

[54] **TWO STAGES OF ISOPARAFFIN-OLEFIN  
ALKYLATION WITH RECYCLE OF  
ALKYLATE-CONTAINING HYDROCARBON**

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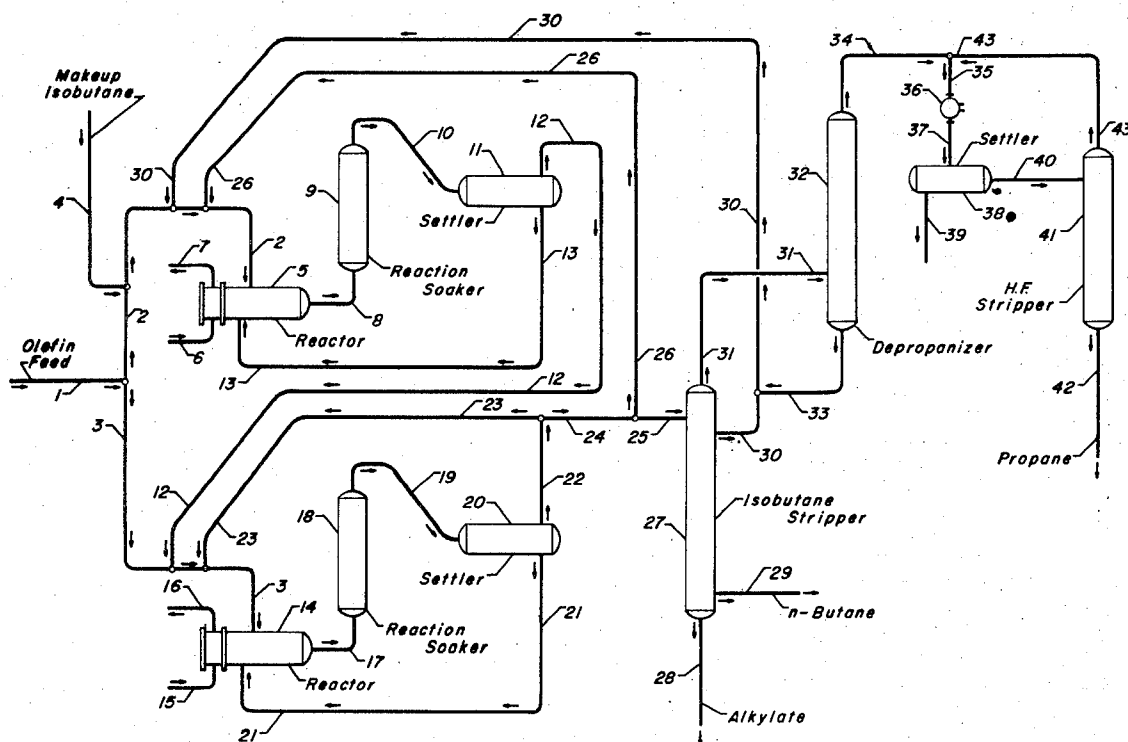
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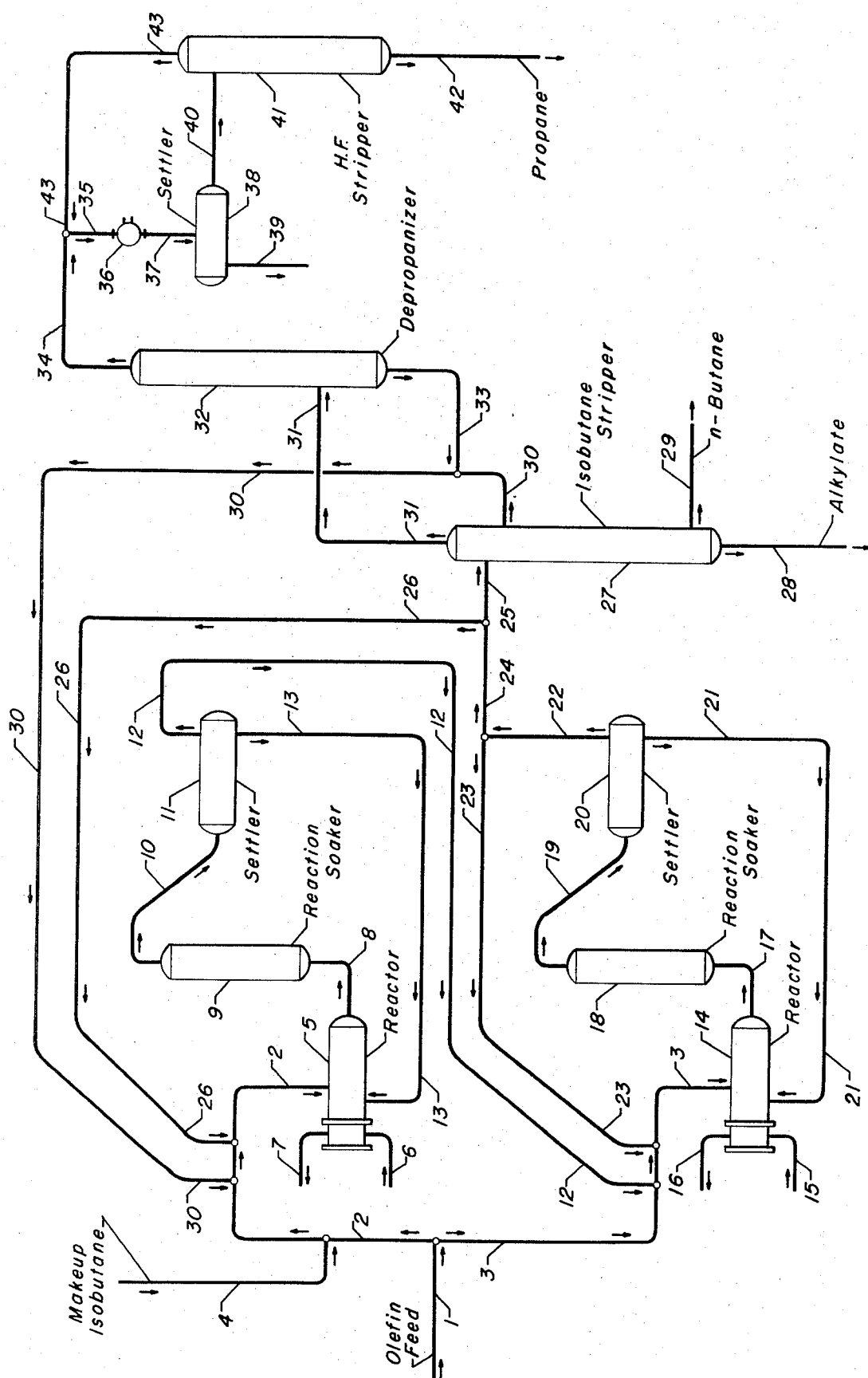
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**ABSTRACT**

A process for alkylating an isoparaffin with an olefin-acting reactant by contacting the isoparaffin with a first portion of the olefin-acting reactant and with a first alkylation catalyst in a first alkylation zone; contacting the hydrocarbons recovered from the first alkylation zone with a second portion of the olefin-acting reactant and with a second alkylation catalyst in a second alkylation zone; recovering the product of the process from a portion of the hydrocarbon effluent from the second alkylation zone; and recycling a portion of the hydrocarbon effluent from the second alkylation zone back into the alkylation zones to provide optimum alkylation conditions.

**4 Claims, 1 Drawing Figure**





## TWO STAGES OF ISOPARAFFIN-OLEFIN ALKYLATION WITH RECYCLE OF ALKYLATE-CONTAINING HYDROCARBON

### CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of my co-pending application Serial No. 236,049, filed on March 20, 1972, now U.S. Patent No. 3,787,518 issued January 22, 1974.

### BACKGROUND OF INVENTION

This invention relates to a process for producing an alkylation reaction product from an isoparaffin and an olefin-acting compound. More specifically, this invention relates to a process for alkylating an isoparaffinic reactant with an olefin-acting reactant, utilizing hydrogen fluoride catalyst, to provide valuable motor fuel components. In one aspect, the present invention relates to a hydrogen fluoride catalyzed isoparaffin-olefin alkylation process in which a particular method for utilization of reactants and reaction products is employed to provide optimum alkylation conditions and a high quality product, while the amount of isoparaffin recycle and the associated utilities and equipment utilized are substantially reduced.

Alkylation of isoparaffinic hydrocarbons, such as isobutane, isopentane and the like, with olefinic hydrocarbons such as propylene, butylene, and amylene, and olefin-acting compounds such as  $C_3$ - $C_5$  alkyl halides, sulfates, etc., is well known as a commercially important method for producing gasoline boiling range hydrocarbons. The  $C_3$ - $C_{10}$  hydrocarbons generally produced by the isoparaffin-olefin alkylation reaction are termed "alkylate". Alkylate is particularly valuable as a motor fuel blending stock because of its high motor and research octane ratings. Alkylate is generally used to improve the overall octane ratings of available gasoline pools to comply with the requirements of modern automobile motors. High octane alkylate fuel components are particularly important in providing motor fuels of sufficiently high quality when it is desired not to employ alkyl lead compounds in motor fuel to meet octane requirements. A continuing goal of the art is to provide an alkylation process which produces an alkylate product having higher motor and research octane ratings than is possible using conventional processes and to reduce the cost and difficulty of producing the alkylate.

In general, commercial isoparaffin-olefin alkylation processes employ isobutane and sometimes isopentane as the isoparaffinic reactant and propylene, butylenes and amylene, or a mixture thereof, as the olefin-acting reactant. Catalysts utilized include hydrogen fluoride, sulfuric acid, zeolites, and other like acidic or acid-acting materials. In alkylation operations using hydrogen fluoride catalyst, the isoparaffin, olefin-acting agent and hydrogen fluoride are typically contacted in an alkylation reactor, forming a reaction mixture. After the alkylation reaction is substantially complete, the reaction mixture is withdrawn from the reactor and is settled into hydrocarbon and catalyst phases in a separation zone such as a settling vessel, and the catalyst thus separated is recycled to the reactor for further use. The hydrocarbon phase produced by the settling operation is further process, typically by fractionation, to recover the alkylate product and to separate unconsumed

isoparaffin for further use by recycle to the alkylation reactor.

It has been found necessary to perform commercial isoparaffin-olefin alkylation operations at fairly specific reaction conditions, such as temperature, pressure, and concentrations of catalyst and reactants, in order to produce an acceptable yield of the desired high quality alkylate product. One of the conditions required to provide a product having the desired utility as a high octane blending stock has been a large excess of isoparaffin relative to the amount of olefin employed in the reactor, e.g., an isoparaffin/olefin mole ratio of about 8:1 to about 30:1. The primary limitations on the amount of excess isoparaffin utilized are the capital and utilities costs of the equipment needed to separate the excess isoparaffin from the product subsequent to the alkylation step. The quality of the alkylate is found to be higher when the isoparaffin/olefin mole ratio in the alkylation step is raised. The improvement is found even when the mole ratio is raised to levels found uneconomical in the prior art. The quality of the alkylate produced in commercial alkylation operations is thus limited by the amount of excess isoparaffin which must be recovered and recycled to the alkylation reactor after fractionation of the hydrocarbon phase of the reactor effluent. The large amount of isoparaffin which must be passed, unreacted, through the alkylation reactor and settler, and subsequently separated from the alkylate product by fractionation, necessitates the use of fractionation equipment of large capacity in order to provide an adequate separation of, for example,  $C_3$ +alkylate from isobutane reactant which is to be recycled to the reactor. The expense and difficulty of providing a large isoparaffin throughput, fractionation and recycle in order to produce alkylate of adequate quality may be obviated, in part, through the use of the process of this invention.

### SUMMARY OF THE INVENTION

An object of the present invention is to provide a process for alkylating an isoparaffin with an olefin-acting compound to produce an alkylation reaction product possessing superior qualities as a motor fuel component.

A further object of the present invention is to provide a process for alkylating an isoparaffinic reactant with an olefin-acting reactant wherein a smaller scale of isoparaffin fractionation and recycle is required in order to obtain a high quality motor fuel alkylate product.

In a broad embodiment, the present invention relates to a process for producing an alkylation reaction product from an isoparaffinic reactant and an olefin-acting reactant which comprises the steps of: contacting a first portion of the olefin-acting reactant with the isoparaffinic reactant and with a first hydrogen fluoride alkylation catalyst in a first alkylation zone at alkylation conditions; removing the resultant hydrocarbons from contact with the first alkylation zone and the first alkylation catalyst to form a first hydrocarbon effluent stream; contacting a second portion of the olefin-acting reactant with at least a portion of the first hydrocarbon effluent stream and with a second hydrogen fluoride alkylation catalyst in a second alkylation zone at alkylation conditions; removing the resultant hydrocarbons from contact with the second alkylation zone and the second alkylation catalyst to form a second hydrocarbon effluent stream; dividing the second hydrocarbon

effluent stream into two portions to form an effluent recycle stream and a reaction product stream; introducing at least a portion of the effluent recycle stream into the second alkylation zone; and recovering the alkylation reaction product from the reaction product stream.

In a limited embodiment, the present invention relates to a process for producing an isoparaflinic alkylation reaction product from an isobutane feed and a  $C_3$ - $C_5$  olefin feed which comprises the steps of: contacting about 50 vol. percent of the  $C_3$ - $C_5$  olefin feed with the isobutane feed and with a first hydrogen fluoride alkylation catalyst in a first alkylation zone at alkylation conditions; removing the resultant hydrocarbons from the first alkylation zone and from contact with the first hydrogen fluoride catalyst to form a first hydrocarbon effluent stream; contacting the remainder of the  $C_3$ - $C_5$  olefin feed with the first hydrocarbon effluent stream and with a second hydrogen fluoride alkylation catalyst in a second alkylation zone at alkylation conditions; removing the resultant hydrocarbons from the second alkylation zone and from contact with the second hydrogen fluoride catalyst to form a second hydrocarbon effluent stream; dividing the second hydrocarbon effluent stream into two portions to form an effluent recycle stream and a reaction product stream; introducing the effluent recycle stream into the second alkylation zone; and recovering the alkylation reaction product from the reaction product stream.

Among the important advantages included in the process of this invention, relative to prior art processes, are those which derive from a substantial decrease in the overall molar excess amount of the isoparaflin required per mole of olefin utilized. By passing only a portion of the olefin reactant to the first alkylation reactor, a significantly smaller amount of the isoparaflin is required in the first reactor to provide the required molar excess of isoparaflin in relation to the moles of olefin reactant utilized in the first reactor. The hydrocarbon effluent from the first reactor is then contacted with a second portion of the olefin reactant in a second reactor, whereby the same relatively smaller molar amount of isoparaflin is utilized to provide the required molar excess of isoparaflin in both the first and the second reaction systems.

The overall isoparaflin fractionation requirement in the process of the present invention is further substantially reduced by recycling a portion of the hydrocarbon effluent from the second alkylation settler back into one or both of the alkylation reactors. Thus, the hydrocarbon effluent from the second alkylation zone, in one embodiment, is divided into two portions. One portion of the hydrocarbon effluent from the second alkylation zone is passed directly to conventional fractionation operations to separate isoparaflin for recycle and recover the alkylate product. The remainder of the hydrocarbon effluent from the second alkylation zone is passed, as an effluent recycle stream, back into the second alkylation reactor, in order to provide a part of the molar excess of isoparaflin required in the second reactor.

In a more limited embodiment, a portion of the hydrocarbon effluent from the second alkylation zone is passed, as an effluent recycle stream, into the first alkylation reactor, in order to provide a part of the molar excess of isoparaflin required in the first alkylation zone. By employing the foregoing embodiments of the

present invention, a very high mole ratio of isoparaflin to olefin-acting reactant can be obtained in both the first alkylation zone and the second alkylation zone. The alkylate product of the process will thereby be produced with a substantially superior octane rating and generally superior quality compared to alkylate produced by a conventional commercial operation. At the same time, the amount of isoparaflin which must be separated from the alkylate product, e.g., by fractionation in an isobutane stripper, is maintained at a very low level.

Further objects, embodiments and advantages of the present process will be apparent to those skilled in the art from the following description of the drawing and detailed description of the invention.

#### DESCRIPTION OF THE DRAWING

The attached drawing is a schematic illustration of one embodiment of the process of the present invention. In the particular embodiment set forth, the isoparaflin is isobutane and the olefin-acting reactant comprises a mixture of propylene and butylenes. The scope of the present invention is not intended to be limited to the embodiment shown, and various other suitable reactants and embodiments will be obvious to those skilled in the art from the description hereinafter provided.

Referring to the drawing, a conventional olefin feed to an isobutane-olefin alkylation process is charged continuously through conduit 1. The olefins are charged at a rate of about 300 moles/hour propylene and 300 moles per hour butylenes. In addition, smaller amounts of other hydrocarbons which are conventionally present in a commercial olefin feedstock, including 120 moles/hour isobutane, 35 moles/hour n-butane and 70 moles/hour propane, are charged through conduit 1 in admixture with the olefins. The continuously charged hydrocarbons in conduit 1 are divided into two streams of equal volume and passed into conduits 2 and 3. The olefinic feedstocks passed into conduits 2 and 3 thus both comprise 150 moles/hour propylene, 150 moles/hour butylenes, 60 moles/hour isobutane, 17.5 moles/hour n-butane and 35 moles/hour propane. Make-up isobutane is charged via conduit 4 into conduit 2 and admixed in conduit 2 with the portion of the olefin feedstock therein. The make-up isobutane stream is passed through conduit 4 at a rate of 500 moles/hour of isobutane, with conventional amounts of non-reactive contaminants including about 15 moles/hour n-butane and about 10 moles/hour propane. The admixed make-up isobutane and olefin feed continues through conduit 2, and recycled isobutane from conduit 30 is passed into conduit 2 and admixed with the contents thereof. The recycle isobutane is passed into conduit 2 at the rate of 2,400 moles/hour isobutane, with some other non-reactive hydrocarbon recycle resulting from imprecise fractionation, including 240 moles/hour n-butane and 140 moles/hour propane. Hydrocarbon effluent recycle from reactor 14 and settler 20, hereinafter more fully described, is passed through conduit 26 into conduit 2 and admixed with the above-described fresh and recycle hydrocarbons therein. The effluent recycle stream is conduit 26 is charged into conduit 2 at the rate of 1210 moles/hour isobutane, 145 moles/hour n-butane, 110 moles/hour propane and 300 moles/hour  $C_5$ + hydrocarbons. The total hydrocarbons charge to reactor 5 thus comprise 150 moles/

hours propylene, 150 moles/hour butylenes, 4170 moles/hour isobutane, with non-reactive hydrocarbons including 295 moles/hour propane, 417.5 moles/hour n-butane and 300 moles/hour  $C_5+$  hydrocarbons. The isobutane/olefin mole ratio in the feed to reactor 5 is thus equal to or better than the mole ratios economically available in prior art commercial operations. The combined feed is passed through conduit 2 into reactor 5 and admixed with hydrogen fluoride alkylation catalyst to form a reaction mixture. The hydrogen fluoride alkylation catalyst is charged to reactor 5 through conduit 13. The catalyst contains about 80 wt. percent acid and less than about 1 wt. percent water, with the remainder being conventional organic diluent. Alkylation conditions maintained in reactor 5 include a temperature of about 90°–100°F. and a pressure sufficient to maintain the reactants and catalyst in the liquid phase. An acid/hydrocarbon volume ratio of about 1 to about 2 is also maintained. Heat generated in the alkylation reaction is withdrawn using indirect heat exchange. Cooling water is charged through conduit 6 into reactor 5, and passed in indirect heat exchange with the reaction mixture. Used cooling water is withdrawn via conduit 7. After a contact time of about 0.1 minute to about 5 minutes, the reaction mixture in reactor 5 is withdrawn and passed through conduit 8 into reaction soaker 9. The reaction mixture of catalyst, reactants are reaction products is maintained in reaction soaker 9 for about 1 minute to about 10 minutes at a temperature and pressure about the same as employed in reactor 5. The reaction mixture is then withdrawn and passed through conduit 10 into settler 11. The reaction mixture is allowed to stand without agitation in settler 11, whereby the hydrogen fluoride catalyst forms a heavier phase and the hydrocarbon components of the reaction mixture form a lighter phase. The lower, catalyst phase is withdrawn from the bottom of settler 11 through conduit 13 and passed back to reactor 5 for further catalytic use. It may be necessary to treat a portion of the recycle catalyst to maintain the desired acid strength, etc. This can be done by passing a slip stream of catalyst from conduit 13 to conventional regeneration means. Such a regeneration operation being conventional and not essential to an understanding of the present invention, the mode of performance thereof will be obvious to those skilled in the art, and this operation is not included in the drawing and description thereof. Referring again to settler 11, the hydrocarbon phase formed therein, which includes the total hydrocarbon effluent from reactor 5 and reaction soaker 9, is withdrawn from the top of settler 11 via conduit 12. The hydrocarbon effluent from settler 11 is charged into conduit 12 at the rate of 3870 moles/hour isobutane, 295 moles/hour propane, 417.5 moles/hour n-butane, and 600 moles/hour  $C_5+$  hydrocarbons. The hydrocarbon effluent from settler 11 passed into conduit 12 is passed into conduit 3 and commingled with the portion of fresh olefin feed therein. A hydrocarbon effluent recycle stream in conduit 23, removed from reactor 14 and settler 20, more fully described hereinafter, is passed into conduit 3 at the rate of 1,210 moles/hour isobutane, 110 moles/hour propane, 145 moles/hour n-butane and 300 moles/hour  $C_5+$  hydrocarbons. The total combined hydrocarbon feed to reactor 14 through conduit 3 is thus charged at the rate of 5140 mole/hour isobutane, 150 moles/hour propylene, 150 moles/hour butylenes, 580 moles/hour n-butane, 440

moles/hour propane and 900 moles/hour  $C_5+$  hydrocarbons. The isobutane/olefin mole ratio of the hydrocarbon charge to reactor 14 is thus about 17:1. The other reaction conditions employed in reactor 14 are similar to those employed in reactor 5, i.e., a temperature of about 90°–100°F., acid/hydrocarbon volume ratio of about 1:1 to about 2:1 and a pressure sufficient to maintain the reaction mixture components in the liquid phase. Hydrogen fluoride catalyst containing about 80 wt. percent acid, less than about 1 wt. percent water, with the remainder made up of organic diluent, is charged to reactor 14 through conduit 21 and intimately admixed with the hydrocarbon feed from conduit 3 to form the reaction mixture. Cooling water is charged through conduit 15 and passed in indirect heat exchange with the reaction mixture in reactor 14. Used cooling water is withdrawn through conduit 16. After a contact time of about 0.1 minute to about 5 minutes, the reaction mixture is withdrawn from reactor 14 and passed through conduit 17 into reaction soaker 18. The reaction mixture of catalyst, reactants and reaction products is maintained in reaction soaker 18 for a contact time of about 1 minute to about 10 minutes at a temperature and pressure substantially the same as employed in reactor 14. The reaction mixture is then withdrawn and passed through conduit 19 into settler 20. The reaction mixture is allowed to stand with agitation in settler 20, in order to facilitate separation of the catalyst and hydrocarbons into separate phases. The heavier, catalyst phase is withdrawn from the bottom of settler 20 through conduit 21 and recycled to reactor 14 for further catalytic use as described. A portion of the catalyst in conduit 21 may be passed to a conventional regeneration operation if desired. The upper, hydrocarbon phase in settler 20 is withdrawn through conduit 22. The hydrocarbon effluent from settler 20 is passed into conduit 22 at the rate of about 440 moles/hour propane, 4,840 moles/hour isobutane, 580 moles/hour n-butane and 1,200 moles/hour  $C_5+$  hydrocarbons. The hydrocarbon effluent stream in conduit 22 is divided into two portions. A first portion is passed into conduit 23 as an effluent recycle stream and then passed into conduit 3 and further utilized as described above. A second portion of the hydrocarbon effluent from settler 20 is passed from conduit 22 into conduit 24. The hydrocarbon effluent in conduit 24 is divided into two portions. A first portion of the hydrocarbon effluent stream in conduit 24 is passed into conduit 26 as a second effluent recycle stream. This effluent stream recycle is passed from conduit 24 through conduit 26 to conduit 2 as described above. A second portion of the hydrocarbon stream in conduit 24 is charged through conduit 25 into isobutane stripper 27 at the rate of 2,420 moles/hour isobutane, 220 moles/hour propane, 290 moles/hour n-butane and 600 moles/hour  $C_5+$  hydrocarbons. In isobutane stripper 27, the portion of hydrocarbon effluent from settler 20 passed through conduit 25 is fractionated to separate a recycle isobutane stream and a product alkylate stream. The vessel employed contains conventional trays, reboiling means, refluxing means, etc. Alkylate product ( $C_5+$  hydrocarbons) is removed as a bottoms product from isobutane stripper 27 through conduit 28, passed out of the operation, and recovered for motor fuel or other desired uses at the rate of 600 moles/hour. Normal butane, a by-product of the process in the embodiment described, is withdrawn as a side cut through

conduit 29 at the rate of 50 moles/hour plus 10 moles/hour isobutane impurity. Recycle isobutane is withdrawn as a side cut on a higher tray in isobutane stripper 27 through conduit 30. The recycle isobutane stream is passed out of isobutane stripper 27 through conduit 30 at the rate of 2,160 moles/hour isobutane, 215 moles/hour n-butane and 140 moles/hour propane. The recycle isobutane stream in conduit 30 is passed into conduit 2 as described above. An overhead stream is withdrawn from isobutane stripper 27 and passed through conduit 31 into depropanizer 32. The overhead stream is passed from the iso stripper at the rate of 80 moles/hour propane, 250 moles isobutane and 25 moles/hour n-butane. In depropanizer 32, the feed from conduit 31 is fractionated to separate propane from isobutane and n-butane. The isobutane and n-butane are withdrawn, at the rate of 240 moles/hour isobutane and 25 moles/hour n-butane, as a bottoms product and passed through conduit 33 into conduit 30 for use in the recycle isobutane stream. Propane, admixed with some hydrogen fluoride and isobutane, is withdrawn overhead through conduit 34, at the rate of 80 moles/hour propane and 10 moles/hour isobutane, and passed through conduit 34 into conduit 35 in admixture with hydrogen fluoride in conduit 43. The mixture of propane, isobutane and hydrogen fluoride in conduit 35 is passed into condenser 36 and condensed to liquefy the propane and acid. The liquefied propane, isobutane and hydrogen fluoride are then passed through conduit 37 into settler 38. Most of the hydrogen fluoride passed into settler 38 settles out as a heavy phase of relatively pure acid and is withdrawn through conduit 39. This relatively concentrated acid may, if desired, be passed back into the recycle catalyst streams in conduit 13 and conduit 21, by means not shown. The liquefied propane phase in settler 38 is withdrawn and passed through conduit 40 into hydrogen fluoride stripper 41, wherein the propane is fractionated to separate any remaining acid. The acid is withdrawn overhead through conduit 43, passed back into conduit 35, and treated as described above. The propane is withdrawn as a by-product from the bottom of hydrogen fluoride stripper 41 through conduit 42 at the rate of 80 moles/hour propane and 10 moles/hour isobutane. Certain conventional equipment and operations necessary for the operation of the embodiment described in the foregoing have been omitted from the drawing and description thereof, e.g., pumps, valves, reboilers, etc. The use and placement of such conventional items will be obvious to those skilled in the art.

The foregoing description illustrates some of the advantages of the present invention over prior art, when embodied in an isobutane  $C_3$ - $C_4$  olefin alkylation process. For example, reaction conditions in reactor 5 and reactor 14 include isobutane/olefin mole ratio of about 13:1 and 17:1 respectively, which are in the high range of economical operation in conventional alkylation processes. Yet fractionation requirements in isobutane stripper 29 need only be sufficient to separate isobutane equivalent to an overall isobutane-olefin mole ratio of about 4:1, a range which will not produce high quality alkylate in conventional operations. The alkylate produced is of equal or superior quality to that produced in conventional alkylation processes in which a 13:1 isobutane/olefin mole ratio is employed, while the fractionation requirements are substantially reduced, with the attendant savings in capital and utilities costs.

In one obvious modification, the amount of isobutane utilized overall can be increased, whereby the alkylation reaction conditions in the present process will include an isobutane/olefin mole ratio higher than described, resulting in an even more valuable product. The amount of isobutane to be recycled in such a modification is less than or equal to that in a conventional operation, while the product is significantly improved.

#### DETAILED DESCRIPTION OF INVENTION

The alkylation process of the present invention may be applied, in general, to the alkylation of  $C_3$ - $C_6$  isoparaffins. The preferred isoparaffins are isobutane and isopentane, particularly isobutane. A mixture of two or more isoparaffins may also be employed, if desired. A suitable isoparaffin feedstock for use in the present process may contain some non-reactive contaminants such as normal paraffins. For example, a conventional commercial isobutane alkylation feedstock generally contains about 95 wt. percent isobutane, 4 wt. percent n-butane and 1 wt. percent propane.

Olefin-acting compounds suitable for use in the process of the present invention as an olefin-acting reactant include  $C_2$ - $C_6$  olefins, alkyl halides, alkyl sulfates, alkyl phosphates, alcohols, etc., and mixtures thereof.  $C_3$ - $C_5$  olefins and alkyl halides are preferred, particularly propylene, butylenes and amylenes. It is to be understood the process of the present invention may be applied to the alkylation of mixtures of two or more olefin-acting compounds, with the same benefits and improvements resulting as would be obtained using a single olefin-acting compound. For example, many conventional olefin feedstocks in commercial isoparaffin-olefin alkylation operations contain mixtures of propylene and butylenes, butylenes and amylenes, or propylene, butylene and amylenes. Application of the present process to such mixtures results in improvements in the quality of the product equal to those obtained from a single olefin. Similarly, a mixture of  $C_3$ - $C_5$  alkyl halides and olefins in any proportion is also suitable in many cases, e.g., when the halide is fluoride. The particularly preferred  $C_3$ - $C_5$  olefin feedstocks are conventionally derived from petroleum refining processes such as catalytic cracking and may therefore contain substantial amounts of saturates, lighter and heavier olefins, etc. Such conventional  $C_3$ - $C_5$  olefin feedstocks are suitable for use to provide the olefin-acting reactant in the present process.

The alkylation catalyst employed in the present process in hydrogen fluoride. Generally, hydrogen fluoride alkylation catalyst contains about 75 wt. percent or more of titratable acid, about 5 wt. percent or less water, with the remainder being organic diluent. Such a hydrogen fluoride alkylation catalyst is suitable for use in both the first and second alkylation reactors and zones in the present process. A particularly preferred catalyst contains about 80 wt. percent acid, less than 1 wt. percent water, the remainder being organic diluent.

Numerous alkylation reactors suitable for use in the process of this invention are known in the art. For example, but not by way of limitation, the alkylation reactors described in U.S. Pat. Nos. 3,456,033, 3,469,949 and 3,501,536 may suitably be employed for both alkylation reactions when alkylating an isoparaffin with an olefin using hydrogen fluoride catalyst. Particular alkylation conditions necessarily associated with the particular alkylation reactors described in the above-listed

patents or in connection with other suitable conventional alkylation reactors, are also well known and may be used in embodiments of the present invention. The scope of the present invention is intended to include, for example, embodiment of the present process in which reactants and hydrogen fluoride catalyst are contacted in the alkylation reactors to form alkylation reaction mixtures and the hydrocarbons and catalyst are subsequently separated by settling for further processing. Particular alkylation zones and optimum alkylation conditions in specific embodiments of the present process depend upon the composition of the particular olefin-acting reactant and the particular isoparaffin.

In general, alkylation conditions suitable for use in an embodiment of the present process in which the isoparaffin is preferably isobutane include a temperature of about 0°F. to about 200°F., a pressure sufficient to maintain the reactants and the hydrogen fluoride catalyst in the liquid phase, and a contact time between the hydrocarbons and catalyst of about 0.1 minute to about 30 minutes. In a preferred embodiment, a catalyst/hydrocarbon volume ratio of about 0.1 to about 10 is preferred, and a temperature of about volume F. to about 150°F. is preferably employed.

In a particularly preferred embodiment, the reaction mixtures of catalyst, reactants and reaction products formed in the alkylation reactors are passed through reaction soakers. In the description of the preferred embodiments herein provided, it is intended that both an alkylation reactor and a reaction soaker, if one is utilized, are included within the scope of the term "alkylation zone." Suitable reaction soakers are well known in the art. For example, the reaction soakers described in U.S. Patents No. 3,560,587 and No. 3,607,970 may suitably be employed in the present process. Such reaction soakers are typically vessels equipped with perforated trays, baffle sections, or the like, to maintain the reaction mixture of catalyst and hydrocarbons charged from the alkylation reactor as a fairly homogeneous mixture, or emulsion, for a predetermined length of time. The mixture of catalyst and hydrocarbons is maintained in the reaction soaker for a time which depends on the composition of the reaction mixture. A reaction soaker residence time of about 1 minute to about 30 minutes is preferred. The temperature and pressure maintained in the reaction soaker are the same as the temperature and pressure maintained in the alkylation reactor.

Means for separating the reaction mixture into a hydrocarbon phase and catalyst phase is necessary to separate the hydrogen fluoride catalyst from the hydrocarbons. The effluent from an alkylation reactor or reaction soaker is conventionally settled to provide the hydrocarbon effluent from the alkylation zone, which contains alkylation reaction products and reactants. When utilizing hydrogen fluoride, the effluent from an alkylation reactor or soaker comprises a mixture of isoparaffin, reaction products, catalyst and catalyst-soluble organic materials, possibly with small amounts of olefin-acting compounds, light hydrocarbon gases, etc. When this mixture is allowed to stand unstirred, i.e., settled, the reaction products, isoparaffin and light hydrocarbon gases form a hydrocarbon phase. The hydrogen fluoride and catalyst-soluble organic materials form a separate phase. The hydrocarbon phase is then easily mechanically separated from the catalyst phase to provide the hydrocarbon effluent streams. The sec-

ond hydrocarbon effluent stream is, in turn, employed to provide the effluent recycle and reaction product recovery streams. The temperature and pressure employed in such a settling operation are substantially the same as those described in above in connection with alkylation reaction conditions. The hydrocarbons and the catalyst are preferably maintained in the liquid phase during the separation operation.

Some means for withdrawing heat from the alkylation zones is necessary for operation of the process. A variety of means for accomplishing the heat withdrawal are well known. For example, in a preferred embodiment the heat generated in the alkylation reaction may be withdrawn directly from the alkylation reactor by indirect heat exchange between cooling water and the reaction mixture in the reactor.

The hydrocarbon effluent stream recovered from the first alkylation zone by settling the reaction mixture to separate the catalyst is combined with a second portion of the olefin-acting reactant and charged to the second alkylation reactor, wherein the combined olefin hydrocarbon effluent are contacted with a second hydrogen fluoride catalyst. It is contemplated that sufficient isoparaffin is charged to the first alkylation zone so that no further make-up isoparaffin, or isoparaffin recovered from fractionation, need be added to the hydrocarbons charged to the second reactor. Under some conditions, it may be advantageous to charge some further fresh isoparaffin to the second alkylation reactor, and such a modification is within the scope of the present process.

In general, the benefits and advantages of the present process are provided when the isoparaffinic reactant is charged into a series of at least two separate alkylation zones and contacted with at least two different portions of the olefin-acting reactant therein. One obvious modification of the present process is to divide the olefin-acting reactant into a plurality of portions, e.g., three or more. The isoparaffin and a first portion of the olefin-acting reactant are contacted in a first alkylation zone, the hydrocarbons are separated from the first catalyst to form a hydrocarbon effluent stream which is then charged to the second reactor. This charge stream is contacted with a second portion of the olefin-acting reactant in the second alkylation zone. The hydrocarbon effluent from the second alkylation zone is divided into an effluent recycle stream and a charge stream to the third alkylation reactor. The effluent recycle stream is passed back into the first and/or second reactors, and the charge stream is contacted with a third portion of the olefin-acting reactant in a third alkylation zone, etc. A portion of the hydrocarbon effluent from the last alkylation zone in the series is utilized to provide a reaction product stream, which is fractionated to recover the alkylation reaction product and separate the isoparaffin contained therein for recycle to the first alkylation zone.

Where it is desired to employ two alkylation zones and to divide the olefin-acting reactant into two portions, as in the preferred embodiments, it is preferred that the portions of olefin-acting reactant be such that neither portion contains less than about 10 vol. percent of the olefin-acting reactant. For example, in a continuous operation, the first portion of olefin may be fed to the first alkylation zone at a rate of 10 moles/hour along with a suitable corresponding amount of isoparaffin sufficient to provide the desired molar excess



thereof in the first reactor. The second portion of olefin is, in this case, preferably fed into the second alkylation zone at a rate of at least about 1 mole/hour and not more than about 100 moles/hour. Preferably the two portions of olefin-acting compound do not vary in the amount of olefin-acting compound they contain by more than about 1:5 to about 5:1. Best results are achieved in a two-reactor system, as described in the preferred embodiment, when the two portions of olefin-acting reactant contain roughly equal molar and volumetric amounts of the olefin-acting reactant. In this way, the amount of isoparaffin required in order to provide an optimum molar excess in each alkylation zone is kept to a minimum, while the highest quality product possible can thereby be obtained from both the first and second reactors.

In a preferred embodiment of the present invention, wherein two alkylation zones are employed, the hydrocarbon effluent from the second alkylation zone is divided into at least two portions. The term "hydrocarbon effluent stream" is intended to include all hydrocarbons recovered from an alkylation reactor when separated from the catalyst. For example, in an operation utilizing hydrogen fluoride in an alkylation reactor, the catalyst is separated from the resultant hydrocarbons after the reaction. The settled hydrocarbon phase removed from the settler in the hydrocarbon effluent stream in such an operation. As stated, in one preferred embodiment, the hydrocarbon effluent stream from the second alkylation zone is divided into at least two portions. The term "divided" is intended to mean that the volumetric concentration of each and every compound and component, in each and every portion formed when the hydrocarbon effluent stream is divided, is substantially the same. Thus, the division of a hydrocarbon effluent stream is intended to be a physical division and to exclude flashing and fractionation-type separations. One portion of the hydrocarbon effluent stream from the second alkylation zone is recycled to the second alkylation zone in a broad embodiment. This stream is therefore termed an effluent recycle stream. The term "effluent recycle stream" is intended to include that portion of a hydrocarbon effluent stream from an alkylation zone which is divided from the hydrocarbon effluent stream and passed back into the reactor of the alkylation zone. The term effluent recycle stream is also intended to include a stream divided from the hydrocarbon effluent from the second alkylation zone and passed back into the reactor of the first alkylation zone. Similarly, when, for example, a series of three or more alkylation zones is employed, an effluent recycle stream would include a portion of the hydrocarbon effluent stream from, e.g., a third alkylation zone, which is passed into the reactors of the first and second alkylation zones. For example, in a modification of the preferred embodiment, another portion divided from the hydrocarbon effluent stream from the second alkylation zone is passed back into the reactor of the first alkylation zone as a second effluent recycle stream.

The portion of a hydrocarbon effluent stream which is divided out to be employed as an effluent recycle stream may be from about 1 vol. percent of the hydrocarbon effluent stream to about 75 vol. percent. In a preferred embodiment employing two alkylation zones, wherein the hydrocarbon effluent stream from the second alkylation zone is divided to form at least two por-

tions, one of which is passed to conventional fractionation to separate the alkylate product, the other being recycled to the reactor of the second alkylation zone as an effluent recycle stream, it is preferred that this effluent recycle stream contain about 25 vol. percent to about 60 vol. percent of the hydrocarbon effluent stream from the second alkylation zone. In the modification of this embodiment, where a second effluent recycle stream is divided out of the hydrocarbon effluent stream from the second alkylation zone and passed back into the alkylation reactor of the first alkylation zone, it is preferred that this other effluent recycle stream contain about 25 vol. percent to about 60 vol. percent of the hydrocarbon effluent stream from the second alkylation zone.

In any event, a portion of the hydrocarbon effluent stream from the second alkylation zone, where two alkylation zones are employed, or a portion of the hydrocarbon effluent stream from the last alkylation zone in the series, is passed to a conventional separation operation, such as fractionation in an isobutane stripper, in order to recover the alkylate product. The portion of the hydrocarbon effluent from the last alkylation zone in the series which is charged to the separation operation to recover the alkylate product is herein termed the "reaction product stream."

The alkylation reaction product produced in the preferred embodiment of the present process, when isobutane is employed as the isoparaffin, and propylene and butylenes are utilized as the olefin-acting reactant, includes  $C_3$ - $C_8$  saturated hydrocarbons resulting from the alkylation reactions of the isoparaffin with the olefin-acting reactant in both the first and second alkylation zones. The primary products include, for example, dimethylpentanes and trimethylpentanes. It is known that more highly branched hydrocarbons possess superior properties as motor fuel components, and the present invention is directed, in part, to providing an alkylation product containing a higher ratio of more highly branched hydrocarbons, such as trimethylpentanes, to less branched hydrocarbons, such as dimethylhexanes. The foregoing is accomplished through the use of the series flow of isoparaffin and through recycle of one or more portion of the hydrocarbon effluent from the second alkylation zone to provide optimum alkylation conditions, including an extremely high mole ratio of isoparaffin to olefin in the alkylation reactors. It is thus apparent that the present invention provides a process for producing a superior motor fuel alkylate product by a method more economical and convenient than has been available in the prior art.

I claim as my invention:

1. A process for alkylating an isoparaffin selected from the group consisting of isobutane and isopentane with an olefin selected from the group consisting of propylene, butylenes and amylene which comprises

- contacting said isoparaffin with a portion of said olefin and a first hydrogen fluoride alkylation catalyst at alkylation conditions in a first reaction zone;
- separating the reaction zone effluent into a first catalyst phase and a first liquid hydrocarbon phase;
- supplying said liquid hydrocarbon phase, without fractionation thereof, to a second reaction zone together with the remainder of said olefin and a second hydrogen fluoride alkylation catalyst and therein subjecting the mixture to alkylation conditions;



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- d. separating the second reaction zone effluent into a second catalyst phase and a second liquid hydrocarbon phase;
- e. dividing said second liquid hydrocarbon phase, prior to fractionation thereof, into a first portion, a second portion and a third portion;
- f. recycling said first portion to said second zone and supplying said second portion to said first zone;
- g. fractionating said third portion of said second liquid hydrocarbon phase to separate said isoparaffin from alkylate;
- h. recycling said separated isoparaffin to said first zone; and
- i. recovering said alkylate.

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2. The process of claim 1 wherein the portion of said olefin supplied to said first zone comprises about 20 vol. percent to about 80 percent of the olefin feed to the process.

3. The process of claim 1 wherein said first portion of said second liquid hydrocarbon phase comprises about 25 vol. percent to about 60 vol. percent of said second phase.

4. The process of claim 1 wherein said second portion of said second liquid hydrocarbon phase comprises about 25 vol. percent to about 60 vol. percent of said second phase.

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