

UNITED STATES PATENT OFFICE

2,361,368

HYDROCARBON CONVERSION

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Application June 27, 1940, Serial No. 342,652

6 Claims. (Cl. 260—683.4)

This invention relates to the conversion of hydrocarbons to improved motor fuels and relates more particularly to the conversion of normally liquid saturated hydrocarbons and mixtures thereof containing a preponderance of straight-chain paraffins into products consisting predominantly of branched-chain paraffinic hydrocarbons.

There are usually available in modern petroleum refineries or in the production fields large quantities of straight-run naphthas, natural gasolines and "distillates" which contain considerable amounts of straight-chain paraffinic hydrocarbons. Such naphthas and gasolines have low octane numbers and therefore are not considered desirable for use as a motor fuel either as such or as a blend with other hydrocarbons. Substantially all such naphthas and natural gasolines, however, do contain minor amounts of branched-chain hydrocarbons which are potentially suitable for use as high anti-knock motor fuels but which are so diluted with straight-chain paraffinic hydrocarbons that their effectiveness is usually almost completely masked for practical purposes.

It is an object of our invention to provide a process for the conversion of normally liquid saturated hydrocarbons containing substantial amounts of straight-chain paraffinic hydrocarbons to saturated branched-chain hydrocarbons of high octane number suitable for premium fuels.

Another object of our invention is to provide a process whereby naphthas and natural gasolines of low octane number are converted into hydrocarbon fuels having branched-chain paraffinic hydrocarbons of suitable octane number and volatility for use as premium motor fuels.

A further object of our invention is to provide a method for the production of valuable branched-chain paraffinic hydrocarbons of gasoline boiling range from low anti-knock naphtha containing a substantial amount of straight-chain paraffinic hydrocarbons.

A still further object of our invention is to provide an improved process whereby normal paraffins can be more completely isomerized to branched-chain isomers in high yields.

Yet another object of our invention is to provide a substantially paraffinic aviation fuel of suitable vapor pressure and boiling range from straight-run naphthas and natural gasolines.

Still another object of our invention is to accelerate the rate of isomerization by removing at least a portion of the branched-chain paraf-

5 fins from the feed by alkylation followed by fractionation, thus concentrating the normal paraffins in the feed to the isomerizer.

Another object of our invention is to convert light normally liquid paraffinic naphthas into high octane paraffinic aviation safety fuels.

Other objects and advantages of our invention will become apparent from the following description read in conjunction with the drawing which forms a part of the specification.

The single figure illustrates schematically a form of apparatus suitable for carrying out one preferred embodiment of our invention.

Our process, in brief, contemplates the conversion of normally liquid branched-chain hydrocarbons in a substantially saturated paraffinic naphtha to branched-chain paraffinic hydrocarbons of higher molecular weight by alkylation, their separation by fractionation, and the conversion of the unalkylated straight-chain paraffins to the corresponding isoparaffinic hydrocarbons by isomerization and blending the combined products to yield a motor fuel of increased anti-knock value and improved distribution of hydrocarbons. Isomerization of normal paraffins is never complete even under the most favorable practical conditions, an equilibrium between the isomeric and normal paraffins occurring at some stage of the process. In the case of normal pentane this equilibrium at 330° F. is about 80% isopentane to 20% normal pentane. In the case of normal hexane the situation is more complex but we have found that an appreciable amount of normal hexane exists even in the most highly isomerized mixtures. Hence, in order to convert higher percentages of the normal paraffins to the more valuable isomers it is necessary to bring about a separation of the normal and branched-chain hydrocarbons so that the equilibrium can be disturbed. This can be effected by fractionation in certain simple cases but in the more usual highly complex cases where there is serious overlapping of the boiling ranges of the normal and branched-chain isomers, fractionation alone is not practical. In our improved process this is accomplished by elevating the boiling range of a substantial part of the branched-chain isomers by alkylation and subsequently separating by fractionation the resulting higher-boiling alkylated isomers, thus increasing the ultimate conversion of normal paraffins to isoparaffins.

It is probably true that the higher-boiling isomeric hydrocarbons, if present, would not in themselves disturb the equilibrium which might

be set up in isomerizing normal pentane to isopentane, or normal hexane to isohexane, and fractionation of alkylate from unconverted low-boiling normal paraffinic hydrocarbons would therefore be unnecessary. However, if it is desired to convert as much as possible of the low-boiling normal paraffinic hydrocarbons to the isomeric form, or if it is desired to avoid degradation of the higher-boiling alkylate to less valuable products of lower octane-number or fewer carbon atoms per molecule, the alkylate should be separated from the low-boiling constituents. Under the conditions of operation in the presence of aluminum chloride there will be conversion of the valuable higher-boiling alkylate to hydrocarbons of lower molecular weight, and/or conversion of the high antiknock hydrocarbons to hydrocarbons of lower knock rating. Since we desire to obtain the highest yield possible of the most valuable hydrocarbons suitable for aviation fuel, and since the production of isomeric low-boiling hydrocarbons at the expense of higher-boiling high octane number hydrocarbons is not compatible with our process for producing a balanced aviation or motor fuel of high octane number, the fractionation of the alkylate from low-boiling normal paraffinic hydrocarbons is an essential part of our process.

As has been suggested the feed stock to our process can be any substantially saturated normally liquid hydrocarbon fraction rich in straight-chain paraffinic hydrocarbons. For example, straight-run gasolines from paraffinic or mixed base crude oil, such as those from Mid-Continent, Michigan and Pennsylvania oil fields, are usually high in straight-chain hydrocarbons and substantially free of olefins. Natural gasoline fractions are also eminently suitable for our purpose and may be found in considerable quantities in the vicinity of natural gas wells and similar production areas. So-called distillates from high pressure wells are also suitable.

It is preferable that our feed stock be free or substantially free of aromatic and olefinic hydrocarbons since such hydrocarbons greatly impair or reduce the activity of the catalyst and decrease appreciably the amount of product obtainable per unit of catalyst. Generally speaking, we prefer feed stocks which contain less than 5% and especially those containing less than 0.5% to 1% of aromatic hydrocarbons, and having very little or no olefinic hydrocarbons. This, therefore, eliminates to a large extent cracked naphthas or other mixtures of unsaturated hydrocarbons available from petroleum refining. Cycloparaffinic or naphthenic hydrocarbons are not seriously objectionable. A substantially aromatic-free feed stock can be obtained for our process either by fractionation of a straight-run naphtha into a cut boiling below the boiling point of the simplest aromatics, for example, below 150° F., or by the solvent extraction of a straight-run naphtha of wider boiling range with a selective solvent. A suitable naphtha for our purpose is one having a boiling range of from about 30° F. to about 158° F. and desirably not above 152° F. On the other hand, some natural gasolines of higher boiling range having less than 5% aromatics and especially those containing less than 0.5% to 1% of aromatic hydrocarbons can be used in their entirety after stabilization. We particularly prefer a mixture of hydrocarbons having present a substantial amount of hydrocarbons having 5 and 6 carbon atoms per molecule.

Referring now to our drawing; a feed stock substantially as described enters through line 10 leading to alkylation reactor 11. A stream of olefinic hydrocarbons enters through line 12 and can be sent directly to alkylator 11 through valve 13 or mixed with the feed stock in line 10 by opening valve 14 in line 15. The olefinic hydrocarbons are preferably normally gaseous hydrocarbons of from two to four carbon atoms per molecule. It is generally desirable to use an olefinic stream in which the major portion of the olefins is ethylene, and special narrow cuts high in ethylene are very suitable. However, ethane and methane can be tolerated and hydrogen may be even beneficial as hereinafter described.

The alkylation product of ethylene with the isoparaffinic hydrocarbons of the feed stock produces isoparaffinic hydrocarbons within the gasoline boiling range, while with the use of the higher-boiling gaseous olefins, hydrocarbons higher boiling than are usually found in gasoline may be obtained. In the event, therefore, that it is desirable to produce an "aviation safety fuel" characterized by the presence of hydrocarbons of more than eight carbon atoms per molecule, the presence of propylene and butylene becomes advisable. A mixture of any two or more of these olefins, diluted if necessary by the corresponding paraffinic hydrocarbons, is a suitable olefinic feed stock.

As catalysts for our process, we can employ an aluminum halide such as, for example, aluminum chloride or aluminum bromide or an aluminum halide-hydrocarbon complex formed by the reaction of anhydrous aluminum halide with paraffinic hydrocarbons in the presence of a promoter such as hydrogen halide, for example, hydrogen chloride or hydrogen bromide. A suitable catalyst for our purpose is the hydrocarbon complex formed during the isomerization of aromatic-free straight-run naphthas.

Generally speaking, sulfuric acid is not desirable for our process, since under ordinary conditions it does not promote the alkylation of isoparaffinic hydrocarbons with ethylene. However, in those cases where no ethylene is present and only propylene and the butylenes are available for alkylation, sulfuric acid can be employed as the catalyst. Sulfuric acid can also be used if a promoter, such as silver sulfate or mercury sulfate, is added, which permits the utilization of ethylene for alkylation.

An aluminum halide catalyst either in the form of a complex or as a slurry in, for example, hydrocarbons of the type exemplified by the feed stock, enters through line 16 and can be sent directly to alkylation reactor 11 by opening valve 17 or can be mixed with the incoming feed stock and olefins by opening valve 18 in line 19 which joins line 10. Generally speaking, it is preferable to add the catalyst directly to the reactor rather than with the feed streams.

The catalyst concentration in alkylation reactor 11 may be from about 15 to about 90% by weight, preferably about 60% by weight of the feed contained in the reactor and may be not only aluminum chloride or an aluminum chloride-hydrocarbon complex, but may be a mixture of these two containing from 10 to 90% aluminum chloride and from 10 to 90% of the hydrocarbon complex.

Alkylation reactor 11 is maintained at a temperature of from about -30° F. to about 250° F., preferably about 80° F. to about 120° F. The tem-

perature can be controlled by a jacket 20 about alkylation reactor 11 through which a heating or cooling medium flows from line 21 and discharges through line 22. Intimate contact between the reactants must be maintained and a stirrer 23 can be used to obtain vigorous agitation of the feed stock, olefins and catalysts in the reactor. In place of a stirring mechanism we can use other means for obtaining intimate contact such as jet injectors, turbo mixers, packed towers, etc. The pressure in alkylation reactor 11 can be the vapor pressure of the reactants and the products at the operating temperature, or we can employ a hydrogen partial pressure of from about 50 to about 1000 pounds per square inch, preferably about 200 to about 800 pounds per square inch. Hydrogen, therefore, can be added by line 24 and valve 25. The olefins should be added to the reactor in an amount such that the ratio of isoparaffinic hydrocarbons to the olefins is at least 1:1 and preferably considerably higher, for example, 3:1 to 4:1. The ratio of isoparaffinic hydrocarbons to olefinic hydrocarbons can be increased by limiting the amount of olefins fed to the reactor or by recycling isoparaffinic hydrocarbons after fractionation of the alkylate.

The alkylate plus unreacted olefins, unconverted paraffinic hydrocarbons, and hydrogen, if present, together with the catalyst are withdrawn from alkylation reactor 11 through line 26 and directed to separator 27 wherein a separation is made between the catalyst and the hydrocarbons. The catalyst is withdrawn through line 28 and can be recycled to the operation by opening valve 29 in line 30 which joins line 16. In the event the catalyst is spent as regards alkylation it can be withdrawn through line 31 by opening valve 32 and discarded or regenerated as desired. Spent catalyst may also be useable in an isomerization reaction, to be described later, and can be directed thereto by opening valve 33 in line 34.

In the event that hydrogen was employed in the alkylation reaction the pressure can be reduced and the hydrogen taken overhead from separator 27 through line 35 and returned for further use through valved line 36 which joins line 24 or discarded through valved line 37. The alkylate plus the unreacted olefins and unconverted paraffinic hydrocarbons is withdrawn from separator 27 through line 38 and directed to fractionator 39. In the event that hydrogen was not released in separator 27 it can be taken overhead from fractionator 39 through line 40 and discarded by opening valve 41 in line 42. It can also be recycled to the alkylation reactor by opening valve 43 in line 44 and valve 45 in line 46 which joins line 24. Any olefins which were not completely reacted in alkylation reactor 11 can be taken overhead through line 40 and recycled to the reactor through line 44, and valve 47 in line 48 which joins line 12. Top-cooling means 49 and bottom-heating means 50 assist in the fractionation of the hydrocarbons in fractionator 39. Any methane and ethane present with the hydrogen in line 40 can be removed (by means not shown) before recycling the hydrogen or otherwise using it.

Unreacted straight-chain hydrocarbons and others, particularly those having less than eight carbon atoms per molecule, and preferably the pentanes and hexanes are withdrawn from fractionator 39 by line 51. During the alkylation, particularly if ethylene was employed as the olefinic hydrocarbon, branched-chain pentanes, 75

hexanes, and/or heptanes have been converted to branched-chain heptanes, octanes and nonanes, respectively. The alkylated hydrocarbons are of a highly branched-configuration, and accordingly of high octane number, while possessing a boiling range within the limits desirable for premium fuels, although deficient in the more volatile constituents.

The unconverted straight-chain paraffinic hydrocarbons, on the other hand, are extremely low in octane number, although of suitable volatility for blending with the alkylate to form a balanced fuel. It therefore becomes desirable to convert these straight-chain paraffinic hydrocarbons to branched-chain hydrocarbons having the same number of carbon atoms per molecule and, accordingly, they are directed from line 51 through line 52 and valve 53 to isomerization reactor 54. In the event that considerable quantities of isoparaffinic hydrocarbons remain in the feed, these can advantageously be recycled from line 51 through line 55 and valve 55a to line 10 leading to reactor 11. By adjusting valves 53 and 55a, it is possible to recycle a portion of the isoparaffinic hydrocarbons to reactor 11 and direct the remainder to isomerization reactor 54, but generally speaking we prefer to direct all of the fraction in line 51 to isomerizer 54. The alkylated hydrocarbons together with any higher-boiling straight-chain hydrocarbons, such as for example, heptane and octane, are withdrawn through line 56 and may be sent to storage through line 57 and valve 58 but preferably are directed to blending tank 59 through line 60 and valve 61 for blending with lower boiling isoparaffinic hydrocarbons preferably obtained from the isomerization reaction (to be described in more detail later).

In the event that there were present in the feed stock branched-chain hydrocarbons having more than seven carbon atoms per molecule, these may have been alkylated and therefore are desirably separated from the alkylate boiling within the gasoline range. These higher alkylates are very suitable for "safety aviation fuels" because of their high octane number and avoid fire hazard because of their high flash point. The higher alkylates are withdrawn from fractionator 39 through line 62 and can be sent to storage through line 63 by opening valve 64. On the other hand, it may be desirable to include the higher boiling alkylates with those boiling ordinarily in the gasoline range in which case the higher-boiling alkylate can be directed to line 56 by opening valve 65 in line 66 which joins line 56. Alternately, the entire alkylate can be withdrawn through line 62 and directed to blending tank 59. Any heavy polymers or tarry matter which might have been formed are withdrawn from fractionator 39 through valved line 67.

Referring now to the isomerization reaction, the predominantly straight-chain paraffinic hydrocarbons in line 52 are mixed with a hydrogen halide from line 68 and catalyst from line 69 and directed to isomerization reactor 54. As catalysts we can employ an aluminum halide, which can be aluminum chloride or aluminum bromide in anhydrous form, or can be the complex formed by the reaction of an aluminum halide and paraffinic, naphthenic or even olefinic hydrocarbons in the presence of a promoter, such as hydrogen chloride or hydrogen bromide. The complex formed during this isomerization reaction or in the previous alkylation reaction is a suitable catalyst for our process. The aluminum chloride or

aluminum bromide is preferably introduced into the reaction zone in the form of a slurry, or as a suspension or solution in, for example, a portion of the feed stock to the reactor.

The concentration of catalyst present in the reaction can vary within wide limits depending primarily upon the temperature, reaction time and the catalyst activity. We prefer to carry out our reaction under a partial pressure of hydrogen, the hydrogen entering the reaction vessel 54 through line 70. The hydrogen halide, for example, hydrogen chloride or hydrogen bromide, added through line 68 acts as an activator, although the hydrogen halide can be dispensed with in certain cases (particularly in the case of aluminum bromide). In place of the hydrogen halide we can employ any compound which in the presence of the catalyst affords a hydrogen halide, particularly hydrogen chloride or hydrogen bromide, under the reaction conditions, preferably in an amount sufficient to supply a concentration in the reaction zone of about one to two mols of hydrogen halide per mol of aluminum halide, which will usually be in the range of from about 0.03% to 3.0% by weight of hydrogen halide based on the charge. Our preferred promoter is hydrogen chloride but hydrogen bromide, carbon tetrachloride, alkyl halides such as methyl chloride, ethyl chloride, etc., or the corresponding bromine compounds, can be used.

The reactions are carried out under relatively high total pressure, for example, from about 250 to about 3000 pounds per square inch and preferably about 500 to about 1500 pounds per square inch. Of this total pressure, the partial pressure of hydrogen is from about 50 to 2500 pounds per square inch, preferably 400 to 1000 pounds per square inch. The hydrogen need not be a pure product but may contain such impurities as methane, ethane, etc., in which case the total pressure can be somewhat higher than that specified above. The reaction can be carried out at temperatures ranging from about 100° F. to about 450° F., preferably about 250° to 350° F.

In our process it is quite possible to include "butanes" (including normal and/or isobutane) with the initial feed stock, in which case the isobutane present, if any, will be converted to alkylated hydrocarbons in the alkylation reaction, and will therefore be withdrawn either with the lower-boiling liquid hydrocarbons by line 51 or with the higher boiling liquid hydrocarbons in line 52, depending upon the olefins used for alkylation. Unconverted butane will pass overhead from fractionator 39 through line 40 with the hydrogen, if any, and can be directed to isomerization reactor 54 from line 40 by opening valve 71 in line 72 which joins line 52. On the other hand, we can introduce butane directly into the feed stream to reactor 54 by line 73 which joins line 72 leading to line 52. It is also possible to introduce fresh feed at this point and operate the reactor 11 entirely on recycle stock from the fractionation of isomerized hydrocarbons. This in general produces a higher boiling product which is sometimes desirable.

Isomerization reactor 54 can be maintained at the proper temperature by a jacket 74 through which flows a heating medium from line 75 which discharges through line 76. Other means for maintaining temperature within the reactor can be employed such as, for example, heating coils, induction heating, etc., such expedients being well known to those skilled in the art. It is essential to the isomerization reaction that in-

timated contact between the catalyst and the reactants be obtained which can be accomplished as illustrated by a stirrer 77 which provides violent agitation of the catalyst and reactants, or by such other means as jet injectors, turbo-mixers, packed towers, turbulent flow, etc.

The catalyst and reactants from isomerization reactor 54 pass by line 78 to separator 79. A cooling means 80 in line 78 can be employed to reduce the temperature of the product in line 78, particularly in those instances when the isomerization has been carried out in the upper temperature range. In separator 79 the catalyst settles and separates from the hydrocarbons, hydrogen and hydrogen halide and can be withdrawn through line 81. If spent for isomerization the catalyst can be discharged through line 82 by opening valve 83 for discard or for the recovery of aluminum halide. If, however, it is still active, it can be recycled to the isomerization reactor by opening valve 84 in line 85 and valve 86 in line 87 which joins line 69. When low temperature isomerization has been employed in isomerization reactor 54, the complex formed therein by the reaction of the aluminum halide and the paraffinic hydrocarbons is a very suitable catalyst for carrying out the alkylation reaction and therefore the complex can be directed through line 88 to line 16 where it can supplement or replace fresh catalyst.

The hydrocarbons together with the unreacted hydrogen and hydrogen halide pass from separator 79 to fractionator 89 by line 90. Top-cooling means 91, bottom-heating means 92, which can be reflux and reboiler means or cooling and heating coils of any desired description, aid in the separation of the various products from separator 79. Hydrogen together with hydrogen halide, if present, pass overhead through line 93 and can be discarded by opening valve 94 in line 95. However, it is usually desirable to recycle either or both of these to the isomerization reaction by opening the valve in line 96 which joins line 70 or by recycling it to the alkylation reactor by opening valve 97 in line 98 which joins line 24. It is possible to direct a part to the isomerization reaction and part to the alkylation reaction by the proper manipulation of valves 97 and 99. The isomerized hydrocarbons which comprise chiefly isopentane and isohexane, together with isobutane if butanes were present, are withdrawn from fractionator 89 by line 105 and can be withdrawn from the system by opening valve 106 in line 107. However, we prefer to employ the isomerized hydrocarbons in our motor fuel. Accordingly, by opening valve 108 in line 109 we can direct them to line 110 by opening valve 111 therein which leads to blending tank 59 wherein they are blended with the higher-boiling alkylates from line 60. Alternatively, we can return these to the alkylation reaction for the production of further quantities of higher-boiling hydrocarbons by opening valve 112 in line 113 which joins line 10. It is also possible to recycle a part of the isomerized hydrocarbons to the alkylation reaction and to direct the remainder to blending tank 59 by the proper manipulation of valves 111 and 112. The relative proportions which may be directed to the various uses will be governed to a great extent by the final blend desired in tank 59 or by the desire for further quantities of higher-boiling alkylates for possible use as aviation safety fuel. Heavier products can be withdrawn from fractionator 89 by opening valve 114 in line 115.

Although we have previously described the operation of the isomerization reaction as taking place in the low temperature range of from 100° F. to 450° F., our process can be carried out by gradually increasing the temperature from 100° F. to 450° F. or to some intermediate temperature less than 450° F. and higher than 100° F. In this case the catalyst, which becomes more and more spent as it is recycled, can be utilized further. In this way we can completely exhaust the catalytic activity of our catalyst as regards isomerization. Moreover, our catalyst can also be suitably utilized by withdrawing the catalyst from alkylation as it becomes gradually spent for optimum activity and directing it to isomerization reactor 54 by line 34, as previously described, and thereupon, starting with a low temperature, gradually increase the temperature until complete exhaustion of the catalyst has been obtained.

By our process, using for example a naphtha having a boiling range of from about 30° F. to 152° F. obtained from the fractionation of a straight-run naphtha from a Mid-Continent crude and having an octane number of about 67-68, we can obtain a motor fuel of 80 to 90 octane number with a yield of 100 to 120 percent by volume based on naphtha.

Although we have described our process as regards certain apparatus, for the sake of clarity and simplicity certain details have been omitted; for example, top-cooling coils in any or all of the fractionating towers can be replaced by supplying reflux to the towers from an outside source or by cooling and condensing the top products from the fractionator towers and returning a portion of them to act as reflux. Similarly, in place of the bottom-heating means in the fractionators, we can withdraw a portion of the heavy product, heat it to increase the temperature sufficiently, and return the heated products to the fractionator whereby heat is supplied to the products to be fractionated. Also, we have omitted certain details as regards pumps, heat exchangers, cooling means, pressure release valves, etc., all of which will occur readily to one skilled in the art and which would naturally be used in any commercial plant employing our process.

In addition to increasing the octane number considerably, we also obtain a balanced fuel, comprising branched-chain hydrocarbons having from at least five to eight or nine carbon atoms per molecule. By our process, the boiling range is extended considerably over that found in the products from such processes as the polymerization of butylenes, or the alkylation of isobutane with butylenes, which are used for the production of "isooctane," and the volatility characteristics of our product are therefore much superior. Moreover, such fuels have excellent lead response and high heat content—both desirable for aviation fuels.

We have also converted a comparatively low octane-number naphtha of too great volatility to a high octane number gasoline of suitable volatility by the production of branched-chain hydrocarbons from straight-chain paraffins, and by the alkylation of low-boiling constituents to higher-boiling constituents, thereby lowering the vapor pressure. In addition, we have provided a process in which the catalyst can be advantageously employed to give optimum yields per unit of catalyst used, and can be cycled from either process to the other under the conditions set forth.

Although we have described our process in rela-

tion to certain preferred embodiments thereof, it should be understood that this is by way of illustration and not by way of limitation, and that we are to be limited only insofar as is set forth in the appended claims.

We claim:

1. The method of preparing a charging stock for an isomerization system which comprises fractionating a light paraffinic naphtha to remove heptanes and heavier hydrocarbons from a C₅-C₈ fraction containing both normal and isoparaffinic hydrocarbons, alkylating said C₅-C₈ fraction with a hydrocarbon stream containing a normally gaseous olefin in the presence of an aluminum chloride catalyst whereby the C₅-C₈ isoparaffins are converted to branched-chain paraffins of higher boiling point and the C₅-C₈ normal paraffins are unreacted, separating the catalyst and the hydrocarbon product stream, separating said higher boiling point hydrocarbons from the unreacted normal paraffinic C₅-C₈ hydrocarbons whereby the concentration of normal paraffin in the C₅-C₈ fraction is increased by the removal of the isoparaffins therefrom by the final separation step which in turn is made possible by the alkylation step, and isomerizing said concentrated normal paraffinic C₅-C₈ hydrocarbons with said separated catalyst in the presence of hydrogen chloride and hydrogen whereby a greater amount of normal paraffinic C₅-C₈ hydrocarbons originally present in said light paraffinic naphtha are converted to isoparaffinic C₅-C₈ hydrocarbons than would otherwise be possible.

2. In the method of isomerizing normal paraffins in the presence of an aluminum chloride catalyst to produce aviation gasoline constituents, the improvement comprising contacting a hydrocarbon fraction comprising predominantly normal and isoparaffinic hydrocarbons having five and six carbon atoms per molecule with a normally gaseous olefin in the presence of an aluminum chloride catalyst and hydrogen under conditions adapted to promote the alkylation of at least a part of the isoparaffinic hydrocarbons with said olefin, separating the alkylation product stream and the aluminum chloride catalyst, separating the unreacted hydrocarbons from the alkylation product stream to produce a residual fraction predominating in normal paraffinic hydrocarbons, and isomerizing the residual normal paraffinic fraction in the presence of aluminum chloride catalyst separated from the alkylation step.

3. In the method of isomerizing normal paraffins in the presence of an aluminum chloride catalyst to produce aviation gasoline constituents, the improvement comprising contacting a hydrocarbon fraction comprising predominantly normal and iso-paraffinic hydrocarbons having five and six carbon atoms per molecule with a normally gaseous olefin in the presence of an aluminum chloride catalyst under conditions adapted to promote the alkylation of at least a part of the isoparaffinic hydrocarbons with said olefins, separating the alkylation product stream and the aluminum chloride catalyst, separating the unreacted hydrocarbons from the alkylation product stream to produce a residual fraction predominating in normal paraffinic hydrocarbon, isomerizing the residual normal paraffinic fraction in the presence of aluminum chloride, catalyst separated from the alkylation product, separating the isomerization product stream and the aluminum chloride catalyst, separating from the isomerization product stream an aviation gasoline fraction comprising isoparaffinic hydrocarbons having five and

six carbon atoms per molecule, and utilizing in said first-mentioned contacting step at least a part of the aluminum chloride catalyst separated from said isomerization product stream.

4. A process for the production of motor fuel constituents which comprises the steps of contacting a hydrocarbon fraction comprising essentially normal and iso-paraffinic hydrocarbons having five and six carbon atoms per molecule with ethylene in the presence of an aluminum chloride catalyst under conditions adapted to promote the alkylation of at least a part of the said isoparaffinic hydrocarbons with said ethylene, separating the alkylation product stream and the aluminum chloride catalyst, separating from the alkylation product stream a fraction predominating in normal paraffins having five and six carbon atoms per molecule, contacting the last-mentioned fraction with an aluminum chloride catalyst and hydrogen halide under conditions adapted to convert at least a substantial part of said normal paraffins into branched chain hydrocarbons, separating the isomerization product stream and the aluminum chloride catalyst, and supplying separated aluminum chloride catalyst to said first-mentioned contacting step.

5. A process for the production of motor fuel constituents which comprises the steps of contacting a hydrocarbon fraction comprising essentially normal and isoparaffinic hydrocarbons having five and six carbon atoms per molecule with an olefin in the presence of an aluminum chloride catalyst under conditions adapted to promote the alkylation of at least a part of the said isoparaffinic hydrocarbons with said olefin, separating the alkylation product stream and the aluminum chlo-

ride catalyst, separating from the alkylation product stream a fraction predominating in normal paraffins having five and six carbon atoms per molecule, contacting the last mentioned fraction with an aluminum chloride catalyst and hydrogen halide under conditions adapted to convert at least a substantial part of said normal paraffins into branched-chain hydrocarbons, separating the conversion product stream and the aluminum chloride catalyst, and supplying separated aluminum chloride catalyst to said first mentioned contacting step.

6. In the method of producing aviation gasoline constituents by operations including alkylation and isomerization in the presence of an aluminum chloride catalyst, the improvement comprising contacting a hydrocarbon fraction comprising predominantly normal and isoparaffinic hydrocarbons having five and six carbon atoms per molecule with an olefin in the presence of an aluminum chloride catalyst under conditions adapted to promote the alkylation of at least a part of the isoparaffinic hydrocarbons with said olefin, separating the unreacted hydrocarbons from the alkylation product stream to produce a residual fraction predominating in normal paraffinic hydrocarbons, isomerizing the residual normal paraffinic fraction in the presence of an aluminum chloride catalyst, recovering separate bodies of an aluminum chloride catalyst from said alkylation and from said isomerization respectively, and supplying separated catalyst from at least one of said operations to the other.

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