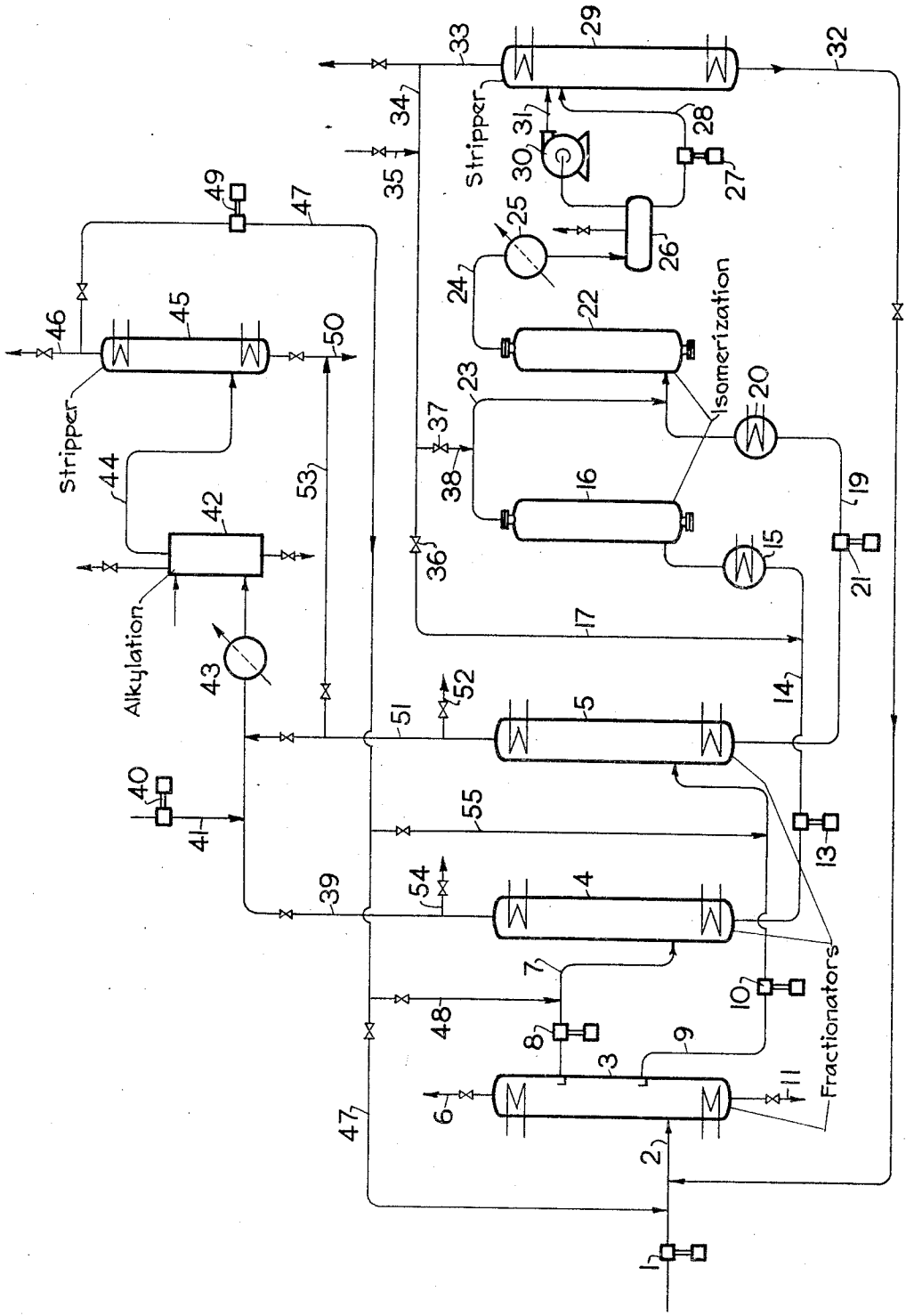
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MANUFACTURE OF MOTOR FUEL

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MANUFACTURE OF MOTOR FUEL

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This invention relates to the production of high anti-knock hydrocarbon motor fuel fractions.

The invention provides a more efficient and economical method for obtaining branched-chain hydrocarbons from straight-chain hydrocarbon mixtures such as natural gasoline, low-boiling fractions of straight-run gasoline, and relatively low-boiling olefinic fractions obtained by fractionating the distillate products of thermal or catalytic hydrocarbon conversions. A method whereby these materials can be treated to obtain as substantially the sole products of the process, hydrocarbon fractions consisting essentially of single branched-chain hydrocarbons or mixtures of branched-chain hydrocarbons having the same number of carbon atoms, is often greatly desired. Resort to the use of processes wherein cracking is the principal reaction is, in such cases, undesirable since the materials treated are converted to a wide range of hydrocarbons of which but a relatively small part may comprise the desired branched-chain hydrocarbons. The use of processes wherein isomerization methods available heretofore are used is often unsatisfactory, since in these processes the isomerization of higher hydrocarbons such as those having from five to ten carbon atoms to the molecule, particularly pentane, is generally unavoidably accompanied by hydrocarbon decomposition. The extent to which this hydrocarbon decomposition is encountered in these processes often renders the economical and efficient production of only the desired branched-chain hydrocarbons on a large scale difficult, if not impossible.

An object of the present invention is the provision of an improved process for the production of branched-chain hydrocarbons highly desirable as components of high anti-knock hydrocarbon motor fuels, from hydrocarbon mixtures predominating in straight-chain hydrocarbons. A more specific object of the invention is an improved process for the production of high anti-knock motor fuel fractions wherein straight-chain hydrocarbons having from four to ten carbon atoms to the molecule are converted more efficiently to higher-boiling branched-chain hydrocarbons in the absence of any substantial hydrocarbon decomposition. A still further object of the invention is the provision of an improved process for the production of higher-boiling hydrocarbon fractions predominating in branched-chain hydrocarbons having the same number of carbon atoms to the molecule from lower-boiling straight-chain hydrocarbons.

In the improved process of the invention, a mixture of substantially paraffinic hydrocarbons is introduced into a fractionating zone wherein a fraction predominating in normal butane and at least one fraction predominating in a straight-chain hydrocarbon having from five to ten carbon atoms to the molecule are segregated. The butane fraction is catalytically converted to isobutane. The higher hydrocarbon fraction or fractions are admixed with effluence of the butane conversion zone and subjected to isomerizing conditions at which the higher hydrocarbon or hydrocarbons are converted to branched-chain isomeric hydrocarbons in the absence of any substantial hydrocarbon decomposition. Isomerization products are returned to the fractionating zone, wherein fractions predominating in branched-chain hydrocarbons are segregated. At least a part of the branched-chain hydrocarbons thus obtained are admixed with an olefinic hydrocarbon fraction, and the resulting mixture subjected to alkylating conditions. Saturated hydrocarbons originally present in the olefinic fraction and unreacted branched-chain hydrocarbons are separated from the products of alkylation and passed to the fractionating zone, in which the paraffinic charge and isomerization products are fractionated.

In order that the invention may be more readily understood, it will be described in detail with reference to the attached drawing showing one form of apparatus suitable for carrying out the process of the invention.

Referring to the drawing, a mixture of substantially paraffinic hydrocarbons such as, for example, natural gasoline or a straight-run gasoline, is drawn from an outside source and forced by means of pump 1 through line 2 into a fractionating zone. In the drawing, fractionators 3, 4, and 5 are shown as constituting this fractionating zone. It will be understood that in actual practice more than three fractionators will generally be used to effect the indicated fractionation. Within fractionator 3, material lower-boiling than C_4 hydrocarbons is removed overhead through valved line 6. A fraction consisting essentially of butane is separated and forced through line 7 by means of pump 8, into fractionator 4. A fraction consisting essentially of a paraffin hydrocarbon having from 5 to 10 carbon atoms to the molecule, for example pentane, is also separated within fractionator 3 and forced through line 9 by means of pump 10 into fractionator 5. Higher-boiling hydrocarbons are eliminated from the lower part of fractionator 3 through valved line 11. Within fractionator 4, isobutane is separated as a vapor fraction from normal butane, and within fractionator 5 isopentane is separated as a vapor fraction from normal pentane.

Normal butane is withdrawn from the lower part of fractionator 4 and forced by means of pump 13 through line 14 and heater 15, into an isomerizing zone. This isomerizing zone may comprise a reaction chamber 16 containing a suitable isomerization catalyst. Suitable isomerization catalysts comprise, for example, those of the Friedel-Crafts type, such in particular as aluminum chloride and aluminum bromide. These catalysts are preferably deposited upon or mixed with various carrier substances such as activated alumina, activated bauxite, activated carbon, and other aluminous and/or silicious adsorptive materials. Modified catalysts of this type, such as the mixture of an aluminum halide with other metal halides in either the solid or molten state may be used. Particularly effective catalysts comprise a mixture of aluminum chloride dissolved in a mixture of molten metal halides such, for instance, as molten mixtures comprising

$AlCl_3$—NaCl—KCl, $AlCl_3$—$SbCl_3$,
$AlCl_3$—NaCl—$ZnCl_2$

The temperature to be maintained within reaction chamber 16 may range, for example, from about 50° C. to about 300° C., and preferably from about 100° C. to about 200° C. Under these conditions, butane will be converted to isobutane in its passage through reaction chamber 16.

The isomerization reaction in the presence of these catalysts is preferably carried out in the presence of a free hydrogen halide promoter such as, for example, hydrogen chloride. Hydrogen chloride is therefore introduced into line 14 through line 17. Generally, concentrations of hydrogen chloride in the order of from about 2% to about 10% by weight of the charge to the butane isomerization zone are sufficient. Larger or smaller amounts may, however, be used.

Normal pentane withdrawn from the lower part of fractionator 5 is forced through line 19 and heater 20 by means of pump 21 into a second isomerizing zone such as, for example, a reaction chamber 22. Within reaction chamber 22, normal pentane is contacted with an aluminum halide isomerization catalyst, preferably selected from those described above. Although but one reaction chamber is shown in the drawing as constituting each of the isomerization zones, it is to be understood that more than one reaction chamber or reactor may be used in each of the zones.

It is well known that butane, the first member of the isomerizable hydrocarbons, is, in relation to its higher homologues, comparatively stable. It may be treated under relatively severe conditions with even highly active isomerization catalysts with only minor amounts of decomposition. The higher hydrocarbons, such as those having from five to ten carbon atoms to the molecule, and especially pentane, however, are particularly prone to undergo decomposition in the presence of isomerization catalysts. By the term "decomposition" as used throughout this specification and the attached claims is meant the rupture of carbon to carbon and/or carbon to hydrogen bonds of the hydrocarbon molecule, to result in the formation of hydrocarbons of lower molecular weight than the hydrocarbon being isomerized. When these higher hydrocarbons are isomerized in accordance with the methods utilized heretofore, an appreciable amount of isomerization can, under certain conditions, be attained. The extent to which hydrocarbon decomposition is unavoidably encountered in these methods generally acts as a serious deterrent to the practical application of these processes to the isomerization of hydrocarbons having from five to ten carbon atoms to the molecule. These decomposition reactions are detrimental not only because they occasion considerable loss of the hydrocarbon being treated by converting it to undesirable by-products, but because these by-products, even when formed in relatively small amounts, generally bring about rapid destruction of the activity of the isomerization catalyst. In the process of the invention, these difficulties are avoided by catalytically isomerizing the hydrocarbons having more than four carbon atoms to the molecule in the presence of isobutane, which has been found to suppress hydrocarbon decomposition in the presence of the isomerization catalysts.

In the process of the invention, the entire effluence of reaction chamber 16 comprising isobutane, unreacted butane, and hydrogen chloride, is passed through line 23 into line 19, thereby admixing with the normal pentane prior to the entry of the pentane into reaction chamber 22. The passage of the effluence of reaction chamber 16 directly into reaction chamber 22 not only eliminates the need of separate fractionation and recycling of the products of the separate isomerizing zones, but permits the full utilization of the heat content of this stream to aid in maintaining the desired temperature in reaction chamber 22. Since the C_4 hydrocarbon decomposition suppressor and the hydrogen halide promoter constitute the predominant part of the charge to the pentane isomerizing zone, a considerable saving in heating requirement is thereby attained. The temperature to be maintained within reaction chamber 22 will generally be somewhat lower than that maintained within reaction chamber 16. It is to be pointed out, however, that the presence of the butanes enables the pentane isomerization to be carried out at temperatures substantially in excess of those at which pentane can be isomerized at all economically in processes utilized heretofore. The temperature within reaction chamber 22 is maintained within the broad range of, for example, from about 30° C. to about 150° C. The particular type of catalyst used will determine to a substantial degree the temperatures within this broader range which are preferred for any one operation. Thus, when isomerizing pentane with a solid, supported aluminum halide catalyst, a temperature of from about 40° C. to about 60° C. may suitably be used. When the pentane isomerization is executed in the presence of a catalyst of the molten salt type, a higher temperature of from about 80° C. to about 120° C. is generally preferred. Within reaction chamber 22, normal pentane will, under these conditions, be converted to isopentane, and due to the presence of isobutane the pentane isomerization will be effected in the absence of any substantial pentane decomposition.

Isomerization products comprising isobutane, isopentane, unreacted normal butane and pentane, and hydrogen chloride are withdrawn from isomerizing zone 22 and passed through line 24 and cooler 25 into an accumulator 26. In passing through cooler 25, the reaction products are cooled to a temperature sufficiently low to effect the condensation of at least a substantial part of the C_4 hydrocarbons. Additional cooling means not shown in the drawing may be utilized if desired. Condensed products comprising C_4 and C_5 hydrocarbons are forced by

means of pump 27 from accumulator 26 through line 28, to a stripping column 29. Gaseous materials comprising hydrogen chloride and uncondensed hydrocarbons are forced from accumulator 26 by means of compressor 30 through line 31, into stripping column 29. Within stripping column 29, a normally gaseous fraction comprising hydrogen chloride is separated from a liquid hydrocarbon fraction comprising C_4 and C_5 hydrocarbons. A high pressure, for example in excess of 350 lbs., is preferably maintained in stripping column 29 to aid in effecting the desired separation. The liquid fraction comprising C_4 and C_5 hydrocarbons is recycled through valved line 32 to line 2, leading into fractionator 3. The normally gaseous fraction comprising hydrogen chloride is eliminated from stripping column 29 through valved line 33 and passed at least in part through lines 34 and 17, into line 14. Make-up hydrogen chloride is introduced into the system through valved line 35, leading into line 34, as needed.

The amount of isobutane to be maintained within reaction chamber 22 may vary considerably within the scope of the invention in accordance with the particular catalyst used. Whereas normal butane has little, if any, effect in suppressing decomposition reactions in the presence of supported aluminum halide catalyst, it does have a favorable effect in the presence of aluminum halide catalysts of the molten salt type. Therefore, when utilizing the molten salt type catalysts, this added effect of the normal butane present in the effluence of reaction chamber 16 permits the maintenance of lesser amounts of isobutane in reaction chamber 22 than if a supported aluminum chloride catalyst were used. Maintenance of a molecular excess of isobutane within reaction chamber 22 is, however, desirable. To aid in maintaining any desired proportion of isobutane to pentanes, controlled amounts of C_4 hydrocarbons may be recycled, when needed, with the hydrogen chloride from stripping column 29 through line 34. When recycling C_4 hydrocarbons with the hydrogen chloride promoter, the greater amount of the gaseous stream recycled through line 34 can be by-passed through valved line 38 into line 23, and only a sufficient amount of the mixture passed into line 17 to provide the desired amount of promoter to reaction chamber 16, by judicious control of valves 36 and 37. Means not shown in the drawing may be used to recycle C_4 hydrocarbons in a separate stream to reaction chamber 22, should this be required.

The effectiveness of isobutane in suppressing pentane decomposition in the presence of an aluminum chloride catalyst is shown in the following examples:

Example I

A mixture of normal pentane and isobutane in equal molar proportions was treated at 90° C. under a hydrogen chloride pressure of 50 lbs. per sq. in. with a molten salt catalyst having the following composition in weight per cent: $AlCl_3$—75%, $ZnCl_2$—10%, NaCl—7.5%, KCl—7.5%. Analysis of the products showed an 85% conversion of pentane to isopentane in mol per cent. Only a negligible amount of pentane decomposition was observed. The remainder of the pentane charged was unchanged.

Example II

A mixture of pentane and isobutane consisting of 33⅓ mol per cent pentane and 66⅔ mol per cent isobutane was passed over activated alumina impregnated with aluminum chloride at a temperature 50° C. and a pressure of 60 lbs. per sq. in. Hydrogen chloride in the amount of 1 mol per cent of the hydrocarbon charge was added. At the end of thirty hours of continuous operation, a conversion of normal pentane to isopentane of 50 mol per cent was obtained with only a negligible amount of pentane decomposition. The remainder of the pentane charged was unchanged.

It is to be pointed out that the unusual effectiveness in suppressing hydrocarbon decomposition in the presence of the aluminum halide isomerization catalysts is apparently restricted to the C_4 paraffin hydrocarbons and is not possessed by propane, ethane, or methane.

The isomerization reactions within chambers 16 and 22 may be executed in either the liquid or the vapor phase. When effecting the isomerization in the liquid phase, it is preferred to use a catalyst of the molten salt type described above. Since normal butane aids in suppressing the hydrocarbon decomposition reaction in the presence of the molten salt type catalyst, a highly advantageous method of carrying out the process of the invention comprises the execution of the butane isomerization in chamber 16 in the presence of a supported aluminum halide catalyst, and the isomerization of the higher hydrocarbon in chamber 22 in the presence of a catalyst of the molten salt type. When executing the process of the invention in this wise, the effluent chamber 16 will generally suffice to effect the complete suppression of any substantial hydrocarbon decomposition within chamber 22. The pressure to be maintained within the isomerization zones may vary widely within the scope of the invention. Pressures in the order of from about 50 to about 300 pounds have been found highly suitable. When operating in the liquid phase, a pressure sufficiently high to maintain the hydrocarbon in the liquid phase is maintained.

Isobutane is eliminated overhead from fractionator 40 through line 39. A substantially olefinic hydrocarbon fraction predominating in hydrocarbons having the same number of carbon atoms to the molecule is drawn from an outside source by means of pump 40 and forced through line 41 into line 39, wherein it is admixed with the isobutane. The olefinic hydrocarbon fraction may be obtained from any suitable source such as, for example, by fractionation of the distillate products of a thermal or catalytic hydrocarbon conversion operation. These fractions, as they are generally more readily obtained, comprise the olefine in admixture with the paraffin hydrocarbon having the same number of carbon atoms to the molecule as the olefine. Thus, a suitable fraction comprises a butane-butylene fraction. The resulting mixture of isobutane, butylene, and butane is passed into an alkylating zone. The alkylating zone may comprise an alkylation unit comprising one or several stages provided with means for contacting the hydrocarbon stream therein with a suitable alkylation catalyst such as sulfuric acid or the like, and for separating the product from the catalyst. For the sake of simplicity, the alkylating zone is depicted in the drawing by reactor 42. Within reactor 42, conditions are maintained to bring about the alkylation of branched-chain saturated hydrocarbons with olefines. Thus, the reaction may be carried

out at a temperature in the range of, for example, from about 5° C. to about 25° C. at a pressure sufficiently high to maintain the reactants in the liquid phase. A cooler or refrigerating means 43 is positioned before reactor 42 to aid in maintaining the desired temperature. The rate at which the olefine fraction is introduction into the system is controlled to maintain an excess of the less reactive isoparaffin molecule relative to the olefinic hydrocarbon within the alkylating zone. It is to be understood that the manner in which the reaction is effected as well as the operating conditions employed, may be varied to produce the results particularly desired.

Alkylation products, which, when treating isobutane with a butylene-butane fraction, comprise branched-chain hydrocarbons having eight carbon atoms to the molecule, unconverted isobutane, and normal butane originally present in the olefinic fraction, after having been neutralized, are passed through line 44 into a stripping column 45. Within stripping column 45, unreacted isobutane and the normal butane which was originally present in the olefinic hydrocarbon fraction charged to the system is separated as a vapor fraction from a liquid hydrocarbon fraction comprising the alkylate. The vapor fraction is removed overhead from stripping column 45 through valved line 46, and forced in part or in its entirety by means of pump 49 through valved lines 47 and 48 into line 7, passing into fractionator 4. It is seen that in the process of the invention both the paraffinic and olefinic constituents of fractions such as the butylene-butane fractions which are usually available in abundance in many refinery operations are utilized efficiently in the production of desired branched-chain hydrocarbons without preliminary separation of the olefinic and paraffinic constituents. The alkylate, consisting essentially of branched-chain hydrocarbons having eight carbon atoms to the molecule, is withdrawn from stripping column 45 through valved line 50.

Isopentane withdrawn from the upper part of fractionator 5 through valved line 51 may be removed in part or in its entirety from the system through valved line 52 as a final product. A part or all of the isopentane, which is itself a highly desirable motor fuel component, may be passed through valved line 53 and combined with the alkylate withdrawn from fractionator 45 through line 50. All, or a part of the isopentane, may be passed through lines 51 and 39 to reactor 42 to be alkylated with the olefine therein. A valved line 54 is provided for the elimination of any part or all of the isobutane from the system when isopentane is passed to the alkylating zone.

The invention is not limited to the use of butane-butylene as the olefinic fraction, and other olefinic fractions such as, for example, a propylene, butylene, amylene, cyclopentene, cyclohexene, or higher olefinic fraction, may be used. When such fractions are used, the saturated constituents thereof are passed from stripping column 45, through line 47 to line 2, leading to fractionator 3. If a hydrocarbon fraction comprising hydrocarbons of the same number of carbon atoms as those passed through line 47 is being fractionated in fractionator 5, the hydrocarbon stream flowing through line 47 is by-passed through valved line 55 into line 9.

Although the above-detailed description has been limited for the sake of simplicity to the isomerization of the butane and pentane content of the paraffinic hydrocarbon mixture charged, it is to be understood that a straight-chain paraffinic hydrocarbon having from six to ten carbon atoms may be separated and isomerized instead of the pentane. The invention, furthermore, contemplates the separate isomerization, in the presence of effluence of the butane isomerization zone, of more than one straight-chain hydrocarbon having from five to ten carbon atoms to the molecule. Though the invention is directed primarily to the production of branched-chain hydrocarbons from mixtures predominating in straight-chain hydrocarbons, it is not beyond the scope of the process to separate a higher branched-chain saturated hydrocarbon within the charge fractionating zone and subject it to separate catalytic isomerization in the presence of effluence of the first isomerizing zone to a more highly-branched isomer. The more highly-branched hydrocarbon thus obtained may, if desired, be passed to the alkylation zone. The additional isomerization and fractionating means which may be required for the execution of these various modifications of the invention have been omitted from the drawing for the purpose of avoiding undue complexity. When a plurality of hydrocarbons having from five to ten carbon atoms are isomerized, any single, several, or all of the resulting branched-chain paraffin hydrocarbons produced in the isomerization steps may be passed to the alkylating zone. Although but one alkylating unit is shown in the drawing, additional alkylating units may be provided to effect the alkylation in separate units of isobutane and one or more branched-chain saturated hydrocarbons having from five to ten carbon atoms to the molecule. The process of the invention thus enables the production of a wide variety of branched-chain hydrocarbon fractions optionally predominating in branched-chain hydrocarbons of the same number of carbon atoms, with a minimum of operative steps and in the absence of any hydrocarbon decomposition.

I claim as my invention:

1. In a process for the production of branched-chain hydrocarbons in the absence of any substantial hydrocarbon decomposition, the steps which comprise fractionating a substantially paraffinic hydrocarbon mixture comprising C_4 and C_5 hydrocarbons in a fractionating zone to separate fractions respectively rich in normal butane and normal pentane therefrom, contacting the normal butane fraction at a temperature in the range of from about 100° C. to about 200° C. with an aluminum halide catalyst in a first isomerizing zone, contacting the pentane fraction in admixture with the effluence of the first isomerizing zone at a temperature in the range of from about 40° C. to about 120° C. with an aluminum halide catalyst in a second isomerizing zone, separating isobutane and isopentane from the effluence of the second isomerizing zone, contacting said isobutane and isopentane in admixture with a hydrocarbon fraction predominating in butylene and butane at alkylating conditions with an alkylation catalyst, thereby reacting isobutane and isopentane with butylene, separating butane, isobutane, and isopentane as a vapor fraction from the products of alkylation, and passing said vapor fraction to said fractionating zone.

2. In a process for the production of branched-chain hydrocarbon fractions in the absence of any substantial hydrocarbon decomposition, the steps which comprise fractionating a substantially paraffinic hydrocarbon mixture comprising

hydrocarbons having from four to ten carbon atoms to the molecule in a fractionating zone to separate fractions respectively rich in normal butane and a higher saturated hydrocarbon having from five to ten carbon atoms to the molecule therefrom, contacting the normal butane fraction at a temperature in the range of from about 50° C. to about 300° C., with an aluminum halide catalyst in a first isomerizing zone, contacting the higher hydrocarbon fraction in admixture with the effluence of the first isomerizing zone at a temperature in the range of from about 30° C. to about 150° C. with an aluminum halide catalyst in a second isomerizing zone, separating branched-chain hydrocarbons from the effluence of the second isomerizing zone, contacting the branched-chain hydrocarbons in admixture with a hydrocarbon fraction predominating in butylene and butane at alkylating conditions with an alkylation catalyst, thereby reacting branched-chain hydrocarbons with butylene, separating butane and unreacted branched-chain hydrocarbons as a vapor fraction from the alkylation products, and passing said vapor fraction to said fractionating zone.

3. In a process for the production of branched-chain hydrocarbon fractions in the absence of any substantial hydrocarbon decomposition, the steps which comprise fractionating a substantially paraffinic hydrocarbon mixture comprising hydrocarbons having from four to ten carbon atoms to the molecule in a fractionating zone to separate fractions respectively rich in normal butane and a higher saturated hydrocarbon having from five to ten carbon atoms to the molecule therefrom, contacting the normal butane fraction at a temperature in the range of from about 100° C. to about 200° C., with an aluminum halide catalyst in a first isomerizing zone, contacting the higher hydrocarbon fraction in admixture with the effluence of the first isomerizing zone at a temperature in the range of from about 40° C. to about 50° C. with a catalyst comprising an aluminum halide and an adsorbent support material in a second isomerizing zone, separating the branched-chain hydrocarbons from the effluence of the second isomerizing zone, contacting the branched-chain hydrocarbons in admixture with a hydrocarbon fraction predominating in straight-chain olefine and paraffin hydrocarbons of the same number of carbon atoms at alkylating conditions with an alkylation catalyst, thereby reacting branched-chain hydrocarbons with the olefine, separating the straight-chain paraffin and unreacted branched-chain hydrocarbons as a vapor fraction from the alkylation products, and passing the vapor fraction to said fractionating zone.

4. In a process for the production of branched-chain hydrocarbon fractions in the absence of any substantial hydrocarbon decomposition, the steps which comprise fractionating a substantially paraffinic hydrocarbon mixture comprising hydrocarbons having from four to ten carbon atoms to the molecule in a fractionating zone to separate fractions respectively rich in normal butane and a higher saturated hydrocarbon having from five to ten carbon atoms to the molecule therefrom, contacting the normal butane fraction at a temperature in the range of from about 50° C. to about 300° C. with an aluminum halide catalyst in a first isomerizing zone, contacting the higher hydrocarbon fraction in admixture with the effluence of the first isomerizing zone at a temperature in the range of from about 80° C. to about 110° C. with a molten salt mixture comprising an aluminum halide in a second isomerizing zone, separating branched-chain hydrocarbons from the effluence of the second isomerizing zone, contacting the branched-chain hydrocarbons in admixture with a hydrocarbon fraction predominating in butylene and butane at alkylating conditions with an alkylation catalyst, thereby reacting branched-chain hydrocarbons and butylene, separating butane and unconverted branched-chain hydrocarbons as a vapor fraction from the alkylation products, and passing said vapor fraction to said fractionating zone.

5. In a process for the production of branched-chain hydrocarbons in the absence of any substantial hydrocarbon decomposition, the steps which comprise fractionating a substantially paraffinic hydrocarbon mixture comprising C_4 and C_5 hydrocarbons in a fractionating zone to separate fractions respectively rich in normal butane and normal pentane therefrom, contacting the normal butane fraction under isomerizing conditions with an aluminum halide catalyst in a first isomerizing zone, contacting said pentane fraction in admixture with the effluence of the first isomerizing zone under isomerizing conditions with an aluminum halide catalyst in a second isomerizing zone, separating isobutane and isopentane from the effluence of the second isomerizing zone, contacting said isobutane and isopentane in admixture with a hydrocarbon fraction predominating in butylene and butane at alkylating conditions with an alkylation catalyst, thereby reacting isobutane and isopentane with butylene, separating butane, isobutane, and isopentane as a vapor fraction from the products of alkylation, and passing the vapor fraction to said fractionating zone.

6. In a process for the production of branched-chain hydrocarbons in the absence of any substantial hydrocarbon decomposition, the steps which comprise fractionating a substantially paraffinic hydrocarbon mixture comprising C_4 and C_5 hydrocarbons in a fractionating zone to separate fractions respectively rich in normal butane and normal pentane therefrom, contacting the normal butane fraction under isomerizing conditions with an aluminum halide catalyst in a first isomerizing zone, contacting the pentane fraction in admixture with the effluence of the first isomerizing zone under isomerizing conditions with an aluminum halide catalyst in a second isomerizing zone, separating isobutane and isopentane from the effluence of the second isomerizing zone, contacting said isobutane and isopentane in admixture with a hydrocarbon fraction predominating in straight-chain olefine and paraffin hydrocarbons having the same number of carbon atoms at alkylating conditions with an alkylation catalyst, thereby reacting isobutane and isopentane with said olefine, separating the straight-chain paraffin and unreacted branched-chain hydrocarbons as a vapor fraction from the alkylation products, and passing the vapor fraction to said fractionating zone.

7. In a process for the production of branched-chain hydrocarbons in the absence of any substantial hydrocarbon decomposition, the steps which comprise fractionating a substantially paraffinic hydrocarbon mixture comprising hydrocarbons having from four to ten carbon atoms to the molecule in a fractionating zone to separate fractions respectively rich in normal butane and a higher saturated hydrocarbon having from

five to ten carbon atoms to the molecule therefrom, contacting the normal butane fraction under isomerizing conditions with an aluminum halide isomerization catalyst in a first isomerizing zone, contacting the higher hydrocarbon fraction in admixture with the effluence of the first isomerizing zone under isomerizing conditions with an aluminum halide catalyst in a second isomerizing zone, separating branched-chain hydrocarbons from the effluence of the second isomerizing zone, contacting the branched-chain hydrocarbons in admixture with a hydrocarbon fraction predominating in straight-chain olefine and paraffin hydrocarbons having the same number of carbon atoms at alkylating conditions with an alklation catalyst, thereby reacting branched-chain hydrocarbons with the olefine, separating the straight-chain paraffin and unreacted branched-chain hydrocarbons as a vapor fraction from the alkylation products, and passing the vapor fraction to said fractionating zone.

8. In a process for the production of branched-chain hydrocarbon fractions in the absence of any substantial hydrocarbon decomposition, the steps which comprise fractionating a substantially paraffinic hydrocarbon mixture comprising hydrocarbons having from four to ten carbon atoms to the molecule to separate fractions respectively rich in normal butane and a higher saturated hydrocarbon having from five to ten carbon atoms to the molecule therefrom, contacting the normal butane fraction under isomerizing conditions with an aluminum halide catalyst in a first isomerizing zone, contacting the higher hydrocarbon fraction in admixture with the effluence of the first isomerizing zone under isomerizing conditions with an aluminum halide catalyst in a second isomerizing zone, separating isobutane from the effluence of the second isomerizing zone, contacting the isobutane in admixture with a hydrocarbon fraction predominating in butylene and normal butane at alkylating conditions with an alkylation catalyst, thereby reacting isobutane with butylene, separating normal butane and unreacted isobutane as a vapor fraction from the alkylation products, and passing the vapor fraction to said fractionating zone.

9. In a process for the production of branched-chain hydrocarbon fractions in the absence of any substantial hydrocarbon decomposition, the steps which comprise fractionating a substantially paraffinic hydrocarbon mixture comprising hydrocarbons having from four to ten carbon atoms to the molecule in a fractionating zone to separate fractions respectively rich in normal butane and a higher saturated hydrocarbon having from five to ten carbon atoms to the molecule therefrom, contacting the normal butane fraction under isomerizing conditions with an aluminum halide isomerization catalyst in a first isomerizing zone, contacting the higher hydrocarbon fraction in admixture with the effluence of the first isomerizing zone under isomerizing conditions with an aluminum halide catalyst in a second isomerizing zone, separating isobutane from the effluence of the second isomerizing zone, contacting the isobutane in admixture with a hydrocarbon fraction predominating in a straight-chain olefine and paraffin of the same number of carbon atoms at alkylating conditions with an alkylation catalyst, thereby reacting isobutane with the olefine, separating the straight-chain paraffin and unreacted isobutane as a vapor fraction from the alkylation products, and passing said vapor fraction to said fractionating zone.

10. In a process for the production of branched-chain hydrocarbons in the absence of any substantial hydrocarbon decomposition, the steps which comprise fractionating a substantially saturated hydrocarbon mixture comprising hydrocarbons having from four to ten carbon atoms to the molecule in a fractionating zone to separate fractions respectively rich in normal butane, and a saturated isomerizable hydrocarbon having from five to ten carbon atoms to the molecule therefrom, contacting the normal butane fraction under isomerizing conditions with an aluminum halide isomerization catalyst in a first isomerizing zone, contacting the higher hydrocarbon fraction in admixture with the effluence of the first isomerizing zone under isomerizing conditions with an aluminum halide catalyst in a second isomerizing zone, passing the hydrocarbon isomerization products to said fractionating zone, separting a fraction predominating in a branched-chain hydrocarbon having from four to ten carbon atoms to the molecule in said fractionating zone, contacting said branched-chain hydrocarbon fraction in admixture with a hydrocarbon fraction predominating in butylene and butane at alkylating conditions with an alkylation catalyst, thereby reacting said branched-chain hydrocarbon with butylene, separating butane and the unreacted branched-chain hydrocarbon as a vapor fraction from the alkylation products, and passing said vapor fraction to said fractionating zone

11. In a process for the production of branched-chain hydrocarbons in the absence of any substantial hydrocarbon decomposition, the steps which comprise fractionating a substantially saturated hydrocarbon mixture in a fractionating zone to separate fractions respectively rich in normal butane, and a saturated isomerizable hydrocarbon having from five to ten carbon atoms to the molecule therefrom, contacting the normal butane fraction under isomerizing conditions with an aluminum halide isomerization catalyst in a first isomerizing zone, contacting the higher hydrocarbon fraction in admixture with the effluence of the first isomerizing zone under isomerizing conditions with an aluminum halide catalyst in a second isomerizing zone, passing the hydrocarbon isomerization products to said fractionating zone, separating a fraction predominating in a branched-chain hydrocarbon having from four to ten carbon atoms to the molecule in said fractionating zone, contacting said branched-chain hydrocarbon fraction in admixture with a hydrocarbon fraction predominating in straight-chain olefine and paraffin hydrocarbons having the same number of carbon atoms at alkylating conditions with an alkylating catalyst, thereby reacting the branched-chain hydrocarbon with said olefine, separating the straight-chain paraffin and the unreacted branched-chain hydrocarbon as a vapor fraction from the alkylation products and passing said vapor fraction to said fractionating zone.

12. In a process for the production of branched-chain hydrocarbons in the absence of any substantial hydrocarbon decomposition, the steps which comprise fractionating a substantially paraffinic hydrocarbon mixture comprising hydrocarbons having from four to ten carbon atoms to the molecule in a fractionating zone to separate fractions respectively rich in normal butane and a higher saturated hydrocarbon having from five to ten carbon atoms to the molecule therefrom

contacting the normal butane fraction in admixture with a hydrogen halide promoter at isomerizing conditions with an aluminum halide isomerization catalyst in a first isomerizing zone, contacting the higher hydrocarbon fraction in admixture with the effluence of the first isomerizing zone under isomerizing conditions with an aluminum halide catalyst in a second isomerizing zone, separating the hydrogen halide promoter and branched-chain hydrocarbons from the effluence of the second isomerizing zone, recycling hydrogen halide promoter to the first isomerizing zone, contacting the branched-chain hydrocarbons in admixture with a hydrocarbon fraction predominating in butylene and butane at alkylating conditions with an alkylation catalyst, thereby reacting branched-chain hydrocarbons with butylene, separating normal butane and unreacted branched-chain hydrocarbons as a vapor fraction from the alkylation products, and passing the vapor fraction to said fractionating zone.

13. In a process for the production of branched-chain hydrocarbons in the absence of any substantial hydrocarbon decomposition, the steps which comprise fractionating a substantially paraffinic hydrocarbon mixture comprising hydrocarbons having from four to ten carbon atoms to the molecule in a fractionating zone to separate fractions respectively rich in normal butane and a higher saturated hydrocarbon having from five to ten carbon atoms to the molecule therefrom, contacting the normal butane fraction in admixture with a hydrogen halide promoter at isomerizing conditions with an aluminum halide isomerization catalyst in a first isomerizing zone, contacting the higher hydrocarbon fraction in admixture with the effluence of the first isomerizing zone under isomerizing conditions with an aluminum halide catalyst in a second isomerizing zone, separating hydrogen halide, isobutane, and a higher branched-chain hydrocarbon from the effluence of the second isomerizing zone, recycling a part of said isobutane to the second isomerizing zone, contacting the remaining isobutane and higher branched-chain hydrocarbon in admixture with a hydrocarbon fraction predominating in butylene and butane at alkylating conditions with an alkylation catalyst, thereby reacting branched-chain hydrocarbons with butylene, separating normal butane and unreacted branched-chain hydrocarbons as a vapor fraction from the alkylation products, and passing the vapor fraction to said fractionating zone.

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