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(54) **CATALYTIC DISPROPORTIONATION OF BUTANE USING IONIC LIQUIDS**

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(57) **ABSTRACT**

Processes for the disproportionation and isomerization of a C_4 hydrocarbon feed using a liquid catalyst comprising an ionic liquid and a carbocation promoter are described. The ionic liquid is unsupported, and the reactions occur at temperatures below about 300° C.

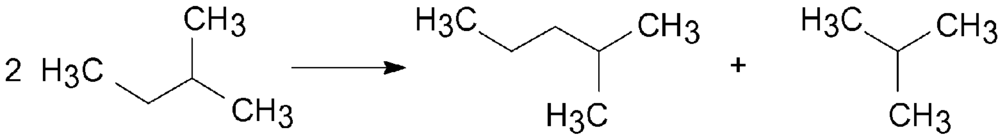


FIG. 1

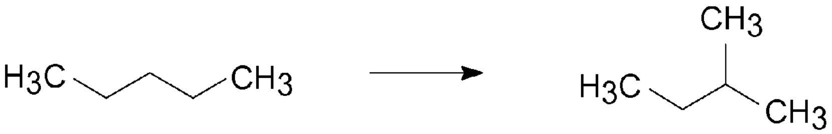


FIG. 2

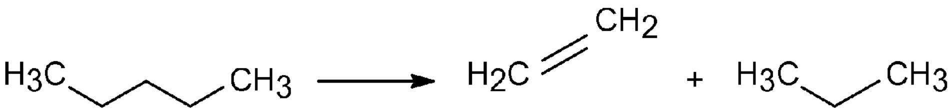
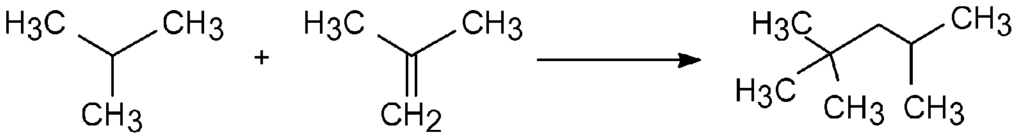


FIG. 3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CH3
+
H3C
CH3
CH2
H3C
CH3
H3C
CH3
CH3

FIG. 4

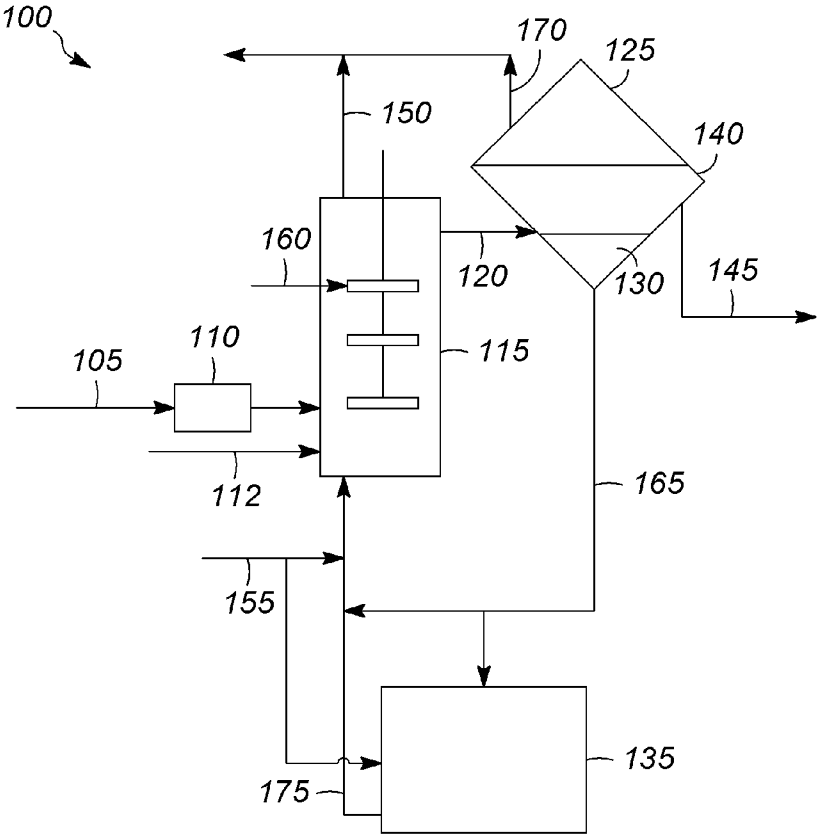

100
170
125
150
140
160
120
130
145
110
115
105
112
165
155
135
175

FIG. 5

CATALYTIC DISPROPORTIONATION OF BUTANE USING IONIC LIQUIDS

[0001] This application claims the benefit of Provisional Application Ser. No. 61/841,266, entitled METHOD FOR TUNING PRODUCT COMPOSITION BASED ON VARYING TYPES AND RATIOS OF FEED, filed Jun. 28, 2013, which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] The Reid vapor pressure (RVP) of gasoline has been utilized by the Environmental Protection Agency as a means of regulating volatile organic compounds emissions by transportation fuels and for controlling the formation of ground level ozone. As these regulations become more stringent and as more ethanol (which has a high vapor pressure) is blended into gasoline, C_5 paraffins need to be removed from the gasoline pool. Moreover, the need to remove components may also extend to some C_6 paraffins. This may result in refiners being oversupplied with C_5 paraffins and possibly C_6 paraffins.

[0003] Disproportionation reactions offer a possible solution to this problem. The disproportionation of paraffins (e.g., isopentane (iC_5)) involves reacting two moles of hydrocarbon to form one mole each of two different products, one having a carbon count greater than the starting material and the other having a carbon count less than the starting material, as shown in FIG. **1**. The total number of moles in the system remains the same throughout the process, but the products have different carbon counts from the reactants. Additional secondary disproportionation-type reactions can occur in which two hydrocarbons having different carbon numbers react to form two different hydrocarbons having different carbon numbers from those of the feed where the total number of carbons in the products does not change from the total number in the feed (e.g., pentane and octane reacting to form hexane and heptane).

[0004] There are a number of different catalysts that have been shown to produce the desired paraffin disproportionation reaction, including zeolites, sulfated zirconias, $AlCl_2/SiO_2$, ionic solids, platinum on chlorided Al_2O_3/Ga_2O_3 supports, supported ionic liquids, $Pt/W/Al_2O_3$ and HF/TiF_4. However, these processes have a number of disadvantages. The processes using zeolites, sulfated zirconias, $AlCl_2/SiO_2$, ionic solids, and platinum on Al_2O_3/Ga_2O_3 supports require elevated temperatures (e.g., 120-450° C.) to carry out the transformation. The HF/TiF_4 system is capable of disproportionation at 51° C., but it utilizes dangerous HF. The supported ionic liquid is active from about 85-125° C. and is composed of the Brønsted acidic trimethylammonium cation. Since the ionic liquid's organic cation is composed of this Brønsted acid, the acid concentration within this catalyst is stoichiometric with respect to the ionic liquid and quite high. Moreover, the supported ionic liquid is deactivated by leaching of the ionic liquid from the support. Additionally, the use of a support increases the cost of the catalyst and may result in a chemical reaction of the support with the acidic ionic liquid over time, as happens when $AlCl_3$ is immobilized on silica.

[0005] Isomerization processes have been used to improve the low octane numbers (RON) of light straight run naphtha. Isomerization processes involve reacting one mole of a hydrocarbon (e.g., normal pentane) to form one mole of an isomer of that specific hydrocarbon (e.g., isopentane), as shown in FIG. **2**. The total number of moles remains the same throughout this process, and the product has the same number of carbons as the reactant.

[0006] Current isomerization processes use chlorided alumina, sulfated zirconia, or zeolites in conjunction with platinum. Process temperatures range from about 120° C. for chlorided alumina up to about 260° C. for zeolite type catalysts. These reactions are run at temperatures which allow the feed to reach equilibrium. At lower temperatures, the equilibrium favors the branched isomers possessing the higher octane number. Isomerization processes utilizing ionic liquids have been developed. For example, US 2003/019767 describes an isomerization process for a paraffin hydrocarbon feed using an ionic liquid as a catalyst. The ionic liquid is formed from an N-containing heterocyclic and/or N-containing aliphatic organic cation and an inorganic anion derived from metal halides. The examples show a catalyst:hydrocarbon weight ratio of 1:1 or 1.5:1. The hydrocarbon feeds examined were normal pentane, normal heptane, normal octane, and 3-methylhexane.

[0007] US 2004/059173 teaches an isomerization process for linear and/or branched paraffin hydrocarbons. The catalyst comprises an ionic liquid. Over 25 wt % of a cyclic hydrocarbon additive is included. The ionic liquid is formed from an N-containing heterocyclic and/or N-containing aliphatic organic cation and an inorganic anion derived from metal halides. The ionic liquid:hydrocarbon ratio in the examples is fixed at 1:1 volume ratio. Metal salt additives or Brønsted acids can be included. The feed is a mixture of C_7 hydrocarbons.

[0008] U.S. Pat. No. 7,053,261 discusses isomerization of linear and/or branched paraffin hydrocarbons using an ionic liquid catalyst in combination with a metal salt additive. The ionic liquid is formed from an N-containing heterocyclic and/or N-containing aliphatic organic cation and an inorganic anion derived from metal halides. The ionic liquid:hydrocarbon ratio in the examples is fixed at 1:1 volume ratio. The results of the gas chromatograph on the paraffin phase were not reported. The feed is a mixture of C_7 hydrocarbons.

[0009] All of these references describe isomerization of the feed; none describes disproportionation reactions. All of the references describe the use of ionic liquids having an acid concentration of at least about 3.0 M. The Brønsted acidic ionic liquid used in US Publication 2003/0109767 was [trimethylammonium][Al_2Cl_7], which has a molar concentration of HCl that ranges from 3.0-4.1 M if the density is in the range of 1.1 to 1.5 g/mL. For US Publications 2004/0059173 and U.S. Pat. No. 7,053,261 the Brønsted acidic ionic liquid used was [trimethylammonium][$Al_{1.8}Cl_{6.4}$], which has a molar concentration of HCl that ranges from 3.3-4.5 M if the density is in the range of 1.1 to 1.5 g/mL. These estimated densities are within the ranges measured for similar ionic liquids.

[0010] None of the references indicate the composition of the product mixture; as a result, it is unclear what was actually formed in the reactions. Assuming that all of the other products were disproportionation products (which is unlikely to be correct as Ibragimov et al. teach that cracking occurs in addition to disproportionation (see below), but it sets an upper limit on the greatest possible conversion, yield, etc. for the disproportionation products). The conversion rates corrected for mass or volume were calculated as follows: using the reported iso-selectivity, the selectivity to other compounds was calculated as (100-iso-selectivity). The % conversion was determined from the reported %-iso yield and % iso-selectivity. The % conversion thus determined was used to determine the reaction rate by the following formula: volume rate=(% conversion/time (h))×(mL HC/mL IL) or as mass rate=(% conversion/time (h))×(g HC/g IL). The % conversion was then used with the computed selectivity to other compounds to set an upper limit on the yield of disproportionation products. The yield of the other compounds and yield of isomers was then calculated using the calculated selectivity to other compounds and the total yield. Since the reaction rate is dependent on the ratio of ionic liquid:hydrocarbon, the rates were corrected according to these ratios.

[0011] With respect to US 2003/0109767, the corrected conversion rates for mass were very low. For n-C_5, the corrected conversion rate for mass ranged was between 3.5 and 18.2. For n-C_7, it ranged from 2.6 to 9.3, for n-C_8, it was 3.3, and for 3-methylhexane, it was 4.7. For US 2005/059173, the corrected conversion rates for volume ranged from 0.6 to 47.1 for the C_7 mixture. For U.S. Pat. No. 7,053,261, the corrected conversion rates for volume ranged from 5.4 to 371.3 in the presence of an additional metal salt.

[0012] Isomerization is also described in "Isomerization of Light Alkanes Catalysed by Ionic Liquids: An Analysis of Process Parameters," Ibragimov et al., Theoretical Foundations of Chemical Engineering (2013), 47(1), 66-70. The desired reaction is stated to be isomerization, and the main isomerization products from n-hexane are said to isobutane, isopentane, and hexane isomers. However, isobutane and isopentane are not the isomerization products of n-hexane as isomerization has been defined above. In addition, the article discusses the fact that a significant amount of an undesirable disproportionation reaction begins to occur after about 2-3 hrs. The article indicates that the disproportionation reaction dominates when the ratio of catalyst to hydrocarbon ratio is 2:1, and that cracking and disproportionation dominate at 333K. Because cracking is occurring, the number of moles formed is increased. The optimum isomerization temperature was 303K. The maximum volume rate they obtained was 26 at their high mixing speeds (900 rpm or more) at 0.5 hr.

[0013] Some processes involve isomerization and then a cracking reaction in which one mole of a hydrocarbon forms two moles of product, each with a lower carbon number than the starting material. In FIG. **3**, the products are illustrated as an alkene and an alkane. Additionally, the total number of moles increases throughout the process.

[0014] Alkylation processes involving ionic liquids are also known. In alkylation reactions, one mole of an alkane and one mole of an alkene react to form one mole of an alkane having a carbon number equal to the sum of the carbon numbers of the starting alkane and alkene, as shown in FIG. **4**. In an alkylation process, the total number of moles in the system is reduced.

[0015] There is a need for improved processes for disproportionation and isomerization of hydrocarbons.

SUMMARY OF THE INVENTION

[0016] One aspect of the invention is a hydrocarbon conversion process. In one embodiment, the process includes disproportionating a hydrocarbon feed comprising normal C_4 alkane or branched C_4 alkane by contacting the hydrocarbon feed with a liquid catalyst in a reaction zone under disproportionation conditions to form a product mixture comprising at least about 0.2 wt % C_3— alkanes and C_{5+} alkanes in 1 hr based on the C_4 alkanes in the hydrocarbon feed, wherein the liquid catalyst comprises an unsupported ionic liquid and a carbocation promoter, and wherein a mass ratio of liquid catalyst to hydrocarbon feed is less than 0.75:1.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG. **1** illustrates the disproportionation reaction of iso-pentane.

[0018] FIG. **2** illustrates the isomerization reaction of n-pentane.

[0019] FIG. **3** illustrates a cracking reaction of n-pentane.

[0020] FIG. **4** illustrates an alkylation reaction of isobutane and isobutene.

[0021] FIG. **5** is a schematic of one embodiment of the process of present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0022] A process for the disproportionation and/or isomerization of a hydrocarbon feed using a liquid catalyst comprising ionic liquids and carbocation promoters is described. The ionic liquids are unsupported and allow the reactions to occur at temperatures below about 300° C.

[0023] The disproportionation reaction involves contacting a hydrocarbon feed comprising a C_n alkane with a liquid catalyst in a reaction zone to form a product mixture containing C_{n-} alkanes and C_{n+} alkanes, wherein the liquid catalyst comprises an unsupported ionic liquid and a carbocation promoter, and wherein n=4-12.

[0024] The isomerization reaction involves contacting the hydrocarbon feed comprising a normal C_n alkane (or iso C_n alkane) with a liquid catalyst in a reaction zone to form a product mixture containing iso C_n alkanes (or normal C_n alkanes), wherein the liquid catalyst comprises an unsupported ionic liquid and a carbocation promoter, and wherein n=4-12.

[0025] Disproportionation and isomerization occur simultaneously. There is a substantial disproportionation reaction for some hydrocarbon, which can be seen by the fact that significant amounts of C_{n+} and C_{n-} alkanes form. In some embodiments, the product mixture can contain at least about 3 wt % C_{n+} alkanes in 1 hr based on the C_n alkane fraction in the hydrocarbon feed, or at least 5 wt %, or at least about 7 wt %, or at least about 10%, or at least about 15 wt %, or at least about 20 wt %. There is a corresponding formation of the C_{n-} fraction. There can be at least about 3 wt % C_{n-} alkanes in 1 hr based on the C_n alkane fraction in the hydrocarbon feed, or at least 5 wt %, or at least about 7 wt %, or at least about 10%, or at least about 15 wt %, or at least about 20 wt %. The percentages are based on the C_n alkane fraction in the hydrocarbon feed.

[0026] It is more complex to evaluate the C_{n+} and C_{n-} fractions when the feed comprises more than one C_n alkane. When the feed comprises more than one C_n alkane, the amount of C_{n+} alkane based on the highest carbon number in the feed can be used. For example if, the feed comprises C_5 and C_6, the amount of C_{n+} can be evaluated using the C_7 fraction. When the feed comprises C_5 and C_8, the increase may be evaluated using the C_9 fraction.

[0027] For a feed comprising C_5, at least about 5 wt % each of C_{4-} and C_{6+} forms within 30 min, or at least about 10 wt %, or at least about 15 wt %. At least about 10 wt % each of C_{4-} and C_{6+} forms within 1 hr, or at least about 15 wt %, or at least about 20 wt %.

[0028] For a feed comprising C_7, at least about 3 wt % each of C_{6-} and C_{8+} forms within 1 hr, or at least about 5 wt %, or at least about 7 wt %.

[0029] Longer reaction times may be needed for C_4 hydrocarbons due to slower reaction rates. In some embodiments, for a feed comprising normal C_4, at least about 0.2 wt % each of C_3 and C_{5+} forms in 32 hr, or at least about 0.25 wt %, or at least about 0.3 wt %. In some embodiments, for a feed comprising normal C_4, at least about 1 wt % each of C_3 and C_{5+} forms in 50 hr, or at least about 1.5 wt %, or at least about 2.0 wt %. In some embodiments, at least about 0.2 wt % each of C_3 and C_{5+} forms in 1 hr, or at least about 0.3 wt %. In some embodiments, at least about 0.5 wt % each of C_3 and C_{5+} forms in 8 hr, or at least about 0.6 wt %, or at least about 0.7 wt %, or at least about 0.8 wt %, or at least about 0.9 wt %. In some embodiments, at least about 1.0 wt % each of C_3 and C_{5+} forms in 25 hr, or at least about 1.1 wt %, or at least about 1.2 wt %, or at least about 1.3 wt %.

[0030] Another indication of the existence of the disproportionation reaction is that the number of moles in the product is nearly equal to the number of moles initially present.

[0031] There can also be a substantial isomerization reaction, which can be seen by the fact that significant amounts of iso C_n alkanes form from normal C_n alkanes, and normal C_n alkanes form from iso C_n alkanes initially. The product mixture can contain at least about 2 wt % normal C_n alkanes in 1 hr based on the iso C_n fraction in the hydrocarbon feed, or at least about 3 wt %, or at least 4 wt %, or at least about 5 wt %, or at least about 7 wt %, or at least about 10 wt %. The product mixture can contain at least about 5 wt % iso C_n alkanes in 1 hr based on the normal C_n fraction in the hydrocarbon feed, or at least about 10 wt %, or at least about 15 wt %, or at least about 20 wt %.

[0032] For normal C_5 isomerization, at least about 10 wt % of iso C_5 forms within 30 min, or at least about 15 wt %. At least about 15 wt % iso C_5 forms within 1 hr, or at least about 20 wt %.

[0033] For iso C_5 isomerization, at least about 2 wt % of normal C_5 forms within 1 hr min, or at least about 3 wt %, or at least about 4 wt %, or at least about 5 wt %.

[0034] For normal C_7 isomerization, at least about 5 wt % of iso C_7 forms within 1 hr, or at least about 10 wt %,

[0035] For normal C_4 isomerization, at least about 10 wt % of iso C_4 forms within 1 hr, or at least about 15 wt %, or at least about 20 wt %. For normal C_4 isomerization, at least about 30 wt % of iso C_4 forms within 8 hr, or at least about 35 wt %, or at least about 40 wt %, or at least about 45 wt %, or at least about 50 wt %.

[0036] The conversion rate for volume can be calculated as volume rate=(% conversion/time (h))×(mL HC/mL IL), where the mL of IL is determined by taking the mass of the ionic liquid and carbocation promoter and dividing by the density of the pure ionic liquid. The conversion rate for volume for some conversions is at least about 60 in the absence of an added metal salt, or at least about 70, or at least about 80, or at least about 90, or at least about 100, or at least about 120, or at least about 140, or at least about 160, or at least about 180, or at least about 200, or at least about 250, or at least about 300, or at least about 350, or at least about 400, or at least about 450, or at least about 500.

[0037] The conversion rate for mass can be calculated as mass rate=(% conversion/time (h))×(g HC/g IL), where the mass of the IL is taken to be the summed mass of the IL and carbocation promoter. The conversion rate for mass in the absence of an added metal salt for some conversions is at least about 20, or at least about 30, or at least about 40, or at least about 50, or at least about 60, or at least about 70, or at least about 80, or at least about 90, or at least about 100, or at least about 110, or at least about 120, or at least about 130, or at least about 140, or at least about 150, or at least about 175, or at least about 200, or at least about 220 or at least about 230, or at least about 240, or at least about 250, or at least about 250.

[0038] The present invention provides a method of disproportionating a hydrocarbon feed using less ionic liquid, which is expensive, and obtaining better results at a faster rate. It also provides a method of isomerizing a hydrocarbon feed using less ionic liquid, and obtaining better results at a faster rate.

[0039] The hydrocarbon feed can be straight chain paraffins, branched chain paraffins, cycloparaffins, naphthenes, or combinations thereof. The hydrocarbon feed may contain a single C_n alkane, such as pentane, or mixtures of two or more alkanes, such as pentane and hexane, or pentane, hexane, and heptane.

[0040] In some embodiments, the hydrocarbon feed can be a mixture of 2, 3, 4, 5, or 6 or more consecutive carbon numbers. Typically, there will be one, two, or three carbon numbers that form most of the feed. For example, there could be greater than about 50% of one carbon number, or greater than about 60%, or greater than about 70%, or greater than about 80%. In some embodiments, two or three carbon numbers (or more) could form greater than about 50% of the feed, or greater than about 60%, or greater than about 70%, or greater than about 80%.

[0041] In some embodiments, the C_n alkane can be substantially pure C_n alkane, e.g., greater than about 90% of a C_n alkane, such as pentane, or greater than about 95%, or greater than about 97%, or greater than about 98%, or greater than about 99%.

[0042] In some embodiments, the C_n alkane can be substantially pure normal C_n alkane or substantially pure iso C_n alkane, e.g., greater than about 90% of a specific normal or iso C_n alkane, such as normal pentane, or greater than about 95%, or greater than about 97%, or greater than about 98%, or greater than about 99%.

[0043] In other embodiments, mixtures of normal C_n alkane and iso C_n alkane (both a single C_n alkane, such as pentane, and two or more C_n alkanes, such as pentane and hexane) are used. The ratio of normal C_n alkane to iso C_n alkane is typically in the range of about 90:10 to about 10:90, or about 80:20 to about 20:80, or about 70:30 to about 30:70, or about 60:40 to about 40:60, or about 50:50.

[0044] As discussed above, the disproportionation reaction of a C_n alkane produces C_{n-} and C_{n+} alkanes. For example, the disproportionation of C_5 produces C_{4-} and C_{6+} alkanes. The presence of the C_{n+} fraction distinguishes the disproportionation reaction (FIG. **1**) from isomerization reactions which produce isomers of the C_n starting material (FIG. **2**), or isomerization and cracking which produces isomers of the C_n starting material and C_{n-} alkanes due to cracking (FIGS. **2** and **4**). The hydrocarbon feed can be dried to remove water before being contacted with the liquid catalyst. The feed can also be treated to remove undesirable reactive compounds such as alkenes, dienes, nitriles, and the like using known treatment processes.

[0045] The hydrocarbon feed can be a fluid. The fluid can be a liquid, a vapor, or a mixture of liquid and vapor. When a liquid or liquid-vapor mixture is used, the method is one of the few liquid-liquid disproportionation methods available.

[0046] The processes can produce mixtures of alkanes having desirable RVP and RON. The RVP and RON values are calculated on the C_{5+} fraction. The RVP was calculated as the vapor pressure for the system when the vapor:liquid ratio is 4:1 by volume using the Peng Robinson fluid properties model. The RON was calculated with linear volumetric blending, and the RON values used for this calculation were based on the values listed in Phillips 66 Reference Data for Hydrocarbons and Petro-Sulfur Compounds, Bulletin No. 521.

[0047] In one embodiment, the product mixture of alkanes has an RVP in the range of about 1 to about 25, or about 8 to about 16, and an RON in a range of about 50 to about 110, or about 60 to about 100. In another embodiment, the product mixture of alkanes has a similar RVP and RON. The octane numbers can be increased by isomerization of the linear paraffins to the corresponding branched compounds.

[0048] In some embodiments, the RVP of the product mixture is less than the RVP of the hydrocarbon feed. In some embodiments, the RVP is reduced at least about 5 numbers compared to the hydrocarbon feed, or at least about 7 numbers, or at least about 8 numbers. For example, the RVP for pure (i.e., greater than 99%) normal pentane is 15.6, and the RVP for the product mixture made from substantially pure normal pentane is 13.0 to 13.5. The RVP for pure (i.e., greater than 99%) isopentane is 20.4, and the RVP for the product mixture made from substantially pure isopentane is 12.3 to 12.5.

[0049] When the mass ratio of branched alkanes to normal alkanes (i/n) produced from converted pentane feed is in the range of about 6:1 to about 17:1, the selectivity for isoparaffins is in the range of about 70 to about 90%, and when it is in the range of about 7:1 to about 17:1, the selectivity for isoparaffins is in the range of about 80 to about 90%. The high branched to normal ratios for alkanes obtainable with this system are notable, especially in comparison to the methods employing dehydrogenation and metathesis catalysts to effect disproportionation. Generally, when these catalysts are employed, the major isomers formed within the C_{n-} and C_{n+} systems are normal paraffins. The formation of large amounts of normal paraffins is typically not desired due to their low octane numbers.

[0050] The formula for calculating the i/n ratio of the product for pure alkanes is (wt. % iC_{n-}+x wt. % iC_n+wt. % iC_{n+})/(wt. % nC_{n-}+y wt. % nC_n+wt. % nC_{n+}) with n– greater than or equal to 4, x=1 and y=0 when C_n=normal alkane and x=0 and y=1 when C_n=isoalkane. For example, for C_5, the calculation would be (wt. % iC_4+x wt. % iC_5+wt. % iC_6+wt. % iC_7+wt. % iC_8)/(wt. % nC_4+y wt. % nC_5+wt. % nC_6+wt. % nC_7+wt. % nC_8); where x=1 and y=0 when C_n=nC_5 and x=0 and y=1 when C_n is iC_5). Although C_{9+} alkanes will be present in small amounts, they should not substantially affect the i/n ratio as reported. In addition, the C_{3-} compounds are not included because they don't have normal and iso isomers.

[0051] The lower reactivity of normal pentane (nC_5) has made it generally difficult to for the development of a commercial process using nC_5. However, disproportionation of nC_5 at reasonable rates has been demonstrated in more than one embodiment of the present invention.

[0052] In order for these reactions to proceed, a stable carbocation likely needs to be present. Carbocations readily undergo skeletal rearrangement at low temperatures. Even at −90° C., rapid rearrangement is observed for degenerate 1, 2-methide shifts. Frequently, carbocations are transient intermediates and are short-lived. However, persistent carbocations have been observed in superacidic media.

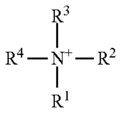
[0053] Ionic liquids offer a number of unique features which make them particularly well suited as reaction mediums for low temperature disproportionation and isomerization. These features include: (1) extremely low volatility, resulting in little to no solvent loss, (2) high chemical diversity, allowing for specific properties to be readily incorporated into the solvent, (3) good thermal stability, (4) readily recyclable, (5) wide liquid ranges, and (6) in some cases (e.g., 1-ethyl-3-methylimidazolium chloroaluminates), they have been shown to be superacidic.

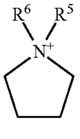
[0054] The liquid hydrocarbon feed comprises a C_n alkane where n=4-12. A normal C_n alkane is converted to a product mixture comprising iso C_n hydrocarbons, normal and iso C_{n-} hydrocarbons and normal and iso C_{n+} hydrocarbons, and an iso C_n alkane is converted to a product mixture comprising normal C_n hydrocarbons, normal and iso C_{n-} hydrocarbons and normal and iso C_{n+} hydrocarbons. A blend of normal and iso C_n alkane is converted to a product mixture comprising normal and iso C_n hydrocarbons, normal and iso C_{n-} hydrocarbons and normal and iso C_{n+} hydrocarbons, and the highest concentration of C_{n+} hydrocarbons is the C_{n+1} hydrocarbon. For example, for a feed of n-pentane, the product mixture would be isopentane, C_{4-} hydrocarbons and C_{6+} hydrocarbons, and for a feed of isopentane, the product mixture would be n-pentane, C_{4-} hydrocarbons and C_{6+} hydrocarbons, with the highest concentration being C_6 hydrocarbons for the C_{n+} fractions. A feed comprising a blend of n-pentane and isopentane would produce a product mixture of n-pentane and isopentane, C_{4-} hydrocarbons and C_{6+} hydrocarbons. The process is particularly useful for conversion of C_4, C_5, C_6, and C_7 alkanes.

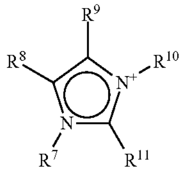
[0055] The liquid catalyst comprises an ionic liquid and a carbocation promoter. The ionic liquid is in liquid form; unlike prior art processes, it is not supported on an oxide support. In addition, the ionic liquids employed herein do not contain Brønsted acidic organic cations, so the acid concentration within the present systems is less than prior art processes using ionic liquids containing Brønsted acidic organic cations. The acid concentration within the liquid catalyst is less than about 2.5 M, or less than about 2.25 M, or less than about 2.0 M, or less than about 1.75 M, or less than about 1.5 M.

[0056] One or more ionic liquids can be used.

[0057] The ionic liquid comprises an organic cation and an anion. Suitable organic cations include, but are not limited to:







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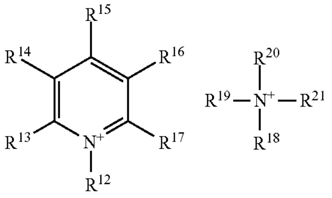


where R^1-R^{21} are independently selected from C_1-C_{20} hydrocarbons, C_1-C_{20} hydrocarbon derivatives, halogens, and H. Suitable hydrocarbons and hydrocarbon derivatives include saturated and unsaturated hydrocarbons, halogen substituted and partially substituted hydrocarbons and mixtures thereof. C_1-C_8 hydrocarbons are particularly suitable.

[0058] The anion can be derived from halides, sulfates, bisulfates, nitrates, sulfonates, fluoroalkanesulfonates, and combinations thereof. The anion is typically derived from metal and nonmetal halides, such as metal and nonmetal chlorides, bromides, iodides, fluorides, or combinations thereof. Combinations of halides include, but are not limited to, mixtures of two or more metal or nonmetal halides (e.g., $AlCl_4^-$ and BF_4^-), and mixtures of two or more halides with a single metal or nonmetal (e.g., $AlCl_3Br^-$). In some embodiments, the metal is aluminum, with the mole fraction of aluminum ranging from $0<Al<0.25$ in the anion. Suitable anions include, but are not limited to, $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, $AlCl_3Br^-$, $Al_2Cl_6Br^-$, $Al_3Cl_9Br^-$, $AlBr_4^-$, $Al_2Br_7^-$, $Al_3Br_{10}^-$, $GaCl_4^-$, $Ga_2Cl_7^-$, $Ga_3Cl_{10}^-$, $GaCl_3Br^-$, $Ga_2Cl_6Br^-$, $Ga_3Cl_9Br^-$, $CuCl_2^-$, $Cu_2Cl_3^-$, $Cu_3Cl_4^-$, $ZnCl_3^-$, $FeCl_3^-$, $FeCl_4^-$, $Fe_3Cl_7^-$, PF_6^-, and BF_4^-.

[0059] The ionic liquid is combined with one or more carbocation promoters. In some embodiments, the carbocation promoter is added to the ionic liquid. In other embodiments, the carbocation promoter is generated in situ. However, in situ production might not provide reproducible results if the activity is dependent only on the minor impurities of the synthetic precursors.

[0060] Suitable carbocation promoters include, but are not limited to, halo-alkanes, mineral acids alone or combined with alkenes, and combinations thereof. Suitable halo-alkanes include but are not limited to 2-chloro-2-methylpropane, 2-chloropropane, 2-chlorobutane, 2-chloro-2-methylbutane, 2-chloropentane, 1-chlorohexane, 3-chloro-3-methylpentane, or combinations thereof. In some embodiments, the carbocation promoters are not cyclic alkanes.

[0061] Suitable mineral acids include, but are not limited to, HCl, HBr, H_2SO_4, and HNO_3. Although HF can also be used, it is less desirable due to safety issues. If the mineral acid is not strong enough to protonate off a hydrogen from a C—H bond, isobutene or another alkene can be added with the mineral acid to produce the desired carbocation promoter. The mineral acid can be generated in situ by the addition of a compound that reacts with the ionic liquid. In situ acid generation can also occur as a result of reaction with water present in the system. The mineral acid may also be present as an impurity in the ionic liquid. In some embodiments, the acid concentration within the liquid catalyst is less than about 2.5 M, or less than about 2.25 M, or less than about 2.0 M, or less than about 1.75 M, or less than about 1.5 M.

[0062] 2-chloropropane, and 2-chlorobutane were used successfully as carbocation promoters. HCl was generated in situ by the addition of methanol to the ionic liquid, resulting in the partial degradation of the $Al_2Cl_7^-$ anion with concomitant formation of HCl. This method was sufficient to catalyze the disproportionation.

[0063] The molar ratio of the carbocation promoter to the ionic liquid in the liquid catalyst is typically in the range of about 0:1 to about 3:1, or about 0.1:1 to about 1:1. This relates to forming the carbocation promoter from the halo-alkane or mineral acid. This ratio is important relative to the specific type of anion. For example, if the anion is $AlCl_4^-$, a reaction is unlikely to occur or will be poor because the aluminum is fully coordinated. However, if the anion is $Al_2Cl_7^-$, there is some aluminum present that can coordinate to the carbocation promoter's anion, assisting in generating the carbocation from the carbocation promoter.

[0064] The mass or volume ratios of liquid catalyst (ionic liquid and carbocation promoter) to hydrocarbon feed are less than 1:1. This is desirable because the ionic liquid is an expensive component in the process. In some embodiments, the mass ratio of liquid catalyst to hydrocarbon feed is not more than about 0.75:1, or not more than about 0.7:1, or not more than about 0.65:1, or not more than about 0.60:1, or not more than about 0.55:1, or not more than about 0.50:1. In some embodiments, the volume ratio of ionic liquid to hydrocarbon feed is not more than about 0.8:1, or not more than about 0.7:1, or not more than about 0.6:1, or not more than about 0.5:1, or not more than about 0.45:1, or not more than about 0.4:1, or not more than about 0.35:1, or not more than about 0.3:1, or not more than about 0.25:1.

[0065] The hydrocarbon feed is contacted with the liquid catalyst at temperatures below the decomposition temperature of the ionic liquids. The temperature is typically about 300° C. or less, or about 275° C. or less, or about 250° C. or less, or about 225° C. or less, or about 200° C. or less, or about 175° C. or less, or about 150° C. or less, or about 125° C. or less, or about 100° C. or less, or about 90° C. or less, or about 80° C. or less, or about 70° C. or less, or about 60° C. or less, or in the range of about 0° C. to about 200° C., or about 0° C. to about 175° C., or about 0° C. to about 150° C., or about 10° C. to about 150° C., or about 25° C. to about 150° C., or about 30° C. to about 150° C., or about 40° C. to about 150° C., or about 50° C. to about 150° C., or about 55° C. to about 150° C.

[0066] The pressure in the reaction zone is typically in the range of about 0 MPa to about 20.7 MPa. In some embodiments, the pressure should be sufficient to ensure that the hydrocarbon feed is in a liquid state. Small amounts of vapor may also be present, but this should be minimized. In some embodiments, increased amounts of vapor are acceptable.

[0067] The reaction typically takes places in the presence of a gas. Suitable gases include, but are not limited to nitrogen, hydrogen, argon, helium, hydrogen chloride and the like.

[0068] For some hydrocarbons, the residence time in the reaction zone is generally less than about 10 hr, or less than 7 hr, or less than 5 hr, or less than 4 hr, or less than 3 hr, or less than 2 hr, or less than 1 hr. In some embodiments, butanes may react more slowly than hydrocarbons with higher numbers of carbons. Significant isomerization of normal C_4 takes place within 1 hr. Substantial amounts of disproportionation of normal C_4 may take longer in some embodiments. For example, disproportionation may take at least about 0.5 hr, or at least about 1 hr, or at least about 2 hr, or at least about 3 hr, or at least about 5 hr, or at least about 10 hr, or at least about 15 hr, or at least about 20 hr, or at least about 25 hr, or at least about 30 hr, or at least about 35 hr, or at least about 40 hr, or at least about 45 hr, or at least about 50 hr.

[0069] The reaction time and conversion are based on the time needed to reach equilibrium of the initial reaction products, such as 2-methylpentane and isobutane from the disproportionation of isopentane. The reaction time is a function of the degree of mixing, the reaction temperature, the concentration of the carbocation promoter, the molar ratio of the carbocation promoter to ionic liquid, and the mass/volume ratio of ionic liquid to hydrocarbon being reacted. Generally, increasing any of these conditions will increase the reaction rate. Under some conditions, greater than 90% conversion is possible.

[0070] The % selectivity for the disproportionation reaction is defined as: [(sum of the wt % C_{n-} and C_{n+} compounds)/(100−wt % C_n feed)]×100. For some embodiments, the % selectivity for the disproportionation reaction is typically at least about 40%, or at least about 45%, or at least about 50%, or at least about 55%, or at least about 60%, or at least about 65%, or at least about 70%, or at least about 75%, or at least about 80%, or at least about 85%, or at least about 90%, or at least about 94%.

[0071] For blends, the selectivity for the disproportionation reaction would be similar as above. For example, for a blend consisting of 50% isopentane and 50% n-pentane, the % selectivity for the disproportionation reaction is defined as: [(sum of the wt. % C_{4-} and C_{6+} compounds)/(100−wt. % C_n feed)]×100, where the C_n feed is taken to be the summed wt. % of isopentane and n-pentane. A simple equation similar to this may not be adequate for more complex blends.

[0072] The % selectivity for the isomerization reaction to isoparaffins ($S_{iso-isom}$) is defined as (z(wt. % isoparaffin C_n))/(100−wt. % C_n feed)×100, where z=0 when the C_n feed is isoparaffin and z=1 when the C_n feed is n-paraffin. The % selectivity for isoparaffin disproportionation is defined as (wt % isoparaffins of C_{n-}+wt % isoparaffins C_{n+})/(100−wt % C_n feed)×100 ($S_{iso-disp}$). The % selectivity for isoparaffins is defined as (wt. % isoparaffins of C_{n-}+wt. % isoparaffins C_{6+}+z(wt. % isoparaffin C_6))/(100−wt. % C_6 feed)×100, where z=0 when the C_n feed is isoparaffin and z=1 when the C_n feed is n-paraffin ($S_{isoparaffin}$); or $S_{isoparaffin}=S_{iso-isom}+S_{iso-disp}$. For some embodiments, the selectivity for isoparaffins is typically at least about 40%, or at least about 45%, or at least about 50%, or at least about 55%, or at least about 60%, or at least about 65%, or at least about 70%, or at least about 75%, or at least about 80%, or at least about 85%, or at least about 90%.

[0073] For blends, the selectivity for isoparaffins would be similar as above. For example, for a blend consisting of 50% isopentane and 50% n-pentane, the % selectivity for the isoparaffins reaction is defined as: [(sum of the wt. % iC_4 and iC_{6+} compounds)/(100−wt. % C_n feed)]×100, where the C_6 feed is taken to be the summed wt. % of isopentane and n-pentane. A simple equation similar to this may not be adequate for more complex blends.

[0074] The selectivity is highly dependent on the type of feed used. For example, for iC_5, the selectivity for the disproportionation reaction typically can be in the range of about 92-94%. However, the selectivity for the disproportionation reaction for nC_5 is much lower, e.g., in the range of about 67-76% because a substantial amount of isomerization to isopentane occurs.

[0075] Conversion for the disproportionation and isomerization reactions is defined as 100−wt % C_n feed. The conversion is typically at least about 50%, or at least about 55%, or at least about 60%, or at least about 65%, or at least about 70%, or at least about 75%, or at least about 80%, or at least about 85%, or at least about 90%.

[0076] For blends, the conversion would be the same as above. For example, for a blend consisting of 50% isopentane and 50% n-pentane, the % conversion is equal to 100−wt % C_n feed, where the C_n feed taken to be the summed wt % of isopentane and n-pentane.

[0077] For example, with an iC_5 feed, initially the products are primarily the isoparaffins of the C_4 and C_6 compounds along with some nC_5. Because iC_5 is more thermodynamically preferred, the amount of nC_5 that forms is relatively small, and the dominating pathway is disproportionation. Since the kinetic products are isoparaffins, the selectivity for isoparaffins can be similar to disproportionation. However, the mixture is not completely at equilibrium, so as the product continues to react, some of the initially formed isoparaffins of the disproportionation products begin to convert to their corresponding n-paraffins. As this occurs, the selectivity for isoparaffins decreases, but the selectivity for disproportionation does not.

[0078] With a feed of nC_5, the initial products are again primarily the isoparaffins of the C_4 and C_6 compounds and iC_5. Because nC_5 is thermodynamically disfavored, the amount of iC_5 that forms is substantially greater relative to the formation of nC5 from the iC5 feed. In this case, significant amounts of nC_5 are converted to iC_5. Since the initial products are isoparaffins, the selectivity for isoparaffins remains high. However, since a significant portion of nC_5 is converted to iC_5, the selectivity for disproportionation is less than it was when iC_5 is used. As the reaction progresses, iC_5 and nC_5 continue to disproportionate and the selectivity for disproportionation increases during the reaction. Conversely, the selectivity for isoparaffins decreases as the mixture equilibrates because the initially formed isoparaffin disproportionation products convert to their normal isomers.

[0079] With nC_4, the initial product is primarily iC_4. Small but significant amounts of C_3 and nC_5 and iC_5 form over longer reaction times, e.g., about 2 hr or more, or about 3 hr or more, or about 5 hr or more, or about 10 hr or more, or about 15 hr or more, about 20 hrs or more, or about 25 hrs or more, or about 30 hrs or more, or about 35 hrs or more, or about 40 hrs or more, or about 45 hrs or more, or about 50 hrs or more.

[0080] For butanes, the mass ratio of branched butane to normal butane (iC_4/nC_4) produced from converted normal butane feed is typically at least about 0.3:1 in 1 hr. It is typically at least about 0.5:1, or at least about 0.75:1, or at least about 1:1, or at least about 1.1:1, or at least about 1.2:1, or at least about 1.3:1, or at least about 1.4:1, or at least about 1.5:1, or at least about 1.6:1, or at least about 1.7:1, or at least about 1.8:1, or at least about 1.9:1, or at least about 2:1, or at least about 2.5:1, or at least about 3:1, or at least about 5:1, or at least about 7.5:1, or at least about 10:1, or at least about 15:1.

[0081] At higher temperatures, the relative concentration of normal paraffins increases, which ultimately results in decreased selectivities for isoparaffins relative to lower temperatures.

[0082] Although the reaction will proceed simply by contacting the hydrocarbon feed and the liquid catalyst, the reaction rate is generally too slow to be commercially viable. The reaction rate can be substantially increased by increasing the stirring speed of the reaction. This indicates that under some conditions the rate of reaction is mass transfer limited and is not reflective of the true elementary steps of the reaction. In addition to simply stirring the reaction mixture, a baffle can be included in the reactor to aid in obtaining good mixing. The baffle helps to prevent a vortex from forming in the reactor. The formation of a vortex would reduce the amount of mixing even in the presence of stirring.

[0083] One embodiment of the process **100** is a continuous-flow reactor as shown in FIG. **5**. Feed **105**, including the liquid hydrocarbon and carbocation promoter (if present), passes over a drying bed **110** and is continuously introduced to the reactor **115** while simultaneously withdrawing product **120**. The liquid catalyst (or ionic liquid alone) **112** is introduced to the reactor **115**. The carbocation promoter can be added with the hydrocarbon feed, or with the ionic liquid, or both. The reactor desirably includes a stirrer 160 to mix the hydrocarbon feed **105** and the liquid catalyst. The gaseous products **150** can be separated in the reactor **115**. The effluent **120** is sent to a settler **125**, where the heavier ionic liquid phase separates as a bottom layer **130**. The used ionic liquid stream **165** can be recycled to the reactor **115** and/or the regenerator **135**. The upper hydrocarbon layer phase **140** is removed from the settler **125**, yielding the liquid product **145**. The gaseous products **170** are separated in settler **125**. These gaseous products **170** can be combined with gaseous products **150** which could then be used as feed in alkylation units (not shown). The used ionic liquid **165** can be regenerated in regenerator **135** to remove deactivated liquid catalyst so it can be reused. Fresh ionic liquid **155** can be added to the regenerated ionic liquid stream **175** as needed and sent to the reactor **115**. Fresh ionic liquid can also be added to the regenerator **135**, as needed.

[0084] The ionic liquid can be regenerated in a variety of ways. The ionic liquid containing the conjunct polymer could be contacted with a reducing metal (e.g., Al), an inert hydrocarbon (e.g., hexane), and hydrogen and heated to about 100° C. The conjunct polymer will be transferred to the hydrocarbon phase, allowing for the conjunct polymer to be removed from the ionic liquid phase. See e.g., U.S. Pat. No. 7,651,970; U.S. Pat. No. 7,825,055; U.S. Pat. No. 7,956,002; US 2007/0142213; US 2007/0249486, each of which is incorporated herein by reference. Another method involves contacting the ionic liquid containing the conjunct polymer with a reducing metal (e.g., Al) in the presence of an inert hydrocarbon (e.g. hexane) and heating to about 100° C. The conjunct polymer will be transferred to the hydrocarbon phase, allowing for the conjunct polymer to be removed from the ionic liquid phase. See e.g., U.S. Pat. No. 7,674,739 B2; US 2007/0249485 A1; US 2010/0147740 A1, each of which is incorporated herein by reference. Still another method of regenerating the ionic liquid involves contacting the ionic liquid containing the conjunct polymer with a reducing metal (e.g., Al), HCl, and an inert hydrocarbon (e.g. hexane), and heating to about 100° C. The conjunct polymer will be transferred to the hydrocarbon phase, allowing for the conjunct polymer to be removed from the IL phase. See e.g., US 2007/0142217, which is incorporated herein by reference. The ionic liquid can be regenerated by adding a homogeneous metal hydrogenation catalyst (e.g., $(PPh_3)_3RhCl$) to the ionic liquid containing the conjunct polymer and an inert hydrocarbon (e.g. hexane). Hydrogen would be introduced, and the conjunct polymer would be reduced and transferred to the hydrocarbon layer. See e.g., US 2007/0142218, which is incorporated herein by reference. Another method for regenerating the ionic liquid involves adding HCl, isobutane, and an inert hydrocarbon to the ionic liquid containing the conjunct polymer and heating to about 100° C. The conjunct polymer would react to form an uncharged complex, which would transfer to the hydrocarbon phase. See e.g., US 2007/0142216, which is incorporated herein by reference. The ionic liquid could also be regenerated by adding a supported metal hydrogenation catalyst (e.g. Pd/C) to the ionic liquid containing the conjunct polymer and an inert hydrocarbon (e.g. hexane). Hydrogen would be introduced and the conjunct polymer would be reduced and transferred to the hydrocarbon layer. See e.g., US 2007/0142215, which is incorporated herein by reference. Still another method involves adding a suitable substrate (e.g. pyridine) to the ionic liquid containing the conjunct polymer. After a period of time, an inert hydrocarbon would be added to wash away the liberated conjunct polymer. In another method, the ionic liquid precursor would be added to the ionic liquid containing the conjunct polymer followed by an inert hydrocarbon. After a given time of mixing, the hydrocarbon layer would be separated, resulting in a regenerated ionic liquid. See, e.g., US 2007/0142211, which is incorporated herein by reference. Another method involves adding the ionic liquid containing the conjunct polymer to an electrochemical cell containing two aluminum electrodes and an inert hydrocarbon. A voltage would be applied and the current measured to determine the extent of reduction. After a given time, the inert hydrocarbon would be separated, resulting in a regenerated ionic liquid. See, e.g., US 2010/0130804, which is incorporated herein by reference.

[0085] The contacting step may be practiced in laboratory scale experiments through full scale commercial operations. The process may be operated in batch, continuous, or semi-continuous mode. The contacting step can take place in various ways, with both concurrent and co-current flow processes being suitable. The order of addition of the reactants is not critical. For example, the reactants can be added individually, or some reactants may be combined or mixed before being combined or mixed with other reactants.

[0086] Disproportionation of nC_5 and iC_5 has also been achieved at temperatures as low as 45° C. The reaction was faster with iC_5 than with nC_5. Gas chromatograph (GC) analysis revealed that the primary compounds formed were isoparaffins using the analytical method ASTM UOP690-99; very few C_{3-} hydrocarbons formed. The products of the reaction for n-C_5 were broadly divided into the following categories: C_{3-}, n-C_4, iC_4, IC_5, C_6 paraffins (C_6P) and C_{7+} hydrocarbons. The products of the reaction for iso C_5 were broadly divided into the following categories: C_{3-}, n-C_4, iC_4, nC_5, C_6 paraffins (C_6P) and C_{7+} hydrocarbons. The selectivity to these products was constant over a wide range of isopentane conversions. However, at higher conversions, the selectivity to C_6 paraffins decreased, while the selectivity to iC_4 and C_{7+} hydrocarbons increased, which is likely the result of secondary disproportionation-type reactions. An analysis of both the headspace and the liquid phase revealed that C_{3-} hydrocarbons form in small amounts.

[0087] In some places, demand for iC_4 exceeds supply, and disproportionation could help alleviate this problem.

[0088] For iso-pentane conversion, the selectivity to the various products (product selectivity being defined as [wt % compound/(100−wt % C_n feed)]*100) was nearly constant up to about 52% conversion at 55° C. Higher isopentane conversions resulted in decreased selectivity to C_6 paraffins and higher selectivities to iC_4 and C_{7+} hydrocarbons, which was likely the result of secondary disproportionation-type reactions.

[0089] With iso-pentane conversion, the extent of isomerization to n-pentane was minimal, but observable, because the reactant was already present in the more thermodynamically favored state. It was consistently observed that the selectivity for isomerization of isopentane to n-pentane centered around 7%, regardless of the % conversion of isopentane.

[0090] A significant stir rate dependence on the reaction rate was observed. Under the conditions used, the benefits of increased mixing began to taper off at stir rates greater than 700 rpm, which indicates that much of the kinetics of the reaction below 700 rpm is mass transfer limited.

[0091] The other products that form during the disproportionation reaction of isopentane were mainly isobutane and C_{6+} isoparaffins. The selectivity to these products was also nearly constant with isopentane conversion. However, at higher conversions, the selectivity to the C_6 paraffins decreased, while there was a concomitant increase in selectivity for isobutane and C_{7+} isoparaffins. It is important to note that very little C_{3-} formed in the reactions at 55° C. as revealed by a headspace analysis and by the analytical method ASTM UOP980-07.

[0092] Under similar conditions (e.g., volume of ionic liquid, temperature, stir rate, etc.), the rate of nC_5 conversion is dependent on the type of ionic liquid used, as the same reaction proceeds at a much greater conversion rate in [1-butyl-1-methylpyrrolidinium][Al_2Cl_7] than in [tributyl(hexyl) phosphonium][Al_2Cl_6Br] ([(^{n}Bu)$_3$P(Hex)][Al_2Cl_6Br]). Despite the increase in reactivity, the selectivities for the products were similar to what was observed with the ionic liquid [(^{n}Bu)$_3$P(Hex)][Al_2Cl_6Br].

[0093] Isomerization and disproportionation of n-hexane has been found to occur at temperatures as low as 45° C. in several different ionic liquids (e.g., [(^{n}Bu)$_3$P(Hex)][Al_2Cl_6Br], [1-butyl-1-methylpyrrolidinium][Al_2Cl_7], [1-butyl-3-methylimidazolium][Al_2Cl_7] and trihexyl(tetradecyl)phosphonium heptachloroaluminate ([(n-Hex)$_3$P (tetradecyl)][Al_2Cl_7])). The promoter used in all of these reactions, except for [1-butyl-3-methylimidazolium][Al_2Cl_7], was 2-chloro-2-methylpropane, which served to generate the active tert-butyl cation. Trace amounts of water or HCl present in [1-butyl-3-methylimidazolium][Al_2Cl_7] was sufficient for the catalysis to occur. A wide range of compounds were formed, including naphthenes, n-paraffins, isoparaffins and even some aromatic complexes, but the major products are paraffins.

[0094] Increasing the concentration of 2-chloro-2-methylpropane increased the conversion, and the yield for the higher and lighter molecular weight complexes. The major light components formed were identified by headspace analysis as iC_4, iC_5, 2-methylpentane and unreacted nC_6. However, it did little to change the selectivity for isomerization. Similarly, increasing the reaction time, temperature, and ratio of mass of ionic liquid to mass of hydrocarbon feed increased the overall conversion. It is desirable to minimize the amount of ionic liquid used due to the cost and potential increase in the amount of feed processed per unit ionic liquid.

EXAMPLES

Example 1

Experimental Set Up

[0095] Unless otherwise indicated, the set-up included a 300 mL Hastelloy C autoclave equipped with a Hastelloy C mechanical stirrer, Hastelloy C baffle, pressure gauge, Hastelloy C thermowell, thermocouple, Hastelloy C dipleg that was connected to the autoclave using a stainless steel nut and stainless steel connector, gold faced inconel rupture disc and stainless steel valves to introduce the feed and withdraw a liquid aliquot for GC analysis. The rupture disc vented to a knock out pot. The house nitrogen passed through a pressure regulator to a high surface sodium column and was then split: feeding to the charger for feed introduction or to a line for various uses (i.e., 2-methyl-2-chloropropane/C_5P introduction). The dipleg was constructed such that the height positions it in the paraffin layer. Upon opening the valve, the withdrawn paraffin layer passed through a column of silica, to the GC valve and then through a metering valve into a waste container. The reaction mixture was analyzed using the GC method described in ASTM UOP690-99. All peaks were integrated with a response factor of 1. Due to the presence of LPG in the liquid sample and sampling from a heated autoclave, the concentration of LPG present within the sample can be understated from the true values. Despite this potential deviation, the conclusions herein remain valid. The $S_{isoparaffin}$ was calculated by summing the wt % contribution of the C4-C8 isoparaffins that are separable using the ASTM UOP690-99 method, but does not include the contributions from the C9+ fraction. Consequently, these values represent lower limits for the selectivity. Similarly, the $S_{iso\text{-}disp}$ were determined using this analytical method and is also a lower limit. The RVP was calculated on the C_{5+} fraction as the vapor pressure for the system when the vapor:liquid ratio is 4:1 by volume using the Peng Robinson fluid properties model. The RON was calculated on the C_{5+} fraction with linear volumetric blending and the RON values used for this calculation were based on the values listed in Phillips 66 Reference Data for Hydrocarbons and Petro-Sulfur Compounds, Bulletin No. 521.

Example 2

Synthesis of [(^{n}Bu)$_3$P(Hex)][Al_2Cl_6Br]

[0096] An oven-dried round bottom flask was charged with [(^{n}Bu)$_3$P(Hex)][Br]. The material was attached to a rotary evaporator and dried under vacuum at 110° C. for at least 14 h. The dried [(^{n}Bu)$_3$P(Hex)][Br] was immediately brought into a nitrogen glovebox and stored there. A synthesis was achieved by massing 17.589 g (47.88 mmol) of [(^{n}Bu)$_3$P (Hex)][Br] into an oven-dried flask equipped with a stir bar in the nitrogen glovebox. To this was added 12.775 g (95.81 mmol) of $AlCl_3$ at ambient temperature. The mixture was stirred and the solids slowly reacted over the course of one week to produce a homogenous pale-yellow liquid.

Example 3

Synthesis of [1-butyl-1-methylpyrrolidinium][Al_2Cl_7]

[0097] An oven-dried round bottom flask was charged with [1-butyl-1-methylpyrrolidinium][Cl]. The material was attached to a rotary evaporator, dried under vacuum at 110° C. for at least 14 h, and then sealed under vacuum with a connecting adapter. The dried [1-butyl-1-methylpyrrolidinium][Cl] was immediately brought into a nitrogen glovebox and stored there. A synthesis was achieved by massing 57.14 g (322 mmol) of [1-butyl-1-methylpyrrolidinium][Cl] into an oven-dried flask equipped with a stir bar in the nitrogen glovebox. To this was added 83.93 g (629 mmol) of $AlCl_3$ at ambient temperature and the mixture stirred. The solids reacted to produce a homogenous liquid.

Example 4

Synthesis of with [1-butyl-3-methylimidazolium][Al_2Cl_7]

[0098] An oven-dried round bottom flask was charged with 1-butyl-3-methylimidazolium chloride. The material was attached to a rotary evaporator, dried under vacuum at 110° C. for at least 14 h and then sealed under vacuum with a connecting adapter. Afterwards, the dried 1-butyl-3-methylimidazolium chloride was stored in a nitrogen glovebox. A synthesis was achieved by massing 50.04 g (286 mmol) of 1-butyl-3-methylimidazolium chloride into an oven-dried flask equipped with a stir bar in the nitrogen glovebox. To this was added 76.40 g (573 mmol) of $AlCl_3$ at ambient temperature, and the mixture stirred. The solids react to produce a homogenous liquid.

Example 5

iC_5—Stir Rate Effect at 350 rpm with [(^{n}Bu)$_3$P(Hex)][Al_2Cl_6Br]

[0099] A 300 mL stainless steel autoclave, stainless steel baffle, and 75 mL stainless steel sample cylinder were dried in a 120° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 50.39 g of [(^{n}Bu)$_3$P(Hex)][Al_2Cl_6Br], and the autoclave head was attached. To the sample cylinder, 1.451 g of 2-chloro-2-methylpropane, which had previously been dried over activated sieves, was added. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was charged with 119 g of iso-pentane from a pressurized feed charger without displacing the nitrogen present in the autoclave. The iso-pentane passed over a high surface sodium column to remove any water before entering the autoclave. Similarly, the nitrogen used to pressurize the charger and for all other work passed over a separate high surface sodium column. The sample cylinder was charged with 18 g of iso-pentane using the same method described above and attached to the autoclave. The autoclave was heated to 55° C., and the 2-chloro-2-methylpropane/iso-pentane solution in the sample cylinder was added with an over-pressure of nitrogen. After complete addition, the initial pressure in the autoclave was 145 psi (1 MPa), and the autoclave was then set to stir at 350 rpm. The reaction was monitored periodically by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The mass ratio of liquid catalyst to iso-pentane was 0.38 and the volume ratio was 0.19. The mass rate of reaction was 38, and the volume rate was 75 after 1.4 h. The results of the run are shown in Tables 1 and 2.

TABLE 1

Disproportionation and Isomerization of iso-Pentane at 55° C., 350 rpm, wt % of reaction mixture

t (h)	% Conv.	C3−	iC4	nC4	iC5	nC5	C6P	C7+	i/n	S. Disp.	$S_{isoparaffin}$
1.4	20	0.00	7.20	0.02	80.46	1.31	6.84	4.13	11.2	93	82
2.7	28	0.01	10.38	0.04	72.48	2.04	9.93	5.09	9.94	92	84
4.4	36	0.01	13.64	0.07	64.29	2.70	12.75	6.54	9.48	92	85

TABLE 2

Time (h)	1.4	2.7	4.4	NA feed
Wt. %				
C3P	0.00	0.01	0.01	0.00
C4P	7.22	10.43	13.71	0.00
C5P	81.77	74.53	66.99	99.86
C6P	6.84	9.94	12.74	0.00
C7P	1.67	2.47	3.32	0.00
C8P	0.52	0.73	1.00	0.00
C9+	1.56	1.51	1.80	0.00
C5N	0.00	0.00	0.00	0.00
C6N	0.00	0.00	0.00	0.00
C7N	0.01	0.00	0.00	0.00
C8N	0.34	0.34	0.38	0.00
C6A	0.00	0.00	0.00	0.00
C7A	0.00	0.00	0.00	0.00
C8A	0.05	0.05	0.05	0.00
nC4-nC5 unknowns	0.00	0.00	0.00	0.14
mmoles (based on wt %)				
C3P	0	0	0	0
C4P	124	179	236	0
C5P	1133	1033	928	1384
C6P	79	115	148	0
C7P	17	25	33	0
C8P	5	6	9	0
C9+	12	12	14	0
C5N	0	0	0	0
C6N	0	0	0	0
C7N	0	0	0	0
C8N	3	3	3	0
C6A	0	0	0	0
C7A	0	0	0	0

TABLE 2-continued

Time (h)	1.4	2.7	4.4	NA feed
C8A	0	0	1	0
nC4-nC5 unknowns	0	0	0	2
Total mmoles	1374	1374	1372	1386

Example 6

iC5—Stir Rate Effect at 700 rpm with $[(^{n}Bu)_3P(Hex)][Al_2Cl_6Br]$

[0100] A 300 mL stainless steel autoclave, stainless steel baffle, and 75 mL stainless steel sample cylinder were dried in a 120° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 50.352 g of $[(^{n}Bu)_3P(Hex)][Al_2Cl_6Br]$, and the autoclave head was attached. To the sample cylinder, 1.453 g of 2-chloro-2-methylpropane, which had previously been dried over activated sieves, was added. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was charged with 112 g of iso-pentane from a pressurized feed charger without displacing the nitrogen present in the autoclave. The iso-pentane passed over a high surface sodium column to remove any water before entering the autoclave. Similarly, the nitrogen used to pressurize the charger and for all other work passed over a separate high surface sodium column. The sample cylinder was charged with 15 g of iso-pentane using the same method described above and attached to the autoclave. The autoclave was heated to 55° C., and the 2-chloro-2-methylpropane/iso-pentane solution in the sample cylinder was added with an over-pressure of nitrogen. After complete addition, the initial pressure in the autoclave was 115 psi (0.793 MPa), and the autoclave was then set to stir at 700 rpm. The reaction was monitored periodically by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The mass ratio of liquid catalyst to iso-pentane was 0.40 and the volume ratio was 0.20. The mass rate of reaction was 47, and the volume rate was 93 after 1.5 h. The results of the run are shown in Tables 3 and 4.

TABLE 3

Disproportionation and Isomerization of iso-Pentane at 55° C., 700 rpm, wt % of reaction mixture

t (h)	% Conv.	C3−	iC4	nC4	iC5	nC5	C6P	C7+	i/n	S. Disp.	$S_{isoparaffin}$
1.5	28	0.02	10.35	0.04	72.07	1.94	9.83	5.74	10.5	93	83
2.7	39	0.02	14.84	0.10	61.22	2.82	13.35	7.65	9.5	93	84
4.4	52	0.03	20.18	0.18	47.98	3.66	16.71	11.25	9.1	93	84

TABLE 4

Time (h)	1.5	2.7	4.4	NA feed
Wt. %				
C3P	0.02	0.02	0.03	0.00
C4P	10.39	14.93	20.35	0.00
C5P	74.02	64.05	51.64	99.86
C6P	9.83	13.34	16.71	0.00
C7P	2.55	3.79	5.53	0.00
C8P	0.82	1.25	1.99	0.00
C9+	1.99	2.17	3.13	0.00
C5N	0.00	0.00	0.00	0.00
C6N	0.00	0.00	0.00	0.00
C7N	0.00	0.01	0.01	0.00
C8N	0.33	0.37	0.51	0.00
C6A	0.00	0.00	0.00	0.00
C7A	0.00	0.00	0.01	0.00
C8A	0.06	0.06	0.09	0.00
nC4-nC5 unknowns	0.00	0.00	0.00	0.14
mmoles (based on wt %)				
C3P	0	0	1	0
C4P	179	257	350	0
C5P	1026	888	716	1384
C6P	114	155	194	0
C7P	25	38	55	0
C8P	7	11	17	0
C9+	16	17	24	0
C5N	0	0	0	0
C6N	0	0	0	0
C7N	0	0	0	0
C8N	3	3	5	0
C6A	0	0	0	0
C7A	0	0	0	0
C8A	1	1	1	0
nC4-nC5 unknowns	0	0	0	2
Total mmoles	1371	1370	1363	1386

Example 7

iC5—Stir Rate Effect at 1700 rpm with $[(^{n}Bu)_3P(Hex)][Al_2Cl_6Br]$

[0101] A 300 mL stainless steel autoclave, stainless steel baffle, and 75 mL stainless steel sample cylinder were dried in a 120° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 50.398 g of $[(^{n}Bu)_3P(Hex)][Al_2Cl_6Br]$, and the autoclave head was attached. To the sample cylinder 1.453 g of 2-chloro-2-methylpropane, which had previously been dried over activated sieves, was added. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was charged with 106 g of iso-pentane from a pressurized feed charger without displacing the nitrogen present in the autoclave. The iso-pentane passed over a high surface sodium column to remove any water before entering the autoclave. Similarly, the nitrogen used to pressurize the charger and for all other work passed over a separate high surface sodium column. The sample cylinder was charged with 23 g of iso-pentane using the same method described above and attached to the autoclave. The autoclave was heated to 55° C., and the 2-chloro-2-methylpropane/iso-pentane solution in the sample cylinder was added with an over-pressure of nitrogen. After complete addition, the initial pressure in the autoclave was 139 psi (0.958 MPa), and the autoclave was set to stir at 1700 rpm. The reaction was monitored periodically by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The mass ratio of liquid catalyst to iso-pentane was 0.40 and the volume ratio was 0.20. The mass rate of reaction was 41, and the volume rate was 82 after 2.5 h. The results of the run are shown in Tables 5 and 6.

TABLE 5

Disproportionation and Isomerization of iso-Pentane at 55° C., 1700 rpm, wt % of reaction mixture

t (h)	% Conv.	C3−	iC4	nC4	iC5	nC5	C6P	C7+	i/n	S. Disp.	$S_{isoparaffin}$
2.5	41	0.01	15.70	0.13	58.64	2.94	14.48	8.09	9.6	93	84
3.7	49	0.02	19.55	0.19	50.66	3.51	16.73	9.34	9.3	93	85

TABLE 6

Time (h)	2.5	3.7	NA feed
Wt. %			
C3P	0.01	0.02	0.00
C4P	15.83	19.74	0.00
C5P	61.58	54.17	99.86
C6P	14.48	16.73	0.00
C7P	4.06	4.97	0.00
C8P	1.31	1.59	0.00
C9+	2.30	2.33	0.00
C5N	0.00	0.00	0.00
C6N	0.00	0.00	0.00
C7N	0.01	0.00	0.00
C8N	0.36	0.39	0.00
C6A	0.00	0.00	0.00
C7A	0.00	0.01	0.00
C8A	0.06	0.07	0.00
nC4-nC5 unknowns	0.00	0.00	0.14
mmoles (based on wt %)			
C3P	0	0	0
C4P	272	340	0
C5P	854	751	1384
C6P	168	194	0
C7P	41	50	0
C8P	11	14	0
C9+	18	18	0
C5N	0	0	0
C6N	0	0	0
C7N	0	0	0
C8N	3	3	0
C6A	0	0	0
C7A	0	0	0
C8A	1	1	0
nC4-nC5 unknowns	0	0	2
Total mmoles	1368	1371	1386

Example 8

iC5—Stir Rate at 700 rpm with $[(^{n}Bu)_3P(Hex)][Al_2Cl_6Br]$ in Hastelloy C Autoclave at 55° C.

[0102] A 300 mL Hastelloy C autoclave, Hastelloy C baffle, and 75 mL stainless steel sample cylinder were dried in a 120° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 50.416 g of $[(^{n}Bu)_3P(Hex)][Al_2Cl_6Br]$, and the autoclave head was attached. To the sample cylinder 1.422 g of 2-chloro-2-methylpropane, which had previously been dried over activated sieves, was added. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was charged with 114 g of iso-pentane from a pressurized feed charger without displacing the nitrogen present in the autoclave. The iso-pentane passed over a high surface sodium column to remove any water before entering the autoclave. Similarly, the nitrogen used to pressurize the charger and for all other work passed over a separate high surface sodium column. The sample cylinder was charged with 16 g of iso-pentane using the same method described above and attached to the autoclave. The autoclave was heated to 55° C., and the 2-chloro-2-methylpropane/iso-pentane solution in the sample cylinder was added with an over-pressure of nitrogen. After complete addition, the initial pressure in the autoclave was 140 psi (0.965 MPa), and the autoclave was set to stir at 700 rpm. The reaction was monitored periodically by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The mass ratio of liquid catalyst to iso-pentane was 0.40 and the volume ratio was 0.20. The mass rate of reaction was 70, and the volume rate was 140 after 0.5 h. The results of the run are shown in Tables 7 and 8.

TABLE 7

Disproportionation and Isomerization of iso-Pentane at 55° C., 700 rpm, Hastelloy C autoclave, wt. % of reaction mixture

t (h)	% Conv.	C3−	iC4	nC4	iC5	nC5	C6P	C7+	i/n	S. Disp.	$S_{isoparaffin}$
0.5	14	0.00	5.04	0.01	85.85	0.94	4.98	3.16	11.4	93	82
2.8	38	0.14	14.04	0.11	62.48	3.13	12.89	7.08	8.1	92	83
4.5	54	0.03	20.70	0.25	46.32	4.41	16.82	11.45	7.6	92	82

TABLE 8

Time (h)	0.5	2.8	4.5	NA feed
Wt. %				
C3P	0.00	0.14	0.03	0.00
C4P	5.05	14.16	20.94	0.00
C5P	86.79	65.61	50.73	99.86
C6P	4.99	12.88	16.83	0.00
C7P	1.19	3.60	5.73	0.00
C8P	0.38	1.15	2.05	0.00
C9+	1.30	2.07	3.08	0.00
C5N	0.00	0.00	0.00	0.00
C6N	0.00	0.00	0.00	0.00
C7N	0.00	0.01	0.01	0.00
C8N	0.25	0.33	0.50	0.00
C6A	0.00	0.00	0.00	0.00
C7A	0.00	0.00	0.01	0.00
C8A	0.02	0.03	0.05	0.00
nC4-nC5 unknowns	0.00	0.00	0.00	0.14
mmoles (based on wt %)				
C3P	0	3	1	0
C4P	87	244	360	0
C5P	1203	909	703	1384
C6P	58	150	195	0
C7P	12	36	57	0
C8P	3	10	18	0
C9+	10	16	24	0
C5N	0	0	0	0
C6N	0	0	0	0
C7N	0	0	0	0
C8N	2	3	4	0
C6A	0	0	0	0
C7A	0	0	0	0
C8A	0	0	1	0
nC4-nC5 unknowns	0	0	0	2
Total mmoles	1375	1371	1364	1386

Example 9

iC5—Stir Rate at 700 rpm with [1-Butyl-1-methylimidazolium][Al_2Cl_7] at 55° C. in a Hastelloy C Autoclave

[0103] A 300 mL Hastelloy C autoclave, Hastelloy C baffle, and 75 mL stainless steel sample cylinder were dried in a 120° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 55.310 g of [1-butyl-1-methylimidazolium][Al_2Cl_7], and the autoclave head was attached. To the sample cylinder 2.311 g of 2-chloro-2-methylpropane, which had previously been dried over activated sieves, was added. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was charged with 111 g of iso-pentane from a pressurized feed charger without displacing the nitrogen present in the autoclave. The iso-pentane passed over a high surface sodium column to remove any water before entering the autoclave. Similarly, the nitrogen used to pressurize the charger and for all other work passed over a separate high surface sodium column. The sample cylinder was charged with 28 g of iso-pentane using the same method described above and attached to the autoclave. The autoclave was heated to 55° C., and the 2-chloro-2-methylpropane/iso-pentane solution in the sample cylinder was added with an overpressure of nitrogen. After complete addition, the initial pressure in the autoclave was 150 psi (1.034 MPa), and the autoclave was set to stir at 700 rpm. The reaction was monitored periodically by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The mass ratio of liquid catalyst to iso-pentane was 0.41 and the volume ratio was 0.20. The mass rate of reaction was 150, and the volume rate was 310 after 0.6 h. The results of the run are shown in Tables 9 and 10.

TABLE 9

Disproportionation and Isomerization of iso-Pentane at 55° C., 700 rpm, with [1-butyl-3-methylimidazolium][Al_2Cl_7] in a Hastelloy C autoclave, wt. % of reaction mixture

t (h)	% Conv.	C3−	iC4	nC4	iC5	nC5	C6P	C7+	i/n	S. Disp.	$S_{isoparaffin}$
0.6	37	0.01	13.86	0.08	62.83	3.11	11.50	8.59	8.2	92	80
1.7	69	0.04	27.55	0.56	31.04	5.47	18.18	17.15	6.9	92	80

TABLE 9-continued

Disproportionation and Isomerization of iso-Pentane at 55° C., 700 rpm, with [1-butyl-3-methylimidazolium][Al_2Cl_7] in a Hastelloy C autoclave, wt. % of reaction mixture

t (h)	% Conv.	C3−	iC4	nC4	iC5	nC5	C6P	C7+	i/n	S. Disp.	$S_{isoparaffin}$
2.9	75	0.07	31.33	1.10	24.52	5.47	18.13	19.38	6.6	93	79
4.5	76	0.09	32.31	1.56	23.41	5.34	18.37	18.90	6.4	93	80

TABLE 10

Time (h)	0.6	1.7	2.9	4.5	NA feed
Wt. %					
C3P	0.01	0.04	0.07	0.09	0.00
C4P	13.95	28.12	32.44	33.88	0.00
C5P	65.94	36.51	29.98	28.75	99.86
C6P	11.50	18.17	18.12	18.38	0.00
C7P	3.68	7.80	8.61	8.65	0.00
C8P	1.37	3.36	4.18	4.25	0.00
C9+	3.01	5.09	5.43	5.09	0.00
C5N	0.00	0.00	0.00	0.00	0.00
C6N	0.00	0.00	0.00	0.00	0.00
C7N	0.01	0.01	0.01	0.01	0.00
C8N	0.45	0.84	0.93	0.86	0.00
C6A	0.00	0.00	0.00	0.00	0.00
C7A	0.00	0.03	0.04	0.04	0.00
C8A	0.08	0.06	0.23	0.06	0.00
nC4-nC5 unknowns	0.00	0.00	0.00	0.00	0.14
mmoles (based on wt %)					
C3P	0	1	2	2	0
C4P	240	484	558	583	0
C5P	914	506	416	398	1384
C6P	133	211	210	213	0
C7P	37	78	86	86	0
C8P	12	29	37	37	0
C9+	23	40	42	40	0
C5N	0	0	0	0	0
C6N	0	0	0	0	0
C7N	0	0	0	0	0
C8N	4	7	8	8	0
C6A	0	0	0	0	0
C7A	0	0	0	0	0
C8A	1	1	2	1	0
nC4-nC5 unknowns	0	0	0	0	2
Total mmoles	1365	1357	1361	1368	1386

Example 10

iC5 $[(^{n}Bu)_3P(Hex)][Al_2Cl_6Br]$ in Hastelloy C Autoclave at 95° C.

[0104] A 300 mL Hastelloy C autoclave, Hastelloy C baffle, and 75 mL stainless steel sample cylinder were dried in a 120° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 50.419 g of $[(^{n}Bu)_3P(Hex)][Al_2Cl_6Br]$, and the autoclave head was attached. To the sample cylinder 3.680 g of 2-chloro-2-methylpropane, which had previously been dried over activated sieves, was added. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was charged with 102 g of iso-pentane from a pressurized feed charger without displacing the nitrogen present in the autoclave. The iso-pentane passed over a high surface sodium column to remove any water before entering the autoclave. Similarly, the nitrogen used to pressurize the charger and for all other work passed over a separate high surface sodium column. The sample cylinder was charged with 15 g of iso-pentane using the same method described above and then attached to the autoclave. The autoclave was heated to 95° C., and the 2-chloro-2-methylpropane/iso-pentane solution in the sample cylinder was added with an over-pressure of nitrogen. After complete addition, the initial pressure in the autoclave was 165 psi (1.138 MPa), and the autoclave was set to stir at 1700 rpm. The reaction was monitored periodically by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The mass ratio of liquid catalyst to iso-pentane was 0.46 and the volume ratio was 0.23. The mass rate of reaction was 260, and the volume rate was 520 after 0.6 h. The results of the run are shown in Tables 11 and 12.

TABLE 11

Disproportionation and Isomerization of iso-Pentane at 95° C., wt % of reaction mixture

t (h)	% Conv.	C3−	iC4	nC4	iC5	nC5	C6P	C7+	i/n	S. Disp.	$S_{isoparaffin}$	RON	RVP (psi)
0.6	72	0.37	27.78	1.72	28.32	4.2	16.21	21.36	6.3	94	73	80.0	12.5
1.8	76	0.82	31.73	3.91	23.66	5.4	17.15	17.29	4.6	93	76	77.6	12.3

TABLE 11-continued

Disproportionation and Isomerization of iso-Pentane at 95° C., wt % of reaction mixture

t (h)	% Conv.	C3−	iC4	nC4	iC5	nC5	C6P	C7+	i/n	S. Disp.	$S_{isoparaffin}$	RON	RVP (psi)
3.1	77	1.05	31.50	5.12	23.14	5.71	17.1	16.38	4.0	92	74	ND	ND
4.6	77	1.21	31.56	6.14	22.79	5.90	16.91	15.42	3.7	92	73	ND	ND

TABLE 12

	Time (h)				
Wt. %	0.6	1.8	3.1	4.6	NA feed
C3P	0.37	0.82	1.05	1.21	0.00
C4P	29.50	35.64	36.62	37.70	0.00
C5P	32.51	29.06	28.85	28.69	99.86
C6P	16.22	17.16	17.10	16.91	0.00
C7P	7.66	8.19	7.96	7.56	0.00
C8P	3.42	3.88	3.79	3.57	0.00
C9+	9.74	4.63	4.04	3.81	0.00
C5N	0.00	0.00	0.00	0.00	0.00
C6N	0.00	0.00	0.00	0.00	0.00
C7N	0.01	0.02	0.02	0.02	0.00
C8N	0.51	0.56	0.53	0.48	0.00
C6A	0.00	0.00	0.00	0.00	0.00
C7A	0.04	0.04	0.04	0.03	0.00
C8A	0.01	0.02	0.02	0.02	0.00
nC4-nC5 unknowns	0.00	0.00	0.00	0.00	0.14
mmoles (based on wt %)					
C3P	8	19	24	27	0
C4P	508	613	630	649	0
C5P	451	403	400	398	1384
C6P	188	199	198	196	0
C7P	76	82	79	75	0
C8P	30	34	33	31	0
C9+	76	36	31	30	0
C5N	0	0	0	0	0
C6N	0	0	0	0	0
C7N	0	0	0	0	0
C8N	5	5	5	4	0
C6A	0	0	0	0	0
C7A	0	0	0	0	0
C8A	0	0	0	0	0
nC4-nC5 unknowns	0	0	0	0	2
Total mmoles	1343	1391	1402	1411	1386

Example 11

nC5 with $[(^{n}Bu)_3P(Hex)][Al_2Cl_6Br]$ at 95° C. in a Hastelloy C Autoclave

[0105] A 300 mL Hastelloy C autoclave, Hastelloy C baffle, and 75 mL stainless steel sample cylinder were dried in a 120° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 50.409 g of $[(^{n}Bu)_3P(Hex)][Al_2Cl_6Br]$, and the autoclave head was attached. To the sample cylinder 3.679 g of 2-chloro-2-methylpropane, which had previously been dried over activated sieves, was added. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was charged with 102 g of n-pentane from a pressurized feed charger without displacing the nitrogen present in the autoclave. The n-pentane passed over a high surface sodium column to remove any water before entering the autoclave. Similarly, the nitrogen used to pressurize the charger and for all other work passed over a separate high surface sodium column. The sample cylinder was charged with 15 g of n-pentane using the same method described above and then attached to the autoclave. The autoclave was heated to 95° C., and the 2-chloro-2-methylpropane/n-pentane solution in the sample cylinder was added with an over-pressure of nitrogen. After complete addition, the initial pressure in the autoclave was 160 psi (1.103 MPa), and the autoclave was then set to stir at 1700 rpm. The reaction was monitored periodically by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The mass ratio of liquid catalyst to n-pentane was 0.46 and the volume ratio was 0.24. The mass rate of reaction was 130, and the volume rate was 240 after 1 h. The results of the run are shown in Tables 13 and 14.

TABLE 13

Disproportionation and Isomerization of n-Pentane at 95° C., wt % of reaction mixture

t (h)	% Conv.	C3−	iC4	nC4	iC5	nC5	C6P	C7+	i/n	S. Disp.	$S_{isoparaffin}$	$S_{isoisom}$
1.0	59	0.42	18.63	1.71	19.46	41.34	10.27	8.14	16.9	67	90	33
2.2	70	0.94	22.7	3.08	20.83	29.43	12.54	10.30	12.1	70	87	30
3.5	76	0.91	25.1	4.06	21.56	23.72	13.57	11.03	10.4	72	86	28

TABLE 13-continued

Disproportionation and Isomerization of n-Pentane at 95° C., wt % of reaction mixture

t (h)	% Conv.	C3−	iC4	nC4	iC5	nC5	C6P	C7+	i/n	S. Disp.	$S_{isoparaffin}$	$S_{isoisom}$
4.8	80	1.05	26.39	4.78	21.83	20.06	14.26	11.63	9.4	73	86	27
8.0	85	1.35	27.64	6.10	21.68	14.82	14.78	12.84	8.0	74	83	25

TABLE 14

	Time (h)					
Wt. %	1.0	2.2	3.5	4.8	8.0	NA feed
C3P	0.42	0.94	0.91	1.05	1.35	0.00
C4P	20.35	25.78	29.16	31.17	33.74	0.00
C5P	60.81	50.26	45.28	41.90	36.50	99.60
C6P	10.27	12.55	13.59	14.25	14.78	0.00
C7P	4.17	5.17	5.67	5.96	6.24	0.00
C8P	1.63	2.11	2.40	2.57	2.82	0.00
C9+	2.02	2.71	2.58	2.67	4.10	0.00
C5N	0.00	0.00	0.00	0.00	0.00	0.00
C6N	0.00	0.00	0.00	0.00	0.00	0.00
C7N	0.01	0.02	0.02	0.02	0.02	0.00
C8N	0.26	0.32	0.36	0.38	0.41	0.00
C6A	0.00	0.00	0.00	0.00	0.00	0.00
C7A	0.01	0.02	0.02	0.02	0.02	0.00
C8A	0.06	0.13	0.03	0.03	0.04	0.00
nC4-nC5 unknowns	0.00	0.00	0.00	0.00	0.00	0.34
nC5-nC6 unknowns	0.00	0.00	0.00	0.00	0.00	0.05
mmoles (based on wt %)						
C3P	10	21	21	24	31	0
C4P	350	444	502	536	580	0
C5P	843	697	628	581	506	1380
C6P	119	146	158	165	172	0
C7P	42	52	57	59	62	0
C8P	14	18	21	23	25	0
C9+	16	21	20	21	32	0
C5N	0	0	0	0	0	0
C6N	0	0	0	0	0	0
C7N	0	0	0	0	0	0
C8N	2	3	3	3	4	0
C6A	0	0	0	0	0	0
C7A	0	0	0	0	0	0
C8A	1	1	0	0	0	0
nC4-nC5 unknowns	0	0	0	0	0	5
nC5-nC6 unknowns	0	0	0	0	0	1
Total mmoles	1396	1403	1409	1413	1412	1386

Example 12

nC5 with [1-butyl-1-methylpyrrolidinium][Al_2Cl_7] at 95° C.

[0106] A 300 mL Hastelloy C autoclave, Hastelloy C baffle, and 75 mL stainless steel sample cylinder were dried in a 120° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 52.795 g of [1-butyl-1-methylpyrrolidinium][Al_2Cl_7] and the autoclave head was attached. To the sample cylinder 5.24 g of 2-chloro-2-methylpropane, which had previously been dried over activated sieves, was added. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was charged with 98 g of n-pentane from a pressurized feed charger without displacing the nitrogen present in the autoclave. The n-pentane passed over a high surface sodium column to remove any water before entering the autoclave. Similarly, the nitrogen used to pressurize the charger and for all other work passed over a separate high surface sodium column. The sample cylinder was charged with 33 g of n-pentane using the same method described above and attached to the autoclave. The autoclave was heated to 95° C., and the 2-chloro-2-methylpropane/n-pentane solution in the sample cylinder was added with an over-pressure of nitrogen. After complete addition, the initial pressure in the autoclave was 260 psi (1.793 MPa), and the autoclave was set to stir at 1700 rpm. The reaction was monitored periodically by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The mass ratio of liquid catalyst to n-pentane was 0.44 and the volume ratio was 0.21. The mass rate of reaction was 220, and the volume rate was 450 after 0.6 h. The results of the run are shown in Tables 15 and 16.

TABLE 15

Disproportionation and Isomerization of n-Pentane at 95° C. with [1-butyl-1-methylpyrrolidinium][Al_2Cl_7], wt. % of reaction mixture

t (h)	% Conv.	C3−	iC4	nC4	iC5	nC5	C6P	C7+	i/n	S. Disp.	$S_{isoparaffin}$	$S_{isoisom}$	RON	RVP (psi)
0.6	57	0.49	18.16	2.44	18.55	42.87	10.02	7.48	13.0	68	89	32	ND	ND
1.9	84	1.22	28.59	5.73	22.01	15.60	14.75	12.00	8.7	74	85	26	76.1	13.5

TABLE 15-continued

Disproportionation and Isomerization of n-Pentane at 95° C. with [1-butyl-1-methylpyrrolidinium][Al_2Cl_7], wt. % of reaction mixture

t (h)	% Conv.	C3−	iC4	nC4	iC5	nC5	C6P	C7+	i/n	S. Disp.	$S_{isoparaffin}$	$S_{isoisom}$	RON	RVP (psi)
3.2	89	1.70	30.42	7.70	21.66	10.57	15.38	12.54	7.1	76	83	24	77.1	13.2
4.4	91	1.96	30.79	8.72	21.31	9.06	15.51	12.65	6.5	76	81	23	77.4	13.0

TABLE 16

Time (h)	0.6	1.9	3.2	4.4	NA feed
Wt %					
C3P	0.49	1.22	1.70	1.96	0.00
C4P	20.60	34.32	38.12	39.51	0.00
C5P	61.41	37.61	32.23	30.37	99.60
C6P	10.02	14.76	15.39	15.50	0.00
C7P	3.93	6.04	6.24	6.25	0.00
C8P	1.52	2.64	2.85	2.89	0.00
C9+	1.71	2.97	3.00	3.05	0.00
C5N	0.00	0.00	0.00	0.00	0.00
C6N	0.00	0.00	0.00	0.00	0.00
C7N	0.01	0.01	0.02	0.02	0.00
C8N	0.25	0.39	0.41	0.41	0.00
C6A	0.00	0.00	0.00	0.00	0.00
C7A	0.01	0.02	0.02	0.02	0.00
C8A	0.04	0.01	0.02	0.02	0.00
nC4-nC5 unknowns	0.00	0.00	0.00	0.00	0.34
nC5-nC6 unknowns	0.00	0.00	0.00	0.00	0.05
mmoles (based on wt %)					
C3P	11	28	39	44	0
C4P	354	591	656	680	0
C5P	851	521	447	421	1380
C6P	116	171	179	180	0
C7P	39	60	62	62	0
C8P	13	23	25	25	0
C9+	13	23	23	24	0
C5N	0	0	0	0	0
C6N	0	0	0	0	0
C7N	0	0	0	0	0
C8N	2	4	4	4	0
C6A	0	0	0	0	0
C7A	0	0	0	0	0
C8A	0	0	0	0	0
nC4-nC5 unknowns	0	0	0	0	5
nC5-nC6 unknowns	0	0	0	0	1
Total mmoles	1402	1421	1435	1441	1386

Example 13

nC7—Stir Rate at 1700 rpm with [(^{n}Bu)$_3$P(Hex)][Al_2Cl_6Br] at 55° C.-80° C. in a Hastelloy C Autoclave

[0107] A 300 mL Hastelloy C autoclave, Hastelloy C baffle, and 75 mL stainless steel sample cylinder were dried in a 110° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 50.425 g of [(^{n}Bu)$_3$P(Hex)][Al_2Cl_6Br], 201 mL of n-heptane (pre-dried by storing over activated 3A MS for several days) and then the autoclave head was attached. The sample cylinder was charged with 8.833 g of a 82.29 wt % n-heptane and 17.71 wt % 2-chloro-2-methylpropane mixture, both of which had previously been dried over activated sieves. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was heated to 55° C., and then the 2-chloro-2-methylpropane/n-heptane solution in the sample cylinder was added with an over-pressure of nitrogen. The nitrogen used to provide this overpressure was passed over a high surface sodium column. After complete addition, the initial pressure in the autoclave was 340 psi (2.34 MPa), and the autoclave was set to stir at 1700 rpm. The reaction was monitored by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. After about 24 the temperature was increased to 80° C. At the end of the reaction (45 h), an aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and into a sample cylinder. The sample cylinder was then charged to about 300 psi using nitrogen prior to offline analysis. The mass ratio of liquid catalyst to n-heptane was 0.36 and the volume ratio was 0.20. The mass rate of reaction was 2, and the volume rate was 3 after 45 h. The results of the run are shown in Table 17 and were determined using the UOP980 method offline.

TABLE 17

Disproportionation and Isomerization of n-heptane at 55-80° C., 1700 rpm, with [(^{n}Bu)$_3$P(Hex)][Al_2Cl_6Br] in a Hastelloy C autoclave, wt % of reaction mixture

t (h)	% Conv.	C3−	iC4	nC4	iC5	nC5	C6P	nC7	C7P	C8P	Heavies	i/n	S. Disp.	S. Isom. C7P
0.0 (feed)	NA	0.00	0.00	0.00	0.04	0.00	0.00	99.25	99.55	0.00		NA	NA	NA
45	26	0.07	3.90	0.14	3.31	0.16	2.89	73.44			15.14			

Example 14

nC7—Stir Rate at 1700 rpm with [1-Butyl-1-methylimidazolium][Al_2Cl_7] at 95° C. in a Hastelloy C Autoclave

[0108] A 300 mL Hastelloy C autoclave, Hastelloy C baffle, and 50 mL stainless steel sample cylinder were dried in a 110° C. oven for at least 5 h and then placed in a glovebox antechamber and evacuated over night. The autoclave and sample cylinder were then brought into a nitrogen glovebox. The autoclave was charged with 55.335 g of [1-butyl-1-methylimidazolium][Al_2Cl_7], 211 mL of n-heptane (pre-dried by storing over activated 3A MS for at least 1 week) and then the autoclave head was attached. The sample cylinder was charged with 15.358 g of a 62.30 wt % n-heptane and 37.70 wt % 2-chloro-2-methylpropane mixture, both of which had previously been dried over activated sieves. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was heated to 95° C., and then the 2-chloro-2-methylpropane/n-heptane solution in the sample cylinder was added with an over-pressure of nitrogen. The nitrogen used to provide this overpressure was passed over a high surface sodium column. After complete addition, the initial pressure in the autoclave was 280 psi (1.93 MPa), and the autoclave was set to stir at 1700 rpm. The reaction was monitored by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The mass ratio of liquid catalyst to n-heptane was 0.40 and the volume ratio was 0.21. The mass rate of reaction was 110, and the volume rate was 210 after 1 h. The results of the run are shown in Tables 18 and 19 and were determined using the UOP690 method. Alternatively, the aliquot could be introduced to a sample cylinder, after passing through the SiO_2 column, and analyzed offline. If this method was used, after introduction of the sample to the sample cylinder, the cylinder would then be charged to about 300 psi using nitrogen prior to offline analysis and analyzed using the UOP980 method.

TABLE 18

Disproportionation and Isomerization of n-heptane at 95° C., 1700 rpm, with [1-butyl-3-methylimidazolium][Al_2Cl_7] in a Hastelloy C autoclave, wt. % of reaction mixture

t (h)	% Conv.	C3−	iC4	nC4	iC5	nC5	C6P	nC7	C7P	C8P	nC8-nC10	C10+	i/n	S. Disp.	$S_{isoisom}$
0.0 (feed)	NA	0.00	0.00	0.00	0.04	0.00	0.00	99.25	99.55	0.00			NA	NA	NA
1.0	44	0.58	7.63	0.89	7.58	0.77	7.06		66.21	3.26	3.07	2.43	15	77	22

TABLE 19

Time (h)	1.0	NA Feed
Wt. %		
C3P	0.58	0.00
C4P	8.52	0.00
C5P	8.35	0.04
C6P	7.06	0.00
C7P	66.21	99.55
C8P	3.26	0.00
C9P	1.62	0.00
C10P	1.40	0.00
C10+	2.43	0.00
C5N	0.00	0.00
C6N	0.00	0.01
C7N	0.03	0.40
C8N	0.40	0.00
C6A	0.00	0.00
C7A	0.06	0.00
C8A	0.04	0.00
nC4-nC5	0.00	
nC5-nC6 unknowns	0.00	0.00
mmoles (based on wt %)		
C3P	13	0
C4P	147	0
C5P	116	1
C6P	82	0
C7P	661	993
C8P	29	0
C9P	13	0
C10P	10	0
C10+	16	0
C5N	0	0
C6N	0	0
C7N	0	4
C8N	4	0
C6A	0	0
C7A	1	0
C8A	0	0
nC4-nC5	0	
nC5-nC6 unknowns	0	0
Total mmoles	1090	998

Example 15

nC4—Stir Rate at 1700 rpm with [(^{n}Bu)$_3$P(Hex)][Al_2Cl_6Br] in Hastelloy C Autoclave at 95° C.-105° C.

[0109] A 300 mL Hastelloy C autoclave, Hastelloy C baffle, and 75 mL stainless steel sample cylinder were dried in a 110° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 50.467 g of [(^{n}Bu)$_3$P(Hex)][Al$_2$Cl$_6$Br], and the autoclave head was attached. 3.692 g of 2-chloro-2-methylpropane, which had previously been dried over activated 3A molecular sieves, was added to the sample cylinder. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was charged with 103.1 g of n-butane from a pressurized feed charger without displacing the nitrogen present in the autoclave. The sample cylinder was charged with 10.9 g of n-butane using the same method described above and attached to the autoclave. The autoclave was heated to 105° C. At this temperature, stirring was stopped, and the 2-chloro-2-methylpropane/iso-pentane solution in the sample cylinder was added with an overpressure of nitrogen. The nitrogen used to pressurize the charger and for all other work passed over a separate high surface sodium column. After complete addition, the autoclave was set to stir at 1700 rpm, and the initial pressure in the autoclave was 420 psi (2.90 MPa) and the temperature was 101° C. The temperature was difficult to maintain above 100° C., so the reaction was cooled to 95° C. where it was easier to maintain temperature. The reaction was in the 98-101° C. region for about 1 h before being allowed to cool to 95° C. The reaction was monitored periodically by GC offline. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO$_2$ column, and into a sample cylinder. The sample cylinder was then charged to about 300 psi (2.07 MPa) using nitrogen prior to offline analysis. The mass ratio of the liquid catalyst to n-butane was 0.48, and the volume ratio of liquid catalyst to n-butane was 0.22 using the following densities: 1.22 g/mL for the liquid catalyst and 0.57 g/mL for n-butane. The mass reaction rate was 5, and the volume reaction rate was 10. The results of the run are shown in Table 20 and were determined using the ASTM UOP980 method.

TABLE 20

Disproportionation and Isomerization of n-butane at 95° C., 1700 rpm, Hastelloy C autoclave, wt. % of reaction mixture

t (h)	C3−	iC4	nC4	iC5	nC5	C6P	C7+	iC4/nC4
0 (feed)	0.01	0.18	99.09	0.00	0.00	0.00	0.60	0.00
3.5	0.07	6.76	91.97	0.71	0.08	0.16	0.14	0.07
27.0	0.09	13.67	84.53	0.93	0.15	0.17	0.33	0.16

Example 16

iC4 and nC7 Reverse Disproportionation—Stir Rate at 1700 rpm with [(^{n}Bu)$_3$P(Hex)][Al$_2$Cl$_6$Br] in Hastelloy C Autoclave at 95° C.

[0110] A 300 mL Hastelloy C autoclave, Hastelloy C baffle, and 75 mL stainless steel sample cylinder were dried in a 110° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 50.428 g of [(^{n}Bu)$_3$P(Hex)][Al$_2$Cl$_6$Br], 40.368 g of n-heptane (pre-dried by storing over activated 3A molecular sieves for several days), and the autoclave head was attached. 1.501 g of 2-chloro-2-methylpropane, which had previously been dried over activated 3A molecular sieves, and 12.868 g of n-heptane were added to the sample cylinder. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was charged with 65 g of iso-butane from a pressurized feed charger without displacing the nitrogen present in the autoclave. The autoclave was heated to 95° C. Once the temperature was reached, the 2-chloro-2-methylpropane/n-heptane solution in the sample cylinder was added with an over-pressure of nitrogen. The nitrogen used to pressurize the charger and for all other work passed over a separate high surface sodium column. After complete addition, stirring was set to 1700 rpm, and the initial pressure in the autoclave was 360 psi (2.48 MPa). The reaction was monitored periodically by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO$_2$ column, and then passing it directly into a GC sample loop. At the end of the reaction, an aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO$_2$ column, and into a sample cylinder. The sample cylinder was then charged to about 300 psi (2.07 MPa) using nitrogen prior to offline analysis. The mass ratio of liquid catalyst to hydrocarbon feed was 0.44. The volume ratio of liquid catalyst to hydrocarbon feed was 0.22 using the following densities: 1.22 g/mL for the liquid catalyst, 0.68 g/mL for n-heptane and 0.55 g/mL for isobutane. The mass reaction rate was 2, and the volume reaction rate was 3 after 28 h. The results of the run are shown in Table 21 and were determined using the ASTM UOP980 method offline. The feed composition (t (O)) is based on the mass of the added reagents.

TABLE 21

Reverse Disproportionation of n-Heptane and iso-Butane at 95° C., 1700 rpm, Hastelloy C autoclave, wt % of reaction mixture

t (h)	C3−	iC4	nC4	iC5	nC5	C6P	nC7	Heavies
0 (feed)		55					45	
28	0.27	56.99	1.38	3.16	0.08	1.70	23.80	11.39

Example 17

nC4/nC5—Stir Rate at 1700 rpm with [1-butyl-3-methylimidazolium][Al$_2$Cl$_7$] in Hastelloy C Autoclave at 100° C.

[0111] A 300 mL Hastelloy C autoclave, Hastelloy C baffle, and 75 mL stainless steel sample cylinder were dried in a 110°

C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 55.387 g of [1-butyl-3-methylimidazolium][Al_2Cl_7], and the autoclave head was attached. 5.6 g of 2-chloro-2-methylpropane, which had previously been dried over activated 3A molecular sieves, was added to the sample cylinder. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was charged with 103 g of n-butane from a pressurized feed charger without displacing the nitrogen present in the autoclave, but was then vented down to 86 g of n-butane. The sample cylinder was charged with 31 g of n-pentane from a pressurized feed charger without displacing the nitrogen present in the sample cylinder. The autoclave was heated to 103° C. while stirring at 100 rpm. Once this temperature was reached, stirring was stopped and the 2-chloro-2-methylpropane/n-pentane solution in the sample cylinder was added with an over-pressure of nitrogen. The nitrogen used to pressurize the charger and for all other work passed over a separate high surface sodium column. After complete addition, the reaction mixture was stirred at 1700 rpm and the temperature increased to 110° C. The pressure in the autoclave at this point was 600 psi (4.14 MPa). After 0.1 h, during which time the temperature fluctuated from 104-111° C., stirring was stopped, the reaction mixture was allowed to settle for 5 minutes, and the paraffinic layer was analyzed by GC. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The GC method employed was UOP690. Afterwards, a liquid sample was removed by filtering through a SiO_2 column into a sample cylinder. The liquid contained within the sample cylinder was pressurized with nitrogen to 300 psi (2.07 MPa) and was then analyzed offline using an analogous method. During sampling, the reaction cooled to 91° C. Afterwards, the reaction was reheated to 100° C. with stirring at 1700 rpm, which took 0.7 h to achieve, and the pressure at this point was 350 psi (2.41 MPa). The reaction was continued for an additional 17.6 h at this temperature, and the mixture was then analyzed is a similar manner. The results of the run are shown in Table 22 and were determined using the UOP690 method online. The mass ratio of liquid catalyst to hydrocarbon feed was 0.52, and the volume ratio was 0.23 using the following densities: 1.34 g/mL for the liquid catalyst, 0.626 g/mL for n-pentane and 0.57 g/mL for n-butane. The mass reaction rate was 650, and the volume reaction rate was 1500 after 0.1 h.

TABLE 22

Isomerization and disproportionation of a n-butane/n-pentane feed at 100° C., 1700 rpm, Hastelloy C autoclave, wt. % of feed and reaction mixture

	C3P	iC4	nC4	iC5	nC5	C6P	C7P	C8P	nC4-nC5[b]	nC5-nC6[b]	nC8-nC9[b]	nC9-nC10[b]	nC10+[b]
HC													
nC5[a]	0.00	0.00	0.00	0.03	99.05	0.00	0.00	0.00	0.88	0.03	0.00	0.00	0.00
nC4[a]	0.01	0.17	99.71	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00	0.00
time (h)													
0.1	0.44	15.52	52.06	11.64	13.97	3.87	0.81	0.49	0.64	0.11	0.11	0.06	0.05
18.4	4.35	42.59	24.64	15.16	4.17	6.80	1.03	0.67	0.19	0.00	0.13	0.05	0.10

[a] Composition of the pure hydrocarbon feed,

[b] Unknowns within these ranges

Example 18

nC4/nC5—Stir Rate at 1700 rpm with [1-butyl-3-methylimidazolium][Al_2Cl_7] in Hastelloy C Autoclave at 100° C.

[0112] A 300 mL Hastelloy C autoclave, Hastelloy C baffle, and 500 mL stainless steel sample cylinder were dried in a 110° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 55.404 g of [1-butyl-3-methylimidazolium][Al_2Cl_7], and the autoclave head was attached. 11.821 g of 2-chloro-2-methylpropane, which had previously been dried over activated 3A molecular sieves, was added to a 500 mL sample cylinder. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The sample cylinder was charged with 61.9 g of n-pentane, which was passed over a high surface sodium column, followed by 200.9 g of n-butane from a pressurized feed charger. The sample cylinder was then charged to about 600 psi (4.14 MPa) with nitrogen. A portion of the stock solution was analyzed by GC offline. The autoclave was charged with 130.3 g of the n-butane/n-pentane/2-chloro-2-methylpropane stock solution at room temperature, without displacing the nitrogen present in the autoclave. The initial temperature and pressure were 26° C. and 340 psi (2.34 MPa). The reaction mixture was set to stir at 1700 rpm while the autoclave was heated to 100° C.; it took 1.2 h to reach temperature, and the initial pressure was 980 psi (6.76 MPa). After a total of 18.8 h, the pressure was 1090 psi (7.52 MPa) within the autoclave. At this time, the reaction mixture was cooled to 85° C., which took 1.6 h, and it was then analyzed by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The GC method employed was UOP690. Afterwards, a liquid sample was removed by filtering through a SiO_2 column into a sample cylinder. The liquid contained within the sample cylinder was pressurized with nitrogen to about 300 psi (2.07 MPa) and was then analyzed offline using an analogous method. The results of the run are shown in Table 23 and were determined using the UOP690 method. The GC of the feed (0.0 h in Table 23) is the wt. % of the components in the 500 mL sample cylinder, without integrating 2-chloro-2-methylpropane. The mass ratio of liquid catalyst to hydrocarbon feed was 0.49, and the volume ratio was 0.21 using the following densities: 1.34 g/mL for the liquid catalyst, 0.626 g/mL for n-pentane and 0.57 g/mL for n-butane. The mass reaction rate was 6, and the volume reaction rate was 14 after 20.4 h.

TABLE 23

Isomerization and disproportionation of a n-butane/n-pentane feed at 100° C., 1700 rpm, Hastelloy C autoclave, wt. % of feed and reaction mixture

time (h)	C3P	iC4	nC4	iC5	nC5	C6P	C7P	C8P	nC4-nC5[a]	nC5-nC6[a]	nC8-nC9[a]	nC9-nC10[a]	nC10+[a]
0.0	0.01	0.13	73.81	0.01	25.26	0.00	0.00	0.00	0.21	0.01	0.00	0.00	0.06
20.4	1.35	40.64	33.77	13.40	3.78	5.30	0.73	0.57	0.08	0.00	0.10	0.04	0.09

[a] Unknowns within these ranges

Example 19

nC4—Stir Rate at 1700 rpm with [1-butyl-3-methylimidazolium]$[Al_2Cl_7]$ in Hastelloy C Autoclave at 100° C.

[0113] A 300 mL Hastelloy C autoclave, Hastelloy C baffle, and 75 mL stainless steel sample cylinder were dried in a 110° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 55.394 g of [1-butyl-3-methylimidazolium]$[Al_2Cl_7]$ and the autoclave head was attached. 5.818 g of 2-chloro-2-methylpropane, which had previously been dried over activated 3A molecular sieves, was added to the sample cylinder. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was charged with 120 g of n-butane from a pressurized feed charger, which was then vented down to 94 g of n-butane in the autoclave. The sample cylinder was charged with 15 g of n-butane from a pressurized feed charger without displacing the nitrogen present in the sample cylinder. The autoclave was heated to 100° C. while stirring at 138 rpm. Once the temperature was achieved, stirring was stopped, and the 2-chloro-2-methylpropane/n-butane solution in the sample cylinder was added with an over-pressure of nitrogen. The nitrogen used to pressurize the charger and for all other work passed over a separate high surface sodium column. After complete addition, stirring was started again at 1700 rpm; the initial pressure in the autoclave was 540 psi (3.72 MPa), and the temperature was 112° C. After 0.2 h, during which time the temperature fluctuated from 98-112° C., stirring was stopped, the reaction mixture was allowed to settle, and the paraffinic layer was analyzed by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The GC method employed was UOP690. Afterwards, a liquid sample was removed by filtering through a SiO_2 column into a sample cylinder. The liquid contained within the sample cylinder was pressurized with nitrogen to 300 psi (2.07 MPa) and was then analyzed offline using an analogous method. After GC analysis, the reaction was stirred at 1700 rpm and the temperature had cooled to 96° C. Reheating to 100° C. took 0.6 h. The reaction was continued for an additional 21.1 h at this temperature. The mixture was then analyzed in a similar manner. The results of the run are shown in Table 24 and were determined using the UOP690 method online. The mass ratio of liquid catalyst to hydrocarbon feed was 0.56, and the volume ratio was 0.24 using the following densities: 1.34 g/mL for the liquid catalyst and 0.57 g/mL for n-butane. The mass reaction rate was 240, and the volume reaction rate was 570 after 0.2 h.

TABLE 24

Isomerization and disproportionation of n-butane at 100° C., 1700 rpm, Hastelloy C autoclave, wt. % of feed and reaction mixture

time (h)	C3P	iC4	nC4	iC5	nC5	C6P	C7P	C8P	nC4-nC5[a]	nC5-nC6[a]	nC8-nC9[a]	nC9-nC10[a]	nC10+[a]
0.0	0.01	0.17	99.71	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00	0.00
0.2	0.37	21.55	72.71	3.04	0.77	0.79	0.19	0.31	0.11	0.00	0.02	0.00	0.05
21.9	0.85	52.78	38.09	5.06	1.38	0.78	0.07	0.30	0.11	0.00	0.07	0.05	0.15

[a] Unknowns within these ranges

Example 20

nC4—Stir Rate at 1700 rpm with [1-butyl-3-methylimidazolium]$[Al_2Cl_7]$ in Hastelloy C Autoclave at 90° C.

[0114] A 300 mL Hastelloy C autoclave, Hastelloy C baffle, and 75 mL stainless steel sample cylinder were dried in a 110° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 55.392 g of [1-butyl-3-methylimidazolium]$[Al_2Cl_7]$, and the autoclave head was attached. 5.823 g of 2-chloro-2-methylpropane, which had previously been dried over activated 3A molecular sieves, was added to the sample cylinder. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was charged with 117 g of n-butane from a pressurized feed charger, which was then vented down to 101 g of n-butane in the autoclave. The sample cylinder was charged with 15.7 g of n-butane from a pressurized feed charger without displacing the nitrogen present in the sample cylinder. The autoclave was heated to 90° C. with stirring at 115 rpm. Once the temperature had stabilized, stirring was stopped, and the 2-chloro-2-methylpropane/n-butane solution in the sample cylinder was added with an over-pressure of nitrogen. The nitrogen used to pressurize the charger and for all other work passed over a separate high surface sodium column. After complete addition, the initial pressure in the autoclave was 320 psi (2.21 MPa), and the autoclave was set to stir at 1700 rpm. After 97 h, stirring was stopped and the reaction mixture was allowed to settle and the paraffinic layer was analyzed by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The GC method employed was UOP690. Afterwards, a liquid sample was removed by filtering through a SiO_2 column into a sample cylinder. The liquid contained within the sample cylinder was pressurized with nitrogen to 300 psi (2.07 MPa) and was then analyzed offline using an analogous method. The results of the run are shown in Table 25 and were determined using the UOP690 method online. The mass ratio of liquid catalyst to hydrocarbon feed was 0.52, and the volume ratio was 0.22 using the following densities: 1.34 g/mL for the liquid catalyst and 0.57 g/mL for n-butane. The mass reaction rate was 0.8, and the volume reaction rate was 2 after 97 h.

TABLE 25

Isomerization and disproportionation of n-butane at 90° C., 1700 rpm, Hastelloy C autoclave, wt. % of feed and reaction mixture

time (h)	C3P	iC4	nC4	iC5	nC5	C6P	C7P	C8P	nC4-nC5[a]	nC5-nC6[a]	nC8-nC9[a]	nC9-nC10[a]	nC10+[a]
0.0	0.01	0.17	99.71	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00	0.00
97	0.33	33.74	60.38	3.03	0.77	0.61	0.14	0.45	0.11	0.00	0.08	0.06	0.10

[a] Unknowns within these ranges

Example 21

nC4—Stir Rate at 1700 rpm with [1-butyl-3-methylimidazolium][Al_2Cl_7] in Hastelloy C Autoclave at 100° C.

[0115] A 300 mL Hastelloy C autoclave, Hastelloy C baffle, and 500 mL stainless steel sample cylinder were dried in a 110° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 55.390 g of [1-butyl-3-methylimidazolium][Al_2Cl_7], and the autoclave head was attached. 8.754 g of 2-chloro-2-methylpropane, which had previously been dried over activated 3A molecular sieves, was added to the 500 mL sample cylinder. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. Nitrogen and any other gaseous compounds were removed from the autoclave by evacuation using standard Schlenk techniques on a Schlenk line. The sample cylinder was charged with 165 g of n-butane. The autoclave was charged with 113 g of the n-butane/2-chloro-2-methylpropane stock solution at room temperature. The initial temperature and pressure were 27° C. and 60 psi (0.41 MPa). The reaction mixture was set to stir at 1700 rpm while the autoclave was heated to 100° C. It took 1 h to reach temperature, and the pressure was 320 psi (2.21 MPa). After a total of 19.4 h, the pressure was 360 psi (2.48 MPa) within the autoclave. At this time, the reaction mixture was analyzed by GC. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The GC method employed was UOP690. Afterwards, a liquid sample was removed by filtering through a SiO_2 column into a sample cylinder. The liquid contained within the sample cylinder was pressurized with nitrogen to about 300 psi (2.07 MPa) and was then analyzed offline using an analogous method. The results of the run are shown in Table 26 and were obtained using the UOP690 method. The mass ratio of liquid catalyst to hydrocarbon feed was 0.57, and the volume ratio was 0.24 using the following densities: 1.34 g/mL for the liquid catalyst and 0.57 g/mL for n-butane. The mass reaction rate was 4, and the volume reaction rate was 9 after 19.4 h.

TABLE 26

Isomerization and disproportionation of n-butane feed at 100° C., 1700 rpm, Hastelloy C autoclave, wt % of feed and reaction mixture

time (h)	C3P	iC4	nC4	iC5	nC5	C6P	C7P	C8P	nC4-nC5[a]	nC5-nC6[a]	nC8-nC9[a]	nC9-nC10[a]	nC10+[a]	iC4/nC4
0.0	0.01	0.17	99.71	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.00
19.4	0.34	33.54	58.91	4.10	1.09	1.04	0.19	0.41	0.08	0.00	0.04	0.03	0.08	0.57

[a] Unknowns within these ranges

Example 22

nC4—Stir Rate at 1700 rpm with [1-butyl-3-methylimidazolium][Al_2Cl_7] in Hastelloy C Autoclave at 100° C.

[0116] A 300 mL Hastelloy C autoclave equipped with a Hastelloy C dipleg and Hastelloy B nut and connector, Hastelloy C baffle, and 75 mL stainless steel sample cylinder were dried in a 110° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 55.391 g of [1-butyl-3-methylimidazolium][Al_2Cl_7] and the autoclave head was attached. 5.894 g of 2-chloro-2-methylpropane, which had previously been dried over activated 3A molecular sieves, was added to the sample cylinder. The sample cylinder was closed under nitrogen, and both the autoclave and sample cylinder were removed from the glovebox. The autoclave was charged with 104 g of n-butane from a pressurized feed charger without displacing the nitrogen present in the autoclave. The composition of the n-butane feed is listed in Table 27, entry 1. The sample cylinder was charged with 15.25 g of n-butane from a pressurized feed charger without displacing the nitrogen present in the sample cylinder. The autoclave was heated to 100° C. with stirring at 100 rpm. Once the temperature was reached, stirring was stopped, and the 2-chloro-2-methylpropane/n-butane solution in the sample cylinder was added with an over-pressure of nitrogen. The nitrogen used to pressurize the charger and for all other work passed over a separate high surface sodium column. Once the addition was complete, stirring was set to 1700 rpm. Initially, the temperature increased to 102° C., and the pressure was 740 psi (5.10 MPa) within the autoclave. During the first 0.6 h, the temperature fluctuated from 98-102° C. After this time, the temperature stabilized at 100° C. and the initial pressure was 720 psi (4.96 MPa). After an additional 7.2 h, the pressure had increased to 830 psi (5.72 MPa), and the reaction mixture was analyzed by GC (entry 2, Table 27). In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The GC method employed was UOP690. Afterwards, a liquid sample was removed by filtering through a SiO_2 column into a sample cylinder. The liquid contained within the sample cylinder was pressurized with nitrogen to 300 psi (2.07 MPa) and was then analyzed offline using an analogous method. Once the stirring was recommenced, the temperature increased to 113° C., and, after 0.6 h, it stabilized at 100° C. with a pressure of 410 psi (2.83 MPa). The reaction was continued for an additional 14.5 h at this temperature, and the mixture was analyzed is a similar manner (entry 3, Table 27). Afterwards, the autoclave was cooled to ambient temperature, and a portion of the product was vented off. Fresh n-butane was added to the partially emptied autoclave. The composition of this new mixture is shown in entry 4, Table 27. The autoclave was then heated back to 100° C. with stirring at 1700 rpm, which took 1 h to achieve, and the pressure was 300 psi (2.07 MPa). After an additional 16.9 h of reaction, the product was analyzed. The results of the run are shown in Table 27 and were determined using the UOP690 method online. The mass ratio of liquid catalyst to hydrocarbon feed was 0.51 and the volume ratio was 0.22 using the following densities: 1.34 g/mL for the liquid catalyst and 0.57 g/mL for n-butane. The mass reaction rate was 15, and the volume reaction rate was 35 after 7.8 h.

TABLE 27

Isomerization and disproportionation of n-butane at 100° C., 1700 rpm, Hastelloy C autoclave, wt. % of feed and reaction mixture

Entry	time (h)	C3P	iC4	nC4	iC5	nC5	C6P	C7P	C8P	nC4-nC5[a]	nC5-nC6[a]	nC8-nC9[a]	nC9-nC10[a]	nC10+[a]	iC4/nC4
1	0.0	0.01	0.17	99.71	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.00
2	7.8	0.97	52.69	39.89	4.18	1.13	0.62	0.07	0.23	0.12	0.00	0.00	0.00	0.05	1.32
3	22.9	1.38	57.72	33.11	5.19	1.41	0.70	0.05	0.18	0.12	0.00	0.00	0.00	0.07	1.74
4	22.9	0.66	31.01	64.14	3.03	0.75	0.35	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.48
5	40.8	0.72	50.72	42.75	3.75	1.02	0.48	0.04	0.19	0.12	0.00	0.02	0.01	0.07	1.19

[a] Unknowns within these ranges

Example 23

nC4—Stir Rate at 1700 rpm with [1-butyl-3-methylimidazolium][Al_2Cl_7] in Hastelloy C Autoclave at 100° C. Using HCl

[0117] A 300 mL Hastelloy C autoclave equipped with a Hastelloy C dipleg and Hastelloy B nut and connector, and Hastelloy C baffle were dried in a 110° C. oven for at least 8 h. The dried autoclave and sample cylinder were brought into a nitrogen glovebox and allowed to cool to ambient temperature. The autoclave was charged with 55.390 g of [1-butyl-3-methylimidazolium][Al_2Cl_7], and the autoclave head was attached. The autoclave was closed under nitrogen and removed from the glovebox. Nitrogen and any other gaseous compounds were removed from the autoclave by evacuation using standard Schlenk techniques and a Schlenk line. The autoclave was charged with 2.5 g of anhydrous HCl at ambient temperature. Afterwards, 123 g of n-butane was added to the autoclave from a pressurized feed charger. The reaction mixture was set to stir at 1700 rpm, and the autoclave was heated to 100° C. with stirring at 1700 rpm. It took 1.2 h to reach temperature, and the initial pressure was 460 psi (3.17 MPa). After a total of 4.8 h, the pressure was 440 psi (3.03 MPa) within the autoclave, and an aliquot was removed for GC analysis. In order to analyze the paraffinic layer, the stirring was stopped, and the product was allowed to settle for 5 minutes. An aliquot was sampled directly from the autoclave by opening a valve from the autoclave, passing the paraffinic layer through a SiO_2 column, and then passing it directly into a GC sample loop. The GC method employed was UOP690 (entry 2, Table 28). Entry 1 in Table 28 is the composition of the butane feed. Afterwards, a liquid sample was removed by filtering through a SiO_2 column into a sample cylinder. The liquid contained within the sample cylinder was pressurized with nitrogen to 300 psi (2.07 MPa) and was then analyzed offline using an analogous method. Afterwards, stirring was set to 1700 rpm, and the pressure was 320 psi (2.21 MPa). The reaction was continued for an additional 17.0 h; the pressure was 320 psi (2.21 MPa) and had not increased.

The reaction temperature was increased to 120° C.; it took 1 h to reach temperature. At this temperature, the pressure within the autoclave was 510 psi (3.52 MPa). The reaction was stirred at this temperature for 3.9 h, and the pressure had increased to 530 psi (3.65 MPa). The temperature was then increased to 130° C. It took 0.5 h to reach temperature, and the reaction was allowed to continue at that temperature for an additional 2.7 h. Afterwards, the temperature was decreased to 100° C.; it took 0.7 h to reach temperature. After maintaining the temperature at 100° C. for 0.1 h, the pressure within the autoclave was 350 psi (2.41 MPa), and the product mixture was analyzed in a similar manner (entry 3, Table 28), as discussed above. Afterwards, stirring was set to 1700 rpm, and the reaction mixture heated to 120° C. It took 1.1 h to reach temperature, and the pressure at this temperature was 500 psi (3.45 MPa). The reaction mixture was allowed to continue to react at this temperature for an additional 13.5 h. At this time, the pressure within the autoclave was 510 psi (3.52 MPa). The reaction mixture was then cooled to 24° C. and analyzed by GC (entry 4, Table 28). The results of the run are shown in Table 28 and were determined using the UOP690 method online. The mass ratio of liquid catalyst to hydrocarbon feed was 0.47, and the volume ratio was 0.20 using the following densities: 1.34 g/mL for the liquid catalyst and 0.57 g/mL for n-butane. The mass reaction rate was 3, and the volume reaction rate was 8 after 4.8 h.

TABLE 28

Isomerization and disproportionation of n-butane at 100-130° C. Using HCl, 1700 rpm, Hastelloy C autoclave, wt. % of feed and reaction mixture

Entry	time (h)	C3P	iC4	nC4	iC5	nC5	C6P	C7P	C8P	nC4-nC5[a]	nC5-nC6[a]	nC8-nC9[a]	nC9-nC10[a]	nC10+[a]	iC4/nC4	% C4P Conv.
1	0.0	0.01	0.17	99.71	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0
2	4.8	0.01	7.37	92.45	0.00	0.00	0.00	0.00	0.00	0.16	0.00	0.00	0.00	0.00	0.08	7
3	30.7	0.34	57.95	40.95	0.46	0.13	0.00	0.00	0.02	0.12	0.00	0.00	0.00	0.00	1.42	59
4	45.3	2.11	59.83	33.93	3.00	0.82	0.13	0.00	0.00	0.12	0.00	0.00	0.00	0.00	1.76	66

[a] Unknowns within these ranges

[0118] While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention. It being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims.

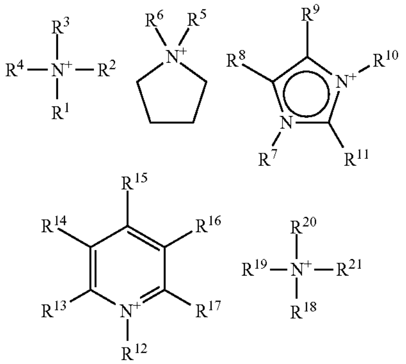
What is claimed is:

1. A hydrocarbon conversion process comprising:

disproportionating a hydrocarbon feed comprising normal C_4 alkane or branched C_4 alkane by contacting the hydrocarbon feed with a liquid catalyst in a reaction zone under disproportionation conditions to form a product mixture comprising at least about 0.2 wt % C_{3-} alkanes and C_{5+} alkanes in 1 hr based on the C_4 alkanes in the hydrocarbon feed, wherein the liquid catalyst comprises an unsupported ionic liquid and a carbocation promoter, and wherein a mass ratio of liquid catalyst to hydrocarbon feed is less than 0.75:1.

2. The process of claim **1** wherein the ionic liquid comprises an organic cation and an anion.

3. The process of claim **2** wherein the organic cation is selected from the group consisting of:



where R^1-R^{21} are independently selected from C_1-C_{20} hydrocarbons, C_1-C_{20} hydrocarbon derivatives, halogens, and H.

4. The process of claim **2** wherein the anion is derived from halides, sulfates, bisulfates, nitrates, sulfonates, fluoroalkanesulfonates, or combinations thereof.

5. The process of claim **2** wherein the anion is selected from the group consisting of $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, $AlCl_3Br^-$, $Al_2Cl_6Br^-$, $Al_3Cl_9Br^-$, $AlBr_4^-$, $Al_2Br_7^-$, $Al_3Br_{10}^-$, $GaCl_4^-$, $Ga_2Cl_7^-$, $Ga_3Cl_{10}^-$, $GaCl_3Br^-$, $Ga_2Cl_6Br^-$, $Ga_3Cl_9Br^-$, $CuCl_2^-$, $Cu_2Cl_3^-$, $Cu_3Cl_4^-$, $ZnCl_3^-$, $FeCl_3^-$, $FeCl_4^-$, $Fe_3Cl_7^-$, PF_6^-, and BF_4^-.

6. The process of claim **1** wherein the carbocation promoter comprises a haloalkane, a mineral acid, or combinations thereof.

7. The process of claim **6** wherein the carbocation promoter comprises the haloalkane, and wherein the haloalkane comprises 2-chloro-2-methylpropane, 2-chloropropane, 2-chlorobutane, 2-chloro-2-methylbutane, 2-chloropentane, 1-chlorohexane, 3-chloro-3-methylpentane, or combinations thereof.

8. The process of claim **6** wherein the carbocation promoter comprises the mineral acid, and wherein the mineral acid comprises HCl.

9. The process of claim **1** further comprising stirring the hydrocarbon feed and the liquid catalyst while contacting the hydrocarbon feed with the liquid catalyst.

10. The process of claim **1** wherein a molar ratio of the carbocation promoter to ionic liquid is in a range of about 0:1 to about 3:1.

11. The process of claim **1** further comprising separating the ionic liquid from the product mixture.

12. The process of claim **11** further comprising regenerating the separated ionic liquid.

13. The process of claim **1** further comprising: drying the hydrocarbon feed before contacting the hydrocarbon feed with the liquid catalyst; or treating the hydrocarbon feed to remove one or more of alkenes, dienes, or nitriles; or both.

14. The process of claim **1** wherein a concentration of acid in the ionic liquid is less than about 2.5 M.

15. The process of claim **1** further comprising isomerizing the hydrocarbon feed concurrently with disproportionating the hydrocarbon feed.

16. The process of claim **15** wherein the product mixture has a ratio of branched C_4 alkane to normal C_4 alkane of at least about 0.3 in 1 hr.

17. The process of claim **1** wherein the hydrocarbon feed comprises a mixture of at least C_4 and C_5 alkanes.

18. The process of claim **1** wherein the product mixture further comprises at least about 0.3 wt % C_{3-} alkanes and C_{5+} alkanes in 1 hr based on the C_4 alkanes in the hydrocarbon feed.

19. The process of claim **1** wherein the product mixture comprises at least about 0.5 wt % C_{3-} alkanes and C_{5+} alkanes in 8 hr based on the C_4 alkanes in the hydrocarbon feed.

20. The process of claim **1** wherein the product mixture comprises at least about 1 wt % C_{3-} alkanes and C_{5+} alkanes in 25 hr based on the C_4 alkanes in the hydrocarbon feed.

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