

1           ALKYLATION PROCESS USING AN ALKYL HALIDE PROMOTED  
2                            IONIC LIQUID CATALYST

3  
4                            FIELD OF THE INVENTION

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6       The present invention relates to a process for the alkylation of light isoparaffins with  
7       olefins using a catalyst comprising an ionic liquid and an alkyl halide.

8  
9                            BACKGROUND OF THE INVENTION

10  
11      In general, conversion of light paraffins and light olefins to more valuable cuts is very  
12      lucrative to the refining industries. This has been accomplished by alkylation of  
13      paraffins with olefins, and by polymerization of olefins. One of the most widely used  
14      processes in this field is the alkylation of isobutane with C<sub>3</sub> to C<sub>5</sub> olefins to make  
15      gasoline cuts with high octane number using sulfuric and hydrofluoric acids. This  
16      process has been used by refining industries since the 1940's. The process was driven  
17      by the increasing demand for high quality and clean burning high-octane gasoline.

18  
19      Alkylate gasoline is a high quality and efficient burning gasoline that constitutes  
20      about 14% of the gasoline pool. Alkylate gasoline is typically produced by alkylating  
21      refineries isobutane with low-end olefins (mainly butenes). Currently, alkylates are  
22      produced by using HF and H<sub>2</sub>SO<sub>4</sub> as catalysts. Although these catalysts have been  
23      successfully used to economically produce the best quality alkylates, the need for  
24      safer and environmentally friendlier catalysts systems has become an issue to the  
25      industries involved.

26  
27      The quest for an alternative catalytic system to replace the current environmentally  
28      unfriendly catalysts has been the subject of varying research groups in both academic  
29      and industrial institutions. Unfortunately, thus far, no viable replacement to the  
30      current processes has been put into practice at commercial refineries.

31  
32      Ionic liquids are liquids that are composed entirely of ions. The so-called "low  
33      temperature" ionic liquids are generally organic salts with melting points under 100

1 degrees C, often even lower than room temperature. Ionic liquids may be suitable for  
2 example for use as a catalyst and as a solvent in alkylation and polymerization  
3 reactions as well as in dimerization, oligomerization acetylation, metatheses, and  
4 copolymerization reactions.

5  
6 One class of ionic liquids is fused salt compositions, which are molten at low  
7 temperature and are useful as catalysts, solvents and electrolytes. Such compositions  
8 are mixtures of components which are liquid at temperatures below the individual  
9 melting points of the components.

10  
11 Ionic liquids can be defined as liquids whose make-up is entirely comprised of ions as  
12 a combination of cations and anions. The most common ionic liquids are those  
13 prepared from organic-based cations and inorganic or organic anions. The most  
14 common organic cations are ammonium cations, but phosphonium and sulphonium  
15 cations are also frequently used. Ionic liquids of pyridinium and imidazolium are  
16 perhaps the most commonly used cations. Anions include, but not limited to,  $\text{BF}_4^-$ ,  
17  $\text{PF}_6^-$ , haloaluminates such as  $\text{Al}_2\text{Cl}_7^-$  and  $\text{Al}_2\text{Br}_7^-$ ,  $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ , alkyl sulphates  
18  $(\text{RSO}_3^-)$ , carboxylates  $(\text{RCO}_2^-)$  and many other. The most catalytically interesting  
19 ionic liquids for acid catalysis are those derived from ammonium halides and Lewis  
20 acids (such as  $\text{AlCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{FeCl}_3$ , etc). Chloroaluminate ionic liquids are  
21 perhaps the most commonly used ionic liquid catalyst systems for acid-catalyzed  
22 reactions.

23  
24 Examples of such low temperature ionic liquids or molten fused salts are the  
25 chloroaluminate salts. Alkyl imidazolium or pyridinium chlorides, for example, can  
26 be mixed with aluminum trichloride ( $\text{AlCl}_3$ ) to form the fused chloroaluminate salts.  
27 The use of the fused salts of 1-alkylpyridinium chloride and aluminum trichloride as  
28 electrolytes is discussed in U.S. Patent No. 4,122,245. Other patents which discuss the  
29 use of fused salts from aluminum trichloride and alkylimidazolium halides as  
30 electrolytes are U.S. Patent Nos. 4,463,071 and 4,463,072.

31  
32 U.S. Patent No. 5,104,840 describes ionic liquids which comprise at least one  
33 alkylaluminum dihalide and at least one quaternary ammonium halide and/or at least

1 one quaternary ammonium phosphonium halide; and their uses as solvents in catalytic  
2 reactions.

3  
4 U.S. Patent No. 6,096,680 describes liquid clathrate compositions useful as reusable  
5 aluminum catalysts in Friedel-Crafts reactions. In one embodiment, the liquid  
6 clathrate composition is formed from constituents comprising (i) at least one  
7 aluminum trihalide, (ii) at least one salt selected from alkali metal halide, alkaline  
8 earth metal halide, alkali metal pseudohalide, quaternary ammonium salt, quaternary  
9 phosphonium salt, or ternary sulfonium salt, or a mixture of any two or more of the  
10 foregoing, and (iii) at least one aromatic hydrocarbon compound.

11  
12 Other examples of ionic liquids and their methods of preparation may also be found in  
13 U.S. Patent Nos. 5,731,101; 6,797,853 and in U.S. Patent Application Publications  
14 2004/0077914 and 2004/0133056.

15  
16 In the last decade or so, the emergence of chloroaluminate ionic liquids sparked some  
17 interest in  $\text{AlCl}_3$ -catalyzed alkylation in ionic liquids as a possible alternative. For  
18 example, the alkylation of isobutane with butenes and ethylene in ionic liquids has  
19 been described in U.S. Patent Nos. 5,750,455; 6,028,024; and 6,235,959 and open  
20 literature (Journal of Molecular Catalysis, 92 (1994), 155-165;  
21 "Ionic Liquids in Synthesis", P. Wasserscheid and T. Welton (eds.), Wiley-VCH  
22 Verlag, 2003, pp 275).

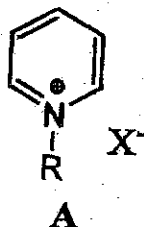
23  
24 Aluminum chloride-catalyzed alkylation and polymerization reactions in ionic liquids  
25 may prove to be commercially viable processes for the refining industry for making a  
26 wide range of products. These products range from alkylate gasoline produced from  
27 alkylation of isobutane and isopentane with light olefins, to diesel fuel and lubricating  
28 oil produced by alkylation and polymerization reactions.

29

## SUMMARY OF INVENTION

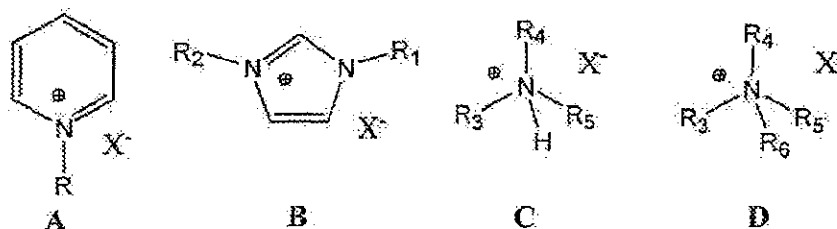
In a first aspect, there is provided an alkylation process comprising contacting a hydrocarbon mixture comprising at least one olefin having from 2 to 6 carbon atoms and at least one isoparaffin having from 4 to 6 carbon atoms under alkylation conditions including an isopentane to olefin molar ratio of from 2 to 8, in the presence of an acidic ionic liquid catalyst in an alkylation zone, said catalyst comprising a mixture of at least one acidic ionic liquid and at least one alkyl halide; wherein the at least one olefin and the at least one isoparaffin are alkylated.

In a second aspect, there is provided an alkylation process comprising contacting a hydrocarbon mixture comprising at least one olefin having 2 to 6 carbon atoms and at least one isoparaffin having from 4 to 6 carbon atoms under alkylation conditions in the presence of an acidic ionic liquid catalyst in an alkylation zone, said catalyst comprising a mixture of at least one acidic ionic liquid and at least one alkyl halide; wherein the acidic ionic liquid is a chloroaluminate ionic liquid prepared by mixing aluminium trichloride ( $\text{AlCl}_3$ ) and a hydrocarbyl substituted pyridinium halide having the general formula A:



where  $\text{R}=\text{H}$ , methyl, ethyl, propyl, butyl, pentyl or hexyl group and  $\text{X}$  is a halide; wherein the isoparaffin and the olefin having 2 to 6 carbon atoms are alkylated; and wherein the alkylation conditions include an isopentane to olefin molar ratio of from 2 to 8.

The present disclosure relates to an alkylation process comprising contacting a hydrocarbon mixture comprising at least one olefin having from 2 to 6 carbon atoms and at least one isoparaffin having from 4 to 6 carbon atoms with a catalyst under alkylation conditions, said catalyst comprising a mixture of at least one acidic ionic liquid and at least one alkyl halide. In one embodiment, the acidic ionic liquid is a chloroaluminate ionic liquid prepared by mixing aluminum trichloride ( $\text{AlCl}_3$ ) and a hydrocarbyl substituted pyridinium halide, a hydrocarbyl substituted imidazolium halide, trialkylammonium hydrohalide or tetraalkylammonium halide of the general formulas A, B, C and D, respectively,



where R=H, methyl, ethyl, propyl, butyl, pentyl or hexyl group and X is a halide and preferably a chloride, and R<sub>1</sub> and R<sub>2</sub>=H, methyl, ethyl, propyl, butyl, pentyl or hexyl group and where R<sub>1</sub> and R<sub>2</sub> may or may not be the same, and R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> and R<sub>6</sub>=methyl, ethyl, propyl, butyl, pentyl or hexyl group and where R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> may or may not be the same.

## DETAILED DESCRIPTION

The present invention relates to an alkylation process comprising contacting a hydrocarbon mixture comprising at least one olefin having from 2 to 6 carbon atoms and at least one isoparaffin having from 4 to 6 carbon atoms with a catalyst under alkylation conditions, said catalyst comprising a mixture of at least one acidic ionic liquid and at least one alkyl halide.

One component of a feedstock to the process of the present invention is at least one olefin having from 2 to 6 carbon atoms. This component may, for example, be any refinery hydrocarbon stream which contains olefins.

Another component of a feedstock to the process of the present invention is at least one isoparaffin having from 3 to 6 carbon atoms. This component may, for example, be any refinery hydrocarbon stream which contains isoparaffins.

The processes according to the present invention are not limited to any specific feedstocks and are generally applicable to the alkylation of  $C_3$ - $C_6$  isoparaffins with  $C_2$ - $C_6$  olefins from any source and in any combination.

In accordance with the present invention, a mixture of hydrocarbons as described above is contacted with a catalyst under alkylation conditions. A catalyst in accordance with the present invention comprises at least one acidic ionic liquid and at least one alkyl halide. The present process is being described and exemplified with reference to certain specific ionic liquid catalysts, but such description is not intended to limit the scope of the invention. The processes described may be conducted using any acidic ionic liquid catalysts by those persons having ordinary skill based on the teachings, descriptions and examples included herein.

The specific examples used herein refer to alkylation processes using ionic liquid systems, which are amine-based cationic species mixed with aluminum chloride. In such systems, to obtain the appropriate acidity suitable for the alkylation chemistry, the ionic liquid catalyst is generally prepared to full acidity strength by mixing one

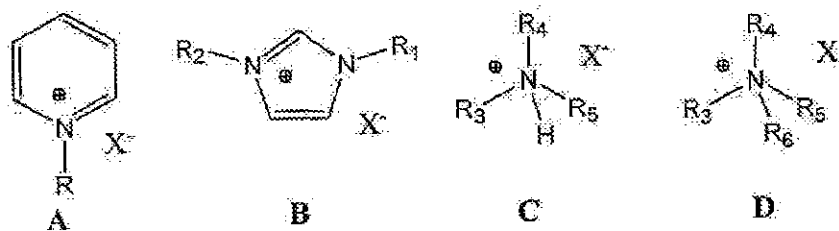
1 molar part of the appropriate ammonium chloride with two molar parts of aluminum  
 2 chloride. The catalyst exemplified for the alkylation process is a 1-alkyl-pyridinium  
 3 chloroaluminate, such as 1-butyl-pyridinium heptachloroaluminate.



4  
 5 1-Butyl-pyridinium heptachloroaluminate

6  
 7 In general, a strongly acidic ionic liquid is necessary for paraffin alkylation, e.g.  
 8 isoparaffin alkylation. In that case, aluminum chloride, which is a strong Lewis acid  
 9 in a combination with a small concentration of a Broensted acid, is a preferred  
 10 catalyst component in the ionic liquid catalyst scheme.

11  
 12 As noted above, the acidic ionic liquid may be any acidic ionic liquid. In one  
 13 embodiment, the acidic ionic liquid is a chloroaluminate ionic liquid prepared by  
 14 mixing aluminum trichloride ( $\text{AlCl}_3$ ) and a hydrocarbyl substituted pyridinium halide,  
 15 a hydrocarbyl substituted imidazolium halide, trialkylammonium hydrohalide or  
 16 tetraalkylammonium halide of the general formulas A, B, C and D, respectively.



17  
 18  
 19  
 20  
 21 where  $\text{R}=\text{H}$ , methyl, ethyl, propyl, butyl, pentyl or hexyl group and  $\text{X}$  is a halide and  
 22 preferably a chloride, and  $\text{R}_1$  and  $\text{R}_2=\text{H}$ , methyl, ethyl, propyl, butyl, pentyl or hexyl  
 23 group and where  $\text{R}_1$  and  $\text{R}_2$  may or may not be the same, and  $\text{R}_3$ ,  $\text{R}_4$ , and  $\text{R}_5$  and  
 24  $\text{R}_6=\text{methyl}$ , ethyl, propyl, butyl, pentyl or hexyl group and where  $\text{R}_3$ ,  $\text{R}_4$ ,  $\text{R}_5$  and  $\text{R}_6$   
 25 may or may not be the same.  
 26

1 The acidic ionic liquid is preferably selected from the group consisting of 1-butyl-4-  
2 methyl-pyridinium chloroaluminate, 1-butyl-pyridinium chloroaluminate, 1-butyl-3-  
3 methyl-imidazolium chloroaluminate and 1-H-pyridinium chloroaluminate.

4  
5 In a process according to the invention an alkyl halide is used as a promoter. This may  
6 be done by, for example, introducing a catalytically effective amount of an  
7 appropriate alkyl halide to the reaction mixture as a component of the feed stream or  
8 by introducing it directly into the ionic liquid catalyst. The alkyl halide acts to  
9 promote the alkylation by reacting with aluminum chloride to form the prerequisite  
10 cation ions in similar fashion to the Friedel-Crafts reactions. The alkyl halides that  
11 may be used include alkyl bromides, alkyl chlorides and alkyl iodides. A variety of  
12 alkyl halides may be used, but alkyl halide derivatives of the isoparaffins or the  
13 olefins that comprise the feed streams in the alkylation process are preferable. Such  
14 alkyl halides include but are not limited to isopentyl halides, isobutyl halides, butyl  
15 halides, propyl halides and ethyl halides. Alkyl chloride versions of these alkyl  
16 halides are preferable when chloroaluminate ionic liquids are used as the catalyst  
17 systems. Other alkyl chlorides or halides having from 1 to 8 carbon atoms may be  
18 also used. The alkyl halides may be used alone or in combination.

19  
20 For chloroaluminate ionic liquids, the alkyl halide is preferably an alkyl chloride such  
21 as ethyl chloride, tertiary butyl chloride, isopentyl chloride or butyl chlorides. The  
22 alkyl chlorides of choice are those derived from the isoparaffin and olefins used in a  
23 given alkylation reaction. For the alkylation of isobutane with butenes in  
24 chloroaluminate ionic liquids, for example, the preferable alkyl halides would be 1-  
25 butyl chloride, 2-butyl chloride or tertiary butyl chloride or a combination of these  
26 chlorides. Most preferably, the alkyl chloride is a derivative of the olefin stream to  
27 invoke hydride transfer and the participation of the isoparaffin. The alkyl halides are  
28 used in catalytic amounts. Ideally, the amounts of the alkyl halides should be kept at  
29 low concentrations and not exceed the molar concentration of the catalyst  $\text{AlCl}_3$ . The  
30 amounts of the alkyl halides used may range from 0.05 mol%-100 mol% of the Lewis  
31 acid  $\text{AlCl}_3$ . Concentrations of the alkyl halides in the range of 0.05 mol%-10 mol%  
32 of the  $\text{AlCl}_3$  are preferable in order to keep the acidity of the catalyst at the desired

1 performing capacity. Also, the amount of the alkyl halide should be proportional to  
2 the olefin and not exceed the molar concentration of the olefin.

3  
4 Without being bound to any theory, when ethyl chloride, for example is added to  
5 acidic chloroaluminate ionic liquids, ethyl chloride reacts with  $\text{AlCl}_3$  to form  
6 tetrachloroaluminate ( $\text{AlCl}_4^-$ ) and ethyl cation. Hydride shift from the isoparaffin  
7 (isopentane or isobutane) to the generated ethyl cation leads to the tertiary cation  
8 which propagates the inclusion of the isoparaffin in the reaction and, hence, the  
9 alkylation pathway.

10  
11 A metal halide may be employed to modify the catalyst activity and selectivity. The  
12 metal halides most commonly used as inhibitors/modifiers in aluminum chloride-  
13 catalyzed olefin-isoparaffin alkylations include  $\text{NaCl}$ ,  $\text{LiCl}$ ,  $\text{KCl}$ ,  $\text{BeCl}_2$ ,  $\text{CaCl}_2$ ,  
14  $\text{BaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{PbCl}_2$ ,  $\text{CuCl}$ ,  $\text{ZrCl}_4$  and  $\text{AgCl}$ , as described by Roebuck and  
15 Evering (Ind. Eng. Chem. Prod. Res. Develop., Vol. 9, 77, 1970). Preferred metal  
16 halides are  $\text{CuCl}$ ,  $\text{AgCl}$ ,  $\text{PbCl}_2$ ,  $\text{LiCl}$ , and  $\text{ZrCl}_4$ .

17  
18  $\text{HCl}$  or any Brønsted acid may be employed as co-catalyst to enhance the activity of  
19 the catalyst by boosting the overall acidity of the ionic liquid-based catalyst. The use  
20 of such co-catalysts and ionic liquid catalysts that are useful in practicing the present  
21 invention is disclosed in U.S. Published Patent Application Nos. 2003/0060359 and  
22 2004/0077914. Other co-catalysts that may be used to enhance the activity include  
23 IVB metal compounds preferably IVB metal halides such as  $\text{ZrCl}_4$ ,  $\text{ZrBr}_4$ ,  $\text{TiCl}_4$ ,  
24  $\text{TiCl}_3$ ,  $\text{TiBr}_4$ ,  $\text{TiBr}_3$ ,  $\text{HfCl}_4$ ,  $\text{HfBr}_4$  as described by Hirschauer et al. in U.S. Patent No.  
25 6,028,024.

26  
27 Due to the low solubility of hydrocarbons in ionic liquids, olefins-isoparaffins  
28 alkylation, like most reactions in ionic liquids is generally biphasic and takes place at  
29 the interface in the liquid state. The catalytic alkylation reaction is generally carried  
30 out in a liquid hydrocarbon phase, in a batch system, a semi-batch system or a  
31 continuous system using one reaction stage as is usual for aliphatic alkylation. The  
32 isoparaffin and olefin can be introduced separately or as a mixture. The molar ratio  
33 between the isoparaffin and the olefin is in the range 1 to 100, for example,

1 advantageously in the range 2 to 50, preferably in the range 2 to 20. In a semi-batch  
2 system the isoparaffin is introduced first then the olefin, or a mixture of isoparaffin  
3 and olefin. Catalyst volume in the reactor is in the range of 2 vol% to 70 vol%,  
4 preferably in the range of 5 vol% to 50 vol%. Vigorous stirring is desirable to ensure  
5 good contact between the reactants and the catalyst. The reaction temperature can be  
6 in the range -40°C to +150°C, preferably in the range -20°C to +100°C. The pressure  
7 can be in the range from atmospheric pressure to 8000 kPa, preferably sufficient to  
8 keep the reactants in the liquid phase. Residence time of reactants in the vessel is in  
9 the range a few seconds to hours, preferably 0.5 min to 60 min. The heat generated  
10 by the reaction can be eliminated using any of the means known to the skilled person.  
11 At the reactor outlet, the hydrocarbon phase is separated from the ionic phase by  
12 decanting, then the hydrocarbons are separated by distillation and the starting  
13 isoparaffin which has not been converted is recycled to the reactor.

14  
15 Typical alkylation conditions may include a catalyst volume in the reactor of from 5  
16 vol% to 50 vol%, a temperature of from -10°C to +100°C, a pressure of from 300 kPa  
17 to 2500 kPa, an isopentane to olefin molar ratio of from 2 to 8 and a residence time of  
18 5 min to 1 hour.

19  
20 In one embodiment of a process according to the present invention, high quality  
21 gasoline blending components of low volatility are recovered from the alkylation  
22 zone. Those blending components are then preferably blended into gasoline.

23  
24 The following Examples are illustrative of the present invention, but are not intended  
25 to limit the invention in any way beyond what is contained in the claims which  
26 follow.

27

EXAMPLES

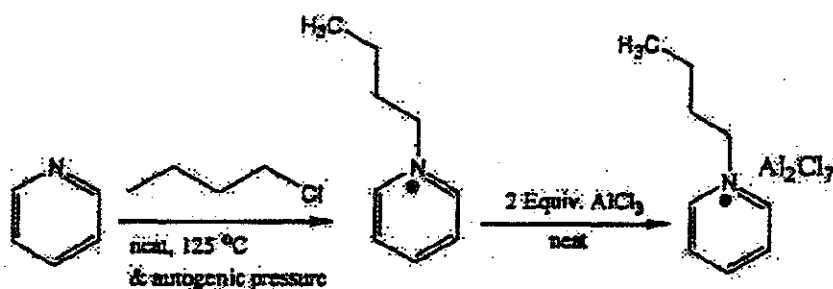
Example 1 Preparation of Fresh 1-Butylpyridinium Chloroaluminate Ionic Liquid  
Catalyst A (Fresh IL-A)

1-butyl-pyridinium chloroaluminate is a room temperature ionic liquid prepared by mixing neat 1-butyl-pyridinium chloride (a solid) with neat solid aluminum trichloride in an inert atmosphere. The syntheses of butylpyridinium chloride and the corresponding 1-butyl-pyridinium chloroaluminate are described below.

In a 2-L Teflon-lined autoclave, 400 gm (5.05 mol.) anhydrous pyridine (99.9% pure purchased from Aldrich) were mixed with 650 gm (7 mol.) 1-chlorobutane (99.5% pure purchased from Aldrich). The autoclave was sealed and the neat mixture was allowed to stir at 125°C under autogenic pressure over night. After cooling off the autoclave and venting it, the reaction mix was diluted and dissolved in chloroform and transferred to a three liter round bottom flask. Concentration of the reaction mixture at reduced pressure on a rotary evaporator (in a hot water bath) to remove excess chloride, un-reacted pyridine and the chloroform solvent gave a tan solid product. Purification of the product was done by dissolving the obtained solids in hot acetone and precipitating the pure product through cooling and addition of diethyl ether. Filtering and drying under vacuum and heat on a rotary evaporator gave 750 gm (88% yields) of the desired product as an off-white shiny solid. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were consistent with the desired 1-butyl-pyridinium chloride and no impurities were observed.

1-butylpyridinium chloroaluminate was prepared by slowly mixing dried 1-butylpyridinium chloride and anhydrous aluminum chloride (AlCl<sub>3</sub>) according to the following procedure. The 1-butylpyridinium chloride (prepared as described above) was dried under vacuum at 80°C for 48 hours to get rid of residual water (1-butylpyridinium chloride is hygroscopic and readily absorbs water from exposure to air). Five hundred grams (2.91 mol.) of the dried 1-butylpyridinium chloride were transferred to a 2-Liter beaker in a nitrogen atmosphere in a glove box. Then, 777.4 gm (5.83 mol.) of anhydrous powdered AlCl<sub>3</sub> (99.99% from Aldrich) were added in

1 small portions (while stirring) to control the temperature of the highly exothermic  
 2 reaction. Once all the  $\text{AlCl}_3$  was added, the resulting amber-looking liquid was left to  
 3 gently stir overnight in the glove box. The liquid was then filtered to remove any  
 4 un-dissolved  $\text{AlCl}_3$ . The resulting acidic 1-butyl-pyridinium chloroaluminate was  
 5 used as the catalyst for the alkylation of isopentane with ethylene.



10 **Example 2** Alkylation of isopentane with Ethylene without the presence of a  
 11 promoter

12

13 A 0.3L (300 cc) autoclave was charged with 40 gm of ionic liquid catalyst, 100 gm  
 14 anhydrous isopentane and 10 gm ethylene. The reaction was then stirred at ~1200 rpm  
 15 and heated to 50°C at autogenic pressures. The starting pressure was  $1.99 \times 10^3$  kPa (288 psig). The  
 16 reaction was allowed to run until the pressure dropped down into the single digits  
 17 range 34.5 kPa (5 psig). In this case after 28 minutes reaction time). In the case of slow going  
 18 reaction, the reaction was allowed to run for 1hr long. At the end of the reaction, the  
 19 reactor was vented out and a gas sample was checked by GC for ethylene  
 20 concentration. The liquid reaction mixture was allowed to settle into 2 phases. The  
 21 organic phase was decanted and analyzed for product distribution by GC analysis.  
 22 The reaction results are shown in Table 1.

23

1 Example 3 Alkylation of isoPentane with Ethylene in the Presence of HCl as Co-  
2 catalyst.

3  
4 Table 1 below shows the results of the alkylation of ethylene with isopentane in the  
5 presence of ethyl chloride and in the presence of isopentyl chloride. The alkylation of  
6 isopentane with ethylene was done according to the following procedure.

7  
8 A 0.3L (300 cc) autoclave was charged with 40 gm of ionic liquid catalyst, 100 gm  
9 anhydrous isopentane, 10 gm ethylene, and 0.35 gm of anhydrous HCl. The reaction  
10 was then stirred at ~1200 rpm and heated to 50°C at autogenic pressures. The starting  
11 pressure was  $2.21 \times 10^3$  kPa (320 psig). The reaction was allowed to run until the pressure dropped  
12 down into the single digits range 62.1 kPa (9 psig) in this case after 4 minutes reaction time). In  
13 the case of slow going reaction, the reaction was allowed to run for 1hr long. At the  
14 end of the reaction, the reactor was vented out and a gas sample was checked by GC  
15 for ethylene concentration. The liquid reaction mixture was allowed to settle into 2  
16 phases. The organic phase was decanted and analyzed for product distribution by GC  
17 analysis. The reaction results are shown in Table 1.

18  
19 Example 4 Alkylation of isoPentane with Ethylene in the Presence of  
20 Chloroethane as a Promoter

21  
22 The reaction described in Example 3 was repeated but chloroethane ( $\text{CH}_3\text{CH}_2\text{Cl}$ ) was  
23 added in place of hydrochloric acid (HCl). The reaction was run on 100 gm  
24 isopentane, 10 gm ethylene and 0.9 gm chloroethane in 40 gm 1-butylpyridinium  
25 chloroaluminate ionic liquid catalyst. The use of chloroethane was as effective as  
26 using HCl in the reaction. Table 1 summarizes the reaction results and conditions.

27  
28 Example 5 Alkylation of Isopentane with Ethylene in the Presence of 2-Chloro-2-  
29 methylButane (Isopentyl Chloride) as Promoter

30  
31 The reaction described in Example 4 was repeated but isopentyl chloride was added in  
32 place of chloroethane. The reaction was run on 100 gm isopentane, 10 gm ethylene  
33 and 1.2 gm of isopentyl chloride in 40 gm 1-butylpyridinium chloroaluminate ionic

liquid catalyst. Isopentyl chloride appeared to be more effective than chloroethane and HCl in the alkylation of isopentane with ethylene. The reaction was extremely exothermic and there was no need to raise the reaction temperature to 50°C (reaction temperature). The pressure dropped instantaneously to the single digit mark from starting pressure of  $2.32 \times 10^3$  kPa (337 psig). Table 1 summarizes the reaction results and conditions.

As shown in Table 1, when ethyl chloride or isopentyl chloride was added, the reaction time was noticeably shortened. The alkylation in the presence of isopentyl chloride was much quicker (almost instantaneous). The reactions were highly exothermic and there was no need to heat them up. The experimental results clearly indicate the very profound effect the addition of alkyl chlorides has on the progress of alkylations in ionic liquids.

|                | No HCl or R-Cl                       | W/HCl                                | W/Ethyl-Cl                           | W/Isopentyl-Cl                       |
|----------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| Start Pressure | $1.99 \times 10^3$ kPa<br>(288 psig) | $1.65 \times 10^3$ kPa<br>(240 psig) | $2.28 \times 10^3$ kPa<br>(331 psig) | $2.32 \times 10^3$ kPa<br>(337 psig) |
| End Pressure   | 34.5 kPa<br>(5 psig)                 | 75.8 kPa<br>(11 psig)                | 62.1 kPa<br>(9 psig)                 | 48.3 kPa<br>(7 psig)                 |
| Reaction Time  | 28 min                               | 4 min                                | 6 min                                | 2 min                                |
| % Selectivity  |                                      |                                      |                                      |                                      |
| C3-            | 0.04                                 | 0                                    | 0.01                                 | 0                                    |
| C4             | 0.86                                 | 1.88                                 | 1.93                                 | 4.97                                 |
| C5             | 67.78                                | 67.7                                 | 62.79                                | 65.53                                |
| C6             | 1.14                                 | 2.6                                  | 2.44                                 | 5.19                                 |
| C7             | 22.33                                | 19.32                                | 22.53                                | 14.78                                |
| C8             | 2.94                                 | 3.25                                 | 3.68                                 | 3.27                                 |
| C9             | 2.41                                 | 2.12                                 | 2.93                                 | 2.65                                 |
| C10            | 1.5                                  | 1.59                                 | 1.78                                 | 1.64                                 |
| C11            | 0.5                                  | 0.8                                  | 0.93                                 | 0.95                                 |
| C12+           | 0.5                                  | 0.75                                 | 0.98                                 | 1.02                                 |
| Total          | 100                                  | 100                                  | 100                                  | 100                                  |

Table 1

1 The alkylations in the previous Examples were done using pure isopentane feeds.  
2 Table 2 shows a comparison between different catalyst schemes in the alkylation of  
3 refinery pentanes with ethylene using HCl, water or ethyl chloride as promoters.  
4 Analysis of the refinery pentanes showed the feed stock to contain 86.4% iso-pentane,  
5 8% n-pentane, 0.9% n-butane, 3.4% C<sub>6</sub>S-C<sub>6</sub>S and 0.2% olefins (C<sub>4</sub> and C<sub>5</sub> olefins).  
6 The refinery pentane stream also contained 88ppm sulfur (as mercaptans) and 0.4ppm  
7 nitrogen. The reactions were done as described in Examples 6, 7, 8 and 9.

8  
9 Example 6 Alkylation of Refinery Pentanes with Ethylene in 1-Butylpyridinium  
10 Chloroaluminate-No Promoters

11  
12 The refinery isopentane feed with specs described earlier was dried with over a  
13 molecular sieve to remove any residual water. Then, 101 gm of the dried feed was  
14 with 10 gm of pure ethylene in 42 gm ionic liquid catalyst according to the procedure  
15 described in Example 1. Table 2 summarizes the reaction and the results.

16  
17 Example 7 Alkylation of Refinery Pentanes with Ethylene in 1-Butylpyridinium  
18 Chloroaluminate-with HCl as Promoter

19  
20 Using the procedure described in Example 3, dried 101 gm of refinery isopentane feed  
21 with the specs described earlier was alkylated with 10 gm of pure ethylene in 42 gm  
22 ionic liquid catalyst in the presence of 0.6 gm HCl. Table 2 summarizes the reaction  
23 and the results.

24  
25 Example 8 Alkylation of Refinery Pentanes with Ethylene in 1-Butylpyridinium  
26 Chloroaluminate-with H<sub>2</sub>O as Promoter

27  
28 Using the procedure described in Example 3, 101 gm of the dried refinery isopentane  
29 feed with the specs described earlier was alkylated with 10 gm of pure ethylene in 42  
30 gm ionic liquid catalyst 0.1 gm water. Table 2 summarizes the reaction and the  
31 results.

32

1 Example 9 Alkylation of Refinery Pentanes with Ethylene in 1-Butylpyridinium  
2 Chloroaluminate with Ethyl Chloride as Promoter

3

4 Using the procedure described in Example 3, 101 gm of the dried refinery isopentane  
5 feed with the specs described earlier was alkylated with 10 gm of pure ethylene in 42  
6 gm ionic liquid catalyst 1gm of ethyl chloride. Table 2 summarizes the reaction and  
7 the results.

8

9 Table 2 summarizes the results of alkylations of refinery isopentane feed with pure  
10 ethylene described in Examples 6, 7, 8 and 9.

11

|                  | Ref. Feed<br>No HCl or<br>R-Cl         | Ref feed<br>W/HCl                      | Ref Feed<br>W/Ethyl-Cl                 | Ref Feed<br>W/H <sub>2</sub> O         |
|------------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| Start Pressure   | 1.56X10 <sup>3</sup> kPa<br>(226 psig) | 1.72X10 <sup>3</sup> kPa<br>(249 psig) | 2.03X10 <sup>3</sup> kPa<br>(295 psig) | 2.16X10 <sup>3</sup> kPa<br>(313 psig) |
| End Pressure     | 717 kPa<br>(104 psig)                  | 68.9 kPa<br>(10 psig)                  | 89.6 kPa<br>(13 psig)                  | 103 kPa<br>(15 psig)                   |
| Reaction<br>Time | 64 min.                                | 19 min.                                | 24 min.                                | 28 min.                                |
| %Selectivity     |                                        |                                        |                                        |                                        |
| C3-              | 0.21                                   | 0.07                                   | 0.05                                   | 0.19                                   |
| C4               | 0.77                                   | 1.19                                   | 1.39                                   | 1.27                                   |
| C5               | 81.34                                  | 69.35                                  | 62.69                                  | 68.93                                  |
| C6               | 2.82                                   | 3.06                                   | 3.87                                   | 2.97                                   |
| C7               | 8.74                                   | 18.36                                  | 21.03                                  | 18.18                                  |
| C8               | 3                                      | 3.8                                    | 5.05                                   | 3.93                                   |
| C9               | 1.41                                   | 2.02                                   | 2.55                                   | 2.14                                   |
| C10              | 0.82                                   | 1.26                                   | 1.70                                   | 1.24                                   |
| C11              | 0.37                                   | 0.42                                   | 0.83                                   | 0.53                                   |
| C12+             | 0.53                                   | 0.48                                   | 0.84                                   | 0.61                                   |
| Total            | 100                                    | 100                                    | 100                                    | 100                                    |

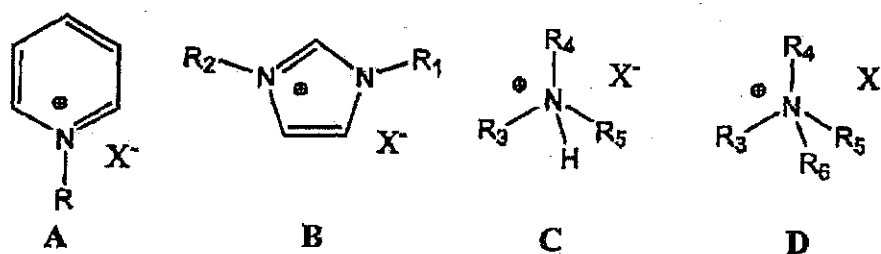
12 Table 2(Aikylation of Refinery Feed in Butylpyridinium Chloride-2AlCl<sub>3</sub>/EtCl)

13

- 1 There are numerous variations on the present invention which are possible in light of
- 2 the teachings and supporting examples described herein. It is therefore understood
- 3 that within the scope of the following claims, the invention may be practiced
- 4 otherwise than as specifically described or exemplified herein.

# WHAT IS CLAIMED IS:

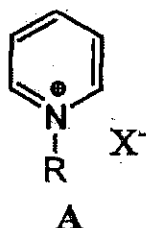
1. An alkylation process comprising contacting a hydrocarbon mixture comprising at least one olefin having from 2 to 6 carbon atoms and at least one isoparaffin having from 4 to 6 carbon atoms under alkylation conditions including an isopentane to olefin molar ratio of from 2 to 8, in the presence of an acidic ionic liquid catalyst in an alkylation zone, said catalyst comprising a mixture of at least one acidic ionic liquid and at least one alkyl halide; wherein the at least one olefin and the at least one isoparaffin are alkylated.
2. The process according to claim 1, where the acidic ionic liquid is a chloroaluminate ionic liquid prepared by mixing aluminum trichloride ( $\text{AlCl}_3$ ) and a hydrocarbyl substituted pyridinium halide, a hydrocarbyl substituted imidazolium halide, trialkylammonium hydrohalide or tetraalkylammonium halide of the general formulas A, B, C and D, respectively,



where R=H, methyl, ethyl, propyl, butyl, pentyl or hexyl group and X is a halide, and R<sub>1</sub> and R<sub>2</sub>=H, methyl, ethyl, propyl, butyl, pentyl or hexyl group and where R<sub>1</sub> and R<sub>2</sub> may or may not be the same, and R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> and R<sub>6</sub>=methyl, ethyl, propyl, butyl, pentyl or hexyl group where R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> and R<sub>6</sub> may or may not be the same.

3. The process according to claim 1, wherein the acidic ionic liquid 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) and 1-H-pyridinium chloroaluminate (HP).

4. An alkylation process comprising contacting a hydrocarbon mixture comprising at least one olefin having 2 to 6 carbon atoms and at least one isoparaffin having from 4 to 6 carbon atoms under alkylation conditions in the presence of an acidic ionic liquid catalyst in an alkylation zone, said catalyst comprising a mixture of at least one acidic ionic liquid and at least one alkyl halide; wherein the acidic ionic liquid is a chloroaluminate ionic liquid prepared by mixing aluminium trichloride ( $\text{AlCl}_3$ ) and a hydrocarbyl substituted pyridinium halide having the general formula A:



- where R=H, methyl, ethyl, propyl, butyl, pentyl or hexyl group and X is a halide; wherein the isoparaffin and the olefin having 2 to 6 carbon atoms are alkylated; and wherein the alkylation conditions include an isopentane to olefin molar ratio of from 2 to 8.
5. The process according to claim 1 or claim 4, wherein the catalyst further comprises an HCl co-catalyst.
6. The process according to claim 1 or claim 4, wherein the isoparaffin is selected from the group consisting of isobutane, isopentanes and mixtures thereof.
7. The process according to claim 1 or claim 4, wherein the olefin is selected from the group consisting of ethylene, propylene, butylenes, pentenes and mixtures thereof.
8. The process according to claim 1 or claim 4, wherein the alkylation conditions include a catalyst volume in the reactor 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, and a residence time of 1 minute to 1 hour.

9. The process according to claim 1 or claim 4, further comprising blending said components into gasoline.
10. The process according to claim 1 or claim 4, wherein the alkyl halide has from 1 to 8 carbon atoms.
11. The process according to claim 10, where the alkyl halide is selected from the group consisting of methyl halide, ethyl halide, propyl halide, 1-butyl halide, 2-butyl halide, tertiary butyl halide, pentyl halides, isopentyl halide, hexyl halides, isohexyl halides, heptyl halides, isoheptyl halides, octyl halides and isooctyl halides.
12. The process according to claim 10, where the alkyl halide is selected from the group consisting of alkyl bromides, alkyl iodides, and alkyl chlorides.
13. The process according to claim 2, wherein the acidic ionic liquid is selected from the group consisting of 1-butyl-pyridinium chloroaluminate (BP), and 1-H-pyridinium chloroaluminate (HP).
14. The alkylation process of claim 1 or claim 4, wherein the halide is chloride.