Oct. 23, 1962 J. J. WISE 3,060,249

VAPOR PHASE ISOMERIZATION PROCESS

Filed March 23, 1960 4 Sheets-Sheet 1

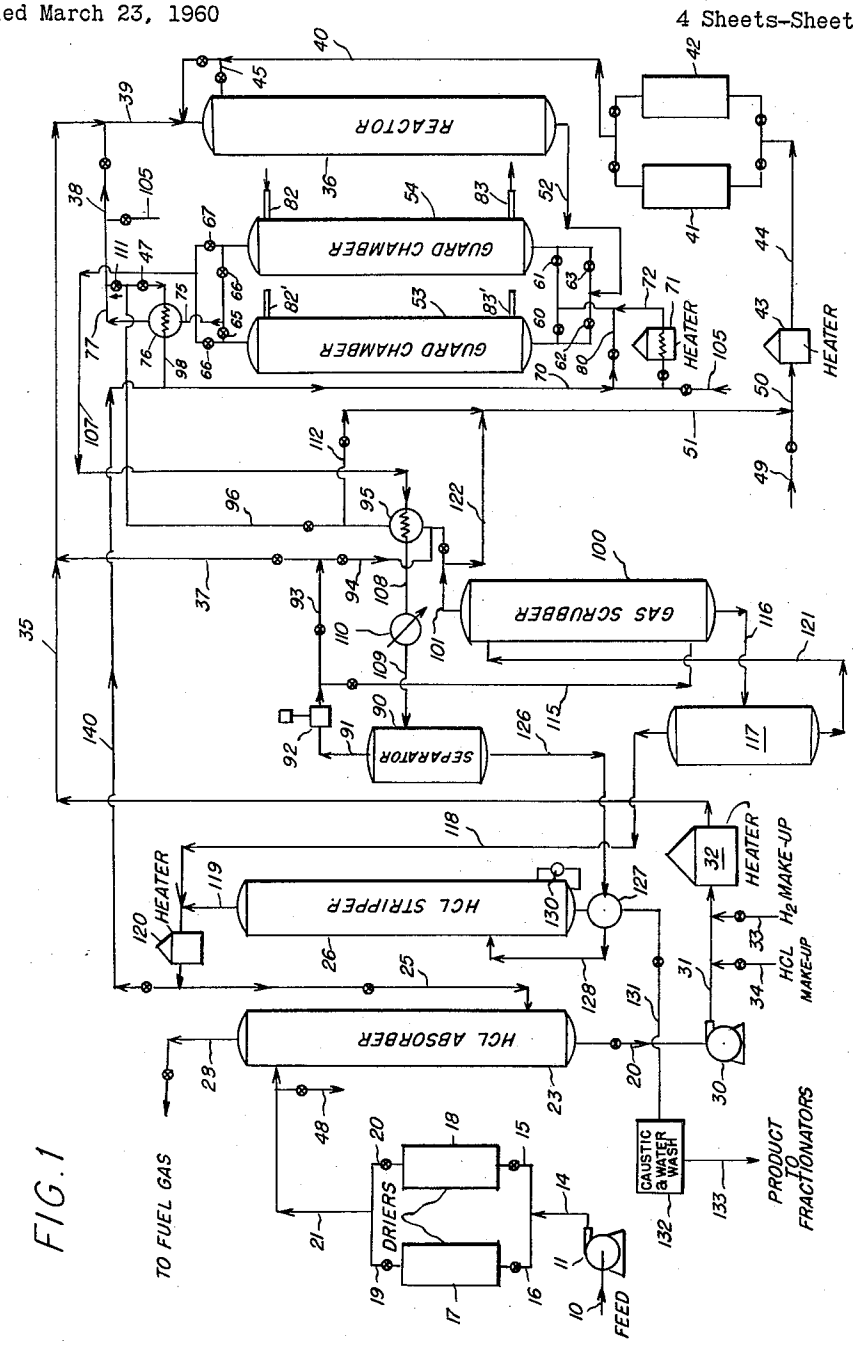


FIG. 1

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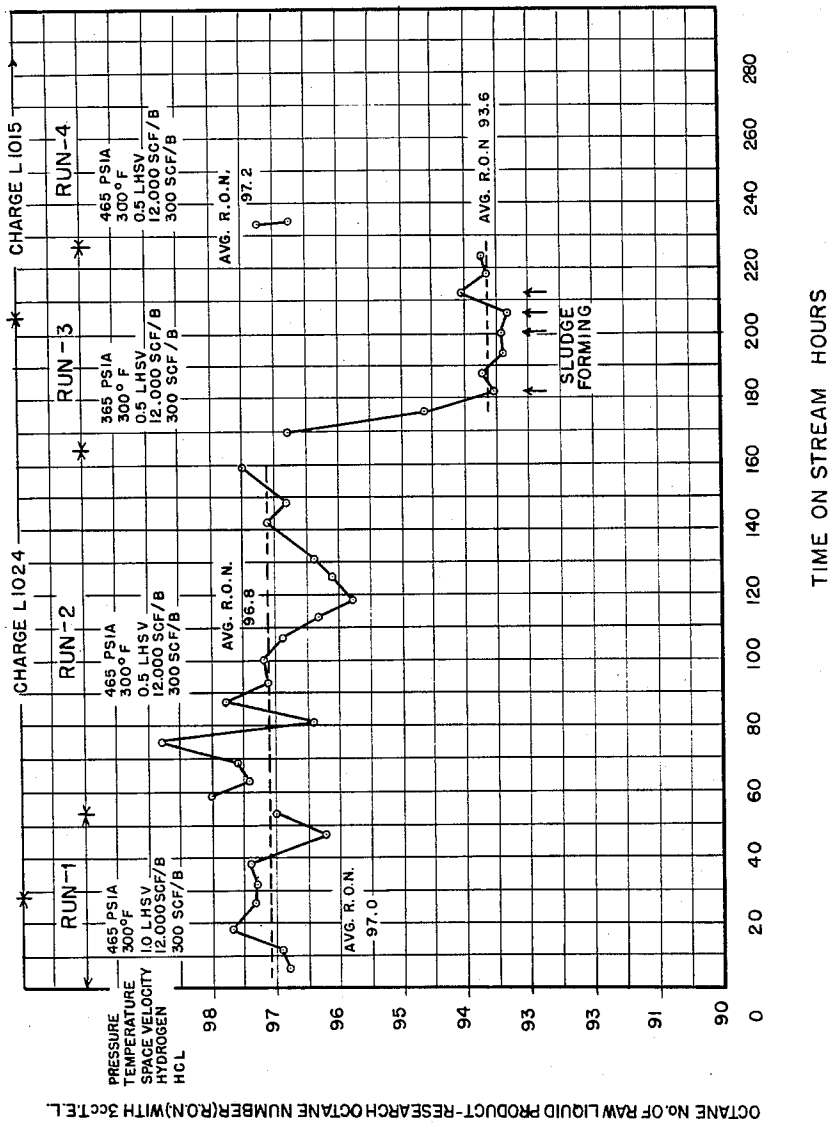
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Oct. 23, 1962 J. J. WISE 3,060,249

VAPOR PHASE ISOMERIZATION PROCESS

Filed March 23, 1960 4 Sheets-Sheet 2

FIG. 2



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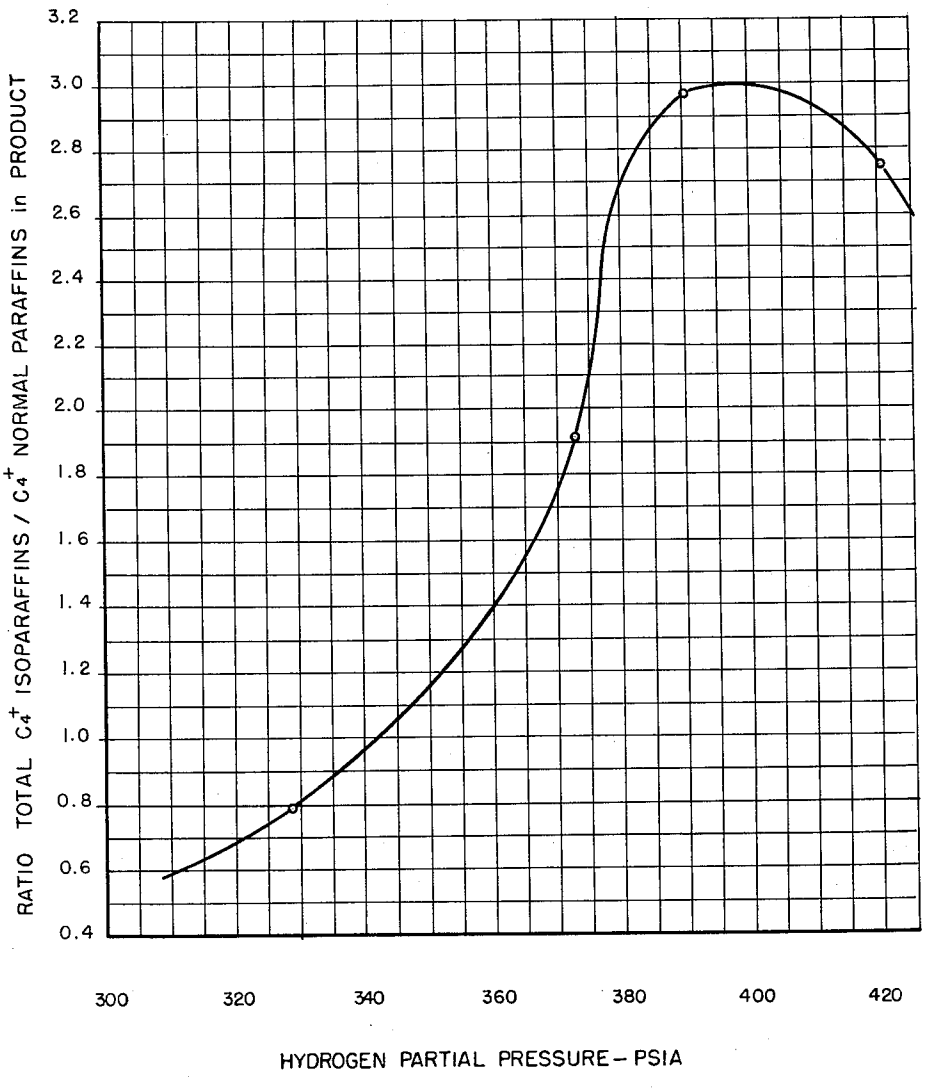
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Oct. 23, 1962 J. J. WISE 3,060,249

VAPOR PHASE ISOMERIZATION PROCESS

Filed March 23, 1960 4 Sheets-Sheet 3

FIG. 3



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Oct. 23, 1962 J. J. WISE 3,060,249

VAPOR PHASE ISOMERIZATION PROCESS

Filed March 23, 1960 4 Sheets-Sheet 4

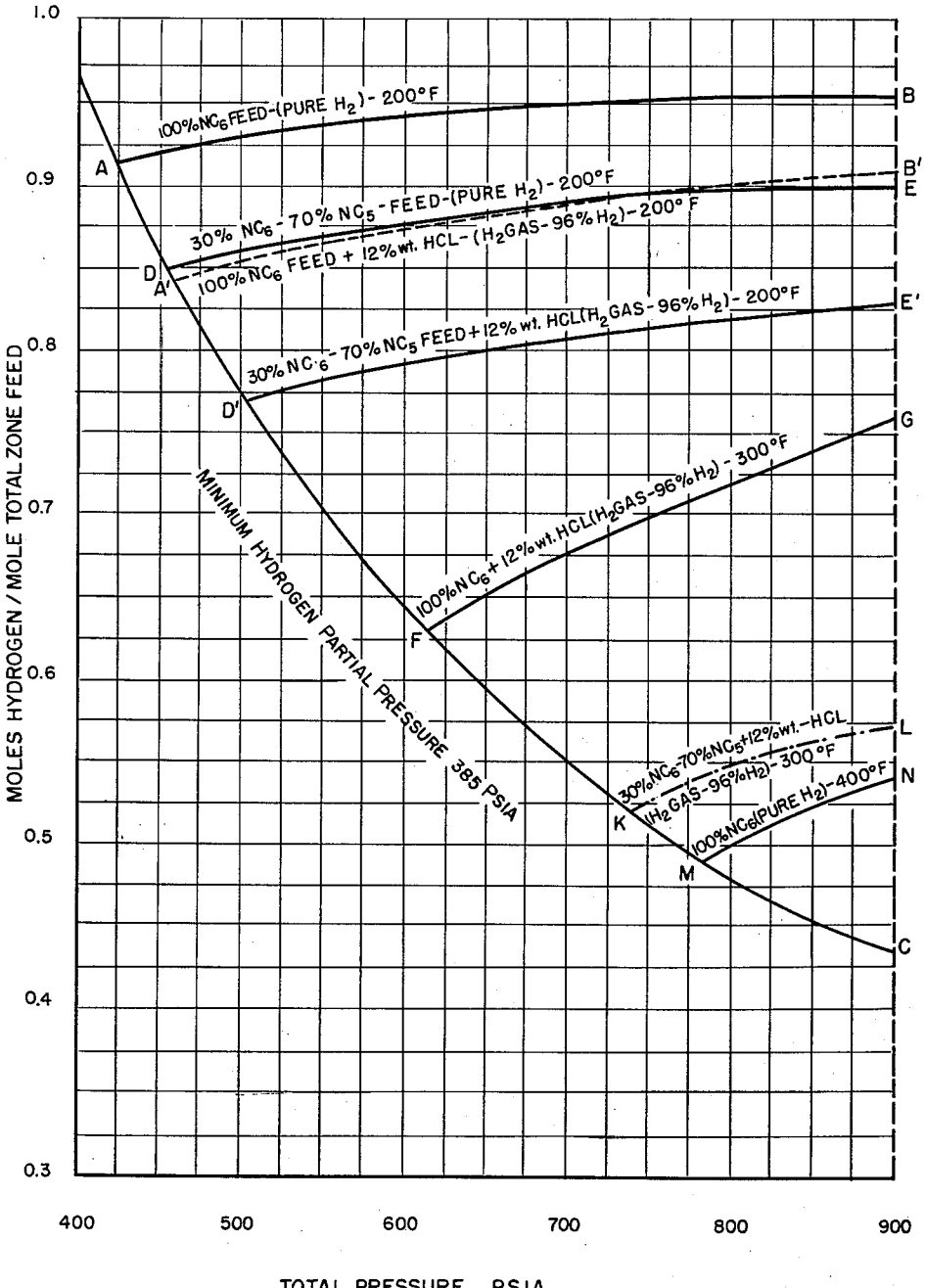


FIG. 4

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United States Patent Office 3,060,249 Patented Oct. 23, 1962

3,060,249

VAPOR PHASE ISOMERIZATION PROCESS

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Filed Mar. 23, 1960, Ser. No. 17,015
9 Claims. (Cl. 260—683.75)

This invention relates to a process for isomerization of saturated, aliphatic hydrocarbons in the gaseous or vapor phase in the presence of metal halide Friedel-Crafts-type catalysts. It is particularly concerned with an improved process for gaseous phase isomerization of hydrocarbon feed fractions made up primarily of saturated, aliphatic hydrocarbons within the range of C_4 to C_6 hydrocarbons and particularly feed stocks containing substantial amounts of saturated, straight chain C_6 hydrocarbons to produce high yields of corresponding branched chain, aliphatic hydrocarbons of high anti-knock value.

The use of metal halide catalysts of the Friedel-Crafts type for isomerization of C_4 to C_6 paraffin hydrocarbons is known in the prior art. Usually such processes have been conducted in the presence of suitable isomerization promoters, such as halogens and halogen compounds, particularly hydrogen halides. Most of such operations have been conducted in the liquid phase, particularly when the feed stock contained substantial amounts of paraffinic hydrocarbons having five to six carbon atoms per molecule. In general, such liquid phase operations have been of the batch or semi-batch type and have employed temperatures within the range of about 100 to 450° F. and pressures within the range of 500 to 4,000 pounds per square inch gauge. A promoter, such as hydrogen chloride, is usually added to the isomerizer in amounts ranging from 3 to 10% by weight of the feed. In some liquid phase operations, hydrogen partial pressures ranging up to 50 atmospheres have been employed in the isomerization zone for the purpose of repressing undesirable side reactions, such as cracking to lower molecular weight hydrocarbons, and prolonging catalyst life. It has been indicated in the prior art, however, that the use of excessive hydrogen partial pressures will inhibit the isomerization reaction. In the liquid phase processes, a metal halide-hydrocarbon complex is formed which acts as the isomerization catalysts. This complex is highly corrosive, particularly in the presence of hydrogen chloride. As a consequence, special alloy metals must be used for the reactor construction, and corrosion problems are still encountered in the product exchangers and recovery equipment unless special alloys are also employed for construction of this equipment.

Isomerization over Friedel-Crafts-type catalyst in the gaseous phase has apparently been restricted almost exclusively to normal butane feeds. Operation in the liquid phase has been preferred for isomerization of C_5 and C_6 paraffins because the reaction equilibrium constants for isomer formation are much more favorable at temperatures permissible in liquid phase operation than those which would ordinarily be required for gaseous phase operation. While some reference has been made to the possibility of isomerization of normal pentane and hexanes in the gaseous phase over metal halide-type catalysts in publications dealing primarily with vapor phase isomerization of normal butane, the operating conditions disclosed usually do not appear to be such as would insure the gas phase in the case of pentane and hexanes. Such prior art suggestions as have been found for gaseous phase isomerization of feeds containing substantial amounts of saturated, aliphatic C_5 or C_6 hydrocarbons over Friedel-Crafts-type catalysts are either entirely indifferent to addition of free hydrogen to the isomerization zone and to hydrogen partial pressure or suggest

the use of indefinite small amounts of hydrogen for the purpose of inhibiting side reactions, such as cracking. It has been suggested for an operation directed primarily to normal butane isomerization, but mentioning normal pentane, that hydrogen may be employed to carry aluminum chloride vapors into the gas phase reaction zone during the on-stream isomerization period. In this operation, the reaction was conducted at temperatures in the range of 150 to 400° F. and total pressures in the range of atmospheric to about 350 pounds per square inch. The rate of aluminum halide vapor introduction was controlled in this operation below the saturation point of the particle form porous catalyst carrier in the isomerization zone so that the effluent gaseous products from the isomerization zone remained free of aluminum halide.

A difficulty which has been noted in connection with isomerization of feeds containing normal pentane and hexane, and particularly normal hexane, is the tendency for the isomerization reaction to be inhibited and sludge to form at excessive rate due to the presence of relatively small amounts of benzene, C_5 to C_7 naphthenes or C_7 paraffins in the isomerization feed stock. Reduction of the content in the feed of the last-mentioned compounds to levels at which reaction inhibition and excessive sludge formation would be avoided is both difficult and costly.

A major object of this invention is the provision of an improved process for isomerization of saturated, aliphatic hydrocarbons having at least four carbon atoms per molecule in the gaseous phase in the presence of a Friedel-Crafts-type metal halide catalyst, which process is characterized by high yields of high octane isomer in the product and extended catalyst life for the isomerization reaction.

Another object is the provision of an improved gaseous phase process for isomerization of hydrocarbon feeds made up primarily of saturated, aliphatic hydrocarbons in the range of C_4 to C_6 hydrocarbons and containing substantial amounts of at least C_6 saturated, straight chain hydrocarbons, which process overcomes the above-mentioned problems heretofore encountered in the isomerization of such feeds.

A specific object is the provision of an improved process for isomerization of hydrocarbon fractions containing substantial amounts of C_6 saturated, straight chain hydrocarbons in the presence of metal halide Friedel-Crafts-type catalysts and suitable gaseous isomerization promoters, which process permits operation at low temperature levels conductive of high yields of high anti-knock value isoparaffin products without appreciable complex formation and attendant corrosion problems and without excessive side reactions and sludge formation, which have been found to inhibit isomerization and greatly reduce the effective active life of the catalyst.

Another specific object is the provision in a gaseous phase process for isomerization of C_4 and higher molecular weight saturated, aliphatic hydrocarbons in the presence of a metal halide Friedel-Crafts-type catalyst of an improved method for prolonging the effective life of the isomerization catalyst and for recovering and returning to the isomerization zone catalyst carried therefrom in the effluent product stream.

These and other objects will become more readily understood from the following description of the invention.

In a broad form, this invention involves a process wherein saturated, aliphatic hydrocarbon material having at least four carbon atoms per molecule is passed in the gaseous phase through a confined isomerization zone in which it is subjected to contact with a metal halide catalyst of the Friedel-Crafts type under conditions of temperature within the range of about 200 to 400° F. and

residence time of about 0.1 to 3 minutes suitable for effecting conversion of the hydrocarbon material to high yields of branched chain, aliphatic hydrocarbons of high anti-knock value. In accordance with the improvement of this invention, the total pressure is maintained within the range of about 400 to about 900 pounds per square inch absolute (hereinafter abbreviated as p.s.i.a.). Free hydrogen is continuously introduced into the isomerization zone at a rate controlled to provide a hydrogen partial pressure at least equal to a critical minimum of approximately 385 p.s.i.a. and below a maximum which is not in excess of about 800 p.s.i.a. The rate of hydrogen introduction is further controlled to provide a proportion of hydrogen relative to total gaseous material flowing through the isomerization zone, exclusive of any metal halide vapors, which is sufficient to maintain the hydrocarbon material in the gaseous phase under the temperature and total pressure conditions involved. In all cases, the proportion of free hydrogen to saturated, aliphatic C_4 and higher molecular weight hydrocarbon material is greater than about 0.43 mole and less than about 0.97 mole of hydrogen per mole of total gaseous material other than metal halide introduced to the isomerization zone.

In a preferred form, this invention involves a process in which the isomerization feed is made up primarily of saturated, aliphatic hydrocarbon material within the range of C_4 to C_6 hydrocarbons, which feed contains at least a substantial quantity of saturated, straight chain C_6 hydrocarbon material and appreciable amounts of at least one undesirable material selected from the group consisting of benzene, C_5 to C_7 naphthenes and C_7 paraffin hydrocarbons. The isomerization feed is passed in the gaseous phase with hydrogen chloride promoter through an isomerization zone containing a bed of particle form catalyst comprising aluminum chloride sorbed on a particle form, porous carrier, such as alumina or bauxite, at a temperature in the range of 200 to 400° F. and at a rate providing a residence time within the range of about 0.2 to 2 minutes suitable for effecting conversion of the saturated, aliphatic hydrocarbons, particularly the paraffinic hydrocarbons, to high anti-knock rating, isoparaffinic hydrocarbons of corresponding number of carbon atoms per molecule. In accordance with the preferred method of this invention, vaporized aluminum chloride mixed with a suitable inert carrier gas is introduced into the isomerization zone at least intermittently during the isomerization on-stream period at a rate in excess of about 0.005% by weight of the hydrocarbon feed and preferably within the range of about 0.85 to 1.7% by weight of the hydrocarbon feed, such rate being sufficient to insure the presence of some aluminum chloride vapors in the effluent product stream which is withdrawn from the isomerization zone. The total pressure within the isomerization zone is maintained within the range of about 400 to about 900 p.s.i.a., and free hydrogen is introduced into said zone at a rate controlled to provide a proportion of hydrogen relative to total gaseous feed to said zone, exclusive of any metal halide, which is in the range of about 0.43 to 0.97 mole of free hydrogen per mole of said total gaseous feed, the proportion being less than that which would provide a hydrogen partial pressure in the isomerization zone in excess of about 800 p.s.i.a., but at least equal to the greater of (*a*) the ratio of a hydrogen partial pressure of about 385 p.s.i.a. to the total pressure in the isomerization zone as expressed in the formula:

$$\frac{\text{Moles of hydroxgen}}{\text{Moles of total zone feed}} = \frac{385}{\text{Total pressure in p.s.i.a.}}$$

and (*b*) that required to maintain the hydrocarbon material in the gaseous phase.

In a further improvement, metal halide, such as aluminum chloride, is withdrawn from the isomerization zone in the gaseous product separated from the hydrocarbon product and recycled to the reaction zone. Preferably, the gaseous product is passed through a bed of solid adsorbent material to effect separation of the metal halide. Metal halide is subsequently stripped from the adsorbent material by a suitable inert stripping gas and introduced into the reactor with the stripping gas. In one preferred embodiment, a non-condensed, hydrogen-rich gas stream is separated from the isomerization products, and a portion of this stream is employed as the stripping gas. Another portion of the hydrogen-rich gas stream is treated to remove hydrogen halide and hydrocarbon gases and then employed as a carrier gas to vaporize and carry fresh make-up metal halide into the isomerization reactor.

In its broadest aspects, this invention is applicable to the gaseous phase isomerization of saturated, aliphatic hydrocarbons, particularly straight chain, saturated hydrocarbons, having at least four carbon atoms per molecule. The invention is particularly applicable to isomerization of feed stocks containing at least a substantial quantity (i.e., about 30% by volume or more) of straight chain, saturated C_6 hydrocarbon material. In addition to normal butane, normal pentane and normal hexane, the feed stock may contain substantial amounts of 2-methyl pentane or 3-methyl pentane or mixtures thereof. In some cases, the feed may also contain relatively small amounts of other isoparaffinic C_4 to C_6 hydrocarbons. The isomerization feed stock may comprise a fraction derived from light natural or straight run gasoline, or it may be derived by distillation from the products of any of a number of hydrocarbon conversion processes, such as cracking, reforming or hydrocracking. In the case of stocks containing large percentages of other than straight chain hydrocarbons boiling within the range of the desired isomerization feed fraction, solvent extraction or separation by adsorbents or molecular sieves may be employed to separate the desired straight chain, saturated hydrocarbon feed material from the other hydrocarbons. For example, molecular sieves of types well known in the art may be employed for effecting separation of isoparaffins from normal paraffins in an isomerization product stream so that the normal paraffins may be recycled to the isomerization process. In the case of cracked source stocks or other feed stocks containing olefins, it is generally necessary to substantially remove the olefins prior to isomerization, either by suitable, conventional methods (e.g., by catalytic hydrogenation) or by treatment with sulfuric acid. The sulfur content of the isomerization feed should be below about 20 parts per million by weight, and feed stocks from high sulfur crudes may require treatment by conventional means well known to the art to reduce sulfur content prior to isomerization. Since the presence of water causes excessive loss of catalyst from the isomerization zone, it is desirable to maintain the water content of the isomerization feed below about 20 parts per million by weight. Where necessary, the moisture content of the feed stock may be reduced by well known methods, such as contact with suitable desiccant materials.

As a practical matter, it has been found that feed fractions consisting principally of normal hexane or of mixtures of C_4 to C_6 or C_5 and C_6 straight chain, saturated hydrocarbons, which have been prepared by the usual practical refinery methods, also contain appreciable amounts of what have heretofore been considered as undesirable components, such as benzene, C_5 to C_7 naphthenes and C_7 paraffins. It has been found that, under such conditions as have been heretofore known for conducting gaseous phase isomerization of hydrocarbons, inhibition of the isomerization reaction and/or excessive sludge formation and catalyst consumption occurs when the hydrocarbon feed stock contains appreciable amounts of these compounds. For example, these difficulties will occur when C_4 to C_6 normal paraffin feed stock contains as little as 0.2% by volume benzene or 5% by volume C_5 to C_7 naphthenes or 3% by volume C_7 paraffins. The

removal of these compounds or the reduction of the feed content thereof would require very costly pretreatment of the hydrocarbon feed stock. This is unnecessary, however, in the process of this invention, which is capable of processing feeds containing substantial amounts of benzene, C_5 to C_7 naphthenes and C_7 paraffins over long periods of sustained operation without serious inhibition of the isomerization reaction or sludge formation and without excessive consumption of the isomerization catalyst. The gaseous phase isomerization process of this invention can tolerate, without difficulty, as much as 0.2 to 2% by volume of benzene or 5 to 25% by volume of C_5 to C_7 naphthenes or 3 to 10% by volume of C_7 paraffins or proportionately lesser percentages of mixtures of these compounds in the isomerization feed stock. It will be understood, of course, that the invention is also applicable to feed stocks containing lesser amounts of these compounds.

The catalyst employed in the process of this invention is a metal halide catalyst of the Friedel-Crafts type, such as an aluminum halide or a halide of zirconium, zinc, tin, antimony, boron, etc., or mixtures of the same. Preferably, an aluminum halide is employed, particularly aluminum chloride or aluminum bromide. It is desirable to support the metal halide on a porous, solid carrier capable of sorbing the metal halide. The porous support may take the form of natural or treated clays, such as fuller's earth, kaolin, bentonite, montmorillonite and superfiltrol; treated clay-like materials, such as tonsil, celite and sil-o-cel; artificially prepared or synthetic materials, such as magnesium oxide, silica gel, alumina gel, activated permutites and the like; or the zeolites, activated carbon, diatomaceous earth, kieselguhr, infusorial earth and the like. Adsorptive aluminas, bauxite or porocel are particularly desirable carrier materials. Activated alumina is an example of one very satisfactory form of alumina which may be employed as the carrier material. Activated alumina is a well known crystalline alpha alumina monohydrate prepared by partial dehydration of crystalline alpha alumina trihydrate. Another highly satisfactory form of alumina is currently marketed by the Aluminum Corporation of America under the name F–10 Alumina. F–10 Alumina is partially dehydrated chi alumina. It is prepared by precipitation of alpha alumina trihydrate from an aluminate solution below 140° F. After filtering and drying, the material is calcined between 536 and 842° F. to effect partial dehydration of the alumina. The carrier material may take the form of particles of palpable size, as distinguished from finely divided powders. For example, the particles may fall in the size range of about 4 to 100 mesh and preferably 8 to 28 mesh by Tyler standard screen analysis. The particles may take the form of pellets, rods, capsules, pills, spheres, tablets or granules of irregular shape, such as obtained by grinding. The term "particle form," as employed herein in describing and claiming this invention, is intended to generically cover the carrier material in any or all of the shapes and sizes above discussed. It is important, prior to preparation of the supported catalyst, to reduce the moisture content of the carrier below the point where water would be released under the isomerization conditions for which the catalyst is to be employed. This is accomplished by calcining or drying by any of the customary methods at temperatures usually in the range of about 800 to 1,500° F. Thus, for example, a bauxite carrier may be dried by heating for about 18 to 24 hours to 950 to 1,000° F. or 2 to 4 hours at 1,300° F.

A chi alumina, such as the one identified above as F–10 Alumina, which was calcined during manufacture at temperatures in the range of 750 to 1,470° F. until the ignition loss on a sample thereof at 2,000° F. was only 3%, was found to be highly suitable for use as a carrier material. The metal halide may be initially combined with the carrier material in any of a number of conventional ways. Thus, the carrier may be finely ground, ultimately mixed with measured amounts of anhydrous metal halide in powdered form, and the resulting mixture pilled with or without a binder material. Alternatively, the particle form carrier, such as alumina, may be mixed with measured amounts of metal halide in the form of particles or pieces and a mixture heated in a closed container to a temperature above the sublimation temperature of the metal halide whereby the metal halide becomes impregnated upon the carrier particles.

In still another method for initial preparation of the catalyst, the metal halide, for example, aluminum halide, may be sublimed by means of a suitable, heated, inert carrier gas and the mixture then passed through a bed of adsorbent carrier particles under temperature and pressure conditions at which the metal halide is sorbed by the porous carrier material. The gas employed to carry the sublimed metal halide should be one which both exists in the gaseous phase and also is substantially inert with regard to the metal halide under the conditions employed for the sublimation and impregnation steps. The term "inert carrier gas" is employed herein in this sense in describing and claiming the invention. The inert carrier gases employed may vary widely in other characteristics. Carrier gases which may be employed alone or in admixture with each other include, by way of example, nitrogen, carbon dioxide, hydrogen, methane, ethane, propane, normal or isobutane. Halogens or hydrogen halides, such as chlorine or hydrogen chloride, may be employed; but, in this case, it is preferred to exclude C_4 and higher molecular weight hydrocarbons from the system during the sublimation and impregnation operation. Similarly, dry air may be employed as the carrier gas in the absence of hydrogen and hydrocarbons or other combustible materials. The metal halide may be sublimed by passing heated carrier gas over a mass of heated metal halide or through a bed made up of chunks or particles of metal halide. The temperature required for the sublimation varies, depending upon the rate of sublimation desired, the pressure on the system, the composition of the metal halide and the amount of carrier gas employed. In general, for sublimation of aluminum chloride, for example, the temperature employed may range from 250° F. at essentially atmospheric pressure to as high as 500° F. for pressures of 500 to 600 p.s.i.a. In cases where higher pressures are involved, somewhat higher temperatures may be employed. In the impregnation zone, the pressure may, in some cases, be as low as atmospheric pressure during impregnation; but usually the pressures employed correspond, in general, to those employed for the isomerization reaction, i.e., 400 to 900 p.s.i.a. Temperatures in the impregnation zone are generally maintained within 50 to 100° F. plus or minus of the temperatures to be employed for the isomerization reaction. Usually, the initial impregnation of the carrier is continued until the carrier has become saturated with metal halide under the conditions involved. However, this is not, in all cases, essential, since the carrier may be subsequently saturated with metal halide as a result of the addition of the same to the isomerization zone during the on-stream period, as described hereinafter. The amount of metal halide required to saturate the porous carrier varies, depending upon the metal halide, porous carrier material and conditions involved. For example, porous aluminas may contain from about 15 to 25% by weight of aluminum chloride when saturated, silica gel may sorb up to 28% by weight, and certain absorptive clays may become saturated with as little as 8% by weight aluminum halide. When activated alumina or partially dehydrated chi alumina is employed as the porous carrier, the composite for initial use in the isomerization process of this invention may contain 5 to 20% and preferably 15 to 20% by weight of aluminum chloride, i.e., sufficient to essentially saturate the carrier.

When operating in accordance with the method of this

invention, actual catalyst consumption is very small, being of the order of 0.1 to 0.3% by weight of total hydrocarbon feed. However, due to the high proportion of hydrogen gas introduced with the feed in accordance with the method of this invention, appreciable amounts of metal halide are released from the porous carrier during operation and carried from the isomerization zone in the effluent gas stream. This is particularly true when the operation is conducted near the lower end of the allowable pressure range, under which conditions the required proportion of hydrogen to hydrocarbon is particularly high. In general, the amount of metal halide carried from the reactor in the product vapors may range from as low as 0.005% by weight total hydrocarbon feed to slightly less than about 2.0% by weight. In order to make up for the metal halide swept from the reaction zone by the reactant vapors, in the preferred form of the invention, metal halide vapors are introduced into the isomerization zone, either intermittently or continuously, during the on-stream period. The amount so added in order to compensate for the small amount of catalyst actually consumed and the catalyst escaping in the effluent product vapors varies, depending upon the operating conditions and the nature of the hydrocarbon feed stock, proportion of hydrogen gas introduced with the feed and the nature of the catalyst and porous carrier material. In some cases, the total rate of metal halide addition may be only slightly in excess of about 0.005% by weight of the hydrocarbon feed. Usually, it will exceed 0.10% by weight of the feed. In most operations, it is desirable to introduce the metal halide at a rate somewhat is excess of that which would merely maintain the porous carrier saturated so that the entering vapors contain slightly more metal halide than the porous carrier is in condition to pick up by sorption under the operating conditions involved. Hence, usually the metal halide is introduced during the on-stream period at a rate within the range of about 0.1 to 2.0% by weight and preferably 0.85 to 1.7% by weight of the hydrocarbon feed. Best results have thus far been obtained when aluminum chloride is added to the reactor during the on-stream period at rates within the range of about 2 to 4 pounds per barrel of total hydrocarbon feed. The metal halide is introduced to the reaction zone during the on-stream period as a vapor mixed with a suitable inert carrier gas. Any of the inert carrier gases mentioned hereinabove in connection with the initial impregnation of the porous carrier may be employed, excepting air. Particularly suitable inert carrier gases are normal butane or hydrogen or mixtures of hydrogen and hydrogen chloride. The metal halide may be heated to form vapors which are mixed with the inert carrier gas, or the heated carrier gas may be passed in contact with metal halide in a sublimation zone to effect vaporization of the metal halide. The mixture of metal halide and inert carrier gas may be separately introduced into the isomerization zone or mixed with the hydrocarbon or hydrogen feed streams prior to introduction. The pressure maintained in the sublimation zone is approximately the same or slightly higher than that employed in the isomerization zone, and the temperature is similar to that employed during initial impregnation of the porous carrier material.

Metal halide which is removed from the reactor in the product stream may be separated from the conversion products in any of a number of ways. For example, the product stream, the whole of which is in the gaseous phase under the conditions of operation, may be cooled to condense the metal halide, with or without the addition of a scrubbing fluid, such as cool normal butane under pressure; and, thereafter, the condensed metal halide may be separated from the conversion products. As shown hereinafter, metal halide is preferably removed from the gaseous product stream by passage of the product, either without cooling or after partial cooling, through a bed of porous, solid adsorbent material to effect sorption of the metal halide thereon, thereby effecting the separation from the gaseous conversion products. In accordance with the preferred form of the invention, separated metal halide is recycled to the isomerization zone during the on-stream period as a portion of the metal halide supply thereto. Since the amount of metal halide carried from the reactor in the gaseous products usually exceeds the amount of metal halide actually consumed in the operation, the recovered metal halide which is recycled to the reactor usually constitutes a major portion of the total metal halide supplied during the on-stream period. Usually, it is preferred to recycle essentially all of the recovered metal halide and to make up the difference between the desired total rate of metal halide supply to the reactor during the on-stream period and the recycle metal halide by introduction of fresh metal halide in the manner discussed hereinabove. While it is preferred to introduce the recycle and make-up metal halide into the reactor continuously during the isomerization operation, it is also contemplated that the metal halide may be introduced intermittently at intervals of the order of 0.5 to 16 hours. If desired, the periods of introduction of recycle metal halide and make-up metal halide may be staggered so as to more closely approach continuous metal halide introduction. It will be understood that, when the introduction of metal halide into the isomerization zone during the on-stream period is intermittent, the instantaneous rate of introduction will be somewhat higher than the rates specified hereinabove, which are intended to indicate the average overall rates.

The isomerization reaction is conducted in the presence of a suitable promoter material. Any of a number of suitable promoters well known in the art may be employed, such as hydrogen halides, bromine, chlorine, chloroform, carbon tetrachloride, lower alkyl halides such as methyl, ethyl, propyl and butyl chlorides or bromides and nitroparaffins such as nitroethane or nitropropane. Gaseous hydrogen halides, particularly hydrogen chloride or hydrogen bromide, are preferred isomerization promoters. The amount of gaseous promoter added may range broadly from about 0.4 to about 30% by weight of the hydrocarbon feed and preferably from about 2 to about 25% by weight.

Reactant residence time and temperature to be employed in the isomerization zone are, to some extent, interrelated and should be correlated with respect to each other to provide the desired conversion and selectivity of conversion for the particular feed stock concerned. Reaction severity increases with increasing temperature and decreasing residence time, and required severity of conditions increases generally with decrease in molecular weight of the hydrocarbon feed. In general, the reactant residence time, i.e., time of contact with the catalyst bed in the isomerization zone, should be broadly within the range of about 0.1 to 3 minutes and preferably within the range of about 0.2 to 2.0 minutes. Reaction temperature should be maintained within the range of about 200 to 400° F. and preferably 300 to 400° F. in the process of this invention.

Total pressure maintained in the isomerization zone should be within the range of 400 to 900 p.s.i.a. and preferably within the range of 400 to 600 p.s.i.a. Contrary to previous belief, it has been discovered, that, in the vapor phase isomerization of straight chain, saturated C_4 to C_6 hydrocarbons over Friedel-Crafts-type catalyst, careful control of the proportion of hydrogen in the total feed mixture and of the partial pressure of hydrogen in the isomerization zone is of critical importance to the attainment of a product of maximum octane number and containing maximum proportions of desired branched chain isomers. Careful control of the hydrogen is also of critical importance to the ability to attain the desired conversion results at low catalyst consumption and in an

operation which can be sustained over long periods of time without interruption. It has been found important in the present invention to introduce hydrogen or hydrogen-containing gas into the isomerization reactor at a rate controlled to provide a hydrogen partial pressure of at least about 385 p.s.i.a. when the reaction temperature is in the range of 200 to 400° F. and the reactant residence time is within the range of about 0.2 to 2.0 minutes. The critical minimum hydrogen partial pressure varies slightly with residence time within the range of 0.2 to 2.0 minutes and to a somewhat lesser extent with a temperature within the range of 200 to 400° F., increasing with increase in residence time and temperature. However, this variation is small, being less than about ±5% for variations from 400° F. and 1 minute residence time within the range indicated. The invention is also applicable to operations in which the reactant residence time is as low as 0.1 minute and as high as 3 minutes; but it will be understood that the variation in the critical minimum hydrogen partial pressure may be somewhat greater than that above indicated for these extreme limits. Since little advantage has been found in providing hydrogen partial pressures in excess of about 800 p.s.i.a., the hydrogen partial pressure in the isomerization zone is maintained within the range of about 385 to 800 p.s.i.a. In addition, it is very important to provide a sufficient proportion of hydrogen in the total gaseous mixture introduced to the isomerization zone to maintain the hydrocarbon feed in the gaseous phase. Expressed in another way, in accordance with this invention, the rate of hydrogen introduction to the isomerization zone is controlled to provide a proportion of hydrogen to total zone feed which is at least equal to the greater of (*a*) the ratio of a hydrogen partial pressure of about 385 p.s.i.a. to the total pressure in the isomerization zone as expressed in the formula:

$$\frac{\text{Moles of hydrogen}}{\text{Moles of total zone feed}} = \frac{385}{\text{Total pressure in p.s.i.a.}}$$

and (*b*) that required to maintain the hydrocarbon feed in the gaseous phase. The term "total zone feed," as employed herein in describing and claiming this invention, is intended to mean the total gaseous feed to the isomerization zone, excepting metal halide. This includes hydrocarbon feed stock, promoter and the hydrogen gas stream with any gaseous diluents therein. Unless otherwise expressly stated, the terms "gas" and "gaseous" are employed herein in describing and claiming this invention in a sense sufficiently broad to include any material which exists in the gaseous phase under the operating conditions involved, irrespective of the normal phase of such material under ordinary atmospheric conditions. It has been found that, when the rate of hydrogen introduction is controlled in the manner above described, the proportion of hydrogen to hydrocarbon feed will generally be in excess of about 0.43 and below about 0.97 and preferably below about 0.90 mole of hydrogen per mole of total zone feed. It has been found that, when the proportion of hydrogen to total zone feed is permitted to fall below the critical minimum above expressed, the isomerization reaction is substantially inhibited with resultant decrease in the percentage of desired branched chain isomers and loss of octane rating in the liquid product. This appears to occur in operations conducted on both essentially pure normal paraffinic C_4 to C_6 hydrocarbon feeds and on straight chain, aliphatic fractions of hydrocarbons within the range of C_4 to C_6 hydrocarbons prepared by usual refinery operations, which fractions usually contain appreciable amounts of any or all of benzene, C_5 to C_7 naphthenes and C_7 paraffinic hydrocarbons. Particularly in the case of the latter feed stocks, it has been found that the inhibition of the isomerization reaction is accompanied by excessive sludge formation and catalyst consumption. It has been found to be important to control the rate of hydrogen supply in the manner above indicated, not only in those preferred operations in which metal halide is also introduced into the isomerization reactor during the on-stream period, but also for those less preferred operations in which there is no metal halide addition during the on-stream period.

Hydrogen consumption in the process of this invention is small, ranging from about 50 to 200 standard cubic feet per barrel of feed, depending upon operating conditions and the feed stock.

While this invention is particularly applicable in once-through or single pass isomerization operations, since it permits high single pass conversion of normal paraffins to products containing high proportions of isoparaffins, the process is also applicable to recycle operations.

The invention may be more fully understood by reference to the accompanying drawings, of which

FIGURE 1 is a diagrammatic flow plan of a system arranged for operation in accordance with the process of this invention;

FIGURE 2 is a graph showing the importance of careful control of hydrogen partial pressure in the process of this invention;

FIGURE 3 is a graph showing the effect of changes in the partial pressure of hydrogen on the isoparaffin to paraffin hydrocarbon ratio in the isomerization product; and

FIGURE 4 is a graph showing the variation of miniimum hydrogen requirements with total pressure for various normal hexane-containing feed compositions in the gaseous phase isomerization process of this invention.

Referring to FIGURE 1, there is shown therein a digrammatic flow plan of a system adapted for conduct of the isomerization process of this invention. For the purpose of describing the arrangement and operation of this system, the processing of a saturated, aliphatic C_4 to C_6 petroleum hydrocarbon feed fraction, prepared by usual refinery distillation procedures, will be discussed. The feed fraction, which is a 170° F. end point light naphtha, contains about 5.8% by volume saturated, aliphatic C_4 hydrocarbons, 11.2% by volume isopentane, 21.9% by volume normal pentane, 1.7% by volume dimethyl C_4 hydrocarbons, 20.5% by volume methyl pentanes, 20.9% by volume normal hexane, 15.4% by volume C_5 to C_7 naphthenes, 1.2% by volume benzene and 1.4% by volume C_7 paraffinic hydrocarbons. The feed stock is drawn via conduit **10** into pump **11**, by which it is forced via conduits **14** and **15** to drier **18** containing a suitable desiccant material, such as granular alumina. The dried feed stock passes from the drier **18** via conduits **20** and **21** to the hydrogen chloride absorber **23**. It will be noted that two drier towers **17** and **18** are shown. These are arranged connected for parallel flow so as to permit alternative operation, one drier being employed for the purpose of removing moisture from the naphtha feed, while the desiccant in the other drier is being revivified by usual methods.

In the specific example, the feed stock does not contain olefins or substantial percentages of sulfur compounds. However, it will be appreciated that, when the feed stock does contain olefins, it should be treated to effect removal thereof prior to use for isomerization. This may be effected by treatment of the feed stock with 90 to 98% sulfuric acid or with chlorosulfonic acid under conditions well known in the art. Subsequent to the acid treating, the naphtha may be subjected to caustic washing in suitable scrubbing towers, not shown, for the purpose of removing sulfur compounds. In some instances, the olefins and sulfur content of the naphtha feed stock may have been reduced by subjecting the same to a conventional catalytic hydrogenation treatment in which the olefins are converted to saturated hydrocarbons and the sulfur compounds are converted to hydrogen sulfide. Since methods for removing olefins and sulfur compounds from feed stocks are well known in the art, it is considered unnecessary to further describe these methods herein. The liquid feed stock is passed down-

wardly through the hydrogen chloride absorber tower 23 countercurrently to a gaseous stream entering via conduit 24 from the hydrogen chloride stripper 26. The hydrogen chloride absorber may be operated at pressures in the range of 50 to 400 p.s.i.g., with top temperatures ranging from 50 to 125° F. and bottom temperatures ranging from 100 to 200° F. In a typical operation, when the tower is maintained at a pressure of about 250 p.s.i.g., the top temperature is about 100° F., and the bottom temperature is about 150° F. The naphtha feed dissolves the hydrogen chloride content and any C_4 or heavier hydrocarbons in the gas stream entering via conduit 25 so that an overhead gas may be withdrawn from the top of the absorber which is essentially free of hydrogen chloride. The overhead gas which is made up of a small amount of hydrogen and C_1 to C_3 hydrocarbons is passed via conduit 28 to the refinery fuel gas system. Naphtha feed stock containing dissolved hydrogen chloride passes via conduit 29 and pump 30 and conduit 31 to heater 32. It is usually preferable to introduce make-up hydrogen via conduit 33 and make-up hydrogen chloride via conduit 34 into a naphtha feed stream passing to heater 32. The mixture is heated to a suitable isomerization charge temperature in heater 32, for example, a temperature of 300° F. At a total pressure of about 435 p.s.i.a., the gaseous feed stream passes via conduits 35 and 39 to the isomerization reactor 36. While only one reactor 36 is shown, it will be understood that a plurality of such reactors may be employed connected for either parallel or series flow. It is preferred to provide a plurality of reactors connected in parallel flow so that the operation may be continuous, one or more reactors being employed for conducting the isomerization reaction while a spare reactor is off-stream for revivification of the catalyst. While, in accordance with the present invention, it is possible to operate the reactors for extended periods of time, eventually it becomes desirable to shut down a given reactor in order to remove from the solid carrier material carbonaceous impurities which gradually accumulate. In general, the catalyst may be regenerated by stripping the remaining metal halide from the porous carrier with a suitable inert stripping gas, usually at elevated temperature, and thereafter burning the carbonaceous deposits with a mixture of air and inert gas. Thereafter, the porous carrier may be cooled and reimpregnated with metal halide in the manner described hereinbefore. The reactor 36 may be of any shape and construction suitable for supporting therein a bed of the particle form catalyst. For example, the reactor may be a vertical, cylindrical chamber having reactant inlet and outlet nozzles connected through its opposite, closed ends and having across its lower section a perforated grid or support plate adapted to support the particle form catalyst mass. While the reactor, as shown in the drawing, is arranged for downward flow of the gaseous hydrocarbons, it will be understood that, in some operations, it may be more desirable to pass the gaseous reactant upwardly through the bed in the reactor.

A bed of isomerization catalyst is maintained in the reactor, the bed being made up of particles of porous carrier material impregnated with metal halide. In the present illustration, the catalyst in the reactor 36 is comprised of about 18% by weight aluminum chloride deposited upon granules of 8 to 14 mesh (Tyler) adsorbent alumina, which has been dried by calcining at 750 to 1,470° F. so that ignition loss on heating a sample thereof at 2,000° F. was 3% by weight. The dried alumina was placed in the reactor in the form of a bed and heated to about 250° F. Hydrogen gas heated to about 260° F. was passed at about 400 p.s.i.a. into contact with chunks of solid aluminum chloride in a suitable aluminum chloride pick-up chamber to effect sublimation of the aluminum chloride. The hydrogen gas stream mixed with sublimed aluminum chloride vapors was then passed at about 250° F. and 400 p.s.i.a. through the bed of porous alumina in the reactor 36 until the aluminum chloride content of the composite mass in the reactor reached about 18% by weight. The catalyst was then considered ready for initial contact with hydrocarbon reactants under desired isomerization conditions.

Isomerization conditions maintained in the reactor 36 are, for example, temperature —300° F., total pressure —435 p.s.i.a., and space velocity —0.5 volume of hydrocarbon feed per hour per volume of catalyst bed in the reactor (hydrocarbon volume measured as liquid at 60° F.) This space velocity corresponds to a reactant residence time in the catalyst bed under conditions employed of about 0.54 minute. The gaseous hydrogen chloride content of the stream entering the reactor is about 300 standard cubic feet per barrel of hydrocarbon feed. The gaseous hydrogen chloride enters the reactor system in part as make-up hydrogen chloride introduced into the hydrocarbon feed stream via conduit 34 and in part as recycle hydrogen chloride mixed with recycle hydrogen, which is introduced into the heated reactant feed stream via conduit 37. Additional hydrogen chloride may enter the reactor 36 along with recycle metal halide via conduits 38 and 39. The rate of hydrogen gas introduction to the reactor is controlled to provide a hydrogen partial pressure in the gaseous reactant stream of at least about 385 p.s.i.a. and to maintain the hydrocarbon reactants in the gaseous phase under the temperature and pressure conditions involved. In this illustration, the amount of hydrogen gas entering the reactor 36 is about 12,000 standard cubic feet per barrel of hydrocarbon feed. This amounts to about 20% by weight of the total zone feed (zone feed meaning total gaseous material passing to the reactor excepting metal halide vapors). Recycle hydrogen is introduced via conduit 37 into the heated reactant feed stream passing to the reactor via conduit 35. As will be further discussed thereinafter, some hydrogen may enter the reactor from the guard chambers via conduit 38 and from the aluminum chloride pick-up chambers via conduit 40. Make-up hydrogen may be added to the system before the heater 32 via conduit 33. Alternatively, make-up hydrogen may be added to the hydrocarbon feed stream downstream of the heater 32, or the make-up hydrogen may be separately introduced directly into reactor 36 through suitable inlets, not shown. Hydrogen consumed in the operation may amount to about 50 to 200 standard cubic feet of hydrogen per barrel of hydrocarbon feed.

Aluminum chloride vapors mixed with an inert gas are introduced, in part from conduits 40 and 44 and in part from conduit 39, into the reactor 36 at the total average rate of about four pounds of aluminum chloride per barrel of hydrocarbon feed. Two pick-up drums 41 and 42 are provided for vaporizing the aluminum chloride supplied to the reactor. It will be noted that the pick-up drums are arranged connected in parallel so as to permit alternate use thereof, one drum being filled with fresh aluminum chloride, while the other drum is in use. Aluminum chloride is placed in the pick-up drums in particle form or in the form of chunks; and a hot, inert gas which has been heated in heater 43 to a temperature of about 300° F. is introduced from the conduit 44 into the pick-up drum in use and passed upwardly through the mass of aluminum chloride therein. By this means, the aluminum chloride is vaporized and carried from the pick-up drum to the reactor via conduits 40 and 44. In this arrangement, the vaporized aluminum chloride-inert gas mixture is admixed with the hydrocarbon reactant stream just prior to introduction to the reactor 36. It will be understood that alternatively the aluminum chloride-inert gas mixture may be separately introduced into the reactor 36 from conduit 40 via conduit 45. It will also be understood that suitable heaters or jackets may be provided in connection with pick-up drums 41 and 42 to assist in the sublimation of the aluminum chloride.

Usually, it is convenient to maintain the pick-up drum which is in use at a pressure only slightly above that in the reactor 36. As has been indicated hereinbefore, the inert carrier gas employed in the pick-up drums 41 and 42 may consist of a portion of the hydrocarbon feed which has been bypassed around the hydrogen chloride absorber 23 via conduit 48 and introduced to the heater 43 via conduits 49 and 50. In some operations, it is preferable to employ normal butane as the carrying gas rather than the hydrocarbon stream containing higher molecular weight hydrocarbons. Usually, when hydrocarbon material is employed as the carrier gas, it is preferred to exclude hydrogen chloride from the aluminum chloride pick-up system in order to prevent sludge formation in the pick-up drums and associated transfer conduits. Alternatively, fresh hydrogen chloride may be employed as the carrier gas, in which event the hydrogen chloride may be introduced via conduit 49. Preferably, a portion of the recycle hydrogen stream, which may or may not have been purified to remove hydrogen chloride and hydrocarbons, may be introduced via conduits 51 and 50 to heater 43 for use as the aluminum chloride carrier gas. The amount of inert carrying gas employed will depend in part upon the desired rate of aluminum chloride feed and upon the temperature to which the aluminum chloride is heated. In the present illustration, about 300 standard cubic feet of enriched hydrogen gas is supplied to the pick-up drums per pound of aluminum chloride to be sublimed and carried to the reactor. In the present illustration, aluminum chloride is introduced into reactor 36 from the pick-up drums on an intermittent basis, the flow from the pick-up drums alternating with that from the guard chamber 53 or 54. In general, the aluminum chloride consumption in the reactor amounts in this example to only about 0.5 pound per barrel of hydrocarbon feed.

Gaseous isomerization reaction products containing slightly less than about four pounds of aluminum chloride vapors per barrel of feed are withdrawn from reactor 36 via conduit 52 and passed upwardly through one of the guard chambers 53 or 54. The guard chambers 53 and 54 are packed with a suitable porous material capable of sorbing the metal halide vapors and thereby effecting separation of the metal halide from the gaseous reaction products. The adsorbent material employed in the guard chamber may consist of any of the porous carrier materials described hereinabove as suitable catalyst supports. In this example, a dried bauxite is employed which is in the form of granular particles falling in the size range 8 to 16 mesh (Tyler) and having a density of about 55 pounds per cubic foot. It is usually preferable to employ two or more guard chambers so that one may be employed to effect separation of the metal halide from the gaseous reactant stream while the bauxite in the other chamber is being stripped to effect removal of metal halide therefrom. Although not in all cases necessary, it is usually desirable to maintain a somewhat lower temperature in the guard chamber than that maintained in the isomerization reactor during the period when the guard chamber is being employed to sorb metal halide from the reactant stream; for example, where the reactor temperature is 300° F., the temperature in the bauxite guard chamber is maintained at about 250° F., the pressure being about the same as that in the reactor, namely, 435 p.s.i.a. It will be understood, however, that other conditions may be employed in the guard chamber, it merely being necessary to so correlate the temperature and pressure conditions in the guard chamber in such a manner as to insure essentially complete removal of the metal halide from the reaction product stream. In general, the temperature in the guard chamber may range from 50 to 250° F. over a pressure range varying from atmospheric to 450 p.s.i.a. When the guard chamber has become essentially saturated with metal halide, metal halide vapors will begin to appear in the reactant stream leaving the guard chamber, at which point the gaseous reaction product stream is diverted to another guard chamber containing fresh bauxite; for example, when the gaseous reaction products are passing through guard chamber 54, valves 63 and 67 are open, and valves 61, 62, 66 and 68 are closed. When the bauxite in chamber 54 has become saturated with metal halide, valves 62 and 68 are opened so as to permit flow of gaseous reaction products through chamber 53, and valves 60, 63, 65 and 67 are closed. Cycle hydrogen is then introduced via conduit 70 to heater 71, from which it passes via conduit 72 to the conduit containing valve 61, which is then opened so as to permit heated hydrogen stripping gas to pass upwardly through the guard chamber 54. The heated hydrogen gas, which may enter the guard chamber 54 at a temperature of about 450° F., gradually heats the bauxite in chamber 54 to about 400° F. so that metal halide sorbed thereon is stripped from the bauxite and withdrawn in the vapor state from the top of guard chamber 54. Valve 66 is opened so as to permit the mixture of stripping gas and sublimed aluminum chloride vapors to pass via conduit 75, heat exchanger 76, conduits 77, 38 and 39, back to the isomerization reactor 36. Stripping gas is passed through chamber 54 until at least most of the metal halide has been removed from the bauxite, after which the chamber is ready for cooling. This may be accomplished by lowering the temperature of the stripping gas introduced to chamber 54; for example, by bypassing the flow around the heater 71 through conduit 80. Alternatively, heat transfer tubes may be provided in the guard chamber, and a suitable cooling fluid may be passed therethrough using inlet and outlet connections 82 and 83. It will also be understood that the heat transfer tubes may be employed for heating the guard chamber prior to the stripping operation by passage of a suitable heating fluid through the heat transfer tubes; for example, high pressure steam may be employed. When the guard chamber has been finally cooled to about 250° F. in this illustration, it is again ready for use in removing metal halide from the reaction product stream. It will be noted that the stripping gas supplied to the guard chambers from conduit 70 originates as an overhead stream from the hydrogen chloride stripping tower 26 and is comprised of a mixture of hydrogen, hydrogen chloride and low molecular weight hydrocarbons, such as C_1 to C_3 hydrocarbons. In general, this stream may contain about 30% by weight hydrogen and about 20% by weight hydrogen chloride. Alternatively, the stripping gas for the guard chambers may consist of a portion of the hydrogen-rich gas stream which was removed from the top of separator 90 via conduit 91. This gas stream may be passed to the guard chambers via compressor 92, conduit 93, conduit 94, exchanger 95, conduit 96, conduit 97, exchanger 76, conduits 98 and 70, heater 71, conduit 72 and manifold means-containing valve 61. This stream may be comprised of about 25% hydrogen and 17% hydrogen chloride by weight, the remainder being low molecular weight hydrocarbons. In still another alternative, enriched hydrogen gas may be employed as the stripping gas, in which event, the stripping gas stream is obtained from the overhead from gas scrubber 100, from which it flows via conduit 101, exchanger 95, conduit 96, conduit 97, exchanger 76 and conduits 98 and 70 through heater 71. This gas may be essentially pure hydrogen. If desired, a hydrocarbon such as normal butane may be employed as the stripping gas in the guard chambers, in which event, the hydrocarbon may be admitted to the heater 71 via conduit 105. When it is desired to effect removal of the aluminum chloride from the guard chamber without substantial heating of the guard chamber, it is useful to increase the hydrogen chloride content of the stripping gas. This may be done by introducing hydrogen chloride to the heater via conduit 105 to mix with hydrogen stripping gas supplied from any of the sources hereinabove mentioned. It will be noted that, in the arrange-

ment herein described, the stripping gas stream leaving the guard chamber **54** along with sublimed aluminum chloride vapors at a temperature of about 400° F. is partially cooled to a temperature of the order of 300 to 325° F. in exchanger **76** prior to introduction to the reactor **36**. This cooling is accomplished by exchanging heat between the hot stripping gas stream and a stripping gas feed stream entering the exchanger from conduit **97**, as hereinabove described. The amount of metal halide recovered from the guard chamber and recycled to the reactor usually consists of the major portion of the metal halide which is introduced to the reactor during the on-stream period. Thus, for example, of a total of four pounds of metal halide per barrel of hydrocarbon feed introduced into the reactor **36**, three and a half pounds may be supplied from the guard chamber as recycle metal halide, whereas the remainder is supplied from one of the pick-up drums **41** and **42** as fresh make-up metal halide. It will be understood that, in less preferred forms of the invention, metal halide recovered from the guard chambers may be diverted via conduit **105** to a separate system in which the metal halide is condensed and separated from the stripping gas instead of being recycled via conduit **38** to the reactor **36**. In this event, all of the metal halide introduced into the reactor during the on-stream period is obtained from the pick-up chambers **41** and **42**.

The gaseous reaction products which have been essentially freed of metal halide pass via conduit **107**, exchanger **95**, conduit **108**, condenser **110** and conduit **109** to the separator **90**. In this illustration, separator **90** is maintained at a pressure of about 400 to 410 p.s.i.a. and at a temperature of the order of 60 to 125° F. A non-condensed stream consisting of about 95% hydrogen, the remainder being hydrogen chloride and C_1 to C_4 hydrocarbons, is withdrawn from the top of separator **90** via conduit **91**. As hereinbefore described, a portion of this stream may be employed as stripping gas for the guard chambers **53** and **54**. Another and major portion of the stream may pass via conduits **93** and **37** to conduit **35**, in which it is mixed with the hydrocarbon feed stream flowing to the reactor **36**. Alternatively, where it is desired to increase the amount of heat exchange in the exchanger **95**, hydrogen cycle gas is passed via conduits **93** and **94** to and through heat exchanger **95**, from which it passes via conduits **96**, **111**, **38** and **39** to reactor **36**. In this event, a portion of the hydrogen gas stream passing through conduit **96** may be bypassed through conduit **112**, from which it flows through conduits **51** and **50** to the heater **43** for use in the aluminum chloride pick-up chambers **41** and **42**.

As has been previously indicated, it is preferred to employ an enriched or purified hydrogen stream in the aluminum chloride pick-up chambers. For this purpose, a portion of the hydrogen-rich gas stream from separator **90** is passed from conduit **93** into conduit **115**, through which it passes to gas scrubber **100**. The gas stream then passes upwardly through the gas scrubber **100** countercurrently to a suitable liquid scrubbing medium to effect removal of hydrogen chloride and low molecular weight hydrocarbons. Normal butane or normal pentane may be employed as the scrubbing liquid in scrubber **100**. The gas scrubber may be operated at a temperature of the order of 60 to 100° F. and pressures in the range of 650 to 900 p.s.i.g. The rich scrubbing liquid leaves the bottom of scrubber **100** via conduit **116**, through which it passes to flash drum **117**, maintained at a pressure of the order of 250 p.s.i.g., for example. Dissolved hydrogen chloride and low molecular weight hydrocarbons are released from the scrubbing fluid in the flash chamber **117** and passed therefrom via conduit **118** to join the overhead stream from the hydrogen chloride stripper **26** prior to passage through heater **120**. Scrubbing fluid, such as normal butane, is recovered from the bottom of the flash drum **117** at a temperature of about 60 to 100° F. and returned to the top of the gas scrubber **100** via conduit **121**. Essentially pure hydrogen gas is withdrawn from the top of scrubber **100** via conduit **101**, from which it passes via conduit **122** and conduts **51** and **50** to the heater **43** for use in aluminum chloride chambers **41** and **42**. As hereinabove stated, a portion of the enriched hydrogen gas stream may be employed for stripping purposes in guard chambers **53** and **54**; but usually it is preferred to employ cycle gas from the separator **90** which has not been further purified.

Liquid hydrocarbon products containing some dissolved hydrogen chloride are withdrawn from the bottom of separator **90** and passed via conduit **126**, exchanger **127** and conduit **128** to the hydrogen chloride stripper **26**. The stripper **26** is maintained under conditions suitable for effecting removal of hydrogen and hydrogen chloride from the liquid hydrocarbon product material. As an example, stripper **26** is maintained at a pressure of about 250 p.s.i.g. with a top temperature ranging from 100 to 150° F. and a bottom temperature ranging from about 300 to 400° F. Heat in the stripping tower is obtained by means of reboiler **130**. Liquid isomerization products containing reduced percentages of normal paraffins and increased percentages of branched chain isoparaffins, as compared to the feed stock, are withdrawn from the stripper **26** via exchanger **127** and conduit **131**. The liquid products are treated in a suitable caustic and water washing system **132** for the purpose of removing any remaining traces of hydrogen chloride and then withdrawn to storage via conduit **133**.

The overhead stream from stripper **26** contains hydrogen, hydrogen chloride and C_1 to C_3 hydrocarbons. This stream may be withdrawn via conduit **119** and passed through a suitable heater or exchanger **120**, from which it passes via conduit **25** to hydrogen chloride absorber **23**. As hereinabove mentioned, hydrogen chloride is recovered from the stream in the absorber **23**. Also as previously mentioned, a portion of the overhead stream from the hydrogen chloride stripper **26**, together with gas recovered from the flash tower **117**, may be passed via conduits **140** and **70** to the guard chamber system wherein it may be employed as stripping gas.

The C_4 to C_7 isomerized product recovered from conduit **133** may be employed as such as a low boiling range blending constituent in preparation of high octane motor fuels. The isomerized product stream may be blended with a heavy reformate such as that obtained from a process for reforming naphthas over suitable dehydrogenation catalysts or with a naphtha fraction obtained from catalytic cracking operations. Alternatively, the isomerized product stream may be employed as a source of feed material for an alkylation process. In this connection, it may be desirable to fractionate the C_4 to C_6 isomerized product so that the isobutane and isopentane may be separately employed for alkylation of C_3 to C_4 olefinic hydrocarbons under suitable conditions. It will be understood that it is also within the scope of this invention to fractionate the product stream from the isomerization unit to effect recovery therefrom of normal paraffins so that the normal paraffins may be recycled as a portion of the feed to the isomerization reactor. Systems for effecting separation of paraffins from branched chain isomers are well known in the art and may include separation by simple fractionation or the use of molecular sieves, for example.

EXAMPLE 1

A reactor having an internal diameter of about 2¼ inches was filled with about 2.4 pounds of the particle form alumina identified hereinbefore as F–10 Alumina, so as to provide a bed having a vertical depth of about 16 inches. The alumina employed was composed principally of chi alumina and was prepared by the method discussed hereinabove. The alumina had been calcined at temperatures in the range of 750 to 1,450° F. to effect dehydration. Analysis of a sample of the alumina showed

96% by weight alumina, 0.9% by weight sodium oxide, 0.09% by weight ferric oxide, 0.09% silica and 0.58% chlorine. Loss on ignition at 2,000° F. was about 3% by weight. The alumina was made up of 8 to 14 mesh (Tyler) particles having a packed bulk density of 55 pounds per cubic foot. Pore volume as determined by helium and mercury displacement in accordance with the method described by L. C. Drake and H. L. Ritter in Industrial and Engineering Chemistry, Analytical edition, volume 17, pages 789–791 (1945) was 0.3 milliliter per gram. Surface area as determined by absorption of nitrogen according to the method of Brunnauer et al., Journal of the American Chemical Society, volume 60, pages 309 et seq. (1938) was 100 square meters per gram. Average pore diameter as determined by methods described by Drake et al. (supra) was 80 angstroms. The alumina was impregnated by passage through the bed thereof of a stream of hydrogen containing sublimed aluminum chloride vapors in the manner described in connection with FIGURE 1. Impregnation conditions included a temperature of 250° F. and a pressure of 400 p.s.i.g. Impregnation was continued until the content of aluminum chloride in the bed was about 15% by weight. This catalyst was employed over a period of continuous, sustained operation for effecting isomerization of two similar 170° F. end point light naphtha feed stocks derived by usual refinery distillation of straight run petroleum stocks. The two feed naphthas differed in minor respect as regards exact hydrocarbon composition. Both of these feed stocks contained appreciable quantities of benzene, C_5 to C_7 naphthenes and C_7 paraffins. The composition and octane rating of the two feed stocks are indicated on Table I. During the operation, hydrogen chloride was added as a promoter at the rate of about 300 standard cubic feet per barrel of the hydrocarbon feed stock. Aluminum chloride vapors mixed with hydrogen carrier gas was added to the reactor continuously during the operation at a rate of about 4.1 pounds per barrel of the hydrocarbon feed. This amounted to 1.3% by weight of the total zone feed, exclusive of the aluminum chloride vapors. Except for a preliminary period during which space velocity was 1.0, the space velocity was maintained at about 0.5 volume of hydrocarbon feed stock (measured at 60° F.) per hour per volume of catalyst bed in the reactor. Total hydrogen (calculated as pure hydrogen) supplied to the reactor, including that added with the aluminum chloride vapors, amounted to 12,000 standard cubic feet per barrel of hydrocarbon feed. This amounted to 0.895 mole of hydrogen per mole of total zone feed, exclusive of aluminum chloride vapors. During that portion of the operation conducted in accordance with this invention, the total pressure was maintained at about 465 p.s.i.a., thereby providing a hydrogen partial pressure of about 416 p.s.i.a. However, during an intermediate period of the operation, the total pressure was permitted to drop to about 365 p.s.i.a., corresponding to a hydrogen partial pressure of 326 p.s.i.a., in order to show the effect of permitting the hydrogen partial pressure to drop below the critical minimum. Operating conditions and composition and properties of the products taken at intervals during the sustained period of operation are summarized in Table I.

Table 1

Charge Stock	L–1024, 170° F. E.P. Lt. Naph.	L–1025, 170° F. E.P. Lt. Naph.	L–1024	L–1024	L–1025	L–1025
			Run Number			
			119A–16	119B–30	119C–18	119D–2
Processing Conditions:						
Total Pressure, p.s.i.a.			465	465	365	465
Temperature, °F.			300	300	300	300
Space Velocity, vol./hr./vol.			1.0	0.5	0.5	0.5
Residence Time, min.			0.27	0.54	0.42	0.54
Hydrogen Introduced, moles/mole Total Zone Feed (Calculated as Pure Hydrogen)			0.895	0.895	0.894	0.894
Hydrogen Introduced, s.c.f./bbl. Hydrocarbon Feed			12,000	12,000	12,000	12,000
Hydrogen Purity, percent wt. Hydrogen			100	100	100	100
HCl Introduced, wt. percent of Hydrocarbon Feed			11.1	11.1	11.1	11.1
$AlCl_3$ Introduced During On-stream Period:						
lb./bbl. Hydrogen Feed			≈9	4.1	4.1	4.1
Percent wt. Hydrogen Feed			≈4	1.8	1.8	1.8
$AlCl_3$ Introduction—Intermittent or Continuous			Continuous			
$AlCl_3$ Concentration on Catalyst Composite, wt. percent $AlCl_3$			[1]≈15–20	[1]≈15–20	[1]≈15–20	[1]≈15–20
Hydrogen Partial Pressure, p.s.i.a.			416	416	336	416
Yields Based on Hydrocarbon Feed,[2] percent vol. (No Loss Basis):						
Methane						
Ethane						
Propane			2.1	2.1	1.6	2.4
Total Dry Gas			2.1	2.1	1.6	2.4
Isobutane	0 5	1.1	6.8	6.2	4.7	6.9
Normal Butane	5.3	6.7	5.0	4.9	5.3	5.3
Total C4's	5.8	7.8	11.8	11.1	10.0	12.2
Isopentane	11.2	14.0	20.6	22.6	15.8	20.8
Normal Pentane	21.9	23.8	10.7	10.2	15.3	10.3
Total Paraffinic C_5's	33.1	37.8	31.3	32.8	31.1	31.1
2,2-Dimethyl Butane	0.4	0.3	9.1	9.5	2.8	7.9
2,3-Dimethyl Butane	1.3	1.2	4.3	4.1	4.4	4.6
2-Methyl Pentane	11.9	11.1	14.4	15.9	13.5	14.4
3-Methyl Pentane	8.6	6.9	9.2	8.7	8.6	9.2
Normal Hexane	20.9	17.3	7.4	7.1	12.1	7.2
Total Paraffinic C_6's	43.1	36.8	44.4	45.3	41.4	43.3
Total C_5–C_7 Naphthenes	15.4	13.0	9.7	8.6	14.1	10.7
Benzene	1.2	1.1	1.0	0.8	1.0	1.0
Total C_7 Paraffins	1.4	3.5	1.1	1.0	1.0	0.6
Grand Total	100.0	100.0	101.4	101.7	100.2	101.3

See footnotes at end of table.

Table I—Continued

Charge Stock	L-1024, 170° F. E.P. Lt. Naph.	L-1025, 170° F. E.P. Lt. Naph.	L-1024	L-1024	L-1025	L-1025
			Run Number			
			119A-16	119B-30	119C-18	119D-2
General:						
Hydrogen Consumption, s.c.f./bbl. Hydrocarbon Feed (Calculated)				155	35	98
Yield C_5+ Product, Percent vol. of Total Hydrocarbon Feed			87.5	88.5	88.6	86.7
Yield C_5+ Product, Percent vol. of C_5+ Feed			92.9	94.0	96.1	94.0
Net C_4 Make, Percent vol. of Hydrocarbon Feed			6.0	5.3	2.2	4.4
Ratio Isoparaffinic C_4's/Normal C_4's in Product			1.4	1.3	0.9	1.3
Ratio Isoparaffinic C_5's/Normal C_5's in Product			1.9	2.2	1.0	2.0
Ratio Isoparaffinic C_6's/Normal C_6's in Product			5.0	5.4	2.4	5.0
Ratio Dimethyl Butanes/Normal C_6's and Methyl C_5's in Product			0.43	0.43	0.21	0.41
Product Octane Number:						
Liquid Product—Research Octane Number +3 cc. TEL	90.5	91.6	97.0	96.8	93.6	97.2
C_5+ Product Calc. Research Octane Number +3 cc. TEL			94.3	94.7	91.6	94.6

[1] Assumed to be saturated (≈15–20% wt. $AlCl_3$) since $AlCl_3$ continuously admitted.
[2] For charge stock data, refer to initial composition.

Referring to FIGURE 2, there is presented a graph plotting the number of hours on-stream since the start of the isomerization operation described above under Example 1 against the research octane number of the C_4 plus liquid hydrocarbon product leaded with 3 cc. of tetraethyl lead. It will be noted that a number of points representing product samples taken at different intervals during the operation are plotted on FIGURE 2. Operating conditions and charge stock employed during different periods of the sustained operation are indicated in FIGURE 2 above the graph. Referring both to FIGURE 2 and to Table I, it will be noted that, when the hydrogen partial pressure was permitted to drop to 326 p.s.i.a., the product octane dropped off rapidly by about 3.5 research octane numbers, i.e., from an average of 97.0 to 97.1 to an average of about 93.6. During this period, it was noted that sludge was forming on the catalyst. When the hydrogen partial pressure was again increased to 416 p.s.i.a., product octane increased to the level attained prior to pressure reduction. Reference to the data in Table I shows that, during the period when the hydrogen partial pressure was low, there was a marked decrease in the isomers formed. For example, during the period when the hydrogen partial pressure was 326 p.s.i.a., the ratio of isopentane to normal pentane and the ratio of dimethyl butane to other hexanes in the product were only about half the corresponding ratios during the period of operation when the hydrogen partial pressure was 416 p.s.i.a.

EXAMPLE 2

An isomerization catalyst was prepared by mixing 3 pounds of alumina of the same type employed for Example 1 with 0.6 pound of solid aluminum chloride particles in a 2-liter capacity, closed shaker bomb. The bomb was heated slowly over a period of one hour to a temperature of 360° F. and then maintained at this temperature for 75 minutes, whereby the aluminum chloride was sublimed and sorbed by the alumina. The bomb was cooled over a period of 0.5 hour to room temperature, and then the catalyst was removed. The catalyst was screened to remove fines. The screened material consisted of particles of 8 to 14 mesh size range and were found to contain about 18% aluminum chloride, the remainder being the porous alumina carrier. About 0.7 pound of this catalyst was arranged as a bed in the same reactor described in Example 1. A feed stock consisting of 97.4% by volume normal hexane, 1.8% by volume 3-methyl pentane and 0.8% by volume residue was subjected to isomerization over this catalyst in a series of runs conducted under conditions summarized in Table II.

Table II

Run Number	22	31	41	38
Processing Conditions:				
Total Pressure, p.s.i.a	430	430	430	430
Temperature, ° F	400	400	400	400
Space Velocity, vol./hr./vol	0.68	0.34	0.19	0.18
Residence Time, min	0.8	0.9	1.1	0.9
H_2 Introduced, moles/mole Total Zone Feed (Calculated as Pure H_2)	0.77	0.87	0.91	0.93
H_2 Introduced, s.c.f./bbl. Hydrocarbon Feed	4,000	8,000	12,400	16,100
H_2 Purity, percent wt. H_2	100	100	100	100
HCl Introduced, wt. percent Hydrocarbon Feed	7.7	7.7	7.7	7.7
$AlCl_3$ Introduced during On-Stream Period	None	None	None	None
$AlCl_3$ Concentration on Catalyst Composite, wt. percent $AlCl_3$	17.9	17.9	14.2	13.3
H_2 Partial Pressure, p.s.i.a	329	373	391	400
Yields Based on Hydrocarbon Feed (No Loss Basis):				
Dry Gas, C_1–C_3, wt. percent	1.3	2.4	2.9	4.5
Isobutane, vol. percent	4.4	6.7	12.8	12.5
Butenes, vol. percent	0.1		0.5	
Normal Butane, vol. percent	1.0	0.8	1.3	2.2
Isopentane, vol. percent	4.8	4.6	8.3	7.9
Pentenes, vol. percent				0.1
Normal Pentane, vol. percent	2.7	2.0	1.8	2.1
Cyclopentane, vol. percent	0.4	0.2	0.5	0.2
2,2-Dimethyl Butane, vol. percent	2.6	5.1	9.0	10.9
2,3-Dimethyl Butane, vol. percent	5.8	8.2	7.4	6.8
2-Methyl Pentane, vol. percent	15.5	23.6	21.6	20.4
3-Methyl Pentane, vol. percent	9.6	15.2	13.6	12.9
Normal Hexane, vol. percent	50.2	30.2	21.4	21.9
Residue	1.9	2.3	1.5	0.7
General:				
Normal Hexane Conversion, vol. percent (No Loss Basis)	48.5	69.0	78.0	77.5
Yield C_4 Free Liquid, vol. percent (No Loss Basis)	93.5	91.4	85.1	83.8
Ratio Isoparaffin/Normal Paraffin in C_4+ Product	0.79	1.92	2.96	2.73
Ratio Isoparafinic C_6's/Normal Parafinic C_6's in Product	0.67	1.7	2.4	2.3
Ratio Isoparaffinic Dimethyl Butanes/Normal C_6's and Methyl C_5's in Product	0.11	0.19	0.29	0.32
Calc. R.O.N. (+3 cc. TEL):				
C_4 and Normal C_5+ Free Liquid	96.6	96.6	97.6	97.7
C_4 Free Liquid	79.7	86.2	89.4	89.2

NOTE.—Hydrocarbon Feed Stock:
3-Methyl Pentane—1.8% vol.
Normal Hexane—97.4% Vol.
Residue—0.8% vol.

It will be noted that the runs were, in general, conducted under similar operating conditions except that the proportion of hydrogen relative to the hydrocarbon feed was varied. The hydrocarbon space velocity was adjusted for different hydrogen charge rates so that the reactant residence time in the catalyst bed remained essentially constant for all runs. Since the total pressure was maintained constant, the hydrogen partial pressure changed with change in hydrogen to hydrocarbon feed ratio.

Fresh catalyst prepared in a manner similar to that described above was used in each run. Although the aluminum chloride content of the catalyst used in each run was slightly different, it was sufficiently high for all runs, so that the change in content did not seriously affect the isomerization results under the space velocity conditions employed. Yields and octane ratings of the resulting isomerization products are summarized in Table II. It will be noted that, with increasing hydrogen partial pressure, the conversion of normal hexane, the ratio of isoparaffins to normal paraffins in the C_4 plus product, the ratio of isoparaffinic C_6's to normal paraffinic C_6's, and the ratio of isoparaffinic dimethyl butanes to normal C_6's and methyl C_5's in the product all increased up to a certain critical hydrogen partial pressure. Beyond this minimum hydrogen partial pressure little, if any, further improvement is obtained. These data clearly demonstrate the critical importance of maintaining the hydrogen partial pressure above a critical minimum level to the attainment of a product of maximum octane rating and containing maximum proportions of desirable branched chain isomers.

Referring to FIGURE 3, the ratio of branched chain paraffin to normal paraffin in the C_4 to C_6 hydrocarbon product from the several runs covered in Example 2 is plotted against the hydrogen partial pressure in the isomerization zone. It will be noted that the ratio of total C_4 plus isoparaffins to C_4 plus normal paraffins in the product decreases rapidly with decreasing hydrogen partial pressure below a hydrogen partial pressure of about 385 p.s.i.a. Increasing hydrogen partial pressure beyond 385 p.s.i.a. results in little, if any, further improvement in isomer formation.

Referring now to FIGURE 4, curve A—C thereon graphically indicates the minimum proportion of hydrogen relative to total zone feed (exclusive of metal halide vapors), expressed as moles of hydrogen per mole of total zone feed required to maintain the minimum allowable critical hydrogen partial pressure of about 385 p.s.i.a. in the isomerization zone for different total pressures within the range of 400 to 900 p.s.i.a. Curve A—B shows the minimum mole proportion of pure hydrogen relative to total zone feed required to maintain the hydrocarbon feed stock in the gaseous phase for an isomerization reaction in which the operating temperature is 200° F., there is no hydrogen chloride promoter addition, the hydrogen introduced to the zone is pure hydrogen and the hydrogen feed stock is pure normal hexane.

Curve A'—B' shows the proportion of hydrogen required when the hydrogen gas introduced consists of 96% hydrogen and 4% C_1 to C_3 hydrocarbons, and hydrogen chloride is introduced at a rate of 12% by weight of the hydrocarbon feed stock, the hydrocarbon feed stock being 100% normal hexane and the temperature being 200° F. Curves D—E and D'—E' show the mole proportion of pure hydrogen required to maintain the hydrocarbon feed stock in the gaseous phase when the hydrocarbon feed stock consists of 30% by weight normal hexane and 70% by weight normal pentane, other conditions being the same as for curves A—B and A'—B', respectively.

Curves F—G and M—N show the minimum proportion of pure hydrogen required to maintain the hydrocarbon feed stock in the gaseous phase at 300° F. and 400° F., respectively, other conditions being the same as for curve A—B.

Curve K—L shows the minimum proportion of pure hydrogen required to maintain the hydrocarbon feed stock in the vapor phase at 300° F., other conditions being the same as for curve D—E.

As has been shown hereinabove, in the process of this invention, it is important to control the rate of hydrogen introduction into the isomerization reactor to provide a hydrogen partial pressure of at least about 385 p.s.i.a., and also to provide a proportion of hydrogen relative to total zone feed sufficient to maintain the hydrocarbon feed material in the gaseous phase under the selected isomerization conditions. The minimum proportion of hydrogen required to satisfy these two requisites will usually be different for each requisite at any given set of operating conditions. The minimum amount of hydrogen required to maintain the hydrogen partial pressure at least equal to the critical minimum varies with total pressure in the isomerization zone, as is shown by curve A—C in FIGURE 4. The minimum proportion of hydrogen required to maintain the hydrocarbon feed in the gaseous phase varies as shown in FIGURE 4 with the composition of the hydrocarbon feed stock, the temperature, the total pressure, the amount of gaseous promoter other than hydrogen introduced and the purity of the hydrogen gas introduced. In any case, the minimum proportion of hydrogen relative to total zone feed which may be tolerated in the process of this invention must be at least equal to the greater of (*a*) that at which the hydrogen partial pressure is about 385 p.s.i.a. and (*b*) that required to maintain the hydrocarbon feed in the gaseous phase. FIGURE 4 may be employed to estimate the minimum hydrogen proportion required over the range of feed stocks and other conditions shown thereon. For example, assume that the isomerization feed stock consists of 30% normal hexane and 70% normal pentane; the desired temperature is to be 200° F.; total pressure—450 p.s.i.a.; hydrogen chloride promoter added—12 weight percent of feed; and the hydrogen gas used is 96% purity. It will be noted that, in this case, the proportion of hydrogen required to maintain the gaseous phase, as indicated by curve D'—E', is 0.75 mole of hydrogen per mole of total zone feed; whereas the amount required to provide a hydrogen partial pressure of 385 p.s.i.a. is 0.86 mole of hydrogen per mole of total zone feed. In this example, the latter amount represents the minimum proportion of hydrogen which could be employed in accordance with the process of this invention. In another example, assume that the feed stock is 100% normal hexane, the hydrogen introduced is pure hydrogen, no hydrogen chloride is introduced, the temperature is 200° F., and the total zone pressure is 700 p.s.i.a. In this case, the proportion of hydrogen, as required by the hydrogen partial pressure curve A—C, is only 0.55 mole of hydrogen per mole of total zone feed; whereas that required by the appropriate curve A—B is 0.95 mole of hydrogen per mole of total zone feed. The latter proportion, being the greater, is controlling in this example. By reference to curve M—N, it will be apparent that the proportions of hydrogen to total feed employed for the runs tabulated in Table II are such that in all cases the reactant was in the vapor phase and the minimum allowable hydrogen proportion was governed by the critical minimum hydrogen partial pressure requirement. From curve A—C, it will be apparent that the minimum allowable proportion of hydrogen to total feed for the total zone feed and total pressure and temperature conditions involved in the runs presented in Table II is about 0.90 mole ratio. It will be apparent that the minimum proportion of hydrogen required for operation in accordance with the process of this invention may be estimated by interpolation for other feed stocks and operating conditions from the graph in FIGURE 4. For more accurate estimates, curves similar to A—B, A'—B', D—E, K—L, etc. may be added to the graph on the basis of suitable vapor pressure calculations of known type. It will be apparent that, in general for feed stocks of lower average molecular weight than those shown on the graph, the curves showing the minimum proportion of hydrogen required to maintain the feed stock in the gaseous phase will fall either below curve A—B or below curve A—C. Since operations cannot be conducted below curve A—C in accordance with the method of this invention, it will be apparent that, in

all cases, the minimum proportion of hydrogen relative to total zone feed which may be employed in accordance with the method of this invention shall not be less than the minimum proportion falling within the area A—B—C—A on the graph of FIGURE 4. It will be understood that greater proportions of hydrogen may be employed in any given case than the minimum amounts shown on the graph; but it is generally preferred not to use in excess of 0.9 mole of hydrogen per mole of total zone feed. Also, it will be apparent from the graph in FIGURE 4 that the minimum proportion of hydrogen which may be employed in any case within the operating range of this invention is 0.43 mole of hydrogen per mole of total zone feed. As has been indicated hereinabove, some adjustment may be required in curve A—C for operations conducted outside the range of 200 to 400° F. and about 0.2 to 2 minutes residence time.

It should be understood that the specific examples of operating conditions, apparatus arrangement and applications of this invention described herein are exemplary in character and are not to be construed as limiting the scope of the invention thereto unless expressly so stated.

I claim:

1. In a process wherein saturated, aliphatic hydrocarbon feed material having at least four carbon atoms per molecule is isomerized under isomerization conditions, including temperature within the range of about 200 to 400° F. and residence time within the range of about 0.1 to 3 minutes, by passage through a mass of particle form catalyst in a confined isomerization zone, said catalyst comprising a metal halide of the Friedel-Crafts type on a porous carrier and wherein the feed material contains materials other than the saturated hydrocarbons to be isomerized, which tend to cause rapid deterioration of the isomerization operation, and wherein metal halide vapors are introduced into said zone mixed with a suitable inert carrier gas at least intermittently during the isomerization on-stream period and gaseous product containing the isomerized hydrocarbon material is withdrawn from said zone, the improvement in combination therewith which comprises: controlling the rate of metal halide vapor introduction into said zone during the on-stream period in excess of that required to saturate said particle form carrier material and sufficient to insure the presence of metal halide vapors in the gaseous product withdrawn from said zone in an amount averaging at least 0.005% by weight of the total hydrocarbon material introduced to said zone during the on-stream period, controlling the total pressure in said isomerization zone within the range of about 400 to about 900 p.s.i.a. and introducing free hydrogen to said zone at a rate controlled to provide a hydrogen partial pressure within the range of approximately 385 to about 800 p.s.i.a. and a proportion of hydrogen relative to total gaseous material flowing through the isomerization zone, exclusive of any metal halide, which is sufficient to maintain said hydrocarbon material in the gaseous phase, said proportion being in any case greater than 0.43 mole and less than 0.97 mole of hydrogen per mole of total gaseous material other than any metal halide supplied to said isomerization zone.

2. A process according to claim 1 characterized further by the steps of introducing a hydrogen halide promoter into said isomerization zone in an amount within the range of about 0.4% to about 30% by weight of said saturated hydrocarbon material; withdrawing gaseous product containing hydrogen, hydrogen halide, isomerized hydrocarbons and some metal halide vapors from said isomerization zone; passing said gaseous product through at least one bed of particle form adsorbent capable of sorbing said metal halide, thereby separating the same from said gaseous product; periodically diverting said gaseous product from said bed and passing the same through at least one alternative bed of adsorbent to remove metal halide; passing a heated stripping gas through said first named bed to remove sorbed metal halide and introducing said stripping gas and resulting metal halide vapors into said isomerization zone during the isomerization reaction; withdrawing gaseous product essentially free of metal halide from the bed of adsorbent in use and cooling said gaseous product to condense normally liquid material; separating from the condensed material a non-condensed gas stream rich in hydrogen and containing normally gaseous hydrocarbons and hydrogen halide; heating a portion of said non-condensed gas stream and employing the same as said stripping gas to remove metal halide from the adsorbent bed not in use; treating another portion of said non-condensed gas stream to remove hydrogen halide and hydrocarbon gases, thereby providing a hydrogen-enriched gas stream; heating said hydrogen-enriched gas stream and passing the same into contact with a mass of metal halide to effect sublimation of the metal halide; withdrawing the hydrogen-enriched gas stream containing vaporized metal halide from said last named bed and introducing the same into said isomerization zone at a rate controlled so that the total amount of metal halide introduced into said isomerization zone by said hydrogen-enriched gas stream and by said stripping gas stream amounts to about 0.1% to 2% by weight of the hydrocarbon material passed through said isomerization zone.

3. A process according to claim 1 further characterized in that the amount of metal halide introduced into said isomerization zone during the on-stream period exceeds 0.1% by weight of the hydrocarbon material introduced and in that metal halide vapors are separated from the gaseous product withdrawn from said isomerization zone and recycled, at least in part, during the on-stream period.

4. The process of claim 1 further characterized in that said isomerization catalyst is comprised of aluminum chloride supported on a porous, particle form carrier material; in that a suitable gaseous isomerization promoter material is introduced into said isomerization zone in addition to hydrogen and hydrocarbons; and in that said proportion of hydrogen to total zone feed is less than about 0.97 mole of hydrogen per mole of total zone feed, but in no case less than a minimum amount falling within the area ABCA in the graph of FIGURE 4 hereof, the allowable minimum proportion depending upon the total pressure and temperature and upon the composition of the non-hydrogen portion of the total zone feed.

5. In a process for isomerization of a feed made up primarily of saturated, straight chain hydrocarbon material within the range of C_4 to C_6 hydrocarbons and containing at least a substantial quantity of saturated, straight chain C_6 hydrocarbon material and appreciable amounts of at least one undesirable material selected from the group consisting of benzene, C_5 to C_7 naphthenes and C_7 paraffinic hydrocarbons, wherein the feed is passed in the gaseous phase under isomerization conditions, including a temperature within the range of about 200 to 400° F. and residence time within the range of about 0.2 to 2 minutes, through a mass of particle form catalyst in a confined isomerization zone, said catalyst comprising a metal halide of the Friedel-Crafts type on a porous carrier, and wherein metal halide vapors are introduced into said zone at least intermittently during the isomerization on-stream period and gaseous product containing the isomerized hydrocarbon material is withdrawn from said zone, the improvement in combination therewith which comprises: controlling the rate of metal halide introduction into said zone in excess of that required to saturate said carrier material and sufficient to maintain the metal halide content of the gaseous product withdrawn from said zone substantially in excess of 0.005% by weight based on the total hydrocarbon material introduced into said zone, and controlling the total pressure within said zone within the range of about 400 to about 900 p.s.i.a. and introducing free hydrogen into said zone at a rate

controlled to provide a proportion of hydrogen to total zone feed which is less than that which would provide a hydrogen partial pressure in excess of about 800 p.s.i.a., but at least equal to the greater of (*a*) the ratio of a hydrogen partial pressure of about 385 p.s.i.a. to the total pressure in said isomerization zone, as expressed in the formula:

$$\frac{\text{Moles of hydrogen}}{\text{Moles of total zone feed}} = \frac{385}{\text{Total pressure in p.s.i.a.}}$$

and (*b*) that required to maintain said hydrocarbon material in the gaseous phase.

6. A process according to claim 5 further characterized by the steps of withdrawing gaseous, isomerized product containing some metal halide vapor from said isomerization zone, passing said gaseous product through a bed of solid adsorbent capable of sorbing said metal halide, withdrawing gaseous product essentially free of metal halide from said bed, periodically diverting the flow of gaseous product from said bed of adsorbent and passing the gaseous product through a second bed of adsorbent to remove said metal halide, passing a suitable stripping gas through said first named bed to remove metal halide therefrom and introducing said stripping gas and entrained metal halide vapors into said isomerization zone as at least part of the metal halide vapors which are introduced during the isomerization on-stream period.

7. A process according to claim 6 further characterized in that said metal halide is aluminum halide and further characterized by the steps of cooling the gaseous product withdrawn from said first named bed of adsorbent to effect condensation of normally liquid products, separating non-condensed gas rich in hydrogen from the condensed products and employing a portion of said non-condensed gas as said stripping gas to remove aluminum halide from said bed of adsorbent and to carry the same into said isomerization zone.

8. In a process for isomerization of a feed made up primarily of saturated, straight chain hydrocarbon material within the range of C_4 to C_6 hydrocarbons and containing at least a substantial quantity of saturated, straight chain C_6 hydrocarbon material and appreciable amounts of at least one undesirable material selected from the group consisting of benzene, C_5 to C_7 naphthenes and C_7 paraffinic hydrocarbons, wherein the feed is passed in the gaseous phase with hydrogen halide promoter under isomerization conditions, including a temperature within the range of about 200 to 400° F. and a residence time within the range of about 0.2 to 2 minutes, through an isomerization zone to effect isomerization of said saturated, straight chain hydrocarbon material in the presence of an isomerization catalyst comprised of aluminum halide on a porous, particle form carrier material, and gaseous product containing the isomerized hydrocarbon material is withdrawn from said zone, the improvement in combination therewith which comprises: introducing vaporized aluminum halide mixed with a substantially inert carrier gas into said isomerization zone substantially continuously during the on-stream period at a rate sufficiently in excess of that required to saturate said particle form carrier material to maintain the aluminum halide content of the gaseous product withdrawn from said isomerization zone substantially in excess of 0.005% by weight, the amount of aluminum halide so introduced into said zone being within the range of 0.1% to 2% by weight of said hydrocarbon feed; controlling the total pressure within said zone within the range of about 400 to about 900 p.s.i.a.; and introducing free hydrogen into said zone at a rate controlled to provide a proportion of hydrogen relative to total zone feed which is within the range of about 0.43 to 0.97 mole of hydrogen per mole of total zone feed, said proportion being less than that corresponding to a hydrogen partial pressure in excess of about 800 p.s.i.a., but at least equal to the greater of (*a*) the ratio of a hydrogen partial pressure of about 385 p.s.i.a to the total pressure of said zone, as expressed in the formula:

$$\frac{\text{Moles of hydrogen}}{\text{Moles of total zone feed}} = \frac{385}{\text{Total pressure in p.s.i.a.}}$$

and (*b*) that required to maintain said hydrocarbon material in the gaseous phase.

9. The process of claim 8 further characterized in that said catalyst is comprised of aluminum chloride on a particle form, porous, high alumina content adsorbent, said promoter is hydrogen chloride, and the aluminum halide vapor introduced to said zone is aluminum chloride.

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