July 19, 1949. M. P. MATUSZAK 2,476,750

PROCESS FOR PRODUCING MOTOR FUEL BY ALKYLATION

Filed Oct. 8, 1947 3 Sheets-Sheet 1

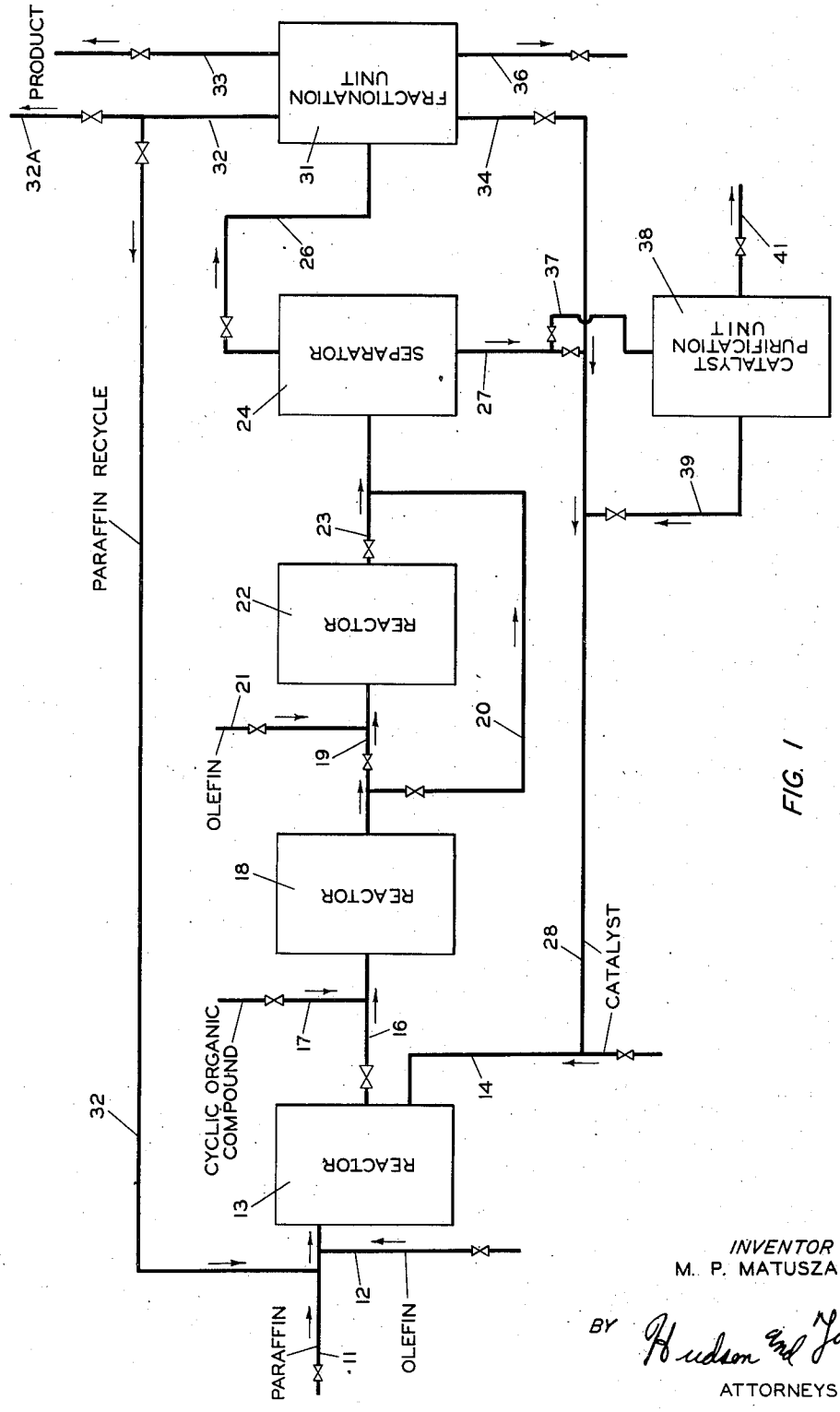


FIG. 1

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Filed Oct. 8, 1947 3 Sheets-Sheet 2

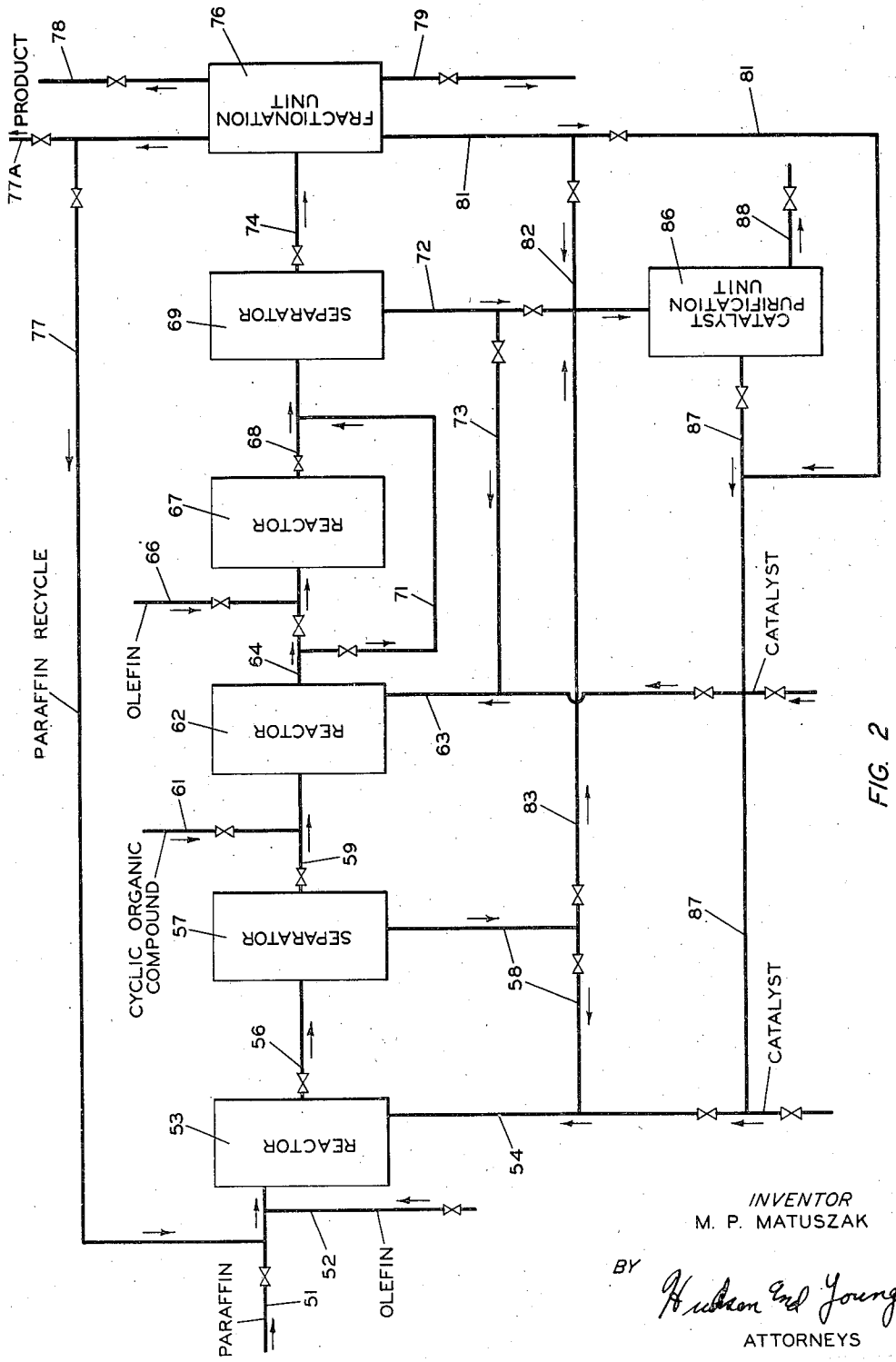


FIG. 2

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Filed Oct. 8, 1947 3 Sheets-Sheet 3

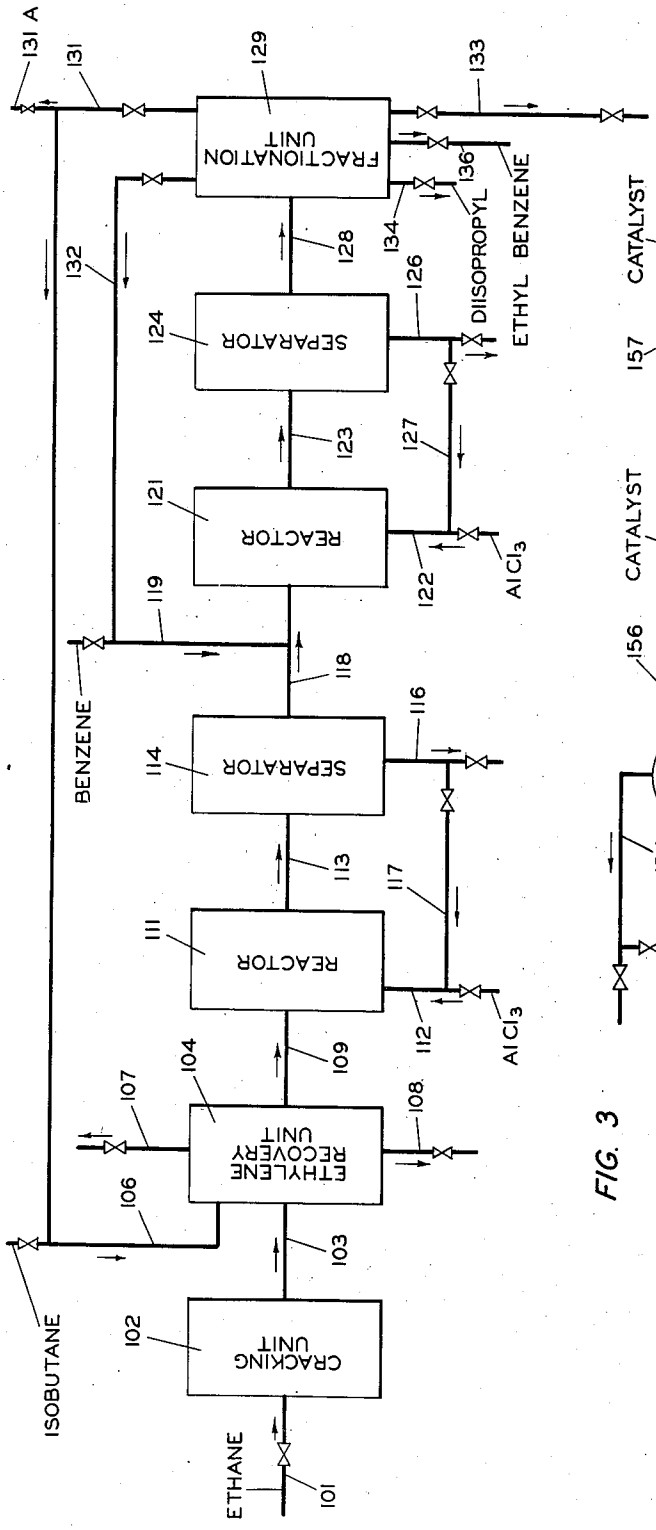


FIG. 3

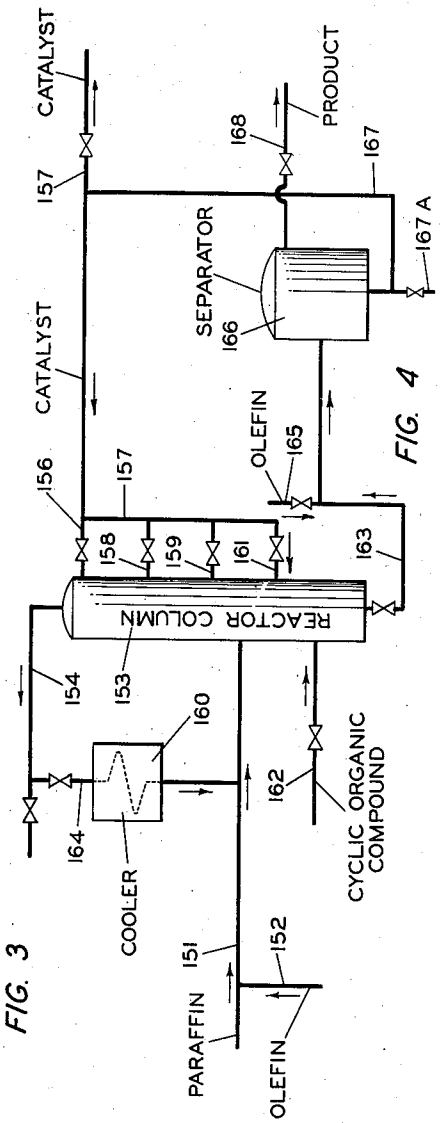


FIG. 4

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Patented July 19, 1949

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UNITED STATES PATENT OFFICE

2,476,750

PROCESS FOR PRODUCING MOTOR FUEL BY ALKYLATION

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Application October 8, 1947, Serial No. 778,607

18 Claims. (Cl. 260—683.4)

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This invention relates to an alkylation process. In one embodiment it relates to a method of removing reaction by-products from the effluent of a catalytic alkylation process. In another embodiment it relates to a method of removing organically combined halogen (herein designated "organic halogen") such as fluorine or chlorine from paraffin hydrocarbon materials contaminated therewith. In another embodiment it relates to an improved method of alkylating a low-boiling paraffin, usually an isoparaffin, with an alkylating agent, usually a low-boiling olefin, to make a higher-boiling paraffin (known in the art as alkylate) which is useful as a high octane base or blending stock for motor and aviation fuel.

This invention is a continuation-in-part of my co-pending application Serial No. 602,247, filed June 29, 1945, and now Patent No. 2,432,482. In one embodiment, it comprises, in combination, catalytic alkylation of a paraffin with an alkylating agent in a first alkylation zone, subsequent addition of an excess of a relatively easily alkylatable compound of the type of benzene and catalytic alkylation thereof in a second alkylation zone with by-products formed in the first alkylation zone, subsequent catalytic alkylation of the excess added easily alkyltable compound with added olefin in a third alkylation zone, and isolation of resultant composite alkylate boiling in the motor-fuel range as the main product of the process.

The principal object of this invention is to provide an improved alkylation process.

Another object is to provide an improved method of removing reaction by-products contained in the effluent material from a catalytic alkylation process.

Another object is to provide an improved method of removing organic halogen from paraffin hydrocarbon materials containing the same.

Another object is to provide an improved method of removing organic sulfates from paraffin hydrocarbon materials containing the same.

Another object is to provide an improved method of removing fluorine from paraffin hydrocarbon material contaminated therewith, such as alkylate made by alkylation of an isoparaffin with an olefin by means of hydrofluoric acid as a catalyst.

Numerous other objects will be obvious to one skilled in the art from the accompanying disclosure and discussion.

Ordinarily, the paraffin is an isoparaffin, selected because of its relatively high reactivity,

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and it is preferably isobutane, primarily because of its availability at relatively low cost. The alkylating agent is usually one or more olefins, but in some applications it may be one or more olefin derivatives, such as alcohols, alkyl halides, or the like. The alkylation catalyst may be any that is effective for promoting alkylation of the selected paraffin with the selected alkylating agent such as anhydrous hydrogen fluoride, sulfuric acid or others. Hydrofluoric acid is preferred for alkylation of an isoparaffin with olefins heavier than ethylene or with polar non-primary alkyl compounds. When ethylene or a primary alkyl compound is the alkylating agent, the catalyst may be advantageously a mixture of hydrofluoric acid and boron fluoride; this catalyst may also be used in alkylation of normal paraffins. Ordinarily, however, when a normal paraffin is being alkylated, or when the alkylating agent is ethylene, the preferred catalyst is one comprising aluminum chloride or bromide, promoted with an alkyl halide or a hydrogen halide, usually hydrogen chloride, as in the commercial manufacture of diisopropyl and other hydrocarbons from isobutane and ethylene.

In the paraffin-alkylation step, conditions for which depend upon the particular reactants and catalyst and may be selected in accordance with knowledge available to the art, some undesired by-products are formed, resulting in objectionable consumption of reactants or catalyst, or both, and in objectionable contamination of the product and the surviving reactants. The principal by-products are compounds or complexes formed from hydrocarbons and alkylation catalyst, polymers formed from alkylating agent, and heavy alkylates that boil above the desired motor-fuel range. The proportions of these undesired by-products, and even their identities, depend considerably upon the particular materials and the particular conditions present, but their formation has long been recognized for every catalytic paraffin-alkylation process, no matter whether the catalyst comprises hydrofluoric acid, aluminum chloride, sulfuric acid, or any of many less widely used alkylation catalysts.

In the past, little has been done to counteract the formation of these various undesired by-products except to remove and withdraw the most objectionable ones at considerable trouble and expense. For example, when a halogen-containing catalyst is used, a small proportion of organic halogen appears in the alkylate and in the surviving reactants, and these materials

in consequence may be subjected to a treating step designed to remove the organic halogen, such as contacting at a suitable temperature with solid metal oxides or other materials that adsorb the organic halogen compounds, or catalytically split out the halogen as the hydrogen halide, or react to form metal halides. Treating with bauxite or similar material exemplifies such a treating step for removing a halogen like chlorine or fluorine. When fluorine is the halogen, considerable difficulty arises because of the formation of silicon tetrafluoride from silica present in the bauxite or similar contacting agent; the silicon tetrafluoride is carried along in the hydrocarbon stream and subsequently causes trouble by becoming hydrolyzed by moisture, forming silicic acid that plugs equipment and necessitates expensive shutdowns for removal. Eliminating or minimizing the formation of the organic halogen compounds is obviously highly desirable. Similarly, counteracting the formation of other undesired by-products is highly desirable.

In the process of this invention, substantial counteracting of the formation of by-products is obtained by mixing with the alkylation reaction mixture, after the paraffin alkylation is substantially completed, an excess of a relatively easily alkylatable compound. This compound, in the presence of the alkylation catalyst, undergoes alkylation with any surviving alkylating agent added as such and with various by-products of the paraffin alkylation. A process utilizing somewhat similar alkylation and directed primarily to reduction of organic halogen, has been described in my co-pending application Serial No. 602,247, filed June 29, 1945, and now Patent No. 2,432,482. In the process of the present invention, in partial contrast, a relatively larger proportion of easily alkylatable compound is required, to react primarily with the by-products other than, for example, organic halogen compounds; furthermore, the present process is broader than that of my above mentioned copending application in that it may be applied to halogen-free systems, although reduction of organic halogen is not to be excluded in particular applications. When organic halogen compounds are present, the organic halogen is liberated as hydrogen halide, which becomes available for reuse; simultaneously, the added easily alkylatable compound becomes alkylated. Similar reactions occur with other catalyst-hydrocarbon compounds or complexes; for example, when sulfuric acid is the catalyst, by-product alkyl sulfates or bisulfates alkylate the added compound with regeneration of sulfuric acid. In somewhat analogous fashion, other by-products are consumed in alkylating the added easily alkylatable compound; such materials as polymers, so-called "acid-soluble oil" formed in hydrofluoric acid and sulfuric acid alkylations, and alkylates boiling above the motor-fuel range contribute substantially to alkylating the added compound, presumably through some preliminary or concurrent fragmentation under the influence of the catalyst.

The added easily alkylatable compound preferably should be one that is not undesirable in the product, so that separation of it or of its alkylates that boil in the motor-fuel range need not be effected; however, such separation may be practiced without going beyond the broad concept of this invention. In a modern petroleum refinery, a stream comprising benzene and/or other low-boiling easily alkylatable aromatic hydrocarbons that may be formed, for example, in cracking steps generally constitutes a highly satisfactory compound and may be preferred because of ready availability at low cost. Especially advantageous is such a material when it is already being used for blending with motor-fuel hydrocarbons produced by paraffin alkylation, for then there is substantially no additional cost for the added easily alkylatable compound. However, other compounds may be suitably utilizable in particular applications of the process. Among compounds that may be used in this way are furan, phenol, pyrrol, thiophene, and similar alkylatable compounds that may be characterized as having at least two conjugated double bonds in a ring; but usually benzene or other low-boiling aromatic hydrocarbon, such as toluene, is preferable because of the absence of an element other than carbon and hydrogen.

Intimate mixing of the added compound with the paraffin-alkylation reaction mixture, including an alkylation catalyst, is essential. The mixing period required depends upon the added compound, upon the reactivity of the various paraffin-alkylation by-products, and upon the activity of the catalyst, but a suitable period, which is ordinarily measurable in minutes, usually in the range of 1 to 20 minutes, can be readily found by trial for any specific application. In general, the conditions are similar to those in the paraffin-alkylation step, so that heating, cooling, or other special conditioning is not necessary though such conditioning may be advantageous in particular applications. In some applications, special mixing means may be unnecessary, provided that the added compound is adequately dispersed into the reaction mixture effluent from the paraffin-alkylation zone, as by ejection from one or more jets; in such applications, substantial alkylation of the added compound occurs during passage of the reaction mixture to the next step, especially when baffles are provided to maintain intimate mixing during this passage. Preferably, the added compound should not be present within the paraffin-alkylation zone, wherein it would compete undesirably with the paraffin for the alkylating agent fed to this zone, but traces added in recycled material may be economically permissible.

In one embodiment, the by-product-alkylation step and the preceding paraffin-alkylation step may be conducted with two separate bodies of catalyst. Although the two bodies may be of different catalysts, such as hydrofluoric acid for the paraffin-alkylation step and sulfuric acid for the by-product-alkylation step, it is usually preferable to have both of one catalyst. By use of the two separate bodies of catalyst, any carry-over, to the paraffin-alkylation step, of surviving added compound (e. g., benzene) in solution in recycled catalyst is avoided. Such carry-over is disadvantageous to the extent that the added compound competes with the paraffin for the olefin or other alkylating agent fed to the process. This application requires an intermediate separation step for separating the reaction mixture effluent from the paraffin-alkylation step into a hydrocarbon phase, which is passed to the by-product-alkylation step, and into a catalyst phase, which is recycled to the first step or is passed in part to a purification or catalyst-recovery system.

Regardless of whether or not a separate body of catalyst has been used, the reaction mixture effluent from the by-product alkylation step is

passed to a final alkylation step, wherein at least part of the excess added compound is alkylated with an added olefin that is consumed so rapidly under the prevailing conditions that any objectionable by-products are negligible. When, as is preferred, the excess added compound is benzene, the olefin added in this step is preferably ethylene-free and is most preferably propylene, inasmuch as this particular olefin has a relatively small tendency to form objectionable by-products and inasmuch as the resulting alkylated benzene is mainly cumene, which is an especially desirable motor-fuel ingredient. This advantageous conversion of excess benzene to cumene results in an increased yield and in an improved quality of the motor fuel formed by the process.

The reaction mixture effluent from the final alkylation step is passed to a settler for separation into hydrocarbon and catalyst phases. The catalyst phase is recycled to its point of original introduction into the system or is in part passed to a catalyst purification or recovery step. The hydrocarbon phase is freed from traces of catalyst and is fractionated into desired product, by-product, and recycle fractions. If the same catalyst is used in all alkylation steps then only one catalyst regeneration system is necessary.

It will be appreciated that the final alkylation step eliminates in large measure the benzene or other relatively easily alkylatable compound from the catalyst phase. By proper adjustment of the proportion of olefin added to this step, substantially no excess or unconsumed benzene remains in the catalyst, which consequently is rendered substantially unobjectionable for use in the paraffin-alkylation step. Although use of one and the same body of catalyst for all alkylation steps presents a need for relatively fine control, it is advantageous when equipment is limited or unobtainable in the amount required for use of two separate bodies of catalyst or when the scale of operation justifies it for economical reasons. Accordingly, such use of one body of catalyst for all alkylation steps is considered within the scope of this invention.

In the accompanying drawing Figure 1, Figure 2, Figure 3 and Figure 4 each illustrates one embodiment of my invention. Referring to Figure 1 of the drawing an alkylatable paraffin hydrocarbon is passed through line 11 to reactor 13. An alkylating agent, such as an olefin, is introduced into reactor 13 through line 12 by way of line 11. An alkylation catalyst, for example, an anhydrous hydrofluoric acid is introduced into reactor 13 by way of line 14. The contents of reactor 13 are maintained under alkylation conditions and are mixed by any suitable means, such as a mechanical stirrer, which is not shown. The reaction mixture effluent from reactor 13 passes through line 16 to reactor 18. An easily alkylatable cyclic organic compound, such as benzene, is introduced into reactor 18 by way of lines 17 and 16. The contents of reactor 17 are maintained under alkylation conditions and are mixed by any suitable means not shown. The reaction mixture effluent from reactor 18 passes through line 19 to reactor 22. An alkylating agent, such as an olefin, is introduced into reactor 22 by way of lines 21 and 19. The contents of reactor 22 are maintained under alkylating conditions and are mixed by any suitable means not shown. If desirable, at least a portion of the reaction mixture effluent from reactor 18 may by-pass reactor 22 by way of line 20 and enter separator 24 by way of line 23. The reaction mixture effluent from reactor 22 passes through line 23 to separator 24 where the reaction mixture is separated by gravity into a hydrocarbon phase and a catalyst phase. The catalyst phase is recycled to reactor 13 by way of lines 27, 28 and 14 and is reused in each of the reactors, namely 13, 18 and 22. However, at least a portion of said catalyst may be withdrawn from line 27 and passed through line 37 to catalyst purification unit 38 where the catalyst is regenerated. The purified catalyst is returned to the system through lines 39, 28 and 14 to reactor 13. If desirable, however, at least a portion of the purified catalyst may be withdrawn from the system through line 41. The hydrocarbon phase from separator 24 passes through line 26 to fractionation unit 31. The unreacted paraffin in the original feed is recycled through lines 32 and 11 to reactor 13. However, at least a portion of this paraffin recycle material may be removed from the system through line 32A. The product coming within the motor fuel boiling range is removed from the fractionation unit 31 through line 33. Any catalyst that might have been carried over from separator 24 to fractionation unit 31 is recycled through lines 34, 28 and 14 to reactor 13. The heavy material boiling above the motor fuel boiling range is removed from fractionation unit 31 through line 36.

Referring to Figure 2 of the drawing an alkylatable paraffin hydrocarbon is passed through line 51 to reactor 53. An alkylating agent, such as an olefin, is introduced into reactor 53 by way of lines 52 and 51. An alkylation catalyst, such as sulfuric acid, is introduced into reactor 53 by way of line 54. The contents of reactor 53 are maintained under alkylation conditions and are mixed by any suitable means not shown. The reaction mixture effluent from reactor 53 is passed through line 56 to separator 57 where the mixture is separated by gravity into a hydrocarbon phase and a catalyst phase. The catalyst phase is recycled through lines 58 and 54 to reactor 53. However, if desirable, at least a portion of the catalyst phase may be passed from line 58 through line 83 to catalyst purification unit 86 where it is purified. The hydrocarbon phase from separator 57 passes through line 59 to reactor 62. An easily alkylatable cyclic organic compound, such as benzene, is introduced into reactor 62 by way of lines 61 and 59. A suitable alkylation catalyst, such as sulfuric acid, is introduced into reactor 62 by way of line 63. The contents of reactor 62 are maintained under alkylation conditions and are mixed by any suitable means not shown. The reaction mixture effluent from reactor 62 is passed through line 64 to reactor 67. An alkylating agent, such as an olefin, is introduced into reactor 67 by way of lines 66 and 64. The resulting reaction mixture is maintained under alkylating conditions in reactor 67 and is mixed by any suitable means not shown. At least a portion of the reaction mixture effluent from reactor 62 may by-pass reactor 67 and be introduced directly into separator 69 by way of lines 71 and 68. The reaction mixture effluent from reactor 67 is passed through line 68 to separator 69 where it is separated by gravity into a hydrocarbon phase and a catalyst phase. At least a portion of the catalyst phase may be recycled through lines 72, 73 and 63 to reactor 62. Also, at least a portion of the catalyst phase may pass through line 72 to catalyst purification unit 86. The hydrocarbon effluent from separator 69 passes through line 74 to fractionation unit 76. The unreacted paraffin contained in the original

feed is removed from fractionation unit 76 and recycled through lines 77 and 51 to reactor 53. However, at least a portion of the recycled paraffin may be removed, if desired, from the system through line 77A. The product coming within the motor fuel boiling range is removed through line 78. Any higher boiling material such as tar that may be formed in the system is removed from fractionation unit 76 through line 79. Any catalyst that may be carried over into fractionation unit 76 from separator 69 is removed through lines 81 and at least a portion of this catalyst material may be recycled through lines 81, 87 and 54 to reactor 53 or to reactor 62 by way of lines 81, 87 and 63. Also, at least a portion of the catalyst may be withdrawn from line 81 and introduced into catalyst purification unit 86 by way of lines 82 and 72. The used catalyst which is introduced into catalyst purification unit 86 from separators 57 and 69 and from fractionation unit 76 is purified and returned to the system by way of line 87. If desired, at least a portion of the purified catalyst may be removed from the system through line 88.

Referring to Figure 3 of the drawing, a hydrocarbon suitable for cracking to produce ethylene, for example ethane, is introduced through line 101 to cracking unit 102 where it is cracked under appropriate conditions to produce ethylene. The reaction mixture effluent from cracking unit 102 is passed through line 103 to ethylene recovery unit 104 where the ethylene is absorbed under suitable conditions of temperature and pressure in isobutane which is introduced into the ethylene recovery unit 104 through line 106. The light materials, such as methane and hydrogen, are removed from the ethylene recovery unit 104 through line 107 and the materials heavier than isobutane are removed through line 108. The isobutane which contains the ethylene is removed from ethylene recovery unit 104 and is passed through line 109 to reactor 111. A catalyst, such as aluminum chloride, preferably dissolved in an aluminum chloride-hydrocarbon complex, is introduced into reactor 111 by way of line 112. The contents of reactor 111 are maintained under appropriate alkylation conditions and are mixed by any suitable means not shown. The reaction mixture effluent from reactor 111 passes through line 113 to separator 114 where it is separated by gravity into a catalyst phase and a hydrocarbon phase. The catalyst phase is removed through line 116 and recycled to reactor 111 through lines 117 and 112. However, at least a portion of the catalyst may be removed from the system through line 115 for purification or use elsewhere, if desired. The hydrocarbon phase from separator 114 passes through line 118 to reactor 121. An easily alkylatable cyclic material, such as benzene, is introduced into reactor 121 by way of lines 119 and 118. Aluminum chloride catalyst, preferably dissolved in an aluminum chloride-hydrocrabon complex, is introduced into reactor 121 through line 122. The contents of reactor 121 are maintained under appropriate alkylating conditions and are mixed by any suitable means not shown. The reaction mixture effluent material from reactor 121 is passed through line 123 to separator 124 where it is separated by gravity into a catalyst phase and a hydrocarbon phase. The catalyst phase is withdrawn through line 126 and at least a portion passed to a purification system not shown or for use in any manner desired; however, at least a portion of the catalyst phase is recycled to reactor 121 by way of lines 127 and 122. The hydrocarbon phase from reactor 124 is passed through 128 to fractionation unit 129. A recycle isobutane stream is removed from fractionation unit 128 and is recycled to ethylene recovery unit 104 through lines 131 and 106. However, a portion of this recycle isobutane-containing stream may be removed from the system through line 131A if desired. Unreacted benzene is romeved through line 132 and returned to reactor 121 by way of lines 119 and 118. The reaction product from isobutane and ethylene which comprises chiefly diisopropyl is removed through line 134. Ethyl benzene formed is removed from fractionating unit 129 through line 136. Any high boiling product may be removed from fractionation unit 179 through line 133.

Referring to Figure 4 of the drawing, an alkylatable paraffin hydrocarbon is introduced into the reactor column 153 through line 151. An alkylating agent, such as an olefin, is introduced into reactor column 153 by way of lines 152 and 154. A suitable alkylation catalyst, such as sulfuric acid, is introduced through line 157 and introduced into reactor column 153 at multiple points through lines 156, 158, 159 and 161. The reactor column is maintained under suitable alkylation conditions wherein the alkylation reaction takes place and the unreacted original paraffin material is taken overhead through line 164 and removed from the system if desired, or at least a portion of this product may be recycled through line 164, cooler 160 and line 151 to the reauctor column 153. An easily alkylatable cyclic organic compound, such as benzene, is introduced into the reactor column 153 through line 162 where it is contacted with the catalyst and reaction products of the paraffin-olefin alkylation step. The reaction mixture effluent of reactor column 153 is passed through line 163 to separator 166. An olefin is introduced through line 165 into the reaction mixture effluent from reactor column 153 passing through line 163 before reaching separator 166. The total reaction mixture is separated by gravity in separator 166 into a catalyst phase and a hydrocarbon phase. The catalyst phase is recycled to the system through line 167, however at least a portion may be removed from the system through line 167A and passed to a purification system not shown or used in any way desired. The hydrocarbon phase is removed from separator 166 through line 168 for further fractionation and purification as desired. Reaction column 153 is preferably operated at such temperature and pressure that butanes and lighter hydrocarbons are removed overhead in the vapor phase and compounds heavier than butane are withdrawn as liquid kettle products.

In the accompanying diagrammatic drawing including Figures 1, 2, 3 and 4 reference to some equipment, such as pumps, gauges, and the like which obviously would be necessary to actually operate the process of my invention have been intentionally omitted. Only sufficient equipment has been shown to illustrate the process of the invention and it is intended that no undue limitation be read into this invention by reference to the drawing and discussion thereof.

This invention may be employed in combination with steps other than a paraffin alkylation step. For example, it may be combined with a paraffin-isomerization step or a paraffin-disproportionation step wherein by-products are formed because of the presence of certain elements or

radicals in the catalyst used, such as halogen or the sulfate radical. The effluent of such step is treated substantially as has been described for paraffin alkylation. The term paraffin-reconstruction may be considered as being generic to paraffin alkylation, paraffin isomerization and paraffin-disproportionation.

Among the advantages provided by this invention by its clean-up action on any unreacted alkylating agent and on other materials such as organic halogen or organic sulfate compounds are decreased catalyst consumption; decreased expense and labor for removal of undesirable by-products; and increased yield of organic material suitable for use in motor fuels. The removal of olefins is desirable when normal butane, for example, is removed from the reaction mixture and is subsequently catalytically isomerized to isobutane.

Example I

In a continuous operation like that illustrated by Figure 2 of the drawing, isobutane is alkylated in the presence of a hydrofluoric acid catalyst with one or more olefins having mainly three to five carbon atoms per molecule. In general, substantially conventional alkylation conditions may be used, such as an isobutane-to-olefin mol ratio in the feed of approximately 4:1 to 10:1, a catalyst-to-hydrocarbon volume ratio of approximately 0.5:1 to 2:1, a temperature of approximately 80 to 120° F., a titratable acidity of approximately 80 to 95 weight per cent hydrogen fluoride, a contact time or residence time of the reaction mixture in the contactor or mixer-reactor of approximately 5 to 20 minutes, and a pressure adequate to maintain the reaction mixture in liquid phase. The reaction mixture effluent from the contactor is passed to a separator for separation into hydrocarbon and catalyst phases by gravity. The catalyst phase is recycled to the isobutane-alkylation step, but part of it ordinarily is passed, continuously or intermittently, to a catalyst purification or recovery step, wherein it is subjected to fractional distillation to free it from dissolved impurities, mainly from heavy unsaturated hydrocarbons collectively known as acid-soluble oil. The hydrocarbon phase is passed to a by-product alkylation step, wherein it is mixed with approximately its own volume of hydrofluoric acid and with approximately 2 to 5 per cent of its own volume of refinery "blending benzene" having an A. P. I. gravity of approximately 30.5° and an A. S. T. M. distillation range for the first 95 per cent evaporated of approximately 167 to 177° F., which indicate a high content of benzene. This blending benzene is so called because of earlier utilization for blending with alkylate and other motor-fuel ingredients to form a high-quality aviation gasoline. Ordinary technical benzene, such as that derived from coal or from petroleum hydrocarbons by aromatization or the like may be substituted for the blending benzene. The mixing and other conditions in the by-product-alkylation step are substantially like the corresponding conditions in the paraffin-alkylation step. The reaction mixture is then passed to a third or final alkylation step, wherein it is mixed with an olefin, preferably ethylene-free and further preferably propylene, which is added in a proportion at least equimolecular with respect to the unconsumed benzene in the reaction mixture and preferably slightly in excess. The conditions in this final alkylation step are generally similar to those in the preceding alkylation steps except that the contact time is ordinarily shorter, approximately 1 to 10 minutes, in correspondence with the relatively high reactivity of the benzene, which appears to outweigh its relatively low concentration. Any excess olefin appears to be substantially consumed without undergoing polymerization, apparently mostly in secondary or further alkylation of benzene, accompanied by some primary alkylation of isobutane. As soon as the added olefin is consumed, the reaction mixture is passed to a settler for separation into hydrocarbon and catalyst phases by gravity. The catalyst phase is recycled to the by-product-alkylation step; ordinarily little of this catalyst phase needs to be removed for purification. The hydrocarbon phase is passed to fractionation means for fractional distillation into various fractions. A minor low-boiling azeotropic fraction of hydrofluoric acid and isobutane may be obtained and may be passed to the by-product-alkylation step, but ordinarily this low-boiling material is included with a major fraction of unreacted isobutane, which is recycled to the paraffin-alkylation step. A motor-fuel fraction is withdrawn as the main product of the process; it comprises both isoparaffinic and aromatic alkylates, including cumene, and has a desirably high quality for use in aviation gasoline. A minor fraction of high-boiling hydrocarbons is withdrawn and may be subjected, if desired, to cracking for production of olefins.

Example II

In a continuous operation like that illustrated by Figure 2 of the drawing, isobutane is alkylated substantially as described in Example I, and the reaction mixture effluent from this paraffin-alkylation step is passed directly to the by-product-alkylation step. Subsequent steps are substantially like those of Example I, inasmuch as the major difference from Example I is the use of one body of catalyst for the three alkylation steps.

Example III

A gaseous stream having approximately 12 mol per cent ethane and 88 mol per cent propane is subjected to cracking, yielding an effluent having the following approximate composition, in mol per cent: hydrogen, 16; methane, 30; ethylene, 24; ethane, 7; propylene, 11; propane, 11; butane and heavier, 1. This effluent is cooled and is compressed to about 800 p. s. i. After being again cooled, it is subjected to absorption at approximately 40 to 100° F. by mineral seal oil, which removes most of the propylene and heavier hydrocarbons. Among these heavier hydrocarbons is a small proportion of aromatic oils formed in the cracking step; if desired, these may be suitably recovered and subsequently used as part of the benzene in the benzene-alkylation step. The unabsorbed gas has the following approximate composition, in mol per cent: hydrogen, 25; methane, 52; ethylene, 17; ethane, 5; heavier, 1. This gas is passed to an ethylene recovery column for removal of hydrogen and methane and for absorption of ethylene and heavier hydrocarbons by liquid isobutane at a pressure of approximately 500 p. s. i. and a kettle temperature of approximately 230° F. The ethylene-denuded gas has approximately 32 and 65 mol per cent of hydrogen and methane, respectively, with

generally less than 3 mol per cent of heavier hydrocarbons. The solution of ethylene in isobutane is passed to a first aluminum chloride-catalyzed alkylation zone, in which alkylation of isobutane with ethylene to form diisopropyl as the main product is carried out under such conditions that the yield of diisopropyl based on ethylene reacted in this step is a maximum, being usually approximately 2.2 to 2.4 pounds of diisopropyl per pound of ethylene reacted. The conditions are interdependent to some degree and may vary somewhat, but the following may be taken as fairly typical: isobutane-to-ethylene mol ratio, approximately 4:1 to 6:1; volume ratio of hydrocarbon phase to catalyst phase, approximately 2:1 to 3:1; temperature, approximately 100 to 130° F.; viscosity of catalyst, approximately 200 to 400 centistokes at 100° F.; residence time in reactor, approximately 10 to 20 minutes. The catalyst phase, which comprises aluminum chloride-hydrocarbon compounds or complexes of incompletely understood nature, is maintained at the activity necessary to effect conversion of approximately 90 to 94 per cent of the ethylene introduced by addition of aluminum chloride and/or hydrogen chloride or equivalent promoter and by withdrawing some of the catalyst phase for purification or recovery of the aluminum chloride. When the ethylene conversion reaches approximately 90 to 94 per cent, the reaction mixture is passed to a separator system. The separated catalyst phase is returned to the reactor or is removed for recovery of aluminum chloride. The hydrocarbon phase is passed to a second aluminum chloride-catalyzed alkylation zone, to which is added also benzene approximately 2 to 6 times in molecular excess of the unreacted ethylene. In this zone the ethylene is substantially completely consumed in alkylation of benzene to ethylbenzene. Some polyethylated benzene, mostly diethylbenzene, is also formed, especially when the ratio of benzene to ethylene is relatively low; in addition, a small proportion of alkylated benzene other than ethylated benzene is formed as a result of minor side reactions, which are advantageous in that they decrease the content of organic chlorine. Although the catalyst used in this benzene-alkylation step is substantially identical when fresh to that introduced into the isobutane-alkylation step, being prepared, for example, by mixing approximately 7 to 10 parts by weight of kerosene and 1 part of anhydrous aluminum chloride and some hydrogen chloride at 150 to 200° F. for 0.5 to 2.5 hours, it is not permitted to enter the isobutane-alkylation zone because it acquires a content of benzene, which would compete with the isobutane for the ethylene. Consequently, when the reaction between ethylene and benzene in the benzene-alkylation zone is completed, the reaction mixture is passed to a second settling system which is distinct and separate from the settling system following the isobutane-alkylation zone. The catalyst phase is recycled from the settling system to the benzene-alkylation zone or is removed for purification and recovery of aluminum chloride. The hydrocarbon phase is passed to a fractionation system for separation into various hydrocarbon fractions. Ethane and propane may be recycled to the cracking unit for formation of ethylene. Isobutane is recycled to the ethylene-recovery unit for use as absorbent for ethylene. Motor-fuel hydrocarbons may be withdrawn as a single fraction, or they may be fractionated to recover specific hydrocarbons; for example, unreacted benzene may be recovered as a separate fraction and may be recycled to the benzene-alkylation zone. Ordinarily, the ethylbenzene is obtained in this way as a separate fraction and is passed to further processing steps for ultimate utilization as styrene in the manufacture of synthetic rubber, but if desired it may be utilized together with the diisopropyl and other products of the process as a motor-fuel ingredient. A small proportion of products heavier than motor fuel is withdrawn as a tarry by-product of the process.

It is to be understood that this invention should not be unnecessarily limited to the above discussion and description and that modifications and variations may be made without departing substantially from the invention or from the scope of the claims.

I claim:

1. An improved paraffin alkylation process which comprises reacting an alkylatable paraffin and an olefin in a first alkylation zone maintained under alkylation conditions in the presence of an alkylation catalyst; reacting a resulting reaction mixture effluent from said first alkylation zone with an alkylatable cyclic organic compound in a second alkylation zone maintained under alkylation conditions; reacting a resulting reaction mixture effluent from said second alkylation zone with an olefin in a third alkylation zone maintained under alkylation conditions, and removing from a resulting reaction effluent a hydrocarbon fraction boiling within the motor fuel boiling range as a product of the process.

2. An improved paraffin alkylation process which comprises reacting an isoparaffin with an olefin in a first alkylation zone maintained under alkylation conditions in the presence of an alkylation catalyst producing an alkylate containing undesirable reaction by-product compounds; contacting a resulting reaction mixture effluent from said first alkylation zone with an easily alkylatable cyclic organic compound in amount stoichiometrically greater than the amount of said undesirable by-product compounds contained therein in a second reaction zone maintained under alkylation conditions such that said undesirable by-product compounds react with a portion of said cyclic organic compound; reacting a resulting reaction mixture effluent from said second alkylation zone with an olefin in amount stoichiometrically equivalent to the amount of unreacted cyclic organic compound contained therein in a third alkylation zone maintained under alkylation conditions such that said olefin reacts with unreacted cyclic organic compound, and removing from a resulting reaction effluent a hydrocarbon fraction boiling within the motor fuel boiling range as a product of the process.

3. The process of claim 2 wherein said alkylation catalyst is anhydrous hydrofluoric acid.

4. The process of claim 2 wherein said alkylation catalyst is sulfuric acid.

5. The process of claim 2 wherein said alkylation catalyst is an aluminum chloride-hydrocarbon complex.

6. The process of claim 2 wherein said easily alkylatable cyclic organic compound is benzene.

7. The process of claim 2 wherein said cyclic organic compound is furan.

8. The process of claim 2 wherein said isoparaffin is isobutane.

9. The process of claim 2 wherein said olefin is butene.

10. An alkylation process which comprises reacting isobutane with butenes in a first alkylation zone maintained under alkylation conditions in the presence of hydrofluoric acid as an alkylation catalyst to produce an alkylate containing organic fluorine compounds; contacting a resulting reaction mixture comprising hydrocarbons and catalyst effluent from said first alkylation zone with an alkylatable cyclic organic compound, in amount stoichiometrically in excess of the amount of organic fluorine compounds present in said effluent, in a second alkylation zone maintained under alkylation conditions such that a portion of said cyclic organic compound reacts with said organic fluorine compounds; contacting a resulting reaction mixture comprising hydrocarbons and catalyst effluent from said second alkylation zone with an olefin in amount at least stoichiometrically equivalent to the amount of unreacted cyclic organic compound contained therein in a third alkylation zone maintained under alkylation conditions whereby said olefin reacts with said unreacted cyclic organic compound; passing a resulting reaction mixture effluent from said third alkylation zone to a separation zone where it is separated into a hydrofluoric acid catalyst phase and hydrocarbon phase; recycling at least a portion of said catalyst phase to said first alkylation zone; passing said hydrocarbon phase to a fractionation zone and removing therefrom a hydrocarbon fraction boiling within the motor fuel boiling range as a product of the process.

11. An improved paraffin alkylation process which comprises reacting an isoparaffin with an olefin in a first alkylation zone maintained under alkylation conditions in the presence of an alkylation catalyst producing an alkylate containing undesirable reaction by-product compounds; treating a resulting hydrocarbon phase from said first alkylation zone with an easily alkylatable cyclic organic compound in an amount stoichiometrically in excess of the amount of the undesirable reaction by-product compounds contained in said alkylate containing hydrocarbon phase in a second alkylation zone maintained under alkylation conditions in the presence of a fluid alkylation catalyst such that a portion of said cyclic organic compound reacts with said undesirable by-product compounds; treating a reaction mixture effluent comprising hydrocarbons and fluid catalyst from said second alkylation zone with an olefin in an amount stoichiometrically equivalent to the amount of unreacted cyclic organic compound in a third alkylation zone maintained under alkylation conditions such that said unreacted cyclic compound reacts with said olefin; passing a resulting reaction mixture effluent comprising hydrocarbons and catalyst from said third alkylation zone to a separation zone; separating said reaction mixture into a catalyst phase and a hydrocarbon phase; returning at least a portion of said catalyst phase from said separation zone to said second alkylation zone, and recovering from the resulting hydrocarbon phase a fraction boiling in the motor fuel boiling range as a product of the process.

12. An improved alkylation process for the production of diisopropyl which comprises reacting an isobutane-ethylene mixture in the presence of a halogen-containing fluid alkylation catalyst in a first alkylation zone producing an alkylate containing undesirable reaction by-product compounds; treating a resulting alkylate-containing hydrocarbon phase with benzene in a second alkylation zone maintained under alkylation conditions in the presence of a halogen-containing alkylation catalyst such that the benzene reacts with said undesirable by-product compounds; passing a resulting reaction mixture effluent from said second alkylation zone together with an added olefin to a third alkylation zone maintained under alkylation conditions, and passing a resulting reaction mixture effluent from said third alkylation zone to a separation zone where it is allowed to separate into a catalyst phase and a hydrocarbon phase and separating from said hydrocarbon phase a fraction containing diisopropyl as a product of the process.

13. An improved paraffin alkylation process which comprises reacting an isoparaffin with an olefin in an alkylation zone maintained under alkylation conditions in the presence of a fluid alkylation catalyst producing an alkylate containing undesirable reaction by-product compounds; introducing said catalyst into said alkylation zone at multiple points intermediate the upper and lower portions of said alkylation zone; withdrawing from upper portion of said alkylation zone unreacted paraffinic and olefinic materials; treating a resulting reaction mixture comprising alkylate and catalyst with an alkylatable cyclic organic compound in amount stoichiometrically in excess of the amount of undesirable reaction by-products contained in said reaction mixture in a lower portion of said alkylation zone under conditions such that said cyclic organic compound reacts with said undesirable reaction by-product compounds; treating a resulting reaction mixture effluent comprising hydrocarbons and catalyst with an olefin in amount substantially stoichiometrically equavalent to the unreacted cyclic organic compound contained in said resulting reaction mixture effluent; introducing a resulting reaction mixture comprising hydrocarbons and catalyst into a separation zone where said resulting reaction mixture is separated into a catalyst phase and a hydrocarbon phase, and withdrawing said hydrocarbon phase as a product of the process.

14. An improved paraffin reconstruction process which comprises contacting a paraffin in a first zone with a fluid paraffin reconstruction catalyst to produce a reconstructed paraffin and undesirable reaction by-product compounds, contacting a resulting reaction mixture effluent from said first zone with an easily alkylatable cyclic organic compound in amount stoichiometrically greater than the amount of said undesirable by-product compounds contained therein in a second reaction zone maintained under alkylation conditions such that said undesirable by-product compounds react with a portion of said cyclic organic compound; reacting a resulting reaction mixture effluent from said second reaction zone with an olefin in amount stoichiometrically equivalent to the amount of unreacted cyclic organic compound contained therein in a third reaction zone maintained under alkylation conditions such that said olefin reacts with unreacted cyclic organic compound, and removing from a resulting reaction effluent a hydrocarbon fraction boiling within the motor fuel boiling range as a product of the process.

15. The process of claim 1 wherein the cyclic organic compound has at least two conjugated double bonds in the ring.

16. The process of claim 1 wherein the third

alkylation step is effected with a substantially ethylene-free olefin.

17. The process of claim 16 wherein the ethylene-free olefin is propylene.

18. The process of claim 12 wherein the catalyst in the first alkylation zone is an aluminum chloride-hydrocarbon complex and the zone is operated to give an ethylene conversion of 90–94% and in which process ethyl benzene is recovered.

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