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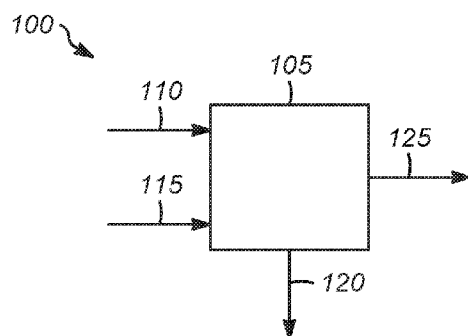


FIG. 1

(57) Abstract: A process utilizing a micro-emulsion is described. The micro-emulsion is formed by contacting an ionic liquid, a co-solvent, a hydrocarbon, an optional surfactant, and an optional catalyst promoter. The micro-emulsion comprises a hydrocarbon component, which comprises the hydrocarbon, and an ionic liquid component which comprises the ionic liquid. The ionic liquid comprises a halometallate anion and a cation. The hydrocarbon comprises an olefin, a paraffin, or both. 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. An olefin can optionally be added to an oligomerization reaction zone containing the micro-emulsion. A product mixture comprising an oligomer product is produced in the oligomerization reaction zone containing the micro-emulsion.

## OLEFIN OLIGOMERIZATION PROCESSES USING HALOMETALLATE IONIC LIQUID MICRO-EMULSIONS

This application claims the benefit of US Provisional Application Serial No.  
5 62/141056, entitled Hydrocarbon Processes Using Halometallate Ionic Liquid 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  
post-reaction separation. High interfacial surface area between two liquid phases is needed to  
10 achieve high activity. As an example, for alkylation and for oligomerization using ionic liquid  
catalysts, large ionic liquid droplets implies low surface area, which leads to slow mass transfer  
of olefin 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 also lead  
to slow product mass transfer out of the ionic liquid droplets back to the hydrocarbon phase  
15 and to low C<sub>8</sub> alkylate selectivities in motor fuel alkylation and heavier oligomer products in  
oligomerization.

High ionic liquid inventory and/or smaller ionic liquid droplets are used to  
counter the mass transfer limitations of the reaction kinetics. However, smaller droplets which  
are typically generated by shear force are also more difficult to separate than larger droplets  
20 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 oligomerization 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 H<sub>2</sub>SO<sub>4</sub> 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.

Alternative methods for generating liquid-liquid mixtures which allow both efficient reaction and easy separation after the reaction is over are needed for oligomerization processes.

#### SUMMARY OF THE INVENTION

5           One aspect of the invention is an oligomerization process. In one embodiment, the process includes forming a micro-emulsion by contacting an ionic liquid, a co-solvent, a hydrocarbon, an optional surfactant, and an optional catalyst promoter. The micro-emulsion comprises a hydrocarbon component comprising the hydrocarbon, and an ionic liquid component comprising the ionic liquid. The ionic liquid comprises a halometallate anion and  
10   a cation. The hydrocarbon comprises an olefin, a paraffin, or both. 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. An olefin can optionally be added to an oligomerization reaction zone containing the micro-emulsion. A product mixture comprising an oligomer product is produced in an oligomerization reaction zone containing the  
15   micro-emulsion.

#### BRIEF DESCRIPTION OF THE DRAWINGS

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

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

Fig. 3 is a graph showing the volume normalized particle size distribution of a  
20   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.

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

## DETAILED DESCRIPTION OF THE INVENTION

Conventional liquid-liquid reactions, including oligomerization, 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 ionic liquid 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. In order to avoid using small droplets, more ionic liquid can be used (e.g., higher ionic liquid to hydrocarbon volume ratio), but this requires significantly higher and un-utilized ionic liquid inventory, which, in addition to increasing costs, also has the potential to lead to increased rate of undesired side-reactions.

Rather than utilizing shear force to generate meta-stable droplets, in the present invention, the ionic liquid catalyst is stabilized in the form of a micro-emulsion. The micro-emulsion contains a hydrocarbon component comprising an olefin, 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 catalytic

applications including oligomerization, 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%. 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%. 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*, 14<sup>th</sup> 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 oligomerization 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.

5 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 the phase boundary in a bi-continuous micro-emulsion. Consequently, diffusion of the reactants from the bulk hydrocarbon phase into the interior of  
10 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  
15 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 m<sup>2</sup>/gram of ionic liquid catalyst. Surface areas of 100-900 m<sup>2</sup>/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  
20 ionic liquid droplet size distribution may have a Sauter mean diameter of 55 microns which corresponds to a surface area of about 0.047 m<sup>2</sup>/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 (about 5-10% by  
25 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  
30 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 olefin), increasing the amount of oligomer product, adding an additional liquid having a polarity less than the polarity of the co-solvent (including an inert or semi-inert hydrocarbon, such as adding an additional paraffin ), adding ionic liquid, or combinations thereof. Once the micro-emulsion is no longer stable, a second phase of ionic liquid is formed which may be settled by gravity. Other separation process could be used including, but not limited to, sonication, electrostatic precipitation, filtration, adsorption, centrifugal separation, distillation, vaporization, or combinations thereof. These separation processes could be used in addition to gravity separation, or in place of it.

The process can be used for a variety of hydrocarbon conversion processes, including olefin oligomerization. Olefin oligomerization involves reacting olefins with each other to form a product with increased molecular weight. The olefin typically has 3 to 16 carbon atoms, or 3 to 12 carbon atoms, or 4 to 12 carbon atoms, or 4 to 7 carbon atoms, or 4 to 5 carbon atoms.

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

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

The micro-emulsion is introduced into the reaction zone (or is formed there). For example, in an oligomerization process, a micro-emulsion is formed from a hydrocarbon,

a co-solvent, an ionic liquid, and optionally a surfactant and/or a catalyst promoter. In some embodiments, the hydrocarbon comprises an olefin. Alternatively, the hydrocarbon component in the micro-emulsion comprises a hydrocarbon that is not an olefin (such as a paraffin), and the olefin is introduced into the reaction zone after the micro-emulsion is formed. In other  
5 embodiments, the hydrocarbon component comprises an olefin and a paraffin, and a second olefin (the same or different from the olefin in the hydrocarbon component of the micro-emulsion) is added to the oligomerization reaction zone. The olefins in the micro-emulsion and/or the additional olefins oligomerize to form the oligomer product.

After the reaction, the micro-emulsion is broken, resulting in two distinct liquid  
10 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 oligomer product, 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  
15 of the hydrocarbons.

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

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

At least a portion of the recovered ionic liquid can be regenerated before being recycled. Various methods for regenerating ionic liquids could be used. For example, US  
30 7,651,970; US 7,825,055; US 7,956,002; US 7,732,363, each of which is incorporated herein by reference, describe contacting ionic liquid containing the conjunct polymer with a reducing metal (e.g., Al), an inert hydrocarbon (e.g., hexane), and hydrogen and heating to about 100°C

to transfer the conjunct polymer to the hydrocarbon phase, allowing for the conjunct polymer to be removed from the ionic liquid phase. Another method involves contacting ionic liquid containing conjunct polymer with a reducing metal (e.g., Al) in the presence of an inert hydrocarbon (e.g. hexane) and heating to about 100°C to transfer the conjunct polymer to the hydrocarbon phase, allowing for the conjunct polymer to be removed from the ionic liquid phase. See e.g., US 7,674,739 B2; which is incorporated herein by reference. Still another method of regenerating the ionic liquid involves contacting the ionic liquid containing the conjunct polymer with a reducing metal (e.g., Al), HCl, and an inert hydrocarbon (e.g. hexane), and heating to about 100°C to transfer the conjunct polymer to the hydrocarbon phase. See e.g., US 7,727,925, which is incorporated herein by reference. The ionic liquid can be regenerated by adding a homogeneous metal hydrogenation catalyst (e.g.,  $(PPh_3)_3RhCl$ ) to ionic liquid containing conjunct polymer and an inert hydrocarbon (e.g. hexane), and introducing hydrogen. The conjunct polymer is reduced and transferred to the hydrocarbon layer. See e.g., US 7,678,727, which is incorporated herein by reference. Another method for regenerating the ionic liquid involves adding HCl, isobutane, and an inert hydrocarbon to the ionic liquid containing the conjunct polymer and heating to about 100°C. The conjunct polymer reacts to form an uncharged complex, which transfers to the hydrocarbon phase. See e.g., US 7,674,740, which is incorporated herein by reference. The ionic liquid could also be regenerated by adding a supported metal hydrogenation catalyst (e.g. Pd/C) to the ionic liquid containing the conjunct polymer and an inert hydrocarbon (e.g. hexane). Hydrogen is introduced and the conjunct polymer is reduced and transferred to the hydrocarbon layer. See e.g., US 7,691,771, which is incorporated herein by reference. Still another method involves adding a suitable substrate (e.g. pyridine) to the ionic liquid containing the conjunct polymer. After a period of time, an inert hydrocarbon is added to wash away the liberated conjunct polymer. The ionic liquid precursor [butylpyridinium][Cl] is added to the ionic liquid (e.g. [butylpyridinium][ $Al_2Cl_7$ ]) containing the conjunct polymer followed by an inert hydrocarbon. After mixing, the hydrocarbon layer is separated, resulting in a regenerated ionic liquid. See, e.g., US 7,737,067, which is incorporated herein by reference. Another method involves adding ionic liquid containing conjunct polymer to a suitable substrate (e.g. pyridine) and an electrochemical cell containing two aluminum electrodes and an inert hydrocarbon. A voltage is applied, and the current measured to determine the extent of reduction. After a given time, the inert hydrocarbon is separated, resulting in a regenerated ionic liquid. See, e.g., US 8,524,623, which is incorporated herein by reference. . Ionic liquids can also be regenerated by contacting with silane compounds (U.S. Patent No. 9,120,092), borane compounds (U.S. Publication

No.2015/0314281), Brønsted acids, (U.S. Patent No. 9,079,176), or C<sub>1</sub> to C<sub>10</sub> Paraffins (U.S. Patent No. 9,079,175), each of which is incorporated herein by reference. Regeneration processes utilizing silane and borane compounds are described in U.S. Application Serial Nos. 14/269,943 and 14/269,978, each of which is incorporated herein by references.

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

10           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.

15           Typical oligomerization reaction conditions for processes utilizing ionic liquid micro-emulsions are significantly colder than solid acid catalysts which are generally operated at temperatures in the range of about 150°C to about 300°C. Colder reaction temperature may result in fewer secondary reaction products, such as cracking of oligomer back to lighter products. For the current invention utilizing ionic liquid micro-emulsions, typical oligomerization reaction conditions include a temperature in the range of about -20°C to about 100°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 olefin maintain a liquid rather than vapor state through the operating temperature range.

20           The pressure is typically in the range of about 0.001 MPa to about 8.0 MPa, or about 0.002 MPa to about 5 MPa, or about 0.1 MPa to about 8 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.

25           The residence time in the contact zone is in the range of a few seconds to several hours, or about 0.5 min to about 4 hours, or about 1 min to about 4 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, or about 2 min to about 10 min. If shorter residence time is desired, more ionic liquid can be used.

30           The molar space velocity of the olefin is defined as the amount of olefin fed to the reaction zone in moles, divided by the amount of ionic liquid in the reaction zone in moles,

divided by the residence time in the reaction zone in hours. The molar space velocity of olefin is in the range of about 200 hr<sup>-1</sup> to about 5000 hr<sup>-1</sup>, or about 500 hr<sup>-1</sup> to about 5000 hr<sup>-1</sup>, or about 1500 hr<sup>-1</sup> to about 5000 hr<sup>-1</sup>, or about 200 hr<sup>-1</sup> to about 4000 hr<sup>-1</sup>, or about 200 hr<sup>-1</sup> to about 3000 hr<sup>-1</sup>.

5 In some embodiments, the hydrocarbon further comprises a paraffin. The paraffin has between two and 25 carbon atoms. Preferably the paraffin is a normal paraffin. In some embodiments, the paraffin and olefin are present in the product of an upstream process, and are not separated before entering the reaction zone. For instance, olefins and paraffins are both generated in a fluid catalytic cracking zone. The fluid catalytic cracking product is distilled  
10 to separate ranges of products by boiling point, but both paraffins and olefins are present in any particular boiling range product and are not further separated. The ratio of olefins to paraffins may be in the range of about 0.1:1 to about 3:1 by weight, or about 0.2:1 to about 3:1 by weight, or about 0.3:1 to about 3:1 by weight, or about 0.2:1 to about 1:1 by weight, or about 0.2:1 to about 0.5:1 by weight.

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

The composition of the reaction mixture is altered to destroy the micro-emulsion. This can be done in a variety of ways. A portion of the co-solvent could be removed,  
25 for example by changing the pressure in the reactor to vaporize the co-solvent. Another way to change the composition is to add one or more of olefin, oligomer product, an additional liquid that has a polarity less than the polarity of the co-solvent (e.g., an inert or semi-inert hydrocarbon, such as an additional paraffin), or an ionic liquid. Any of these will change the composition of the reaction mixture so that the micro-emulsion is no longer stable. The ionic  
30 liquid phase (which may contain other materials) will separate from the hydrocarbon phase (which may contain other materials) due to density differences.

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

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

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

The reaction rate and selectivity may be changed by changing the amounts of the components in the micro-emulsion. For example, if the co-solvent is more viscous than the hydrocarbon, increasing the ratio of 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 olefin. With higher concentration of olefin, selectivity to the lighter oligomer would improve. Adding a second co-solvent with a lower viscosity or using a different co-solvent with a lower viscosity may result in a faster reaction if the reaction is mass-transfer limited. Decreasing the size of the micelles, reverse micelles, or bi-continuous structures in the micro-emulsion may result in faster reaction. Decreasing the size of micelles, reverse micelles, or 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.

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 80 mole olefin/mole ionic liquid/hour, or greater than about 200 mole olefin/mole ionic liquid/hour, or greater than about 500 mole olefin/mole ionic liquid/hour, or greater than about 800 mole olefin/mole ionic liquid/hour, or about 80 mole olefin/mole ionic liquid/hour to about 2000 mole olefin/mole ionic liquid/hour, or about 80 mole olefin/mole ionic liquid/hour to about 1500 mole olefin/mole ionic liquid/hour, or about 80 mole olefin/mole ionic liquid/hour to about 1000 mole olefin/mole ionic liquid/hour, or about 80 mole olefin/mole ionic liquid/hour to about 800 mole olefin/mole ionic liquid/hour, or about 500 mole olefin/mole ionic liquid/hour to about 1500 mole olefin/mole ionic liquid/hour.

The selectivity to a particular product or group of products is defined as the amount of the particular product or group of products in weight percent, divided by the amount of products. For example for the oligomerization of butene, the selectivity for C<sub>8</sub> hydrocarbons is the wt% of hydrocarbons containing exactly 8 carbon atoms in the product divided by the wt% of all of the products (which excludes all isomers of un-reacted butenes, co-solvent, ionic liquid, and paraffin diluent).

In some embodiments, the selectivity to dimeric oligomerization products is greater than about 35 wt%. Here, dimeric oligomerization products are defined as products containing greater than or equal to  $2n - (n/2)$  carbon atoms but less than  $2n + (n/2)$  carbon atoms, where  $n$  is carbon weighted average number of carbon atoms in the olefin reactant.

5 Without being bound by theory, selectivity to dimeric oligomerization products is higher if the olefin feed rate is slower, if residence time is longer, or if temperature is lower. 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  
10 component. The micro-emulsion is formed from an ionic liquid, a hydrocarbon, 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 olefin and/or co-solvent may be present in the ionic liquid component.

15 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,  
20 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 or  
25 micelles, as shown in Figs. 3-4. When an added surfactant is present, reverse micelles or micelles may be larger. In some embodiments, reverse micelles or micelles with added surfactant have diameters about 2 to about 7 times larger than similar compositions without added surfactant. Not wishing to be bound by theory, the presence of an added surfactant may increase the surface tension of reverse micelles or micelles and allow larger reverse micelles  
30 or 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 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.

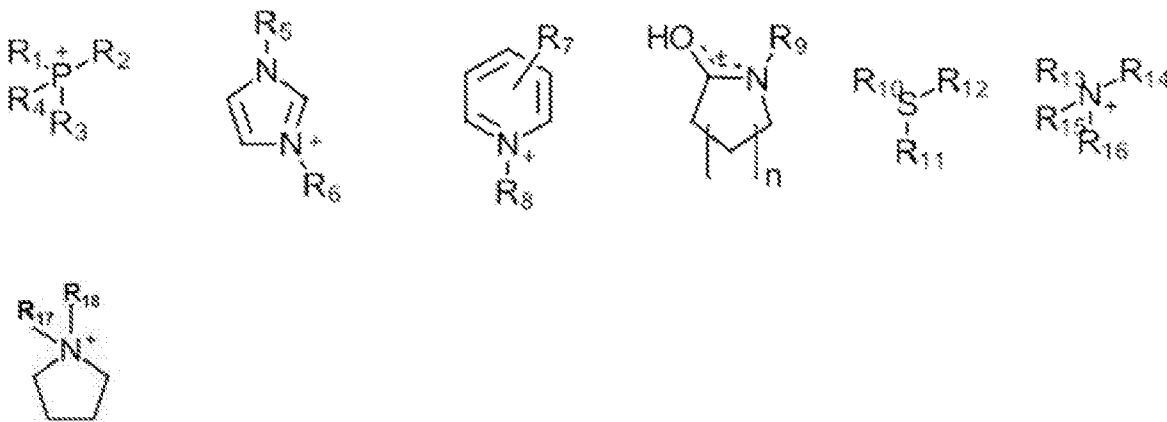
In some embodiments, the size distribution of the reverse micelles or micelles may be changed by changing the co-solvent. Not wishing to be bound by theory, using a more polar co-solvent may lead to larger reverse micelles due to the higher solubility of the co-solvent in the reverse micelles and due 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.

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.

- 5                    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-  
10    lactamiums and trialkylsulfoniums. Mixtures of cations may be used as well. Examples of suitable cations include, but are not limited to:



- where R<sub>1</sub>-R<sub>3</sub> are independently selected from alkyl groups, alkene groups, naphthene groups,  
15    and aryl groups having 1 to 12 carbon atoms, and R<sub>4</sub> is independently selected from alkyl groups, alkene groups, naphthene groups, and aryl groups having 1 to 15 carbon atoms; and

- where R<sub>5</sub>-R<sub>18</sub> 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  
20    naphthene groups.

In some embodiments, the anion is a halometallate or anion with acidic character, and in most embodiments with Lewis acidic character. Halometallate anions may contain a metal selected from Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, In, Sn, Sb, La, Ce, Hf, Ta, W, or combinations thereof, and a halide selected from F, Cl, Br, I, or

combination thereof. The halometallate may be a simple halometallate or a composite in which more than one metal is used. For catalytic applications requiring Lewis acidity (such as alkylation, isomerization, and disproportionation), the ratio of moles of halide to moles of metal in the anion is less than 4. The anion may be formally an anion, or it may be an anion associated with a metal halide. For instance, the anion may be  $\text{AlCl}_4^-$  associated with  $\text{AlCl}_3$ . In some embodiments, such as those where the ionic liquid comprises an imidazolium based cation, the ratio of moles of halide to moles of metal in the anion must be less than 4 in order for a micro-emulsion to form.

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

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

In order to form a micro-emulsion containing reverse micelles, there must be at least some solubility of the amphiphile in both the hydrocarbon component and the ionic liquid component of the micro-emulsion. Here, at least some solubility of the amphiphile in the hydrocarbon component is defined as the amphiphile being soluble in an amount of at least 0.5 mole ppm in the hydrocarbon component. If the cation and anion are both not amphiphilic, an additional surfactant may be needed to act as the amphiphile. The solubility of the ionic liquid or 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 oligomerization where the medium usually contains olefins, such as butenes), 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, 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, and 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 oligomerization reaction rate for olefins is decreased by more than 25% for a mole ratio of surfactant to ionic liquid of 1:1 compared to the same conditions with no additional surfactant. As an example of compatible surfactant anions,  $Cl^-$ ,  $AlCl_4^-$  or  $Al_2Cl_7^-$  may be used as the anion with an  $Al_2Cl_7^-$  ionic liquid (as may the bromide versions). Examples of cationic quaternary ammonium salts are cetyltrimethylammonium chloride, and benzyldimethyltetradecylammonium chloride. Anionic surfactants may also be suitable; however, most include sulfonate groups which are expected to be reactive with, or coordinate to, the Lewis acidic ionic liquid. Ideally, the cation of the sulfonate salt or phosphonate salt may be selected to match the cation of the ionic liquid or selected to be compatible with the cation of the ionic liquid. For instance, if the ionic liquid is tributylhexylphosphonium heptachloroaluminate, the surfactant could be tributylhexylphosphonium dodecyl sulfonate. As demonstrated below, the use of a surfactant allows use of less co-solvent, and, in some cases, it results in larger reverse micelles.

Another optional material is a catalyst promoter. In many hydrocarbon conversion reactions, such as oligomerization, a 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 materials are mixed in specific ratios such as to stabilize ionic liquid micro-emulsions, including reverse micelles. The ionic liquid is typically present in an amount of about 0.05 wt% to about 40 wt% of the micro-emulsion, or about 0.05 wt% to about 35 wt%, or about 0.05 wt% to about 30 wt%, or about 0.05 wt% to about 25 wt%, or about 0.05 wt% to about 20 wt%, or about 0.05 wt% to about 15 wt%, or about 0.05 wt% to about 10 wt%, or about 0.05 wt% to about 5 wt%, or about 0.05 wt% to about 1 wt%. If more ionic liquid is

used, shorter reaction time or lower temperature is required to achieve the same olefin conversion.

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

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

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

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

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

The micro-emulsion can be formed by contacting or otherwise mixing the hydrocarbon, the co-solvent, the ionic liquid, the optional surfactant, and the optional catalyst promoter. The hydrocarbon has a polarity less than the polarity of the co-solvent. In some

embodiments, the co-solvent is miscible in the hydrocarbon component, at least up to the desired composition. The ionic liquid comprises a halometallate anion and a cation. In some embodiments, the ionic liquid is at least slightly soluble in the co-solvent. By slightly soluble, we mean that at least 1 wt% of the ionic liquid is soluble in the co-solvent. The ionic liquid is present in an amount of about 0.05 wt% to about 40 wt% of the micro-emulsion.

The materials can be combined in different ways. For example, the hydrocarbon and co-solvent can be combined first, and then combined with ionic liquid. Alternatively, the ionic liquid and the co-solvent can be combined first, and then combined with the hydrocarbon. The optional surfactant and optional catalyst promoter can be added at different times and to different combinations of the materials. For example, the catalyst promoter and optional surfactant can be added to the hydrocarbon, the co-solvent, the ionic liquid, or any combinations of these materials. In another alternative, all of the 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 hydrocarbon component comprises the 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. 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 co-solvent is greater than the polarity of the hydrocarbon, 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

Oligomerization of 2-butenes was demonstrated using ionic liquid micro-emulsions. A mixture of hydrocarbons containing 7-15 carbon atoms was obtained as the  
5 product, and dichloromethane was used as the co-solvent.

A micro-emulsion comprising 1-butyl-3-methylimidazolium-heptachloroaluminate (BMIm-  $\text{Al}_2\text{Cl}_7$ ) ionic liquid was generated by charging a mixture of 0.89 g (0.50 final vol%) ionic liquid, 97.493 g (55 final vol%) dichloromethane as the co-solvent, and 19.22 g n-hexane (22 final vol%) into a 300 cc autoclave, equipped with a 1-3/8"  
10 pitched blade turbine impeller.

The vessel was pressurized with nitrogen to 2.4 MPa(g) (350 psig). A mixture of 18.3 g of cis- and trans-2-butene with 9 wt % n-pentane (used as a tracer) was added continuously at room temperature over the course of 5 min while mixing with a pitched-blade impeller at 1200 rpm. Initial temperature was 23 °C. Since micro-emulsions are not expected  
15 to settle, these reactions were then chemically quenched by adding 20 g of 50 wt% 1-butanol in hexane. The mixture was analyzed by GC under pressure. The products were not individually identified. Rather, they were lumped by carbon number based on retention time. For instance, products that eluted between n-heptane and n-octane were reported as  $\text{C}_8$ , and products that eluted between n-octane and n-nonane were reported as  $\text{C}_9$ .

20 Butenes conversion was calculated based on the n-pentane tracer. Selectivities are reported as a weight percent of the  $\text{C}_{4+}$  product. Table 1 shows the conditions for the two runs, and Table 2 shows the butene conversion and selectivities by carbon number.

The percent olefin (butene) conversion is defined as (the amount of olefin added to the reactor minus the amount of olefin remaining after the reaction (or at the reactor outlet))  
25 divided by the total amount of olefin added to the reactor times 100.

### Comparative Example 1

Conditions were the same as example 1, except that instead of using both dichloromethane and n-hexane, 67.23 g n-hexane (77 final vol%) was used. The amount of n-

hexane has equal volume to the total of dichloromethane and n-hexane used in Example 1. Without dichloromethane, a micro-emulsion did not form. Rather, the ionic liquid formed a separate liquid phase.

- Olefin conversion was 38.5% in the micro-emulsion case (example 1) and only 15.8% in the comparison experiment (Comparative Example 1). This is consistent with the exotherms observed during reaction; 2°C for the comparison experiment and 6°C for the micro-emulsion experiment. Clearly reaction in the micro-emulsion system is substantially faster than the conventional system. Selectivities were similar in both cases, with significant products distributed among compounds containing 7-15 carbons.
- 10 Table 1: Conditions of 2-butene oligomerization tests

|                                        | Ex. 1                  | Comp. Ex. 1            |
|----------------------------------------|------------------------|------------------------|
| n-C <sub>6</sub> g                     | 19.22                  | 67.23                  |
| 2-butenes g (from isco)                | 18.3                   | 18.3                   |
| CH <sub>2</sub> Cl <sub>2</sub> g      | 97.493                 |                        |
| BMIM-Al <sub>2</sub> Cl <sub>7</sub> g | 0.89                   | 0.89                   |
|                                        |                        |                        |
| Temp C                                 | 23                     | 23                     |
| Reaction time hrs                      | 5 min + 2 min settling | 5 min + 2 min settling |
| CH <sub>2</sub> Cl <sub>2</sub> vol%   | 55%                    | 0%                     |
| n-C <sub>6</sub> vol %                 | 22%                    | 77%                    |
| 2-butenes vol%                         | 22%                    | 22%                    |
| BMIM vol%                              | 0.50%                  | 0.50%                  |
| olefin whsv (hr <sup>-1</sup> )        | 248.27                 | 246.88                 |

| Results                    | Ex. 1 | Comp. Ex. 1 |
|----------------------------|-------|-------------|
| C <sub>4</sub> Conversion% | 38.5% | 15.8%       |

|                                                      |       |       |
|------------------------------------------------------|-------|-------|
| C <sub>4</sub> wt% selectivity                       | 0.7%  | 1.0%  |
| C <sub>5</sub> wt% selectivity                       | 0.3%  | 0.6%  |
| C <sub>6</sub> wt% selectivity                       | 0.7%  | 0.3%  |
| C <sub>7</sub> wt% selectivity                       | 6.6%  | 7.2%  |
| C <sub>8</sub> wt% selectivity                       | 13.5% | 13.5% |
| nC <sub>8</sub> -nC <sub>9</sub> wt% selectivity*    | 24.7% | 21.2% |
| nC <sub>9</sub> -nC <sub>10</sub> wt% selectivity*   | 10.5% | 11.4% |
| nC <sub>10</sub> -nC <sub>11</sub> wt% selectivity*  | 6.5%  | 7.2%  |
| nC <sub>11</sub> -nC <sub>12</sub> wt% selectivity*  | 13.0% | 13.2% |
| nC <sub>12</sub> -nC <sub>13</sub> wt% selectivity*  | 8.9%  | 9.9%  |
| nC <sub>13</sub> -nC <sub>14</sub> wt% selectivity*  | 8.2%  | 8.0%  |
| nC <sub>14</sub> -nC <sub>15</sub> wt% selectivity*  | 6.2%  | 5.8%  |
| nC <sub>15</sub> -nC <sub>16+</sub> wt% selectivity* | 0.2%  | 0.8%  |

\*products eluting between the specified n-paraffins on a

#### Example 2 – Phase diagram

In this example n-hexane is used as the hydrocarbon, tributylhexylphosphonium  
 5 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.  
 10 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  
 15 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  
5 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  
10 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 3

Particle size distributions of micro-emulsions were measured by dynamic light  
15 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  
20 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  
25 normalized average particle size of  $12 \pm 2$  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  $3 \pm 2$   
30 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 4

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- $\text{Al}_2\text{Cl}_7$  was used in formulation 1, tributylmethylphosphonium- $\text{Al}_2\text{Cl}_7$  was used in formulation 2, 1-butyl-3-methylimidazolium- $\text{Al}_2\text{Cl}_7$  was used in formulation 3 and caprolactamium- $\text{Al}_2\text{Cl}_7$  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 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- $\text{Al}_2\text{Cl}_7$ | 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 <sub>2</sub> Cl <sub>7</sub>           | 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 <sub>2</sub> Cl <sub>7</sub>           | 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 <sub>2</sub> Cl <sub>7</sub> | 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%.

- 5 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  
5 arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims.

### SPECIFIC EMBODIMENTS

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

A first embodiment of the invention is a process comprising forming a micro-emulsion comprising contacting an ionic liquid, a co-solvent, a hydrocarbon, an optional surfactant, and an optional catalyst promoter to form the micro-emulsion, the micro-emulsion comprising a hydrocarbon component comprising the hydrocarbon and an ionic liquid  
15 component comprising the ionic liquid, the ionic liquid comprising a halometallate anion and a cation, the hydrocarbon comprising an olefin, a paraffin or both, 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; optionally adding an olefin to an oligomerization reaction zone containing the micro-emulsion; and producing a  
20 product mixture in the oligomerization reaction zone containing the micro-emulsion, the oligomerization reaction zone being operated at oligomerization reaction conditions, the product mixture comprising an oligomer product. 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  
25 wt% of the micro-emulsion. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the 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  
30 through the first embodiment in this paragraph further comprising altering a composition of the product mixture to destroy the micro-emulsion; and separating the oligomer product from one or more of the ionic liquid, the co-solvent, and the olefin. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first

embodiment in this paragraph wherein the composition of the product mixture is altered by removing a portion of the co-solvent, increasing an amount of the olefin, increasing an amount of the oligomer product, adding an additional liquid having a polarity less than the polarity of the co-solvent, adding additional ionic liquid, or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the cation of the ionic liquid comprises a tetraalkyl phosphonium cation, a dialkylimidazolium cation, an alkylimidazolium cation, a pyridinium cation, an alkyl pyridinium cation, a dialkylpyridinium cation, an alkylpyrrolidinium cation, a dialkylpyrrolidinium cation, a trialkylammonium cation, a tetraalkylammonium cation, a lactamium cation, an alkyl-lactamium cation, a trialkylsulfonium cation, or combinations thereof; and wherein the halometallate anion contains a metal selected from Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, In, Sn, Sb, La, Ce, Hf, Ta, W, or combinations thereof, and a halide selected from F, Cl, Br, I, or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein a viscosity of the co-solvent is less than about 1 centipoise at 25°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the co-solvent comprises a halogenated hydrocarbon, a halocarbon, a halogenated aromatic, or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the surfactant is present, wherein the surfactant comprises a quaternary ammonium salt, a ternary ammonium salt, a phosphonium salt, a sulfonate salt, a phosphonate salt, or a disubstituted amide, and wherein a molar ratio of the surfactant to the ionic liquid is less than about 2.5:1; or wherein the catalyst promoter is present, wherein the catalyst promoter comprises an anhydrous hydrogen halide, a halogenated hydrocarbon, or combinations thereof, and wherein a molar ratio of the catalyst promoter to the ionic liquid is about 0.1:1 to about 1:1; or both. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the 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 reaction mixture to destroy the micro-emulsion; recovering the ionic liquid; regenerating at least a portion the recovered 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 the hydrocarbon further comprises the paraffin, and wherein a ratio of the olefin to the paraffin is in a range of about 0.1:1 to about 3:1 by weight. 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 olefin has 3 to 16 carbon atoms. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein a molar space velocity of the olefin is about 200 hr<sup>-1</sup> to about 5000 hr<sup>-1</sup>. 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 oligomerization  
10 conditions include at least one of a temperature in a range of about -20°C to about 100°C, a pressure in a range of about 1 kPa(a) to about 8 MPa(a), or a residence time in a range of about 1 min to about 30 min.

A second embodiment of the invention is a process comprising forming a micro-emulsion comprising contacting an ionic liquid, a co-solvent, a hydrocarbon, an optional  
15 surfactant, and an optional catalyst promoter 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 ionic liquid comprising a halometallate anion and a cation, the hydrocarbon comprising an olefin, a paraffin, or both, the co-solvent having a polarity greater than a polarity of the hydrocarbon, the ionic liquid being present in an  
20 amount of about 0.05 wt% to about 40 wt% of the micro-emulsion; optionally adding an olefin to an oligomerization reaction zone containing the micro-emulsion; producing a product mixture in the oligomerization reaction zone containing the micro-emulsion, the oligomerization reaction zone being operated at oligomerization reaction conditions, the product mixture comprising an oligomer product; altering a composition of the reaction  
25 mixture by removing a portion of the co-solvent, increasing an amount of the hydrocarbon, increasing an amount of oligomer product, adding an additional liquid having a polarity less than the polarity of the co-solvent, adding ionic liquid, or combinations thereof, to destroy the micro-emulsion; and separating the oligomer product from one or more of the ionic liquid, the co-solvent, and the hydrocarbon. An embodiment of the invention is one, any or all of  
30 prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the halometallate anion contains a metal selected from Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, In, Sn, Sb, La, Ce, Hf, Ta, W, or combinations thereof, and a halide selected from F, Cl, Br, I, or combinations thereof, and wherein the cation 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. 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 halogenated hydrocarbon, a halocarbon, a halogenated aromatic, or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the surfactant is present, wherein the surfactant comprises a quaternary ammonium salt, a ternary ammonium salt, a phosphonium salt, a sulfonate salt, a phosphonate salt, or a disubstituted amide, and wherein a molar ratio of the surfactant to the ionic liquid is less than about 2.5:1; or wherein the catalyst promoter is present, wherein the catalyst promoter comprises an anhydrous hydrogen halide, a halogenated hydrocarbon, or combinations thereof, and wherein a molar ratio of the catalyst promoter to the ionic liquid is about 0.1:1 to about 1:1; or both. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the 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.

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 oligomerization process comprising:

forming a micro-emulsion comprising:

contacting an ionic liquid, a co-solvent, a hydrocarbon, an optional surfactant, and an optional catalyst promoter to form the micro-emulsion, the micro-emulsion comprising  
5 a hydrocarbon component comprising the hydrocarbon and an ionic liquid component comprising the ionic liquid, the ionic liquid comprising a halometallate anion and a cation, the hydrocarbon comprising an olefin, a paraffin or both, 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;

10 optionally adding an olefin to an oligomerization reaction zone (105) containing the micro-emulsion; and

producing a product mixture in the oligomerization reaction zone (105) containing the micro-emulsion, the oligomerization reaction zone (105) being operated at oligomerization reaction conditions, the product mixture comprising an oligomer product

2. The process of claim 1 further comprising:

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

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

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

4. The process of claim 2 further comprising:

recovering the ionic liquid;

regenerating at least a portion the recovered ionic liquid; and

recycling the regenerated ionic liquid.

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

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

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

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

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

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; the hydrocarbon further comprises the paraffin, and wherein a ratio of the olefin to the paraffin is in a range of 0.1:1 to 3:1 by weight; and a molar space velocity of the olefin is  $200 \text{ hr}^{-1}$  to  $5000 \text{ hr}^{-1}$ .

10. The process of any one of claims 1-4 wherein the oligomerization conditions include at least one of: a temperature in a range of  $-20^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , a pressure in a range of 1 kPa(a) to 8 MPa(a), or a residence time in a range of 1 min to 30 min.

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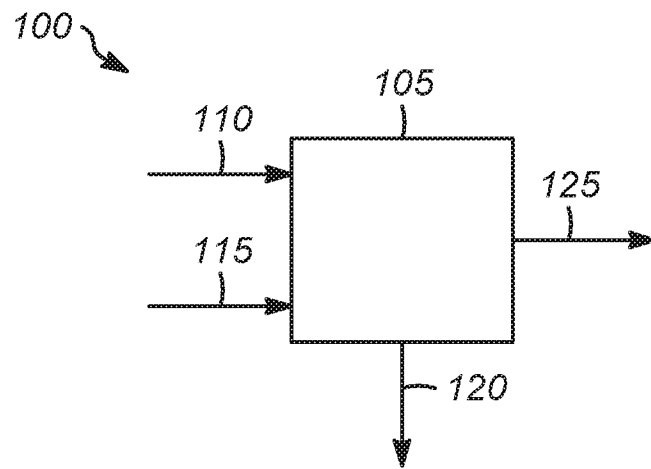


FIG. 1

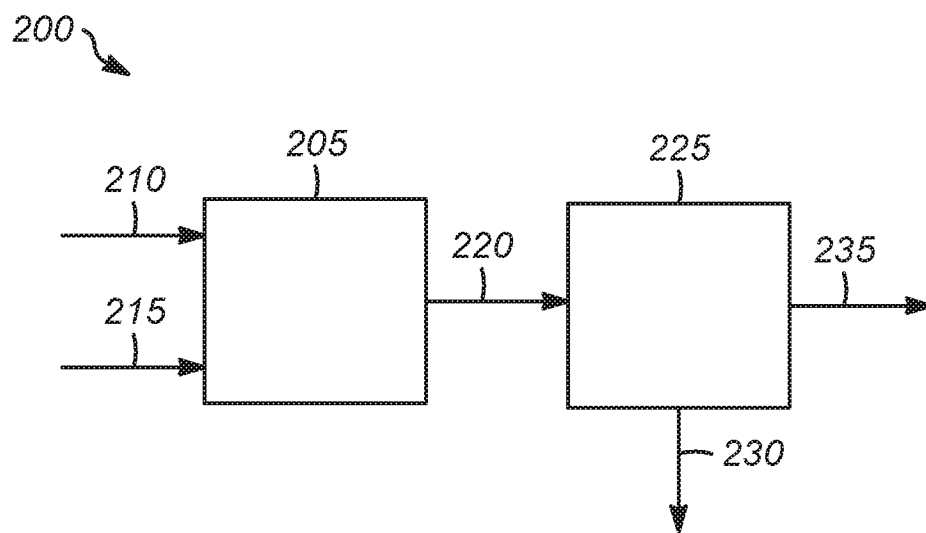


FIG. 2

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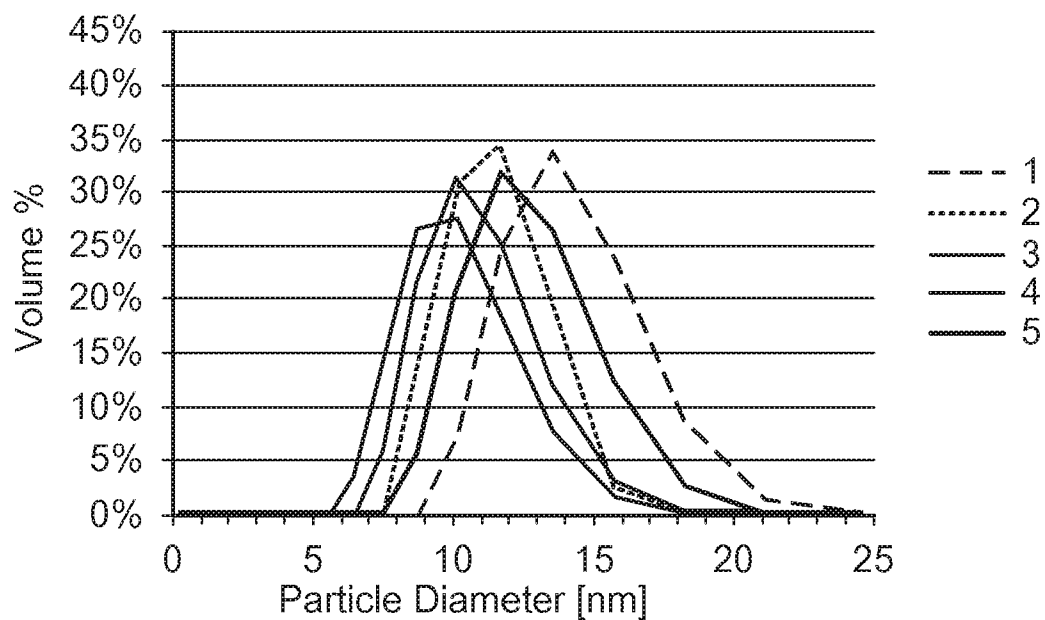


FIG. 3

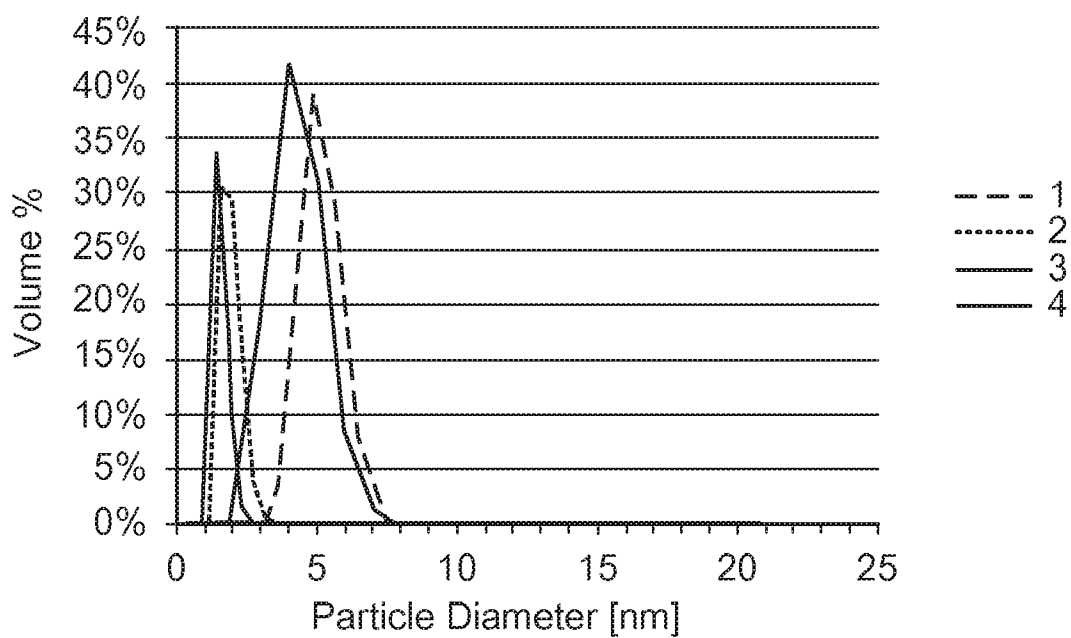


FIG. 4

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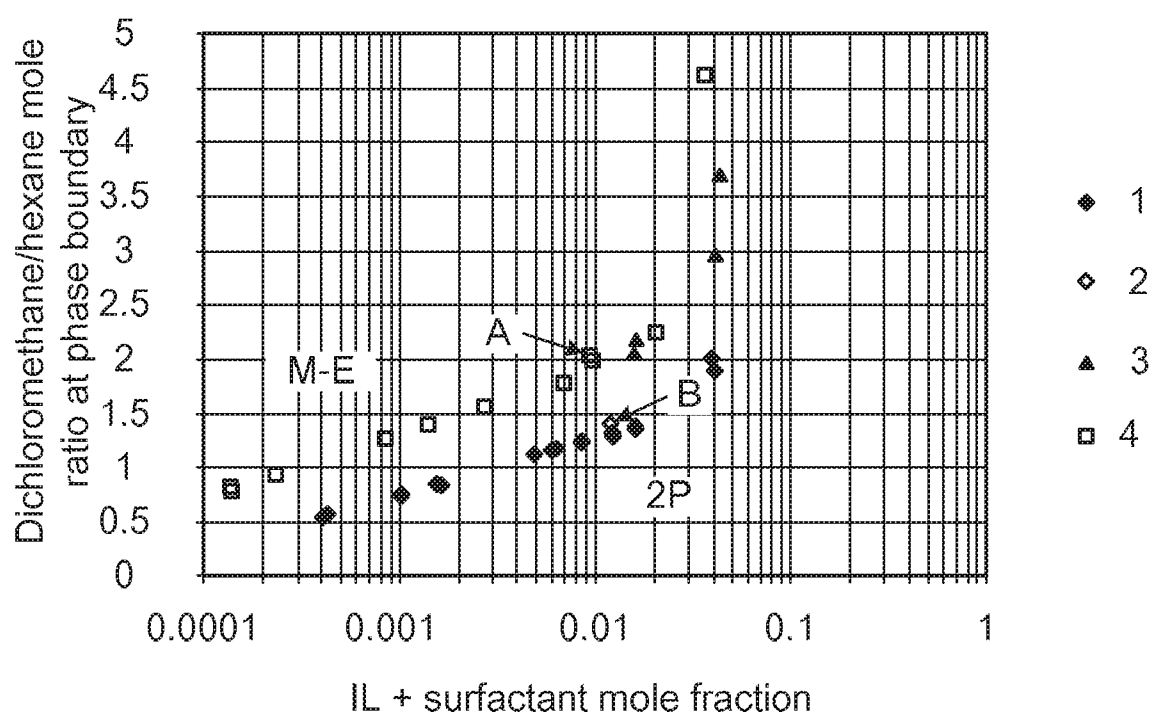


FIG. 5

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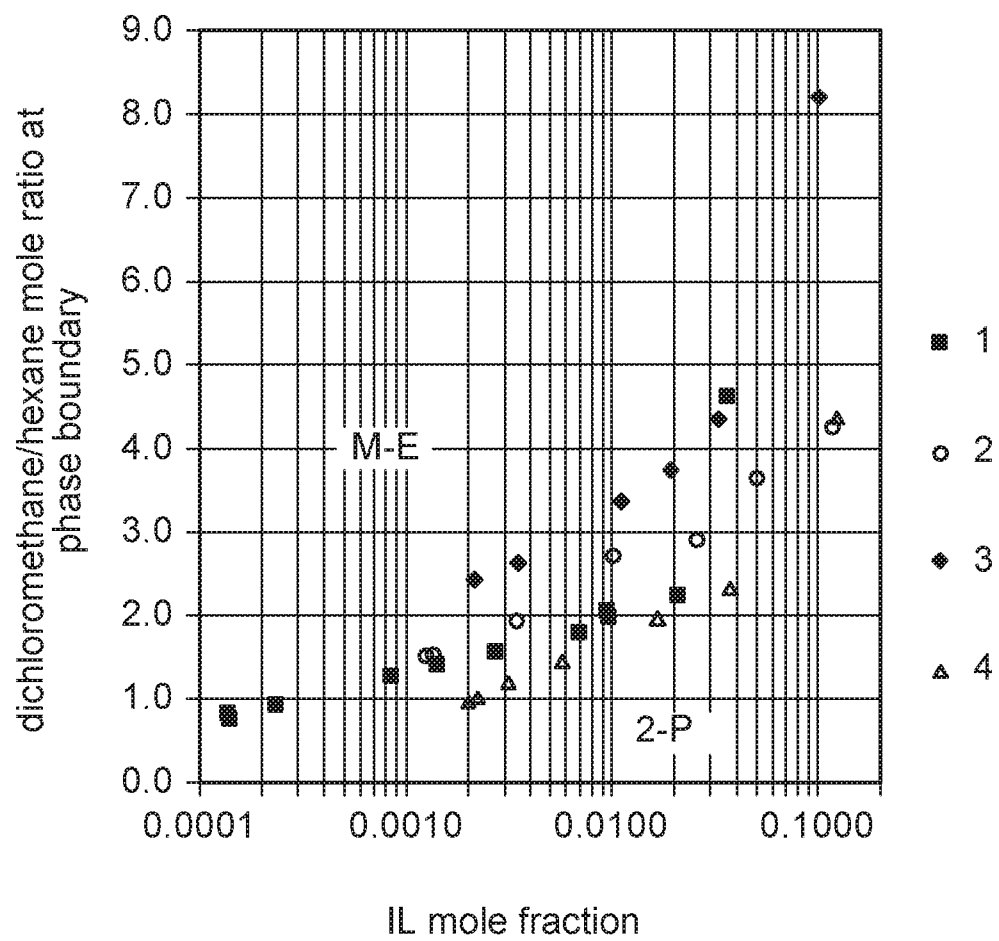


FIG. 6

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2016/025421

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                                                           |                                                                               |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
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| A. CLASSIFICATION OF SUBJECT MATTER                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                                                                           |                                                                               |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| (see extra sheet)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                                                           |                                                                               |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| According to International Patent Classification (IPC) or to both national classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                                                           |                                                                               |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| B. FIELDS SEARCHED                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                                                           |                                                                               |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| Minimum documentation searched (classification system followed by classification symbols)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                           |                                                                               |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| C07C 2/08, 2/26, C08F 110/10, B01J 31/02, 31/16, 31/30, B01F 3/08, B82Y 40/00                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                                                           |                                                                               |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| 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), RUPAT, Espacenet, EAPATIS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                           |                                                                               |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                                           |                                                                               |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| Category*                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | Citation of document, with indication, where appropriate, of the relevant passages                                                                                        | Relevant to claim No.                                                         |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | US 2005/0119423 A1 (LEE H. BERGMAN et al.) 02.06.2005, paragraphs [0010] – [0013], [0016], [0019], [0020], [0022], [0024], [0029], [0031], [0032], [0034], [0047], fig. 1 | 1-10                                                                          |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | US 2010/0197483 A1 (CHEVRON U.S.A. INC.) 05.08.2010, paragraph [0021]                                                                                                     | 1-10                                                                          |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | WO 2010/135064 A2 (CHEVRON U.S.A. INC.) 25.11.2010, claims 1, 2, 6, 7, 16, p. 4, p. 6, lines 14-19, 24-25                                                                 | 6, 7                                                                          |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | WO 2003/089390 A2 (CHEVRON PHILLIPS CHEMICAL COMPANY LP) 30.10.2003, p. 9, lines 4-9, example 1                                                                           | 8                                                                             |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| <input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                           |                                                                               |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| * Special categories of cited documents: <table border="0"> <tr> <td>“A”</td> <td>document defining the general state of the art which is not considered to be of particular relevance</td> <td>“T”</td> <td>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</td> </tr> <tr> <td>“E”</td> <td>earlier document but published on or after the international filing date</td> <td>“X”</td> <td>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</td> </tr> <tr> <td>“L”</td> <td>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)</td> <td>“Y”</td> <td>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</td> </tr> <tr> <td>“O”</td> <td>document referring to an oral disclosure, use, exhibition or other means</td> <td>“&amp;”</td> <td>document member of the same patent family</td> </tr> <tr> <td>“P”</td> <td>document published prior to the international filing date but later than the priority date claimed</td> <td></td> <td></td> </tr> </table> |                                                                                                                                                                           |                                                                               | “A”                                                                                                                                                                                                                                          | document defining the general state of the art which is not considered to be of particular relevance | “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 | “E” | earlier document but published on or after the international filing date | “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 | “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) | “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 | “O” | document referring to an oral disclosure, use, exhibition or other means | “&” | document member of the same patent family | “P” | document published prior to the international filing date but later than the priority date claimed |  |  |
| “A”                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | document defining the general state of the art which is not considered to be of particular relevance                                                                      | “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                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
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| “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)       | “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 |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| “O”                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | document referring to an oral disclosure, use, exhibition or other means                                                                                                  | “&”                                                                           | document member of the same patent family                                                                                                                                                                                                    |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| “P”                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | document published prior to the international filing date but later than the priority date claimed                                                                        |                                                                               |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| Date of the actual completion of the international search                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                           | Date of mailing of the international search report                            |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| 27 May 2016 (27.05.2016)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                           | 23 June 2016 (23.06.2016)                                                     |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |
| Name and mailing address of the ISA/RU:<br>Federal Institute of Industrial Property,<br>Berezhkovskaya nab., 30-1, Moscow, G-59,<br>GSP-3, Russia, 125993<br>Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                                                           | Authorized officer<br><br>G. Ovchinnikova<br><br>Telephone No. (495)531-64-81 |                                                                                                                                                                                                                                              |                                                                                                      |     |                                                                                                                                                                                                 |     |                                                                          |     |                                                                                                                                                                          |     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |     |                                                                          |     |                                           |     |                                                                                                    |  |  |

**INTERNATIONAL SEARCH REPORT**  
Classification of subject matter

International application No.

PCT/US 2016/025421

*C07C 2/08 (2006.01)*  
*C07C 2/26 (2006.01)*  
*C08F 110/10 (2006.01)*  
*B01J 31/02 (2006.01)*  
*B01J 31/16 (2006.01)*  
*B01J 31/30 (2006.01)*  
*B82Y 40/00 (2011.01)*  
*B01F 3/08 (2006.01)*