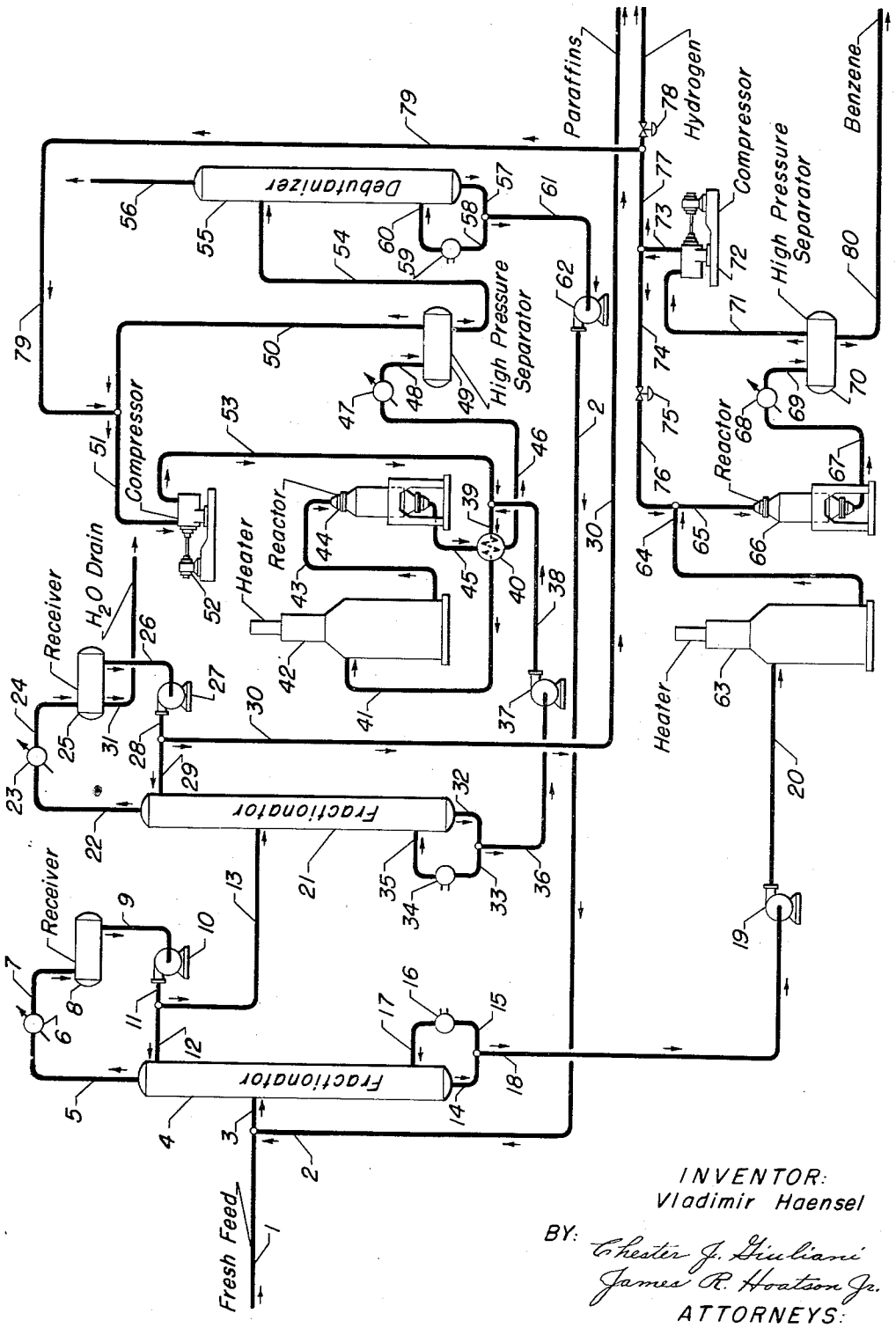
Sept. 13, 1960 V. HAENSEL 2,952,716

HYDROISOMERIZATION PROCESS

Filed Feb. 27, 1958



INVENTOR:
Vladimir Haensel

BY: Chester J. Giuliani
James R. Hoatson Jr.
ATTORNEYS:

United States Patent Office 2,952,716 Patented Sept. 13, 1960

2,952,716

HYDROISOMERIZATION PROCESS

Vladimir Haensel, Hinsdale, Ill., assignor, by mesne assignments, to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware

Filed Feb. 27, 1958, Ser. No. 717,849

10 Claims. (Cl. 260—668)

This invention relates to the hydroisomerization of saturated hydrocarbons in the presence of a hydroisomerization catalyst. More particularly, this invention relates to the hydroisomerization of paraffin hydrocarbons in an integrated process comprising hydroisomerization, dehydrogenation, and recycle of hydrogen produced in the dehydrogenation step as the sole source of makeup hydrogen for the hydroisomerization step. Still more particularly, this invention relates to the vapor phase hydroisomerization of paraffin hydrocarbons boiling above butanes and pentanes in which process high yields of high antiknock hydrocarbon fractions are produced with minimum loss to byproducts such as dry gas and high boiling materials. Along with the production of this high antiknock hydrocarbon fraction there is produced an aromatic hydrocarbon fraction which may be utilized per se or if so desired combined with the above mentioned high antiknock hydrocarbon fraction for the production of the maximum quantity of high antiknock hydrocarbons. Simultaneously with the maximum utilization of available relatively low octane number straight chain paraffin hydrocarbons, this invention relates to a particular series of process steps, the use of which results in maximum hydroisomerization catalyst life and optimum product quality. This invention is particularly directed to an improved process for the production of dimethylbutanes and benzene by the hydroisomerization of relatively straight chain hexane hydrocarbons and by the dehydrogenation of cyclohexane naturally occurring in the hexane hydrocarbon feed streams and produced in the hydroisomerization reaction zone. These objectives are accomplished by the combination process of the present invention as will be set forth hereinafter.

Production of highly branched chain paraffinic hydrocarbons having high antiknock properties and therefore suitable for use in automotive and aviation fuels is of considerable importance in the petroleum refining industry. Furthermore, the recent introduction of automobile engines of high compression ratios has necessitated the utilization of high antiknock fuels in these engines to obtain maximum horsepower output therefrom. Thus, the demand for higher and higher octane number fuels has led to the need for increased quantities of highly branched chain paraffin hydrocarbons for use as blending agents in existing supplies of gasoline. A convenient source of highly branched chain paraffin hydrocarbons is the catalytic isomerization of less highly branched chain paraffin hydrocarbons. Normal butane and normal pentane have been isomerized to isobutane and isopentane, respectively, by various prior art processes utilizing either liquid or vapor phase. However, it is well known in the prior art that cracking occurs along with isomerization and that this cracking increases with increasing molecular weight of the hydrocarbon reactant. There has been considerable difficulty in the successful isomerization of hexane fractions on a commercial scale. A process for such isomerization is particularly attractive when it is realized that a hexane fraction can be converted by proper isomerization and fractionation into a pool of motor fuel blending components having an F–1+3 cc. octane number of over 100. It is therefore an additional object of this invention to provide a process which will result in the production of these desired high octane number hexane isomers.

Prior art processes for the isomerization of saturated hydrocarbons have taught the utilization of various catalytic agents to accelerate the desired molecular rearrangement at the conditions selected. Ordinarily, the catalytic agents utilized have comprised metal halides such as aluminum chloride, aluminum bromide, antimony chloride, etc., which were activated by the addition of the respective hydrogen halide thereto. Furthermore, the prior art has taught that these catalytic agents may be additionally utilized in the presence of added hydrogen. Such catalytic agents are known to be very active and effect high conversions per pass. However, this high activity is accompanied by many disadvantages. One of the greatest disadvantages is the fact that these catalytic materials not only accelerate isomerization reactions, but they also induce decomposition reactions. These decomposition reactions are particularly detrimental to the overall economics of an isomerization process since they cause a loss of a portion of the charging stock as well as increasing catalyst consumption by the reaction of fragmental material with the catalytic agent to form sludge-like materials. As stated hereinabove, the prior art teaches the utilization of hydrogen along with these catalytic agents. This hydrogen has been utilized in an attempt to cause reaction of these fragmental materials which are formed by decomposition with the hydrogen thus resulting in a decrease in sludge formation. While there has been some indication that such utilization of hydrogen is beneficial, processes utilizing the same along with the above mentioned catalytic agents have not been accepted as economically feasible by the petroleum industry. The process of the present invention overcomes these disadvantages by utilization of more recently developed catalysts and thus the use of this process along with these catalysts results in the attainment of isomerization reactions, more specifically hydroisomerization reactions, which have hereinbefore been unavailable to the petroleum industry.

As stated hereinabove, the process of the present invention is particularly directed to the hydroisomerization of hydrocarbon fractions comprising hexane hydrocarbons or hydrocarbons containing six carbon atoms. Hexane hydrocarbons boil from about 45° to about 85° C. (113–185° F.) and analyses of typical hexane fractions show that they contain varying quantities of 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, normal hexane, methylcyclopentane, and cyclohexane. Because of their respective boiling points, these hexane hydrocarbon fractions also contain varying small quantities of cyclopentane (boiling point 120.7° F.) and dimethylpentanes (boiling points 174.6–176.9° F.). The trimethylbutane, 2,2,3-trimethylbutane, which boils at 177.6° F. also falls within the hexane hydrocarbon boiling range but occurs naturally in such small quantities that it is not usually found as a component of these fractions. The boiling points and octane numbers of these six carbon atom hydrocarbons are given in the following table:

TABLE I

	Boiling Point		F-1 Octane No.	
	° C.	° F.	Clear	+3 cc.
2,2-Dimethylbutae	49.7	121.5	92.3	104.0
2,3-Dimethylbutane	58.0	136.4	103.5	>120
2-Methylpentane	60.3	140.5	73.4	93.1
3-Methylpentane	63.3	145.9	74.5	93.4
n-Hexane	68.7	155.7	25.0	65.3
Methylcyclopentane	71.8	161.3	92.0	103.1
Benzene	80.1	176.2	>120	>120
Cyclohexane	80.7	177.3	84.0	97.4

By the process of this invention the high octane number dimethylbutane components and cyclohexane are not passed to the hydroisomerization reactor but are fractionated from the combined feed to the process. Such dimethylbutane components include 2,2-dimethylbutane and 2,3-dimethylbutane. Furthermore, the benzene and cyclohexane components of the combined feed are not passed to the hydroisomerization reactor but are instead passed to a dehydrogenation reactor for the production of aromatic hydrocarbons, namely benzene, with the concurrent production of hydrogen which is utilized as the sole source of makeup hydrogen in the process. When processing hexanes in the process of this invention, the hydroisomerization reaction zone feed will comprise 2-methylpentane, 3-methylpentane, normal hexane, and methylcyclopentane. This hydroisomerization reaction zone feed will be converted therein to an equilibrium mixture of hexane isomers including the dimethylbutanes and cyclohexane. In this manner a total gasoline pool having an F-1+3 cc. octane number of greater than 100 is produced and methylcyclopentane is converted to cyclohexane thus increasing the quantity of benzene which can ultimately be produced as the second product from the process.

One embodiment of the present invention relates to a process for the hydroisomerization of an isomerizable saturated hydrocarbon fraction characterized by an average molecular weight greater than about 80, such hydroisomerization being carried out at hydroisomerization conditions in the presence of hydrogen and a hydroisomerization catalyst comprising a hydrogenation component deposited on an acid-acting support, which comprises separating dehydrogenatable cycloparaffins naturally occurring in the fresh feed and produced in the hydroisomerization process from the combined feed to the hydroisomerization process, dehydrogenating said cycloparaffins in the presence of a dehydrogenation catalyst at dehydrogenation conditions to produce hydrogen and aromatic hydrocarbons, removing said aromatic hydrocarbons from the process, and recycling at least a portion of said hydrogen to the hydroisomerization process as the sole source of makeup hydrogen therefor.

Another embodiment of the present invention relates to a combination hydroisomerization-dehydrogenation process for the simultaneous production of dimethylbutanes and benzene, said process self-sufficient in hydrogen requirement, which comprises passing to a first fractionation zone an isomerizable hexane hydrocarbon fraction in combination with liquid phase hydroisomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially cyclohexane-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction comprising cyclohexane, passing said cyclohexane bottoms fraction to a dehydrogenation zone herein after described, passing said substantially cyclohexane-free overhead hexane fraction from said first fractionation zone to a second fractionation zone as feed therefor, fractionating said hydrocarbons to produce an overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane, removing said overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes as one product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane along with hydrogen at least some of which is produced by dehydrogenation as hereinafter described to a hydroisomerization zone maintained at a temperature of from about 300° F. to about 500° F. and at a pressure of from about 100 to about 1000 pounds per square inch wherein methylpentanes, normal hexane, and methylcyclopentane are isomerized at a liquid hourly space velocity of from about 0.1 to about 10 in the presence of a hydroisomerization catalyst comprising a hydrogenation component deposited on an acid-acting support to an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethylbutanes, methylpentanes, normal hexane, methylcyclopentane, and cyclohexane, recycling the hydroisomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover cyclohexane therefrom and to allow recovery therefrom of 2,2- and 2,3-dimethylbutane produced in the process in said second fractionation zone as aforesaid and to separate methylpentanes, normal hexane, and methylcyclopentane as aforesaid for reuse and internal recycle in said process, dehydrogenating said cyclohexane from the bottoms of said first fractionation zone in a dehydrogenation zone in the presence of a dehydrogenation catalyst at dehydrogenation conditions to hydrogen and benzene, removing said benzene as the second product from the process, and recycling at least a portion of said hydrogen to the hydroisomerization zone as the sole source of makeup hydrogen therefor.

A specific embodiment of this invention relates to a combination hydroisomerization and dehydrogenation process for the simultaneous production of dimethylbutanes and benzene, said process self-sufficient in hydrogen requirement, which comprises passing to a first fractionation zone an isomerizable hexane hydrocarbon fraction in combination with liquid phase hydroisomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially cyclohexane-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction comprising cyclohexane, passing said cyclohexane bottoms fraction to a dehydrogenation zone hereinafter described, passing said substantially cyclohexane-free overhead hexane fraction from said first fractionation zone to a second fractionation zone as feed therefor, fractionating said hydrocarbons to produce an overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane, removing said overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes as one product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane along with hydrogen at least some of which is produced by dehydrogenation as hereinafter described to a hydroisomerization zone maintained at a temperature of from 300° F. to about 500° F. and at a pressure of from about 100 to about 1000 pounds per square inch wherein methylpentanes, normal hexane, and methylcyclopentane are isomerized at a liquid hourly space velocity of from about 0.1 to about 10 in the presence of a hydroisomerization catalyst comprising platinum deposited on alumina impregnated with aluminum chloride to an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethylbutanes, methylpentanes, normal hexane, methylcyclopentane, and cyclohexane, recycling the hydroisomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover cyclohexane therefrom and to allow recovery therefrom of 2,2- and 2,3-dimethylbutanes produced in the process in

said second fractionation zone as aforesaid and to separate methylpentanes, normal hexane, and methylcyclopentane as aforesaid for reuse and internal recycle in said process, dehydrogenating said cyclohexane from the bottoms of said first fractionation zone in a dehydrogenation zone in the presence of a dehydrogenation catalyst comprising platinum deposited on acid-free alumina at a temperature of from about 500° F. to about 1000° F., a pressure of from about atmospheric to about 500 pounds per square inch, and at a liquid hourly space velocity of from about 0.1 to about 100 to produce hydrogen and benzene, removing said benzene as a second product from the process, and recycling at least a portion of said hydrogen to the hydroisomerization zone as the sole source of makup hydrogen therefor.

The combination process of this invention has several advantages, all interrelated. The process prevents the buildup of heavier products in the combined feed to the reaction zone since these heavier products are eliminated by removal in the bottoms from the first fractionation zone along with the cyclohexane. The hydroisomerization step of the process is carried out in the presence of hydrogen and more recently developed hydroisomerization catalysts comprising hydrogenation components deposited on acid-acting supports. In the presence of hydrogen and in the presence of these catalysts, sludge formation, which appears to be a concurrent reaction with hydroisomerization is minimized, or for all practical purposes eliminated. This sludge elimination is accomplished by hydrogenation of the fragmental materials leading to the sludge or by hydrogenation of the sludge prior to the accumulation thereof in quantities which cause catalyst deactivation. It has also been theorized, although not yet confirmed, that the hydrogen plays an essential role in one of the proposed reaction steps of the mechanism by which the hydroisomerization process takes place. However, no intention is meant to be inferred therefrom that the particular hydroisomerization reactions which take place herein are to be limited to any particular theory or reaction mechanism. The process of the present invention provides maximum utilization of naphthenic hydrocarbons containing six carbon atoms in the cycloparaffin ring by removal thereof prior to isomerization in the lower portion of the first fractionation zone. By elimination of the cyclohexane and derivatives thereof from the reaction zone combined feed, conversion of cycloparaffins containing five carbon atoms in the cycloparaffin ring, such as methylcyclopentane, to cycloparaffins containing six carbon atoms in the ring is accomplished due to equilibrium factors. Benzene which is naturally occurring in many hexane hydrocarbon fractions is substantially removed along with the cyclohexane from the bottom of the first fractionation zone. This removal, however, is not 100% due to azeotroping of the benzene with the paraffin hydrocarbons. However, benzene which is carried over into the hydroisomerization zone is hydrogenated therein to cyclohexane and this cyclohexane is then recovered by the particular fractionation as set forth hereinabove. By elimination of cyclohexane naturally occurring in the reaction zone feed, by elimination of cyclohexane produced during hydroisomerization, and by reduction of the benzene content of the combined feed, hydrogen consumption in the process is minimized. This results in an economic advantage since large quantities of hydrogen do not have to be furnished to the process. Major hydrogen consumption is that due to hydrogen solubility in the reaction zone effluent in the high pressure separator, described hereinafter. Some hydrogen loss occurs, however, through the small amount of hydrocracking which inherently takes place in the process and through hydrogenation of higher molecular weight fragmental materials which tend to form sludge or by hydrogenation of sludge itself. The process prevents so-called reverse isomerization of high octane number dimethylbutanes to other hexane isomers by separation of these high octane number components prior to isomerization. At any particular isomerization reaction temperature, the formation of hexane isomers is limited by the equilibrium distribution of these isomers. By having the high octane number dimethylbutanes present in the hydroisomerization feed, the conversion of monomethylpentanes and normal hexane to these compounds cannot proceed to the same extent as when these isomers are absent. Furthermore, the equilibrium among hexane isomers is dynamic so that the desired dimethylbutane isomers can undergo reverse isomerization if present in substantial quantities in the hydroisomerization feed. Another advantage of the process of the present invention is that hydroisomerization catalyst deactivation or destruction is minimized or substantially eliminated by distillation drying of the hydroisomerization zone feed and rejection of small quantities of water contained therein is accomplished along with the dimethylbutanes in the overhead from the second fractionation zone. Thus, the hydroisomerization zone feed is a fractionation zone bottoms product and by this means full advantage is taken of maximum distillation drying. All hydroisomerization catalysts depend upon an acid function to promote or to accomplish the desired reaction. This acid function is destroyed or decreased by contact with water. The preferred catalysts of the present invention which operate at elevated temperatures contain this acid function in quantities ranging from about 2 to about 20% by weight thereof, and are thus utilized at intermediate processing conditions. Thus, small amounts of water which can be brought in with the feed stock cause relatively rapid catalyst deactivation. Utilization of the process of the present invention prevents this deactivation. By elimination of dimethylbutanes and cyclohexane from the hydroisomerization zone feed, the quantity of total feed is reduced as well as the combined feed ratio and thus the investment necessary for catalyst can be substantially reduced. By dehydrogenation of dehydrogenatable cycloparaffins, for example, cyclohexane, a second desirable product is produced in the process, namely, aromatic hydrocarbons such as benzene. Not only is this second product produced in substantial quantities but the hydrogen which is produced along with this hydrocarbon is extremely pure and is utilized as the sole source of makeup hydrogen necessary for the hydroisomerization step in the process. This combination results in the process being self-sufficient in hydrogen requirement and thus eliminates the necessity for an outside source of hydrogen and allows installation of the process in locations where the cost of such hydrogen would ordinarily prevent utilization of hydroisomerization for upgrading the octane number of hydrocarbon fractions. These and other advantages will be explained more fully in the following detailed description of the process of this invention.

As set forth hereinabove, this invention relates to a process for the hydroisomerization of an isomerizable saturated hydrocarbon fraction characterized by an average molecular weight greater than about 80. Hydrocarbons within the scope of the above limitation and utilizable in the process of this invention include methylcyclopentane normal hexane, 2-methylpentane, 3-methylpentane, 2-methylhexane, 3-methylhexane, 3-ethylpentane, normal heptane, ethylcyclopentane, normal octane, 2-methylheptane, 3-methylheptane, etc. As stated previously, the process of this invention is particularly applicable to the isomerization of hexane hydrocarbon fractions. These hexane hydrocarbons may be obtained from various sources including fractionation from straight run gasoline, straight run naphtha, natural gasoline, catalytically reformed naphtha, catalytically reformed gasoline, etc. Analyses of typical hexane fractions from various crude oil sources are given in the following Table II.

TABLE II

Analyses of typical C_6 fractions—Fractionation cut 40–74° C. (104–165° F.)

Composition, Vol Percent	Barninus Crude	Pennsylvania	South Louisiana	Gulf Coast	Oklahoma	Wyoming	Arabian	Nat'l Gasol. Texas	Nat'l Gasol. Texas
Cyclopentane	5	2	2	3	3	4	2	2	5
2,2-Dimethylbutane	Tr	3	2	3	1	1	1	2	3
2,3-Dimethylbutane	5	5	5	5	2	3	3	4	6
2-Methylpentane	20	27	25	25	22	22	22	28	28
3-Methylpentane	19	18	18	20	15	14	16	17	15
n-Hexane	32	36	31	30	40	35	44	34	23
Methylcyclopentane	16	6	14	3	14	18	7	9	14
Dimethylpentanes	Tr	Tr	1	1	--------	1	1	Tr	Tr
Cyclohexane	1	Tr	1	7	1	1	2	1	2
Benzene	2	2	1	3	2	1	2	3	4
Total	100	100	100	100	100	100	100	100	100
C_6 Cyclics	19	8	16	13	17	20	11	13	20
Octane No. F-1+3 cc	88	86	88	90	85	86	82	86	92

A detailed description of the processing of one of these hexane hydrocarbon fractions by the process of the present invention will be given hereinafter.

Various hydroisomerization catalysts are utilizable within the generally broad scope of the process of the present invention. These catalysts may be defined as comprising a hydrogenation component deposited on an acid-acting support. The acid-acting support may inherently have this property or its acid-acting characteristics may be added thereto either before or after deposition of the hydrogenation component thereon. Suitable supports may be selected from among the different refractory oxides including silica, alumina, silica-alumina, silica - alumina - magnesia, silica-alumina-zirconia, silica-zirconia, etc. These supports may be naturally occurring or may be prepared synthetically. Other suitable naturally occurring refractory oxides include acid-acting clays such as Filtrol, Tonsil, etc., diatomaceous earths, montmorillonites, etc. Depending upon whether or not the refractory oxide support is naturally occurring or prepared synthetically, and depending upon the method of preparation, and upon the treatment of the support thereafter, these various supports will have surface areas ranging from about 25 to about 500 square meters per gram. In some of these supports the acid-acting function is inherently present, as stated hereinabove, for example, when silica-alumina or silica-alumina-zirconia is used as the support. The effectiveness of this acid-acting function in such a support is controlled by the quantities of the respective components, and by the treatment of the composites, particularly by calcination, prior to or after compositing the hydrogenation component therewith. The preferred catalysts used in the hydroisomerization zone in the process of the present invention comprise a refractory oxide, a hydrogenation component, and a Friedel-Crafts metal halide. In these preferred catalysts the above mentioned refractory oxides have composited therewith a hydrogenation component and then a metal halide of the Friedel-Crafts type. The hydrogenation component will normally be selected from groups VI(B) and VIII of the periodic table or mixtures thereof. Such hydrogenation components include chromium, molybdenum, tungsten, iron, cobalt, nickel, and the so-called platinum group metals. By a platinum group metal is meant a noble metal, excluding silver and gold, and selected from platinum, palladium, ruthenium, rhodium, osmium, and iridium. These metals are not necessarily equivalent in activity in the catalysts utilized in the hydroisomerization step of the process of the present invention and of these metals, platinum and palladium are preferred, and particularly platinum is preferred. A Friedel-Crafts metal halide is associated with the solid composite of refractory oxide and hydrogenation component for use as a catalyst in the process of the present invention. Suitable Friedel-Crafts metal halides include aluminum chloride, aluminum bromide, zinc chloride, ferric chloride, ferric bromide, beryllium chloride, gallium chloride, titanium tetrachloride, zirconium chloride, stannic chloride, etc. Of these Friedel-Crafts metal halides, the aluminum halides are preferred, and of the aluminum halides, aluminum chloride is particularly preferred. Furthermore, these metal halides are not necessarily equivalent when utilized in forming the catalysts described hereinabove. The preferred catalyst composition comprises alumina, platinum, and aluminum chloride. The alumina is preferably synthetically prepared gamma-alumina and is of a high degree of purity. These aluminas may include, in one embodiment, from about 0.01 to about 8% of what is known in the art as combined halogen, based on the weight of the dry alumina, the combined halogen preferably being fluorine. Furthermore, it is generally preferred to utilize from about 0.01 to about 2% by weight of platinum based on the dry alumina. When utilizing other hydrogenation components such as those of the so-called iron group of group VIII of the periodic table or those in group VI(B) of the periodic table, the amount is generally higher, usually within the range of from about 1 to about 25% by weight or more of the alumina on a dry basis. The synthetically prepared alumina-platinum composites are preferentially impregnated with aluminum chloride to form the desired catalysts for use in the hydroisomerization step. This can be accomplished readily by sublimation of the aluminum chloride onto the surface of the particles of the platinum-alumina composite. In a like manner, aluminum chloride can be impregnated on other refractory oxide-hydrogenation component composites. Aluminum chloride sublimes at about 183° C. and thus a suitable impregnation temperature will range from about 190° C. to about 350° C. or higher. The amount of Friedel-Crafts metal halide utilized in preparing these catalysts will range from about 2.0 to about 25% by weight based on the weight of the refractory oxide-hydrogenation metal, more particularly alumina-platinum, prior to impregnation.

As is readily apparent from the description hereinabove, the hydroisomerization step is effected in a hydrogen atmosphere. Sufficient hydrogen should be utilized so that the hydrogen to hydrocarbon ratio of the hydroisomerization zone feed will be within the molar range of from about 0.25 to about 10. The hydroisomerization step in this process is hydrogen consuming and this consumption of hydrogen is readily furnished by supplying hydrogen from the dehydrogenation step as set forth hereinafter.

The hydroisomerization step of the present process may be carried out at varying conditions of temperature, pressure, space velocity, and combined feed ratio. The temperature utilized will generally be dictated by the particular catalyst selected. In the presence of the preferred

catalyst, the temperature will range from about 200° to about 550° F., although temperatures within the more limited range of from about 300° to about 500° F. will generally be utilized. The pressure selected will depend upon the particular temperature utilized and will range from about 100 to about 1000 pounds per square inch or more. The liquid hourly space velocity will range from about 0.1 to about 10 or more, the only limitation being that equilibrium mixtures of isomerized hydrocarbons or a close approach thereto shall be obtained in the hydroisomerization reaction zone effluent. The combined feed ratio which is defined as the total amount of fresh feed entering the reactor and recycle divided by the quantity of fresh feed will range from one up to about 5 or more. Values in between these two apparent limitations are determined by the concentration of cyclohexane in the hydroisomerization reaction zone effluent and further by the concentration of desired high octane number hydrocarbons.

Various dehydrogenation catalysts are utilizable in the dehydrogenation reaction zone in the process of this invention. These dehydrogenation catalysts normally include a dehydrogenation component deposited on an acid-free support. The dehydrogenation component is preferentially metallic and as such is selected from among the metals of group VIII of the periodic table including iron, cobalt, nickel, platinum, palladium, ruthenium, rhodium, osmium, and iridium. In some instances the so-called metal oxide dehydrogenation components are also suitable including metal oxides of the above mentioned group VIII metals as well as the metal oxides of group VI(B) such as chromia, molybdena, and tungsten oxide. These metallic and metal oxide dehydrogenation components are composited with a suitable acid-free support in the preferred embodiment. These acid-free supports include silica, alumina, and various naturally occurring substances such as bauxite, kaolin or clay, etc. Of these various supports, alumina is preferred, and particularly preferred is synthetically prepared gamma-alumina of a high degree of purity. The quantity of dehydrogenation component composited with the support usually ranges from about one to about 25% or more based on the dry weight of the support. When the metallic dehydrogenation component is one of the platinum group metals, the quantity utilized is usually less, for example, from about 0.1 to about 2% by weight of the support since these metallic dehydrogenation components are not only expensive but also relatively scarce.

The dehydrogenation step of the process of the present invention may be carried out at varying conditions of temperature, space velocity, and pressure. Here again, the temperature will generally be dictated by the particular catalyst selected. Since the metallic dehydrogenation catalysts are also hydrogenation catalysts, they must be utilized at sufficiently high temperatures so that dehydrogenation is the favored reaction. Such temperatures may range from about 500° F. to about 1000° F. or more. The pressure will range from about atmospheric to about 500 pounds per square inch or more. Obviously, the pressure utilized will be as low as possible since lower pressures favor the desired dehydrogenation reaction. Liquid hourly space velocity will range from about 0.1 to about 100 or more. Dehydrogenation of naphthenes containing six carbon atoms in the ring is an exceedingly rapid reaction and thus much higher space velocities can be utilized than are operable for the hydroisomerization reactions. These higher space velocities result in the necessity for the utilization of smaller quantities of catalyst in the dehydrogenation reaction zone and thus are favored. Liquid hourly space velocities of from about 5 to about 50 are preferred.

The process of the present invention can perhaps be best understood by reference to the accompanying drawing which is a schematic diagram of the process flow.

Referring to the drawing, a saturated hydrocarbon fraction characterized by an average molecular weight greater than about 80, for example, a hexane fraction separated from a straight run or catalytically reformed naphtha, is passed, as a liquid under pressure, through lines **1** and **3** to the upper portion of fractionation zone **4**. The hydrocarbon fraction passing through lines **1** and **3** is combined in line **1** with recycle reaction zone effluent from line **2** as hereinafter set forth. The combined feed to fractionator **4** is fractionated therein to separate a substantially dehydrogenatable cycloparaffin-free overhead from dehydrogenatable cycloparaffins which occur in the feed or which may be produced during processing by hydroisomerization. Ordinarily these dehydrogenatable cycloparaffins, such as cyclohexane, occur in the feed and their destruction via hydrocracking is prevented by removal at this point. Thus, the hydrocarbon stream from line **3** is fractionated in fractionation zone **4** and the substantially dehydrogenatable cycloparaffin-free portion thereof separated overhead. This cyclohexane-free hydrocarbon fraction passes through line **5**, is condensed in condenser **6**, and passes through line **7** to overhead receiver **8**. The substantially dehydrogenatable cycloparaffin-free hydrocarbons from receiver **8** are withdrawn therefrom through line **9** by pump **10** which discharges into line **11** and supplies reflux to fractionation zone **4** by means of line **12**. The net substantially dehydrogenatable cycloparaffin hydrocarbon stream from fractionation zone **4** passes from line **11** through line **13** to fractionation zone **21** as hereinafter described. Fractionation zone **4** is heated by reboiling a portion of the dehydrogenatable cycloparaffins from the bottom thereof which are withdrawn through lines **14** and **15**, and are passed through heat exchanger **16**. The heated hydrocarbons are then returned to a lower portion of fractionation zone **4** through line **17**. The higher boiling dehydrogenatable cycloparaffin bottoms fraction is withdrawn from the bottom of fractionation zone **4** through lines **14** and **18** by pump **19** and is pumped through line **20** to the dehydrogenation step hereinafter described.

The purpose of fractionation zone **21** is to fractionate the feed thereto to produce a hydrocarbon fraction characterized by a major proportion of hydrocarbons which contain at least two methyl substituents per molecule and to produce a hydroisomerization reaction zone feed. The overhead product from fractionation zone **21** thus comprises dimethylalkanes naturally occurring in the feed and dimethylalkanes from the reaction zone effluent which have been formed as a result of the hydroisomerization of normal paraffins and monomethylalkanes as set forth hereinafter. For example, when processing a hexane fraction, the overhead product which is separated from the process at this point comprises 2,2- and 2,3-dimethyl butanes naturally occurring in the feed and 2,2- and 2,3-dimethylbutanes from the hydroisomerization reaction zone effluent which have been formed as a result of the hydroisomerization of normal hexane and 2- and 3-methylpentane as set forth hereinafter. Also, any water which is dissolved in the feed or produced during the hydroisomerization processing separates overhead at this point due to distillation drying. Therefore, the bottoms from fractionation zone **21** which pass to the hydroisomerization reaction zone are for all practical purposes substantially water free. The above described dimethylalkane hydrocarbon stream passes from fractionation zone **21** overhead through line **22**, is condensed in condenser **23**, and passes through line **24** to overhead receiver **25**. From receiver **25**, the hydrocarbon fraction passes through line **26** to pump **27** which discharges into line **28** and provides reflux for fractionation zone **21** by means of line **29**. The net dimethylparaffin hydrocarbon stream is withdrawn through line **30**. Water which is separated overhead by distillation drying in fractionation zone **21** is removed from overhead receiver **25** by drain line **31**. Fractionator **21** is heated by reboiling a portion of the higher boiling hydrocarbons, which are withdrawn therefrom

through lines 32 and 33 and are passed through heat exchanger 34. The heated hydrocarbons are then returned into a lower portion of fractionation zone 21 through line 35. The higher boiling hydrocarbons, substantially free from dehydrogenatable cycloparaffins as hereinabove described, and substantially free from dimethylalkanes, are withdrawn from fractionation zone 21 through lines 32 and 36 by pump 37.

The net hydrocarbon stream from fractionation zone 21 is passed by pump 37 through lines 38 and 39. From line 39 this hydrocarbon stream is heat exchanged with the hot reaction zone effluent in heat exchanger 40 and then passes through line 41 to heater 42. In heater 42, the stream is heated to the desired reaction temperature, and then passes through line 43 to hydroisomerization reaction zone 44. It is in this reaction zone 44 that the less highly branched chain and straight chain hydrocarbons and naphthenes containing five carbon atoms in the ring are isomerized to an equilibrium mixture of saturated hydrocarbon isomers. As will be set forth hereinafter, the hydrocarbons are processed in the presence of hydrogen which is introduced via line 53 into line 39. This hydrogen also hydrogenates any aromatic hydrocarbons in reaction zone 44.

The conditions utilized in hydroisomerization reaction zone 44 will depend upon the particular hydroisomerization catalyst utilized therein. It was pointed out above that a preferred catalyst in the process of this invention is one comprising a hydrogenation component deposited on an acid-acting support. With such a catalyst, the pressure utilized will range from about 100 to about 1000 pounds per square inch, the temperature will range from about 200° to about 500° F., and the hourly liquid space velocity will range from about 0.1 to about 10. The hydrogen to hydrocarbon ratio in the reaction zone will range from about 0.25 to about 10 mols of hydrogen per mol of hydrocarbon. When the preferred hydroisomerization catalyst comprising platinum and alumina which has been impregnated with a Friedel-Crafts metal halide, such as aluminum chloride, is utilized, the temperature will be in the preferred range of from about 300° to about 500° F. In some instances it is desirable and/or advisable to utilize hydrogen halide along with these catalysts and thus the use of hydrogen chloride, for example, is within the generally broad scope of the present invention.

The hydroisomerization reaction zone effluent passes from reactor 44 through line 45 in indirect heat exchange with the hydroisomerization reaction zone feed through heat exchanger 40 and then passes through line 46, is condensed in condenser 47, and passes through line 48 to high pressure separator 49. The high pressure separator 49 is utilized for separating hydrogen from the isomerized hydrocarbons, which hydrogen is separated and passed through lines 50 and 51 to compressor 52 where its pressure is increased to the desired number of pounds per square inch, and then the hydrogen is discharged through line 53 as hereinabove described. When a hydrogen halide is utilized along with the hereinabove described catalyst as a promoter, a substantial proportion of it will pass through lines 50 and 51 to compressor 52 as hereinabove described.

Makeup hydrogen, to maintain the process in hydrogen balance, is supplied to the hydroisomerization zone through line 79 from dehydrogenation as hereinafter described. This makeup hydrogen passes from line 79 to line 51 wherein it joins the recycle hydrogen from line 50, both hydrogen streams then being compressed by compressor 52. As stated hereinabove, hydrogen consumption in the hydroisomerization process of the present invention is relatively small, that is less than 100 cubic feet of hydrogen per barrel of combined feed to the hydroisomerization reaction zone, and usually this consumption is less than 50 cubic feet of hydrogen per barrel. In a normal operation, this 50 cubic feet per barriel is divided between hydrogen consumed by reaction with hydrocarbons and sludge, if any, and hydrogen lost through solubility in the effluent from the high pressure separator. The loss due to solubility may run in the order of about 30 cubic feet of hydrogen per barrel and thus about 20 cubic feet of hydrogen per barrel can be assigned to reactions.

The cooled hydroisomerization zone effluent after high pressure separation is discharged from separator 49 through line 54 to debutanizer 55. This debutanizer is a conventional fractionation zone by means of which light hydrocarbon gas or low boiling cracked products and dissolved hydrogen are removed from the process. This removal is accomplished through line 56 which may include receiver and reflux means not shown. Debutanizer 55 is heated by passing a portion of the higher boiling hydrocarbons through lines 57 and 58 to heat exchanger 59 from which the heated hydrocarbons are returned to a lower portion of debutanizer 55 via line 60. The net hydroisomerization reaction zone effluent is withdrawn from debutanizer 55 through lines 57 and 61 by means of pump 62 which discharges the liquid hydroisomerization reaction zone effluent through line 2 to fractionator 4 for fractionation as described hereinabove.

As set forth hereinabove, the dehydrogenatable cycloparaffin hydrocarbon fraction, for example, cyclohexane, is withdrawn from the bottom of fractionation zone 4 through lines 14 and 18 by means of pump 19 which discharges this dehydrogenatable cycloparaffin hydrocarbon fraction into line 20. From line 20 these dehydrogenatable cycloparaffin hydrocarbons are passed to heater 63 in which this stream is heated to the desired reaction temperature, and then passes through lines 64 and 65 to dehydrogenation reaction zone 66. It is in this dehydrogenation reaction zone 66 that the dehydrogenatable cycloparaffin hydrocarbons are dehydrogenated to aromatic hydrocarbons and hydrogen. While usually not desired since it tends to reverse the desired direction of the reaction, these dehydrogenatable cycloparaffin hydrocarbons may be dehydrogenated in the presence of hydrogen which is introduced via lines 74 and 76 into line 65. Some hydrogen may be desirable, depending upon the particular catalyst utilized since the hydrogen may tend to reduce or prevent carbon deposition on the catalyst in dehydrogenation zone 66.

The conditions utilized in dehydrogenation reaction zone 66 will depend upon the particular dehydrogenation catalyst utilized therein. With catalysts of the type set forth hereinabove, the pressure utilized in the reaction zone will range from atmospheric to about 500 pounds per square inch or more, the temperature will range from about 500° to about 1000° F. or more, and the hourly liquid space velocity will range from about 0.1 to about 100 or more. A particularly preferred catalyst comprises platinum deposited on an acid-free support such as platinum-alumina in which the platinum content ranges from about 0.01 to about 2.0% by weight. The temperature utilized will be from about 750° to about 900° F. with such a catalyst. Also, the hourly liquid space velocity will be from about 5 to about 50. Low pressures are always most desirable.

The dehydrogenation reaction zone effluent passes from reactor 66 through line 67, is condensed in condenser 68, and passes through line 69 to high pressure separator 70. High pressure separator 70 is utilized for separating hydrogen from the aromatic hydrocarbons produced in the dehydrogenation reaction zone. This hydrogen is separated and passed through line 71 to compressor 72 which discharges through line 73 connected to lines 74 and 77. Line 74 contains pressure control valve 75 which is set so that the desired amount of hydrogen, if any, passes therethrough to lines 76 and 65 as set forth hereinabove. As is readily apparent, the major proportion of the hydrogen is discharged from compressor 72 through lines 73 and 77. Line 77 contains pressure control valve 78 which is set so that the desired amount of hydrogen is

passed from line 77 through line 79 to the hydroisomerization reaction zone as set forth hereinabove, and so that the remainder of the hydrogen is vented. In this manner, the combination process is self sufficient in hydrogen, and makeup hydrogen, if necessary, is supplied to the hydroisomerization reaction zone in a quantity to balance the amount consumed during the reaction and dissolved in the liquid withdrawn from high pressure separator 49. The aromatic hydrocarbon fraction, such as benzene, is withdrawn from high pressure separator 70 through line 80.

The following example is introduced solely for the purpose of illustration and with no intention of unduly limiting the generally broad scope of this invention.

Example

One specific example of the operation of the process with a platinum-alumina-aluminum chloride catalyst in the hydroisomerization reaction zone and a platinum-alumina catalyst in the dehydrogenation zone and as the process is carried out similar to that set forth hereinabove with reference to the drawing is described herewith now in connection with the drawing. The catalyst utilized in the hydroisomerization reaction zone comprises alumina containing 0.4% platinum, said composite having been impregnated with about 17% by weight of aluminum chloride. The catalyst utilized in the dehydrogenation reaction comprises alumina containing 0.7% platinum.

This example illustrates the production of dimethylbutanes via hydroisomerization and the production of benzene and hydrogen via dehydrogenation from a Gulf Coast hexane fraction, boiling point 40–74° C. The composition of this Gulf Coast hexane fraction is as follows: cyclopentane, 3%; 2,2-dimethylbutane, 3%; 2,3-dimethylbutane, 5%; 2-methylpentane, 25%; 3-methylpentane, 20%; normal hexane, 30%; methylcyclopentane, 3%; dimethylpentanes, 1%; cyclohexane, 7%; and benzene, 3%. By this process there is produced from 1000 barrels per day of this hexane fraction 860 barrels per day of a fraction comprising mainly dimethylbutanes and somewhat less than 140 barrels per day of benzene containing a small amount of dimethylpentanes, this difference in volume being accounted for by shrinkage due to the change in specific gravity from cyclohexane to benzene. Referring again to the drawing, this hexane fraction, having an average molecular weight greater than 80, in the quantity of 1000 barrels per day, is passed as a liquid under pressure through line 1 and through line 3 to an upper section of fractionation zone 4. This fresh feed stream has combined therewith in line 1, 2430 barrels per day of recycle hydroisomerization reaction zone effluent from line 2 as hereinafter described. This recycle hexane stream consisting of the liquid hydroisomerization reaction zone effluent contains 504 barrels per day of 2,2-dimethylbutane, 246 barrels per day of 2,3-dimethylbutane, 795 barrels per day of 2-methylpentane, 445 barrels per day of 3-methylpentane, 350 barrels per day of normal hexane, 60 barrels per day of methylcyclopentane, and 30 barrels per day of cyclohexane. Thus, the total combined feed to fractionation zone 4 amounts to 3430 barrels per day comprising 30 barrels per day of cyclopentane, 534 barrels per day of 2,2-dimethylbutane, 296 barrels per day of 2,3-dimethylbutane, 1045 barrels per day of 2-methylpentane, 645 barrels per day of 3-methylpentane, 650 barrels per day of normal hexane, 90 barrels per day of methylcyclopentane, 10 barrels per day of dimethylpentane, 100 barrels per day of cyclohexane, and 30 barrels per day of benzene. The combined feed to fractionation zone 4 is fractionated therein under a 2:1 molal reflux to feed ratio and a substantially cyclohexane-free stream is separated overhead therefrom in the amount of 3290 barrels per day. This 3290 barrels per day contains 30 barrels per day of cyclopentane, 534 barrels per day of 2,2-dimethylbutane, 296 barrels per day of 2,3-dimethylbutane, 1045 barrels per day of 2-methylpentane, 645 barrels per day of 3-methylpentane, 650 barrels per day of normal hexane, and 90 barrels per day of methylcyclopentane. This fractionation zone 4 overhead is withdrawn therefrom through line 5, is condensed in condenser 6, and is passed through line 7 to overhead receiver 8. From receiver 8 the liquid is withdrawn through line 9 by pump 10 which supplies feed to a fractionation zone 21, hereinafter described, via line 13.

Fractionation zone 4 bottoms are withdrawn from line 14 through line 8 by pump 19 and have a composition as follows: 10 barrels per day of dimethylpentanes, 100 barrels per day of cyclohexane, and 30 barrels per day of benzene. These bottoms are then pumped by pump 19 through line 20 to heater 63 and dehydrogenation, described hereinafter.

The feed stream to fractionation zone 21 in the quantity of 2350 barrels per day of the composition described hereinabove is fractionated therein under a 4:1 molal reflux to feed ratio and the overhead passed therefrom through line 22, condensed in condenser 23, and is passed as a liquid through line 24 to overhead receiver 25. Fractionation zone 21 separates a substantially monomethylpentane and normal hexane-free dimethylbutane stream overhead therefrom in an amount of 860 barrels per day. This 860 barrels per day contains 30 barrels per day of cyclopentane, 534 barrels per day of 2,2-dimethylbutane, and 296 barrels per day of 2,3-dimethylbutane. This stream has an F–1 clear octane number of 96.4 and an F–1+3 cc. octane number of 111.1. This fractionation zone overhead is withdrawn from receiver 24 through line 26 by pump 27 and the net product is pumped through lines 28 and 30 to storage.

The substantially dimethylbutane-free bottoms stream from the fractionation zone 21 in the quantity of 2430 barrels per day is the hydroisomerization reaction zone feed. The composition of this stream is as follows: 1045 barrels per day of 2-methylpentane, 645 barrels per day of 3-methylpentane, 650 barrels per day of normal hexane, and 90 barrels per day of methylcyclopentane. This bottoms stream from fractionation zone 21 is withdrawn therefrom through lines 32 and 36 by means of pump 37 which pumps this stream through lines 38 and 39, where it is joined with hydrogen from line 53, through heat exchange zone 40, to line 41 and heater 42. The quantity of hydrogen which is continuously supplied is sufficient to maintain a hydrogen to hydrocarbon ratio of 2:1 in the hydroisomerization zone. This is accomplished by recycling hydrogen from the high pressure separator and from the dehydrogenation zone as hereinafter described back to the hydroisomerization zone. The quantity of hydrogen which is supplied from the dehydrogenation zone as hereinafter described is that necessary to make up for the hydrogen consumed in the reaction and for the hydrogen which is dissolved in the high pressure separator liquid effluent. By means of heat exchanger 40 and heater 42 the combined feed to the reaction zone is heated to a temperature of about 340° F. The reaction is carried out at a pressure of about 500 p.s.i.g. in vapor phase at a liquid hourly space velocity of about 2.0. As set forth hereinabove, hydroisomerization of this feed is accomplished in reaction zone 44 in the presence of the hereinabove described hydroisomerization catalyst and results in the production of 2340 barrels per day of reaction zone effluent containing 504 barrels per day of 2,2-dimethylbutane, 246 barrels per day of 2,3-dimethylbutane, 795 barrels per day of 2-methylpentane, 445 barrels per day of 3-methylpentane, 350 barrels per day of normal hexane, 60 barrels per day of methylcyclopentane, and 30 barrels per day of cyclohexane.

The hydroisomerization reaction zone effluent after heat exchange with the incoming feed is passed via lines 45 and 46 to condenser 47, and the liquid product and hydrogen gas are then passed through line 48 to high

pressure separator 49. The hydrogen gas along with minor amounts of low boiling hydrocarbons formed by cracking in the reaction zone are separated in high pressure separator 49 and passed through lines 50 and 51 to compressor 52. High pressure separator liquid which discharges through line 54 is passed to debutanizer 55 to further separate this small amount of cracked products produced during hydroisomerization and to prepare the liquid recycle stream as hereinabove set forth. The liquid recycle stream passes from debutanizer 55 through lines 57 and 61 to pump 62 wherein it is recycled to fractionation zone 4 via line 2.

As stated hereinabove, the bottoms from fractionation zone 4 are withdrawn therefrom through lines 14 and 18 by pump 19 from which these bottoms pass through line 20 to heater 63. These bottoms comprising 10 barrels per day of dimethylpentanes, 100 barrels per day of cyclohexane, and 30 barrels per day of benzene are heated to 800° F. in heater 63 and are passed therefrom via lines 64 and 65 to dehydrogenation reaction zone 66. The dehydrogenation reaction is carried out at a pressure of about 100 p.s.i.g. in vapor phase at an hourly liquid space velocity of 10. As set forth hereinabove, dehydrogenation of the dehydrogenation reaction zone feed is accomplished in dehydrogenation zone 66 in the presence of the hereinabove described catalyst and results in the production of approximately 140 barrels per day of reaction zone effluent containing 10 barrels per day of dimethylpentanes and about 130 barrels per day of benzene. The dehydrogenation of the hundred barrels per day of cyclohexane in the feed to the dehydrogenation reaction zone results in the production of 4.43×10^5 standard cubic feet of hydrogen per day.

The dehydrogenation reaction zone effluent is withdrawn from dehydrogenation zone 66 through line 67 to condenser 68, and the liquid product and hydrogen gas are then passed through line 69 to high pressure separator 70. The hydrogen gas produced in dehydrogenation zone 66, except for that dissolved in the benzene, is withdrawn from high pressure separator 70 through line 71 by compressor 72 which discharges into line 73. From line 73 this hydrogen or a portion thereof, if so desired, may be directed to the dehydrogenation reaction zone by an appropriate setting of valve 75 and thus the hydrogen will pass through lines 73, 74, 76, and 65 back to dehydrogenation zone 66. In the usual case, valve 75 will be closed and the hydrogen which is discharged from the compressor will pass through lines 73, 77, and 79. Valve 78 in line 77 will be set so that sufficient hydrogen passes from line 77 through line 79 back to the hydroisomerization zone 44 to maintain the combination process in hydrogen balance. The remainder of the hydrogen is vented from line 77 to other uses not shown. As stated hereinabove, the dehydrogenation of 100 barrels per day of cyclohexane results in a hydrogen production of 4.43×10^5 standard cubic feet of hydrogen per day. With a normal consumption of hydrogen in the hydroisomerization zone of 50 cubic feet of hydrogen per barrel, approximately 4.3×10^4 standard cubic feet of hydrogen per day pass from line 77 through line 79 back to the hydroisomerization reactor. The remainder of the hydrogen produced, approximately 4×10^5 standard cubic feet of hydrogen per day, is vented from line 77.

The above example illustrates the production of 860 barrels per day of a hydrocarbon fraction comprising dimethylbutanes having an F–1 clear octane number of 96.4 and an F–1+3 cc. octane number of 111.1, and the simultaneous production of approximately 140 barrels per day of benzene. In the above example, the small amount of cracking which is observed during processing has not been taken into account. This can be done since the liquid volume yields through the hydroisomerization reactor are in the order of 98 volume percent or higher, and the liquid volume yields through the dehydrogenation reactor are approximately 100% except for the loss due to volumetric shrinkage due to the difference in the specific gravity of the feed and the product from the dehydrogenation reactor.

The volume balances in barrels per day in and out of the 1000 barrel per day process exemplified hereinabove are presented in the following Table III:

TABLE III

	Bbls./Day						
	Fresh Feed	Hydroisomerization Zone Effluent	Fractionation Zone Bottoms	Fractionation Zone Overhead	Hydroisomerization Zone Feed	Dehydrogenation Zone Feed	Dehydrogenation Zone Effluent
Cyclopentane	30			30			
2,2-Dimethylbutane	30	504		534			
2,3-Dimethylbutane	50	246		296			
2-Methylpentane	250	795			1045		
3-Methylpentane	200	445			645		
Normal Hexane	300	350			650		
Methylcyclopentane	30	60			90		
Dimethylpentanes	10		10			10	10
Cyclohexane	70	30	100			100	
Benzene	30		30			30	130
	1000	2430	140	860	2430	140	140

As is shown in the above table, the high octane number product is the 860 barrels per day of fractionation zone 21 overhead. The benzene product is the 140 barrels per day of dehydrogenation zone effluent. In addition to the two above products there is also vented from the process in this example approximately 4×10^5 standard cubic feet of hydrogen per day. All this results from feeding to the process 1000 barrels per day of a hexane hydrocarbon fraction shown in the table as the fresh feed.

I claim as my invention:

1. A combination hydroisomerization and dehydrogenation process for the simultaneous production of dimethylbutanes and benzene, said process self-sufficient in hydrogen requirement, which comprises passing to a first fractionation zone an isomerizable hexane hydrocarbon fraction in combination with liquid phase hydroisomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially cyclohexane-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction comprising cyclohexane, passing said cyclohexane bottoms fraction to a dehydrogenation zone hereinafter described, passing said substantially cyclohexane-free overhead hexane fraction from said first fractionation zone to a second fractionation zone as feed therefor, fractionating said hydrocarbons to produce an overhead hydrocarbon fraction containing 2,2- and2,3-

dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane, removing said overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes as one product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane along with hydrogen at least some of which is produced by dehydrogenation as hereinafter described to a hydroisomerization zone maintained at a temperature of from about 300° F. to about 500° F. and at a pressure of from about 100 to about 1000 pounds per square inch wherein methylpentanes, normal hexane, and methylcyclopentane are isomerized at a liquid hourly space velocity of from about 0.1 to about 10 in the presence of a hydroisomerization catalyst comprising a hydrogenation component deposited on an acid-acting support to an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethylbutanes, methylpentanes, normal hexane, methylcyclopentane, and cyclohexane, recycling the hydroisomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover cyclohexane therefrom and to allow recovery therefrom of 2,2- and 2,3-dimethylbutanes produced in the process in said second fractionation zone as aforesaid and to separate methylpentanes, normal hexane, and methylcyclopentane as aforesaid for reuse and internal recycle in said process, dehydrogenating said cyclohexane from the bottom of said first fractionation zone in a dehydrogenation zone in the presence of a dehydrogenation catalyst at dehydrogenation conditions to produce hydrogen and benzene, removing said benzene as the second product from the process, and recycling at least a portion of said hydrogen to the hydroisomerization zone as the sole source of makeup hydrogen therefor.

2. A combination hydroisomerization and dehydrogenation process for the simultaneous production of dimethylbutanes and benzene, said process self-sufficient in hydrogen requirement, which comprises passing to a first fractionation zone an isomerizable hexane hydrocarbon fraction in combination with liquid phase hydroisomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially cyclohexane-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction comprising cyclohexane, passing said cyclohexane bottoms fraction to a dehydrogenation zone hereinafter described, passing said substantially cyclohexane-free overhead hexane fraction from said first fractionation zone to a second fractionation zone, fractionating said hydrocarbons to produce an overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane, removing said overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes as one product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane along with hydrogen at least some of which is produced by dehydrogenation as hereinafter described to a hydroisomerization zone maintained at a temperature of from about 300° F. to about 500° F. and at a pressure of from about 100 to about 1000 pounds per square inch wherein methylpentanes, normal hexane, and methylcyclopentane are isomerized at a liquid hourly space velocity of from about 0.1 to about 10 in the presence of a hydroisomerization catalyst comprising a hydrogenation component deposited on an acid-acting support to an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethylbutanes, methylpentanes, normal hexane, methylcyclopentane, and cyclohexane, recycling the hydroisomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover cyclohexane therefrom and to allow recovery therefrom of 2,2- and 2,3-dimethylbutanes produced in the process in said second fractionation zone as aforesaid and to separate methylpentanes, normal hexane, and methylcyclopentane as aforesaid for reuse and internal recycle in said process, dehydrogenating said cyclohexane from the bottom of said first fractionation zone in a dehydrogenation zone in the presence of a dehydrogenation catalyst at a temperature of from about 500° F. to about 1000° F., a pressure of from about atmospheric to about 500 pounds per square inch, and at a liquid hourly space velocity of from about 0.1 to about 100 to produce hydrogen and benzene, removing said benzene as the second product from the process, and recycling at least a portion of said hydrogen to the hydroisomerization zone as the sole source of makeup hydrogen therefor.

3. A combination hydroisomerization and dehydrogenation process for the simultaneous production of dimethylbutanes and benzene, said process self-sufficient in hydrogen requirement, which comprises passing to a first fractionation zone an isomerizable hexane hydrocarbon fraction in combination with liquid phase hydroisomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially cyclohexane-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction comprising said cyclohexane bottoms fraction to a dehydrogenation zone hereinafter described, passing said substantially cyclohexane-free overhead hexane fraction from said first fractionation zone to a second fractionation zone as feed therefor, fractionating said hydrocarbons to produce an overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane, removing said overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes as one product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane along with hydrogen at least some of which is produced by dehydrogenation as hereinafter described to a hydroisomerization zone maintained at a temperature of from about 300° F. to about 500° F. and at a pressure of from about 100 to about 1000 pounds per square inch wherein methylpentanes, normal hexane, and methylcyclopentane are isomerized at a liquid hourly space velocity of from about 0.1 to about 10 in the presence of a hydroisomerization catalyst comprising a platinum group metal deposited on a refractory oxide support impregnated with a Friedel-Crafts metal halide to an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethylbutanes, methylpentanes, normal hexane, methylcyclopentane, and cyclohexane, recycling the hydroisomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover cyclohexane therefrom and to allow recovery therefrom of 2,2- and 2,3-dimethylbutanes produced in the process in said second fractionation zone as aforesaid and to separate methylpentanes, normal hexane, and methylcyclopentane as aforesaid for reuse and internal recycle in said process, dehydrogenating said cyclohexane from the bottom of said first fractionation zone in a dehydrogenation zone in the presence of a metallic dehydrogenation catalyst comprising a dehydrogenation component deposited on an acid-free support at a temperature of from about 500° F. to about 1000° F., a pressure of from about atmospheric to about 500 pounds per square inch, and at a liquid hourly space velocity of from about 0.1 to about 100 to produce hydrogen and benzene, removing said benzene as the second product from the process, and recycling at least a portion of said hydrogen to the hydroisomerization zone as the sole source of makeup hydrogen therefor.

4. A combination hydroisomerization and dehydrogenation process for the simultaneous production of dimethyl butanes and benzene, said process self-sufficient in hydrogen requirement, which comprises passing to a first fractionation zone an isomerizable hexane hydro-

carbon fraction in combination with liquid phase hydroisomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially cyclohexane-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction comprising cyclohexane, passing said cyclohexane bottoms fraction to a dehydrogenation zone hereinafter described, passing said substantially cyclohexane-free overhead hexane fraction from said first fractionation zone to a second fractionation zone as feed therefor, fractionating said hydrocarbons to produce an overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane, removing said overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes as one product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane along with hydrogen at least some of which is produced by dehydrogenation as hereinafter described to a hydroisomerization zone maintained at a temperature of from about 300° F. to about 500° F. and at a pressure of from about 100 to about 1000 pounds per square inch wherein methylpentanes, normal hexane, and methylcyclopentane are isomerized at a liquid hourly space velocity of from about 0.1 to about 10 in the presence of a hydroisomerization catalyst comprising platinum deposited on alumina impregnated with aluminum chloride to an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethylbutanes, methylpentanes, normal hexane, methylcyclopentane, and cyclohexane, recycling the hydroisomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover cyclohexane therefrom and to allow recovery therefrom of 2,2- and 2,3-dimethylbutanes produced in the process in said second fractionation zone as aforesaid and to separate methylpentanes, normal hexane, and methylcyclopentane as aforesaid for reuse and internal recycle in said process, dehydrogenating said cyclohexane from the bottoms of said first fractionation zone in a dehydrogenation zone in the presence of a dehydrogenation catalyst comprising platinum deposited on an acid-free support at a temperature of from about 500° F. to about 1000° F., a pressure of from about atmospheric to about 500 pounds per square inch, and at a liquid hourly space velocity of from about 0.1 to about 100 to produce hydrogen and benzene, removing said benzene as the second product from the process, and recycling at least a portion of said hydrogen to the hydroisomerization zone as the sole source of makeup hydrogen therefor.

5. A combination hydroisomerization and dehydrogenation process for the simultaneous production of dimethylbutanes and benzene, said process self-sufficient in hydrogen requirement, which comprises passing to a first fractionation zone an isomerizable hexane hydrocarbon fraction in combination with liquid phase hydroisomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially cyclohexane-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction comprising cyclohexane, passing said cyclohexane bottoms fraction to a dehydrogenation zone hereinafter described, passing said substantially cyclohexane-free overhead hexane fraction from said first fractionation zone to a second fractionation zone as feed therefor, fractionating said hydrocarbons to produce an overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane, removing said overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes as one product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane along with hydrogen at least some of which is produced by dehydrogenation as hereinafter described to a hydroisomerization zone maintained at a temperature of from about 300° F. to about 500° F. and at a pressure of from about 100 to about 1000 pounds per square inch wherein methylpentanes, normal hexane, and methylcyclopentane are isomerized at a liquid hourly space velocity of from about 0.1 to about 10 in the presence of a hydroisomerization catalyst comprising platinum deposited on alumina impregnated with aluminum chloride to an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethylbutane, methylpentanes, normal hexane, methylcyclopentane, and cyclohexane, recycling the hydroisomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover cyclohexane therefrom and to allow recovery therefrom of 2,2- and 2,3-dimethylbutanes produced in the process in said second fractionation zone as aforesaid and to separate methylpentanes, normal hexane, and methylcyclopentane as aforesaid for reuse and internal recycle in said process, dehydrogenating said cyclohexane from the bottoms of said first fractionation zone in a dehydrogenation zone in the presence of a platinum-alumina dehydrogenation catalyst at a temperature of from about 500° F. to about 1000° F., a pressure of from about atmospheric to about 500 pounds per square inch, and at a liquid hourly space velocity of from about 0.1 to about 100 to produce hydrogen and benzene, removing said benzene as the second product from the process, and recycling at least a portion of said hydrogen to the hydroisomerization zone as the sole source of makeup hydrogen therefor.

6. A combination hydroisomerization and dehydrogenation process for the simultaneous production of dimethylbutanes and benzene, said process self-sufficient in hydrogen requirement, which comprises passing to a first fractionation zone an isomerizable hexane hydrocarbon fraction in combination with liquid phase hydroisomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially cyclohexane-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction comprising cyclohexane, passing said cyclohexane bottoms fraction to a dehydrogenation zone hereinafter described, passing said substantially cyclohexane-free overhead hexane fraction from said first fractionation zone to a second fractionation zone as feed therefor, fractionating said hydrocarbons to produce an ovehead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane, removing said overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes as one product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane along with hydrogen at least some of which is produced by dehydrogenation as hereinafter described to a hydroisomerization zone maintained at a temperature of from about 300° F. to about 500° F. and at a pressure of from about 100 to about 1000 pounds per square inch wherein methylpentanes, normal hexane, and methylcyclopentane are isomerized at a liquid hourly space velocity of from about 0.1 to about 10 in the presence of a hydroisomerization catalyst comprising platinum deposited on alumina impregnated with aluminum chloride to an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethybutanes, methylpentanes, normal hexane, methylcyclopentane, and cyclohexane, recycling the hydroisomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover cyclohexane therefrom and to allow recovery therefrom of 2,2- and 2,3-dimethylbutanes produced in the process in said second fractionation zone as aforesaid and to separate methylpentanes, normal hexane, and methylcyclopentane as aforesaid for reuse and internal recycle in said process, dehydrogenat-

ing said cyclohexane from the bottom of said first fractionation zone in a dehydrogenation zone in the presence of a dehydrogenation catalyst comprising nickel deposited on an acid-free support at a temperature of from about 500° F. to about 1000° F., a pressure of from about atmospheric to about 500 pounds per square inch, and at a liquid hourly space velocity of from about 0.1 to about 100 to produce hydrogen and benzene, removing said benzene as the second product from the process, and recycling at least a portion of said hydrogen to the hydroisomerization zone as the sole source of makeup hydrogen therefor.

7. A combination hydroisomerization and dehydrogenation process for the simultaneous production of dimethylbutanes and benzene, said process self-sufficient in hydrogen requirement, which comprises passing to a first fractionation zone an isomerizable hexane hydrocarbon fraction in combination with liquid phase hydroisomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially cyclohexane-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction comprising cyclohexane, passing said cyclohexane bottoms fraction to a dehydrogenation zone hereinafter described, pass said substantially cyclohexane-free overhead hexane fraction from said first fractionation zone to a second fractionation zone as feed therefor, fractionating said hydrocarbons to produce an overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane, removing said overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes as one product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane along with hydrogen at least some of which is produced by dehydrogenation as hereinafter described to a hydroisomerization zone maintained at a temperature of from about 300° F. to about 500° F. and at a pressure of from about 100 to about 1000 pounds per square inch wherein methylpentanes, normal hexane, and methylcyclopentane are isomerized at a liquid hourly space velocity of from about 0.1 to about 10 in the presence of a hydroisomerization catalyst comprising platinum deposited on alumina impregnated with aluminum chloride to an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethylbutanes, methylpentanes, normal hexane, methylcyclopentane, and cyclohexane, recycling the hydroisomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover cyclohexane therefrom and to allow recovery therefrom of 2,2- and 2,3-dimethylbutanes produced in the process in said second fractionation zone as aforesaid and to separate methylpentanes, normal hexane, and methylcyclopentane as aforesaid for reuse and internal recycle in said process, dehydrogenating said cyclohexane from the bottoms of said first fractionation zone in a dehydrogenation zone in the presence of a nickel-alumina dehydrogenation catalyst at a temperature of from about 500° F. to about 1000° F., a pressure of from about atmospheric to about 500 pounds per square inch, and at a liquid hourly space velocity of from about 0.1 to about 100 to produce hydrogen and benzene, removing said benzene as the second product from the process, and recycling at least a portion of said hydrogen to the hydroisomerization zone as the sole source of makeup hydrogen therefor.

8. A combination hydroisomerization and dehydrogenation process for the simultaneous production of dimethylbutanes and benzene, said process self-sufficient in hydrogen requirement, which comprises passing to a first fractionation zone an isomerizable hexane hydrocarbon fraction in combination with liquid phase hydroisomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially cyclohexane-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction comprising cyclohexane, passing said cyclohexane bottoms fraction to a dehydrogenation zone hereinafter described, passing said substantially cyclohexane-free overhead hexane fraction from said first fractionation zone to a second fractionation zone as feed therefor, fractionating said hydrocarbons to produce an overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane, removing said overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes as one product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane along with hydrogen at least some of which is produced by dehydrogenation as hereinafter described to a hydroisomerization zone maintained at a temperature of from about 300° F. to about 500° F. and at a pressure of from about 100 to about 1000 pounds per square inch wherein methylpentanes, normal hexane, and methylcyclopentane are isomerized at a liquid hourly space velocity of from about 0.1 to about 10 in the presence of a hydroisomerization catalyst comprising platinum deposited on alumina impregnated with aluminum chloride to an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethylbutanes, methylpentanes, normal hexane, methylcyclopentane, and cyclohexane, recycling the hydroisomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover cyclohexane therefrom and to allow recovery therefrom of 2,2- and 2,3-dimethylbutanes produced in the process in said second fractionation zone as aforesaid and to separate methylpentanes, normal hexane, and methylcyclopentane as aforesaid for reuse and internal recycle in said process, dehydrogenating said cyclohexane from the bottoms of said first fractionation zone in a dehydrogenation zone in the presence of a nickel-kieselguhr dehydrogenation catalyst at a temperature of from about 500° F. to about 1000° F., a pressure of from about atmospheric to about 500 pounds per square inch, and at a liquid hourly space velocity of from about 0.1 to about 100 to produce hydrogen and benzene, removing said benzene as the second product from the process, and recycling at least a portion of said hydrogen to hydroisomerization zone as the sole source of makeup hydrogen therefor.

9. A combination hydroisomerization and dehydrogenation process for the simultaneous production of dimethylbutanes and benzene, said process self-sufficient in hydrogen requirement, which comprises passing to a first fractionation zone an isomerizable hexane hydrocarbon fraction in combination with liquid phase hydroisomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially cyclohexane-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction comprising cyclohexane, passing said cyclohexane bottoms fraction to a dehydrogenation zone hereinafter described, passing said substantially cyclohexane-free overhead hexane fraction from said first fractionation zone to a second fractionation zone as feed therefor, fractionating said hydrocarbons to produce an overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane, removing said overhead hydrocarbon fraction containing 2,2- and 2,3- dimethylbutanes as one product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane along with hydrogen at least some of which is produced by dehydrogenation as hereinafter described to a hydroisomerization zone maintained at a temperature of from about 300° F. to about 500° F. and at a pressure of from about

100 to about 1000 pounds per square inch wherein methylpentanes, normal hexane, and methylcyclopentane are isomerized at a liquid hourly space velocity of from about 0.1 to about 10 in the presence of a hydroisomerization catalyst comprising platinum deposited on alumina impregnated with aluminum chloride to an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethylbutanes, methylpentanes, normal hexane, methylcyclopentane, and cyclohexane, recycling the hydroisomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover cyclohexane therefrom and to allow recovery therefrom of 2,2- and 2,3-dimethylbutanes produced in the process in said second fractionation zone as aforesaid and to separate methylpentanes, normal hexane, and methylcyclopentane as aforesaid for reuse and internal recycle in said process, dehydrogenating said cyclohexane from the bottoms of said first fractionation zone in a dehydrogenation zone in the presence of a chromia-alumina dehydrogenation catalyst at a temperature of from about 500° F. to about 1000° F., a pressure of from about atmospheric to about 500 pounds per square inch, and at a liquid hourly space velocity of from about 0.1 to about 100 to produce hydrogen and benzene, removing said benzene as the second product from the process, and recycling at least a portion of said hydrogen to the hydroisomerization zone as the sole source of makeup hydrogen therefor.

10. A combination hydroisomerization and dehydrogenation process for the simultaneous production of dimethylbutanes and benzene, said process self-sufficient in hydrogen requirement, which comprises passing to a first fractionation zone an isomerizable hexane hydrocarbon fraction in combination with liquid phase hydroisomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially cyclohexane-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction comprising cyclohexane, passing said cyclohexane bottoms fraction to a dehydrogenation zone hereinafter described, passing said substantially cyclohexane-free overhead hexane fraction from said first fractionation zone to a second fractionation zone as feed therefor, fractionating said hydrocarbons to produce an overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane, removing said overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes as one product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes, normal hexane, and methylcyclopentane along with hydrogen at least some of which is produced by dehydrogenation as hereinafter described to a hydroisomerization zone maintained at a temperature of from about 300° F. to about 500° F. and at a pressure of from about 100 to about 1000 pounds per square inch wherein methylpentanes, normal hexane, and methylcyclopentane are isomerized at a liquid hourly space velocity of from about 0.1 to about 10 in the presence of a hydroisomerization catalyst comprising platinum deposited on alumina impregnated with aluminum chloride to an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethylbutanes, methylpentanes, normal hexane, methylcyclopentane, and cyclohexane, recycling the hydroisomerization zone effluent to the first mentioned fraction zone as aforesaid to recover cyclohexane therefrom and to allow recovery therefrom of 2,2- and 2,3-dimethylbutanes produced in the process in said second fractionation zone as aforesaid and to separate methylpentanes, normal hexane, and methylcyclopentane as aforesaid for reuse and internal recycle in said process, dehydrogenating said cyclohexane from the bottoms of said first fractionation zone in a dehydrogenation zone in the presence of a molybdena-alumina dehydrogenation catalyst at a temperature of from about 500° F. to about 1000° F., a pressure of from about atmospheric to about 500 pounds per square inch, and at a liquid hourly space velocity of from about 0.1 to about 100 to produce hydrogen and benzene, removing said benzene as the second product from the process, and recycling at least a portion of said hydrogen to the hydroisomerization zone as the sole source of makeup hydrogen therefor.

References Cited in the file of this patent

UNITED STATES PATENTS

2,372,711	Cornforth	Apr. 3, 1945
2,395,022	Sutton et al.	Feb. 19, 1946
2,396,331	Marschner	Mar. 12, 1946
2,425,074	Waugh	Aug. 5, 1947
2,766,302	Elkins	Oct. 9, 1956