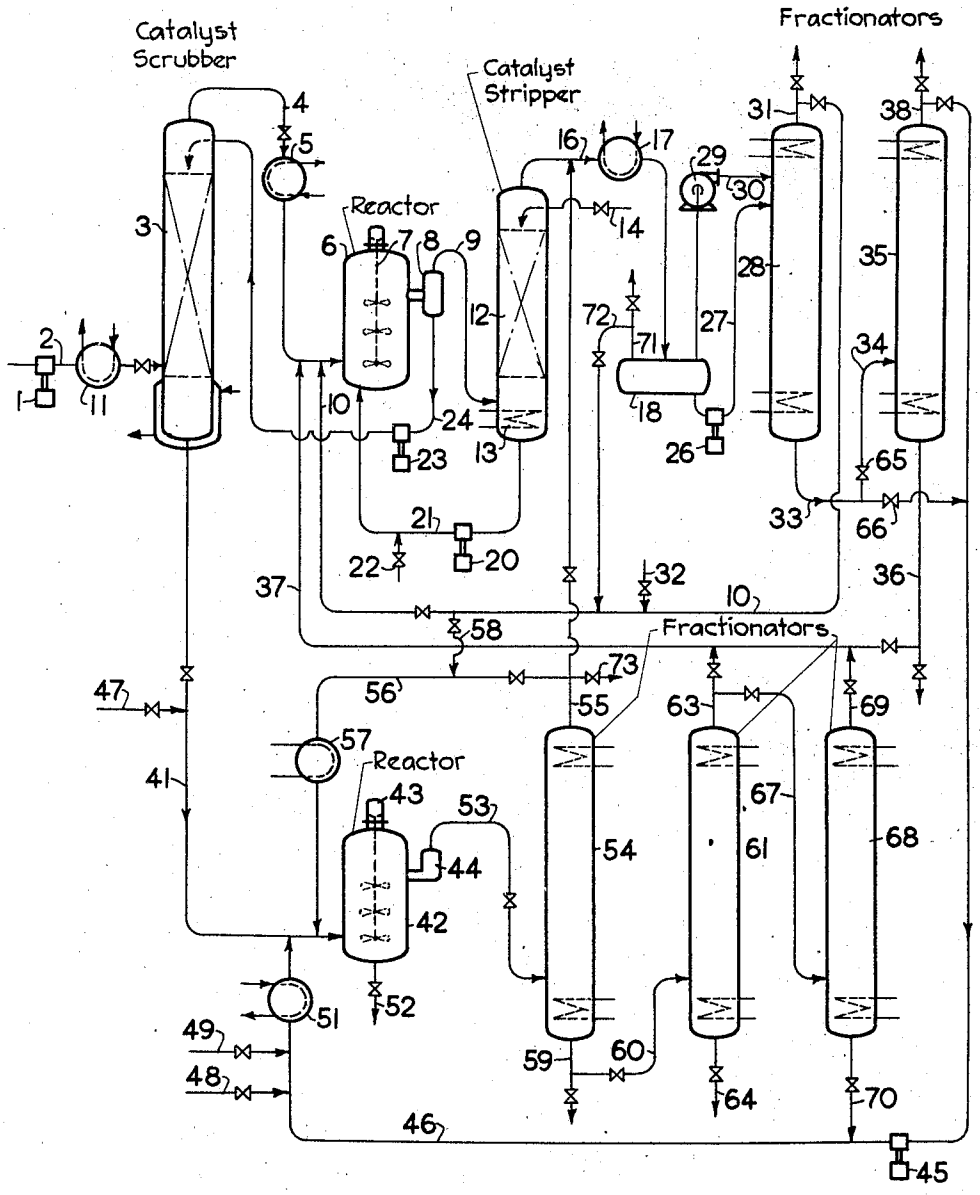
Feb. 12, 1946. W. E. ROSS 2,394,810

PRODUCTION OF BRANCHED CHAIN HYDROCARBONS

Filed Nov. 24, 1942



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Patented Feb. 12, 1946 2,394,810

UNITED STATES PATENT OFFICE

2,394,810

PRODUCTION OF BRANCHED CHAIN HYDROCARBONS

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Application November 24, 1942, Serial No. 466,790

13 Claims. (Cl. 260—683.5)

This invention relates to the production of branched chain hydrocarbons.

An object of the invention is the provision of a more efficient and economical process for the production of branched chain hydrocarbons from straight chain paraffin and olefin hydrocarbons. Another object of the invention is the provision of a process for the more efficient production of branched chain saturated hydrocarbons from saturated hydrocarbons comprising open chain saturated hydrocarbons and unsaturated hydrocarbons comprising ethylene. Still another object of the invention is the provision of a process for the more efficient production of 2,3-dimethyl butane from saturated hydrocarbon fractions comprising butane and unsaturated hydrocarbon fractions comprising ethylene.

Methods whereby the straight chain paraffin and olefin hydrocarbons, particularly the lower boiling of these hydrocarbons, abundantly available in the petroleum industry, can be processed to obtain as the major product a single hydrocarbon of branched structure or a mixture of branched chain hydrocarbons having the same number of carbon atoms to the molecule, are often greatly desired. The use of processes wherein hydrocarbon cracking is the principal reaction is, in such cases, unsuited 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. Resort is therefore often had to the treatment of these materials under non-cracking conditions effecting the conversion of the open chain paraffinic hydrocarbon to a branched or a more highly branched chain product and the combining of the resulting branched chain product with an available olefin hydrocarbon to obtain a desired branched chain product of higher molecular weight than the starting materials. Utilization of several catalysts of entirely different nature, and the consequent increase in operative steps involved, often renders uneconomical the large scale operation of many of the processes, comprising exclusively non-cracking steps, available heretofore for the production of branched chain hydrocarbons from lower molecular weight hydrocarbons. These processes are furthermore limited in their scope of efficient application since they are generally inapplicable to the practical utilization of the abundantly available ethylene, or ethylene-containing hydrocarbon fractions, as a starting material.

Catalysts particularly efficient in their ability to catalyze the conversion of open chain paraffin hydrocarbons to branched or more highly branched chain paraffin hydrocarbons comprise those of the molten salt type consisting of molten mixtures of halide salts at least one of which is a halide of the Friedel-Crafts type. The efficiency of these catalyst melts is adversely affected by the presence of spent or partly spent catalyst components within the melt. It has now been found that the degree to which the catalyst melt is adversely affected is substantially proportional to the amount of spent or partly spent catalyst components in the body of the entire melt, and that removal of these spent components substantially as rapidly as formed results in the maintenance of exceedingly high catalyst activity over longer periods of operation. The catalyst components, which are at least partly spent with respect to their ability to catalyze the hydrocarbon isomerization reaction, may be removed from the catalyst melt efficiently within the system by scrubbing the molten catalyst with incoming hydrocarbon feed, thereby separating a fluid catalyst residue, comprising the spent or partially spent catalyst components, from active catalyst components. Such continuous and thorough scrubbing of the catalyst melt, however, results in a relatively rapid removal of catalyst components from the system, thereby considerably increasing the cost of operation. It has now been found that the fluid catalyst residue comprising the spent catalyst components thus removed in the scrubbing operation, to which a small proportion of fresh aluminum chloride has been preferably added, can be used advantageously to effect the reaction between branched chain saturated hydrocarbon and olefinic hydrocarbons. The fact that the fluid catalyst residue produced as a by-product in the isomerization of a saturated hydrocarbon can be utilized as a catalyst in a subsequent alkylation of branched chain hydrocarbons thus brings within the realm of economic feasibility a novel and exceedingly efficient process for the production of branched chain hydrocarbons of higher molecular weight than the starting materials. However, a still more advantageous feature of such a process resides in the fact that the inherent characteristics of the fluid catalyst residue thus obtained as a by-product in the isomerization of paraffinic hydrocarbons enables the efficient alkylation of isoparaffins with ethylene. Thus, isobutane can be alkylated with ethylene in its presence to a product consisting mainly of the highly desirable 2,3-dimethyl butane. The fluid catalyst residue obtained as a by-product in the isomerization of saturated hydrocarbons, to

which a small amount of aluminum chloride has preferably been added to enhance its activity, thus presents a distinct advantage over the utilization of alkylation catalysts, such as, for example, sulfuric acid, which are found to be impractical for the alkylation of isoparaffins with ethylene, and over the hydrocarbon-aluminum chloride complex sludge type catalysts, such as the complexes formed by reacting aluminum chloride with toluene or a kerosene extract, which are rendered unsuitable because of the apparent tendency of the ethylene to react with the aromatic hydrocarbon constituent of the catalyst.

In accordance with the invention, saturated hydrocarbons, comprising at least one straight chain paraffin hydrocarbon, are contacted under isomerizing conditions with a catalyst comprising a mixture of halide salts, at least one of which is a halide of the Friedel-Crafts type, in a first reaction zone, thereby effecting the conversion of straight chain paraffin hydrocarbons to branched chain paraffin hydrocarbons. A portion of the catalyst melt is continuously passed from the first reaction zone into a scrubbing zone wherein it is scrubbed with incoming hydrocarbon feed. Within the scrubbing zone a fluid catalyst residue, which comprises catalyst components at least partially spent with respect to their ability to catalyze the hydrocarbon isomerization reaction, is separated from active soluble catalyst components. The feed containing dissolved catalyst components is passed to the first reaction zone. A part or all of the hydrocarbon products comprising branched chain paraffin hydrocarbons emanating from the first reaction zone is admixed with olefin hydrocarbons from an outside source. The resulting mixture of hydrocarbons is contacted under alkylating conditions in a second reaction zone with the fluid catalyst residue separated in the scrubbing zone, and to which a small amount of fresh Friedel-Crafts type halide has been preferably added, thereby alkylating branched chain paraffins with olefins. Products from the second reaction zone are fractionated to separate a product comprising branched chain hydrocarbon reaction product therefrom.

In order that the invention may be more fully set forth and more readily understood, reference is made to the single drawing accompanying and forming part of this specification. The single figure in the drawing is a more or less diagrammatic elevational view of one form of apparatus suitable for executing the invention.

An isomerizable saturated hydrocarbon such as, for example, butane from any suitable source is forced by means of pump 1 through valved line 2 into an intermediate part of an extraction zone. The extraction zone may consist of a column 3 provided with suitable packing material, baffles or the like. Within extraction column 3 the butane is contacted in the liquid phase with a portion of the catalyst emanating from the reaction zone as described more fully below. Liquid butane comprising extracted catalyst components is passed from extraction column 3 through valved line 4 and heater 5 into a reaction zone.

The reaction zone may consist of a suitable reactor 6 provided with stirring means 7 and a separating chamber 8. Although but one such reactor is shown within the drawing, it is to be understood that a plurality of such reactors, connected in series or in parallel, may be used. Within reactor 6 the butane is contacted with a suitable isomerization catalyst of the molten salt type. Such catalysts comprise mixtures of molten halide salts, at least one of which is a halide of the Friedel-Crafts type. A particularly efficient isomerization catalyst comprises, for example, a molten mixture of an antimony halide and an aluminum halide. A molten mixture of $AlCl_3$ and $SbCl_3$, containing from about 3 to 24 mol percent of aluminum chloride and modified, if desired, by the presence of a halide of an alkali or an alkaline earth metal, is highly suitable. It is to be understood, however, that the invention is in no wise limited to but one specific catalyst of the molten salt type, and other catalyst melts may be employed such as, for example, any of the following molten mixtures: aluminum chloride-sodium chloride-potassium chloride, aluminum chloride-sodium chloride-zinc chloride, aluminum chloride-sulfur dioxide-zinc chloride, aluminum chloride-sodium chloride-potassium chloride-zinc chloride, etc. A part or all of the halide components of the catalysts may comprise halides other than the chlorides, for example, the bromides.

The temperature to be maintained within reaction chamber 6 may vary, for example, from about 50° C. to about 300° C. and preferably from about 80° C. to about 200° C., and is controlled by judicious heat input into heater 5 and, if needed, by additional heating means not shown in the drawing. The isomerization reaction is preferably executed in the presence of a hydrogen halide such as, for example, hydrogen chloride. The hydrogen chloride is introduced into the charge flowing through line 4 by means of line 10. Under these conditions butane will be converted to isobutane within reactor 6.

The isomerization reaction may be executed in the vapor or liquid phase. When operating in the liquid phase, a pressure at least sufficiently high is maintained within reactor 6 to keep at least a substantial part of the butane in the liquid phase.

Within separation chamber 8 a substantial degree of separation between catalyst melt and hydrocarbon will be effected. The supernatent hydrocarbon layer, which in general will comprise some admixed and dissolved catalyst, is withdrawn from separator 8 and passed through line 9 into a vaporizing zone. The vaporizing zone may suitably consist of the lower part of a column 12, an intermediate part of which is provided with suitable packing means, baffles, or the like. Within column 12 separation of hydrocarbons from entrained catalyst components is effected with the aid of heating coil 13. Since antimony chloride is relatively volatile, its separation from the hydrocarbon within column 12 is aided by the introduction of cold hydrocarbon reflux into the upper part of the column by means of valved line 14. Vapors comprising isobutane, unconverted normal butane and hydrogen chloride promoter are passed from the upper part of column 12 through line 16 and cooler 17 into accumulator 18. In passing through cooler 17 the stream is cooled to a temperature sufficiently low to effect the condensation of butanes. Catalyst components consisting essentially of antimony chloride, separated out as a liquid fraction within column 12, are forced by means of pump 20 through line 21 into reactor 6. Additional aluminum chloride, required to maintain catalyst composition, is added to the catalyst flowing through line 21 by passing this stream through a suitable vessel containing anhydrous $AlCl_3$ or by the addition of the halide salt by means of valved

conduit 22. The catalyst phase, separated out within separator 8, is forced by means of pump 23 through line 24 into the upper part of extraction column 3. The portion of catalyst thus introduced into extraction column 3 will pass countercurrent to the upflow of the liquid hydrocarbon. In its passage through column 3 a portion of catalyst comprising antimony chloride is dissolved in the hydrocarbon stream and passed therewith to reactor 6. Another portion of the catalyst comprising components which are spent, or at least partly spent, with respect to their ability to catalyze the isomerization reaction, remains insoluble in the hydrocarbon stream and is separated therein as a heavier fluid catalyst residue. The hydrocarbon charge to the system is preferably preheated, for example, with the aid of a suitable heat exchanger 11, to a temperature favorable to the extraction operation. This temperature will vary with the nature of the material being treated and the particular catalyst used. In the treatment of paraffinic hydrocarbons temperatures in the approximate range of from 50° C. to 125° C. and preferably from 50° C. to 100° C. are found suitable. The pressure within column 3 is always sufficiently high to maintain at least a substantial portion of the hydrocarbon stream passing therethrough in the liquid phase.

It has been found that the fluid catalyst residue separated within extractor 3 will comprise any hydrocarbon-aluminum chloride complex formed within reactor 6. It has also been found that this material is substantially insoluble in the hydrocarbon feed which contributed to its formation and will not undergo decomposition or disintegration to any substantial degree in the extraction zone, whereas the still active antimony chloride-aluminum chloride catalyst possesses an appreciable degree of solubility in the normal butane. The composition of the fluid catalyst residue separated within column 3 will vary to some degree with the nature of material treated and operating conditions used. The catalyst residue thus obtained as a by-product of the isomerization operation is found to possess appreciable fluidity and will maintain this fluidity at temperatures substantially below room temperatures. The lower part of column 3 may, however, be provided with a jacket for the passage of a heating medium therethrough to aid in maintaining the desired temperature conditions therein.

The rate at which catalyst is withdrawn from separating chamber 8 and passed to the upper part of extractor 3 may vary within the scope of the invention. As pointed out above, however, it is highly advantageous to effect the catalyst withdrawal at a rate sufficiently great to prevent the accumulation to any substantial degree of even partially spent catalyst within the reactor.

From accumulator 18 liquid comprising isobutane and normal butane is forced by means of pump 26 through line 27 into a stripping column 28. Gases and vapors, separately withdrawn from accumulator 18, are forced by means of compressor 29 through line 30 into stripping column 28. Within stripping column 28 the hydrogen chloride promoter is separated from the hydrocarbon material, and removed therefrom through valved line 31. A portion or all of the hydrogen halide promoter passing through line 31 is recycled through valved line 10 to the reaction zone. Make-up hydrogen chloride is introduced into line 10 from an outside source through valved line 32. A liquid fraction comprising normal butane and isobutane is passed through valved lines 33 and 34 into a fractionator 35. Within fractionator 35 a liquid fraction comprising normal butane is separated from a vapor fraction comprising isobutane. The liquid fraction is withdrawn from column 35 through valved line 36 and passed in part or in its entirety through valved line 37 to the isomerization zone. The vapor fraction is removed overhead from column 35 through valved line 38.

The fluid catalyst residue separated within extraction column 3 is withdrawn therefrom through valved line 41 and passed to a second reaction zone. A small amount of fresh aluminum chloride is preferably added thereto by passing a part or all of the stream through a vessel containing anhydrous $AlCl_3$ or by addition of the halide salt through valved conduit 47. The amount of fresh aluminum chloride added to the fluid catalyst residue may vary within the scope of the invention in accordance with the particular materials treated, composition of the isomerization catalyst, operating conditions, etc. Addition of fresh aluminum chloride in amounts ranging from exceedingly small amounts, for example, about one percent, to substantially larger proportions up to, for example, about twenty percent of the resulting catalyst mixture, is suitable. Greater or lesser amounts may be added, however, as occasion requires without adversely affecting that peculiar quality of the resulting mixture which is imparted thereto by the inherent characteristics of the by-product catalyst residue emanating from scrubber 3. If desired, a Friedel-Crafts type halide other than aluminum chloride, and even differing from that utilized in the melt in reactor 6, may constitute the fresh portion of the catalyst component added to the catalyst residue passing through line 41. The second reaction zone may consist of a reactor 42 provided with suitable stirring means 43 and a suitable separating chamber, for example, a separating chamber 44 in communication with the rest of the reactor in such wise that liquid may flow therefrom by gravity into the reactor proper. Although but one such reactor is shown in the drawing, one or more reactors connected in series or in parallel may be used.

A part or all of the isobutane passing through line 38 is forced by means of pump 45 through line 46 into line 41 leading into reactor 42. If desired, additional hydrocarbons comprising branched chain saturated hydrocarbons may be drawn from an outside source and introduced into line 46 by means of valved line 48. A substantially olefinic hydrocarbon fraction such as, for example, a fraction predominating in ethylene is introduced from an outside source through valved line 49 into line 46. Within reactor 42 the mixture of olefinic and paraffinic hydrocarbons is subjected to alkylating conditions to effect the alkylation of isobutane with ethylene, thereby forming branched chain hydrocarbons, which because of the inherent nature of the catalyst produced within the system will comprise mainly 2,3-dimethyl butane. Suitable temperature conditions to be maintained within reactor 42 comprise a temperature within the range of from about 0° C. to about 80° C., preferably from about 20° C. to about 40° C. The temperature within reactor 42 may be maintained by means of a suitable indirect heat exchanger 51 and other means not shown in the drawing. An excess of paraffins with respect to olefins is maintained within re-

actor 42. Thus, the ratio of paraffins to olefins may be as high as 4:1 and even higher, if desired.

The presence of a hydrogen halide is found advantageous to the alkylation reaction, smaller amounts of hydrogen halide being, in general, required within reactor 42 then in reactor 6. Thus, an amount of hydrogen chloride not substantially in excess of about one percent, for example, less than 0.5 percent, of the hydrocarbon charge to reactor 42 has been found suitable. Higher proportions may, however, be used. The hydrogen halide promoter supplied to reactor 42 need not necessarily be the same halide as that introduced into reactor 6.

Within separator 44 separation of hydrocarbons from the catalyst is effected. The catalyst which separates as a lower layer flows back into reactor 42. Spent catalyst in the form of a sludge is removed from reactor 42 through valved line 52. The spent sludgy material thus eliminated through line 52 may be treated to recover $AlCl_3$ therefrom by means not shown in the drawing. Such recovery means may comprise the more drastic means involving distillation or heating to effect decomposition of the aluminum chloride-hydrocarbon complex contained therein. From separator 44 a supernatant hydrocarbon layer comprising the desired alkylate, unreacted olefins and paraffins, and hydrogen halide promoter are passed through valved line 53 into a fractionator 54. Within fractionator 54 a lighter fraction comprising hydrogen chloride, unconverted ethylene and isobutane is separated and removed therefrom through valved line 55. This lighter fraction is passed in part or in its entirety from line 55 through valved line 56 and heater 57 into line 41. Make-up hydrogen halide for the alkylation zone may be diverted from line 10 through valved line 58 into line 56.

Alkylate and unreacted butane, separated as a liquid fraction within fractionator 54, are removed therefrom through valved line 59 and passed in part or in their entirety through valved line 60 into fractionator 61. Within fractionator 61 any normal butane present is stripped from the alkylate and passed through valved line 63 into line 37 leading to reactor 6. The alkylate comprising 2,3-dimethyl butane is withdrawn from fractionator 61 through valved line 64 as a final product.

If desired, all of the hydrocarbon product removed as a liquid fraction from fractionator 28 and comprising both normal and isobutane may be passed directly, by judicious manipulation of valves 65 and 66, into line 46 leading to reactor 42.

It is to be pointed out that the invention is in no wise limited to the production of branched chain hydrocarbons from starting materials consisting of a paraffin and an olefin which is lower boiling than the paraffin. When the olefin introduced into the system is heavier than the paraffinic hydrocarbons passed into reactor 42, unreacted branched chain paraffin hydrocarbons are recycled together with the hydrogen chloride promoter to the alkylation zone through lines 55 and 56. Remaining reaction products, comprising the desired branched chain alkylate, unreacted olefin and some normal paraffins, are fractionated in fractionator 61 to separate the alkylate as a liquid fraction which is withdrawn therefrom through valved line 64. Remaining olefin and paraffin hydrocarbons are passed from fractionator 61 through valved lines 63 and 67 into a fractionator 68 wherein the paraffins are separated as a vapor fraction from a liquid fraction comprising unreacted olefins. The vapor fraction is passed from fractionator 68 through valved lines 69, 37, and 4 into reactor 6. The liquid fraction is drawn from fractionator 68 through valved line 70 and passed through valved lines 46 and 41 to reactor 42.

Under certain conditions it may be desirable to pass at least a part of the lighter fraction comprising the hydrogen halide promoter separated within fractionator 54 to accumulator 18. This may be accomplished by passing the overhead from fractionator 54 through line 55 into line 16. This method of operation is often desirable as additional means for controlling the amount of hydrogen halide recycled to the alkylating zone. Light gases may be withdrawn from accumulator 18 through valved line 71 and passed in part or in their entirety through valved lines 72, 10, 58, 56 and 41 into reactor 42.

Although the process of the invention has been described in its application to the production of a branched chain hydrocarbon fraction comprising 2,3-dimethyl butane from normal butane and ethylene, it is to be understood that the invention is in no wise limited to the use of these particular hydrocarbons as the starting materials. Any saturated hydrocarbon capable of being isomerized to a branched or more highly branched chain saturated hydrocarbon may constitute the saturated hydrocarbon charge to the system. It need not necessarily be a pure hydrocarbon and may have admixed therewith one or more other saturated hydrocarbons which may or may not be isomerized under the conditions of execution of the reaction. Particularly desirable saturated hydrocarbon starting materials comprise fractions such as the butane, pentane, hexane, etc., fractions obtained by fractional distillation of natural or straight run gasoline or saturated hydrocarbon mixtures from any other sources. A saturated hydrocarbon mixture of considerably wider boiling range, which may comprise a substantial portion or all of the hydrocarbons boiling within the gasoline range, such as a natural gasoline, casinghead gasoline or the like may constitute the saturated hydrocarbon charge to the system. In passing through the isomerization stage of the process substantial proportions of branched chain hydrocarbons are produced. The resulting isomerizate may be passed in part or in its entirety to the alkylation zone. It may be desirable to pass only a lower boiling fraction of the isomerizate to the alkylation zone in admixture with olefinic hydrocarbons and combine the resulting alkylate with the remaining higher boiling portion of the isomerizate.

An advantage of the invention resides in the economical and efficient utilization of ethylene or ethylene-containing fractions in the production of a branched chain hydrocarbon product. The invention is, however, not limited to the use of ethylene or ethylene-containing fractions as the olefinic charge to the process. Other olefins or olefinic fractions, such as those comprising, for example, propylene, butylene, amylene, cyclopentene, cyclohexene, or higher olefins, may be used. The olefin may be charged to the alkylation zone in admixture with paraffinic hydrocarbons, thus enabling the use of ethane-ethylene, propane-propylene, butane-butylene, etc. fractions without the need for a preliminary separation of the olefin from the paraffin. When an olefin-containing fraction comprising a sub-

stantial amount of ethane, such as, for example, an ethane-ethylene fraction, is charged to the alkylation zone, ethane is preferably removed from the hydrogen chloride-containing fraction separated from the effluence of the alkylation reactor before this fraction is recycled thereto. This may be accomplished by diverting all or a part of the stream flowing through line 55 through valved line 73, and subjecting it to any suitable treatment for the separation of ethane therefrom by means not shown in the drawing, and returning the substantially ethane-free fraction comprising hydrogen chloride to reactor 42. The means utilized for effecting the separation of ethane may comprise such steps as distillation scrubbing with suitable absorbents for hydrogen chloride, etc.

The process of the invention thus enables the efficient and highly economical 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, a high level of catalyst activity and maximum utilization of catalyst components charged to the system.

It is to be understood that the apparatus shown may be modified as apparent to one skilled in the art without departing from the scope of the invention. Thus for the sake of clarity parts of apparatus such as, for example, certain additional heating means, fractionator reboilers, condensers, means for providing reflux to fractionators, accumulators, catalyst storage means, valves and the like have been omitted from the drawing.

Example

Butane was treated in the isomerization reactor with a molten mixture of antimony trichloride and aluminum chloride containing 11% $AlCl_3$ at a temperature of 90° C. with contact time of 6 minutes and a catalyst to hydrocarbon ratio of 1 to 1 by volume. Hydrogen chloride in the amount of 4 to 5% by weight of the butane charged was introduced into the reactor. Catalyst melt was passed from the reactor to the scrubber and scrubbed therein with incoming butane at a rate sufficiently high to preclude the presence to any substantial degree of spent catalyst components within the reactor. The conversion of butane to isobutane was maintained at 42% per pass. The isobutane product and fluid catalyst residue separated out in the scrubber were introduced into the alkylation reactor. A fresh portion of $AlCl_3$ in the amount of 17% by weight of the resulting mixture was added to the fluid catalyst residue entering the alkylation reactor. Ethylene was introduced into the alkylation reactor at a rate providing a mol ratio of isobutane to ethylene of 3 to 1. With a contact time of 20 minutes and a temperature of 25° C. the hydrocarbon effluence of the alkylation reactor contained 25% by weight of hexanes consisting predominantly of 2,3-dimethyl butane.

I claim as my invention:

1. A process for the production of 2,3-dimethyl butane which comprises contacting normal butane with a catalyst melt comprising aluminum chloride and antimony chloride at isomerizing conditions in a first reaction zone thereby converting normal butane to isobutane, continuously removing a portion of the catalyst melt from the first reaction zone, contacting said portion of catalyst melt with butane passing to the first reaction zone thereby separating active catalyst components from a fluid catalyst residue, adding aluminum chloride to said catalyst residue, separating isobutane from the effluence of the first reaction zone, contacting said isobutane together with added ethylene at alkylating conditions with said aluminum chloride-containing catalyst residue in a second reaction zone thereby reacting isobutane with ethylene to form a branched chain hydrocarbon alkylation product comprising 2,3-dimethyl butane, and separating hydrocarbons comprising said 2,3-dimethyl butane from the effluence of the second reaction zone.

2. In a process for the production of branched chain hydrocarbons, the steps which comprise contacting normal butane with a catalyst melt comprising aluminum chloride and antimony chloride at isomerizing conditions in a first reaction zone thereby converting normal butane to isobutane, continuously removing a portion of the catalyst melt from the first reaction zone, contacting said portion of catalyst melt with butane passing to the first reaction zone thereby separating active catalyst components from a fluid catalyst residue, adding aluminum chloride to said catalyst residue, separating isobutane from the effluence of the first reaction zone, contacting said isobutane together with an added straight chain olefinic hydrocarbon at alkylating conditions with said aluminum chloride-containing catalyst residue in a second reaction zone thereby reacting isobutane with said olefin to form a branched chain hydrocarbon alkylation product, and separating hydrocarbons comprising said alkylation product from the effluence of the second reaction zone.

3. In a process for the production of branched chain hydrocarbons, the steps which comprise contacting saturated hydrocarbons comprising an open chain saturated hydrocarbon with a catalyst melt comprising aluminum chloride and antimony chloride at isomerizing conditions in a first reaction zone thereby converting straight or branched chain saturated hydrocarbons to branched or more highly branched chain saturated hydrocarbons, continuously removing a portion of the catalyst melt from the first reaction zone, contacting said portion of catalyst melt with said saturated hydrocarbons passing to the first reaction zone thereby separating active soluble catalyst components from a fluid catalyst residue, adding aluminum chloride to said catalyst residue, contacting at least a portion of the effluence of the first reaction zone comprising saturated branched chain hydrocarbons together with added ethylene at alkylating conditions with said aluminum chloride-containing catalyst residue in a second reaction zone thereby reacting saturated branched chain hydrocarbons with ethylene to form a branched chain hydrocarbon alkylation product, and separating hydrocarbons comprising said alkylation product from the effluence of the second reaction zone.

4. In a process for the production of branched chain hydrocarbons, the steps which comprise contacting saturated hydrocarbons comprising an open chain saturated hydrocarbon with a catalyst melt comprising aluminum chloride and antimony chloride at isomerizing conditions in a first reaction zone thereby converting straight or branched chain saturated hydrocarbons to branched or more highly branched chain saturated hydrocarbons, continuously removing a portion of the catalyst melt from the first reaction zone, contacting said portion of catalyst melt with saturated hydrocarbons passing to the first

reaction zone thereby separating active soluble catalyst components from a fluid catalyst residue, adding aluminum chloride to said catalyst residue, contacting at least a portion of the effluence of the first reaction zone comprising branched chain hydrocarbons together with an added hydrocarbon fraction predominating in a straight chain olefin at alkylating conditions with said aluminum chloride-containing catalyst residue in a second reaction zone thereby reacting branched chain saturated hydrocarbons with said olefin to form a branched chain hydrocarbon alkylation product, and separating hydrocarbons comprising said alkylation product from the effluence of the second reaction zone.

5. In a process for the production of branched chain hydrocarbons, the steps which comprise contacting normal butane with a catalyst melt comprising a mixture of halide salts at least one of which is a halide of aluminum at isomerizing conditions in a first reaction zone thereby converting normal butane to isobutane, continuously removing a portion of the catalyst melt from the first reaction zone, contacting said portion of catalyst melt with butane passing to the first reaction zone thereby separating active catalyst components from a fluid catalyst residue, adding aluminum halide to said catalyst residue, separating isobutane from the effluence of the first reaction zone, contacting said isobutane together with added ethylene at alkylating conditions with said aluminum halide-containing catalyst residue in a second reaction zone thereby reacting isobutane with ethylene to form a branched chain hydrocarbon alkylation product, and separating hydrocarbons comprising said alkylation product from the effluence of the second reaction zone.

6. In a process for the production of branched chain hydrocarbons, the steps which comprise contacting saturated hydrocarbons comprising an open chain saturated hydrocarbon with a catalyst melt comprising a molten mixture of halide salts at least one of which is a halide of aluminum at isomerizing conditions in a first reaction zone thereby converting straight or branched chain saturated hydrocarbons to branched or more highly branched chain saturated hydrocarbons, continuously removing a portion of the catalyst melt from the first reaction zone, contacting said portion of catalyst melt with said saturated hydrocarbons passing to the first reaction zone thereby separating active catalyst components from a fluid catalyst residue, adding aluminum halide to said catalyst residue, contacting at least a portion of the effluence of the first reaction zone comprising saturated branched chain hydrocarbons together with added ethylene at alkylating conditions with said aluminum halide-containing catalyst residue in a second reaction zone thereby reacting saturated branched chain hydrocarbons with ethylene to form a branched chain hydrocarbon alkylation product, and separating hydrocarbons comprising said alkylation product from the effluence of the second reaction zone.

7. In a process for the production of branched chain hydrocarbons, the steps which comprise contacting saturated hydrocarbons comprising an open chain saturated hydrocarbon with a catalyst melt comprising a molten mixture of halide salts at least one of which is a halide of aluminum at isomerizing conditions in a first reaction zone thereby converting straight or branched chain saturated hydrocarbons to branched or more highly branched chain saturated hydrocarbons, continuously removing a portion of the catalyst melt from the first reaction zone, contacting said portion of catalyst melt with saturated hydrocarbons passing to the first reaction zone thereby separating active catalyst components from a fluid catalyst residue, adding aluminum halide to said catalyst residue, contacting at least a portion of the effluence of the first reaction zone comprising branched chain saturated hydrocarbons together with an added hydrocarbon fraction predominating in a straight chain olefin at alkylating conditions with said aluminum halide-containing catalyst residue in a second reaction zone thereby reacting branched chain saturated hydrocarbons with said olefin to form a branched chain hydrocarbon alkylation product, and separating hydrocarbons comprising said alkylation product from the effluence of the second reaction zone.

8. In a process for the production of branched chain hydrocarbons, the steps which comprise contacting normal butane with a catalyst melt comprising a molten mixture of halide salts at least one of which is a halide of the Friedel-Crafts type at isomerizing conditions in a first reaction zone thereby converting normal butane to isobutane, continuously removing a portion of the catalyst melt from the first conversion zone, contacting said portion of catalyst melt with butane passing to the first reaction zone thereby separating active catalyst components from a fluid catalyst residue, adding a fresh portion of said halide of the Friedel-Crafts type to said catalyst residue, contacting at least a part of the effluence of the first conversion zone comprising isobutane together with added ethylene at alkylating conditions with said Friedel-Crafts type halide-containing catalyst residue in a second reaction zone thereby reacting isobutane with ethylene to form a branched chain hydrocarbon alkylation product, and separating hydrocarbons comprising said alkylation product from the effluence of the second reaction zone.

9. In a process for the production of branched chain hydrocarbons, the steps which comprise contacting saturated hydrocarbons comprising an open chain saturated hydrocarbon in admixture with a promoting amount of a hydrogen halide with a catalyst melt comprising a molten mixture of halide salts at least one of which is a halide of the Friedel-Crafts type at isomerizing conditions in a first reaction zone thereby converting straight or branched chain saturated hydrocarbons to branched or more highly branched chain saturated hydrocarbons, continuously removing a portion of the catalyst melt from the first conversion zone, contacting said portion of catalyst melt with saturated hydrocarbons passing to the first reaction zone thereby separating active catalyst components from a fluid catalyst residue, adding a fresh portion of said Friedel-Crafts type halide to said catalyst residue, contacting at least a portion of the effluence of the first reaction zone comprising saturated branched chain hydrocarbons together with added ethylene at alkylating conditions with said Friedel-Crafts type halide-containing catalyst residue in a second reaction zone thereby reacting saturated branched chain hydrocarbons with ethylene to form a branched chain hydrocarbon alkylation product, and separating hydrocarbons comprising said alkylation product from the effluence of the second reaction zone.

10. In a process for the production of branched chain hydrocarbons, the steps which comprise

contacting saturated hydrocarbons comprising an open chain saturated hydrocarbon with a catalyst melt comprising a molten mixture of halide salts at least one of which is a halide of the Friedel-Crafts type at isomerizing conditions in a first reaction zone thereby converting straight or branched chain saturated hydrocarbons to branched or more highly branched chain saturated hydrocarbons, continuously removing a portion of the catalyst melt from the first reaction zone, contacting said portion of catalyst melt with saturated hydrocarbons passing to the first reaction zone thereby separating active catalyst components from a fluid catalyst residue, adding a Friedel-Crafts type halide to said catalyst residue, contacting at least a portion of the effluence of the first reaction zone comprising saturated branched chain hydrocarbons together with an added hydrocarbon fraction containing straight chain paraffins and olefins at alkylating conditions with said Friedel-Crafts type halide-containing catalyst residue in a second reaction zone thereby reacting saturated branched chain hydrocarbons with said olefins to form a branched chain alkylation product, separating a fraction comprising said alkylation product and a fraction comprising straight chain paraffins from the effluence of the second reaction zone, and passing said fraction comprising straight chain paraffins to said first reaction zone.

11. In a process for the production of antiknock motor fuels, the steps which comprise contacting a hydrocarbon mixture predominating in saturated straight chain hydrocarbons and boiling within the gasoline boiling range with a catalyst melt comprising aluminum chloride and antimony chloride at isomerizing conditions in a first reaction zone thereby effecting the conversion of straight chain saturated hydrocarbons to branched chain saturated hydrocarbons, continuously removing a portion of the catalyst melt from the first reaction zone, contacting said portion of catalyst melt with said hydrocarbon mixure passing to the first reaction zone thereby separating active soluble catalyst components from a fluid catalyst residue, adding aluminum chloride to said catalyst residue, and contacting at least a part of the effluence of the first reaction zone comprising branched chain saturated hydrocarbons together with added ethylene at alkylating conditions with said aluminum chloride-containing catalyst residue in a second reaction zone thereby reacting saturated branched chain hydrocarbons with ethylene.

12. In a process for the production of antiknock motor fuels, the steps which comprise contacting a hydrocarbon mixture predominating in saturated straight chain hydrocarbons and boiling within the gasoline boiling range with a catalyst melt comprising aluminum chloride and antimony chloride at isomerizing conditions in a first reaction zone thereby effecting the conversion of straight chain saturated hydrocarbons to branched chain saturated hydrocarbons, continuously removing a portion of the catalyst melt from the first reaction zone, contacting said portion of catalyst melt with said hydrocarbon mixture passing to the first reaction zone thereby separating active catalyst components from a fluid catalyst residue, adding aluminum chloride to said catalyst residue, and contacting at least a part of the effluence of the first reaction zone comprising branched chain saturated hydrocarbons together with an added hydrocarbon fraction predominating in olefinic hydrocarbons at alkylating conditions with said aluminum chloride-containing catalyst residue in a second reaction zone thereby reacting branched chain hydrocarbons with said olefinic hydrocarbons.

13. In a process for the production of antiknock motor fuels, the steps which comprise contacting a hydrocarbon mixture predominating in saturated straight chain hydrocarbons boiling within the gasoline boiling range with a catalyst melt comprising a molten mixture of halide salts at least one of which is a halide of the Friedel-Crafts type in a first reaction zone thereby effecting the conversion of straight chain saturated hydrocarbons to branched chain saturated hydrocarbons, continuously removing a portion of the catalyst melt from the first reaction zone, contacting said portion of catalyst melt with said hydrocarbon mixture passing to the first reaction zone thereby separating active catalyst components from a fluid catalyst residue, adding a halide of the Friedel-Crafts type to said catalyst residue, and contacting at least a part of the effluence of the first reaction zone comprising branched chain saturated hydrocarbons together with an added hydrocarbon fraction predominating in olefinic hydrocarbons at alkylating conditions with said Friedel-Crafts type halide-containing catalyst residue in a second reaction zone thereby reacting branched chain hydrocarbons with said olefinic hydrocarbons.

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