July 16, 1946. C. S. KUHN, JR 2,403,929

CATALYTIC REFORMING PROCESS

Filed Aug. 22, 1942 2 Sheets-Sheet 1

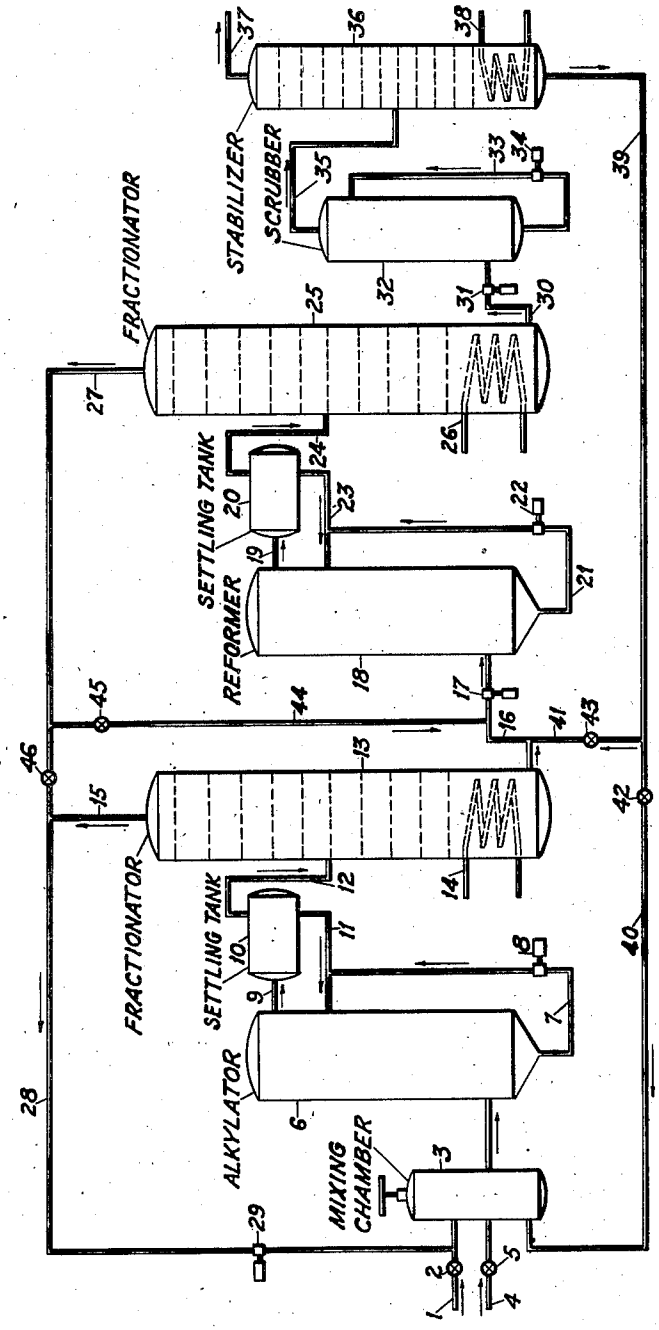


FIG. 1

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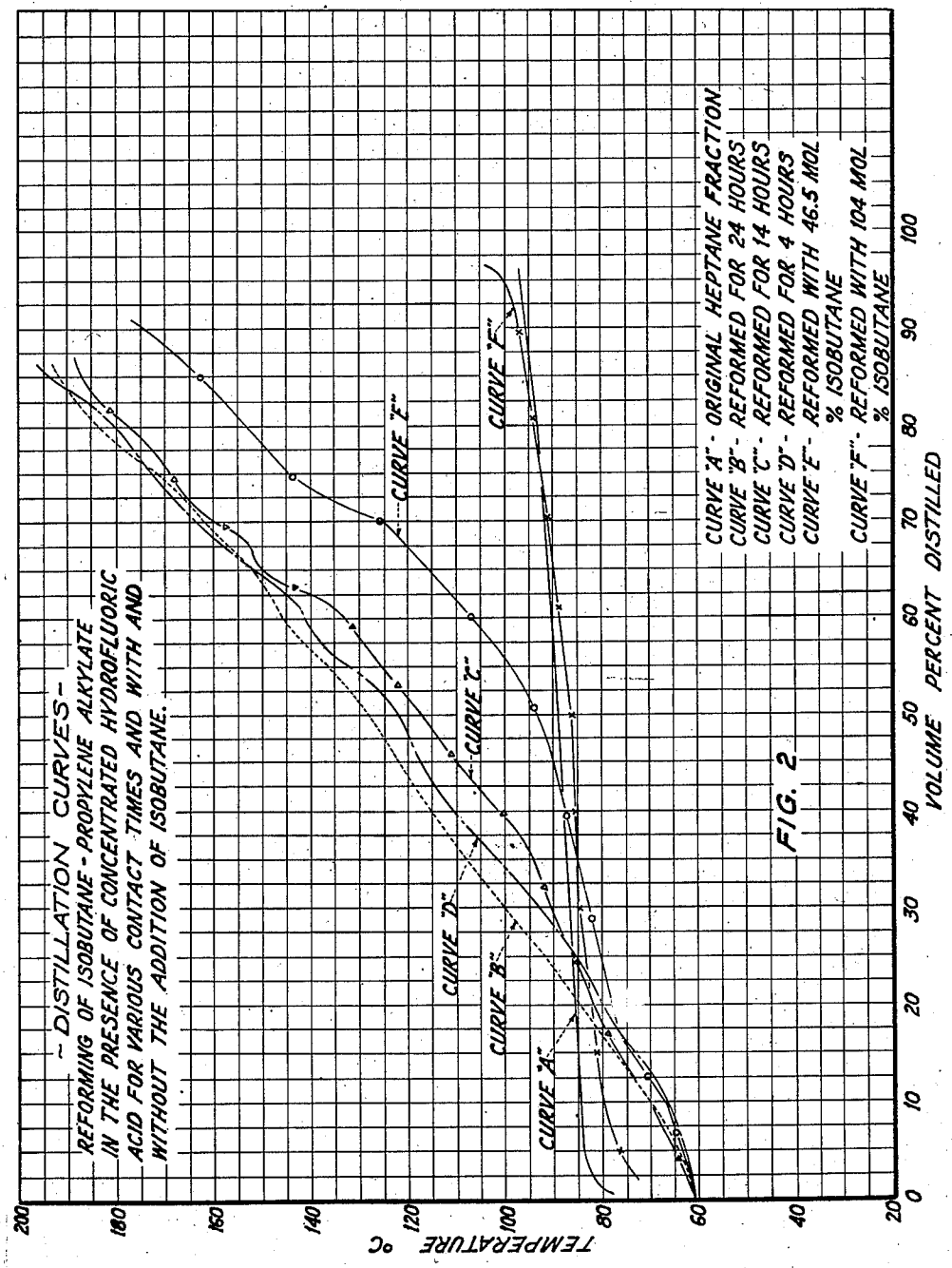


FIG. 2

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UNITED STATES PATENT OFFICE

2,403,929

CATALYTIC REFORMING PROCESS

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Application August 22, 1942, Serial No. 455,775

2 Claims. (Cl. 260—683.4)

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This invention relates to the catalytic rearrangement or reforming of branched-chain hydrocarbons and is especially concerned with the manufacture of complete aviation gasolines using relatively narrow-boiling fractions of such hydrocarbons.

It is well known that in order to insure proper carburetion and combustion of motor fuel, the distribution of hydrocarbons in the gasoline boiling range should be uniform. A preponderance of either light or heavy material leads to uneven carburetion and uneven burning. This is recognized by users, and this recognition is reflected in purchasing specifications which require reasonable distribution of material across the entire boiling range of the fuel. Such requirement is usually arrived at by specifying that the product be such that only given percents of it shall distill over at each of several given temperatures in the boiling range.

During recent years production of high octane value gasolines by synthesis from lighter hydrocarbons has assumed increasing importance and widespread usage. Thus, for example, in processes known to the art, high octane gasolines may be prepared by alkylating normally gaseous isoparaffins with normally gaseous olefins in the presence of such catalysts as sulfuric acid, phosphoric acid, aluminum chloride, etc. Likewise, in my copending application S. N. 320,097, filed February 21, 1940, there is disclosed a similar alkylating process using hydrogen fluoride as a catalyst. Branched-chain hydrocarbons of high octane value are prepared also by polymerization of gaseous olefins, and the polymers are usually hydrogenated to give a saturated product.

Since alkylation processes, as usually conducted, effect predominantly the condensation of one particular isoparaffin with one particular olefin, the resulting alkylate gasoline, although of high octane value, is composed essentially of branched-chain isomers of one paraffinic hydrocarbon. Therefore, the alkylate is of relatively narrow-boiling range, or, at least, it does not have a required uniform distribution of hydrocarbons across the desired gasoline-boiling range. This is one of the reasons why alkylate gasoline is now conventionally blended with gasoline of inferior anti-knock value in order to form blended gasoline of proper distillation characteristics and vapor pressure.

Accordingly, it is an object of this invention to provide a process for treating a relatively narrow-boiling fraction of branched-chain hydrocarbons so as to promote a molecular conversion or rearrangement to yield a mixture of branched-chain hydrocarbons which boils over a relatively wide range. Another object is to afford a process for treating a relatively narrow-boiling fraction of alkylate gasoline or similar gasoline, consisting essentially of branched-chain hydrocarbons in order to yield a complete aviation gasoline of not substantially less octane value. Still another object is to provide a process for synthesizing a complete aviation gasoline from gaseous hydrocarbons. These and other objects will be apparent from the following description of my invention.

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My invention is based upon the discovery that if a relatively narrow-boiling fraction of gasoline-boiling, branched-chain hydrocarbons is treated in the presence of an alkylation catalyst under alkylating conditions of temperature and pressure for a controlled period of time, a gasoline fraction having desired distillation characteristics may be produced therefrom. If desired, the narrow-boiling fraction may be reformed to produce a complete aviation gasoline having the proper distillation characteristics. Moreover, the gasoline-boiling product formed by my process possesses substantially as high an octane rating as that of the original narrow-boiling, branched-chain hydrocarbon fraction.

In general, the conditions under which the alkylation catalysts reform alkylate or other narrow-boiling hydrocarbons are essentially the same as those under which they will produce alkylate from lighter paraffins and olefins, except that sufficient additional reaction time must be provided to obtain a reformed product of the desired characteristics. Thus, for example, when a catalyst consisting essentially of hydrogen fluoride is used, the hydrogen fluoride should be of at least about 90% concentration, and a temperature preferably between about −10 and about +30° C. should be employed. It is to be understood, however, that since hydrofluoric acid, unlike sulfuric acid, is not an oxidizing acid, rather high temperatures up to about 200° C. may be used if desired. Since it is generally preferable to operate with the hydrocarbons in the liquid phase, the critical temperature of the hydrocarbon being reformed will frequently set the upper temperature limit for liquid phase operation. The alkylating conditions for such catalysts as sulfuric acid, aluminum chloride, etc., are well known.

As stated previously, the reforming reaction is preferably carried out with the reactants in the liquid phase and therefore sufficient pressure is

used to maintain the reactants in this liquid phase. Suitable agitating means should be provided in order to afford efficient contacting of the hydrocarbons and the catalyst as is customary in the alkylation art. Liquid phase operation is not essential, however, and lower pressures may be used if desired.

The relative proportions of the catalyst to the total hydrocarbons are similar to those used in alkylation processes. Within certain limits, increasing the amount of catalyst increases the amount of reforming obtained in a given time. In the case of solid or immiscible liquid catalysts, and to a certain extent with a soluble catalyst, increased agitation increases the amount of reforming obtained in a definite time period since the agitation produces better contact between the catalyst and hydrocarbons.

Alkylation reactions are generally carried out in the presence of a large excess of isoparaffins. In this respect, as well as in the reaction time, the reforming reaction is different. The amount of excess isoparaffin over that required to combine with the olefin is generally of the order of upwards of 400 mol percent in the case of alkylation reactions. In contrast thereto, reforming reactions will proceed most rapidly in the absence of additional isoparaffinic hydrocarbons, although limited amounts of light isoparaffins or high-boiling, saturated hydrocarbons up to not over 100 to 200 mol percent of the hydrocarbon being reformed, may be present as will be discussed more in detail later in the description of my invention.

The exact reaction time for each individual reforming operation must be worked out by a consideration of several factors. Thus the reforming time factor is dependent upon the particular alkylate or other isoparaffinic hydrocarbon stock being reformed, the catalyst, the ratio of catalyst to hydrocarbons, the efficiency of contact between catalyst and hydrocarbons, the temperature, the specification characteristics desired in the reformed product, etc. Although the reaction may be speeded up by increasing the temperature, increase in the temperature will in some cases produce an increase in the amount of side reactions such as polymerization of any olefins formed as intermediate products in the reforming reaction. Accordingly, even with non-oxidizing catalysts, the temperature is generally kept below about 80 to 90° C. In general the reaction time used in carrying out the desired amount of rearrangement will vary between about 1 and 24 hours. For a given set of conditions of temperature, catalyst concentration, etc., one of the most important factors in determining the amount of time required for a particular reforming operation is the particular charge stock being subjected to the process. The charge stocks of primary concern for reforming are the various octane and heptane alkylates, and the range of reaction times given is generally suitable for these alkylates. With some of the hexanes, nonanes or decanes the range of reaction time is usually greater than the range given above, particularly where alkylation catalysts less effective for the particular alkylate are used. The time required for reforming also varies with the particular alkylate isomers being treated. For example, the heptanes formed by the alkylation of isopentane with ethylene are considerably slower in reforming to a uniformly boiling hydrocarbon mixture, than

the heptanes formed by the alkylation of isobutane with propylene. It is my belief, although my invention should not be limited to any particular theoretical considerations that under a given set of reaction conditions, the reaction time is primarily dependent upon the configuration of the carbon atoms in the charge stock. This discussion of reaction time is directed to batch operation. Continuous processing, of course, permits the use of much shorter contact times as is well understood in the art.

It is difficult to state definitely which catalyst or catalysts will effect the desired amount of reforming in the shortest period of time, since this also varies with charge stock and the reaction conditions. I have found, however, that with certain alkylates one catalyst is preferable, while with other alkylates another catalyst will be preferred. For example, the heptanes formed by the alkylation of isopentane with ethylene will be reformed most effectively with aluminum chloride, while the heptanes formed by the alkylation of isobutane with propylene will be reformed by hydrogen fluoride substantially as rapidly as with aluminum chloride. For the most part it may be stated that those alkylation catalysts which are most effective for the formation of a particular alkylate are most effective for its catalytic rearrangement.

Aluminum chloride and hydrofluoric acid have been mentioned above as typical catalysts suitable for my reforming process. It is to be understood that any hydrocarbon alkylation catalyst is likewise suitable. The various catalysts must, of course, be used under conditions of temperature, pressure, concentration, etc., at which they are effective as alkylation catalysts. The following are illustrative of alkylation catalysts which are particularly useful in my process: hydrogen fluoride, sulfuric acid, aluminum chloride, aluminum bromide, and boron trifluoride. My invention is not, however, to be construed as limited to the use of the aforementioned catalysts. In general, aluminum chloride represents the preferred catalyst for use with the less highly branched-chain paraffins, whereas hydrogen fluoride represents the preferred catalyst for use with the more highly branched-chain paraffins. Aluminum bromide corresponds rather closely to aluminum chloride, while sulfuric acid more nearly resembles hydrogen fluoride in its catalytic reforming properties.

I am aware that some of the alkylation catalysts will isomerize normal paraffinic hydrocarbons to produce branched-chain paraffinic hydrocarbons. For example, Nenitzescu and Dragen have disclosed that aluminum chloride will isomerize normal hexane and normal heptane to produce branched-chain hexanes and heptanes (cf. Berichte, 66 B, 1892 (1933)). The isomerization of normal paraffins to corresponding branched-chain hydrocarbons by aluminum bromide has been demonstrated by Glazebrook, Phillips and Lovell (cf. J. Am. Chem. Soc. 58, 1944 (1936)). Where these isomerization processes are applied to the gasoline-boiling normal paraffins, there will be concurrent isomerization, cracking of the normal paraffins to low boiling normal paraffins, and reforming of the isomers produced. The isomerization of normal paraffins is usually extremely slow under the comparatively mild conditions used for reforming the branched-chain paraffins. The boiling characteristics of the product from such a combined

process is not controllable within the meaning with which this term is used in my invention. The concurrent isomerization and reforming of gasoline-boiling, normal paraffins is not included within my invention. However, fractionation of such a hydrocarbon mixture to separate out a narrow-boiling, branched-chain paraffin would yield a distillate fraction suitable for treatment by my process to form a hydrocarbon mixture of desired distillation characteristics within the gasoline range. Therefore, the reforming of a narrow-boiling, branched-chain isoparaffin obtained in this way, as well as from any other source, is to be considered as included within the scope of my invention.

The catalysts used in my process are both hydrocarbon soluble and hydrocarbon insoluble catalysts. Aluminum bromide is a typical hydrocarbon soluble catalyst. The hydrocarbon immiscible catalysts are further capable of division into three groups based upon their physical properties under the reaction conditions as follows: solid, immiscible catalysts, typified by aluminum chloride; liquid, immiscible catalysts, typified by sulfuric acid and hydrofluoric acid; and gaseous catalysts, typified by gaseous hydrogen fluoride.

Because of the different physical characteristics of the various catalysts used, certain differences exist in the operating procedures followed in the carrying out of my invention. The essential features of the invention are the same, regardless of the particular type of catalyst selected.

The gaseous catalysts may simply be bubbled up through the hydrocarbon in a packed tower, and this not only serves to produce contact between hydrocarbon and catalyst, but will, in a properly designed reactor, produce all the necessary agitation. The catalyst is very easily recirculated for recontacting with the same batch of hydrocarbons, or with a fresh hydrocarbon for treatment. Continuous operation is very easily performed. On a volumetric basis, the quantity of catalyst used is fairly substantial relative to the quantity of hydrocarbon being reformed, thus requiring, in general, more costly equipment than with the other type catalysts.

Solid, immiscible catalysts, such as aluminum chloride, possess the advantage that bulk separation of the liquid gasoline produced from the solid catalyst is very simple. Considerable agitation is required with catalysts of this type to obtain efficient contacting. Moreover, the aluminum chloride reacts with some of the hydrocarbons to form a sludge, whose regeneration involves considerable additional processing.

Immiscible liquid catalysts such as sulfuric acid and hydrofluoric acid also possess the advantage that bulk separation of product from the catalyst involves a mere settling operation or its equivalent. In addition, hydrogen fluoride offers the further advantage that, since it is quite stable and has a normal boiling point of 19.4° C., it can be distilled at ordinary temperatures and pressures without decomposition. Therefore, the hydrogen fluoride catalyst can be easily and cheaply purified as often as necessary by a simple distillation procedure whereby it may be reused indefinitely in my process. Hydrogen fluoride presents other advantages over sulfuric acid because of its lack of oxidizing effect upon hydrocarbons permitting use at high temperatures without danger of oxidizing the reactants, and low density and viscosity permitting relatively small expense for agitation and admixture of the catalyst and hydrocarbon immiscible layers.

Hydrocarbon soluble catalysts, such as aluminum bromide, possess the advantage that molecular contact is obtained between catalyst and hydrocarbon, hence a minimum of agitation is required. The catalyst may be subsequently removed from the hydrocarbons by chilling, which will cause the catalyst to separate out as a solid, or by distillation of the hydrocarbons from the catalyst, preferably at reduced pressures.

Because the reaction involved in my reforming process is of sufficient intensity to produce hydrocarbons boiling over the entire gasoline range, there also are produced smaller amounts of saturated hydrocarbons boiling over and below the gasoline range. In this connection, I have found that these less valuable saturated portions of the reformed product distilling outside the gasoline range, e. g., below 25° C. and above 168° C., can be utilized for the production of additional gasoline-boiling hydrocarbons by reacting these products together in the presence of essentially anhydrous hydrogen fluoride, or other alkylating catalyst. It should be noted that this reaction is not alkylation since both reactants are saturated hydrocarbons.

Another feature of my invention is based upon my discovery that the distillation characteristics of the final product may be influenced by the addition of minor amounts of either light isoparaffins such as isobutane or isopentane, or by the addition of hydrocarbons boiling above the gasoline range. The amount of this added hydrocarbon should be preferably less than an equimolar quantity, and is of the general order of from 5 to about 40 mol percent of the alkylate charge stock. Since these light and heavy hydrocarbons are end products of the reforming reaction, their presence in the reaction mixture has the effect, also, of slowing down the reforming reaction. Obviously, if too great a quantity of these high and low boiling materials are present in the mixture, the desired catalytic rearrangement will be largely suppressed. As a general practice neither of these added hydrocarbons should be present in an amount much in excess of an equimolar quantity of the branched-chain hydrocarbon being reformed. As mentioned previously, the catalysts differ appreciably in their activity. While the amount of either high- or low-boiling hydrocarbons added or recirculated should be less than about an equimolar quantity (based upon the hydrocarbons being reformed), and preferably should not exceed about fifty mol percent, with some of the more active catalysts, or where the extent of reforming desired is small, somewhat larger amounts of added hydrocarbons may be present. In the case of aluminum chloride, for example, amounts up to 200 mol percent of isobutane may be added, and in some cases such a large addition might be desirable to enable better control of the extent of the reforming reaction.

Without attempting to theorize as to the mechanics of the reaction by which a hexane, heptane or an octane, for example, reacts to form isobutane, isopentane, hexanes, etc., up to 10 to 12 carbon atom saturated hydrocarbons, I have found that the presence of a low-boiling isoparaffin, such as isobutane or isopentane, or a high-boiling hydrocarbon, such as a decane, tends to suppress the reaction towards the formation of these lower and higher boiling products. The result is the formation of a higher percentage of intermediate boiling products, and a slowing down of the reaction.

As stated previously, the high- and low-boiling fractions may be combined and will react together in the presence of an alkylation catalyst under alkylating conditions of temperature and pressure to form additional gasoline-boiling material. This may advantageously be done by recycling these fractions to the reforming reactor. Normally, less than 40 mol percent of the narrow-boiling feed is reformed to material boiling outside of the gasoline range, even in the absence of added high- or low-boiling material. Since the rate of recombination of this recirculated material is generally at least as rapid as the rate of production of these high- and low-boiling materials from the narrow-boiling feed, the total molar ratio of the high- and low-boiling hydrocarbons to the narrow-boiling fraction in the reaction zone is less than 1 to 1. In some cases where the reforming reaction yields substantial amounts of high- and low-boiling material, of the order of 30 to about 50 mol percent, and/or the recombination of the recirculated high- and low-boiling feed material is slow, relative to its rate of formation from the narrow-boiling feed, the amount of the high- and low-boiling material recirculated will be larger than the amount of narrow-boiling fraction fed to the reaction zone. In such a case the total molar ratio of the recirculated hydrocarbons will exceed 1 to 1. While this slows down the reforming of the narrow-boiling fraction, since gasoline-boiling material is being formed from the high- and low-boiling material, the overall result is the same; i. e., the formation of a material boiling over the entire, or a desired portion of the entire, gasoline range. In some cases it is possible that the amount of low-boiling material formed may be much in excess of the amount of high-boiling material. If this is true, and if the amount of this excess low-boiling material (principally isobutane) is large relative to the amount of narrow-boiling hydrocarbon being processed, it may be necessary to withdraw some of this isobutane from the process. In other words, where mol quantities of these recycled hydrocarbons are unequal, the mol excess of the one present in the greater amount should not exceed about 100 to 200 mol percent (depending upon the catalyst being used) of the narrow-boiling hydrocarbon being processed. In the case of this addition of high- and low-boiling hydrocarbons, the high-boiling and low-boiling materials probably react with the branched-chain hydrocarbon being processed, as well as with each other. This same reaction between the reactant hydrocarbon being processed and recycled hydrocarbon or any added saturated isoparaffin undoubtedly occurs where only a single additional component is present. The exact mechanics of the reaction occurring in a two or more component system is not clear, and my invention is not to be considered as bound to any theoretical consideration. The manner in which these added hydrocarbons affect the reaction is immaterial. The result is that the catalytic rearrangement favors the formation of less hydrocarbons boiling above and below the gasoline range. Where only one type of hydrocarbon is added, the material to be reformed should constitute at least 35 to 50 mol percent of the total mixture. As a consequence of the effect of these added hydrocarbons, a simple procedure for controlling and regulating the distillation characteristics of the final product is available.

Inasmuch as my process involves the use of an alkylation catalyst for the treatment of an alkylate charge stock, a simple and novel combined process is possible by using the same alkylation catalyst for the reforming step as was used for the alkylation. In such a process, it is unnecessary to remove the alkylation catalyst from the alkylate product-containing, reaction mixture. Since it is usual to conduct alkylation reactions with the use of a large excess of isoparaffin, this isoparaffin should either be removed, or, where its presence to influence the boiling range of the product is desirable, it may be necessary to only remove a part of it. In any event excess isoparaffin must be removed to an extent which will allow the reforming reaction to proceed. The excess isoparaffin should be reduced to less than 200 mol percent of the alkylate product, and preferably to less than 100 mol percent of the alkylate. The product-catalyst mixture is reformed in the manner heretofore described by further agitation and contacting before separation. Therefore, another feature of my invention is a combined alkylation and reforming operation. In such a combined process where excess isobutane, or other light isoparaffin is formed in the reforming step as described previously, this light isoparaffin may be used in the alkylation step to make additional narrow-boiling alkylate. My invention is not to be construed, however, as limited to the use of the same catalyst for the reforming as was used for the preparation of the initial alkylate charge stock.

In Figure 1 of the drawings there is shown diagrammatically a complete set up for both alkylating and reforming, wherein hydrogen fluoride is the catalyst used in both steps. In this operation a suitable isoparaffin, such as isobutane, is fed through line 1, provided with control valve 2, to a mixing chamber 3, wherein it is mixed with an olefin, such as propylene introduced through line 4, provided with control valve 5. This mixture is then fed to reactor 6, in which a stream of concentrated hydrofluoric acid flows counter current to the hydrocarbon charge. This acid is recycled from the bottom of alkylator 6, to the top thereof through line 7, by means of pump 8. The alkylate, principally heptanes, along with unreacted isobutane and some entrained acid passes from the top of the alkylator through line 9, to settling tank 10, wherein the hydrocarbons and acid separate to two layers. The acid leaves the bottom of this settling tank through line 11 and is returned to the alkylator along with the recycled acid passing through line 7. The hydrocarbons flow from the settling tank through line 12, to fractionator 13, provided with suitable heating coil 14, wherein the isobutane is removed from the alkylate as overhead through line 15. Suitable means (not shown) are provided for returning some isobutane to the fractionator as reflux. The alkylate product from the bottom of this fractionator flows through line 16, provided with pump 17, to reformer 18. In this reformer, as in the alkylator, a stream of concentrated hydrofluoric acid flows counter current to the hydrocarbon charge. The reformed hydrocarbons pass through line 19, to settling tank 20, wherein the mixture of hydrocarbons and entrained acid separate into two layers in the manner previously described. The acid being recycled passes from the bottom of the reformer through line 21, provided with pump 22, to the top thereof. The acid layer from the settling tank 20, is returned to the bulk

of the recycled acid in line 21, through line 23. The hydrocarbons from the settling tank 20, flow by line 24, to fractionator 25, provided with a suitable heating coil 26, wherein isobutane along with small amounts of isopentane are removed by fractional distillation overhead through line 27. Means (not shown) are provided for refluxing part of the fractionator overhead. The overhead from the fractionators in lines 15 and 27, are combined in line 28, and returned to the isobutane feed line 1. This line 28 is provided with a suitable pump 29. The bottoms from the fractionator pass through line 30, provided with pump 31, to scrubber 32, wherein the last traces of hydrogen fluoride are removed by washing with an aqueous alkaline solution circulating through line 33, provided with pump 34. The scrubbed product flows through line 35, to stabilizer 36, where the gasoline fraction is removed by distillation through line 37, as an overhead product. The stabilizer is provided with a suitable heating coil 38, and means (not shown) are provided for refluxing part of the overhead. The bottoms from the stabilizer are fed back through line 39, either to the mixing chamber via line 40, or to the reformer via line 41, wherein these bottoms are reacted in the presence of concentrated hydrofluoric acid and the lighter isoparaffins to give additional quantities of gasoline-boiling range material. Valves 42 and 43 are provided with lines 40 and 41, respectively, whereby the distribution of the return of the stabilized bottoms may be controlled. Line 44 is provided so that a suitable portion of the overhead from fractionator 25 may be recycled directly to the reformer, although these light isoparaffins may also be obtained in the reformer by regulating the amount of excess light isoparaffin taken overhead from the fractionator 13. Valves 45 and 46 are provided for controlling the distribution of the overhead from fractionator 25.

The following specific examples of operation are given to further illustrate the principles of my invention and the advantages obtained by my process. These examples are illustrative only, and are not to be construed as limiting the scope of my invention to the details set forth therein.

Example I

An alkylate charge stock composed principally of branched-chain heptanes in an amount of 4290 parts by weight produced by the reaction of isopentane with ethylene in the presence of anhydrous aluminum chloride, was mixed thoroughly with 1350 parts by weight of anhydrous aluminum chloride for 7 hours at room temperature in a steel autoclave. During this time a gradual pressure rise from about 1 to about 8 pounds per square inch (gage) took place. This pressure rise was caused by the formation of proportionately larger amounts of light isoparaffins having normally a higher vapor pressure than the alkylate charge stock, and was used as a measure of the extent of reaction. Agitation was then discontinued and the hydrocarbon phase separated from the catalyst, washed with water, and dried over anhydrous calcium chloride. The dried hydrocarbons were then fractionated to recover the gasoline distilling in the range 25° to 160° C.

The properties of this fraction and the original alkylate are given in the following table for comparison:

	Original alkylate	Gasoline fraction (25°–160° C.) of reformed product
Octane rating, A. S. T. M. method:		
No TEL	69.9	74.8
Plus 1 cc. TEL/gallon	83	85
Plus 3 cc. TEL/gallon	88.9	92.3
Octane rating, research '39 method:		
No TEL	69.2	73.4
Plus 1 cc. TEL/gallon	79.8	84.4
Plus 3 cc. TEL/gallon	88.6	91.8
A. S. T. M. distillation:		
Initial, °F	172	105
10%, °F	185	137
50%, °F	190	182
70%, °F	192	201
90%, °F	199	222
E. P., °F	208	310
Reid vapor pressure at 100° F	4.5	6.9

It will be noted that the gasoline-boiling fraction of the reformed product meets the distillation and vapor pressure requirements for aviation gasoline and has an unleaded octane number almost 5 points higher than the original alkylate. It possesses the same high lead susceptibility as the original alkylate, i. e., about 2.1.

The gaseous by-product distilling below 25° C. was composed entirely of isobutane, and was reacted with the fraction distilling above 160° C. to produce an additional quantity of aviation boiling range gasoline. To illustrate the procedure for doing this the fraction distilling above 150° C., which amounted to 439 parts by weight, was mixed thoroughly with 300 parts by weight of isobutane and 240 parts by weight of anhydrous aluminum chloride for 7 hours at room temperature in a steel autoclave. During this time a gradual pressure drop from about 29 to about 21 pounds per square inch (gage) took place. In this reaction there was a pressure drop since the the reaction products normally have a lesser vapor pressure than the original high- and low-boiling fractions. As in the previous case, this change in the pressure was used as a measure of the extent of reaction. Agitation was then discontinued, the hydrocarbon phase separated from the catalyst, and the gasoline fraction distilling in the range 25° to 160° C. recovered as in the previous case. This fraction amounted to over 60 percent by weight of the total product and had approximately the same composition as the corresponding fraction obtained by catalytic reforming of the original alkylate.

By repeatedly reacting the light ends with the heavy ends and removing the gasoline range material by fractionation, therefore, substantially all of the original alkylate can be converted to gasoline of high octane rating which meets the distillation and vapor pressure requirements for aviation gasoline. The continuous recycling procedure already described is, of course, preferable for carrying out this process on a commercial scale.

Example II

1380 parts by weight of alkylate (principally branched-chain octanes), having an octane number by the A. S. T. M. method of 93, produced by reaction of isobutane with normal butene in the presence of concentrated hydrofluoric acid, were mixed thoroughly with 1328 parts by weight of hydrofluoric acid for 15 hours at room temperature in a steel autoclave to obtain substantially complete reforming of this alkylate. During this time a gradual pressure rise from about 23 to about 27 pounds per square inch (gage) took

place, which was used as a measure of the extent of reaction. Agitation was then discontinued and the two liquid phases, i. e., the hydrocarbon phase and the hydrofluoric acid phase, allowed to separate. The hydrofluoric acid phase was withdrawn as the bottom layer and the hydrocarbon phase washed with water, dried over anhydrous calcium chloride, and fractionated to recover the gasoline distilling in the range 25° to 168° C.

The gaseous by-product distilling below 25° C. was composed entirely of isobutane, and was reacted with the fraction distilling above 168° C. to produce an additional quantity of gasoline boiling range material. To illustrate the procedure for doing this the fraction distilling above 168° C. which amounted to 317 parts by weight was mixed thoroughly with 216 parts by weight of isobutane and 447 parts by weight of concentrated hydrofluoric acid for 9 hours at room temperature in a steel autoclave. During this time a gradual pressure drop from about 40 to about 35 pounds per square inch (gage) took place which, as in the previous cases, was used as a measure of the extent of reaction. Agitation was then discontinued, the two liquid phases separated, and the hydrocarbon phase fractionated as before to recover the gasoline fraction distilling in the range 25° to 168° C.

The properties of the composite gasoline prepared in this manner are given in the following table:

	No TEL	Plus 3 cc. TEL/gallon
Octane rating:		
A. S. T. M. method	84.2	100.0
Research '39 method	83.3	97.3

A. S. T. M. distillation:					
Vol. per cent distilled	10%	50%	70%	90%	E. P.
Temperature, °F	126	223	247	272	320

Reid vapor pressure at 100° F ..... 8 pounds per square inch

It will be noted that this product has an A. S. T. M. octane number of 100 with only 3 cc. of tetraethyl lead per gallon. Substantially complete reforming was obtained in this case as shown by the high vapor pressure and the appreciable quantity of low- and high-boiling hydrocarbons.

Example III

19.7 parts by weight of alkylate (principally branched-chain heptanes), produced by reaction of isobutane with propylene in the presence of concentrated hydrofluoric acid, were mixed thoroughly with 26 parts by weight of concentrated hydrofluoric acid for 24 hours at room temperature. The liquid product from this reaction was recovered as in Example II. Substantially complete reforming was obtained as shown by the distillation curve, B, of the portion of the product boiling above isopentane in Figure 2.

Example IV

The experiment described in Example III was repeated except that the time of contact between the hydrofluoric acid and the alkylate was 14 hours. The distillation curve, C, of the liquid product boiling above isopentane is given in Figure 2.

Example V

The experiment described in Example III was repeated except that a larger weight ratio of catalyst to alkylate was employed, i. e., 1.56 instead of 1.32, and the time of contact between catalyst and alkylate was only 4 hours. The extent of reforming in this experiment fell midway between that obtained in the two previous examples as shown by the distillation curve, D, of the liquid product boiling above isopentane in Figure 2.

The following examples were performed to show the effect of an added hydrocarbon, boiling outside the gasoline range on the reforming process.

Example VI

The experiment described in Example IV was repeated except that 46.5 mol percent of isobutane was added to the alkylate charge before contacting it with the acid for 14 hours. The extent of reforming in this experiment was appreciably less than that obtained in the absence of isobutane as shown by the distillation curve, E, of the liquid product in Figure 2.

Example VII

The experiment in Example III was repeated except that 104 mol percent of isobutane was added to the alkylate charge before contacting it with the acid for 24 hours. Distillation curve F in Figure 2 shows the extent of the reforming obtained in this experiment.

As mentioned above, the distillation curves for the products of Examples III to VII boiling above isopentane have been plotted in Figure 2. This graph, wherein volume percent of gasoline-boiling material distilled is plotted against distillation temperature, effectively illustrates the utility of my invention. For comparison purposes, the distillation curve of the original heptane fraction obtained by the alkylation of isobutane with propylene is shown as curve A. This curve shows that this heptane alkylate has a narrow-boiling range between 80 and 100° C.

By a comparison of curve A with curves B, C, and D, the effect of the reforming reaction on the boiling range of the alkylate fraction may be readily seen. Approximately 85 percent of the product boiling above isopentane distilled rather uniformly over the entire gasoline range. The lower-boiling material, not shown in the curves, constituted about 30 percent of the original heptane fraction, and was about equally divided between isobutane and isopentane. The isopentane fraction is, of course, suitable for use in gasoline, so about a total of 70 percent of the original heptane fraction was recovered directly as a gasoline fraction of uniform distillation characteristics over the entire gasoline boiling range.

Curves B, C, and D show the effect of time upon the reaction. The extent of reforming is substantially the same over the entire time range of 4 to 24 hours. Curve B shows that somewhat more reforming was obtained at 24 hours than at 14 hours shown in curve C. Where the reforming reaction was allowed to proceed for only 4 hours, substantially the same degree of reforming was obtained by slightly increasing the amount of catalyst used, as shown by curve D lying intermediate curves B and C.

A comparison of curves C and E shows the effect of an added hydrocarbon boiling outside the gasoline range on the process. The effect of the added hydrocarbon, isobutane, was to increase the proportion of intermediate boiling material. In the presence of isobutane (46.5 mol precent) over 65 percent of the material boiling above isopentane boiled within the range from 60 to 120° C. In the absence of isobutane only about 45 percent of the material boiling above isopentane

boiled in this same range. The amount of material boiling above the gasoline range was less than 10 percent, as compared with about 15 percent in the case of reforming in the absence of isobutane. The amount of total low-boiling material, not shown on the graph, was also considerably less, making the total gasoline-boiling material, including isopentane, about 85 percent.

Curve F shows that where the amount of isobutane added, in the case of the hydrofluoric acid catalyst, exceeded an equimolar quantity the reforming reaction was almost completely suppressed. The reaction was allowed to proceed for 24 hours, and the curve shows that in the presence of such a large amount of isobutane, an excessively long time would be required to obtain appreciable reforming.

The curves show that in the absence of added isobutane, the contact time may be varied from about one hour to about 24 hours without appreciably altering the results. This is evidence that with an active catalyst equilibrium is established in the system in a comparatively short time. In case it is desired that the major fraction of the reformed product boil over but a limited portion of the gasoline range, contact times of less than about one hour may be used, the concentration of the catalyst may be lowered, or a low- or high-boiling hydrocarbon added.

It is important to note that the reformed product obtained by my process is not a low octane product as might be expected, but rather it has an octane rating that compares favorably with that of the original alkylate and is frequently higher than that of the original alkylate. When dealing with a narrow-boiling, branched-chain fraction of relatively low octane number, such as the ordinary heptane alkylates, the octane number is raised in addition to obtaining a desired spread in the boiling range. Some of the alkylates, such as the isobutane-butylene alkylate of Example II, which have a very high octane number, will give a somewhat lower octane rating for the reformed product. The reformed product, however, might easily have a higher octane rating than the motor fuel obtained by blending the high octane alkylate with the blending agents available and capable of giving the alkylate the proper boiling characteristics. Also a partial reforming of a high octane alkylate so that it may be blended with available blending agents to give a complete motor fuel may frequently be desirable, and such a partial reforming could be accomplished at a lesser sacrifice of octane number. The improvement in the boiling characteristics of the alkylate will frequently be desirable and necessary for the effective utilization of a particular alkylate, and for the production of a high octane complete fuel. The process is therefore of value for the treatment of high octane alkylates as well as the lower octane alkylates, even though with the former there is some sacrifice in the octane number of the alkylate itself. The octane rating of my reformed products may be easily brought up to aviation requirements by the addition of small and permissible amounts of tetraethyl lead. It is also important to note that my process is capable of producing a complete gasoline, and that in so doing, a larger percentage of the alkylate, and hence a larger percentage of gaseous hydrocarbons going into alkylate, will be represented in the finished product.

The invention has been described with particular reference to alkylate gasolines; however, it is to be understood narrow-boiling, branched-chain hydrocarbon fractions in general may be used. For instance, such a product formed by polymerizing olefins and then hydrogenating the polymers could serve as a stock to be reformed.

Many modifications of my invention will be apparent to those skilled in the art, and only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The process which comprises contacting a mixture of an isoparaffin and an olefin in which the mol ratio of the isoparaffin to the olefin is greater than two to one with an alkylation catalyst consisting essentially of hydrofluoric acid under alkylating conditions of temperature and pressure for said catalyst to form a relatively narrow-boiling alkylate, separating at least a sufficient amount of the isoparaffin from the hydrocarbon product mixture to reduce the isoparaffin-alkylate mol ratio to less than one to one, contacting the alkylate product containing less than one mol of isoparaffin per mol of alkylate with an alkylation catalyst consisting essentially of hydrofluoric acid under alkylating conditions of temperature and pressure to reform said alkylate to higher and lower boiling saturated hydrocarbons, allowing the hydrocarbons and catalyst to remain in contact until the desired amount of the original narrow-boiling fraction has been reformed to give a mixture of hydrocarbons whose boiling range has a desired distribution over the gasoline boiling range, separating the hydrocarbons from the hydrofluoric acid catalyst, fractionating the hydrocarbons to remove saturated hydrocarbons boiling below and saturated hydrocarbons boiling above the desired range, returning the hydrocarbons so separated in admixture for further contacting with the alkylation catalyst, and recovering the desired hydrocarbon fraction of controlled boiling characteristics.

2. The process which comprises contacting a mixture of an isoparaffin and an olefin in which the mol ratio of isoparaffin to the olefin is greater than 2 to 1 with an alkylating catalyst consisting essentially of hydrofluoric acid under alkylating conditions of temperature and pressure for said catalyst to form a relatively narrow-boiling alkylate, separating a sufficient amount of isoparaffin from the hydrocarbon product mixture to reduce the isoparaffin-alkylate mol ratio to less than 1 to 2 contacting the alkylate product containing less than one-half mol of isoparaffin per mol of alkylate product with an alkylation catalyst consisting essentially of hydrofluoric acid under alkylating conditions of temperature and pressure to reform said alkylate to higher and lower boiling saturated hydrocarbons, allowing the hydrocarbons and catalyst to remain in contact until the desired amount of the original narrow-boiling fraction has been reformed to give a mixture of hydrocarbons whose boiling range has a desired distribution over the gasoline boiling range, separating the hydrocarbons from the hydrofluoric acid catalyst, fractionating the hydrocarbons to remove saturated hydrocarbons boiling below and saturated hydrocarbons boiling above the desired range, returning the hydrocarbons so separated in admixture for further contacting with the alkylation catalyst, and recovering the desired hydrocarbon fraction of controlled boiling characteristics.

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