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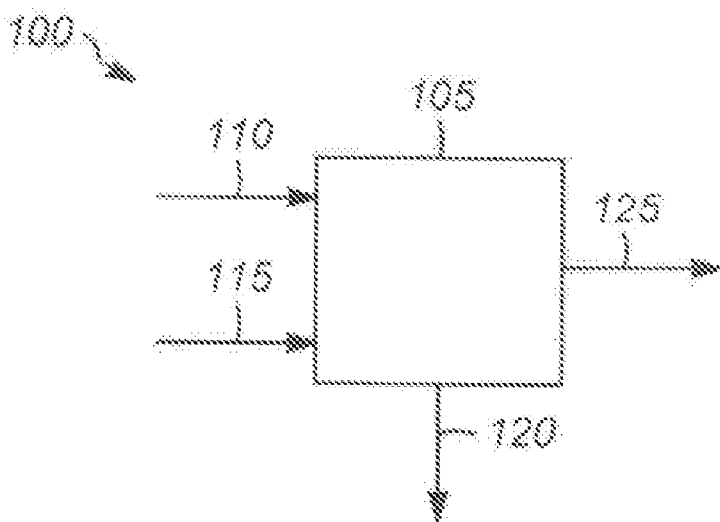


FIG. 1

(57) Abstract: A process for removing a contaminant from a hydrocarbon is described. A micro-emulsion is formed by contacting a lean ionic liquid, a co-solvent, a rich hydrocarbon containing the contaminant, and an optional surfactant. The micro-emulsion comprises a hydrocarbon component, which comprises the hydrocarbon, and an ionic liquid component which comprises the ionic liquid. 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 mixture is produced in a process zone containing the micro-emulsion. The lean hydrocarbon is recovered from the mixture.

CONTAMINANT REMOVAL

USING HALOMETALLATE IONIC LIQUID MICRO-EMULSIONS

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

BACKGROUND OF THE INVENTION

Various hydrocarbon streams, such as vacuum gas oil (VGO), atmospheric residuum, light cycle oil (LCO), and naphtha, may be converted into higher value hydrocarbon fractions such as diesel fuel, jet fuel, naphtha, gasoline, and other lower boiling fractions in refining processes such as hydrocracking and fluid catalytic cracking (FCC). However, hydrocarbon feed streams for these materials often have high amounts of nitrogen and sulfur which are more difficult to convert. For example, the degree of conversion, product yields, catalyst deactivation, and/or ability to meet product quality specifications may be adversely affected by the nitrogen and sulfur content of the feed stream. It is known to reduce the nitrogen content of these hydrocarbon feed streams by catalytic hydrogenation reactions such as in a hydrotreating process unit. However, hydrogenation processes require high pressures and temperatures. The presence of metals such as vanadium and nickel in the feeds are detrimental to catalyst life, as are so-called Conradson carbon compounds which result in high coke generation rates. The presence of metals and Conradson carbon compounds presents a great challenge especially for processing atmospheric residuum feeds.

Various processes using ionic liquids to remove sulfur and nitrogen compounds from hydrocarbon fractions are also known. U.S. Pat. No. 7,001,504 discloses a process for the removal of organosulfur compounds from hydrocarbon materials which includes contacting an ionic liquid with a hydrocarbon material to extract sulfur containing compounds into the ionic liquid. U.S. Pat. No. 7,553,406 discloses a process for removing polarizable impurities from hydrocarbons and mixtures of hydrocarbons using ionic liquids as an extraction medium. U.S. Pat. No. 7,553,406 also discloses that different ionic liquids show different extractive

properties for different polarizable compounds. U. S. Pat. No. 8,608,950 discloses a process for removing metals from a residuum feed using a residuum-immiscible ionic liquid.

Sulfur extraction has also been reported using Lewis hard acid AlCl_3 combined with tert-butyl chloride, n-butyl chloride, and tert-butyl bromide, A Carbonium Pseudo Ionic
5 Liquid with Excellent Extractive Desulfurization Performance, AIChE Journal, Vol. 59, No. 3, p. 948-958, March 2013; and acylating reagents and Lewis acids, Acylation Desulfurization of Oil Via Reactive Adsorption, AIChE Journal, Vol. 59, No. 8, p. 2966-2976, August 2013.

While deep denitrogenation is possible using conventional ionic liquid processes, deep desulfurization is difficult. Alternative methods for extractive feed
10 decontamination are needed.

SUMMARY OF THE INVENTION

One aspect of the invention is a process for removing a contaminant from a hydrocarbon. In one embodiment, the process includes forming a micro-emulsion by
15 contacting a lean ionic liquid, a co-solvent, a rich hydrocarbon, and an optional surfactant. The micro-emulsion comprises a hydrocarbon component comprising the hydrocarbon and an ionic liquid component comprising the ionic liquid. 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 mixture is produced in a process zone containing the
20 micro-emulsion. The lean hydrocarbon is recovered from the mixture.

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.

25 Fig. 3 is a graph showing the volume normalized particle size distribution of a 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.

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DETAILED DESCRIPTION OF THE INVENTION

Conventional contaminant removal processes using ionic liquids often use high shear to generate droplets in a two-phase mixture. The contaminants may include one or more of compounds containing sulfur or nitrogen, metal ions and metal compounds such as metalloporphyrins, and Conradson carbon. In these bi-phasic mixtures, ionic liquid solubility in the hydrocarbon is often negligible, and the extraction occurs in the surface layer of the ionic liquid. Small droplet size thus allows improved mass transfer by increasing the surface to volume ratio of the ionic liquid. 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 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.

Rather than utilizing shear force to generate meta-stable droplets, in the present invention, the ionic liquid is stabilized in the form of a micro-emulsion. The micro-emulsion contains a hydrocarbon component comprising a hydrocarbon, an ionic liquid component comprising the 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 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 contaminant removal applications, but they are also highly reactive and are not compatible with most protic or oxygenated solvents or surfactants.

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.

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.

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.

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% by weight. 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% by weight. Therefore, in order to form a micro-emulsion, an additional component such as a surfactant and/or a co-solvent must be added.

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

 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
10 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
15 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
20 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-
25 Hill, 1992, New York).

 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
30 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 materials for contaminant removal processes.

In one specific type of micro-emulsion, the polar structures containing the ionic liquid are reverse micelles. 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 amphiphilic surfactant reverse micelles have a specific size distribution determined by the nature and relative amount of the surfactant, 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 contaminant removal 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 ionic liquid may be concentrated on the surface of the micelles, reverse micelles, or the phase boundary in a bi-continuous micro-emulsion. Consequently, diffusion of the contaminants from the bulk hydrocarbon phase into the interior of the droplets may not be necessary. This provides additional reduction in mass transfer resistance. Solubility of the contaminants in the hydrocarbon component and/or the ionic liquid component is also likely to control the extent of contaminant removal. Here, the presence of a co-solvent may assist in making the contaminants more soluble in the ionic liquid component, or the change in solubility when the micro-emulsion is broken causes the contaminants to transfer to the ionic liquid.

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, ionic liquid 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. 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 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 contaminant removal, the nature of the micro-emulsion may allow ionic liquid recovery without the specialized equipment typically used in conventional ionic liquid processes. To recover the ionic liquid, 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, increasing the amount of lean hydrocarbon, adding an additional liquid having a polarity less than the polarity of the co-solvent (including an additional hydrocarbon), 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.

Not wishing to be bound by theory, use of a micro-emulsion for contaminant removal may result in more extensive (i.e., deeper) contaminant removal because mass transport of the contaminant to the ionic liquid phase is not necessary. The micro-emulsion exists as essentially one phase in which contaminants can freely associate with solvent (ionic liquid). Upon breaking the micro-emulsion, for instance by addition of a hydrocarbon, the contaminants stay with the ionic liquid and cannot transport back into the hydrocarbon.

Contaminant removal processes involve forming a micro-emulsion by contacting a lean ionic liquid, a co-solvent, a rich hydrocarbon containing one or more contaminants, and an optional surfactant. The micro-emulsion is introduced into the process zone (or is formed there). The micro-emulsion comprises a hydrocarbon component comprising a hydrocarbon having a polarity, an ionic liquid component comprising the ionic liquid. The co-solvent has a polarity greater than the polarity of the hydrocarbon. 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. A mixture is produced in a process zone containing the micro-emulsion. The lean hydrocarbon is recovered from the mixture.

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. 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
5 Application Serial No. 62/141076, entitled HEAT EXCHANGER FOR USE IN ALKYLATION PROCESS USING HALOMETALLATE IONIC LIQUID MICRO-EMULSIONS, (Attorney Docket No. H0048678-8250) filed March 31, 2015, each of which is incorporated herein by reference.

In some embodiments, the lean hydrocarbon is recovered from the mixture by
10 breaking the micro-emulsion, resulting in two distinct liquid phases. One phase is an ionic liquid phase that contains a majority of the ionic liquid and the transferred contaminants. The other phase is a hydrocarbon phase that contains a majority of the hydrocarbon which has a reduced level of contaminants compared to the rich hydrocarbon. If the micro-emulsion is broken by addition of a hydrocarbon of additional ionic liquid, the amount of contaminants and
15 the amount of other hydrocarbons in the rich ionic liquid may be adjusted by adjusting the amount of hydrocarbon or ionic liquid added. In this way, an optimum of desired contaminant removal can be balanced against undesired hydrocarbon losses. Both phases may contain co-solvent, surfactant (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.

20 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 has a higher density than the hydrocarbon, the ionic liquid layer will be below the hydrocarbon layer. If the ionic liquid has a lower density, it will be above the hydrocarbon
25 layer. The presence and amount of co-solvent in the ionic liquid and hydrocarbon phases may affect the density of these phases.

In some embodiments, the lean hydrocarbon is recovered from the mixture by extractive distillation. The extractive distillation is performed at a temperature and pressure such that the lean hydrocarbon is distilled off. Fresh rich hydrocarbon is added to the micro-
30 emulsion. If the co-solvent boils at a temperature below the extractive distillation temperature, the co-solvent is distilled off with the lean hydrocarbon, and fresh or recycled co-solvent is added to the micro-emulsion. If the co-solvent boils at a temperature above the extractive

distillation temperature (which is preferred), then only small amounts of co-solvent are added to the micro-emulsion to compensate for small losses in the distillation. In this embodiment, the micro-emulsion is not broken by the extractive distillation. In some embodiments, at least a portion of the rich micro-emulsion can be removed, and the co-solvent and rich ionic liquid
5 can then be separated.

The rich ionic liquid from the ionic liquid phase or the rich ionic liquid from the extractive distillation process can be recovered and recycled to the reaction zone. Separation of the components of the ionic liquid phase or the rich ionic liquid from the extractive distillation process may be desirable prior to recycling the ionic liquid and optionally one or
10 more other materials (e.g., surfactant) 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. The regeneration step involves decreasing the amount of the contaminant in the rich ionic liquid to produce a regenerated ionic liquid, which can be recycled to the process zone to
15 remove additional contaminant from the rich hydrocarbon. Some regeneration methods also allow for recovery of the extracted contaminants and hydrocarbon, known as the extract. Various methods for regenerating ionic liquids could be used. The rich ionic liquid can be washed with a regeneration solvent. For example, US 8,608,950, US 8,580,107, and US 8,608,943 describe washing the rich ionic liquid with a lighter (lower boiling) hydrocarbon
20 than the extract or washing with water to reduce either the metals or nitrogen content of the ionic liquid. The extract is separated from the ionic liquid, and then the ionic liquid is optionally dried to remove the regeneration solvent.

In some embodiments the ionic liquid comprises a Lewis acidic anion, such as a halometallate. In these embodiments, washing the ionic liquid with water is not an advisable
25 regeneration method since water will react with the anion. In these cases, other regeneration methods are needed. Several methods for regeneration of ionic liquid containing conjunct polymer may be applicable for removing sulfur compounds or nitrogen compounds. For example, 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
30 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. In the case of sulfur and nitrogen compounds, such methods are likely to hydrotreat

the compounds and cause them to release from the ionic liquid. 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
5 e.g., US 7,691,771, which is incorporated herein by reference. In the case of sulfur and nitrogen compounds, such methods are likely to hydrogenate the compounds and cause them to release from the ionic liquid. 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
10 [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. In the case of sulfur and nitrogen compounds, such methods are likely to cause pyridine or other substrate to coordinate to the ionic liquid in place of the
15 sulfur and or nitrogen compounds and cause them to release from the ionic liquid. Ionic liquids may also be regenerated by contacting with silane compounds (U.S. Patent No. 9,120,092), borane compounds (U.S. Publication No.2015/0314281), Bronsted 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
20 compounds are described in U.S. Application Serial Nos. 14/269,943 and 14/269,978, each of which is incorporated herein by references. In the case of sulfur and nitrogen compounds, such methods are likely to cause the compounds to release from the ionic liquid.

The materials of the hydrocarbon phase can be separated using a suitable separation process. The lean hydrocarbon can be recovered. Any surfactant can be recovered,
25 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.

The micro-emulsion forming step may be repeated, for example, when the contaminant content of the hydrocarbon effluent is to be reduced further to obtain a desired
30 contaminant level in the ultimate hydrocarbon product stream from the process. Each micro-emulsion forming step may be referred to as a contaminant removal step. Thus, the invention encompasses single and multiple contaminant removal steps. A contaminant removal zone may

be used to perform a contaminant removal step. As used herein, the term "zone" can refer to one or more equipment items and/or one or more sub-zones. Equipment items may include, for example, one or more vessels, heaters, separators, exchangers, conduits, pumps, compressors, and controllers. Additionally, an equipment item can further include one or more zones or sub-

5 zones. The contaminant removal process or step may be conducted in a similar manner and with similar equipment as is used to conduct other liquid-liquid wash and extraction operations. Suitable equipment includes, for example, columns with: trays, packing, rotating discs or plates, and static mixers. Pulse columns and mixing/settling tanks may also be used.

The micro-emulsion step can take place at a temperature in the range of about -

10 50°C to about 300°C, or about -50°C to about 250°C, or about -50°C to about 200°C, or about -50°C to about 150°C, or about -50°C to about 100°C, or about 0°C to about 350°C, or about 0°C to about 300°C, or about 0°C to about 250°C, or about 0°C to about 200°C, or about 0°C to about 150°C, or about 0°C to about 100°C, or about 20°C to about 350°C, or about -20°C to about 300°C, or about 20°C to about 250°C, or about 20°C to about 200°C, or about 20°C to

15 about 150°C, or about 20°C to about 120°C, or about 20°C to about 100°C, or about 20°C to about 80°C. It is desirable that the ionic liquid, co-solvent, and hydrocarbon maintain a liquid rather than vapor state through the operating temperature range.

The pressure is typically in the range of about 0.7 kPa(a) to about 13.8 MPa(a), or about 0.7 MPa to about 8.0 MPa, or about 0.7 MPa to about 5 MPa, or about 0.7 MPa to

20 about 3 MPa. The pressure is preferably sufficient to keep the materials in the liquid phase. The micro-emulsion forming step typically takes place at atmospheric pressure, although higher or lower pressures could be used, if desired or required to maintain the materials in liquid phase.

If the ionic liquid is a Lewis acidic ionic liquid such as an ionic liquid

25 comprising a halometallate anion, then the micro-emulsion forming step takes place in an inert atmosphere, such as nitrogen, helium, argon, and the like, without oxygen or moisture. An inert atmosphere may be preferable for processes using other ionic liquids as well, for instance to minimize long term oxidation of the ionic liquid.

The residence time in the contact zone is in the range of a few seconds to several

30 hours, or about 5 sec to about 12 hours, or about 30 sec to about 2 hours or about 2 minutes to about 1 hour. If shorter residence time is desired, more ionic liquid can be used.

The settling time may range from about 1 min to about 8 hr, or about 1 min to about 2 hr, or about 1 min to about 1 hr, or about 1 min to about 30 min, or about 1 min to about 10 min.

The weight ratio of rich hydrocarbon to lean ionic liquid may range from about 4:1 to about 100:1 or from about 10:1 to about 100:1 or from about 4:1 to about 50:1 or from about 4:1 to about 20:1 or from about 4:1 to about 10:1.

Examples of hydrocarbon streams that could be decontaminated using the present process include, but are not limited to, at least one of crude oil, de-salted crude oil, straight run naphtha, straight run distillate, atmospheric residuum, vacuum gas oil streams (boiling point (BP) of about 263°C to about 583°C), vacuum residuum, cracked naphtha streams (BP of about 30°C to about 200°C) light cycle oil streams (BP of about 103°C to about 403°C), naphtha streams (BP of about 30°C to about 200°C), coker gas oil streams (BP of about 263°C to about 603°C), kerosene streams (BP of about 150°C to about 275°C), streams made from biorenewable sources, fracking condensate streams, streams from hydrocracking zones, streams from hydrotreating zones including residuum hydrotreating, and streams from fluid catalytic cracking zones.

The sulfur and nitrogen contaminants are one or more species found in the hydrocarbon material that are detrimental to further processing. The total sulfur content may range from about 50 ppm to about 7 wt%, and the nitrogen content may be from about 5 ppm to about 30,000 ppm.

The ionic liquid can remove one or more of the sulfur and nitrogen contaminants in the hydrocarbon feed. The hydrocarbon feed will usually comprise a plurality of nitrogen compounds of different types (for instance, nitriles, indoles and carbazoles) in various amounts, typically in the range of about 5 ppmw to about 30,000 ppmw. Thus, at least a portion of at least one type of nitrogen compound may be removed from the hydrocarbon feed. The same or different amounts of each type of nitrogen compound can be removed, and some types of nitrogen compounds may not be removed. In an embodiment, up to about 92 wt% of the nitrogen can be removed. The nitrogen content of the hydrocarbon feed is typically reduced by at least about 10 wt%, at least about 20 wt%, or at least about 30 wt%, or at least about 40 wt%, at least about 50 wt%, or at least about 60 wt%, or at least about 70 wt%, or at least about 80 wt%, or at least about 90 wt%.

The hydrocarbon feed will typically also comprise a plurality of sulfur compounds of different types in various amounts, typically in the range of about 50 ppmw to about 7 wt%. Examples of sulfur compounds to be removed include, but are not limited to, thiophene, alkylthiophenes such as methylthiophenes, ethyl thiophenes and propylthiophenes, dialkylthiophenes, trialkylthiophenes benzothiophenes, alkylsulfides, and alkyldisulfides. Thus, at least a portion of at least one type of sulfur compound may be removed from the hydrocarbon feed. The same or different amounts of each type of sulfur compound may be removed, and some types of sulfur compounds may not be removed. In an embodiment, up to about 95 wt% of the sulfur can be removed. Typically, the sulfur content of the hydrocarbon feed is reduced by at least about 10 wt%, or at least about 15 wt%, or at least about 20 wt%, or at least about 25 wt%, or at least about 30 wt%, or at least about 35 wt%, or at least about 40 wt%, or at least about 50 wt%, or at least about 60 wt%, or at least about 70 wt%, or at least about 80 wt%, or at least about 90 wt%, or at least 95 about wt%.

In some embodiments, the rich hydrocarbon includes one or more metal in various amounts. Metals generally exist in crude oil or crude oil derived feed-stocks as metalloporphyrin compounds. Examples of metals to be removed include, but are not limited to, nickel, vanadium, iron, cobalt, manganese, molybdenum and chromium. Nickel, vanadium and iron are the most prevalent metals in most feedstocks derived from crude oil. Thus, at least a portion of at least one metal may be removed from the hydrocarbon feed. The same or different amounts of each metal may be removed and some metals may not be removed.

In some embodiments, the rich hydrocarbon includes Conradson carbon. Conradson carbon is carbon which readily leads to coke formation at elevated temperature. Conradson carbon can be determined in standard laboratory analysis tests such as ASTM Method D4530 (Standard Test Method for Determination of Carbon Residue (Micro Method)) or ASTM Method D189 (Standard Test Method for Conradson Carbon Residue of Petroleum Products). At least a portion of the Conradson carbon may be removed from the hydrocarbon feed.

In some embodiments, the rich hydrocarbon includes one or more an aromatic compounds. In many cases, aromatic compounds are a desired portion of the hydrocarbon and may have high octane or potential petrochemicals yield. Thus, in many cases it is desirable to maximize the amount of aromatic compounds retained in the lean hydrocarbon. However, many interactions which allow for contaminant removal also remove aromatics. In some embodiments, contaminant removal with micro-emulsions results in minimal loss of aromatics. In some

embodiments, the concentration of aromatic compounds in the lean hydrocarbon may be at least 95% of the concentration of aromatic compounds in the rich hydrocarbon feed (by weight), or at least 90%, or at least 80%, or at least 70%. Consistent with common terms of art, the ionic liquid used to form the micro-emulsion may be referred to as a “lean” ionic liquid generally meaning an ionic liquid that is not saturated with one or more extracted contaminants. Lean ionic liquid may include one or both of fresh and regenerated ionic liquid and is suitable for accepting or extracting contaminants from the hydrocarbon feed. Likewise, after the micro-emulsion is broken, the ionic liquid may be referred to as “rich”, which generally means an ionic liquid produced by a contaminant removal step or process or otherwise including a greater amount of extracted contaminants than the amount of extracted contaminants included in the lean ionic liquid. A rich ionic liquid may require regeneration or dilution, e.g. with fresh ionic liquid, before recycling the rich ionic liquid to the same or another contaminant removal step of the process. The starting hydrocarbon may be called a rich hydrocarbon, meaning a hydrocarbon containing one or more contaminants. The treated hydrocarbon may be called a lean hydrocarbon, meaning a hydrocarbon produced by the contaminant removal step or otherwise including a lesser amount of contaminants than the amount in the rich hydrocarbon.

Fig. 1 illustrates an embodiment of a contaminant removal process 100 using a single process zone 105. The micro-emulsion 110 is fed into the process zone 105. Alternatively, the materials to form the micro-emulsion could be fed into the process zone 105, and the micro-emulsion could be formed in the process zone 105. A mixture is produced. In some embodiments, the composition of the 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, for example by changing the pressure in the process zone to vaporize the co-solvent. Another way to change the composition is to add an additional material 115 comprising one or more of hydrocarbon, an additional liquid that has a polarity less than the polarity of the co-solvent (e.g., an additional hydrocarbon), 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).

Rich ionic liquid component 120, which may contain some other materials such as a portion of the co-solvent, can be removed from the process zone 105. The contaminants can be removed from the rich ionic liquid component 120 (not shown) which can be recycled

for further use (not shown), if desired. All or a portion of the ionic liquid component 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 product 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 materials and the recovery and/or recycle of the lean hydrocarbon and other materials.

Fig. 2 illustrates another embodiment of a contaminant removal process 200 in which there are different zones. The micro-emulsion (or the components to form the micro-emulsion) 210 is fed into the contacting zone 205.

The mixture 220, which contains the micro-emulsion is sent to a separation zone 225. The composition of the mixture 220 is changed so that the micro-emulsion is destroyed and the ionic liquid separates from the majority of the hydrocarbon component. Rich ionic liquid component 230, which may contain some other materials such as a portion of the co-solvent, can be removed from the separation zone 225 for further processing. The remaining mixture 235 containing the lean hydrocarbon can also be removed for further processing.

The contaminant removal kinetics may be changed by changing the amounts of the materials in the micro-emulsion. For example, if the co-solvent is more viscous than the rich hydrocarbon, increasing the ratio of rich hydrocarbon to co-solvent would decrease the viscosity of the hydrocarbon component, which would result in faster mass transfer. Higher hydrocarbon to co-solvent ratio would also increase the concentration of hydrocarbon. Adding a second co-solvent with a lower viscosity or using a different co-solvent with a lower viscosity may result in a faster mass transfer. Decreasing the size of the micelles, reverse micelles, or bi-continuous structures in the micro-emulsion may result in faster mass transfer. Decreasing the size of the micelles, reverse micelles, or bi-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.

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 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.

5 The micro-emulsion includes a hydrocarbon component and an ionic liquid component. The micro-emulsion is formed from a lean ionic liquid, a rich hydrocarbon, and a co-solvent. The micro-emulsion may optionally contain an additional surfactant.

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

10 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, or about 1 nanometer to about 80 nanometers, or about 1 nanometer to about 60 nanometers, 15 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 presence 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 20 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 25 surfactant is present, 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 3 nanometers to about 20 nanometers, or about 5 nanometers to about 30 100 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

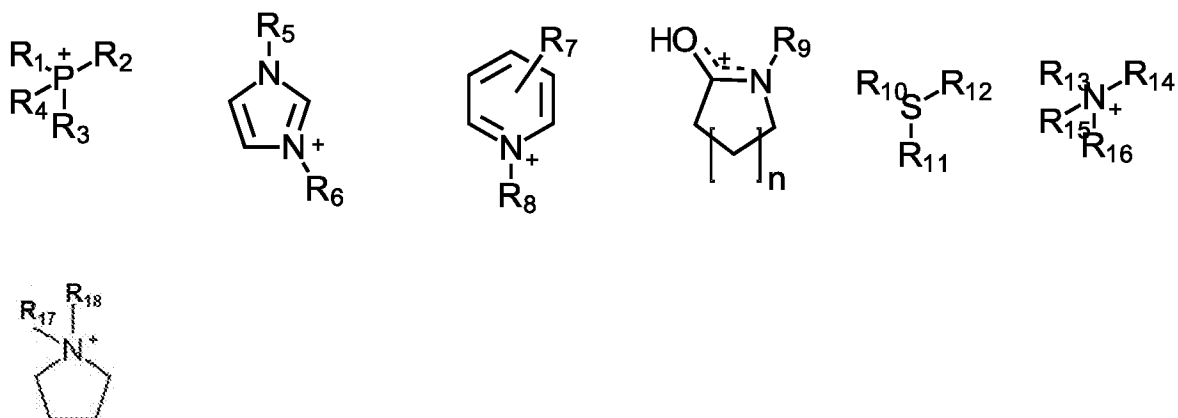
60 nanometers, or about 5 nanometers to about 50 nanometers, or about 5 nanometers to about 40 nanometers, or about 5 nanometers to about 30 nanometers, or about 5 nanometers to about 20 nanometers.

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 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.

In some embodiments, the ionic liquid anion is a halometallate. In those embodiments, 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 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 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 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, phosphorus based organic cations, sulfur based cations, or combinations thereof. Examples of cations include tetraalkyl phosphoniums, dialkylimidazoliums, alkylimidazoliums, pyridiniums, alkyl pyridiniums, alkylpyrrolidiniums, dialkylpyrrolidiniums, trialkylammoniums, tetraalkylammoniums, lactamiums, alkyl-lactamiums and trialkylsulfoniums. Mixtures of cations may be used as well. Examples of 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 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.

Suitable anions include, but are not limited to, halometallate anions, phosphate anions, hydrogen phosphate anions, dihydrogen phosphate anions, alkylphosphate anions, dialkylphosphate anions, alkylphosphonate anions, dialkylphosphonate anions, arylphosphate anions, diarylphosphate anions, sulfate anions, hydrogen sulfate anions, alkylsulfate anions (e.g., methylsulfate), arylsulfate anions, alkylsulfonate anions (e.g., methylsulfonate), arylsulfonate anions (e.g., p-toluenesulfonate), BF₄ anions, PF₆ anions, Br anions, Cl anions, F anions, I anions, dicyanamide anions, tricyanomethanide anions, tetracyanoborate anions, thiocyanate anion, trifluoromethylsulfonate anions, bis(sulfonyl)imide anions, (bis(trifluoromethylsulfonyl)imide) anions, nitrate anions, nitrite anions, carboxylate anions

(e.g., acetate), fluorocarboxylate anions (e.g., trifluoroacetate), and combinations thereof. 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,
5 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. 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
10 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
15 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.

20 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. In some embodiments, the hydrocarbon contains heavy molecules including structures of condensed and aromatic rings, alkylated aromatic rings and alkylated condensed
25 aromatic rings. 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,
30 an additional surfactant may be needed to act as the amphiphile. The solubility of the ionic liquid or the optional surfactant in the ionic liquid component 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, a co-solvent is used to modify the polarity of the hydrocarbon. The co-solvent is more polar than the hydrocarbon.

5 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, 10 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 15 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 20 limited to, chloroform, dichloromethane, chloromethane, chlorobenzene, dichlorobenzene, fluoromethane, difluoromethane, trifluoromethane, and 1-chloro-2,2-dimethylpropane.

In cases where the ionic liquid is not Lewis acidic or where a weaker Lewis acid is utilized, other co-solvents may be used that would otherwise be reactive with stronger Lewis acids. These include, but are not limited to, ethers (e.g., tetrahydrofuran, and diethyl ether), 25 alcohols (e.g., butanol, propanol, and methanol), amides (e.g., dimethylformamide, and dimethylacetamide), esters (e.g., ethyl acetate), ketones (e.g., acetone), nitriles (e.g., acetonitrile), sulfoxides (e.g., dimethylsulfoxide), sulfones (e.g. sulfolane), or combinations thereof.

In some embodiments, the viscosity of the co-solvent is less than about 1 30 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 and as little co-solvent in the micro-emulsion as possible. 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 hydrocarbon. 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, and co-solvent. 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 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 about 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 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 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-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 of classes of such surfactants include, but are not limited to, amphiphilic quaternary ammonium

salts, ternary ammonium salts, phosphonium salts, sulfonate salts, phosphonate salts, di-substituted 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.

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 0.05 about 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 1 wt% to about 30 wt% or about 5 wt% to about 30 wt% or about 10 wt% to about 30 wt% or about 1 wt% to about 20 wt% or about 5 wt% to about 20 wt%.

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.

The amounts of co-solvent and surfactant needed to stabilize the micro-emulsion depend on the amount of ionic liquid and hydrocarbon component present. When
5 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
10 combination of hydrocarbon, co-solvent, ionic liquid, and optional surfactant 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,
15 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
20 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, and the optional surfactant. The hydrocarbon component has a polarity less than the polarity of the co-solvent. In some
25 embodiments, the co-solvent is miscible in the hydrocarbon component, at least up to the desired composition. In some embodiments, the ionic liquid is at least slightly 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
30 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 can be added at different times and to different combinations of the

materials. For example, the 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 materials could be combined at the same time. Other ways of combining the materials would be understood by those skilled in the art.

5 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 hydrocarbon is less than the polarity of the co-solvent, and the co-solvent is miscible in the hydrocarbon. The hydrocarbon component comprises the
10 hydrocarbon and the co-solvent. The ionic liquid is present in an amount of about 0.05 wt% to about 40 wt% of the micro-emulsion.

 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. The ionic liquid and an
15 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 micro-emulsion.

Examples

Feed decontamination was demonstrated using a naphtha range product from a fluid catalytic cracking processes which had been distilled to remove all material boiling below
20 approximately 140 °C. Properties of the feed are shown in Table 1-4. The feed contained 6393 ppm sulfur and 133 ppm nitrogen by weight.

Table 1: GC analysis of heavy naphtha range feed used for feed decontamination.

	Wt%
C4s	0
C5s	0
C6s	0
C7s	0
C8 Aromatics	8
C8 Cyclic Olefins	0
C8 Isoolefins	0
C8 Isoparaffins	0
C8 Naphthenes	0

C8 n-Olefins	0
C8 n-Paraffins	0
C9 Cyclic Olefins	0.4
C9 Isoolefins	0.6
C9 Isoparaffins	0.6
C9 Naphthenes	1.7
C9 n-Olefins	0.5
C9 n-Paraffins	0.3
C9+ Aromatics	71
C10 Cyclic Olefins	0
C10 Isoolefins	0.4
C10 Isoparaffins	1.7
C10 Naphthenes	1.4
C10 n-Olefins	1.4
C10 n-Paraffins	0.7
C11 Cyclic Olefins	0
C11 Isoolefins	0.4
C11 Isoparaffins	0.2
C11 Naphthenes	0.2
C11 n-Olefins	2
C11 n-Paraffins	0.2
C12+ non-Aromatics	8.3
Total	
Aromatics	79
Olefins	5.7
Naphthenes	3.3
Paraffins	3.7
C12+ non-A	8.3

Table 2: sulfur and nitrogen analysis of heavy naphtha range feed

Total Sulfur wppm (X-ray fluorescence)	6393
Total nitrogen (chemiluminescence D4629) wppm	133

Table 3: GC simulated distillation (D2887) of heavy naphtha range feed

wt% distilled	Boiling point (° C)
0.5 (IBP)	137.8
1	138.8
2	139.6
3	140
4	140.6
5	142
6	144.8
7	145.6
8	146.2
9	146.8
10	147.8
11	151.6
12	154.2
13	158.2
14	160.4
15	161.6
16	162.4
17	162.8
18	163.2
19	163.6
20	163.8
21	164
22	164.4
23	164.8
24	165.2
25	165.8
26	166.4
27	167.2
28	167.8
29	169.4
30	170.2
31	170.8
32	171.2
33	171.4
34	171.8
35	172
36	172.2
37	172.4
38	172.8
39	173.4
40	175.8
41	176.6
42	177.4
43	178.4
44	179.2
45	182.2
46	183.2

47	184
48	184.6
49	185.2
50	186
51	187.8
52	189
53	189.6
54	190.2
55	190.6
56	191.2
57	191.6
58	193.8
59	196.2
60	197.6
61	198.2
62	199.2
63	201
64	202
65	202.8
66	203.2
67	203.8
68	204.4
69	205.6
70	207.2
71	208
72	208.6
73	209.2
74	210.4
75	211.4
76	212.2
77	213.4
78	215.2
79	218.2
80	219.6
81	221.8
82	223.2
83	224.6
84	226.2
85	228
86	229
87	229.8
88	230.2
89	230.6
90	231.4
91	232.4
92	233
93	235.8
94	239

95	243.4
96	248
97	254.2
98	321.4
99	409.8
99.5 (FBP)	452

Table 4 – GC analysis of heavy naphtha range feed by D5623 (sulfur compounds in gasoline)

1-propylmercaptan	--
2,3,5-trimethylthiophene	176.5
2,5-dimethylthiophene	12.4
2,7-dimethylbenzothiophene	85.3
2-ethyl-5-methylthiophene	52.4
2-ethylthiophene	13
2-methylbenzothiophene	649.8
2-methylthiophene	--
2-n-butylthiophene	29.9
2-n-propylthiophene	31.8
2-propylmercaptan	--
3-ethylthiophene	84.7
3-methylthiophene	--
Benzothiophene	>1000
butyl sulfide	40.4
Heavies	1326.9
Lights	--
Methyl Sulfide	--
Propyl Disulfide	21.5
propyl sulfide	149.8
sec-butyl sulfide	60.9
tert-butyl disulfide	36.7
Thiophene and benzothiophene Unknowns	715.1
Thiophene/Sec-butylmercaptan	--

5 Example 1 – Feed decontamination by ionic liquid micro-emulsion

13.3 g (31.4 vol%) of the feed described above was combined with 6.60 g of tributylmethylphosphonium heptachloroaluminate ionic liquid (11.5 vol%) and 36.5 g of dichloromethane (57.1 vol%). The mixture was shaken well for 30 seconds, resulting in a clear mixture that did not scatter visible light. To break this micro-emulsion and recover a decontaminated product, 37.0 g of n-pentane was added, shaken, and allowed to separate to two phases by gravity. The top phase was decanted, and the dichloromethane and n-pentane

were removed on a rotary evaporator. The product was washed with water, dried over $\text{Mg}(\text{SO}_4)_2$ and filtered through celite to remove residual IL. Analysis of the product is shown in table 5. The product contained only 297 wppm sulfur, a reduction of 95.4% relative to the feed, and 10 ppm nitrogen, a reduction of 92.5% relative to the feed. The product contained
5 78.1% aromatics, 1.9% $\text{C}_8\text{-C}_{11}$ olefins, 5.1% $\text{C}_8\text{-C}_{11}$ naphthenes, 6.6% $\text{C}_8\text{-C}_{11}$ paraffins and 7.4% C_{12+} non-aromatics.

Comparative Example 1 – Feed decontamination with no polar co-solvent

In this comparative example, the same volume % of feed and IL were used as in Example 1. Instead of adding dichloromethane, n-pentane was added such that the volume %
10 of n-pentane was the same as the volume % of dichloromethane in Example 1. 11.0 g (32.1 vol%) of the feed described above was combined with 14.3 g of n-pentane (55.9 vol%) and 5.57 g of tributylmethylphosphonium heptachloroaluminate ionic liquid (12.0 vol%). The mixture was shaken well for 30 seconds, and allowed to settle. Two distinct phases were formed. The top layer was decanted and filtered through celite to remove residual IL. This layer
15 was analyzed for sulfur and nitrogen content, and by GC to determine hydrocarbon speciation. A portion of the mixture of naphtha feed and pentane was analyzed as well. The product (which included the added pentane) contained 1772 ppm sulfur and 2.3 ppm nitrogen. After re-normalizing the results to discount the addition of pentane by applying the formula: (actual content in product)*(content in pentane-free feed)/(content in feed with pentane), the product
20 contained 3865 wppm sulfur, a reduction of 39.5% relative to the feed; 5 wppm nitrogen a reduction of 96.2% relative to the feed; 77.6 wt% aromatics, 6.5 wt% $\text{C}_8\text{-C}_{11}$ olefins, 3.9 wt% $\text{C}_8\text{-C}_{11}$ naphthenes, 4.4 wt% $\text{C}_8\text{-C}_{11}$ paraffins and 7.6% C_{12+} non-aromatics.

Comparative Example 2 - Feed decontamination with no polar co-solvent

In this comparative example, the same volume % of feed and IL were used as in example 1. Instead of adding dichloromethane, n-pentane was added such that the volume %
25 of n-pentane was the same as the volume % of dichloromethane plus the volume % of n-pentane added to break the micro-emulsion in Example 1. 13.3 g (14.5 vol%) of the feed described above was combined with 55.1 g of n-pentane (80.2 vol%) and 6.60 g of
30 tributylmethylphosphonium heptachloroaluminate ionic liquid (5.3 vol%). The mixture was shaken well for 30 seconds, and allowed to settle. Two distinct phases were formed. The top

phase was decanted, and the n-pentane was removed on a rotary evaporator. The product was washed with water, dried over $\text{Mg}(\text{SO}_4)_2$ and filtered through celite to remove residual IL. Analysis of the product is shown in table 5. The product contained only 4133 wppm sulfur, a reduction of 35.4% relative to the feed, and 8.2 ppm nitrogen, a reduction of 93.8% relative to the feed.

Table 5: Decontamination of heavy naphtha feed

	Example 1 before breaking micro-emulsion	Example 1 after breaking micro-emulsion	Comparative example 1	Comparative example 2
Heavy FCC naphtha g	13.3	13.3	11.0	13.3
n-C5 g	--	37.0	14.3	55.1
CH_2Cl_2 g	36.5	36.5	--	--
TBMP g	6.60	6.60	5.57	6.60
CH_2Cl_2 vol%	57.1%	26.3%	--	--
Naphtha vol%	31.4%	14.5%	32.1%	14.5%
nC5 vol%	--	54.0%	55.9%	80.2%
TBMP vol%	11.5%	5.3%	12.0%	5.3%
S in feed ppm	n.d.	6393	2931	6393
S in product ppm	n.d.	297	1772	4133
DeS	n.d.	95.4%	39.5%	35.4%
N in feed ppm	n.d.	135	60	135
N in product ppm	n.d.	10	2.3	8.2
DeN	n.d.	92.5%	96.2%	93.8%

Example 3 – Phase diagram

10 In this example n-hexane is used as the hydrocarbon, tributylhexylphosphonium heptachloroaluminate is used as the ionic liquid, dichloromethane is used as the co-solvent, and benzyldimethyltetradecylammonium chloride was used as the additional surfactant.

Micro-emulsions were generated by preparing a mixture of ionic liquid and surfactant. Three 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 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 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 boundary was also found. A phase diagram showing the required dichloromethane/hexane ratio to form a clear liquid (the phase boundary) 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. 7) 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. The micro-emulsion used in examples 1-4 is shown as the point indicated as "5" in Fig. 5, although isobutane was used instead of hexane. Typical alkylation conditions systems not containing a micro-emulsion, such as those described in examples in US2013/0345482, are indicated by point "6" in Fig. 5.

Example 4

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 (Malvern Instruments LTD., UK). Compositions were prepared as described in Example 7. 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 5

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 6.

Table 6: 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
5 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
10 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
15 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 for removing a contaminant comprising at least one of sulfur compounds and nitrogen compounds from a hydrocarbon comprising forming a micro-emulsion comprising contacting a lean ionic liquid, a co-solvent,
20 a rich hydrocarbon containing the contaminant, and an optional surfactant to form the micro-emulsion, the micro-emulsion comprising a hydrocarbon component comprising the hydrocarbon and an ionic liquid component comprising the ionic liquid, 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 mixture in a process
25 zone containing the micro-emulsion under contaminant removal conditions; and recovering a lean hydrocarbon from the mixture. 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
30 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 a 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 mixture to destroy the micro-emulsion; and wherein recovering the lean hydrocarbon from the mixture comprises separating the lean hydrocarbon from one or more of a rich ionic liquid, and the co-solvent. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first
5 embodiment in this paragraph wherein the composition of the mixture is altered by removing a portion of the co-solvent, increasing an amount of the lean hydrocarbon, 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
10 embodiments in this paragraph up through the first embodiment in this paragraph wherein recovering the lean hydrocarbon from the mixture comprises distilling the lean hydrocarbon from the mixture while adding additional rich hydrocarbon to the mixture. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first
15 embodiment in this paragraph wherein the ionic liquid comprises a cation and an anion and wherein the cation of the lean 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
20 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 comprises a cation and an anion and wherein the anion comprises a halometallate anion, a phosphate
anion, a hydrogen phosphate anion, a dihydrogen phosphate anion, an alkylphosphate anion, a dialkylphosphate anion, an alkylphosphonate anion, a dialkylphosphonate anion, an
arylphosphate anion, a diarylphosphate anion, a sulfate anion, a hydrogensulfate anion, an
25 alkylsulfate anion, an arylsulfate anion, an alkylsulfonate anion, an arylsulfonate anion, a BF₄
anion, a PF₆ anion, a Br anion, a Cl anion, a F anion, an I anion, a dicyanamide anion, a
tricyanomethanide anion, a tetracyanoborate anion, a thiocyanate anion, a
trifluoromethylsulfonate anion, a bis(sulfonyl)imide anion, a
(bis(trifluoromethylsulfonyl)imide) anion, a nitrate anion, a nitrite anion, a carboxylate anion,
30 a fluorocarboxylate anion, and combination 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 comprises a cation and an anion and wherein anion
comprises a halometallate anion containing 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, an ether, an alcohol, an amide, an ester, a ketone, a nitrile, a sulfoxide, a sulfone, 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, wherein the surfactant comprises a quaternary ammonium salt, a ternary ammonium salt, a phosphonium salt, a sulfonate salt, a phosphonate salt, a di-substituted amide, an ether, or a glyme, 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 co-solvent is present in an amount of about 30 wt% to about 80 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 further comprising altering a composition of the mixture to destroy the micro-emulsion; recovering a rich ionic liquid; removing the contaminants from the rich ionic liquid to produce a regenerated ionic liquid; and recycling the regenerated ionic liquid. 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 contaminant removal conditions include at least one of a temperature in a range of about -50°C to about 300°C, a pressure in a range of about 0.7 Pa(a) to about 13.8 MPa(a), or a residence time in a range of about 5 sec to about 12 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 rich hydrocarbon to lean ionic liquid is in a range of about 4:1 to about 100:1. 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 at least about 70 wt% of the sulfur compounds are removed, or at least about 90 wt% of the nitrogen compounds are removed, or both. 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 sulfur compounds comprise at least one of thiophene, alkylthiophenes, dialkylthiophenes, trialkylthiophenes, benzothiophenes, alkylsulfides, and alkyldisulfides. 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 rich hydrocarbon further comprises

an aromatic compound, and wherein a concentration of the aromatic compound in the lean hydrocarbon is at least about 95% of a concentration of the aromatic compound in the rich hydrocarbon, by weight. 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
5 contaminant comprises at least one of sulfur compounds, nitrogen compounds, metal ions, metal compounds, and Conradson carbon.

A second embodiment of the invention is a process for removing a contaminant comprising at least one of sulfur compounds, nitrogen compounds, metal ions, metal compounds, and Conradson carbon from a hydrocarbon comprising forming a micro-emulsion
10 comprising contacting a lean ionic liquid, a co-solvent, a rich hydrocarbon containing the contaminant, and an optional surfactant to form the micro-emulsion, the micro-emulsion comprising a hydrocarbon component comprising the hydrocarbon and an ionic liquid component comprising the ionic liquid, 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
15 wt% of the micro-emulsion; and producing a mixture in a process zone containing the micro-emulsion under contaminant removal conditions; altering a composition of the mixture to destroy the micro-emulsion; separating the lean hydrocarbon from the mixture and recovering the lean hydrocarbon; separating a rich ionic liquid from the mixture; removing the contaminant from the rich ionic liquid to produce a regenerated ionic liquid; and recycling the
20 regenerated ionic liquid.

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, to make various changes and modifications of the invention and to adapt it to various usages
25 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.

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

What is claimed:

1. A process for removing a contaminant comprising at least one of sulfur compounds, nitrogen compounds, metal ions, metal compounds, and Conradson carbon from a hydrocarbon comprising:

forming a micro-emulsion comprising:

5 contacting a lean ionic liquid, a co-solvent, a rich hydrocarbon containing the contaminant, and an optional surfactant to form the micro-emulsion, the micro-emulsion comprising a hydrocarbon component comprising the hydrocarbon and an ionic liquid component comprising the ionic liquid, the co-solvent having a polarity greater than a polarity of the hydrocarbon, the ionic liquid being present in an amount of 0.05 wt% to 40 wt% of the
10 micro-emulsion; and

producing a mixture in a process zone (105) containing the micro-emulsion under contaminant removal conditions; and

recovering a lean hydrocarbon from the mixture.

2. The process of claim 1 further comprising:

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

wherein recovering the lean hydrocarbon from the mixture comprises separating the lean hydrocarbon from one or more of a rich ionic liquid, and the co-solvent.

3. The process of claim 2 wherein the composition of the mixture is altered by removing a portion of the co-solvent, increasing an amount of the lean hydrocarbon, 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 a rich ionic liquid;

removing the contaminants from the rich ionic liquid to produce a regenerated ionic liquid; and

5 recycling the regenerated ionic liquid.

5. The process of any one of claims 1-4 wherein recovering the lean hydrocarbon from the mixture comprises distilling the lean hydrocarbon from the mixture while adding additional rich hydrocarbon to the mixture.

6. The process of any one of claims 1-4 wherein the ionic liquid comprises a cation and an anion and wherein the cation of the lean 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 anion comprises a halometallate anion, a phosphate anion, a hydrogen phosphate anion, a dihydrogen phosphate anion, an alkylphosphate anion, a dialkylphosphate anion, an alkylphosphonate anion, a dialkylphosphonate anion, an arylphosphate anion, a diarylphosphate anion, a sulfate anion, a hydrogensulfate anion, an alkylsulfate anion, an arylsulfate anion, an alkylsulfonate anion, an arylsulfonate anion, a BF₄ anion, a PF₆ anion, a Br anion, a Cl anion, a F anion, an I anion, a dicyanamide anion, a tricyanomethanide anion, a tetracyanoborate anion, a thiocyanate anion, a trifluoromethylsulfonate anion, a bis(sulfonyl)imide anion, a (bis(trifluoromethylsulfonyl)imide) anion, a nitrate anion, a nitrite anion, a carboxylate anion, a fluorocarboxylate anion, and combination thereof.

7. The process of any one of claims 1-4 wherein the co-solvent comprises a halogenated hydrocarbon, a halocarbon, a halogenated aromatic, an ether, an alcohol, an amide, an ester, a ketone, a nitrile, a sulfoxide, a sulfone, 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, an ether, or a glyme, and wherein a molar ratio of the surfactant to the ionic liquid is less than 2.5:1.

9. The process of any one of claims 1-4 wherein at least one of: the co-solvent is present in an amount of 30 wt% to 80 wt% of the micro-emulsion; and a weight ratio of rich hydrocarbon to lean ionic liquid is in a range of 4:1 to 100:1.

10. The process of any one of claims 1-4 wherein the contaminant removal conditions include at least one of: a temperature in a range of -50°C to 300°C, a pressure in a range of 0.7 kPa(a) to 13.8 MPa(a), or a residence time in a range of 5 sec to 12 hours.

1/4

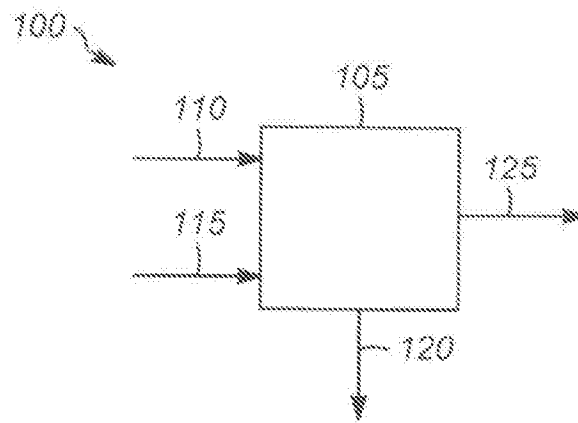


FIG. 1

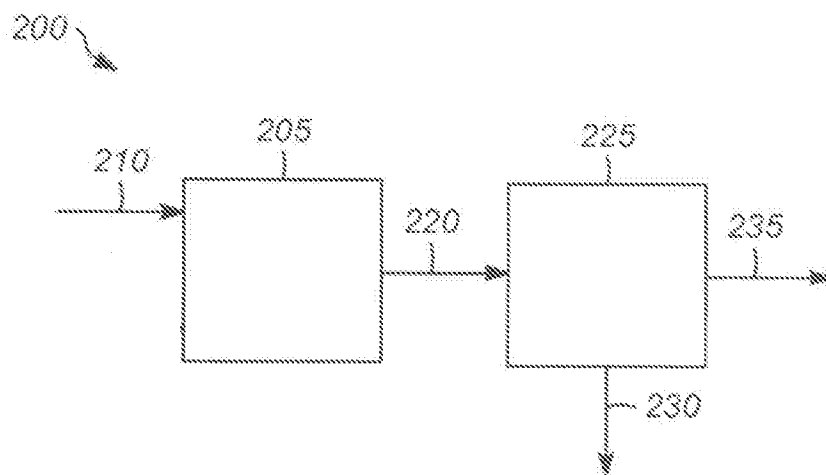


FIG. 2

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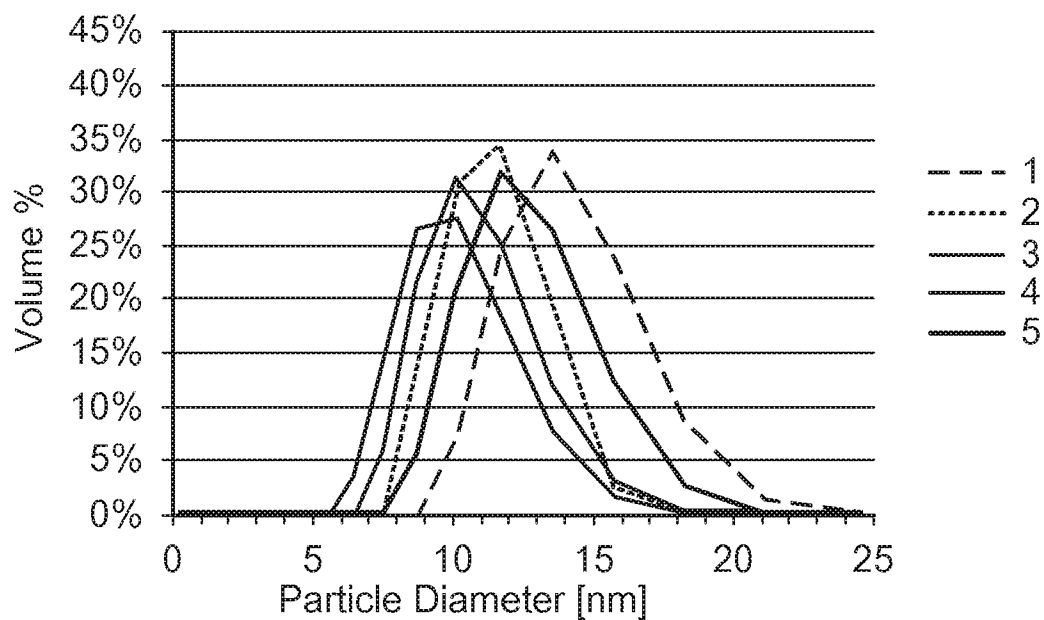


FIG. 3

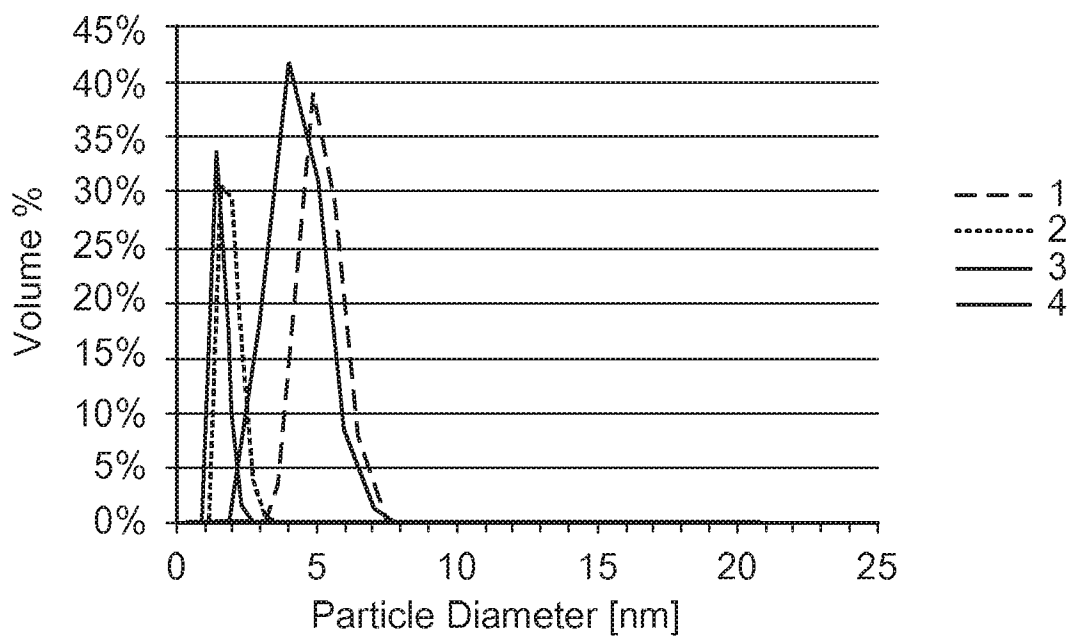


FIG. 4

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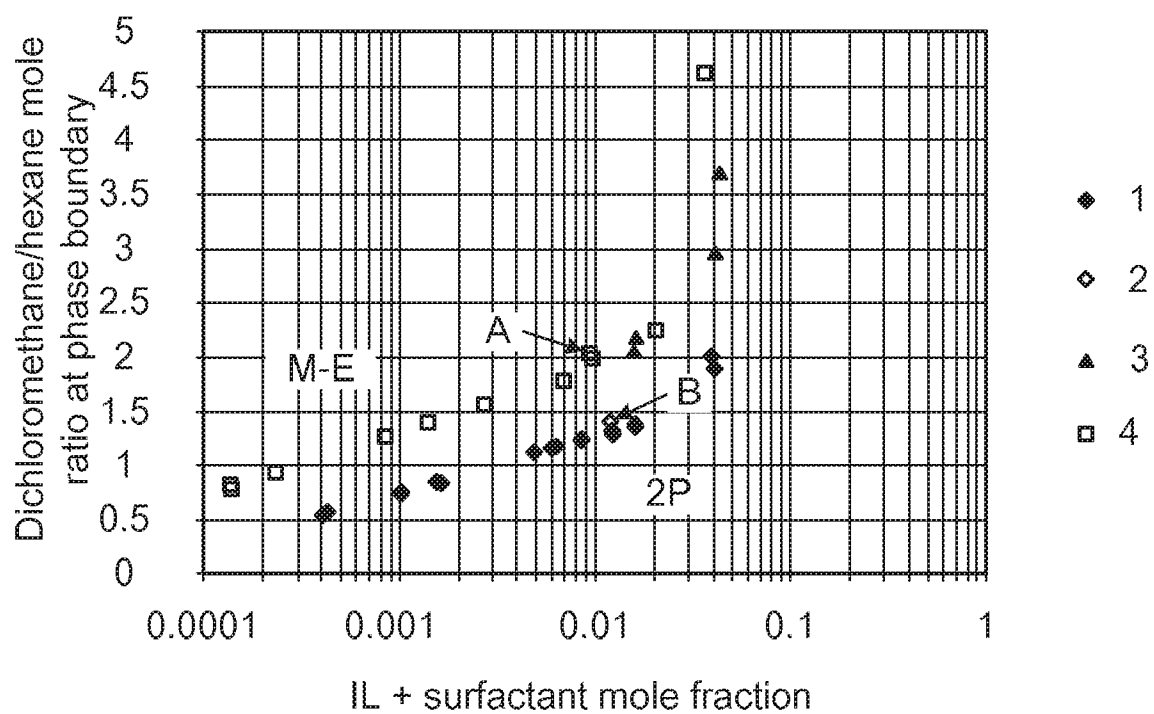


FIG.5

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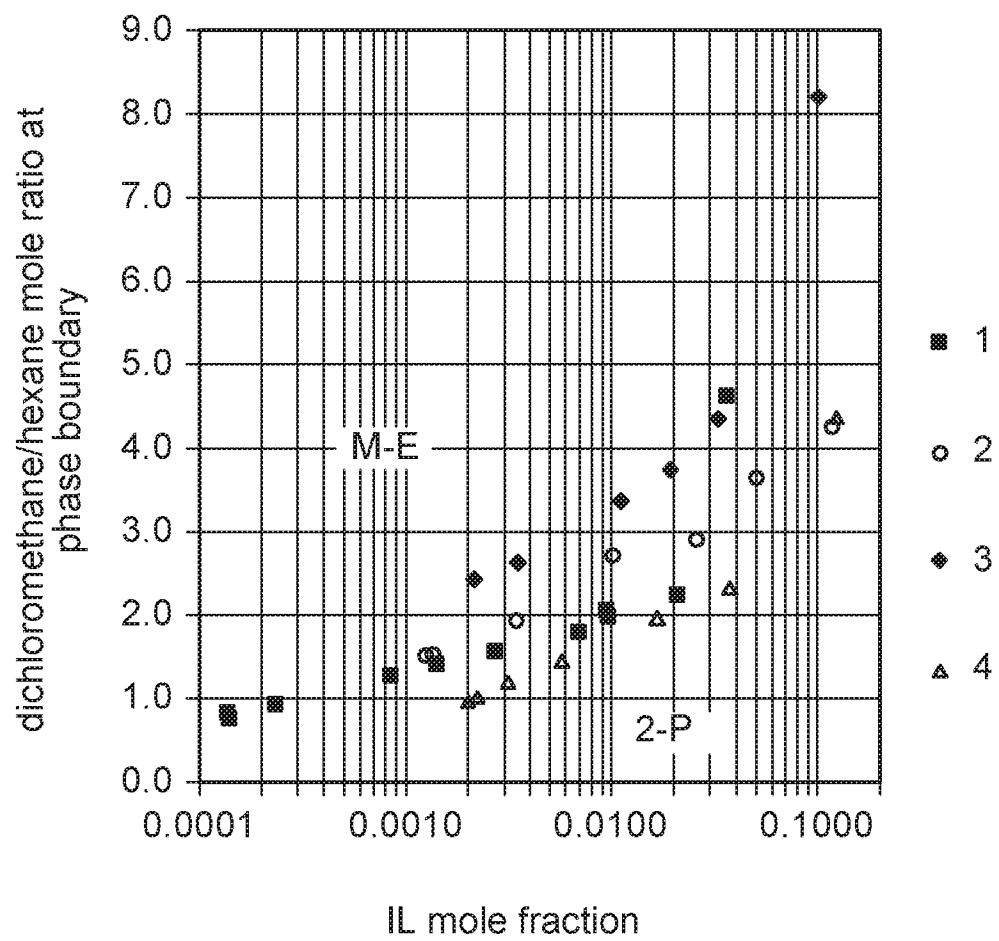


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2016/025425

A. CLASSIFICATION OF SUBJECT MATTER				
<i>C10G 21/12 (2006.01)</i> <i>C07C 2/58 (2006.01)</i> <i>C10G 50/00 (2006.01)</i> <i>C10L 1/08 (2006.01)</i> <i>B01F 3/08 (2006.01)</i>				
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)				
C10G 21/12, 21/06, 50/00, C07C 2/58, 2/56, C10L 1/08, 1/04, 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 7553406 B2 (MERCK PATENT GMBH) 30.06.2009	1-10		
A	US 2012/0121485 A1 (ROBIN DON ROGERS et al) 17.05.2012	1-10		
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.				
<table border="0"> <tr> <td style="vertical-align: top;"> * Special categories of cited documents: “A” document defining the general state of the art which is not considered to be of particular relevance “E” earlier document but published on or after the international filing date “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) “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 </td> <td style="vertical-align: top;"> “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 “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 “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 “&” document member of the same patent family </td> </tr> </table>			* Special categories of cited documents: “A” document defining the general state of the art which is not considered to be of particular relevance “E” earlier document but published on or after the international filing date “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) “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	“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 “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 “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 “&” document member of the same patent family
* Special categories of cited documents: “A” document defining the general state of the art which is not considered to be of particular relevance “E” earlier document but published on or after the international filing date “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) “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	“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 “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 “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 “&” document member of the same patent family			
Date of the actual completion of the international search		Date of mailing of the international search report		
16 June 2016 (16.06.2016)		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 T. Krivoruchko Telephone No. (495) 531-64-81		