

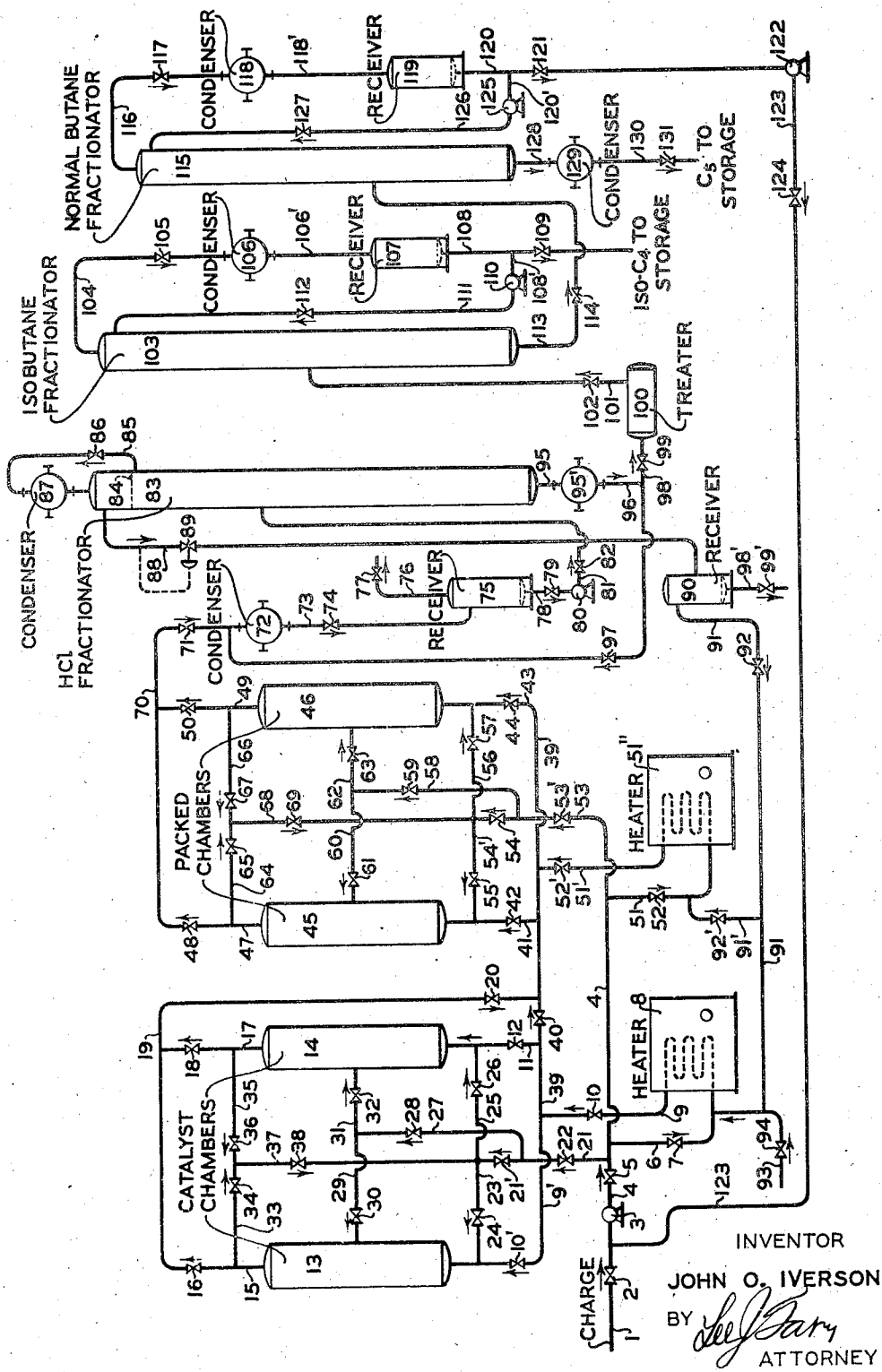
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ISOMERIZATION OF HYDROCARBONS

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ISOMERIZATION OF HYDROCARBONS

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13 Claims. (Cl. 260—683.5)

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This invention relates to a process for the isomerization of paraffin hydrocarbons and particularly those of normal or mildly branched structure to produce more highly branched isomers therefrom.

While the process is particularly applicable to the isomerization of individual hydrocarbons such as normal butane representing normally gaseous isomerizable paraffins and normally liquid paraffin hydrocarbons such as pentanes and hexanes, the process of the invention may be applied to the treatment of hydrocarbon mixtures comprising both paraffins and naphthenes such as, for example, straight-run petroleum fractions of gasoline boiling range, although other types of hydrocarbon conversion reactions in addition to isomerization will take place in such treatments. As a result of these treatments the antiknock properties of the gasolines charged are improved by the sum total of the reactions taking place.

More specifically the present invention is concerned with a mode of operation which involves closely cooperating steps, the process being particularly suitable for use in connection with granular metal halide catalysts of the Friedel-Crafts type such as aluminum chloride.

The isomerization of paraffin and naphthene hydrocarbons to produce more highly branched compounds or compounds with more condensed structure is becoming increasingly important in connection with petroleum refining. The isomerization of normal butane is important in view of the fact that isobutane is considerably more reactive than normal butane and can, for example, be more readily alkylated with olefins such as butenes to produce octanes of high antiknock value. Butenes formed by the dehydrogenation of isobutane yield octenes which when hydrogenated yield octanes of higher antiknock rating than those produced by subjecting normal butane to a similar series of steps. Normal butane generally occurs in larger amounts than isobutane so that its isomerization is frequently necessary if the greatest possible utilization must be made of the gaseous products from petroleum distilling and cracking operations.

In the case of normally liquid hydrocarbon mixtures such as straight run gasoline fractions either of close cut or rather wide boiling range processes involving isomerization of paraffins are of definite value in that the treated fractions have increased antiknock rating so that the process offers a means of greatly improving the quality of gasolines without the excessive losses frequently encountered when fractions are reformed by

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strictly thermal or high temperature thermal-catalytic methods.

The isomerization of paraffin hydrocarbons is more or less readily brought about by contact with such metal halides as aluminum chloride and aluminum bromide. Alternative metal halides not necessarily of equal efficiency include zirconium chloride, zinc chloride, ferric chloride or their bromides, or mixtures of these with each other or with aluminum halides. These halides may be used in a variety of ways for the isomerization of hydrocarbons. One of the oldest and simplest methods consists in refluxing the liquid in the presence of granular and finely divided metal halides preferably with the addition of small amounts of water or hydrogen halide, the lower boiling isomer being taken overhead and condensed. Other methods employ aluminum chloride, for example, supported on relatively inert granular materials over which the hydrocarbon or hydrocarbon mixture to be isomerized is passed in liquid or vapor phase along with the hydrogen halide. More recent developments in continuous processes have involved the passage of hydrocarbons to be isomerized through beds of granular aluminum chloride and the further passage of the hydrocarbon containing dissolved or entrained aluminum chloride into a reactor after the addition of a hydrogen halide. In a packed reactor, this operation serves to maintain a definite amount of active metal halide on the surface of the packing. The present process is concerned with improvements in this type of operation so that some of the operating difficulties commonly encountered are obviated.

In one specific embodiment as applied to normal butane representing saturated isomerizable hydrocarbons the present invention comprises passing said normal butane and hydrogen chloride through a stationary bed of granular aluminum chloride under a temperature and pressure adequate to effect isomerization while simultaneously introducing a portion of the cooler normal butane charge at spaced points in the aluminum chloride bed to control undue temperature rise therein, passing the products from the aluminum chloride contact into contact with granular absorbent material for the removal of aluminum chloride contained in products while introducing further amounts of cooler butane charge at spaced points in the absorbent material to control temperature therein, fractionating the products from contact with the absorbent to produce hydrogen chloride, isobutane and normal butane, recycling said hydrogen chloride to commingle with normal bu-

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tane charge, recovering said isobutane and recycling said normal butane to further isomerizing treatment.

In its broader aspect the feature of employing portions of hydrocarbon charge at a temperature lower than that obtaining in isomerizing reaction zones to counteract the tendency for undue temperatures rises in isomerizing reactors is applicable to any type of continuous flow isomerizing process such as, for example, a process in which isomerization is effected by merely passing the hydrocarbon charge mixed with a hydrogen halide through a stationary bed of granular metal halide either alone or on a support, or in processes where isomerization is effected by the use of relatively finely divided catalyst which is carried upwardly through a reaction zone by an ascending stream of vapors of hydrocarbons followed by separation of hydrocarbons and powdered catalyst with return of the latter to further catalytic use either with or without intermediate regeneration.

The features of the present invention and particularly the use of relatively cool charge to control temperature in the isomerizing zones will be more fully described in connection with the attached drawing which shows diagrammatically by the use of conventional figures in general side elevation an arrangement of apparatus in which the process may be conducted. The description of the operation is given in connection with the treatment of normal butane in the interest of simplifying the description and making it more readily understandable though it is to be understood that a similar characteristic flow may be used on other individual hydrocarbons or on hydrocarbon mixtures particularly those represented by hydrocarbon fractions of gasoline boiling range.

Referring to the drawing normal butane is introduced to the plant by way of line 1 containing valve 2 leading to a charging pump 3 which discharges through line 4 containing valve 5. Recycled normal butane enters line 1 from line 123 containing valve 124 as will be subsequently described. In accordance with the present invention the main portion of the charge to the isomerizing plant is heated and passed to contact with granular aluminum chloride while a minor portion is reserved for effecting cooling in the isomerizing zone wherein there is a tendency for temperatures to rise unduly due to the exothermic nature of the isomerization reaction. Thus, the major portion of the charge is passed from line 4 through line 6 containing valve 7 and through a suitable heater 8 in which the charging material is brought to an optimum temperature for its isomerizing treatment. Unheated portions of the charge are passed through line 21 containing valve 22, and line 53 containing valve 54 for cooling purposes as will be described in proper sequence. Provision is made for passing a portion of the original charge through a secondary heater 51' in line 51 so that this portion of the charge may carry additional heat to the stream of hydrocarbon material from the catalyst supply chambers 13 and 14 and permit substantially vapor phase operation in the reaction chambers 45 and 46 while a substantial amount of liquid phase is maintained in the catalyst supply chambers.

The embodiment of the invention contemplates the use of isomerizing reactors either in parallel, series or series-parallel connection. Thus, in parallel operation of reactors containing aluminum chloride the portion of the heated charge

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passes through line 9 containing valve 10 and line 9' containing valve 10' to contact with granular aluminum chloride contained in catalyst chamber 13 while a substantially equal portion passes through line 11 containing valve 12 into and through the granular catalyst contained in catalyst chamber 14. In this strictly parallel operation of the two catalyst chambers the effluent materials from chamber 13 pass through line 15 containing valve 16 while those from chamber 14 pass through line 17 containing valve 18, the streams combining in line 19 containing valve 20 and passing to the succeeding chambers containing granular material. In case it is desired to operate the two catalyst chambers in series, the effluent materials from chamber 13 may be diverted through line 33 containing valve 34 with valve 16 closed and pass through line 37 containing valve 38 through line 25 containing valve 26 and leading to line 11 and thence through chamber 14 with valves 36 and 24 closed so that the total effluent materials pass through line 17 containing valve 18 to line 19. When chamber 14 is to be used as the first of the series the charge is introduced through line 11 containing valve 12 with valve 26 closed and the effluent materials from chamber 14 pass through line 35 containing valve 36 with valves 18 and 34 closed and thence through line 37 containing valve 38 to line 23 containing valve 24 and into catalyst chamber 13 by way of line 9' with valve 10' closed. The effluent materials in this case pass through line 15 containing valve 16 with valve 34 closed into line 19.

To effect cooling of the reaction zones an unheated portion of the charge passes through line 21 containing valve 22 and may be then passed through line 27 containing valve 28 to intermediate points in the catalyst chambers by way of line 29 containing valve 30 and leading to catalyst chamber 13 or line 31 containing valve 32 and leading to catalyst chamber 14. The cooling or "quenching" fluid is shown as being introduced at one single point in each chamber although it is comprised within the scope of the invention to introduce the cooling material at any point or plurality of points which are found necessary to produce the best results. To provide for intermediate cooling between chambers when they are used in series, a regulated portion of cooling fluid may be introduced either through valve 21' into line 23 or line 25 with valve 28 closed.

In the second stage of the isomerizing process the partially isomerized materials from the first zone in which they were contacted with aluminum chloride are passed to a secondary treating zone containing granular and preferably absorbent material such as, for example, porous refractories, granular aluminas, such as bauxite clays either raw or acid treated, kieselguhr, etc. In this stage further isomerizing action may occur as the partially converted hydrocarbons contact the absorbent which has taken up any aluminum chloride carried over from the first zone and at the same time metal halide-hydrocarbon complexes are absorbed and removed from the reaction products. Thus, in the ordinary operation of the process products of the primary isomerizing zone pass through line 19 and valve 20 into chambers containing granular absorbent material, these chambers being used in parallel, series or series-parallel connection as in the case of the primary chambers, and being provided with means for temperature control by the in-

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roduction of unheated charge. Thus products from line 19 may be introduced by way of line 41 containing valve 42 to a packed chamber 45, and another portion of the primary reaction products may be passed through line 43 containing valve 44 to packed chamber 46. A line 39 containing valve 40 is also provided for the diversion or bypassing of a portion of the original heated charge to the secondary reaction chambers as a means of temperature control therein. When chambers 45 and 46 are operating in parallel, the effluent materials from chamber 45 will follow line 47 containing valve 48 while those from chamber 46 follow line 49 containing valve 50, the two streams uniting in line 70 containing valve 71 and passing to the succeeding fractionating zone. When the packed chambers are utilized in series with chamber 45 as the first chamber the effluent materials from this chamber will pass from line 47 through line 64 containing valve 65 with valves 48 and 67 closed and follow line 68 containing valve 69 and line 56 containing valve 57 to enter line 43, with valves 44 and 55 closed. When chamber 46 is to be used as the first in a series the effluent materials will pass from line 49 through line 66 containing valve 67 with valves 50 and 65 closed and through line 68 containing valve 69 to flow through line 54' and valve 55 into line 41 with valves 42 and 57 closed. In this case the total effluent materials will pass through line 47 containing valve 48 into line 70.

For cooling purposes in the secondary zone containing granular material line 51 containing valve 52 leading through heater 51' and line 51' containing valve 52' serve to admit heated or cooler charge to line 41 or line 43. Line 53 containing valves 53' and 54 permits the passage of cooling fluid to line 58 containing valve 59 which has branch lines 60 containing valve 61 leading to an intermediate point in chamber 45 and branch line 62 containing valve 63 leading to an intermediate point in chamber 46. Again these single points of introduction are merely to illustrate any single or any multiple points which may be used as circumstances may require. To permit intermediate cooling between chambers when they are used in series line 53 leads to both line 54' containing valve 55 and line 56 containing valve 57.

In the preceding description the flow through the catalyst chambers and packed chambers has been indicated as being upward but downflows may also be used without departing from the scope of the invention.

The preferred arrangement of the isomerizing zones permits considerable flexibility in operation. Thus the major amount of isomerization may be brought about in the primary zones designated as "catalyst chambers" in contact with granular aluminum chloride catalyst in the presence of hydrogen chloride; or the aluminum chloride in the primary zone may serve in the absence of added hydrogen chloride merely as a source of supply of catalytic material to be deposited on granular materials in the second zones designated as "packed chambers," to which hydrogen chloride is introduced to assist in the isomerizing action. The choice of operating procedure will depend upon the character of the hydrocarbon or hydrocarbon mixture which it is desired to isomerize. Similarly both temperature, pressure and flow rate may be varied in the primary and secondary zones so that substantially vapor phase conditions may be made to obtain in both zones, liquid phase conditions in both zones or liquid

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phase in the primary zone and vapor phase in secondary zone. In the case of normal butane satisfactory isomerization may be effected in the setup of the present character by passing the normal butane through the aluminum chloride catalyst chambers in substantial liquid phase and effecting isomerization in the succeeding secondary zone in vapor phase. In the case of normally liquid isomerizable hydrocarbons substantially liquid phase conditions may be maintained throughout the primary and secondary zone. In the case of normal butane temperatures of from approximately 150 to 200° F. may be maintained in the primary zone under pressures of the order of 250 to 350 pounds per square inch while slightly higher temperatures of the order of 200 to 220° F. and the same or slightly lower pressure is used in the second zone. The amount of hydrogen chloride present at any stage of the isomerization may be varied to control the rate and character of the reactions. As a rule, amounts of from about 1 to about 20 mole per cent of hydrogen chloride in respect to the hydrocarbon or hydrocarbon mixture undergoing isomerization may be used.

Following the isomerization stages the products are fractionated to recover those of desired characteristics, hydrocarbon recycle stocks and hydrogen chloride. Thus, the total products from the secondary isomerizing zone may be caused to pass through condenser 72 wherein substantially complete liquefaction of all products is obtained and the liquefied material passes through line 73 containing valve 74 to a receiver 75 provided with a gas release line 76 containing a valve 77 for the removal of uncondensed gases.

In the next step the hydrogen chloride is recovered for reuse by a convenient means such as distillation under relatively high pressures above 300 and usually of the order of 450 pounds per square inch. Thus a pump 80 takes suction on the liquid material in receiver 75 by way of line 78 containing valve 79 and discharges through line 81 containing valve 82 into a high pressure fractionating column 83 containing a plate 84 dividing the lower section from the small upper section. The vapors of hydrogen chloride and some light hydrocarbons pass through line 85 containing valve 86 and reflux is condensed during passage through overhead condenser 87 after which hydrogen chloride passes through line 88 containing upstream pressure control valve 89, line 88 leading to an intermediate accumulator 90 for the intermediate storage of hydrogen chloride and whatever hydrocarbons have passed overhead as vapor. From receiver 90 hydrogen chloride is passed through line 91 containing valve 92 to line 93 leading to line 6 and thence to the primary isomerizing step. Hydrogen chloride sufficient to make up any incidental losses in the processing is admitted from line 93 containing valve 94 as required.

To provide for operation in which hydrogen chloride is admitted only to the packed reaction chambers line 91' containing valve 92' is provided to permit the recirculated hydrogen chloride and any hydrogen chloride introduced from line 93 to be introduced into line 51 ahead of secondary heater 51' and thence to the packed chambers.

The bottoms from fractionator 83 pass through line 95 and a cooler 95' and are then split into a stream passing through line 96 and valve 97 and leading to line 70 to increase the amount of liquid and promote more effective condensation in condenser 72. The main stream of bot-

toms is passed through line 98 containing valve 99 to a treating stage designated as 100 where it is treated to remove any traces of hydrogen chloride, aluminum chloride or aluminum chloride complexes preferably by contact with alkaline material such as aqueous caustic soda, before the final fractionation to produce isobutane and normal butane and separate heavy materials. Thus the treated materials from zone 100 pass through line 101 containing valve 102 and enter the isobutane fractionator 103 designed to effect a substantially accurate separation of this hydrocarbon. The vapors from fractionator 103 pass through line 104 containing valve 105 and are liquefied during passage through condenser 106 after which they pass through line 106' to a receiver 107. To assist in controlling the fractionation in fractionator 103 a controlled portion of the condensed liquid is returned to a point near the top of the fractionator by a pump 110 which takes suction in on line 108 by way of line 108' and discharges through line 111 containing valve 112, the main portion of the isobutane as a product of the process following line 108 and valve 109 to storage or use in other processes.

The bottoms from fractionator 103 consisting largely of normal butane together with some heavier hydrocarbons pass through line 113 containing valve 114 to a fractionator 115 operated to effect the separation of normal butane. Thus the vapors of this compound pass through line 116 containing valve 117 and are liquefied by passage through condenser 118 after which they flow through line 118' to a receiver 119. Again to assist in controlling the fractionation in fractionator 115 pump 125 takes a portion of the liquid from receiver 119 by way of line 120 and line 120' and discharges it through line 126 containing valve 127 into a point near the top of the fractionator. The production of normal butane follows line 120 containing valve 121 to recycle pump 122 which discharges through line 123 containing valve 124 into line 1 to commingle with the fresh charge. Hydrocarbons heavier than normal butane are withdrawn as bottoms from fractionator 115 through line 128 and through a condenser 129 and are then removed through line 130 containing valve 131 to a suitable storage.

The following example is given to show typical charge rates, yields and operating conditions used in a process of the present character though without the intent of correspondingly limiting the scope of the invention.

The process is used to isomerize normal butane and the total combined feed to the process including fresh and recycled butane is 1,078 barrels per day. Of this material 269 barrels are preheated to a temperature of 190° F. and passed in series through catalyst supply chambers containing granular aluminum chloride. 695 barrels of the combined feed and 14,600 pounds of hydrogen chloride are passed through the main heater preceding the packed reaction chambers and heated to a temperature of 275° F. 114 barrels per day of the combined feed at a temperature of 157° F. is injected into the reactors which are used in parallel to offset the tendency toward temperature rise due to the exothermic character of the isomerizing reaction. A pressure of 250 pounds per square inch is maintained upon both the saturators and the reactors and the hourly liquid space velocity per volume of reactor packing is 0.25. In operating in this

manner with an overall yield of iso-butane from normal butane of 90 per cent, the plant produces a yield of 520 barrels of iso-butane per stream day.

I claim as my invention:

1. A process for the isomerization of normal butane which comprises passing a portion of a normal butane charge mixed with hydrogen chloride through a stationary bed of granular aluminum chloride at a temperature and pressure adequate to effect isomerization while simultaneously introducing further portions of the normal butane charge at spaced points in the aluminum chloride bed to control the temperature therein, passing the products from the aluminum chloride bed into contact with granular absorbent material while introducing further portions of the butane charge at spaced points in the absorbent material to control the temperature therein, fractionating the products resulting from contact with the absorbent to recover hydrogen chloride, isobutane and normal butane, recycling said hydrogen chloride to commingle with the normal butane charge, recovering said isobutane and recycling said normal butane to further isomerizing treatment.

2. A process for the isomerization of normal butane which comprises passing a portion of a normal butane charge mixed with hydrogen chloride through a stationary bed of granular aluminum chloride at a temperature of from about 150 to about 200° F. and a pressure of from about 250 to about 350 pounds per square inch to effect isomerization while simultaneously introducing further portions of the normal butane charge at spaced points in the aluminum chloride bed to control temperature therein, passing the products from the aluminum chloride bed into contact with granular absorbent material at a temperature of from about 200 to about 220° F. and under a pressure corresponding to substantially vapor phase conditions while introducing further portions of the butane charge at spaced points in the material to control temperature therein, fractionating the products from contact with the absorbent under a pressure substantially in excess of 300 pounds per square inch to recover hydrogen chloride, isobutane and normal butane, recycling said hydrogen chloride to commingle with the normal butane charge, recovering said isobutane and recycling said normal butane to further isomerizing treatment.

3. A process for the isomerization of normal butane which comprises passing a portion of a normal butane charge mixed with hydrogen chloride through a stationary bed of granular aluminum chloride at a temperature of from about 150 to about 200° F. and a pressure of from about 250 to about 350 pounds per square inch to effect isomerization while simultaneously introducing further portions of the normal butane charge at spaced points in the aluminum chloride bed to control temperature therein, passing the products from the aluminum chloride bed into contact with granular absorbent material at a temperature of from about 200 to about 220° F. while introducing further portions of the butane charge at spaced points in the absorbent material to control temperature therein, fractionating the products from contact with the absorbent under a pressure substantially in excess of 300 pounds per square inch to recover hydrogen chloride, isobutane and normal butane, recycling said hydrogen chloride to commingle with the normal butane charge, recovering said

isobutane and recycling said normal butane to further isomerizing treatment.

4. A process for the isomerization of normal butane which comprises passing a portion of a normal butane charge mixed with hydrogen chloride through a stationary bed of granular aluminum chloride at a temperature of from about 150 to about 200° F. and a pressure of from about 250 to about 350 pounds per square inch to effect isomerization with a substantial amount of said butane in liquid phase while simultaneously introducing further portions of the normal butane charge at spaced points in the aluminum chloride bed to control temperature therein, passing the products from the aluminum chloride bed into contact with granular absorbent material at a temperature of from about 200 to about 220° F. and under a pressure corresponding to substantially vapor phase conditions while introducing further portions of the butane charge at spaced points in the absorbent material to control temperature therein, fractionating the products from contact with the absorbent under a pressure substantially in excess of 300 pounds per square inch to recover hydrogen chloride, isobutane and normal butane, recycling said hydrogen chloride to commingle with the normal butane charge, recovering said isobutane and recycling said normal butane to further isomerizing treatment.

5. A process for the isomerization of a normal paraffin hydrocarbon which comprises passing a portion of the charge of said hydrocarbon mixed with hydrogen chloride through a stationary bed of granular aluminum chloride under a temperature and a pressure adequate to effect isomerization while simultaneously introducing further portions of the hydrocarbon charge at spaced points in the aluminum chloride bed to control temperature therein, passing the products from the aluminum chloride bed into contact with granular absorbent material while introducing further portions of the hydrocarbon charge at spaced points in the absorbent material to control temperature therein, fractionating the products from contact with the absorbent to separate hydrogen chloride, a lower boiling isomeric hydrocarbon fraction and unconverted normal paraffin hydrocarbon, recycling said hydrogen chloride to commingle with the paraffin hydrocarbon charge, recovering said isomeric fraction and recycling said unconverted paraffin hydrocarbon to further isomerizing treatment.

6. A process for treating a gasoline fraction composed predominantly of saturated hydrocarbons to increase the antiknock value of said fraction which comprises passing a portion of said fraction mixed with hydrogen chloride through a stationary bed of granular aluminum chloride under a temperature and a pressure adequate to effect a substantial increase in the antiknock value thereof while simultaneously introducing further portions of said fraction at a lower temperature at spaced points in said bed to control temperature therein, passing the products from the aluminum chloride bed to contact with gran-

ular absorbent material while introducing further portions of said fraction at a lower temperature at spaced points along the line of flow through the absorbent material to control temperature therein, fractionating the products from contact with the absorbent to separate hydrogen chloride, a treated fraction of improved antiknock value and a higher boiling fraction, recycling said hydrogen chloride to commingle with the charge, recovering said treated fraction and recycling said higher boiling fraction to further treatment.

7. A process for isomerizing saturated hydrocarbons which comprises heating a portion of the saturated hydrocarbon charging stock to isomerizing temperature, passing the thus heated hydrocarbons together with a hydrogen halide through a stationary bed of granular metal halide isomerizing catalyst under isomerizing conditions, simultaneously introducing another portion of said charging stock to at least one intermediate point of said bed to control the temperature in the bed, passing the products from the catalyst bed through a body of solid absorbent material while introducing an additional portion of said charging stock to at least one intermediate point of said body to control the temperature therein, and fractionating the products discharging from said body to separate isomerized hydrocarbons therefrom.

8. A process for isomerizing paraffinic hydrocarbons which comprises heating a portion of the paraffinic hydrocarbon charging stock to isomerizing temperature, passing the thus heated hydrocarbons together with a hydrogen halide through a stationary bed of granular metal halide isomerizing catalyst under isomerizing conditions, simultaneously introducing another portion of said charging stock to at least one intermediate point of said bed to control the temperature in the bed, passing the products from the catalyst bed through a body of solid absorbent material while introducing an additional portion of said charging stock to at least one intermediate point of said body to control the temperature therein, and fractionating the products discharging from said body to separate isomerized hydrocarbons therefrom.

9. The process as defined in claim 7 further characterized in that said charging stock comprises a naphthene hydrocarbon.

10. The process as defined in claim 7 further characterized in that said catalyst comprises an aluminum halide.

11. The process as defined in claim 8 further characterized in that said catalyst comprises an aluminum halide.

12. The process as defined in claim 7 further characterized in that said catalyst comprises aluminum chloride and in that said hydrogen halide is hydrogen chloride.

13. The process as defined in claim 8 further characterized in that said catalyst comprises aluminum chloride and in that said hydrogen halide is hydrogen chloride.

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