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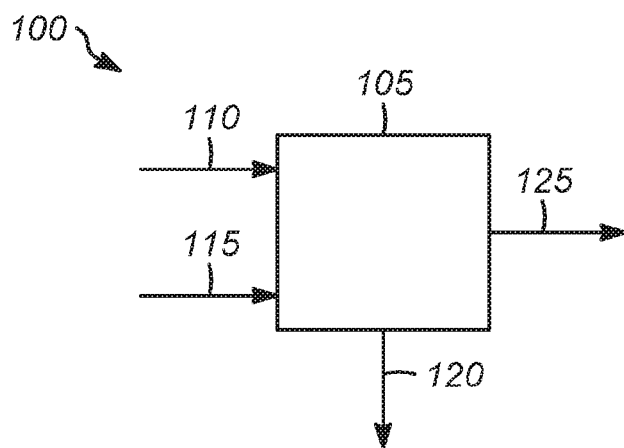
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(54) Title: PARAFFIN PROCESSING USING IONIC MICRO-EMULSIONS

**FIG. 1**

(57) Abstract: A process utilizing a micro-emulsion is described. The micro-emulsion is formed by contacting an ionic liquid, a co-solvent, a hydrocarbon, an optional surfactant, and an optional catalyst promoter. The micro-emulsion comprises a hydrocarbon component comprising the hydrocarbon, and an ionic liquid component comprising the ionic liquid. The ionic liquid comprises a halometallate anion and a cation. The hydrocarbon comprises at least one paraffin having from 4 to about 50 carbon atoms. The co-solvent has a polarity greater than the polarity of the hydrocarbon. The ionic liquid is present in an amount of about 0.05 wt% to about 40 wt% of the micro-emulsion. A product mixture comprising a product is produced in a process zone containing the micro-emulsion. The product comprises at least one of an isomerized paraffin, a disproportionated paraffin, and a reverse disproportionated paraffin.

PARAFFIN PROCESSING USING IONIC MICRO-EMULSIONS

5 This application claims the benefit of US Provisional Application Serial No. 62/141056, entitled Hydrocarbon Processes Using Halometallate Ionic Liquid Micro-Emulsions, filed March 31, 2015, which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

10 In liquid-liquid reactions, an intrinsic tradeoff exists between reactivity and post-reaction separation. High interfacial surface area between two liquid phases is needed to achieve high activity. As an example, in isomerization, disproportionation and reverse disproportionation using ionic liquid catalysts, high mixing speeds are required to improve reaction rate as is shown in US Publication No. 2015/0329444. Large ionic liquid droplets
15 available with conventional mixing result in low surface area and mass transfer-limited reaction of paraffins. Shorter reaction times or lower ionic liquid loading would be achievable if mass transfer resistance were less substantial.

 High ionic liquid inventory and/or smaller ionic liquid droplets are used to counter the mass transfer limitations of the reaction kinetics. However, smaller droplets which
20 are typically generated by shear force, are also more difficult to separate than larger droplets once the reaction is complete. Small ionic liquid droplets require very long or even infinite settling times for complete separation by gravity. Often, specialized equipment such as coalescers or centrifugal separation may be employed. However, coalescers are subject to fouling by pinning of ionic liquid droplets on coalescing elements, and separation by
25 centrifugal force requires a large amount of power. The loss rates of ionic liquid due to inefficient separation and deactivation may introduce a significant cost in ionic liquid catalyst make-up.

 Ionic liquids catalysts are well suited for reactions of paraffins such as isomerization, disproportionation and reverse disproportionation. Isomerization processes are
30 detailed in US Patent Nos. 9,096,483, 9,096,485, 9,102,578, and 9,126,881.

Disproportionation processes are described in US Patent Nos. 9,096,480, 9,096,481, 9,102,577, and 9,181,150. Reverse disproportionation processes are discussed in US Patent No. 9,096,482. However, the processes described in those inventions are biphasic liquid reactions involving ionic liquid droplets generated by mixing. The reactions are relatively slow, or
5 require elevated temperature or significantly high ionic liquid loading.

Alternative methods for generating mixtures which allow faster reaction and/or easy separation after reaction are needed for paraffin isomerization, disproportionation, and reverse disproportionation.

SUMMARY OF THE INVENTION

10 One aspect of the invention is a process utilizing a micro-emulsion. In one embodiment, the process includes forming a micro-emulsion by contacting an ionic liquid, a co-solvent, a hydrocarbon, an optional surfactant, and an optional catalyst promoter. The micro-emulsion comprises a hydrocarbon component comprising a hydrocarbon and an ionic liquid component comprising the ionic liquid. The ionic liquid comprises a halometallate anion
15 and a cation. The hydrocarbon comprises at least one paraffin having from 4 to about 50 carbon atoms. The co-solvent has a polarity greater than a polarity of the hydrocarbon. The ionic liquid is present in an amount of about 0.05 wt% to about 40 wt% of the micro-emulsion. A product mixture comprising a product is produced in a process zone containing the micro-emulsion. The product mixture comprises a product selected from an isomerized paraffin, a
20 disproportionated paraffin, a reverse disproportionated paraffin, or combinations thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is one embodiment of a process of the present invention.

Fig. 2 is another embodiment of a process of the present invention.

Fig. 3 is a graph showing the volume normalized particle size distribution of a
25 composition containing reverse micelles made using an added surfactant.

Fig. 4 is a graph showing the volume normalized particle size distribution of a composition containing reverse micelles made without an added surfactant.

Fig. 5 is a phase diagram showing the dichloromethane/hexane mole ratio as a function of total ionic liquid plus surfactant mole fraction.

Fig. 6 is a phase diagram showing the dichloromethane/hexane mole ratio as a function of the ionic liquid mole fraction for various ionic liquids.

DETAILED DESCRIPTION OF THE INVENTION

Conventional liquid-liquid reactions, including paraffin isomerization, disproportionation and reverse disproportionation using ionic liquids, often use high shear to generate droplets in a two-phase mixture. In these bi-phasic reactions, catalyst solubility in the hydrocarbon phase is often negligible, and the reaction occurs in the surface layer of the catalyst phase. Small droplet size thus allows improved mass transfer by increasing the surface area to volume ratio of the catalyst. This requires the input of energy into the mixture, which is stored as surface energy in the droplets. The surface energy is dissipated as droplets coalesce to form larger droplets either in the reactor/mixer or during gravity settling. However, in some cases, the smallest droplets do not easily separate due to their low terminal settling velocities which are insignificant compared to Brownian motion. Incomplete separation leads to costly losses of ionic liquid. In order to avoid using small droplets, more ionic liquid can be used (e.g., higher ionic liquid to hydrocarbon volume ratio), but this requires significantly higher and unutilized ionic liquid inventory, which, in addition to increasing costs, also has the potential to lead to increased rate of undesired side-reactions.

Rather than utilizing shear force to generate meta-stable droplets, in the present invention, the ionic liquid catalyst is stabilized in the form of a micro-emulsion. The micro-emulsion contains a hydrocarbon component comprising a hydrocarbon, and an ionic liquid component comprising the ionic liquid. The micro-emulsion can be reverse micelles, micelles, or a bi-continuous micro-emulsion. The ionic liquid component typically contains a higher content of co-solvent than the hydrocarbon component.

Reverse micelles are small structures containing an amphiphile, which allows for dispersion of a polar substance in a less-polar liquid. Such micro-emulsions are well known. Commonly, a micro-emulsion containing reverse micelles contains small structures on the order of one to tens of nanometers which consist of a water core surrounded by a surfactant in an organic solvent. Mixtures containing ionic liquid reverse micelles have been made. See, for example, Table 5 of Correa et al., *Nonaqueous Polar Solvents in Reverse Micelle Systems*, Chem. Rev. 2012, vol. 112, p. 4569–4602, which summarizes this work. Previous examples of ionic liquid reverse micelles generally contain a surfactant in addition to the ionic liquid. Furthermore, the prior art does not address the use of halometallate ionic liquids, which are

often used in their Lewis acidic form. Such ionic liquids are very useful for catalytic applications including paraffin isomerization, disproportionation and reverse disproportionation, but they are also highly reactive and are not compatible with most protic or oxygenated solvents or surfactants.

5 In some embodiments of this invention, the micro-emulsion comprises reverse micelles. In these embodiments, the co-solvent is miscible in the hydrocarbon and at least a portion of the co-solvent is contained in the hydrocarbon component. The ionic liquid component is dispersed in the hydrocarbon component. The ionic liquid component is more polar than the hydrocarbon component.

10 In some embodiments, the micro-emulsion comprises micelles. With micelles, there is a core of the hydrocarbon component surrounded by the ionic liquid component and an optional surfactant. The hydrocarbon component core surrounded by the ionic liquid component and the optional surfactant is dispersed in a polar continuous medium which comprises the co-solvent. The co-solvent is more polar than the hydrocarbon component.

15 In some embodiments, the micro-emulsion comprises a bi-continuous micro-emulsion comprising the hydrocarbon component and the ionic liquid component. The ionic liquid component contains at least a portion of the co-solvent, and it is more polar than the hydrocarbon component.

20 In conventional liquid-liquid mixtures containing ionic liquids and hydrocarbons, where shear force is used to generate droplets in a two-phase mixture, ionic liquid solubility in the non-ionic liquid phase is typically very low. This can be characterized by the solubility of the ionic liquid in a typical non-polar hydrocarbon such as n-hexane. The ionic liquid has a solubility in n-hexane of less than about 5 wt%, or less than about 3 wt%, or less than about 1 wt%, or less than about 0.5 wt%, or less than about 0.1 wt%, or less than about 0.01 wt%. As an example, ionic liquids with halometallate anions have very low solubility in hydrocarbons such as n-hexane and are often characterized as immiscible with hexane, such as in Zhao, D; Wu, M; Kou, Y; Min, E, Catalysis Today, 2002, 74, 157-189 Table 2. As such, these ionic liquids do not form solutions or micro-emulsions when combined with non-polar hydrocarbons, but instead form two-phase systems, with the non-polar hydrocarbon phase being substantially free of ionic liquid. By substantially free we mean that the non-polar hydrocarbon phase contains less than about 5 wt%, or less than about 3 wt%, or less than about 1 wt%, or less than about 0.5 wt%, or less than about 0.1 wt%, or less than about 0.01 wt%.

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Therefore, in order to form a micro-emulsion, an additional component such as a surfactant and/or a co-solvent must be added. Moreover, ionic liquid micro-emulsions have not been used in paraffin isomerization, disproportionation and reverse disproportionation processes.

5 In the present invention, micro-emulsions can be made using an ionic liquid, a hydrocarbon, and a co-solvent. The micro-emulsion may optionally contain an additional surfactant and/or a catalyst promoter.

The hydrocarbon and co-solvent each have a polarity. The polarity of the co-solvent is greater than the polarity of the hydrocarbon. Many hydrocarbons, including those in some embodiments of this invention, have polarity close to zero. Many polarity scales are known. Here polarity is defined by the polarity index P' , which is a measure of interactions of a solute relative to other solvents based on solubility constants. This polarity scale is commonly used to distinguish solvents by polarity for predicting solubility. Some hydrocarbons on this scale have P' less than zero. Hydrocarbons with P' less than zero are considered to have polarity less than the polarity of the co-solvent if the co-solvent has P' greater than P' of the hydrocarbon. A detailed description of polarity index is found in Snyder, L. R; Journal of Chromatography, 1974, vol 92, pp. 223-230 and tabulation of polarity index for many liquids is found in table I of that reference, which is incorporated herein by reference. For example, polarity index of n-hexane is 0.0, n-decane is -0.3, toluene is 2.3, benzene is 3.0, and methylene chloride (dichloromethane) is 3.4. In the absence of an available polarity index measurement, relative polarity of two liquids is determined from the magnitude of the liquids' dielectric constants. For instance, isobutane has dielectric constant of 1.8 at 300 K (Hayn, W. M, J. Chem. Eng. Data, 1983, vol 28, pp. 367-369), while the dielectric constant of dichloromethane at 298 K is 9.14 (Dean, J. A; Lange's Handbook of Chemistry and Physics, 14th ed, p. 5.101, McGraw-Hill, 1992, New York).

25 In some embodiments, the micro-emulsion can be made utilizing a surfactant that is compatible with the ionic liquid, while in others, no additional surfactant is used. In the latter case, although not wishing to be bound by theory, it is believed that the ionic liquid itself acts as the amphiphile to stabilize the micro-emulsions. To generate a micro-emulsion using a hydrocarbon as a major component of the mixture, a polar aprotic co-solvent such as dichloromethane is used. The micro-emulsions are useful as high surface-area catalysts for alkylation and other hydrocarbon conversion processes, as well as separation processes.

One specific type of micro-emulsion contains reverse micelles composed at least partly of ionic liquid. Reverse micelles are thermodynamically stable structures composed of a polar core stabilized by an amphiphile (the ionic liquid alone or the ionic liquid and an added surfactant) in a less-polar medium (the hydrocarbon component). The reverse micelles have a specific size distribution determined by the nature and relative amount of the amphiphile, as well as the relative amounts and properties of the polar and less polar media.

The need for high surface area in order to increase the reaction rate and the selectivity of the catalyst is met by the very small size of the micelles, reverse micelles or structures of bi-continuous phases of the micro-emulsion. Furthermore, because the ionic liquid itself may act as the amphiphile, the catalyst may be concentrated on the surface of the micelles, reverse micelles, or a phase boundary in a bi-continuous micro-emulsion. Consequently, diffusion of the reactants from the bulk hydrocarbon phase into the interior of the droplets may not be necessary. This provides additional reduction in mass transfer resistance.

The surface area to volume ratio of the micelles, reverse micelles, or bi-continuous structures in the micro-emulsion is much higher than the surface area to volume ratio of ionic liquid droplets generated by shear mixing alone. The higher surface area to volume ratio may also meet the need to decrease catalyst inventory. In some cases, the micelles, reverse micelles, or bi-continuous structures have volume normalized mean diameter as small as about 3 nm and contain surface areas exceeding 800 m²/gram of ionic liquid catalyst. Surface areas of 100-900 m²/gram of ionic liquid are typical for reverse micelles with an average size of 3-20 nm in diameter. Yet with conventional high shear mixing, a typical ionic liquid droplet size distribution may have a Sauter mean diameter of 55 microns which corresponds to a surface area of about 0.047 m²/gram of ionic liquid. Thus, significantly less ionic liquid needs to be used in a micro-emulsion to provide the same amount of surface area as in conventional ionic liquid systems. The amount of ionic liquid can be low (e.g., about 0.5-15% by volume) compared to traditional ionic liquid alkylation reactions (about 5-30% by volume). The amount of ionic liquid can be adjusted if it is accompanied by a change in the amount of co-solvent in order to stabilize the micro-emulsion or otherwise prevent a second liquid phase from forming, or if higher activity is desired.

In addition to advantages for reactivity, the nature of the micro-emulsion may allow catalyst recovery without the specialized equipment typically used in conventional ionic

liquid processes. To recover the catalyst, the micro-emulsion is broken by changing the reaction mixture composition such that the micro-emulsion is no longer thermodynamically stable. This can be done by any suitable method, including, but not limited to, removing a portion of the polar co-solvent (for example, by vaporization), increasing the amount of the hydrocarbon reactants (such as paraffins) and/or products, adding an additional liquid having a polarity less than the polarity of the co-solvent (including an inert or semi-inert hydrocarbon such as propane), adding ionic liquid, or combinations thereof. Once the micro-emulsion is no longer stable, a second phase of ionic liquid is formed which may be settled by gravity. Other separation process could be used including, but not limited to, sonication, electrostatic precipitation, filtration, adsorption, centrifugal separation, distillation, vaporization, or combinations thereof. These separation processes could be used in addition to gravity separation, or in place of it.

The process can be used for a variety of hydrocarbon conversion processes, including, paraffin disproportionation, paraffin reverse disproportionation, and paraffin isomerization.

In paraffin disproportion, a paraffin typically having from at least 4 to about 50 carbon atoms reacts to form products having one more carbon and one less carbon than the starting paraffin. Successive reactions lead to a distribution of paraffinic products having several more carbons and several fewer carbons than the reactant. In paraffin reverse disproportionation, two paraffins having different numbers of carbons atoms, each typically having from at least 4 to about 50 carbon atoms are reacted to form other paraffins having carbon numbers between those of the initial reactants. In paraffin isomerization, a paraffin typically having at least 4 to about 50 carbon atoms is isomerized to a different configuration having the same number of carbon atoms, e.g., normal butane to isobutane. Since all three of these reaction types involve only rearrangement of atoms or transfer of atoms from one molecule to another, moles of paraffin are conserved in these reactions. Excluding side-reactions which may occur, the number of moles of paraffin in the disproportionation, isomerization, or reverse disproportionation product is equal to the number of moles of converted paraffins. Paraffin isomerization, disproportionation, and reverse disproportionation often occur simultaneously in the same reactor.

The reaction takes place using a micro-emulsion comprising a hydrocarbon component comprising a hydrocarbon having a polarity, an ionic liquid component comprising an ionic liquid, the ionic liquid comprising a halometallate anion and a cation, and a co-solvent having a polarity greater than the polarity of the hydrocarbon. The micro-emulsion can be
5 reverse micelles, micelles, or a bi-continuous micro-emulsion. The ionic liquid component typically contains a higher content of co-solvent than the hydrocarbon component.

The generation of ionic liquid micro-emulsions and processes using ionic liquid micro-emulsions are described in US Application Serial No. 62/141087, entitled HALOMETALLATE IONIC LIQUID MICRO-EMULSIONS, (Attorney Docket No.
10 H0047291-8242) filed March 31, 2015, US Application Serial No. 62/141070, entitled HYDROCARBON PROCESSES USING HALOMETALLATE IONIC LIQUID MICRO-EMULSIONS, (Attorney Docket No. H0047294-8250) filed March 31, 2015, and US Application Serial No. 62/141076, entitled HEAT EXCHANGER FOR USE IN ALKYLATION PROCESS USING HALOMETALLATE IONIC LIQUID MICRO-
15 EMULSIONS, (Attorney Docket No. H0048678-8250) filed March 31, 2015, each of which is incorporated herein by reference.

The micro-emulsion is introduced into the reaction zone (or is formed there), along with the other reaction components. For example, in isomerization, disproportionation, reverse disproportionation processes, a micro-emulsion is formed from paraffins, a co-solvent,
20 an ionic liquid, and optionally a surfactant and/or a catalyst promoter. The reaction zone can be heated and or pressurized with a gas, and reaction occurs to form products including isomerized paraffins with the same number of carbon atoms as the reactants but a different configuration, disproportionated paraffins with fewer and greater number of carbon atoms than the individual reactants, and reverse disproportionated paraffins containing more carbon atoms
25 than at least one reactant but fewer carbon numbers than at least one reactant..

After the reaction, the micro-emulsion is broken, resulting in two distinct liquid phases. One phase is an ionic liquid phase that contains a majority of the ionic liquid. The other phase is a hydrocarbon phase that contains a majority of the hydrocarbon which can include products, and unreacted paraffins (if present). Both phases may contain co-solvent, surfactant
30 (if present) and catalyst promoter (if present). The hydrocarbon phase may contain a minor portion of the ionic liquid, and the ionic liquid phase may contain a minor component of the hydrocarbons.

The ionic liquid phase is separated from the hydrocarbon phase. This separation typically takes place by gravity due to the density difference between the ionic liquid phase and the hydrocarbon phase and/or using one of the other processes discussed above. If the ionic liquid phase has a higher density than the hydrocarbon phase, the layer containing the ionic liquid phase will be below the layer containing the hydrocarbon phase. If the ionic liquid phase has a lower density, it will be above the layer containing the hydrocarbon phase. The presence and amount of co-solvent in the ionic liquid and hydrocarbon phases may affect the density of these phases.

The ionic liquid phase can be recycled to the reaction zone. Separation of the components of the ionic liquid phase may be desirable prior to recycling one or more of the components of the ionic liquid phase to the reaction zone. Such separation may take place by distillation, vaporization, or other means of separation known to those skilled in the art.

At least a portion of the recovered ionic liquid can be regenerated before being recycled. Various methods for regenerating ionic liquids could be used. For example, US 7,651,970; US 7,825,055; US 7,956,002; US 7,732,363, each of which is incorporated herein by reference, describe contacting ionic liquid containing the conjunct polymer with a reducing metal (e.g., Al), an inert hydrocarbon (e.g., hexane), and hydrogen and heating to about 100°C to transfer the conjunct polymer to the hydrocarbon phase, allowing for the conjunct polymer to be removed from the ionic liquid phase. Another method involves contacting ionic liquid containing 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 to transfer the conjunct polymer to the hydrocarbon phase, allowing for the conjunct polymer to be removed from the ionic liquid phase. See e.g., US 7,674,739 B2; 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 to transfer the conjunct polymer to the hydrocarbon phase. See e.g., US 7,727,925, 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 ionic liquid containing conjunct polymer and an inert hydrocarbon (e.g. hexane), and introducing hydrogen. The conjunct polymer is reduced and transferred to the hydrocarbon layer. See e.g., US 7,678,727, 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 reacts to

form an uncharged complex, which transfers to the hydrocarbon phase. See e.g., US 7,674,740, 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 is introduced and the conjunct polymer is reduced and transferred to the hydrocarbon layer. See e.g., US 7,691,771, 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 is added to wash away the liberated conjunct polymer. The ionic liquid precursor [butylpyridinium][Cl] is added to the ionic liquid (e.g. [butylpyridinium][Al₂Cl₇]) containing the conjunct polymer followed by an inert hydrocarbon. After mixing, the hydrocarbon layer is separated, resulting in a regenerated ionic liquid. See, e.g., US 7,737,067, which is incorporated herein by reference. Another method involves adding ionic liquid containing conjunct polymer to a suitable substrate (e.g. pyridine) and an electrochemical cell containing two aluminum electrodes and an inert hydrocarbon. A voltage is applied, and the current measured to determine the extent of reduction. After a given time, the inert hydrocarbon is separated, resulting in a regenerated ionic liquid. See, e.g., US 8,524,623, which is incorporated herein by reference. . Ionic liquids can also be regenerated by contacting with silane compounds (U.S. Patent No. 9,120,092), borane compounds (U.S. Publication No.2015/0314281), Brønsted acids, (U.S. Patent No. 9,079,176), or C₁ to C₁₀ Paraffins (U.S. Patent No. 9,079,175), each of which is incorporated herein by reference. Regeneration processes utilizing silane and borane compounds are described in U.S. Application Serial Nos. 14/269,943 and 14/269,978, each of which is incorporated herein by references.

The materials of the hydrocarbon phase can be separated using a suitable separation process. The product can be recovered. Any unreacted paraffins, surfactant, or catalyst promoter can be recovered, processed, and/or recycled. Suitable separation and recovery processes are well known.

The process can be a batch, semi-batch, or continuous process. The reaction and separation can take place in a single vessel or in multiple vessels.

Typical reaction conditions include a temperature in the range of about 0°C to about 250°C, or about 20°C to about 200°C, or about 50°C to about 150°C, or about 80°C to about 200°C, or about 80°C to about 170°C, or about 80°C to about 150°C, or about 80°C to

about 130°C, or about 90°C to about 150°C. It is desirable that the ionic liquid, co-solvent, and paraffins maintain a liquid rather than vapor state through the operating temperature range.

5 The pressure is typically in the range of about 0.1 MPa to about 8.0 MPa, or about 0.2 MPa to about 5 MPa. The pressure is preferably sufficient to keep the reactants in the liquid phase.

The residence time of the reactants in the reaction zone is in the range of a few minutes to a few days, or about 5 min to about 24 hours, or about 20 min to about 24 hours, or about 40 min to about 20 hours. If shorter residence time is desired, more ionic liquid can be used.

10 Isomerization

Suitable hydrocarbon feed for isomerization reactions includes C₄ to C₂₃ paraffins.

15 Suitable reaction conditions include a temperature up to the decomposition temperature of the ionic liquid, typically of 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.

20 The pressure in the reaction zone is typically in the range of about 0 MPa(g) to about 13.8 MPa(g), or about 0 MPa(g) to about 8.1 MPa(g), or about 0 MPa(g) to about 5 MPa(g), or about 0 MPa(g) to about 3.5 MPa(g). The pressure should be sufficient to ensure that the reaction product is in a liquid state. Small amounts of vapor may also be present, but this should be minimized.

25 The reaction can take place in the presence of a gas. Suitable gases include, but are not limited to methane, ethane, propane, hydrogen, hydrogen chloride, nitrogen and the like.

The reaction can take place in the presence of a catalyst promotor, which is generally an added acid or acid precursor. Suitable acids or acid precursors include, but are

not limited to, HCl, 2-chlorobutane, or tert-butyl chloride, for example. If tert-butyl chloride is used, this also serves as a carbenium ion initiator.

The residence time in the reaction zone is generally less than about 24 hr, or less than about 16 hr, or less than about 12 hr, or less than about 10 hr, or less than about 7 hr, or less than about 5 hr, or less than about 4 hr, or less than about 3 hr, or less than about 2 hr, or less than about 1 hr or less than about 30 min, or less than about 10 min, or about 1 min to about 24 hr, or about 5 min to about 24 hr, or about 10 min to about 24 hr, or about 30 min to about 16 hr, or about 30 min to about 12 hr, or about 1 hr to about 16 hr. The reaction time can be selected so that a predetermined conversion can be obtained. The reaction time is a function of the, the reaction temperature, the concentration of acid, the ratio of hydrocarbon to co-solvent (provided there is not so much hydrocarbon that the micro-emulsion is broken), and the mass/volume ratio of liquid catalyst to hydrocarbon being reacted. Generally, increasing any of these conditions will increase the reaction rate.

Disproportionation

Suitable hydrocarbon feeds for disproportionation reactions include C₄ to C₂₃ paraffins. Feeds comprising two or more paraffins are also acceptable.

Suitable reaction conditions include a temperature of less than the decomposition temperature of the ionic liquid, or about 250°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.

The pressure in the reaction zone is typically in the range of about 0 MPa to about 20.7 MPa, or about 0 MPa to about 8.1 MPa, or about 0 MPa to about 5 MPa, or about 0 MPa to about 3.5 MPa. The pressure should be sufficient to ensure that the reaction product is in a liquid state. Small amounts of vapor may also be present, but this should be minimized.

The reaction can take place in the presence of a gas. Suitable gases include, but are not limited to methane, ethane, propane, hydrogen, hydrogen chloride, nitrogen and the like.

The reaction can take place in the presence of a catalyst promotor, which is generally an added acid or acid precursor. Suitable acids or acid precursors include, but are not limited to, HCl, 2-chlorobutane, or tert-butyl chloride, for example.

The residence time in the reaction zone is generally less than about 24 hr, or less than about 16 hr, or less than about 12 hr, or less than about 10 hr, or less than about 7 hr, or less than about 5 hr, or less than about 4 hr, or less than about 3 hr, or less than about 2 hr, or less than about 1 hr, or less than about 30 min, or less than about 10 min, or about 1 min to about 24 hr, or about 5 min to about 24 hr, or about 10 min to about 24 hr, or about 30 min to about 16 hr, or about 30 min to about 12 hr, or about 1 hr to about 16 hr. The reaction time can be selected so that a predetermined conversion can be obtained. The reaction time is a function of the reaction temperature, the concentration of acid, the ratio of hydrocarbon to co-solvent (provided there is not so much hydrocarbon that the micro-emulsion is broken), and the mass/volume ratio of liquid catalyst to hydrocarbon being reacted. Generally, increasing any of these conditions will increase the reaction rate.

Reverse Disproportionation

The microscopic reverse of pentane disproportionation is the combination of one mole of hexane and one mole of butane to form two moles of pentane. This type of reaction is referred to herein as reverse disproportionation. Reverse disproportionation-type reactions can occur in which two paraffins having different carbon numbers react to form two different paraffins having different carbon numbers from those of the feed where the total number of moles of product and moles of carbon and hydrogen in the products does not change from the total number in the feed (e.g., pentane and octane reacting to form hexane and heptane). Utilizing the equilibrium among the various species, the concentration of the product can be controlled by varying the relative ratios of the species. Consequently, two different paraffinic feed sources of varying carbon count can be reacted to obtain a product containing paraffins of intermediate carbon count.

More generally, this process involves the net transfer of CH₂ units between paraffins, where CH₂ unit refers to the transfer of 1 C and 2 H, not necessarily a methylene unit. The products result from the donation and acceptance of net CH₂ units to and from various paraffins. Thus, two paraffinic feeds having different carbon counts can be reacted to produce a product having an intermediate carbon count. For example, the reaction of butane with a larger paraffin, e.g., C₁₆, produces a product containing paraffins in the C₅ to C₁₅ range.

In addition to the net CH₂ transfer, the process favors the formation of branched paraffins, which are more valuable than normal paraffins because they have more desirable octane numbers and cloud points.

Typically, hydrocarbons having a carbon number from 3-200 or more can be selected as feeds for the process. Depending on the desired product, one or two (or more) hydrocarbon feeds could be selected.

In some embodiments involving reverse disproportion, one larger and one smaller paraffin feed can be used to produce a product composition having an intermediate carbon count. The smaller feed typically has carbon numbers ranging from 3-198, and the larger feed typically has carbon numbers ranging from 5-200. There is generally a difference of at least 2 or more carbon numbers between the two feeds, or at least 3, or at least 4, or at least 5, or at least 6 or more. In some embodiments involving reverse disproportionation, the reaction mixture has an amount of at least one of the intermediate products equal to or in excess of the amount formed by the disproportionation reaction of either feed alone.

In some embodiments, the smaller feed typically has carbon numbers ranging from 4-23, and the larger feed typically has carbon numbers ranging from 6-25. There is generally a difference of at least 2 or more carbon numbers between the two feeds, or at least 3, or at least 4, or at least 5, or at least 6 or more.

The liquid hydrocarbon feed is contacted with the liquid catalyst at temperatures of in the range of about -20°C to about the decomposition temperature of the ionic liquid, or about 250°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.

The pressure in the reaction zone is typically in the range of about 0 MPa to about 20.7 MPa, or about 0 MPa to about 8.1 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 other embodiments, using propane and other light paraffins, the temperatures may not allow for a liquid state. In this case, a gas phase

or a supercritical phase can be used. The reaction typically takes place in the presence of a gas. Suitable gases include, but are not limited to nitrogen, hydrogen, argon, helium, hydrogen chloride and the like.

5 The reaction can take place in the presence of a catalyst promotor, which is generally an added acid or acid precursor. Suitable acids or acid precursors include, but are not limited to, HCl, 2-chlorobutane, or tert-butyl chloride, for example.

The residence time in the reaction zone is generally less than about 24 hr, or less than about 16 hr, or less than about 12 hr, or less than about 10 hr, or less than about 7 hr, or less than about 5 hr, or less than about 4 hr, or less than about 3 hr, or less than about 2 hr, or
10 less than about 1 hr, or less than about 30 min, or less than about 10 min, or about 1 min to about 24 hr, or about 5 min to about 24 hr, or about 10 min to about 24 hr, or about 30 min to about 16 hr, or about 30 min to about 12 hr, or about 1 hr to about 16 hr. The reaction time can be selected so that a predetermined conversion can be obtained. The reaction time is a function of the reaction temperature, the concentration of acid, the ratio of hydrocarbon to co-solvent
15 (provided there is not so much hydrocarbon that the micro-emulsion is broken), and the concentration of acid and the mass/volume ratio of liquid catalyst to hydrocarbon being reacted. Generally, increasing any of these conditions will increase the reaction rate.

If reverse disproportionation is desired, multiple paraffins are fed to the reaction zone. The multiple paraffins may enter the reaction zone in one location or several
20 locations, and may be present in the reaction zone at the start of the reaction.

Fig. 1 illustrates an embodiment of a process 100 in which the reaction and separation processes occur in a single process zone 105. The micro-emulsion 110 is fed into the zone process 105. Alternatively, the components to form the micro-emulsion could be fed into the zone, and the micro-emulsion could be formed in the process zone 105. The paraffin
25 reactant(s) 115 is fed into the process zone 105 where the reaction takes place forming the products. The reaction mixture will contain a mixture of ionic liquid, products, unreacted paraffin(s), co-solvent, surfactant (if present), and catalyst promoter (if present).

The composition of the reaction mixture is altered to destroy the micro-emulsion. This can be done in a variety of ways. A portion of the co-solvent could be removed,
30 for example by changing the pressure in the reactor to vaporize the co-solvent. Another way to change the composition is to add one or more of paraffins, products, an additional liquid that

has a polarity less than the polarity of the co-solvent (e.g., an inert or semi-inert hydrocarbon, such as propane), or an ionic liquid. Any of these will change the composition of the reaction mixture so that the micro-emulsion is no longer stable, producing two separate ionic liquid and hydrocarbon phases. The ionic liquid component (which may contain other materials such as co-solvent) will separate from the hydrocarbon component due to density differences (when the ionic liquid has a higher density than the hydrocarbon).

Ionic liquid stream 120, which may contain some other materials such as a portion of the co-solvent, can be removed from the process zone 105. The ionic liquid stream 120 can be recycled for further use (not shown), if desired. All or a portion of the ionic liquid stream 120 can be further processed as needed before recycle, including but not limited to, regeneration of the ionic liquid, or recovery of co-solvent. The remaining reaction mixture 125 can be removed and sent for further processing (not shown) including, but not limited to separation of the remaining mixture into its various components and the recovery and/or recycle of the components.

Fig. 2 illustrates another embodiment of a process 200 in which the reaction and separation take place in different zones. The micro-emulsion (or the components to form the micro-emulsion) 210 is fed into the reaction zone 205. The paraffin(s) 215 is fed into the reaction zone 205, and the product(s) is formed.

The reaction mixture 220, which contains the mixture of ionic liquid, product(s), unreacted paraffin(s), co-solvent, surfactant (if present), and catalyst promoter (if present), is sent to a separation zone 225. The composition of the reaction mixture 220 is changed so that the micro-emulsion is destroyed and the ionic liquid separates from the majority of the remaining components. Ionic liquid stream 230, which may contain some other components such as a portion of the co-solvent, can be removed from the separation zone 225 for further processing. The remaining reaction mixture 235 can also be removed for further processing.

The reaction rate and selectivity may be changed by changing the amounts of the components in the micro-emulsion. For example, if the co-solvent is more viscous than the paraffin(s), increasing the ratio of paraffin(s) to co-solvent would decrease the viscosity of the hydrocarbon component, which would result in faster mass transfer. Higher paraffin to co-solvent ratio would also increase the concentration of paraffin(s). Adding a second co-solvent with a lower viscosity or using a different co-solvent with a lower viscosity may result in a faster reaction if the reaction is mass-transfer limited. Decreasing the size of the micelles,

reverse micelles, or bi-continuous structures in the micro-emulsion may result in faster reaction. Decreasing the size of micelles, reverse micelles, or b-continuous structures in the micro-emulsion may be accomplished by changing the composition (for instance by changing the amount of co-solvent or surfactant), or mixing with higher shear to improve contacting.

5 Although the micro-emulsion is generated due to thermodynamic stability rather than by shear mixing, adequate mixing is necessary to insure a homogenous mixture and uniform concentration profiles. This mixing facilitates mass transfer in the micro-emulsion and prevents local in-homogeneities in which the micro-emulsion is not stable. The shear rate is defined as the tip speed of the mixing element (such as an impeller) divided by the distance to
10 the nearest surface (such as a baffle or vessel wall). See e.g., US 8,163,856 examples 1-3. In some embodiments, the shear rate is greater than about 300 inverse seconds, or greater than about 350 inverse seconds, or greater than about 400 inverse seconds, or greater than about 425 inverse seconds.

 The micro-emulsion includes a hydrocarbon component and an ionic liquid
15 component. The micro-emulsion is formed from an ionic liquid, a hydrocarbon phase, and a co-solvent. The micro-emulsion may optionally contain an additional surfactant and/or a catalyst promoter.

 The ionic liquid component will primarily contain ionic liquid. However, in some cases, some paraffin(s) and/or co-solvent may be present in the ionic liquid component.

20 In some embodiments, more than about 90% of the reverse micelles or micelles have a diameter less than about 100 nanometers, or less than about 90 nanometers, or less than about 80 nanometers, or less than about 70 nanometers, or less than about 60 nanometers, or less than about 50 nanometers, or less than about 40 nanometers, or less than about 30 nanometers, or less than about 20 nanometers, or about 1 nanometer to about 100 nanometers,
25 or about 1 nanometer to about 80 nanometers, or about 1 nanometer to about 60 nanometers, or about 1 nanometer to about 40 nanometers, or about 1 nanometer to about 20 nanometers, or about 1 nanometer to about 10 nanometers, or about 1 nanometer to about 4 nanometers. The reverse micelles or micelles are typically at least about 1 nanometer in diameter. The reverse micelles or micelles are typically at least about 1 nanometer in diameter. The presence
30 of added surfactant can be used to help control the size of the reverse micelles or micelles, as shown in Figs. 3-4. When an added surfactant is present, reverse micelles or micelles may be larger. In some embodiments, reverse micelles or micelles with added surfactant have

diameters about 2 to about 7 times larger than similar compositions without added surfactant. Not wishing to be bound by theory, the presence of an added surfactant may increase the surface tension of reverse micelles or micelles and allow larger reverse micelles or micelles to be thermodynamically stable. In some embodiments, when an additional surfactant is present,
5 more than about 90% of the reverse micelles or micelles have a diameter in the range of about 3 nanometers to about 100 nanometers, or about 3 nanometers to about 90 nanometers, or about 3 nanometers to about 80 nanometers, or about 3 nanometers to about 70 nanometers, or about 3 nanometers to about 60 nanometers, or about 3 nanometers to about 50 nanometers, or about 3 nanometers to about 40 nanometers, or about 3 nanometers to about 30 nanometers, or about
10 3 nanometers to about 20 nanometers, or about 5 nanometers to about 100 nanometers, or about 5 nanometers to about 90 nanometers, or about 5 nanometers to about 80 nanometers, or about 5 nanometers to about 70 nanometers, or about 5 nanometers to about 60 nanometers, or about 5 nanometers to about 50 nanometers, or about 5 nanometers to about 40 nanometers, or about 5 nanometers to about 30 nanometers, or about 5 nanometers to about 20 nanometers.

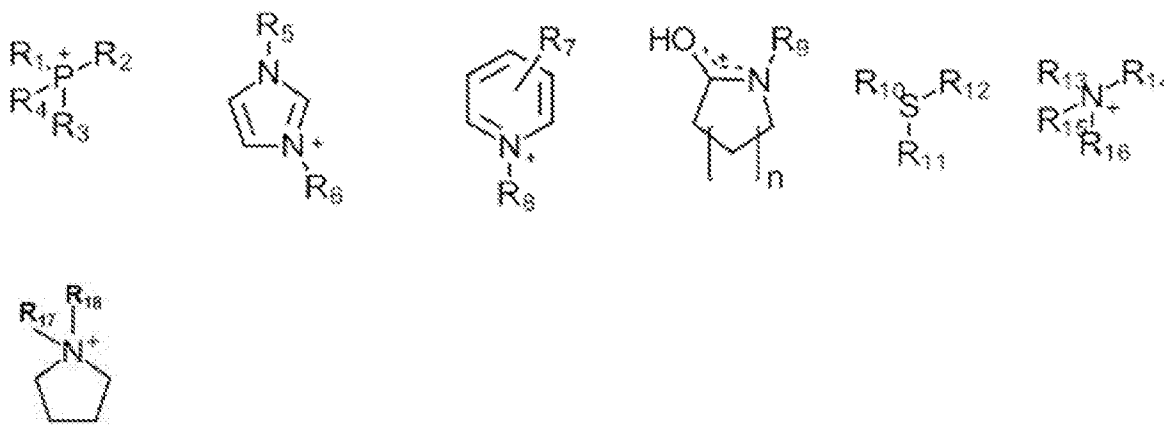
15 In some embodiments, the size distribution of the reverse micelles or micelles may be changed by changing the co-solvent. Not wishing to be bound by theory, using a more polar co-solvent may lead to larger reverse micelles due to the higher solubility of the co-solvent in the reverse micelles and due to the higher surface tension at the interface between the reverse micelles and the hydrocarbon component. The size of micelles may change if the
20 co-solvent is modified to result in a different surface tension of the micelles. For instance, a more polar co-solvent will often reduce the surface tension of micelles resulting in smaller structures.

The micro-emulsion is substantially free of water. The presence of water in the micro-emulsion is undesirable because it is not typically compatible with halometallate ionic
25 liquids. Water reacts with the ionic liquid resulting in facile hydrolysis of the halometallate anion. In cases where the ionic liquid is Lewis acidic, this causes reduction in or neutralization of Lewis acidity. By substantially free of water we mean that the reverse micelles or micelles themselves are not water, and the components in the micro-emulsion do not contain enough water to substantially affect the halometallate anion (i.e., it does not result in appreciable loss
30 of activity for reactions that are catalyzed by the ionic liquid). There is typically less than about 300 wppm water in the micro-emulsion, or less than about 250 wppm water, or less than about 200 wppm water, or less than about 150 wppm water, or less than about 100 wppm water, or less than about 75 wppm water, or less than about 50 wppm water, or less than about 25 wppm

water, or less than about 20 wppm water, or less than about 15 wppm water, or less than about 10 wppm water, or less than about 5 wppm water, or less than about 1 wppm water.

The ionic liquid comprises a cation and an anion. The cation is generally a nitrogen, phosphorous, or sulfur-based organic cation. In some embodiments, the cation is
 5 amphiphilic in nature and at least slightly soluble in the co-solvent. By “slightly soluble” we mean the cation is soluble in an amount of at least 0.5 mole ppm in the co-solvent. If the cation and anion are both not amphiphilic, an additional surfactant may be needed. In many cases, the ionic liquid is fully miscible with the co-solvent.

Suitable cations include, but are not limited to, nitrogen-based organic cations,
 10 phosphorus based organic cations, sulfur based cations, or combinations thereof. Examples of cations include tetraalkyl phosphoniums, dialkylimidazoliums, alkylimidazoliums, pyridiniums, alkyl pyridiniums, dialkyl pyridiniums, alkylpyrrolidiniums, dialkylpyrrolidiniums, trialkylammoniums, tetraalkylammoniums, lactamiums, alkyl-lactamiums and trialkylsulfoniums. Mixtures of cations may be used as well. Examples of
 15 suitable cations include, but are not limited to:



where R₁-R₃ are independently selected from alkyl groups, alkene groups, naphthene groups, and aryl groups having 1 to 12 carbon atoms, and R₄ is independently selected from alkyl
 20 groups, alkene groups, naphthene groups, and aryl groups having 1 to 15 carbon atoms; and

where R₅-R₁₈ are independently selected from hydrogen, alkyl groups, alkene groups, naphthene groups, and aryl groups having 1 to 20 carbon atoms, n is 1 to 8, and the alkyl, naphthene, alkene and aryl groups may be substituted with halogens, or other alkyl, aryl and naphthene groups.

In some embodiments, the anion is a halometallate or anion with acidic character, and in most embodiments with Lewis acidic character. Halometallate anions may contain a metal selected from Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, In, Sn, Sb, La, Ce, Hf, Ta, W, or combinations thereof, and a halide selected from F, Cl, Br, I, or combination thereof. The halometallate may be a simple halometallate or a composite in which more than one metal is used. For catalytic applications requiring Lewis acidity (such as alkylation, isomerization, and disproportionation), the ratio of moles of halide to moles of metal in the anion is less than 4. The anion may be formally an anion, or it may be an anion associated with a metal halide. For instance, the anion may be AlCl_4^- associated with AlCl_3 . In some embodiments, such as those where the ionic liquid comprises an imidazolium based cation, the ratio of moles of halide to moles of metal in the anion must be less than 4 in order for a micro-emulsion to form.

In embodiments in which the micro-emulsion contains reverse micelles, the hydrocarbon component is continuous and the ionic liquid component comprises reverse micelles that are dispersed in the hydrocarbon component. A majority of the hydrocarbon is in the hydrocarbon component. The co-solvent may be in the hydrocarbon component, the ionic liquid component, or both. In embodiments in which the micro-emulsion contains micelles, the hydrocarbon component forms the core of micellular structures which are surrounded by the ionic liquid component and optional surfactant. The micelles are dispersed in a continuous medium comprising the co-solvent.

The hydrocarbon comprises at least a part of the less polar hydrocarbon component of the micro-emulsion. A majority of the hydrocarbon is in the hydrocarbon component. The hydrocarbon may be a paraffin, an olefin, an aromatic, a naphthene, or mixtures of these. When micro-emulsions containing ionic liquid are used to catalyze a hydrocarbon conversion process, the hydrocarbon reactants also serve as a portion of the hydrocarbon component.

In order to form a micro-emulsion containing reverse micelles, there must be at least some solubility of the amphiphile in both the hydrocarbon component and the ionic liquid component of the micro-emulsion. Here, at least some solubility of the amphiphile in the hydrocarbon component is defined as the amphiphile being soluble in an amount of at least 0.5 mole ppm in the hydrocarbon component. If the cation and anion are both not amphiphilic, an additional surfactant may be needed to act as the amphiphile. The solubility of the ionic liquid

or optional surfactant is generally much higher than in the hydrocarbon component and depends on the type of ionic liquid or the optional surfactant and size of the reverse micelles.

In cases where a non-polar hydrocarbon medium is desired (for instance, in paraffin isomerization, disproportionation and reverse disproportionation the medium contains paraffins), a co-solvent is used to modify the polarity of the hydrocarbon. The co-solvent is more polar than the hydrocarbon. The co-solvent should be compatible with the ionic liquid, and it should be miscible with the hydrocarbon. Here, miscible with the hydrocarbon means that the co-solvent is soluble in an amount of at least 1 mol% in the hydrocarbon. Suitable co-solvents are any organic solvent containing at least one atom that is not carbon or hydrogen. Any polar aprotic solvent that is not reactive with the ionic liquid may be suitable. Examples include, but are not limited to, halomethanes, other halogenated hydrocarbons, halocarbons, halogenated aromatics, or combinations thereof. Halogenated hydrocarbons are any compound that contains carbon, hydrogen, and a halogen atom or atoms. Halomethanes are any compound of the formula $\text{CH}_{4-n}\text{X}_n$ where X is selected from F, Cl, Br, I, or a combination thereof. Halocarbons are any compound that contains only carbon and halogens. Halogenated aromatics are an aromatic compound containing one or more halogen atoms, such as chlorobenzene. Halomethanes, halocarbons, halogenated aromatics, and compounds with no hydrogen attached to the adjacent (beta) carbon atom are preferable to compounds with a beta hydrogen (such as halogenated hydrocarbons with more than one carbon) because of the potential to eliminate a halogen and a hydrogen to form a hydrogen halide and an olefin. Suitable co-solvents include, but are not limited to, chloroform, dichloromethane, chloromethane, chlorobenzene, dichlorobenzene, fluoromethane, difluoromethane, trifluoromethane, and 1-chloro-2,2-dimethylpropane.

In some embodiments, the viscosity of the co-solvent is less than about 1 centipoise at 25°C. Preferably, the viscosity of the co-solvent is less than about 0.6 centipoise at 25°C. This is helpful for mass transfer of the olefin in the continuous hydrocarbon component.

The amount of co-solvent is typically in the range of about 30 wt% to about 80 wt% of the micro-emulsion. In some embodiments, it is desirable to include as much hydrocarbon (i.e., paraffin, and products) and as little co-solvent in the micro-emulsion as possible. This results in increased concentration of the paraffin reactants. In some embodiments, the total amount of hydrocarbon is greater than 90% and less than 100% of a

total saturation amount of hydrocarbon, i.e., the saturation amount of the mixture of paraffins, including the reaction products. The saturation amount of the hydrocarbon is the amount of hydrocarbon present at the phase boundary on a phase diagram. The saturation amount depends on the amount of ionic liquid, optional surfactant, optional catalyst promoter, and co-solvent.

5 For example, Fig. 5 shows a phase diagram of the mole ratio of co-solvent (dichloromethane)/hydrocarbon component (hexane) as a function of the mole fraction of ionic liquid plus surfactant at the phase boundary. The presence of a micro-emulsion can be determined visually. A micro-emulsion will appear clear, while a composition in the two phase region will appear cloudy or have two separate phases. The micro-emulsion region (M-E) is
10 above and to left of the phase boundary while the two phase region (2P) is below and to the right of the phase boundary. It is desired to operate in the micro-emulsion region and within 10% of the saturation amount of the hydrocarbon. For example, in a system containing tributylhexylphosphonium heptachloroaluminate ionic liquid, dichloromethane co-solvent, and hexane (hydrocarbon) with no surfactant, and an ionic liquid mole fraction of 0.00084, the mole
15 ratio of dichloromethane/hexane at the phase boundary is 1.28. Thus, the saturation amount of hexane is 43.9 wt%, and the desired amount of hexane should be 39.5 wt% to 43.9 wt%. In a system containing tributylhexylphosphonium heptachloroaluminate ionic liquid, dichloromethane co-solvent, hexane (hydrocarbon), and benzyldimethyltetradecylammonium chloride surfactant, a molar ratio of surfactant to ionic liquid of 2.1:1, and a mole fraction of
20 ionic liquid plus surfactant of 0.0010, the mole ratio of dichloromethane/hexane at the phase boundary is 0.76. Thus, the saturation amount of hexane is 56.8 wt%, and the desired amount of hexane should be 51.1 wt% to 56.8 wt%.

In some embodiments, no additional surfactant is needed because the ionic liquid itself acts as an amphiphile to make a stable micro-emulsion. However, if a non-
25 amphiphilic ionic liquid is used, or if the use of less co-solvent is desired, a surfactant may be added. The surfactant can be cationic, anionic, or neutral. The surfactant can be amphiphilic and non-protic (i.e., it does not contain an acidic H atom bound to N, O, or S). Protic surfactants with very weakly acidic protons, such as ternary ammonium salts and cyclic amides, may also be suitable. Many surfactants that are not reactive with the ionic liquid are suitable. Examples
30 of classes of such surfactants include, but are not limited to, amphiphilic quaternary ammonium salts, ternary ammonium salts, phosphonium salts, sulfonate salts, phosphonate salts, disubstituted amides (e.g., amides of the formula $R-(C=O)-NR_2$, where R groups are generally alkyl or aryl groups but may be substituted as well), ethers, or glymes. Ideally, the anion of

the quaternary ammonium salt, the ternary ammonium salt, or the phosphonium salt may be selected to match the anion of the ionic liquid or selected to be compatible with it. By compatible with the anion of the ionic liquid, we mean that the anion of the additional surfactant does not neutralize the Lewis acidity of the ionic liquid anion or co-ordinate strongly to the ionic liquid anion such that the catalyst activity is substantially decreased. By substantially decreased, we mean that the reaction rate for isobutane alkylation with olefins is decreased by more than 25% for a mole ratio of surfactant to ionic liquid of 1:1 compared to the same conditions with no additional surfactant. As an example of compatible surfactant anions, Cl^- , AlCl_4^- or Al_2Cl_7^- may be used as the anion with an Al_2Cl_7^- ionic liquid (as may the bromide versions). Examples of cationic quaternary ammonium salts are cetyltrimethylammonium chloride, and benzyldimethyltetradecylammonium chloride. Anionic surfactants may also be suitable; however, most include sulfonate groups which are expected to be reactive with, or coordinate to, the Lewis acidic ionic liquid. Ideally, the cation of the sulfonate salt or phosphonate salt may be selected to match the cation of the ionic liquid or selected to be compatible with the cation of the ionic liquid. For instance, if the ionic liquid is tributylhexylphosphonium heptachloroaluminate, the surfactant could be tributylhexylphosphonium dodecyl sulfonate. As demonstrated below, the use of a surfactant allows use of less co-solvent, and in some cases, it results in larger reverse micelles.

Another optional material is a catalyst promoter. In many hydrocarbon conversion reactions, such as paraffin disproportionation, paraffin reverse disproportionation and paraffin isomerization, a Brønsted acidic catalyst promoter is desirable. Two common promoters are anhydrous hydrogen halides (for instance, HCl) and halogenated hydrocarbons (such as 2-chlorobutane or 2-chloro-2-methyl propane (t-butyl chloride)). The halogenated hydrocarbons react in the presence of a Lewis acid to form a hydrogen halide and an olefin. The catalyst promoter may also serve as an initiator for carbenium ions in disproportionation and reverse disproportionation reactions.

The above materials are mixed in specific ratios such as to stabilize ionic liquid micro-emulsions, including reverse micelles. The ionic liquid is typically present in an amount of about 0.05 wt% to about 40 wt% of the micro-emulsion, or about 0.05 wt% to about 35 wt%, or about 0.05 wt% to about 30 wt%, or about 0.05 wt% to about 25 wt%, or about 0.05 wt% to about 20 wt%, or about 0.05 wt% to about 15 wt%, or about 0.05 wt% to about 10 wt%, or about 0.05 wt% to about 5 wt%, or about 0.05 wt% to about 1 wt% or about 1 wt% to about 40 wt%, or about 1 wt% to about 35 wt%, or about 1 wt% to about 25 wt%, or about 1 wt% to

about 15 wt%, or about 1 wt% to about 10 wt%, or about 1 wt% to about 5 wt%, or about 2.5 wt% to about 40 wt%, or about 2.5 wt% to about 35 wt%, or about 2.5 wt% to about 25 wt%, or about 2.5 wt% to about 15 wt%, or about 2.5 wt% to about 10 wt%, or about 2.5 wt% to about 5 wt%. If more ionic liquid is used, shorter reaction time or lower temperature is required to achieve the same paraffin conversion.

The co-solvent is typically present in an amount of about 30 wt% to about 80 wt% of the micro-emulsion, or about 40 wt% to about 80 wt%, or about 30 wt% to about 70 wt%, or about 30 wt% to about 60 wt%, or about 40 wt% to about 70 wt%.

The molar ratio of the surfactant to the ionic liquid is typically less than about 2.5:1, or less than about 1.5:1.

When the catalyst promoter is present, the molar ratio of the catalyst promoter to the ionic liquid is typically about 0.1:1 to about 1:1, or about 0.1:1 to about 0.7:1, or about 0.2:1 to about 0.7:1.

The weight ratio of the ionic liquid to the hydrocarbon is in the range of about 0.025:1 to about 0.3:1, or about 0.025:1 to about 0.2:1, or about 0.05:1 to about 0.3:1, or about 0.08:1 to about 0.3:1, or about 0.05:1 to about 0.2:1, or about 0.05:1 to about 0.15:1.

The relative amounts of the paraffins in the reaction mixture can be tuned to obtain the desired product using the method described in US 2015/0005560. The equilibrium constants for reactions of the paraffins can be used to select appropriate feed ratios. Equilibrium product compositions and non-equilibrium product compositions can be obtained using the process, depending on the extent of approach to equilibrium. Extent of approach to equilibrium is controlled by residence time, the ratio of ionic liquid to hydrocarbon and temperature. Generally, increasing one of these will increase the extent of approach to equilibrium.

The amounts of co-solvent and surfactant needed to stabilize the micro-emulsion depend on the amount of ionic liquid and hydrocarbon present. When surfactant is included in the micro-emulsion, generally less co-solvent is needed. When more ionic liquid is included in the micro-emulsion, generally more surfactant or more co-solvent is needed.

The amounts of each material needed to result in a stable micro-emulsion may be determined by determination of a phase diagram. The phase diagram for a given combination of hydrocarbon, co-solvent, ionic liquid, optional surfactant and catalyst promoter

is constructed by preparing mixtures containing various known amounts of the materials. A particular composition is then determined to be a micro-emulsion or consist of two distinct phases. Determination of whether a composition is a micro-emulsion or two distinct phases is generally completed by assessing turbidity of the mixture or identifying an interface between two phases, but may be accomplished by other means known in the art such as dynamic light scattering, conductivity measurement, or x-ray scattering. A mixture which is a micro-emulsion is then subjected to addition of the hydrocarbon or ionic liquid to determine the composition at which the phase boundary between micro-emulsion and two-phase composition exists. Alternatively, a mixture which is two phases is subjected to addition of co-solvent or surfactant to determine the composition at which the phase boundary between micro-emulsion and two-phase composition exists.

The micro-emulsion can be formed by contacting or otherwise mixing the hydrocarbon component, the co-solvent, the ionic liquid, the optional surfactant, and the optional catalyst promoter. The hydrocarbon component has a polarity less than the polarity of the co-solvent. In some embodiments, the co-solvent is miscible in the hydrocarbon component, at least up to the desired composition. The ionic liquid comprises a halometallate anion and a cation. In some embodiments, the ionic liquid is at least slightly soluble in the co-solvent. By slightly soluble, we mean that at least 1 wt% of the ionic liquid is soluble in the co-solvent. The ionic liquid is present in an amount of about 0.05 wt% to about 40 wt% of the micro-emulsion.

The materials can be combined in different ways. For example, the hydrocarbon and co-solvent can be combined first, and then combined with ionic liquid. Alternatively, the ionic liquid and the co-solvent can be combined first, and then combined with the hydrocarbon. The optional surfactant and optional catalyst promoter can be added at different times and to different combinations of the materials. For example, the catalyst promoter and optional surfactant can be added to the hydrocarbon, the co-solvent, the ionic liquid, or any combinations of these materials. In another alternative, all of the components could be combined at the same time. Other ways of combining the materials would be understood by those skilled in the art.

In one method, an ionic liquid and an optional surfactant are dissolved in a co-solvent to form an ionic liquid component. The ionic liquid comprises a halometallate anion and a cation. The ionic liquid component is introduced into a hydrocarbon to form the micro-

emulsion. The polarity of the co-solvent is greater than the polarity of the co-solvent, and the co-solvent is miscible in the hydrocarbon. The hydrocarbon component comprises the hydrocarbon. If a catalyst promoter is included, it can be added to the ionic liquid component, the hydrocarbon, the co-solvent, or the micro-emulsion.

5 Another method involves mixing the hydrocarbon with a co-solvent to form a hydrocarbon component. The polarity of the co-solvent is greater than the polarity of the hydrocarbon, and the co-solvent is miscible in the hydrocarbon component. The ionic liquid and an optional surfactant are added to the hydrocarbon component to form the micro-emulsion. The ionic liquid is present in an amount of about 0.05 wt% to about 40 wt% of the
10 micro-emulsion. If a catalyst promoter is included, it can be added to the hydrocarbon component, the co-solvent, the ionic liquid, or the micro-emulsion.

Examples

Isomerization and disproportionation were demonstrated simultaneously using n-pentane (nC₅) as the reactant. The products generated included isopentane (iC₅) which is the
15 product of isomerization, as well as butanes (C₄s), hexanes (C₆s), heptanes (C₇s) and octanes (C₈s) which are the products of disproportionation. Minor amounts of propane (C₃) and heavy products with 9 or more carbon atoms (C₉+) were also produced. Reverse disproportionation was demonstrated using n-hexane and n-decane as reactants. Disproportionation and isomerization occurred alongside reverse disproportionation, resulting in a mixture of
20 paraffinic products containing 3 carbons or more. Dichloromethane, CH₂Cl₂, was used as the co-solvent.

Comparative Example 1 – isomerization/disproportionation with no polar co-solvent

To compare cases with and without micro-emulsion formation, in this comparative example, the co-solvent necessary for producing reverse micelles in Example 1 was substituted
25 for an equal volume of propane, which reacts very slowly in disproportionation reactions. In a 300 cc Hastalloy C autoclave fitted with a 1.375" pitched blade turbine impeller, 3.86 g of tributylmethylphosphonium heptachloroaluminate (3.2 vol%), 27.9 g of nC₅ (44 vol%), and 0.341 g of 2-chloro-2-methylpropane were combined in an inert atmosphere. 27 g of propane (53 vol% once pressurized) was added from a pressurized charger. The autoclave was
30 pressurized with N₂ to a total pressure of 1.4 MPa (g) (200 psig). The reactor was heated to 95°C with mixing at 1200 rpm, reaching the target temperature within 20 minutes and resulting

in autogeneous pressure of 3.2 MPa(g) (460 psig). After 16 hours at temperature, stirring was discontinued, and the product was analyzed at reaction pressure by GC with FID detector. Conversion of nC₅ was 6.9%. Selectivity to the isomerization product iC₅ was 42%, and selectivity to disproportionation products was 58%. Overall selectivity was 33% to C₄s, 17% to C₆s, 5.4% to C₇s, 1.3% to C₈s and 0.4% to C₉+. Since C₃ was used as a solvent, the small amount of product C₃ formed could not be precisely determined. Conditions and results are shown in Table 1.

Comparative Example 2 – non-reactivity of CH₂Cl₂ co-solvent

To verify that dichloromethane does not react under reaction conditions, a small amount of dichloromethane was included in a reaction at the same temperature and time conditions as comparative example 1 and example 1. In a 300 cc Hastalloy C autoclave fitted with a 1.375” pitched blade turbine impeller, 4.65 g of tributylmethylphosphonium heptachloroaluminate, 71.4 g of nC₅ (0.99 mol), 6.01 g of dichloromethane (0.071 mol), and 0.42 g of 2-chloro-2-methylpropane were combined in an inert atmosphere. The autoclave was pressurized with N₂ to a total pressure of 1.7 MPa(g) (250 psig). The top (hydrocarbon phase) of the reactor contents was analyzed by GC prior to reaction. Signal from dichloromethane was 0.69% of the total signal (dichloromethane has a low response in in FID detector relative to hydrocarbons). The reactor was heated to 95°C, reaching the target temperature within 20 minutes and resulting in autogeneous pressure of 2.1 MPa(g) (310 psig). After 16 hours at temperature, stirring was discontinued and the product was analyzed at reaction pressure by GC. After reaction, dichloromethane accounted for 0.74% of the signal, indicating that no reaction of dichloromethane occurred.

Example 1 - isomerization/disproportionation with polar co-solvent

In a 300 cc Hastalloy C autoclave fitted with a 1.375” pitched blade turbine impeller, 3.89 g of tributylmethylphosphonium heptachloroaluminate (3.2 vol%), 27.5 g of nC₅ (44 vol%), 70.7 g of dichloromethane (53 vol%), and 0.351 g of 2-chloro-2-methylpropane were combined in an inert atmosphere. The autoclave was pressurized with N₂ to a total pressure of 1.7 MPa(g) (250 psig). The reactor was heated to 95°C, reaching the target temperature within 20 minutes and resulting in autogeneous pressure of 2.4 MPa(g) (350 psig). After 16 hours at temperature, stirring was discontinued, and the reaction was quenched by addition of 10 g of 1-butanol. The product was analyzed at reaction pressure by GC with FID detector. Conversion of nC₅ was

10.9%. Selectivity to the isomerization product iC_5 was 39% and selectivity to disproportionation products was 61%. Overall selectivity was 0.78% to C_3 , 35% to C_4 s, 18% to C_6 s, 5.2% to C_7 s, 1.2% to C_8 s and 0.54% to C_9+ . Conditions and results are shown in Table 1.

5 emulsions

Example #	Comp. 1	Ex 1
Temperature (°C)	95	95
Reaction time (hr)	16	16
IL (g)	3.86	3.89
CH ₂ Cl ₂ (g)	--	70.7
C ₃ (g)	27.0	--
nC ₅ (g)	27.8	27.5
2-chloro-2-methylpropane (g)	0.341	0.351
IL vol% ^a	3.2%	3.2%
CH ₂ Cl ₂ vol% ^a	--	53%
C ₃ vol% ^a	53%	--
nC ₅ vol% ^a	44%	44%
Total initial liquid volume (mL) ^a	101	101

Results

nC ₅ Conversion%	6.9%	10.9%
C ₃ wt% selectivity	n.d.	0.8%
C ₄ wt% selectivity	32.7%	34.6%
iC ₅ wt% selectivity	42.4%	38.9%
C ₆ wt% selectivity	17.3%	18.4%
C ₇ wt% selectivity	5.4%	5.2%
C ₈ wt% selectivity	1.3%	1.2%
C ₉ + wt% selectivity	0.4%	0.54%

^a Volumes are estimated based on pure component densities at 25 °C

Comparative Example 3 – n-hexane/n-decane reverse disproportionation with no polar co-solvent

10 To compare cases with and without micro-emulsion formation, in this comparative example the co-solvent necessary for producing reverse micelles in example 3 was substituted for an equal volume of propane, which reacts very slowly in disproportionation reactions. In a 300 cc Hastalloy C autoclave fitted with a 1.375" pitched blade turbine impeller, 3.86 g of 1-butyl-3-methylimidazolium heptachloroaluminate (1.9 vol%, 0.0176 mol Al), 35.2 g of n-

hexane (36.0 vol%), 4.6 g of n-decane (4 vol%) and 0.30 g of 2-chloro-2-methylpropane were combined in an inert atmosphere. 46.7 g of propane (55 vol% once pressurized) was added from a pressurized charger. The autoclave was pressurized with N₂ to a total pressure of 225 psig. The reactor was heated to 105 °C with mixing at 1200 rpm, reaching the target temperature within 20 minutes and resulting in autogeneous pressure of 575 psig. After 15.5 hours at temperature, stirring was discontinued and the reactor was immediately cooled in an ice bath. The product was analyzed at pressure after cooling by GC with FID detector. Conversion of n-hexane was 5.7%, while no conversion of n-C₁₀ was observed. The distribution of feed and product by carbon number (excluding the C₃ diluent) is shown in Table 2.

Example 3 - n-hexane/n-decane reverse disproportionation with polar co-solvent using 1-butyl-3-methylimidazolium heptachloroaluminate IL (BMIM IL)

In a 300 cc Hastalloy C autoclave fitted with a 1.375" pitched blade turbine impeller, 3.8 g of 1-butyl-3-methylimidazolium heptachloroaluminate (1.7 vol%, 0.0172 mol Al), 37.3 g of n-hexane (36.0 vol%), 4.9 g of n-decane (4 vol%), 127.7 g dichloromethane (58.2 vol%) and 0.31 g of 2-chloro-2-methylpropane were combined in an inert atmosphere. The autoclave was pressurized with N₂ to a total pressure of 2.1 MPa(g) (300 psig). The reactor was heated to 105°C with mixing at 1200 rpm, reaching the target temperature within 20 minutes and resulting in autogeneous pressure of 2.8 MPa(g) (400 psig). After 15.5 hours at temperature, stirring was discontinued, and the reactor was immediately cooled in an ice bath. Nitrogen was vented while still on ice, and no mass loss was measured (excluding the expected loss of nitrogen). The reactor products were immediately quenched in ice water and extracted twice with pentadecane. The pentadecane extract was dried over MgSO₄ and filtered using a 0.2 micron syringe filter. The extract was analyzed by gas chromatography to determine reaction products, and the same procedure was followed on an aliquot of the reactant mixture. Conversion of n-hexane was 6.7%, and conversion of n-decane was 19.5%. Conversion of overall hexanes (i.e. conversion of hexanes not counting isomerization) was 4.7% and conversion of decanes was 17.3%. The distribution of feed and product by carbon number (excluding the C₃ diluent) is shown in Table 2, showing that there was an overall shift of carbon from heavier (C₉-C₁₃) compounds to lighter (C₃-C₉) compounds, indicating that reverse disproportionation occurred in addition to disproportionation and isomerization.

Example 4 - n-hexane/n-decane reverse disproportionation with polar co-solvent using caprolactamium heptachloroaluminate ionic liquid

Caprolactamium chloroaluminate ionic liquid (CPL IL) was prepared as in Example 2 of US 2015/0321977 by addition of 1.8 molar equivalents of AlCl_3 to caprolactamium chloride, which was prepared as in Example 1 of US 2015/0321977. In a 300 cc Hastalloy C autoclave fitted with a 1.375" pitched blade turbine impeller, 3.42 g of caprolactamium chloroaluminate (1.6 vol%, 0.0157 mol Al), 37.3 g of n-hexane (36.0 vol%), 4.9 g of n-decane (4 vol%), 127.9 g dichloromethane (58.4 vol%) and 0.31 g of 2-chloro-2-methylpropane were combined in an inert atmosphere. The autoclave was pressurized with N_2 to a total pressure of 2.1 MPa(g) (300 psig). The reactor was heated to 105 °C with mixing at 1200 rpm, reaching the target temperature within 20 minutes and resulting in autogeneous pressure of 2.5 MPa(g) (360 psig). After 15.5 hours at temperature, stirring was discontinued, and the reactor was immediately cooled in an ice bath. Nitrogen was vented while still on ice, and no mass loss was measured (excluding the expected loss of nitrogen). The reactor products were immediately quenched in ice water and extracted twice with pentadecane. The pentadecane extract was dried over MgSO_4 and filtered using a 0.2 micron syringe filter. The extract was analyzed by gas chromatography to determine reaction products, and the same procedure was followed on an aliquot of the reactant mixture. Conversion of n-hexane was 8.4%, and conversion of n-decane was 25.7%. Conversion of overall hexanes (i.e. conversion of hexanes not counting isomerization) was 5.8% and conversion of decanes was 21.3%. The distribution of feed and product by carbon number (excluding the C_3 diluent) is shown in Table 2, showing that there was an overall shift of carbon from heavier (C_9 - C_{13}) compounds to lighter (C_3 - C_9) compounds, indicating that reverse disproportionation occurred in addition to disproportionation and isomerization.

Table 2

	Comparative 3		Example 3		Example 4	
	Mass (g)	Vol%	Mass (g)	Vol%		
nC10	4.6	4.0%	4.9	4.0%	4.9	4.0%
nC6	35.2	36%	37.3	36%	37.3	36%
CH_2Cl_2	--	--	127.7	58.2%	127.9	58.4%
nC3	46.7	58.6%	--	--	--	--
BMIM IL	3.9	1.9%	3.8	1.7%	--	--

CPL IL	--	--	--	--	3.4	1.6%
t-BuCl	0.30		0.31		0.31	
nC6 conversion	5.7%		6.7%		8.4%	
nC10 conversion	-1.0%		19.5%		25.7%	
Total C6 conv	4.3%		4.7%		5.8%	
Total C10 conv	-1.4%		17.3%		21.3%	
	% carbon distribution					
	feed	Product	feed	Product	feed	Product
C3	0%	0%	0.0%	0.0%	0.0%	0.0%
C4	0.6%	1.8%	0.1%	1.6%	0.0%	2.1%
C5	0.2%	1.8%	0.1%	2.4%	0.0%	2.8%
nC6	85.7%	80.8%	85.7%	80.0%	85.6%	78.5%
iC6	1.3%	2.5%	1.0%	2.6%	1.2%	3.4%
C7	0.2%	0.7%	0.1%	1.2%	0.4%	1.3%
C8	0.1%	0.2%	0.0%	0.5%	0.0%	0.6%
C9	0.1%	0.1%	0.0%	0.3%	0.0%	0.4%
nC10	11.2%	11.3%	12.7%	10.2%	12.7%	9.4%
iC10	0.6%	0.7%	0.1%	0.4%	0.03%	0.6%
C11	0%	0%	0.0%	0.2%	0.01%	0.2%
C12	0%	0.007%	0.1%	0.1%	0.01%	0.2%
C13	0%	0.01%	0.0%	0.0%	0.002%	0.4%

Example 5 – Phase diagram

In the examples below, n-hexane is used as the hydrocarbon, tributylhexylphosphonium heptachloroaluminate is used as the ionic liquid, and dichloromethane is used as the co-solvent.

5 Micro-emulsions were generated by preparing a mixture of ionic liquid and (in some cases) benzyldimethyltetradecylammonium chloride, referred to as “surfactant” below. Four different compositions were prepared with the following surfactant:ionic liquid mole ratios. Formulation 1 had a molar ratio of surfactant:ionic liquid of 2.1:1. Formulation 2 had a molar ratio of surfactant:ionic liquid of 1.7:1. Formulation 3 had a molar ratio of
10 surfactant:ionic liquid of 0.83:1. Formulation 4 had no surfactant. Sufficient dichloromethane was added to dissolve the ionic liquid and surfactant. Following this, n-hexane was added dropwise, with shaking. When turbidity appeared, this composition was recorded as the boundary between the micro-emulsion region and the two-phase region of the phase diagram. A drop or drops of dichloromethane was then added to check that cloudiness disappeared. This
15 was recorded as a second limit for the phase boundary. Additional dichloromethane was added, and the procedure was repeated. As the ionic liquid and surfactant became more dilute in the mixture, less dichloromethane was needed in the mixture to clarify the liquid. When a large amount of surfactant was added to the ionic liquid, less dichloromethane was needed to stabilize the same amount of ionic liquid. However, with little or no surfactant, a phase
20 boundary was also found. A phase diagram showing the required dichloromethane/hexane ratio to form a clear liquid (the phase boundary) for each of the formulations 1-4 as a function of total ionic liquid plus surfactant mole fraction is shown in Fig. 5.

The micro-emulsion region (M-E on Fig. 5) is above and to left of the phase boundary while the two phase region (2-P on Fig. 5) is below and to the right of the phase
25 boundary. Micro-emulsions are broken to produce two phases when the composition is changed from a composition in the micro-emulsion region to the two phase region.

Example 6

Particle size distributions of micro-emulsions were measured by dynamic light scattering (DLS) using a Zetasizer Nano ZS two angle particle and molecular size analyzer
30 (Malvern Instruments LTD., UK). Compositions were prepared as described in Example 5. A composition was prepared with 2.9 wt% tributylhexylphosphonium heptachloroaluminate ionic liquid, 2.9 wt% benzyldimethyltetradecylammonium chloride, 54.6% dichloromethane, and 39.5% hexane. The micro-emulsion was placed in a quartz cuvette (1 cm path length) with

a Teflon stopper. Particle size distributions were measured using the analyzer's particle size mode. 30 scans were collected for each sample assuming viscosity of 0.347 centipoise (the volume weighted average viscosity of n-hexane and dichloromethane in the mixture) of the continuous phase, and refractive index of 1.403 (the volume weighted average refractive index of n-hexane and dichloromethane in the mixture). This composition had measured volume normalized average particle size of 12 ± 2 nm. This composition is indicated with a "B" on Fig. 5. Volume normalized particle size distributions for five repeat measurements (1-5) are shown in Fig. 3.

A composition with 6.16 wt% tributylhexylphosphonium heptachloroaluminate ionic liquid, 62.7 wt% dichloromethane, and 31.2 wt% hexane had measured particle size of 3 ± 2 nm. This composition is indicated with an "A" on Fig. 5. Volume normalized particle size distributions for four repeat measurements (1-4) are shown in Fig. 4. The size of the particles is more than three orders of magnitude smaller than droplets generated by impellers.

Example 7

In the examples below, n-hexane is used as the hydrocarbon, and dichloromethane is used as the co-solvent. Four different ionic liquids were tested: tributylhexylphosphonium- Al_2Cl_7 was used in formulation 1, tributylmethylphosphonium- Al_2Cl_7 was used in formulation 2, 1-butyl-3-methylimidazolium- Al_2Cl_7 was used in formulation 3 and caprolactamium- Al_2Cl_7 was used in formulation 4.

Micro-emulsions were generated by preparing a mixture of ionic liquid and sufficient dichloromethane to dissolve the ionic liquid and surfactant. Following this, n-hexane was added dropwise, with shaking. When turbidity appeared, this composition was recorded as the boundary between the micro-emulsion region and the two-phase region of the phase diagram. A drop or drops of dichloromethane was then added to check that cloudiness disappeared. This was recorded as a second limit for the phase boundary. Additional dichloromethane was added, and the procedure was repeated. As the ionic liquid became more dilute in the mixture, less dichloromethane was needed in the mixture to clarify the liquid. A phase diagram showing the required dichloromethane/hexane ratio to form a clear liquid (the phase boundary) for each of the formulations 1-4 as a function of total ionic liquid mole fraction is shown in Fig. 6. The micro-emulsion region (M-E) is above and to left of the phase boundary

while the two phase region (2P) is below and to the right of the phase boundary. Micro-emulsions are broken to produce two phases when the composition is changed from a

composition in the micro-emulsion region to the two phase region. A list of compositions measured which were on the phase boundary are in Table 3.

Table 3: Compositions on phase boundary between micro-emulsion and two-phase mixture for compositions containing dichloromethane, hexane and four different ionic liquids.

	IL wt%	DCM wt%	Hexane wt %	IL mol fraction	DCM/hexane mole fraction
TBHP-Al ₂ Cl ₇	21%	64.94%	14.29%	3.65E-02	4.61
	6.3%	61.99%	31.73%	9.60E-03	1.98
	6.2%	62.68%	31.16%	9.41E-03	2.04
	12.7%	60.13%	27.22%	2.05E-02	2.24
	4.6%	60.83%	34.56%	6.95E-03	1.79
	1.8%	59.49%	38.68%	2.70E-03	1.56
	1.0%	57.32%	41.72%	1.41E-03	1.39
	1.0%	57.46%	41.58%	1.41E-03	1.40
	0.6%	55.09%	44.33%	8.50E-04	1.26
	0.578%	55.50%	43.92%	8.42E-04	1.28
	0.159%	47.87%	51.97%	2.31E-04	0.93
	0.096%	43.45%	56.45%	1.39E-04	0.78
	0.093%	44.90%	55.01%	1.36E-04	0.83
TBMP-Al ₂ Cl ₇	45%	44.53%	10.63%	1.18E-01	4.25
	24%	59.09%	16.42%	5.05E-02	3.65
	14%	63.73%	22.34%	2.59E-02	2.90
	6%	68.44%	25.67%	1.02E-02	2.71
	2.0%	64.20%	33.75%	3.43E-03	1.93
	0.8%	59.67%	39.51%	1.36E-03	1.53
	0.8%	59.49%	39.76%	1.24E-03	1.52
BMIm-Al ₂ Cl ₇	36.9%	56.19%	6.95%	1.01E-01	8.21
	14.9%	68.99%	16.12%	3.27E-02	4.34
	9.2%	71.42%	19.38%	1.92E-02	3.74
	5.5%	72.58%	21.91%	1.11E-02	3.36
	5.5%	72.58%	21.91%	1.11E-02	3.36
	1.8%	70.85%	27.36%	3.49E-03	2.63
	1.1%	69.70%	29.21%	2.14E-03	2.42
Caprolactamium-Al ₂ Cl ₇	40.6%	48.25%	11.19%	1.22E-01	4.38
	15.7%	58.70%	25.64%	3.66E-02	2.32
	7.5%	60.46%	32.07%	1.63E-02	1.91
	7.5%	60.46%	32.07%	1.63E-02	1.91
	2.7%	56.68%	40.60%	5.69E-03	1.42

	1.5%	53.51%	45.00%	3.08E-03	1.21
	1.1%	49.66%	49.28%	2.19E-03	1.02
	0.9%	48.32%	50.73%	1.96E-03	0.97

As used herein, the term about means within 10% of the value, or within 5%, or within 1%.

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.

SPECIFIC EMBODIMENTS

While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

A first embodiment of the invention is a process utilizing a micro-emulsion comprising forming the micro-emulsion comprising contacting an ionic liquid, a co-solvent, a hydrocarbon, an optional surfactant, and an optional catalyst promoter to form the micro-emulsion, the micro-emulsion comprising a hydrocarbon component comprising a hydrocarbon and an ionic liquid component comprising the ionic liquid, the ionic liquid comprising a halometallate anion and a cation, the hydrocarbon comprising at least one paraffin having from 4 to about 50 carbon atoms, the co-solvent having a polarity greater than a polarity of the hydrocarbon, the ionic liquid being present in an amount of about 0.05 wt% to about 40 wt% of the micro-emulsion; and producing a product mixture in a process zone containing the micro-emulsion under at least one of isomerization, disproportionation, and reverse disproportionation conditions, the product mixture comprising a product selected from an isomerized paraffin, a disproportionated paraffin, a reverse disproportionated paraffin, or combinations thereof. An embodiment of the invention is one, any or all of prior

embodiments in this paragraph up through the first embodiment in this paragraph wherein the ionic liquid is present in an amount of about 0.05 wt% to about 25 wt% of the micro-emulsion. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the ionic liquid is present in an amount of about 0.05 wt% to about 15 wt% of the micro-emulsion. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the micro-emulsion comprises micelles or reverse micelles and wherein more than about 90% of the micelles or reverse micelles have diameter less than about 100 nanometers. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising altering a composition of the product mixture to destroy the micro-emulsion; and separating the product from one or more of the ionic liquid, the co-solvent, and the hydrocarbon. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the composition of the product mixture is altered by removing a portion of the co-solvent, increasing an amount of the hydrocarbon, increasing an amount of the product, adding an additional liquid having a polarity less than the polarity of the co-solvent, adding additional ionic liquid, or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the cation of the ionic liquid comprises a tetraalkyl phosphonium cation, a dialkylimidazolium cation, an alkylimidazolium cation, a pyridinium cation, an alkyl pyridinium cation, a dialkylpyridinium cation, an alkylpyrrolidinium cation, a dialkylpyrrolidinium cation, a trialkylammonium cation, a tetraalkylammonium cation, a lactamium cation, an alkyl-lactamium cation, a trialkylsulfonium cation, or combinations thereof; and wherein the halometallate anion contains a metal selected from Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, In, Sn, Sb, La, Ce, Hf, Ta, W, or combinations thereof, and a halide selected from F, Cl, Br, I, or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein a viscosity of the co-solvent is less than about 1 centipoise at 25°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the co-solvent comprises a halogenated hydrocarbon, a halocarbon, a halogenated aromatic, or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the surfactant is present,

70 wherein the surfactant comprises a quaternary ammonium salt, a ternary ammonium salt, a phosphonium salt, a sulfonate salt, a phosphonate salt, or a disubstituted amide, and wherein a molar ratio of the surfactant to the ionic liquid is less than about 2.5:1. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the catalyst promoter is present, wherein the catalyst promoter comprises an anhydrous hydrogen halide, a halogenated hydrocarbon, or
75 combinations thereof, and wherein a molar ratio of the catalyst promoter to the ionic liquid is about 0.1:1 to about 1:1. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the co-solvent is present in an amount of about 30 wt% to about 80 wt% of the micro-emulsion.

80 An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the hydrocarbon comprises at least one paraffin having from 4 to about 25 carbon atoms. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the isomerization, disproportionation, or reverse disproportionation
85 conditions include at least one of a temperature in a range of about 0°C to about 250°C, a pressure in a range of about 0 MPa to about 20.7 MPa, a residence time in a range of about 5 min to about 24 hours. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein a weight ratio of the ionic liquid to the hydrocarbon is in a range of about 0.025:1 to about
90 0.3:1. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the ionic liquid is present in an amount of about 0.05 wt% to about 5 wt% of the micro-emulsion, and wherein a residence time in the process zone is in a range of about 30 min to about 24 hours. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up
95 through the first embodiment in this paragraph wherein a residence time in a range of or about 1 min to about 24 hours. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising altering a composition of the reaction mixture to destroy the micro-emulsion; recovering the ionic liquid; regenerating at least a portion the recovered ionic liquid; and
100 recycling the regenerated ionic liquid.

A second embodiment of the invention is a process utilizing a micro-emulsion comprising forming the micro-emulsion comprising contacting an ionic liquid, a co-solvent, a hydrocarbon, an optional surfactant, and an optional catalyst promoter to form the micro-

emulsion, the micro-emulsion comprising a hydrocarbon component comprising a hydrocarbon and an ionic liquid component comprising the ionic liquid, the ionic liquid comprising a halometallate anion and a cation, the hydrocarbon comprising at least one paraffin having from 4 to about 50 carbon atoms, the co-solvent having a polarity greater than a polarity of the hydrocarbon, the ionic liquid being present in an amount of about 0.05 wt% to about 25 wt% of the micro-emulsion, the co-solvent being present in an amount of about 30 wt% to about 80 wt% of the micro-emulsion, wherein a weight ratio of the ionic liquid to the hydrocarbon is in a range of about 0.025:1 to about 0.3:1, and wherein the co-solvent comprises a halogenated hydrocarbon, a halocarbon, a halogenated aromatic, or combinations thereof; producing a product mixture in a process zone containing the micro-emulsion under at least one of isomerization, disproportionation, or reverse disproportionation conditions, the product mixture comprising a product selected from an isomerized paraffin, a disproportionated paraffin, a reverse disproportionated paraffin, or combinations thereof, wherein the isomerization, disproportionation, or reverse disproportionation conditions include at least one of a temperature in a range of about 0°C to about 250°C, a pressure in a range of about 0 MPa to about 20.7 MPa, a residence time in a range of about 1 min to about 24 hours; altering a composition of the product mixture to destroy the micro-emulsion by removing a portion of the co-solvent, increasing an amount of the hydrocarbon, increasing an amount of the product, adding an additional liquid having a polarity less than the polarity of the co-solvent, adding additional ionic liquid, or combinations thereof; and separating the product from one or more of the ionic liquid, the co-solvent, and the hydrocarbon. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the surfactant is present, wherein the surfactant comprises a quaternary ammonium salt, a ternary ammonium salt, a phosphonium salt, a sulfonate salt, a phosphonate salt, a disubstituted amide, and wherein a molar ratio of the surfactant to the ionic liquid is less than about 2.5:1; wherein the catalyst promoter is present, wherein the catalyst promoter comprises an anhydrous hydrogen halide, a halogenated hydrocarbon, or combinations thereof, and wherein a molar ratio of the catalyst promoter to the ionic liquid is about 0.1:1 to about 1:1; or both. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the cation of the ionic liquid comprises a tetraalkyl phosphonium cation, a dialkylimidazolium cation, an alkylimidazolium cation, a pyridinium cation, an alkyl pyridinium cation, a dialkylpyridinium cation, an alkylpyrrolidinium cation, a dialkylpyrrolidinium cation, a trialkylammonium cation, a tetraalkylammonium cation, a

lactamium cation, an alkyl-lactamium cation, a trialkylsulfonium cation, or combinations thereof.; and wherein the halometallate anion contains a metal selected from Al, Sc, Ti, V, 140 Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, In, Sn, Sb, La, Ce, Hf, Ta, W, or combinations thereof, and a halide selected from F, Cl, Br, I, or combinations thereof.

Without further elaboration, it is believed that using the preceding description that one skilled in the art can utilize the present invention to its fullest extent and easily ascertain the essential characteristics of this invention, without departing from the spirit and scope thereof, 145 to make various changes and modifications of the invention and to adapt it to various usages and conditions. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting the remainder of the disclosure in any way whatsoever, and that it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

150 In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

What is claimed:

1. A hydrocarbon conversion process utilizing a micro-emulsion comprising:

forming the micro-emulsion comprising:

5 contacting an ionic liquid, a co-solvent, a hydrocarbon, an optional
 surfactant, and an optional catalyst promoter to form the micro-
 emulsion, the micro-emulsion comprising a hydrocarbon component
 comprising a hydrocarbon and an ionic liquid component comprising the
 ionic liquid, the ionic liquid comprising a halometallate anion and a
 cation, the hydrocarbon comprising at least one paraffin having from 4
 to 50 carbon atoms, the co-solvent having a polarity greater than a
10 polarity of the hydrocarbon, the ionic liquid being present in an amount
 of 0.05 wt% to 40 wt% of the micro-emulsion; and

 producing a product mixture in a process zone containing the micro-emulsion
 under at least one of isomerization, disproportionation, and reverse disproportionation
 conditions, the product mixture comprising a product selected from an isomerized paraffin, a
15 disproportionated paraffin, a reverse disproportionated paraffin, or combinations thereof.

2. The process of claim 1 further comprising:

altering a composition of the product mixture to destroy the micro-emulsion;

and

5 separating the product from one or more of the ionic liquid, the co-solvent, and
 the hydrocarbon.

3. The process of claim 2 wherein the composition of the product mixture
is altered by removing a portion of the co-solvent, increasing an amount of the hydrocarbon,
increasing an amount of the product, adding an additional liquid having a polarity less than the
polarity of the co-solvent, adding additional ionic liquid, or combinations thereof.

4. The process of claim 2 further comprising:

recovering the ionic liquid;

regenerating at least a portion the recovered ionic liquid; and

recycling the regenerated ionic liquid.

5. The process of any one of claims 1-4 wherein the micro-emulsion comprises micelles or reverse micelles and wherein more than 90% of the micelles or reverse micelles have diameter less than 100 nanometers.

6. The process of any one of claims 1-4 wherein the cation of the ionic liquid comprises a tetraalkyl phosphonium cation, a dialkylimidazolium cation, an alkylimidazolium cation, a pyridinium cation, an alkyl pyridinium cation, a dialkylpyridinium cation, an alkylpyrrolidinium cation, a dialkylpyrrolidinium cation, a trialkylammonium cation, a tetraalkylammonium cation, a lactamium cation, an alkyl-lactamium cation, a
5 cation, a tetraalkylsulfonium cation, or combinations thereof.; and wherein the halometallate anion contains a metal selected from Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, In, Sn, Sb, La, Ce, Hf, Ta, W, or combinations thereof, and a halide selected from F, Cl, Br, I, or combinations thereof.

7. The process of any one of claims 1-4 wherein the co-solvent comprises a halogenated hydrocarbon, a halocarbon, a halogenated aromatic, or combinations thereof.

8. The process of any one of claims 1-4 wherein the surfactant is present, wherein the surfactant comprises a quaternary ammonium salt, a ternary ammonium salt, a phosphonium salt, a sulfonate salt, a phosphonate salt, a disubstituted amide, and wherein a molar ratio of the surfactant to the ionic liquid is less than 2.5:1; wherein the catalyst promoter
5 is present, wherein the catalyst promoter comprises an anhydrous hydrogen halide, a

halogenated hydrocarbon, or combinations thereof, and wherein a molar ratio of the catalyst promoter to the ionic liquid is 0.1:1 to 1:1; or both.

9. The process of any one of claims 1-4 wherein the co-solvent is present in an amount of 30 wt% to 80 wt% of the micro-emulsion.

10. The process of any one of claims 1-4 wherein the isomerization, disproportionation, or reverse disproportionation conditions include at least one of: a temperature in a range of 0°C to 250°C, a pressure in a range of 0 MPa to 20.7 MPa, a residence time in a range of 1 min to 24 hours.

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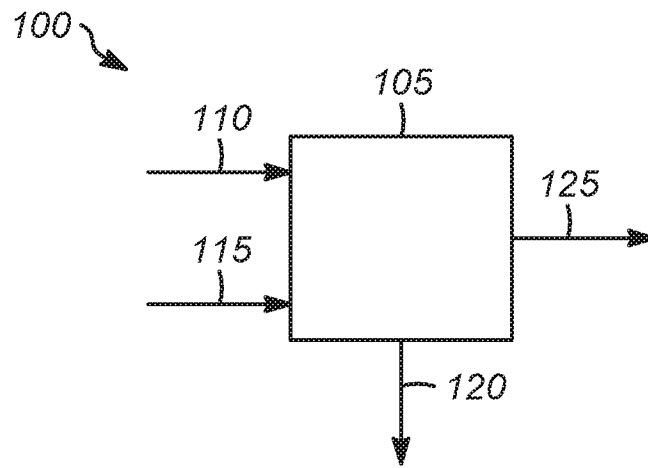


FIG. 1

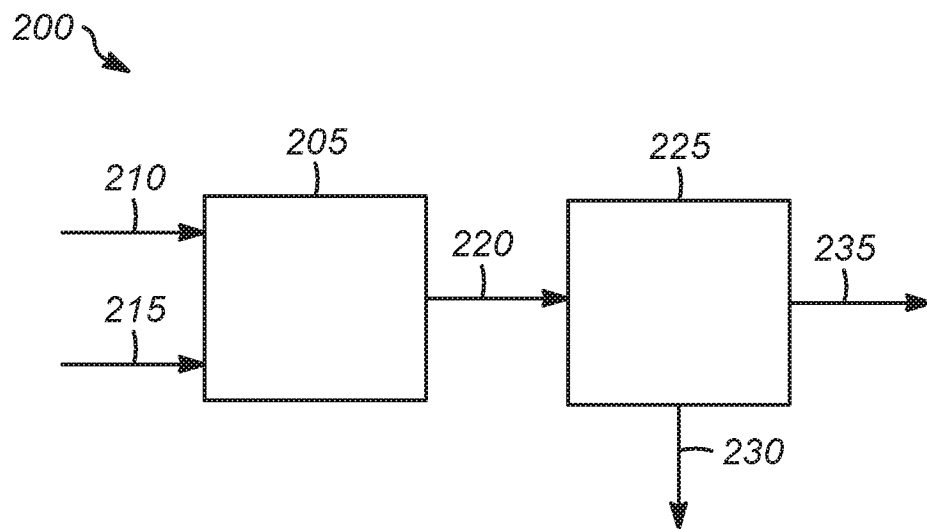


FIG. 2

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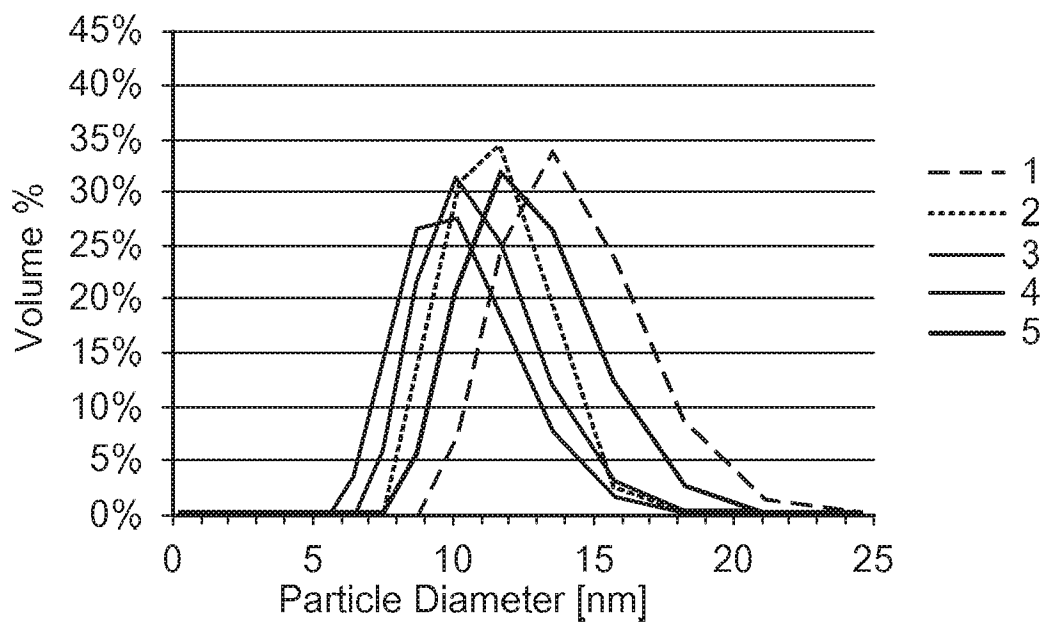


FIG. 3

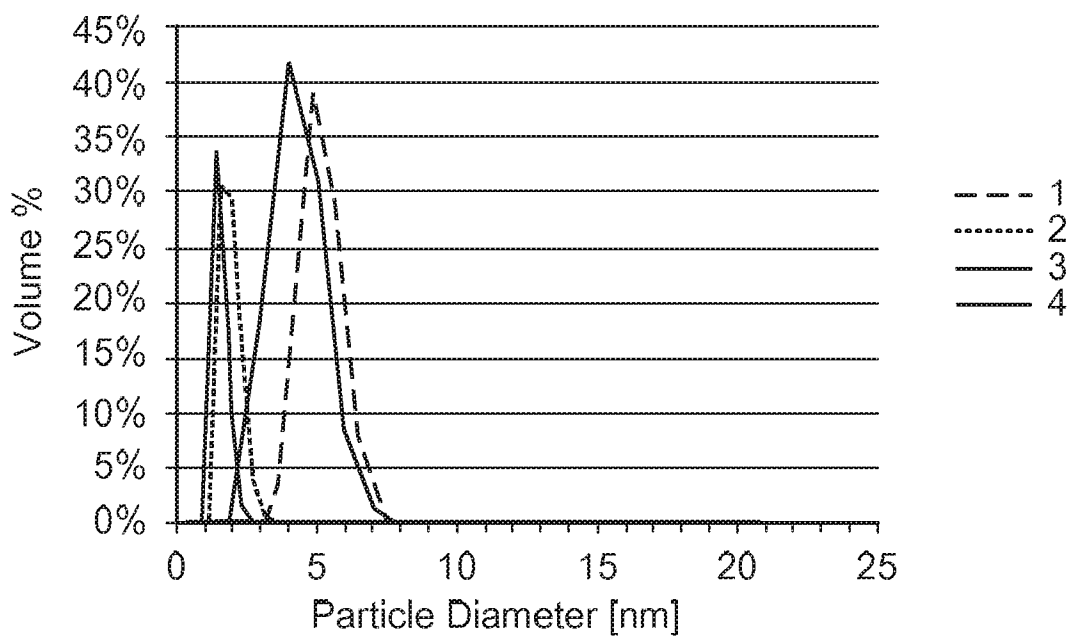


FIG. 4

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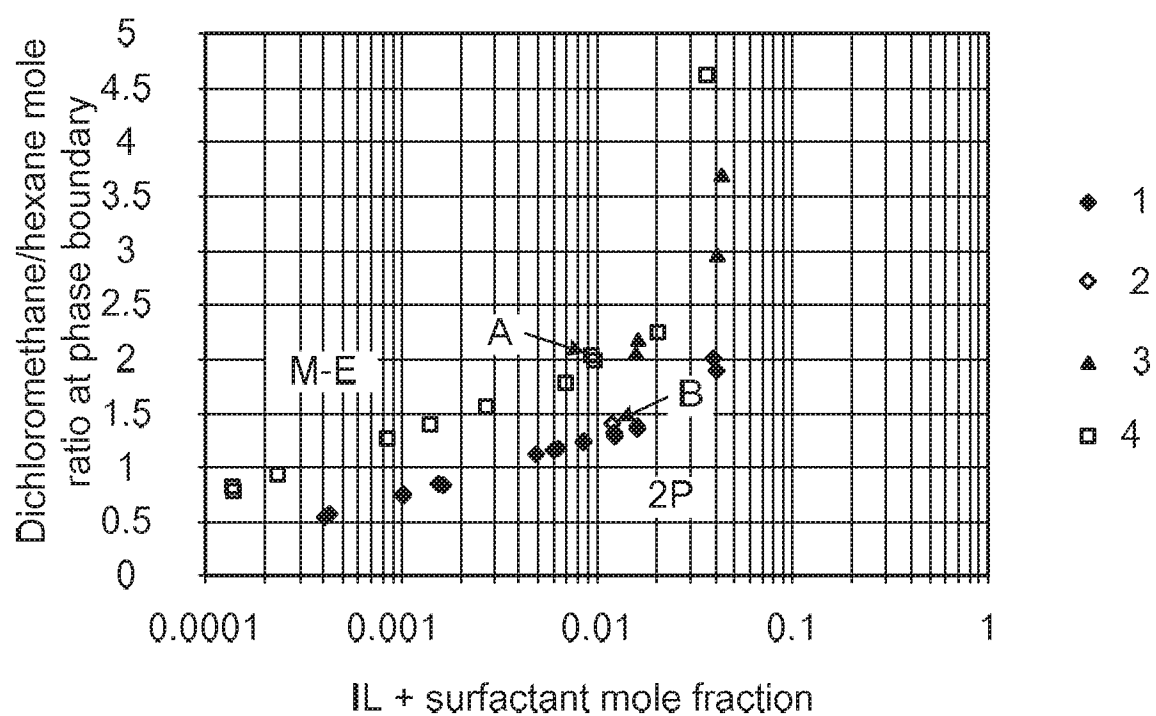


FIG. 5

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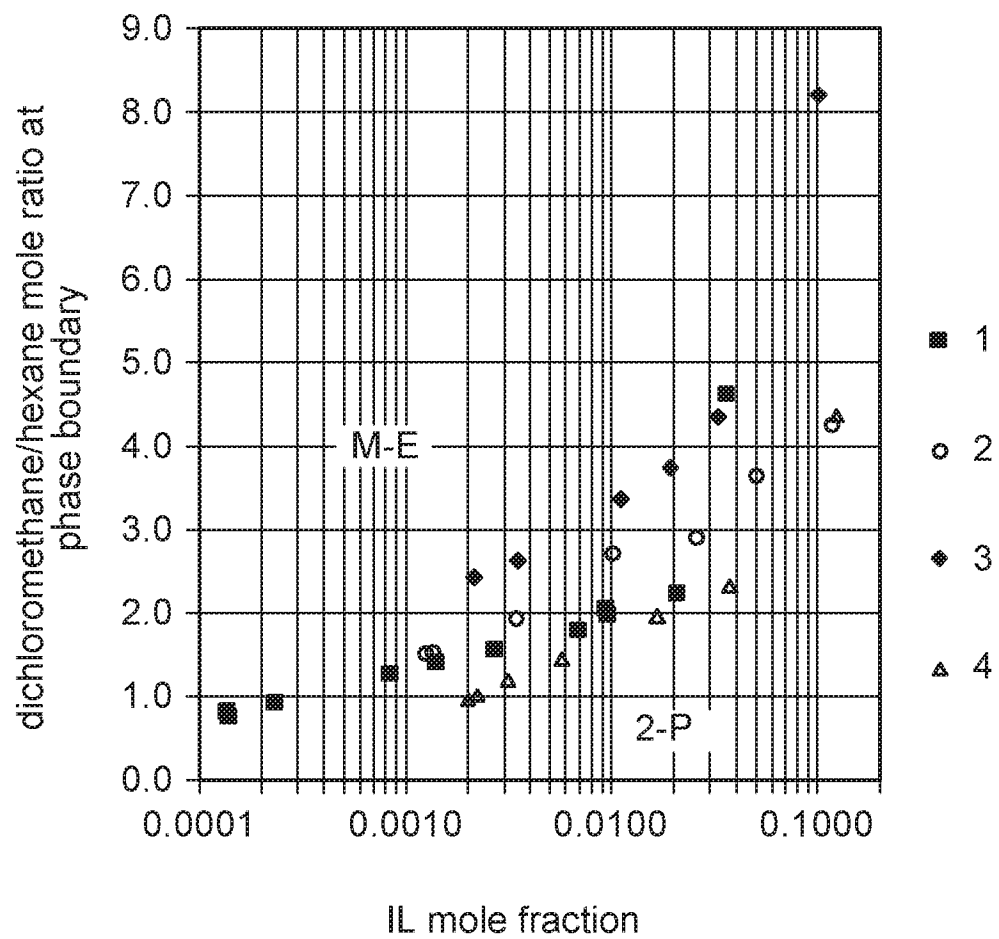


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2016/025414

A. CLASSIFICATION OF SUBJECT MATTER (see extra sheet) According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) B01J 31/22, 31/18, 31/02, 35/12, C07C 5/22, 6/00, B01F 3/08 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, Information Retrieval System of FIPS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005/0119423 A1 (BERGMAN LEE H. et al) 02.06.2005	1-10
A	WO 2010/135064 A2 (CHEVRON U.S.A. INC.) 21.06.2007	1-10
A	US 2007/0142216 A1 (CHEVRON U.S.A. INC.) 21.06.2007	1-10
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	
"E" earlier document but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family	
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 22 June 2016 (22.06.2016)	Date of mailing of the international search report 14 July 2016 (14.07.2016)	
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37	Authorized officer A. Sedov Telephone No. (495) 531-64-81	

INTERNATIONAL SEARCH REPORT
Classification of subject matter

International application No.

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B01J 31/18 (2006.01)
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B01J 35/12 (2006.01)
C07C 5/22 (2006.01)
C07C 6/00 (2006.01)
B01F 3/08 (2006.01)