

IONIC LIQUID CATALYST ALKYLATION USING A LOOP REACTOR

FIELD OF ART

The present invention relates to a process for producing low volatility, high
5 quality gasoline blending components which recirculates at least a portion of a
recovered stream comprising isoparaffins to the process. More particularly, the
present invention relates to an alkylation process utilizing an ionic liquid catalyst
that produces a product comprising gasoline blending components and recirculates
at least a portion of a recovered stream comprising isoparaffins to the alkylation
10 process.

BACKGROUND

Modern refineries employ many upgrading units such as fluid catalytic
cracking (FCC), hydrocracking (HCR), alkylation, and paraffin isomerization. As a
15 result, these refineries produce a significant amount of isopentane. Historically,
isopentane was a desirable blending component for gasoline having a high octane
(92 RON), although it exhibited high volatility (20.4 Reid vapor pressure (RVP)).
As environmental laws began to place more stringent restrictions on gasoline
volatility, the use of isopentane in gasoline was limited because of its high volatility.
20 As a consequence, the problem of finding uses for by-product isopentane became
serious, especially during the hot summer season. Moreover, as more gasoline
compositions contain ethanol instead of MTBE as their oxygenate component, more
isopentane had to be kept out of the gasoline pool in order to meet the gasoline
volatility specification. So, the gasoline volatility issue became even more serious,
25 further limiting the usefulness of isopentane as a gasoline blending component.

An alkylation process, which is disclosed in U.S. Patent Application
Publication 2006/0131209, was developed that is capable of converting the
undesirable, excess isopentane into desirable and much more valuable low-RVP
gasoline blending components. The contents of U.S. Patent Application Publication
30 2006/0131209 are incorporated by reference herein. This alkylation process
involves contacting isoparaffins, preferably isopentane, with olefins, preferably

ethylene, in the presence of an ionic liquid catalyst to produce the low-RVP gasoline blending components. This process eliminates the need to store or otherwise use isopentane and eliminates concerns associated with such storage and usage.

Furthermore, the ionic liquid catalyst can also be used with conventional alkylation
5 feed components (e.g. isobutane, propylene, butene, and pentene).

The ionic liquid catalyst distinguishes this novel alkylation process from conventional processes for converting light paraffins and light olefins to more lucrative products. Conventional processes include the alkylation of paraffins with olefins, and polymerization of olefins. For example, one of the most extensively
10 used processes in the field is the alkylation of isobutane with C₃-C₅ olefins to make gasoline cuts with high octane number. However, this and all conventional processes employ sulfuric acid and hydrofluoric acid catalysts.

Numerous disadvantages are associated with sulfuric acid and hydrofluoric acid catalysts. Extremely large amounts of acid are necessary to initially fill the
15 reactor. The sulfuric acid plant also requires a huge amount of daily withdrawal of spent acid for off-site regeneration. Then the spent sulfuric acid must be incinerated to recover SO₂/SO₃ and fresh acid is prepared. While an HF alkylation plant has on-site regeneration capability and daily make-up of HF is orders of magnitude less, HF forms aerosol. Aerosol formation presents a potentially significant environmental
20 risk and makes the HF alkylation process less safe than the H₂SO₄ alkylation process. Modern HF processes often require additional safety measures such as water spray and catalyst additive for aerosol reduction to minimize the potential hazards. Thus, the ionic liquid catalyst alkylation process fulfills the need for safer and more environmentally-friendly catalyst systems.

25 Benefits of the ionic liquid catalyst alkylation process include the following:

(1) substantial reduction in capital expenditure as compared to sulfuric acid and hydrofluoric acid alkylation plants;

(2) Substantial reduction in operating expenditures as compared to sulfuric acid alkylation plants;

30 (3) substantial reduction in catalyst inventory volume (potentially by 90%)

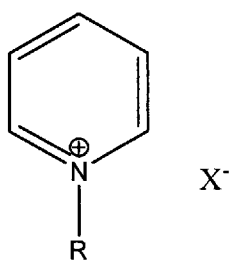
- (4) a substantially reduced catalyst make-up rate (potentially by 98% compared to sulfuric acid plants)
- (5) a higher gasoline yield
- (6) comparable or better product quality (Octane number, RVP, T50)
- 5 (7) significant environment, health and safety advantages;
- (8) expansion of alkylation feeds to include isopentane and ethylene; and
- (9) higher activity and selectivity of the catalyst.

Ionic liquid catalysts specifically useful in the alkylation process described in U.S. Patent Application Publication 2006/0131209 are disclosed in U.S. Patent

10 Application Publication 2006/0135839, which is also incorporated by reference herein. Such catalysts are chloroaluminate liquid catalysts comprising an alkyl substituted pyridium halide or an alkyl substituted imidazolium halide of the general formulas A and B, respectively. Such catalysts further include chloroaluminate liquid catalysts comprising a hydrocarbyl substituted pyridium halide or a

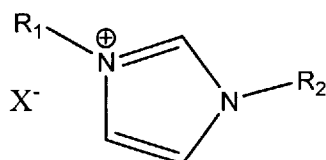
15 hydrocarbyl substituted imidazolium halide of the general formulas A and B, respectively.

(A)



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(B)



where R=H, methyl, ethyl, propyl, butyl, pentyl or hexyl group and X is a haloaluminate and preferably chloroaluminate, and R₁ and R₂=H, methyl, ethyl, propyl, butyl, pentyl, or hexyl group and where R₁ and R₂ may or may not be the same. Preferred catalysts include 1-butyl-4-methyl-pyridinium chloroaluminate (BMP), 1-butyl-pyridinium chloroaluminate (BP), 1-butyl-3-methyl-imidazolium chloroaluminate (BMIM) and 1-H-pyridinium chloroaluminate (HP).

However, the ionic liquid catalyst has unique properties, which requires that the ionic liquid catalyst alkylation process be further developed and modified to achieve superior gasoline blending component products, improved process operability and reliability, and reduced operating costs, etc. More particularly, the ionic liquid catalyst alkylation process requires uniform mixing of the hydrocarbon and catalyst, sufficient interfacial contact between the hydrocarbons and catalyst, good temperature and pressure control, and a high isoparaffin to olefin (I/O) ratio. In addition, alkylation by means of the ionic liquid catalyst is an exothermic reaction requiring the removal of heat generated. Thus, it would be beneficial to the industry if an improved alkylation process for converting isoparaffins and olefins in the presence of an ionic liquid catalyst was available.

One technique that has been used in general alkylation processes is the recycling of effluent. For example, ExxonMobil's auto refrigeration process described at page 243 of Petroleum Refining--Technology and Economics (3rd edition) by James Gary and Glenn Handwerk involves recycling catalyst and isobutane to the reactor where alkylation between the olefins and isobutane takes place. U.S. Patent No. 5,347,064 describes an isoparaffin-olefin alkylation process wherein recycled isobutane is added to a series of alkylation reaction stages. U.S. Patent 4,225,742 discloses an HF alkylation process of isoparaffins with olefins wherein an alkane stream substantially free of alkylate (the product) and comprising principally normal C₃ and C₄ paraffin hydrocarbons is recycled to the reaction zone. However, the industry continues to strive for improved, more efficient processes in order to lower the cost of products, and in particular when using an ionic liquid catalyst.

SUMMARY

Provided is a process for producing low volatility, high quality gasoline blending components incorporating recirculation of at least a portion of a recovered stream comprising primarily isoparaffins. Either all of the product or only a mere
5 portion of the isoparaffins may be recirculated. In any case, the process includes the following steps:

- (a) providing at least one olefin feed stream comprising olefins;
- (b) providing at least one isoparaffin feed stream comprising isoparaffins;
- (c) contacting the at least one olefin feed stream with the at least one
10 isoparaffin feed stream in the presence of an ionic liquid catalyst in an alkylation zone under alkylation conditions to provide at least one product stream, and
- (d) recirculating to the alkylation zone a stream comprised primarily of isoparaffin.

Among other factors, recirculation of a stream comprised primarily of
15 isoparaffin has been found to provide a more efficient and cost effective alkylation process when using an ionic liquid catalyst. Most importantly, the recirculation of a stream comprised primarily of isoparaffin reactant allows the reaction in the presence of an ionic liquid catalyst to maintain a high effective I/O ratio, which minimizes undesired side reactions. One can also use a lower quality of feed while
20 maintaining the high I/O ratio within the reaction.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic illustration of a first embodiment of present invention having an external loop for recirculation of primarily isoparaffin.

25 FIG. 2 is a schematic illustration of a second embodiment of the present invention using a horizontal reactor with recycled vapor of primarily isoparaffin.

DETAILED DESCRIPTION

The present invention provides a process for the production of low volatility,
30 high quality gasoline blending components. According to the broadest aspect of the present invention, the process involves recirculating a portion of at least one

recovered stream from an alkylation reaction comprised primarily of isoparaffin back to the alkylation reaction.

As used herein, the term alkylation reaction refers to the reaction that occurs between olefins and isoparaffins. The term "isoparaffin" means any branched-chain saturated hydrocarbon compound, i.e. a branched-chain alkane with a chemical formula of C_nH_{2n+2} . Examples of isoparaffins are isobutane and isopentane. The term "olefin" means any unsaturated hydrocarbon compound having at least one carbon-to-carbon double bond, i.e. an alkene with a chemical formula of C_nH_{2n} . Examples of olefins include ethylene, propylene, butene, and so on. The olefins can comprise at least one olefin selected from the following olefins: ethylene, propylene, butene, pentene, and mixtures of these. The isoparaffins can comprise at least one isoparaffin selected from the following isoparaffins: isobutane, isopentane, and mixtures of these.

According to one aspect, the process begins by providing at least one olefin feed stream comprising olefins and at least one isoparaffin feed stream comprising isoparaffins. The at least one olefin feed stream and the at least one isoparaffin feed stream contact one another in the presence of an ionic liquid catalyst within at least one alkylation zone under alkylation conditions. The term "alkylation zone" refers to the physical area in which the alkylation between olefins and isoparaffins occurs. Interaction between the olefins and the isoparaffins under the influence of the catalyst provides at least one product stream comprising the gasoline blending components. The at least one alkylation zone may be a single alkylation zone or a plurality of separate and distinct alkylation zones.

The process thereafter requires that at least a portion of a recovered stream comprised primarily of isoparaffin is recirculated to the alkylation zone. By primarily isoparaffin is meant a stream of at least 50 volume % isoparaffin, and in another embodiment at least 70 volume %, and in yet another embodiment at least 90 volume %.

Referring to Figure 1, a process is depicted which uses an external loop for recirculating a stream comprised of primarily isoparaffin. The hydrocarbon feeds 1, comprised of a isoparaffin feed and an olefin feed mixed together, is split and

injected at three different points, 4, 5 and 6, into the alkylation zone/reactor 7.

Effluent 8 from the reactor generally comprises isoparaffin, catalyst and reaction product. Essentially all of the olefin is reacted, as the I/O (isoparaffin/olefin) ratio is maintained as high as practical in order to insure complete reaction. At the

5 beginning of the reaction process the I/O ratio is generally around 10:1 as injected into the reactor 7. However, the effective ratio in the reactor, as the reaction occurs, can be generally 1,000:1, or 10,000:1, or even higher, as almost all of the olefin is reacted and substantially only isoparaffin remains of the reactants.

The effluent 8 is then pumped via pump 9 through a heat exchange 10 in
10 order to remove reaction heat and help control the temperature in the reactor 7. Some part of the effluent can be separated and removed 11, while the remaining portion 12 comprised primarily of isoparaffin, is recirculated to the reactor 7. Additional catalyst 13 can be added to the recirculated stream.

By recirculating the stream of primarily isoparaffin, one can achieve an
15 effective high I/O ratio and insure product quality by employing a lower I/O ratio in the feed, which is more cost effective. The recirculated isoparaffin allows the charged I/O ratio to remain high while the ratio of newly added isoparaffin and olefin can be lower, for example 8:1, or even 6:1. This results in a tremendous savings in isoparaffin cost.

20 Another embodiment is shown in Fig. 2, using a horizontal reactor. Isoparaffin 21 is injected into the reactor 22 at a first nozzle 23. Catalyst 24 is also injected at nozzle 23. Olefin 25 is injected into the reactor at multiple olefin injection points 26, which increases the internal I/O ratio and provides improved mixing inside the reactor. The horizontal reactor is generally run at low pressure so
25 that reaction heat is removed by isoparaffin evaporation. The generated vapor provides extra mixing inside the reactor, and the isoparaffin vapor is removed at 27 and fully condensed in a condenser 28 and recycled 29 back to the reactor 22. Product is removed at 30.

It should be appreciated that the olefins and isoparaffins need not exist in
30 separate olefin feed stream(s) and the isoparaffin feed stream(s). Rather, the olefins and isoparaffins can be mixed or otherwise combined to form one or more

hydrocarbon feed stream(s). Thus, at least one hydrocarbon feed stream can comprise the at least one olefin feed stream and the at least one isoparaffin feed stream.

Alkylation is a exothermic reaction. Thus, it is necessary to remove heat from the at least one alkylation zone by some means in order to maintain the desired reaction temperature or temperature range. A variety of methods are available for removing such reaction heat and maintaining control of the reaction temperature in the alkylation zone. One method of cooling the at least one alkylation zone involves passing the at least one product stream (or part of the at least one product stream) through at least one heat exchanger. This method is illustrated and discussed above in relation to Fig. 1. Another method of cooling the at least one alkylation zone involves evaporation. In this method, as depicted in Fig. 2, reaction heat is removed instantly by isoparaffin evaporation within the alkylation. Other conventional methods, such as cooling jackets, can also be used as are known in the art.

The non-recirculated portion of a product stream(s) may be treated by any known separation technique in order to separate the gasoline blending components from the other constituents in the product stream(s). Generally, the catalyst and hydrocarbon phase, which comprises unreacted isoparaffins and the gasoline blending components, are first separated. Next, the gasoline blending components are separated from the remainder of the hydrocarbon phase. A variety of feasible separation methods are known in the art. An example of a useful method of separating the gasoline blending components from hydrocarbon phase is distillation.

The present process employs an ionic liquid catalyst. Ionic liquid catalysts are well known in the art.

The process can employ a catalytic composition comprising at least one aluminum halide and at least one quaternary ammonium halide and/or at least one amine halohydrate. An example of an aluminum halide which can be used in accordance with the invention is aluminum chloride. Quaternary ammonium halides which can be used in accordance with the invention are described in U.S. Patent No. 5,750,455, which is incorporated by reference herein, which also teaches a method

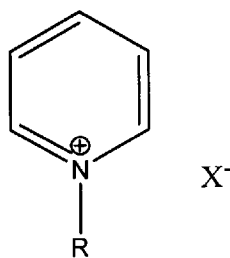
for the preparation of the catalyst. An exemplary ionic liquid catalyst is N-butylpyridinium chloroaluminate ($C_5H_5NC_4H_9Al_2Cl_7$).

The ionic liquid catalyst can also be a pyridinium or imidazolium-based chloroaluminate ionic liquid. These ionic liquid have been found to be much more effective in the alkylation of isopentane and isobutane with ethylene than aliphatic ammonium chloroaluminate ionic liquid (such as tributyl-methyl-ammonium chloroaluminate). The ionic liquid catalyst can be a chloroaluminate ionic liquid comprising a hydrocarbyl substituted pyridinium halide or a hydrocarbyl substituted imidazolium halide. Alternatively, the ionic liquid catalyst can be a chloroaluminate ionic liquid catalyst comprising an alkyl substituted pyridinium halide or an alkyl substituted imidazolium halide. More specifically, the ionic liquid catalyst may be selected from the group consisting of:

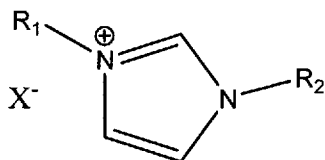
a chloroaluminate ionic liquid catalyst comprising a hydrocarbyl substituted pyridinium halide mixed in with aluminum trichloride or a hydrocarbyl substituted imidazolium and aluminum trichloride preferably in 1 molar equivalent hydrocarbyl substituted pyridinium halide or hydrocarbyl substituted imidazolium halide to 2 molar equivalents aluminum trichloride of the general formulas A and B, respectively;

a chloroaluminate ionic liquid catalyst comprising an alkyl substituted pyridinium chloride and aluminum trichloride or an alkyl substituted imidazolium chloride and aluminum trichloride preferably in 1 molar alkyl substituted pyridinium chloride or alkyl substituted imidazolium chloride to 2 molar equivalents of aluminum trichloride of the general formulas A and B, respectively;

25 (A)



(B)



5 and mixtures thereof,

where R=H, methyl, ethyl, propyl, butyl, pentyl or hexyl group and X is a haloaluminate and preferably a chloroaluminate, and R₁ and R₂=H, methyl, ethyl, propyl, butyl, pentyl, or hexyl group and where R₁ and R₂ may or may not be the same.

10 Preferably the ionic liquid catalyst is selected from the group consisting of 1-butyl-4-methyl-pyridinium chloroaluminate (BMP), 1-butyl-pyridinium chloroaluminate (BP), 1-butyl-3-methyl-imidazolium chloroaluminate (BMIM), 1-H-pyridinium chloroaluminate (HP), and N-butylpyridinium chloroaluminate (C₅H₅NC₄H₉Al₂Cl₇).

15 A metal halide may be employed as a co-catalyst to modify the catalyst activity and selectivity. Commonly used halides for such purposes include NaCl, LiCl, KCl, BeCl₂, CaCl₂, BaCl₂, SiCl₂, MgCl₂, PbCl₂, CuCl, ZrCl₄, and AgCl as published by Roebuck and Evering (Ind. Eng. Chem. Prod. Res. Develop., Vol. 9, 77, 1970). Preferred metal halides are CuCl, AgCl, PbCl₂, LiCl, and ZrCl₄.

20 HCl or any Broensted acid may be employed as an effective co-catalyst to enhance the activity of the catalyst by boosting the overall acidity of the ionic liquid-based catalyst. The use of such co-catalysts and ionic liquid catalysts that are useful in practicing the present invention are disclosed in U.S. Published Patent Application Nos. 2003/0060359 and 2004/0077914. Other co-catalysts that may be
 25 used to enhance the catalytic activity of the ionic liquid catalyst include IVB metal compounds preferably IVB metal halides such as TiCl₃, TiCl₄, TiBr₃, TiBr₄, ZrCl₄, ZrBr₄, HfCl₄, and HfBr₄ as described by Hirschauer et al. in U.S. Patent No. 6,028,024.

Alkylation conditions are maintained in the at least one alkylation zone. The molar ratio between the isoparaffin and the olefin is in the range of 1 to 100, for example, advantageously in the range 2 to 50, preferably in the range 2 to 20.

Catalyst volume in the reactor is in the range of 2 vol% to 70 vol%, preferably in the
5 range of 5 vol% to 50 vol%. The reaction temperature can be in the range -40°C to 150°C, preferably in the range -20°C to 100°C. The pressure can be in the range from atmospheric pressure to 8000 kPa, preferably sufficient to keep the reactants in the liquid phase. Residence time of reactants in the at least one alkylation zone is in the range of a few seconds to hours, preferably 0.5 min to 60 min.

10 Typical alkylation conditions may include a catalyst volume in the at least one alkylation zone of from 5 vol% to 50 vol%, a temperature of from -10°C to 100°C, a pressure of from 300 kPa to 2500 kPa, an isoparaffin to olefin molar ratio of 2 to 10 and a residence time of 1 minute to 1 hour.

Although the present invention has been described in connection with
15 preferred embodiments thereof, it will be appreciated by those skilled in the art that additions, deletions, modifications, and substitutions not specifically described may be made without departing from the spirit and scope of the invention as defined in the appended claims.

WHAT IS CLAIMED IS:

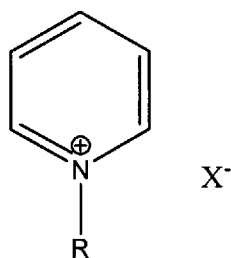
1. A process for the production of low volatility, high quality gasoline blending components comprising:
 - (a) providing at least one olefin feed stream comprising olefins;
 - (b) providing at least one isoparaffin feed stream comprising isoparaffins;
 - (c) contacting the at least one olefin feed stream with the at least one isoparaffin feed stream in the presence of an ionic liquid catalyst in an alkylation zone under alkylation conditions to provide at least one product stream; and
 - (d) recirculating to the alkylation zone a stream comprised of primarily isoparaffin.
2. The process according to claim 1, wherein the olefin feed stream comprise at least one olefin selected from the group consisting of ethylene, propylene, butene, pentene, and mixtures thereof.
3. The process according to claim 1, wherein the isoparaffin feed stream comprise at least one isoparaffin selected from the group consisting of isobutane, isopentane, and mixtures thereof.
4. The process according to claim 1, further comprising:
 - passing a product stream through at least one heat exchanger; and
 - removing heat from the product stream.
5. The process according to claim 1, wherein the stream comprised of primarily isoparaffin is separated from effluent obtained from the contacting in step (c).
6. The process according to claim 1, wherein the stream comprised primarily of isoparaffin is condensed from vaporous overhead in a horizontal reactor in which the contacting in step (c) occurs.

7. The process according to claim 1, wherein the ionic liquid catalyst is selected from the group consisting of:

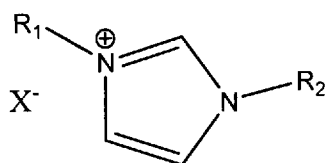
a chloroaluminate ionic liquid catalyst comprising a hydrocarbyl substituted pyridinium halide or a hydrocarbyl substituted imidazolium halide of the general formulas A and B, respectively;

a chloroaluminate ionic liquid catalyst comprising an alkyl substituted pyridinium halide or an alkyl substituted imidazolium halide of the general formulas A and B, respectively;

(A)



(B)



and mixtures thereof,

where R=H, methyl, ethyl, propyl, butyl, pentyl or hexyl group and X is a haloaluminate and preferably a chloroaluminate, and R₁ and R₂=H, methyl, ethyl, propyl, butyl, pentyl, or hexyl group and where R₁ and R₂ may or may not be the same.

8. The process according to claim 7, wherein the ionic liquid catalyst is selected from the group consisting of 1-butyl-4-methyl-pyridinium chloroaluminate (BMP), 1-butyl-pyridinium chloroaluminate (BP), 1-butyl-3-methyl-imidazolium chloroaluminate (BMIM), 1-H-pyridinium chloroaluminate (HP), and N-butylpyridinium chloroaluminate.
9. The process according to claim 7, wherein the catalyst further comprises an HCl co-catalyst.
10. The process according to claim 1, wherein there are multiple injections of olefin into the alkylation zone.
11. The process according to claim 1, wherein there are multiple injections of isoparaffin into the alkylation zone.
12. The process according to claim 1, wherein the I/O ratio of newly added reactants injected into the alkylation zone is in the range of from 6:1 to 10:1.