



(51) International Patent Classification:

B01J 31/22 (2006.01) *B01J 31/02* (2006.01)
B01J 31/18 (2006.01) *B01J 35/12* (2006.01)

(21) International Application Number:

PCT/US2016/025422

(22) International Filing Date:

31 March 2016 (31.03.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/141,076 31 March 2015 (31.03.2015) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,

[Continued on next page]

(54) Title: HEAT EXCHANGER FOR USE IN ALKYLATION PROCESS USING HALOMETALLATE IONIC LIQUID MICRO-EMULSIONS

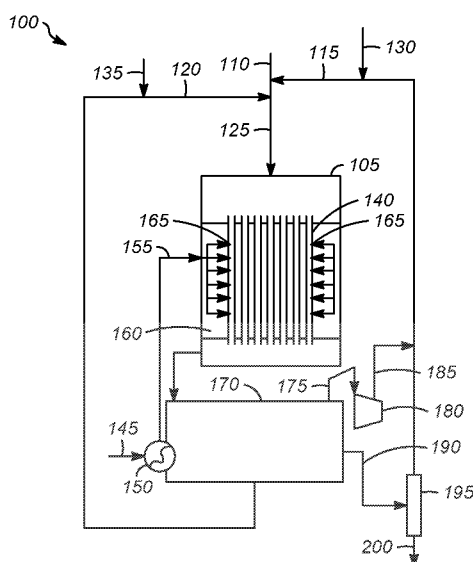


FIG. 1

(57) Abstract: An ionic liquid reaction zone and an alkylation process utilizing the ionic liquid reaction zone are described. The reaction zone comprises at least one shell and tube heat exchanger bundle. The heat exchanger bundle has a shell side and a tube side, and it has an isoparaffin inlet, an olefin inlet, and a product outlet. The tube side has at least one tube. Each tube has an inlet at one end and an outlet at the opposite end. There are at least two inlets along the length of the at least one tube. The olefin inlet is in fluid communication with the at least two inlets along the length of the at least one tube.

WO 2016/161204 A1



SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, **Published:**
GW, KM, ML, MR, NE, SN, TD, TG).

— *with international search report (Art. 21(3))*

HEAT EXCHANGER FOR USE IN ALKYLATION PROCESS USING HALOMETALLATE IONIC LIQUID MICRO-EMULSIONS

This application claims the benefit of US Provisional Application Serial No.
5 62/141076, entitled heat Exchanger for Use in Alkylation Process Using Halometallate Ionic
Liquid Micro-Emulsions, filed March 31, 2015, which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

In liquid-liquid reactions, an intrinsic tradeoff exists between reactivity and
10 post-reaction separation. High interfacial surface area between two liquid phases is needed to
achieve high activity. As an example, for motor fuel alkylation using ionic liquid catalysts,
large ionic liquid droplets implies low surface area, which leads to slow mass transfer of
olefin and isobutane from the bulk hydrocarbon phase to the ionic liquid droplets, and a mass
transfer-limited reaction of olefin inside the ionic liquid droplets. Mass transfer limitations
15 also lead to slow product mass transfer out of the ionic liquid droplets back to the
hydrocarbon phase and to product degradation, hence to low C₈ alkylate selectivities.

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

25 The high activity of ionic liquids used for motor fuel alkylation and related
processes allows for the use of relatively low ionic liquid volume fractions compared to the
high acid volume fractions used in HF or H₂SO₄ processes. However, even at low ratios of
ionic liquid catalyst to hydrocarbon, the loss rates of ionic liquid due to inefficient separation
and deactivation may introduce a significant cost in ionic liquid catalyst make-up.

30 Alkylation is an exothermic reaction, so heat removal is necessary in an
alkylation process. Furthermore, the octane of the resulting product is generally higher when
the reaction is completed at lower temperatures. One method for removing heat from an

alkylation reaction, which is currently practiced in some sulfuric acid units, is vaporization of isobutane in the reactor. This method has the advantage of avoiding internal heat exchangers which may foul with ionic liquid. However, halometallate ionic liquids often utilize HCl as a catalyst promoter, so vaporization of isobutane results in vaporization of HCl as well. The HCl then needs to be compressed with the isobutane and recycled (requiring a corrosion resistant compressor) or replaced with makeup HCl.

Alternative methods for generating liquid-liquid mixtures which allow both efficient reaction, easy separation after the reaction is over, and effective heat removal, are needed for alkylation and for other liquid-liquid reactions.

SUMMARY OF THE INVENTION

One aspect of the invention is an ionic liquid reaction zone. In one embodiment, the reaction zone comprises at least one shell and tube heat exchanger bundle. The heat exchanger bundle has a shell side and a tube side, and it has an isoparaffin inlet, an olefin inlet, and a product outlet. The tube side has at least one tube. Each tube has an inlet at one end and an outlet at the opposite end. There are at least two inlets along the length of the at least one tube. The olefin inlet is in fluid communication with the at least two inlets along the length of the at least one tube.

Another aspect of the invention is an alkylation process. In one embodiment, the process includes forming a micro-emulsion by contacting an ionic liquid, a co-solvent, an isoparaffin, an optional surfactant, and an optional catalyst promoter. The micro-emulsion comprises a hydrocarbon component comprising the isoparaffin and an ionic liquid component comprising the ionic liquid. The ionic liquid comprises a halometallate anion and a cation. The isoparaffin has from 4 to 10 carbon atoms. The co-solvent has a polarity greater than a polarity of the isoparaffin. The ionic liquid being present in an amount of about 0.05 wt% to about 40 wt% of the micro-emulsion. An olefin having from 3 to 8 carbon atoms is passed to an alkylation reaction zone containing the micro-emulsion. The alkylation reaction zone is operated at alkylation reaction conditions to react the olefin and the isoparaffin to generate a reaction mixture comprising an alkylate. At least one of the ionic liquid component, the micro-emulsion, the hydrocarbon component, and the reaction mixture are cooled by transferring heat to the co-solvent. The alkylate is separated from the ionic liquid component. The alkylation reaction zone comprises at least one shell and tube heat exchanger bundle as described above.

BRIEF DESCRIPTION OF THE DRAWINGS

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

Fig. 2 is a graph showing the volume normalized particle size distribution of a composition containing reverse micelles made with an additional surfactant.

5 Fig. 3 is a graph showing the volume normalized particle size distribution of a composition containing reverse micelles made without an additional surfactant.

Fig. 4 is a phase diagram showing the dichloromethane/hexane mole ratio as a function of total ionic liquid plus surfactant mole fraction.

10 Fig. 5 is a phase diagram showing the dichloromethane/hexane mole ratio as a function of the ionic liquid mole fraction for various ionic liquids.

DETAILED DESCRIPTION OF THE INVENTION

Conventional liquid-liquid reactions, including motor fuel alkylation using ionic liquids, often use high shear to generate droplets in a two-phase mixture. In these bi-phasic reactions, catalyst solubility in the hydrocarbon phase is often negligible, and the reaction occurs in the surface layer of the catalyst phase. Small droplet size thus allows improved mass transfer by increasing the surface to volume ratio of the catalyst. This requires the input of energy into the mixture, which is stored as surface energy in the droplets. The surface energy is dissipated as droplets coalesce to form larger droplets either in the reactor/mixer or during gravity settling. However, in some cases, the smallest droplets do not easily separate due to their low terminal settling velocities which are insignificant compared to Brownian motion. Incomplete separation leads to costly losses of ionic liquid.

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

Reverse micelles are small structures containing an amphiphile, which allows for dispersion of a polar substance in a less-polar liquid. Such micro-emulsions are well known. Commonly, a micro-emulsion containing reverse micelles contains small structures on the order of one to tens of nanometers which consist of a water core surrounded by a surfactant in an organic solvent. Mixtures containing ionic liquid reverse micelles have been

made. See, for example, Table 5 of Correa et al., *Nonaqueous Polar Solvents in Reverse Micelle Systems*, Chem. Rev. 2012, vol. 112, p. 4569–4602, which summarizes this work. Previous examples of ionic liquid reverse micelles generally contain a surfactant in addition to the ionic liquid. Furthermore, the prior art does not address the use of halometallate ionic liquids, which are often used in their Lewis acidic form. Such ionic liquids are very useful for catalytic applications including motor fuel alkylation, 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.

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

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

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

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

The surface area to volume ratio of the micelles, reverse micelles, or bi-continuous structures in the micro-emulsion is much higher than the surface area to volume ratio of ionic liquid droplets generated by shear mixing alone. The higher surface area to volume ratio may also meet the need to decrease catalyst inventory. In some cases, micelles, reverse micelles, or bi-continuous structures have volume normalized mean diameter as small as about 3 nm and contain surface areas exceeding 800 m²/gram of ionic liquid catalyst. Surface areas of 100-900 m²/gram of ionic liquid are typical for reverse micelles with an average size of 3-20 nm in diameter. Yet with conventional high shear mixing, a typical ionic liquid droplet size distribution may have a Sauter mean diameter of 55 microns which corresponds to a surface area of about 0.047 m²/gram of ionic liquid. Thus, significantly less ionic liquid needs to be used in a micro-emulsion to provide the same amount of surface area as in conventional ionic liquid systems. The amount of ionic liquid can be low (e.g., about 0.5% by volume) compared to traditional ionic liquid alkylation reactions (5-10% by volume). The amount of ionic liquid can be adjusted if it is accompanied by a change in the amount of co-solvent in order to stabilize the micro-emulsion or otherwise prevent a second liquid phase from forming, or if higher activity is desired.

In addition to advantages for reactivity, the nature of the micro-emulsion may allow catalyst recovery without the specialized equipment typically used in conventional ionic liquid processes. To recover the catalyst, the micro-emulsion is broken by changing the reaction mixture composition such that the micro-emulsion is no longer thermodynamically stable. This can be done by any suitable method, including, but not limited to, removing a portion of the polar co-solvent (for example, by vaporization), increasing the amount of the hydrocarbon (such as isoparaffin for alkylation), increasing the amount of product (such as

alkylate), adding an additional liquid having a polarity less than the polarity of the co-solvent (including an inert or semi-inert hydrocarbon, such as propane), adding ionic liquid, or combinations thereof. Once the micro-emulsion is no longer stable, a second phase of ionic liquid is formed which may be settled by gravity. Other separation process could be used including, but not limited to, sonication, electrostatic precipitation, filtration, adsorption, centrifugal separation, distillation, vaporization, or combinations thereof. These separation processes could be used in addition to gravity separation, or in place of it.

In this invention, the reaction zone a part of a shell and tube heat exchanger, comprising at least one shell and tube bundle. Each shell and tube bundle comprises at least one tube. The reaction zone is either the tube side or the shell side of the heat exchanger. On the other side of the heat exchanger, olefin reactant is fed. The heat exchanger tubes contain at holes through which the olefin enters the reaction zone.

In this process the reaction is operated in plug-flow, with olefin reactant entering the reaction zone in many places along its length. This has the advantages of eliminating back-mixing which leads to undesired reaction of primary alkylate products, as well as preventing high olefin concentration at the reactor inlet that occurs in other alkylation processes. High olefin concentration typically leads to low reaction selectivity to the desired primary alkylation products (i.e., product containing 8 carbons when the reactants are isobutane and butenes). Not wanting to be bound by theory, selectivity to primary alkylation products is higher when olefin concentration is lower because the alkylation reaction is first-order in olefin concentration and competing (and typically undesired) oligomerization reactions have reaction orders that are greater than one in olefin. The use of a micro-emulsion composition is particularly suited for this reactor configuration because in contrast to many other alkylation processes, the reaction occurs in one liquid phase, so mixing is not necessary to shear droplets as it is in other processes. Thus, the reaction can occur in a plug-flow type reactor, such as the tubes or shell of a heat exchanger. Furthermore, fouling of the heat exchanger with ionic liquid is less likely to occur using a micro-emulsion, because ionic liquid is not a separate phase which may adhere to heat exchange surfaces.

In motor fuel alkylation, an isoparaffin having from 4 to 10 carbon atoms is reacted with an olefin having from 2 to 8 carbon atoms, or 3 to 5 carbon atoms, to form an alkylate. The reaction takes place using a micro-emulsion comprising an ionic liquid component comprising ionic liquid and a hydrocarbon component comprising a hydrocarbon. The ionic liquid comprises a halometallate anion and a cation. There is a co-solvent which 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.

In some embodiments, the co-solvent is used both to stabilize micro-emulsion and as a refrigerant to remove heat from the reaction. Heat is removed by evaporation of the refrigerant. In the process, the composition of the mixture changes such that micro-emulsion is broken and the ionic liquid forms a second phase which can be recovered by settling.

For an isobutane alkylation reaction, isobutane typically comprises a majority of the hydrocarbon, and the micro-emulsion is generated by combining ionic liquid, isobutane, and co-solvent/refrigerant. The co-solvent/refrigerant can be a halocarbon (for instance dichloromethane, chloromethane, trifluoromethane, fluoromethane, or difluoromethane). Alternatively, other co-solvent/refrigerants may be used in place of a halocarbon, so long as they are polar (to allow the micro-emulsion to form). In most embodiments, the co-solvent/refrigerant has a boiling point that is less than the boiling point of isobutane (-13 °C at 1 atm (101 kPa)), such that isobutane need not be vaporized in order to remove heat. However, a co-solvent/refrigerant with boiling point lower than isobutane is not necessary. For instance, in some embodiments isobutane is not in as large an excess as it is in traditional alkylation, and vaporization of the refrigerant takes place after most of the isobutane has reacted. In other embodiments, the co-solvent/refrigerant has a higher boiling point than isobutane and isobutane is separated prior to vaporization of the co-solvent/refrigerant or it is vaporized along with the co-solvent/refrigerant. By co-solvent/refrigerant we mean that the material acts as both a co-solvent and a refrigerant.

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. 62/141056, entitled HYDROCARBON PROCESSES USING HALOMETALLATE IONIC LIQUID MICRO-EMULSIONS, (Attorney Docket No. H0047293-8250) filed March 31, 2015, and US Application Serial No. 62/141070, entitled HYDROCARBON PROCESSES USING HALOMETALLATE IONIC LIQUID MICRO-EMULSIONS, (Attorney Docket No. H0047294-8250) filed March 31, 2015, each of which is incorporated herein by reference.

The micro-emulsion is introduced into the reaction zone (or is formed there), along with the other reaction components. For example, in an alkylation process, a micro-emulsion is formed from an isoparaffin, a co-solvent, an ionic liquid, and optionally a

surfactant and/or a catalyst promoter. An olefin is introduced into the reaction zone where it reacts with the isoparaffin to form alkylate.

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

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

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

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

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

Typical alkylation reaction conditions include a temperature in the range of about -100°C to about 100°C, or about -50°C to about 70°C, or about -10°C to about 70°C, or about 0°C to about 70°C, or about 0°C to about 60°C, or about 0°C to about 50°C, or about 20°C to about 60°C, or about 20°C to about 50°C. It is desirable that the ionic liquid, co-solvent, and isoparaffin maintain a liquid rather than vapor state through the operating temperature range.

The pressure is typically in the range of 0.001 MPa to about 8.0 MPa, or about 0.002 MPa to about 5 MPa. The pressure is preferably sufficient to keep the reactants in the

liquid phase. Vacuum pressures may be desirable if vaporization of the co-solvent is used to remove heat and the process is at low temperature.

The residence time of the reactants in the reaction zone is in the range of a few seconds to several hours, or about 0.5 min to about 4 hours, or about 2 min to about 120 min
5 or about 2 min to about 60 min. If shorter residence time is desired, more ionic liquid can be used.

The overall molar ratio between the isoparaffin and olefin feeds is in the range of about 1:1 to about 100:1, or about 5:1 to about 100:1, or about 5:1 to about 70:1, or about 5:1 to about 25:1, or about 5:1 to about 20:1, or about 5:1 to about 15:1. The overall molar
10 ratio is defined as the ratio of the total amount of isoparaffins entering the reaction zone or present in the reaction zone at the start of the reaction to the total amount of olefins entering the reaction zone or present in the reaction zone at the start of the reaction. Both isoparaffins and olefins may enter the reaction zone in one location or several locations, and may be present in the reaction zone at the start of the reaction.

Fig. 1 is an illustration of an alkylation process 100 in which the reaction takes place in a heat exchanger 105. In some embodiments, the heat exchanger 105 is shell and tube heat exchanger. In some embodiments, the isoparaffin is isobutane, and HCl is used as a catalyst promoter. Fresh isobutane feed 110 can be combined with the recycle isobutane stream 115 containing co-solvent/refrigerant and HCl catalyst promoter and recycle ionic
15 liquid stream 120 to form feed stream 125. Fresh co-solvent/refrigerant and/or HCl catalyst promoter 130 and fresh ionic liquid 135 can be added as needed.

In one embodiment, the isoparaffin feed inlet to the shell and tube heat exchanger is connected to the inlet to the tubes. The feed stream 125 enters the shell and tube heat exchanger 105 and flows into the tube side 140 of the heat exchanger 105 where the
20 reaction takes place.

Olefin feed 145 flows through heat exchanger 150. The cooled olefin feed 155 flows into the shell side 160 and flows from the outside of the tubes through inlets 165 along the length of the tubes to the inside of the tubes. To maintain liquid phases on both sides of the heat exchanger 105, the liquid level on the shell side 160 of the heat exchanger
25 would be maintained close to or above the top of the heat exchanger tubes 140.

The reaction mixture then flows to separation zone 170. The pressure is reduced causing the co-solvent/refrigerant to vaporize, cooling the reaction mixture in the separation zone 170. The cooled reaction mixture exchanges heat with the olefin feed 145 in heat exchanger 150.

The vaporization of the co-solvent/refrigerant changes the composition of the reaction mixture, destroying the micro-emulsion which causes separation into an ionic liquid phase and a hydrocarbon phase in the separation zone 170. Other methods of changing the composition of the reaction mixture could be used as discussed above.

5 The recycle ionic liquid stream 120 can be mixed with fresh ionic liquid 135 and recycled to the beginning of the process.

The vaporized co-solvent/refrigerant 175 containing the HCl catalyst promoter is compressed or condensed in a compressor or condenser 180. The compressed/condensed stream 185 is mixed with the recycle isobutane stream 115.

10 The hydrocarbon stream 190 is sent to a product separation zone 195 where the isoparaffin is separated from the alkylate product. The isoparaffin forms recycle isobutane stream 115 while the alkylate product 200 is recovered.

Alternatively, the olefin inlet can be connected to the inlets of the tubes. In this case, the feed stream 125 flows into the shell side 160 where the reaction takes place.
15 The cooled olefin feed 155 would flow into the tube side 140 and flow from the inside of the tubes to the shell side 160 through the inlets 165. The reaction mixture would then flow to the separation zone 170.

The reaction rate and selectivity may be changed by changing the amounts of the components in the micro-emulsion. For example, if the co-solvent is more viscous than
20 the isoparaffin, increasing the ratio of isoparaffin to co-solvent would decrease the viscosity of the hydrocarbon component, which would result in faster mass transfer. Higher isoparaffin to co-solvent ratio would also increase the concentration of isoparaffin. With higher concentration of isoparaffin, selectivity to the desired alkylate product rather than oligomer would improve. Adding a second co-solvent with a lower viscosity or using a
25 different co-solvent with a lower viscosity may result in a faster reaction if the reaction is mass-transfer limited. Decreasing the size of the micelles, reverse micelles, or bi-continuous structures in the micro-emulsion may result in faster reaction. Decreasing the size of micelles, reverse micelles, or 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),
30 or mixing with higher shear to improve contacting.

Although the micro-emulsion is generated due to their 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.

The amount of olefin reacted in moles olefin reacted per mole of ionic liquid is calculated by dividing the total amount of olefin converted in the reaction zone by the total amount of ionic liquid in the reaction zone (or which flowed through the reaction zone). In batch or semi-batch reactions, the amount of moles of olefin converted per mole of ionic liquid is an indication of how much olefin can be converted before catalyst deactivation.

The rate of olefin reaction is calculated by dividing the total amount of olefin converted in the reaction zone per unit time (in hours) divided by the amount of ionic liquid in the reaction zone. In some embodiments, the rate of olefin reaction is greater than about 20 mole olefin/mole ionic liquid/hour, or greater than about 30 mole olefin/mole ionic liquid/hour, or greater than about 40 mole olefin/mole ionic liquid/hour, or greater than about 50 mole olefin/mole ionic liquid/hour, or greater than about 60 mole olefin/mole ionic liquid/hour, or about 20 mole olefin/mole ionic liquid/hour to about 300 mole olefin/mole ionic liquid/hour, or about 20 mole olefin/mole ionic liquid/hour to about 200 mole olefin/mole ionic liquid/hour, or about 20 mole olefin/mole ionic liquid/hour to about 100 mole olefin/mole ionic liquid/hour, or about 20 mole olefin/mole ionic liquid/hour to about 80 mole olefin/mole ionic liquid/hour, or about 30 mole olefin/mole ionic liquid/hour to about 70 mole olefin/mole ionic liquid/hour.

In some embodiments, the selectivity to primary alkylation products is greater than about 50 wt%. Here, primary alkylation products are defined as products containing the number of carbon atoms equal to the sum of the number of carbon atoms in one isoparaffin reactant plus the number of carbon atoms in one olefin reactant. The selectivity to primary alkylation products is defined as the amount of primary alkylation products in weight percent, divided by the amount of products containing a number of carbon atoms greater than the number of carbon atoms in one isoparaffin reactant in weight percent. For example, for the alkylation of isobutane and butene, the selectivity for C₈ hydrocarbons could be greater than about 50 wt% of the C₅₊ hydrocarbons. Without being bound by theory, selectivity to C₈ hydrocarbons is higher, and selectivity to C₅-C₇ hydrocarbons is lower if the olefin feed rate is slower, if the isoparaffin/olefin ratio is higher, if residence time is longer, if temperature is lower, or if a less hydrophobic ionic liquid is used (e.g., tributylmethylphosphonium instead

of tributylhexylphosphonium). C₈ selectivity is probably higher if less co-solvent and more isoparaffin is used. Selectivity may be higher if a less viscous co-solvent is used due to improved mass transfer. Reaction may be faster (conversion is higher for similar conditions) if more promoter or ionic liquid is used, if the co-solvent is less viscous, or if more shear is imparted.

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

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

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, 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, as shown in Figs. 2-3. When an added surfactant is present, reverse micelles may be larger. In some embodiments, reverse 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 and allow larger reverse micelles to be thermodynamically stable. In some embodiments, when an additional 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 100 nanometers, or about 5 nanometers to about 90 nanometers, or about 5 nanometers to about 80 nanometers, or 5

about 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.

5 The presence of added surfactant can be used to help control the size of the reverse micelles or micelles. This was confirmed as described below in example 2 using dynamic light scattering (DLS) for two compositions, one without and one with added surfactant. With added surfactant, the volume averaged particle diameter was larger (12 ± 2 nm) than without added surfactant (3 ± 2 nm).

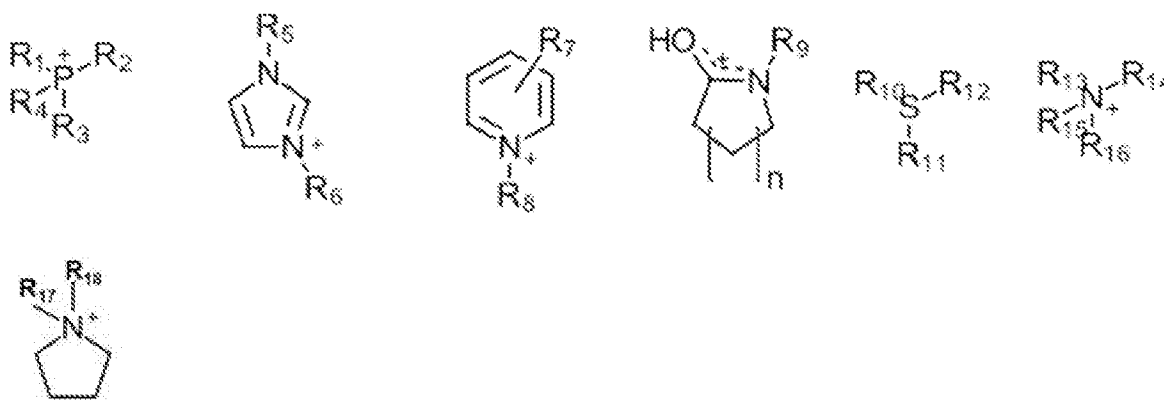
10 In some embodiments, the size distribution of the reverse micelles or micelles may be changed by changing the co-solvent. Not wishing to be bound by theory, using a more polar co-solvent may lead to larger reverse micelles due to the higher solubility of the co-solvent in the reverse micelles and due to the higher surface tension at the interface between the reverse micelles and the hydrocarbon component. The size of micelles may
15 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.

 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
20 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
25 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
30 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, dialkyl 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.

20

In some embodiments, the anion is a halometallate or anion with acidic character, and in most embodiments with Lewis acidic character. Halometallate anions may contain a metal selected from Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, In, Sn, Sb, La, Ce, Hf, Ta, W, or combinations thereof, and a halide selected from F, Cl, Br, I, or combination thereof. The halometallate may be a simple halometallate or a composite in which more than one metal is used. For catalytic applications requiring Lewis acidity (such as alkylation, isomerization, and disproportionation), the ratio of moles of halide to moles of

25

metal in the anion is less than 4. The anion may be formally an anion, or it may be an anion associated with a metal halide. For instance, the anion may be AlCl_4^- associated with AlCl_3 . BF_4^- activated with BF_3 or a Brønsted acid may also be suitable. In some embodiments, such as those where the ionic liquid comprises an imidazolium based cation, the ratio of moles of halide to moles of metal in the anion must be less than 4 in order for a micro-emulsion to form.

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

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

In order to form a micro-emulsion containing reverse micelles, there must be at least some solubility of the amphiphile in both the hydrocarbon component and the ionic liquid component of the micro-emulsion. Here, at least some solubility of the amphiphile in the hydrocarbon component is defined as the amphiphile being soluble in an amount of at least 0.5 mole ppm in the oil phase. If the cation and anion are both not amphiphilic, an additional surfactant may be needed to act as the amphiphile. The solubility of the ionic liquid or 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 (for instance, in motor fuel alkylation where the medium usually contains isobutane), a co-solvent is used to modify the polarity of the hydrocarbon. The co-solvent is more polar than the hydrocarbon. The co-solvent should be compatible with the ionic liquid, and it should be miscible with the hydrocarbon. Here, miscible with the hydrocarbon means that the co-solvent is soluble in an

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

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

In some embodiments, the amount of co-solvent is typically in the range of about 30 wt% to about 80 wt% of the micro-emulsion. When the process is an alkylation process, it is desirable to include as much hydrocarbon (i.e., isoparaffin, olefin, and alkylate) 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 mixture of isoparaffin, olefin, and alkylate). 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, surfactant, catalyst promoter, and co-solvent. For example, Fig. 4 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 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, more co-solvent is desired such that the amount of hydrocarbon is less than 90% of the saturation limit of hydrocarbon. Specifically, if vaporization of the co-solvent is used to remove the heat of reaction, sufficient co-solvent must be present in the reactor or separator such that there is sufficient co-solvent to vaporize.

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, or 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). 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
5 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
10 the ionic liquid is tributylhexylphosphonium heptachloroaluminate, the surfactant could be tributylhexylphosphonium dodecyl sulfonate. As demonstrated below, the use of a surfactant allows use of less co-solvent, and in some cases, it results in larger reverse micelles.

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

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

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

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

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

The amounts of co-solvent and surfactant needed to stabilize the micro-emulsion depend on the amount of ionic liquid and hydrocarbon component present. When

surfactant is included in the micro-emulsion, generally less co-solvent is needed. When more ionic liquid is included in the micro-emulsion, generally more surfactant or more co-solvent is needed.

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

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

The materials can be combined in different ways. For example, the hydrocarbon and co-solvent can be combined first, and then combined with ionic liquid. Alternatively, the ionic liquid and the co-solvent can be combined first, and then combined with the hydrocarbon. The optional surfactant and optional catalyst promoter can be added at different times and to different combinations of the materials. For example, the catalyst promoter and optional surfactant can be added to the hydrocarbon, the co-solvent, the ionic liquid, or any combinations of these material. 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.

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 component comprises the hydrocarbon and the co-solvent. If a catalyst promoter is included, it can be added to the ionic liquid component, the hydrocarbon, the co-solvent, or the micro-emulsion.

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

Examples

Example 1

In the examples below, 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. 4.

The micro-emulsion region (M-E on Fig. 4) is above and to left of the phase boundary while the two phase region (2-P on Fig. 4) 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.

Example 2

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 1. 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. 4. Volume normalized particle size distributions for five repeat measurements (1-5) are shown in Fig. 2.

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. 7. Volume normalized particle size distributions for four repeat measurements (1-4) are shown in Fig 3. The size of these particles is more than three orders of magnitude smaller than droplets generated by impellers.

Example 3

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. 5. 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 2.

Table 2: 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_2Cl_7	21%	64.94%	14.29%	3.65E-02	4.61
	6.3%	61.99%	31.73%	9.60E-03	1.98
	6.2%	62.68%	31.16%	9.41E-03	2.04
	12.7%	60.13%	27.22%	2.05E-02	2.24
	4.6%	60.83%	34.56%	6.95E-03	1.79
	1.8%	59.49%	38.68%	2.70E-03	1.56
	1.0%	57.32%	41.72%	1.41E-03	1.39
	1.0%	57.46%	41.58%	1.41E-03	1.40

	0.6%	55.09%	44.33%	8.50E-04	1.26
	0.578%	55.50%	43.92%	8.42E-04	1.28
	0.159%	47.87%	51.97%	2.31E-04	0.93
	0.096%	43.45%	56.45%	1.39E-04	0.78
	0.093%	44.90%	55.01%	1.36E-04	0.83
TBMP-Al ₂ Cl ₇	45%	44.53%	10.63%	1.18E-01	4.25
	24%	59.09%	16.42%	5.05E-02	3.65
	14%	63.73%	22.34%	2.59E-02	2.90
	6%	68.44%	25.67%	1.02E-02	2.71
	2.0%	64.20%	33.75%	3.43E-03	1.93
	0.8%	59.67%	39.51%	1.36E-03	1.53
	0.8%	59.49%	39.76%	1.24E-03	1.52
BMIm-Al ₂ Cl ₇	36.9%	56.19%	6.95%	1.01E-01	8.21
	14.9%	68.99%	16.12%	3.27E-02	4.34
	9.2%	71.42%	19.38%	1.92E-02	3.74
	5.5%	72.58%	21.91%	1.11E-02	3.36
	5.5%	72.58%	21.91%	1.11E-02	3.36
	1.8%	70.85%	27.36%	3.49E-03	2.63
	1.1%	69.70%	29.21%	2.14E-03	2.42
Caprolactamium-Al ₂ Cl ₇	40.6%	48.25%	11.19%	1.22E-01	4.38
	15.7%	58.70%	25.64%	3.66E-02	2.32
	7.5%	60.46%	32.07%	1.63E-02	1.91
	7.5%	60.46%	32.07%	1.63E-02	1.91
	2.7%	56.68%	40.60%	5.69E-03	1.42
	1.5%	53.51%	45.00%	3.08E-03	1.21
	1.1%	49.66%	49.28%	2.19E-03	1.02
	0.9%	48.32%	50.73%	1.96E-03	0.97

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

While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention. It being understood that various changes may be made in the

function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claim

SPECIFIC EMBODIMENTS

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

A first embodiment of the invention is an apparatus comprising at least one shell and tube heat exchanger bundle, the at least one heat exchanger bundle having a shell side and a tube side, the heat exchanger bundle having an isoparaffin inlet, an olefin inlet, and a product outlet; the tube side having at least one tube, each tube having an inlet at one end and an outlet at the opposite end, at least two inlets along the length of the at least one tube, the olefin inlet being in fluid communication with the at least two inlets along the length of the at least one tube. 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 a separation zone. 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 separation zone is in a separate vessel from the at least one heat exchanger bundle. 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 isoparaffin inlet is in fluid communication with the inlet of the at least one tube and the outlet of the at least one tube in fluid communication with the product outlet. 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 olefin inlet is in fluid communication with the inlet of the at least one tube and the inside of the tube. 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 there are at least two heat exchanger bundles. 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 there is an isoparaffin inlet between the at least two heat exchanger bundles.

A second embodiment of the invention is a process comprising forming a micro-emulsion comprising contacting an ionic liquid, a co-solvent, an isoparaffin, an optional surfactant, and an optional catalyst promoter to form the micro-emulsion, the micro-emulsion comprising a hydrocarbon component comprising the isoparaffin and an ionic liquid component comprising the ionic liquid, the ionic liquid comprising a halometallate anion and a cation, the isoparaffin having from 4 to 10 carbon atoms, the co-solvent having a polarity

greater than a polarity of the isoparaffin, the ionic liquid being present in an amount of about 0.05 wt% to about 40 wt% of the micro-emulsion; and passing an olefin having from 2 to 8 carbon atoms to an alkylation reaction zone containing the micro-emulsion, wherein the alkylation reaction zone is operated at alkylation reaction conditions to react the olefin and the isoparaffin to generate a reaction mixture comprising an alkylate, wherein the alkylation reaction zone comprises at least one shell and tube heat exchanger bundle, the at least one heat exchanger bundle having a shell side and a tube side, the heat exchanger bundle having an isoparaffin inlet, an olefin inlet, and a product outlet; and the tube side having at least one tube, each tube having an inlet at one end and an outlet at the opposite end, at least two inlets along the length of the at least one tube, the olefin inlet being in fluid communication with the at least two inlets along the length of the at least one tube; wherein the olefin is passed through the at least two inlets along the length of the tube, cooling at least one of the ionic liquid, the micro-emulsion, the hydrocarbon, and the reaction mixture; and separating the alkylate from the ionic liquid. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the isoparaffin inlet is in fluid communication with the inlet of the at least one tube, and wherein the micro-emulsion flows into the tube side and the olefin flows into the shell side and wherein the olefin flows from the shell side into the at least one tube through the at least two inlets along the length of the at last one tube; or wherein the olefin inlet is in fluid communication with the inlet of the at last one tube, and wherein the olefin flows into the tube side and the composition flows into the shell side and wherein the olefin flows from the tube side into the shell side through the at least two inlets along the length of the tube. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein cooling at least one of the ionic liquid, the micro-emulsion, the hydrocarbon, and the reaction mixture comprises transferring heat to the co-solvent by vaporizing the co-solvent after generating the reaction mixture. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the co-solvent is vaporized by reducing a pressure of the reaction mixture. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the co-solvent is vaporized in the alkylation reaction zone, and wherein the alkylate is separated from the ionic liquid in a separation zone located after the reaction zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the co-solvent is

vaporized in a separation zone located after the alkylation reaction zone, and wherein the alkylate is separated from the ionic liquid in the separation zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising compressing or condensing the vaporized co-solvent; recycling the compressed or condensed co-solvent to the alkylation reaction zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein separating the alkylate from the ionic liquid comprises altering a composition of the reaction mixture to destroy the micro-emulsion. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the composition of the reaction mixture is altered by at least one of removing a portion of the co-solvent, increasing an amount of alkylate, adding an additional liquid having a polarity less than the polarity of the co-solvent, increasing an amount of the isoparaffin, or increasing an amount of the ionic liquid. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising separating unreacted isoparaffin from the alkylate; recycling at least one of the unreacted isoparaffin and the ionic liquid to the alkylation reactor. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the co-solvent has a boiling point less than a boiling point of the isoparaffin. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the co-solvent has a viscosity of 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 second embodiment in this paragraph wherein the co-solvent comprises a halocarbon, a hydrohalocarbon, or combinations thereof.

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

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

What is claimed:

1. An ionic liquid reaction zone comprising:
at least one shell and tube heat exchanger bundle (105), the at least one heat exchanger bundle (105) having a shell side (160) and a tube side (140), the heat exchanger bundle (105) having an isoparaffin inlet, an olefin inlet, and a product outlet;
5 the tube side (140) having at least one tube, each tube having an inlet at one end and an outlet at the opposite end, at least two inlets along the length of the at least one tube, the olefin inlet being in fluid communication with the at least two inlets along the length of the at least one tube; and
an optionally separation zone (170).
2. The ionic liquid reaction zone of claim 1 wherein the isoparaffin inlet is in fluid communication with the inlet of the at least one tube and the outlet of the at least one tube in fluid communication with the product outlet.
3. The ionic liquid reaction zone of any one of claims 1-2 wherein the olefin inlet is in fluid communication with the inlet of the at least one tube and the inside of the tube.
4. The ionic liquid reaction zone of any one of claims 1-2 wherein there are at least two heat exchanger bundles (105) and wherein there is an isoparaffin inlet between the at least two heat exchanger bundles (105).
5. A process utilizing a micro-emulsion comprising:
forming the micro-emulsion comprising:
contacting an ionic liquid, a co-solvent, a hydrocarbon, an optional surfactant, and an optional catalyst promoter to form the micro-emulsion, the micro-emulsion
5 comprising a hydrocarbon component comprising a hydrocarbon and an ionic liquid component comprising the ionic liquid, the ionic liquid comprising a halometallate anion and a cation, the 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 micro-emulsion; and

producing a product mixture in a process zone containing the micro-emulsion,
10 the product mixture comprising a product, the process zone comprising the a tube side (140)
or the shell side (160) of the shell and tube heat exchanger (105) as in any one of claims 1-2;
cooling at least one of the ionic liquid, the micro-emulsion, the hydrocarbon,
and the product mixture by transferring heat to the co-solvent; and
separating the product from the ionic liquid component.

6. The process of claim 5 wherein the process zone is the tube side (140)
of a shell and tube heat exchanger (105) and wherein an effluent from the tube side (140)
flows into a shell side (160) of the shell and tube heat exchanger (105), and further
comprising reducing a pressure of the effluent in the shell side (160) to vaporize the co-
5 solvent; or

wherein the process zone is a shell side (160) of a shell and tube heat
exchanger (105) and wherein an effluent from the shell side (160) flows into a tube side (140)
of the shell and tube heat exchanger (105), and further comprising reducing a pressure of the
effluent in the tube side (140) to vaporize the co-solvent.

7. The process of any one of claims 5-6 wherein the isoparaffin inlet is in
fluid communication with the inlet of the at least one tube, and wherein the micro-emulsion
flows into the tube side (140) and the olefin flows into the shell side (160) and wherein the
olefin flows from the shell side (160) into the at least one tube through the at least two inlets
5 along the length of the at last one tube; or

wherein the olefin inlet is in fluid communication with the inlet of the at last
one tube, and wherein the olefin flows into the tube side (140) and the composition flows into
the shell side (160) and wherein the olefin flows from the tube side (140) into the shell side
(160) through the at least two inlets along the length of the tube.

8. The process of any one of claims 5-6 wherein cooling at least one of
the ionic liquid, the micro-emulsion, the hydrocarbon, and the reaction mixture comprises
transferring heat to the co-solvent by vaporizing the co-solvent after generating the reaction
mixture.

9. The process of claim 8 wherein the co-solvent is vaporized by reducing
a pressure of the reaction mixture.

10. The process of any one of claims 5-6 wherein separating the product from the ionic liquid component comprises altering a composition of the product mixture to destroy the micro-emulsion.

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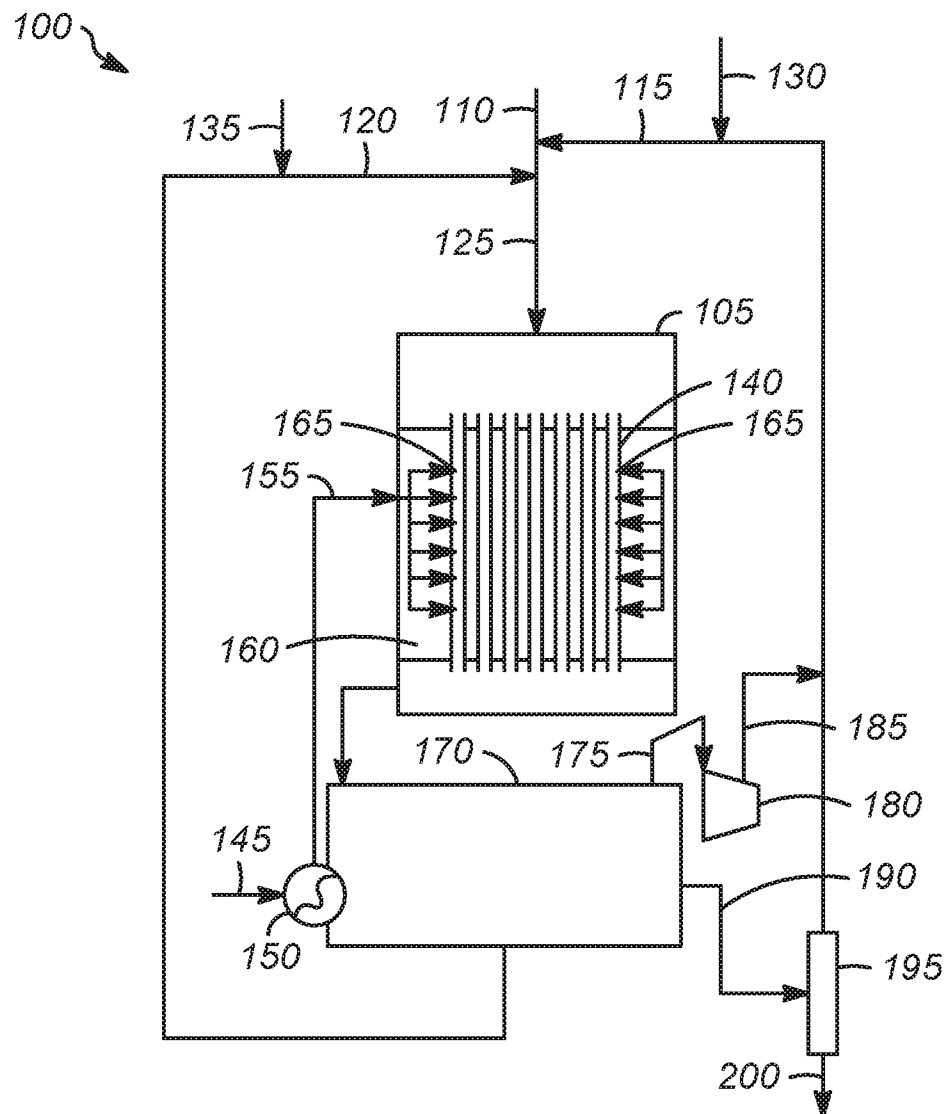


FIG. 1

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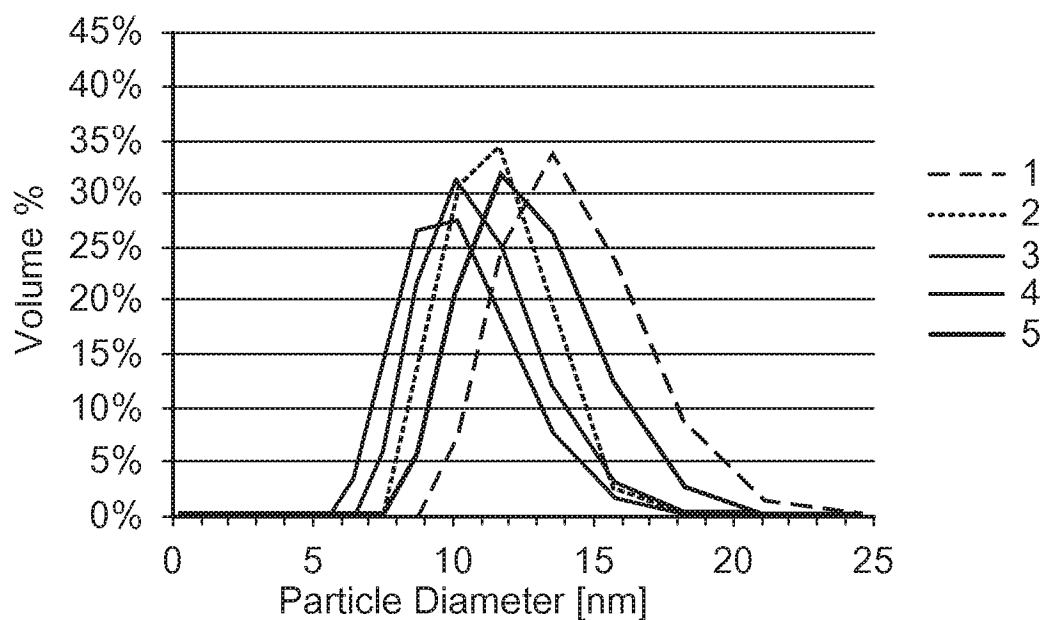


FIG. 2

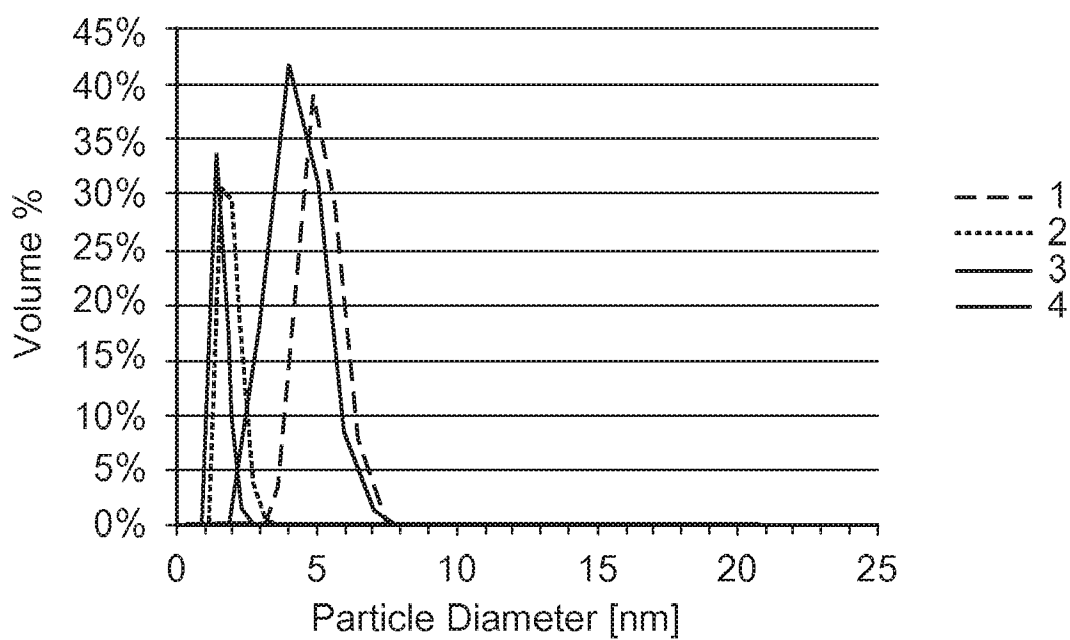


FIG. 3

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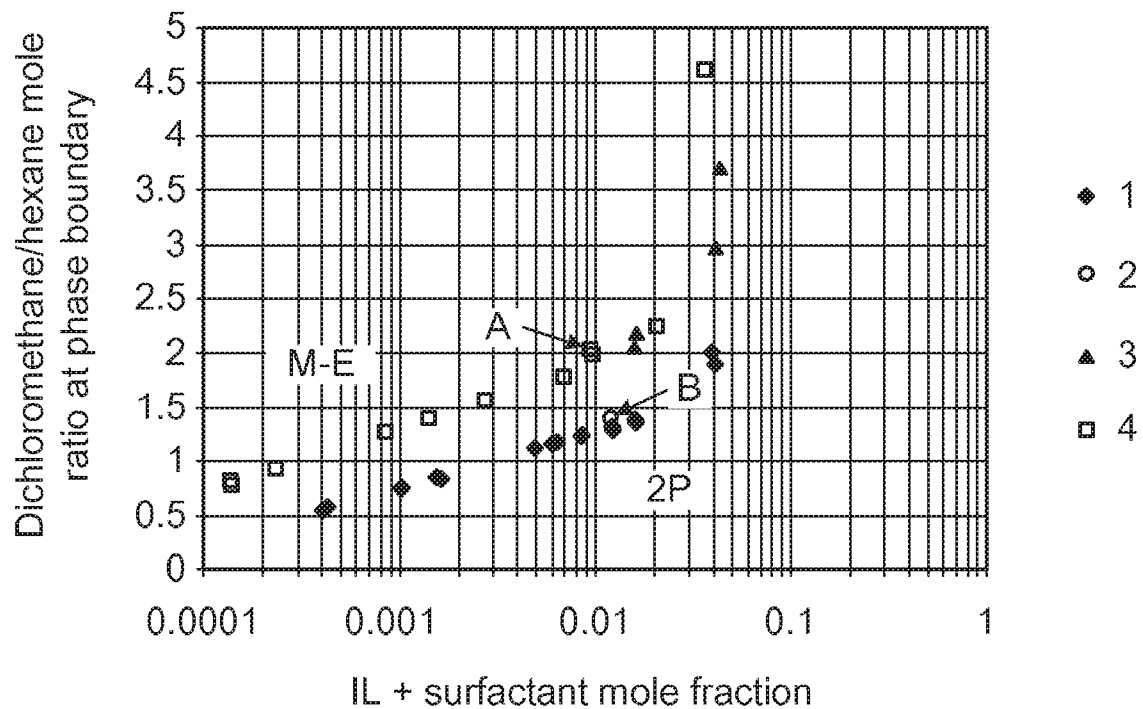


FIG. 4

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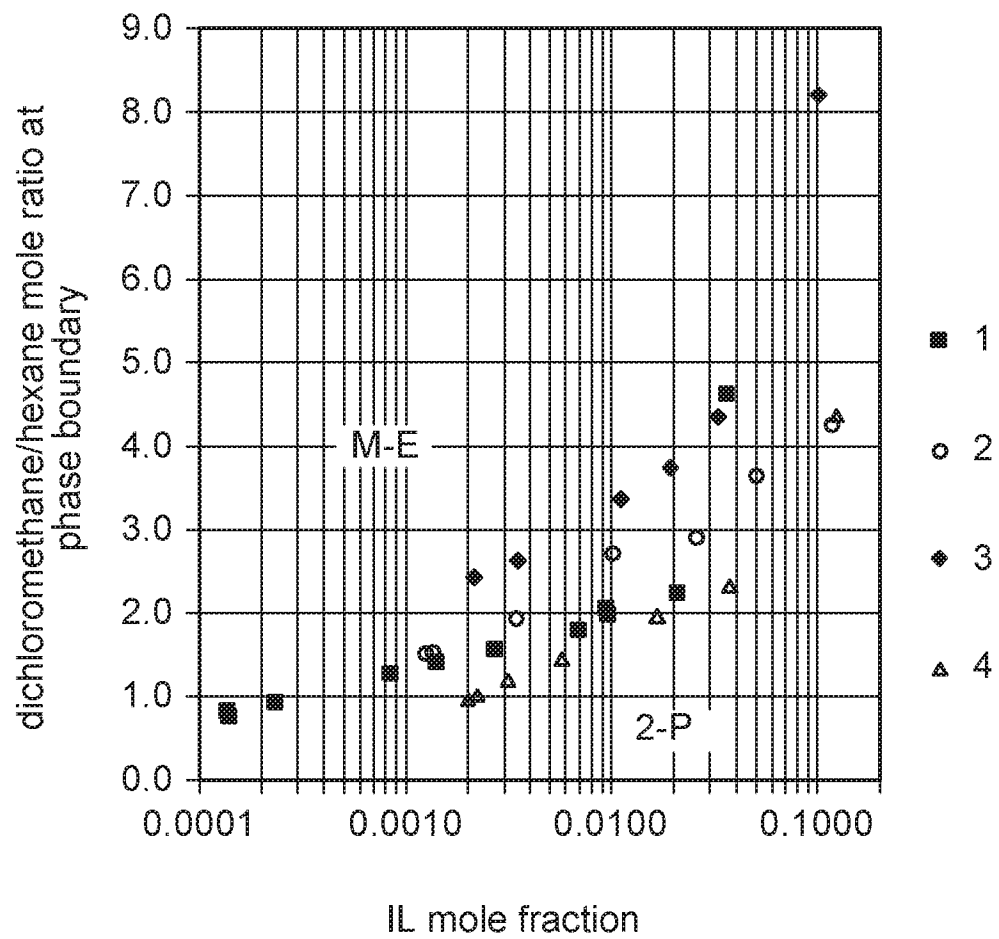


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2016/025422

A. CLASSIFICATION OF SUBJECT MATTER		
B01J 31/22 (2006.01) B01J 31/18 (2006.01) B01J 31/02 (2006.01) B01J 35/12 (2006.01) C07C 2/58 (2006.01)		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
B01J 31/22, C07C 2/58, B01J 31/18, 31/02, 35/12		
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)		
RUPAT BD, PAJ, Espacenet, USPTO DB, EAPATIS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005/0119423 A1 (LEE H. BERGMAN et al.) 02.06.2005, paragraphs 6, 9, 12, 16, 22	1-10
A	WO 2010/135064 A2 (CHEVRON U.S.A. INC. et al.) 25.11.2010	1-10
A	US 2007/0142216 A1 (CHEVRON U.S.A. INC) 21.06.2007	1-10
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "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
20 June 2016 (20.06.2016)		30 June 2016 (30.06.2016)
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37		Authorized officer A. Sedov Telephone No. (495)531-64-81