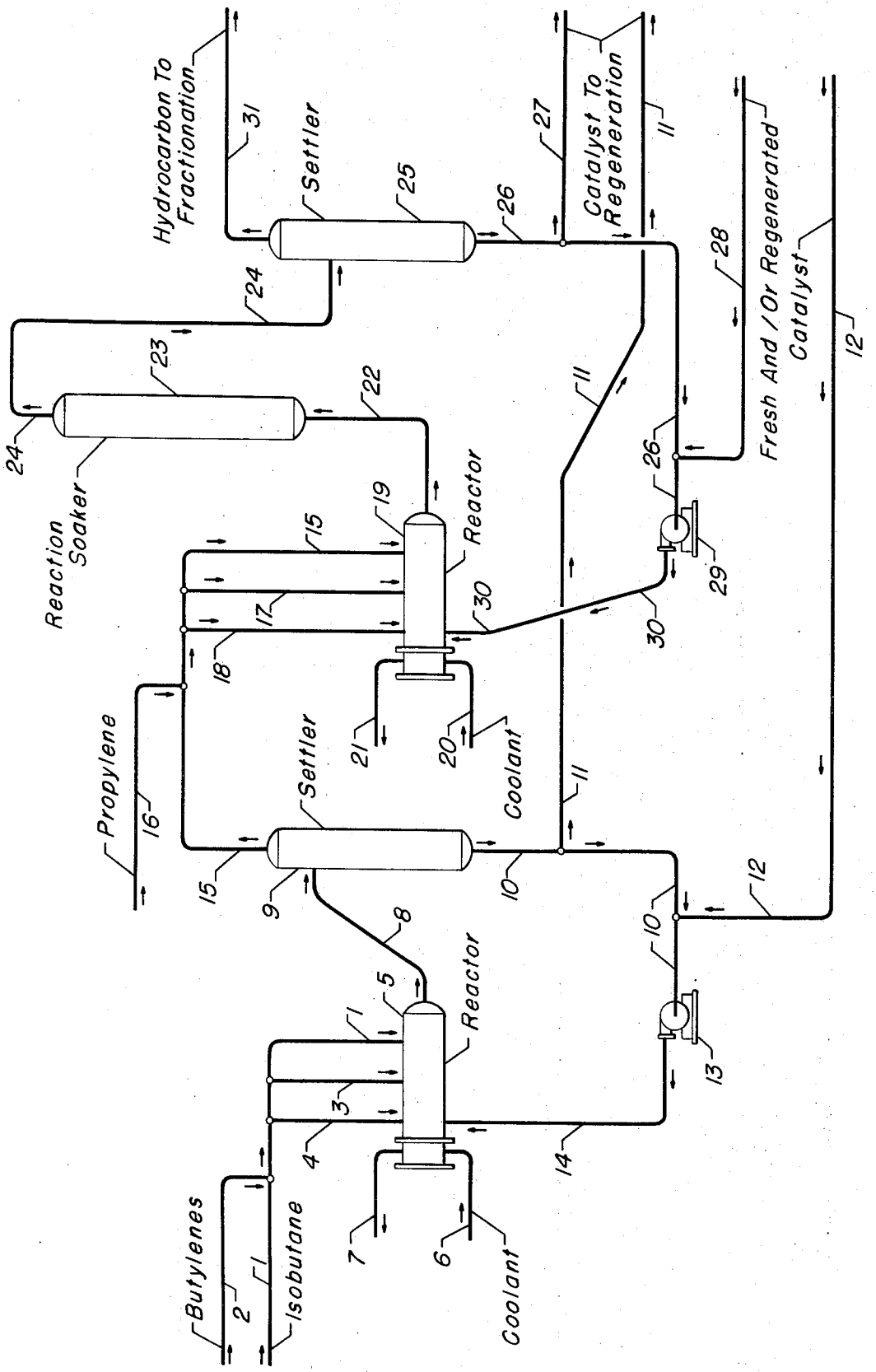
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PLURAL STAGES OF HF ALKYLATION OF ISOPARAFFIN WITH BUTYLENE AND PROPYLENE REACTANTS

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PLURAL STAGES OF HF ALKYLATION OF ISOPARAFFIN WITH BUTYLENE AND PROPYLENE REACTANTS

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ABSTRACT OF THE DISCLOSURE

Plural stages for alkylating an isoparaffin with a butylene reactant and with a propylene reactant utilizing hydrogen fluoride catalyst, the butylene reactant is reacted initially with a catalyst containing 70–95 wt. percent HF and the separated hydrocarbon phase is then reacted with the propylene reactant with a catalyst of higher HF concentration than that utilized in the initial reaction. The catalyst in the second reacion contains 80–99 wt. percent HF. An optimum yield of high quality alkylate product is recovered from the butylene and propylene stages of alkylation.

BACKGROUND OF THE INVENTION

This invention relates to a process for alkylating an alkylatable isoparaffinic hydrocarbon with olefinic hydrocarbons. More specifically, this invention relates to a process for producing an alkylation reaction product from an isoparaffinic reactant, a lighter olefinic reactant and a heavier olefinic reactant, utilizing acid-acting alkylation catalysts. This invention further relates to the process for producing an alkylation reaction product having superior qualities as a component of motor fuels, in comparison to the product produced by existing alkylation processes.

Alkylation of isoparaffinic hydrocarbons, such as isobutane, isopentane and the like, with olefinic hydrocarbons such as propylene, butylene, amylenes, and the like, is well known as a commercially important method for producing gasoline boiling range hydrocarbons. The C_5–C_{10} hydrocarbons generally produced by the alkylation reaction are termed "alkylate." Alkylate is particularly useful as a motor fuel blending stock because of its high motor octane and research octane ratings, such that it can be used to improve the overall octane ratings of gasolines to comply with the requirements of modern automobile motors. Such high octane products are particularly important in producing unleaded motor fuels of sufficient quality when it is desired not to employ alkyl lead compounds in the 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.

Recent trends in motor fuel requirements and projections of future requirements in this area indicate that the production of motor fuels distilling at end points below about 300° F. may be desirable and/or necessary to meet projected standards. Conventional isoparaffin-olefin alkylation processes do not have the capacity to produce an alkylate product having a distillation end point low enough to be useful in providing such low end point motor fuels. The process of the present invention provides a method whereby an alkylate product having a significantly lower distillation end point than possible using conventional processes may be produced, in addition to the increased value of the product of the present process resulting from octane rating improvements.

In general, commercial isoparaffin-olefin alkylation processes employ isobutane as the isoparaffin and propylene and/or butylenes as the olefins. Catalysts utilized include hydrogen fluoride, sulfuric acid and other like acidic or acid-acting materials. The isoparaffin, olefins and catalyst are typically contacted in an alkylation reactor, forming 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 is further processed, for example, by fractionation, to recover the alkylate product and to separate unconsumed reactants, e.g. isoparaffin, for further use.

It has been found preferable to conduct isoparaffin-olefin alkylation processes at particular conditions of temperature and pressure, and at specific concentrations of reactants and catalysts in order to produce an optimum yield of high quality alkylate product. A large molar excess of isoparaffin, relative to olefin, in the reaction mixture, generally about 10:1 to about 30:1, is one of the conditions required to provide even an adequate product. It has been found desirable to employ as large an excess of isoparaffin as possible, since the quality of the alkylate product is improved thereby. Thus, a considerable amount of isoparaffin is generally recovered and recycled to the reactor after separation from the hydrocarbon phase of the reactor effluent. The large amount of isoparaffin which must accordingly be passed, unreacted, through the alkylation reactor and settler and separated from the alkylate product necessitates the use of fractionation equipment of large capacity in order to provide an adequate separation of the product alkylate from the isoparaffin to be recycled. The expense and difficulty of providing a large isoparaffin throughput and recycle may be obviated, in part, through the use of the process of this invention.

It is known that higher quality alkylate may be produced, in the alkylation of propylene and butylenes, or other olefins, with an isoparaffin, when, for example, propylene is separately alkylated with the isoparaffin at one set of reaction conditions while butylenes are alkylated with the isoparaffin at a different set of reaction conditions. However, it has been found necessary to maintain the same high molar excess of isoparaffin to olefin in both the propylene alkylation reaction and the butylenes alkylation reaction in order to provide an adequate product. The separate alkylation of C_3 and C_4 olefins has, therefore, been found uneconomical, because of the expense of providing separate reactors for the C_3 and C_4 olefins when combined with the above-noted difficulties of handling the large molar excess of isoparaffin, necessary to provide a high quality product.

A continuing problem, in connection with the use of the widely employed hydrogen fluoride catalyst, has been the production of alkyl fluorides in the alkylation reactor during the reaction. When the hydrocarbons are separated from the hydrogen fluoride catalyst after the reaction, the alkyl fluorides remain in the hydrocarbon phase. In fractionation of the hydrocarbon phase to recover the alkylate product, the alkyl fluorides remain with the alkylate product because of their boiling point, and are thus very difficult to separate from the product. Such alkyl fluorides are undesirable impurities in the alkylate employed as a motor fuel component, both because they downgrade the quality of the hydrocarbons as fuel and because they are objectionable as air pollutants. This continuing problem in the alkylation art has been evidenced by various attempts to provide a method for reducing the alkyl fluoride content of alkylate. A convenient and thorough method for eliminating these impurities from an alkylation reaction product is provided by the process of the present invention.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process for alkylating an isoparaffin with a lighter olefin and a heavier olefin. A further object of the present invention is to provide a process for producing a superior alkylation reaction product from a lighter olefin, a heavier olefin and an isoparaffin. Another object of the present invention is to provide an isoparaffin-olefin alkylation process having a reduced isoparaffin recycle requirement. Yet another object of this invention is to provide an alkylation process employing hydrogen fluoride catalyst wherein the product is free from alkyl fluorides.

In a broad embodiment, the present invention relates to a process for producing an alkylation reaction product from an isoparaffinic reactant, a heavier olefinic reactant and a lighter olefinic reactant, which comprises the steps of: (a) contacting said isoparaffinic reactant, in admixture with said heavier olefinic reactant, with a first acidic alkylation catalyst in a first alkylation zone at alkylation conditions to form a first reaction mixture; (b) separating a first hydrocarbons stream from at least a portion of said first reaction mixture; (c) contacting at least a portion of said first hydrocarbons stream, in admixture with said lighter olefinic reactant, with a second acidic alkylation catalyst in a second alkylation zone at second alkylation conditions to form a second reaction mixture; (d) separating a second hydrocarbons stream from at least a portion of said second reaction mixture; and (e) recovering said alkylation reaction product from said second hydrocarbons stream.

I have discovered a method whereby a lighter olefinic reactant and a heavier olefinic reactant can be alkylated separately with an isoparaffin at different alkylation conditions preferred for alkylation of the two olefins, providing a superior reaction product from both olefins. Simultaneously, the amount of excess isoparaffin required for optimum alkylation conditions can be reduced. By passing the total charge of isoparaffin reactant into a first alkylation reactor with the heavier olefinic reactant, charging the hydrocarbon effluent from the first reactor and the lighter olefinic reactant to a second alkylation reactor and recovering the alkylate product from the hydrocarbon effluent from the second alkylation reactor, the separate alkylation of the lighter and heavier olefins can be accomplished with an optimum concentration of excess isoparaffin for both the reactions in both reactors without the necessity of providing separate isoparaffin supplies to the two reactions employed. Moreover, the alkylation reaction conditions employed in the second alkylation zone to alkylate the lighter olefinic reactant are ideal for elimination of undesirable alkyl fluorides from the reaction mixture prior to separation and fractionation of the hydrocarbons to provide the alkylation reaction product.

DESCRIPTION OF THE DRAWING

The attached drawing illustrates a particular embodiment of the present invention. In the embodiment shown, isobutane is employed as the isoparaffin, butylenes and propylene are employed as the heavier and lighter olefinic reactants, respectively, and hydrogen fluoride catalysts are employed in both alkylation reactors, the catalysts having different concentrations of hydrogen fluoride therein. The scope of the present invention is not limited to the embodiments illustrated thereby. Further objects, embodiments and illustrations indicative of the broad scope of the present invention will be apparent to those skilled in the art from the description of the drawing and preferred embodiments of the invention hereinafter provided.

Referring to the drawing, isobutane is charged in conduit **1**. The heavier olefinic reactant, comprising butylenes, is charged through conduit **2** and passed into conduit **1** in admixture with isobutane. The mixture of butylenes and isobutane is passed through conduit **1** and a portion thereof is diverted through conduits **3** and **4** and the portions in conduits **1**, **3** and **4** are passed separately into alkylation reactor **5** to insure thorough mixing. In alkylation reactor **5** the isoparaffin and olefin are contacted with low strength hydrogen fluoride catalyst comprising about 80% acid and thoroughly admixed to form a reaction mixture. Reactor **5** is provided with indirect heat exchange means not shown. Coolant is introduced through conduit **6** into reactor **5** and passed in indirect heat exchange with the reactants and catalyst therein. The heat exchanged coolant is withdrawn from reactor **5** through conduit **7**. The reaction mixture is maintained at a temperature of about 75° F. and a pressure sufficient to provide liquid phase operations in reactor **5**. The reactor effluent, comprising catalyst, alkylated hydrocarbons, alkyl fluoride compounds and unreacted hydrocarbons, such as isobutane, and possibly some butylenes, is passed via conduit **8** to settler **9**. In settler **9** low strength hydrogen fluoride catalyst is separated from a hydrocarbon phase containing alkylated hydrocarbons, unreacted hydrocarbons and alkyl fluoride compounds. The low strength hydrogen fluoride catalyst forms a separate heavier phase in settler **9** and is withdrawn through conduit **10**, passed through pump **13** and through conduit **14**, and thus recycled to reactor **5**. A small portion of the low strength catalyst in conduit **10** is withdrawn through conduit **11** and passed to a catalyst regeneration operation not shown. Fresh and/or regenerated catalyst containing a high concentration of hydrogen fluoride, e.g. 97 wt. percent is charged through conduit **12** to conduit **10** in order to maintain the catalyst employed in reactor **5** at an optimum strength. Referring again to settler **9**, the hydrocarbon phase comprising alkylation reaction products, isobutane, alkyl fluorides, etc., is withdrawn and passed through conduit **15**. The lighter olefinic reactant, comprising propylene, is charged through conduit **16** into conduit **15** and admixed with the hydrocarbon materials in conduit **15**. The combined propylene and hydrocarbon effluent from settler **9** are passed further through conduit **15** into reactor **19**. Portions of the combined propylene and hydrocarbon effluent are diverted from conduit **15** to conduit **17** and conduit **18** and passed separately into reactor **19** in order to provide thorough mixing. Reactor **19** is provided with indirect heat exchange means not shown. Coolant is charged to reactor **19** by way of conduit **20**. The coolant is passed in indirect heat exchange with the reaction mixture in reactor **19** and subsequently withdrawn through conduit **21**. The reactants charged to reactor **19** through conduits **15**, **17** and **18** are admixed with high strength hydrogen fluoride catalyst, containing about 95% wt. percent acid, to form a reaction mixture in reactor **19**. The reaction mixture in reactor **19** is maintained at a temperature of about 110° F. in liquid phase operations. After the reaction is substantially complete, the reaction mixture is withdrawn from reactor **19** and passed through conduit **22** into reaction soaker **23**, wherein the reaction mixture is maintained for an additional time at alkylation conditions. The effluent from the reaction soaker is passed through conduit **24** into settler **25**. In settler **25** a heavier high strength hydrogen fluoride catalyst phase separates and is withdrawn through conduit **26**, passed through pump **29** and charged via conduit **30** to reactor **19**. A small portion of the high strength catalyst in conduit **26** is withdrawn through conduit **27** and passed to regeneration not shown. Fresh and/or regenerated catalyst is charged through conduit **28** to conduit **26**. Referring again to settler **25**, a lighter hydrocarbon phase, comprising alkylate product and unreacted isobutane, is withdrawn through conduit **31** and passed to conventional fractionation means, such as a isobutane stripper, for further conventional separation of the alkylate product.

PREFERRED EMBODIMENTS OF THE INVENTION

The isoparaffinic and olefinic reactants which are employed in the process of the present invention are well known in the art. Isobutane is the preferred isoparaffin, although isopentane, isohexane, and the like, may also be utilized, or a mixture of two or more suitable isoparaffins may be employed. A suitable isoparaffinic reactant may contain some non-reactive contaminants such as normal paraffins. For example, a typical commercial isobutane reactant may contain some propane and normal butane.

The preferred heavier olefinic reactant comprises butylenes. A preferred heavier olefinic reactant may comprise, for example, pure 1-butene, pure 2-butene, pure isobutylene, or any mixture of two or all of the butylene isomers. Also preferred for use as the heavier olefinic reactant is a mixture of butylenes with some amylenes or other heavier olefinic reactants. A preferred heavier olefinic feed stock may contain small amounts of such hydrocarbons as normal paraffins, isoparaffins, ethylene, propylene, etc. The lighter olefinic reactant is preferably propylene, and may suitably contain small amounts of paraffins, isoparaffins, ethylene, butylenes, etc. It is preferred that the heavier olefinic reactant be substantially free from the lighter olefin employed and, likewise, that the lighter olefinic reactant be substantially free from heavier olefin employed. A typical preferred isoparaffinic feed stock may contain, for example, 95 wt. percent isobutane, 1 wt. percent propane, and 4 wt. percent normal butane, while a typical preferred heavier olefinic reactant feed stock may contain about 40 wt. percent butylenes, 45 wt. percent isobutane and 15 wt. percent normal butane, and a typical preferred lighter olefinic reactant feed stock may contain 60 wt. percent propylene and 40 wt. percent propane.

Acidic alkylation catalysts which can be utilized in the present invention, in general, include alkylation catalysts known in the art. For example, strong acids such as hydrogen fluoride, sulfuric acid, phosphoric acid, and sometimes hydrogen chloride have all been employed. Other suitable catalysts include metal halides such as aluminum chloride, antimony halides, etc., boron halides, and certain crystalline aluminosilicates catalytically active for alkylation of isoparaffins, such as faujasite, mordenite, etc., either with or without the addition of catalytic amounts of metals or metal ions.

In general, hydrogen fluoride alkylation catalyst is preferred for use as an alkylation catalyst in the present process. Conventional hydrogen fluoride alkylation catalyst comprises about 75 wt. percent or more of titratable acid, about 5 wt. percent or less water with the remainder made up of hydrocarbons and combined fluoride in solution in the acid. Such a conventional alkylation catalyst is suitable for use both as the alkylation catalyst in the first alkylation zone for alkylating with the heavier olefinic reactant and in the second alkylation zone for alkylating with the lighter olefinic reactant. In a particularly preferred embodiment of the process of this invention, two different strength hydrogen fluoride catalysts are employed. A lower strength alkylation catalyst is preferably utilized in the first alkylation zone to alkylate the isoparaffin with the heavier olefinic reactant, comprising butylenes. This lower strength catalyst is characterized by a concentration of titratable acid of about 75 wt. percent to about 90 wt. percent, a water concentration of about 0.1 wt. percent to about 1 wt. percent and a hydrocarbon concentration of about 10 wt. percent to about 25 wt. percent. A different, higher strength hydrogen fluoride alkylation catalyst is preferably utilized in the second alkylation reaction zone in the reaction involving the lighter olefinic reactant, comprising propylene. The higher strength alkylation catalyst is characterized by a titratable acid concentration of about 80 wt. percent to about 98 wt. percent, a water concentration of about 0.1 wt. percent to about 1 wt. percent and a hydrocarbons concentration of about 1 wt. percent to about 15 wt. percent. A particularly preferred lower strength catalyst contains about 75 wt. percent to about 80 wt. percent acid while a particularly preferred higher strength catalyst contains about 90 wt. percent to about 99 wt. percent acid.

Numerous alkylation reaction zones suitable for use in the process of this invention are known in the art. For example, but not by way of limitation, the alkylation reactor described in U.S. Pats. 3,456,033, 3,469,949 and 3,501,536 may suitably be employed for both alkylation reactions when a fluid catalyst such as hydrogen fluoride catalyst is utilized. Isoparaffin-olefin alkylation conditions 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, embodiments of the present process in which reactants and fluid catalysts are contacted in the alkylation zones and catalyst is subsequently separated from the reaction products by settling for further use. The scope of the present invention also includes embodiments wherein fixed beds of catalyst, such as a zeolitic catalyst, are employed in one or both of the reactors and the hydrocarbon effluent from the first reactor may thus be passed to the second reactor without further separation. Particular alkylation zones and optimum alkylation conditions in specific embodiments of the present process depend upon the composition of the particular heavier olefinic reactant feed stream, the particular lighter olefinic reactant feed stream, the isoparaffin feed stream, and the type of catalyst employed. For example, in the preferred embodiment, isobutane and a heavier olefinic reactant comprising about 30 volume percent to about 60 volume percent butylenes are contacted with a hydrogen fluoride catalyst in a first alkylation reaction zone at alkylation conditions including a temperature in the range from about 0° F. to about 200° F., a pressure sufficient to maintain the hydrocarbons and catalyst as liquids, a catalyst/hydrocarbon volume ratio in the first alkylation reactor in the range from about 0.1:1 to about 10:1 and a contact time (defined as the volume of the alkylation reactor divided by the volumetric flow rate, per minute of reactants and catalyst charged) in the first alkylation reactor in the range from about 0.1 minute to about 30 minutes. In this preferred embodiment, a lighter olefinic reactant comprising about 50 volume percent to about 70 volume percent propylene is contacted in a second alkylation reactor with the hydrocarbon effluent from the first alkylation zone and with a hydrogen fluoride catalyst at alkylation conditions including a temperature in the range from about 0° F. to about 200° F., a pressure sufficient to maintain liquid phase operations, a catalyst/hydrocarbon volume ratio, in the second alkylation reactor, of about 0.1:1 to about 10:1 and a contact time in the second alkylation reactor in the range from about 0.1 minute to about 30 minutes.

In a particularly preferred embodiment, alkylation conditions in the first alkylation zone include employment of the preferred low strength hydrogen fluoride alkylation catalyst described above and also include a temperature of about 40° F. to about 110° F., with a temperature of about 50° F. to about 100° F. particularly preferred, a pressure sufficient to maintain the reactants and catalyst as liquid, and a reaction time of about 0.1 minute to about 2 minutes. Preferably, in this particular embodiment, isobutane and butylenes reactants are charged to the first alkylation reactor at a mole ratio of about 20:1 to about 30:1, and a catalyst-to-hydrocarbon volume ratio of about 1:1 to about 2:1 is maintained in the first alkylation zone. Likewise, in this particular preferred embodiment, alkylation conditions in the second alkylation re-

actor include the use of the preferred high strength hydrogen fluoride alkylation catalyst, as described above, and also include a temperature of about 65° F. to about 150° F., with a temperature of about 90° F. to about 120° F. particularly preferred, a pressure sufficient to maintain the reactants and catalyst as liquids, and a reaction time of about 0.1 minute to about 2 minutes. Preferably, the hydrocarbon effluent from the first alkylation zone and the lighter olefinic reactant, comprising propylene, are charged to the second alkylation reactor at a propylene-to-hydrocarbon effluent mole ratio of about 1:20 to about 1:30, and a catalyst-to-hydrocarbon volume ratio of about 1:1 to about 2:1 is maintained in a second alkylation reactor. By maintaining the above-described preferred conditions in the first alkylation zone and second alkylation zone respectively, when using butylenes as the heavier olefinic reactant and propylene as the lighter olefinic reactant, it is possible to provide an optimum yield of high quality alkylate product from both the butylenes alkylation reaction and the propylene alkylation reaction. The desirable high molar ratio of isobutane is also maintained in both the first and second alkylation reaction zones without the necessity of maintaining enough surplus isobutane to provide separate charges of excess isobutane to the separate reactors as taught in prior art. By employing the hydrocarbons recovered from the first alkylation zone to provide the isobutane required in the second alkylation zone, the same charge of isobutane acts, in part, as the excess required in both the heavier olefin alkylation reaction and the lighter olefin alkylation reaction. By utilizing propylene as the lighter olefinic reactant, and maintaining the above-described preferred alkylation conditions in the second alkylation zone, self-alkylation of isobutane, the preferred isoparaffin reactant, is enhanced. Under the preferred conditions employed in the second alkylation zone, propylene reacts with isobutane to provide propane and isobutylene, in what is known in the art as the hydrogen transfer reaction. The isobutylene thus formed reacts in an alkylation reaction with further isobutane to provide primarily high octane C_8 hydrocarbons. Thus, while more isobutane is consumed in the preferred embodiment of the present process than in conventional alkylation processes, the increased consumption is more than offset by the production of additional amounts of superior alkylate product.

A further advantage of employing the preferred alkylation conditions in the second alkylation reaction zone is the substantially complete elimination of undesirable alkyl fluorides from the hydrocarbons which is thereby provided. The higher preferred temperature and higher strength hydrogen fluoride catalyst employed in the preferred embodiment are both conducive to the reaction of alkyl fluorides to produce hydrogen fluoride and hydrocarbons in the second alkylation reactor.

Because of the use of the preferred conditions, the effluent from the second reactor contains a substantially reduced concentration of alkyl fluorides. Further, in the preferred embodiment, the reaction mixture formed in the second alkylation reactor is passed through a reaction soaker. In the description of the preferred embodiments herein provided, it is intended that both the second alkylation reactor and the reaction soaker are included within the scope of the term "second alkylation zone." Suitable reaction soakers are well known in the art. For example, the reaction soakers described in U.S. Pats. 3,560,587 and 3,607,970 may suitably be employed in the present process. Such reaction soakers are commonly vessels equipped with perforated trays, baffle sections, or the like, to maintain the mixture of catalyst and hydrocarbons charged from the second alkylation reactor as a fairly homogenous mixture 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 second alkylation reactor.

Means for separating a hydrocarbon phase from, for example, a fluid catalyst phase, such as hydrogen fluoride, in the effluent from an alkylation reactor or reaction soaker are well known in the alkylation art. Generally, when a fluid catalyst such as hydrogen fluoride is employed, the effluent from an alkylation reactor or soaker comprises a mixture of isoparaffin, reaction products, catalyst and catalyst-soluble organic materials 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, light hydrocarbon gases and some organic fluorides form a hydrocarbon phase containing a small amount of catalyst in solution. The catalyst and catalyst-soluble hydrocarbons form a separate phase. The hydrocarbon phase is then easily mechanically separated from the catalyst phase. The temperature and pressure maintained during such a settling operation in an alkylation process, required when a fluid catalyst is utilized, are substantially the same as those described above in connection with alkylation reaction conditions. The hydrocarbons and the catalyst are preferably maintained in the liquid phase during the separation operation.

Means for withdrawing heat from the alkylation zone are necessary for operation of the process. A variety of means for accomplishing the heat withdrawal are well known. For example, in one 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 hydrocarbons stream, or phase, recovered, in the preferred embodiment, from the first alkylation reactor by settling the reaction mixture effluent therefrom, is preferably combined with the lighter propylene reactant and charged to the second alkylation reactor, wherein this combined hydrocarbons stream is contacted with an alkylation catalyst. It is contemplated that sufficient isoparaffin is charged to the first reactor so that no further isoparaffin need be added to the hydrocarbons charged to the second reactor. Generally, the total isobutane charged to the alkylation process is passed through, in turn, the first alkylation zone and the second alkylation zone. Under some conditions, it may be advantageous to charge some further isobutane to the second alkylation reactor, and such a modification is within the scope of this invention. The second hydrocarbons phase, recovered from the second alkylation separation procedure, is passed to further conventional separation operations and equipment, such as a fractionator, whereby the alkylate product is separated from unconsumed isoparaffin and any catalyst, such as hydrogen fluoride, which is present in the hydrocarbons effluent from the second alkylation zone. Any suitable method utilized in the prior art to separate the alkylate product from the isoparaffin and, for example, hydrogen fluoride, may be employed in the present process.

The alkylation reaction product produced in the improved process of this invention includes primarily C_7 and heavier saturated hydrocarbons resulting from the alkylation reactions of the isoparaffin with both the lighter and the heavier olefinic reactants. The primary products include, for example, dimethylpentanes and trimethylpentanes. It is well known that more highly branched hydrocarbons possess superior properties as motor fuel, and the present invention is, directed in part, to providing alkylate containing a higher ratio of more highly branched hydrocarbons, such as trimethylpentanes, to less branched hydrocarbons, such as dimethylhexanes, from the alkylation process. Thus, it is apparent that the present invention pro-

vides a novel process for producing a superior 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 producing an alkylation reaction product from an isoparaffinic reactant, a butylene reactant and a propylene reactant, which comprises reacting said butylene reactant with said isoparaffinic reactant at an alkylation temperature of from about 40° F. to about 110° F. in contact with a hydrogen fluoride catalyst containing about 70 wt. percent to about 95 wt. percent hydrogen fluoride, separating resultant alkylate-containing hydrocarbon phase from catalyst phase and reacting the same with said propylene reactant at a temperature higher than the first-mentioned temperature and in the range of from about 65° F. to about 150° F. in contact with a hydrogen fluoride catalyst of higher HF concentration than the first-mentioned catalyst and containing from about 80 wt. percent to about 99 wt. percent hydrogen fluoride, and recovering said reaction product.

2. The process of claim 1 further characterized in that said isoparaffinic reactant comprises isobutane.

3. The process of claim 1 further characterized in that said first mentioned alkylation temperature is from about 50° F. to about 100° F. and said first mentioned catalyst comprises about 75 wt. percent to about 80 wt. percent hydrogen fluoride.

4. The process of claim 1 further characterized in that said second mentioned temperature is from about 90° F. to about 120° F. and said second mentioned catalyst comprises about 90 wt. percent to about 99 wt. percent hydrogen fluoride.

References Cited

UNITED STATES PATENTS

2,814,654	11/1957	Kelly	260—683.48
3,236,912	2/1966	Phillips	260—683.49
3,078,321	2/1963	Van Pool et al.	260—683.49
3,007,983	11/1961	Clauson	260—683.46
3,211,803	10/1965	Chapman	260—683.49

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