

1 SEPARATION OF DIENES FROM OLEFINS USING IONIC LIQUIDS

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3 FIELD OF THE INVENTION

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5 The present invention is in the field of organic separations, in particular
6 separation of di-olefins from mono-olefins, and olefins from non-olefins, using
7 olefin-complexing metal salts dissolved, dispersed or suspended in ionic
8 liquids.

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10 BACKGROUND OF THE INVENTION

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12 There are many product streams in the field of petroleum chemistry which
13 include both mono-olefins and di-olefins, for example resulting from
14 hydrocracking, olefin oligomerization and paraffin dehydrogenation. For a
15 variety of reasons it is desirable to separate mono-olefins from di-olefins. For
16 example, normal alpha mono-olefins such as 1-butene, 1-hexene and 1-
17 octene are valuable products; and product specifications often require
18 relatively low levels of di-olefins (also known as dienes). When paraffins are
19 dehydrogenated to form olefins and subsequently used in alkylation
20 chemistry, di-olefin by-products from the dehydrogenation step produce
21 undesired products in the alkylation step. Di-olefins are also known to poison
22 some catalysts and need to be removed before certain reactions can be
23 performed. Di-olefins themselves are often valuable products, but must be
24 separated from unwanted mono-olefins. For example, di-olefins are often
25 used as crosslinking agents and in Diels-Alder reactions.

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27 Methods for selectively converting di-olefins to mono-olefins have been
28 developed. For example, one commercially licensed process employs a
29 selective, supported hydrogenation catalyst to selectively remove di-olefins by
30 converting them to mono-olefins. However, there are several limitations to
31 this type of process. Normal alpha olefins (NAO) may be isomerized to
32 internal olefins in the presence of the catalyst. Hydrogenation can also cause
33 side reactions such as formation of branched hydrocarbons. Some of the

1 olefins may also be hydrogenated, forming paraffins. Further, the
2 hydrogenation process does not remove paraffins, which are often present in
3 the product streams. Additionally, known catalysts are toxic, corrosive,
4 volatile and environmentally harmful

5
6 Another method for separating di-olefins from mono-olefins involves
7 distillation. However, di-olefins are difficult to remove from mono-olefins by
8 distillation because they tend to be extremely close in relative volatility.
9 Therefore, distillation requires a large number of stages and / or high reflux
10 ratios. Paraffins are also difficult to separate from olefins via distillation
11 because there is only a small difference in relative volatility between a
12 paraffin and the corresponding olefin with the same number of carbons.
13 Given purity requirements for commercially viable olefins, it is difficult and
14 expensive to achieve the required separation using distillation.

15
16 Therefore, while the olefins are extremely commercially valuable, the
17 commercially available methods for separating them are expensive, toxic, or
18 both. None of the known processes provide a facile method for obtaining
19 relatively high purity olefin components from olefin-containing streams such
20 as cracked gases. It is a difficult separation to achieve economically by
21 distillation. It is also difficult to control the side reactions and the migration of
22 double bonds which occur in catalytic hydrogenation.

23
24 It would be advantageous to have economical methods for separating di-
25 olefins from mono-olefins, and, preferably, separating both di-olefins and
26 mono-olefins from non-olefins such as paraffins. It would also be
27 advantageous to have such methods which also limit the formation of
28 unwanted products, such as branched hydrocarbons, paraffins, and olefins
29 with internal double bonds. The present invention provides such methods.

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31 Ionic liquids are a category of compounds which are made up entirely of ions
32 and are liquid at or below ambient temperatures. Usually, such compounds
33 produce solids with high melting points (commonly known as 'molten salts').

1 Ionic liquids differ from 'molten salts', in that they have low melting points, and
2 are liquid at ambient temperatures. Moreover, they tend to be liquid over a
3 very wide temperature range, with a liquid range of up to about 300° C. Ionic
4 liquids are non-volatile, with no effective vapor pressure. Most are air and
5 water stable, and are good solvents for a wide variety of inorganic, organic,
6 and polymeric materials.

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8 Ionic liquids are used herein to dissolve, suspend, disperse or otherwise
9 immobilize olefin-complexing metal salts. When a mixture containing mono-
10 and di-olefins is contacted with such an immobilized olefin-complexing metal
11 salt, di-olefins are selectively complexed over mono-olefins, forming a metal
12 salt/olefin complex. Since ionic liquids are non-volatile, the non-complexed
13 mono-olefins may be easily separated via distillation or other conventional
14 methods. Furthermore, the di-olefins may be readily desorbed and recovered
15 from the metal salt/olefin complex, allowing the ionic liquid – metal salt
16 solution to be recovered and recycled. Mono-olefins may also be complexed,
17 allowing facile separation of non-olefins followed by selective desorption of
18 mono- and di-olefins.

19 20 21 SUMMARY OF THE INVENTION

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23 Disclosed herein are methods for separating di-olefins from mono-olefins
24 and, optionally, non-olefins such as paraffins, oxygenates and aromatics. The
25 methods use metal salts which complex both mono-olefins and di-olefins, but
26 which preferentially complex di-olefins in the presence of mono-olefins with a
27 high degree of selectivity. The metal salts are dissolved, dispersed or
28 suspended in ionic liquids. Preferred salts are Group IB salts, more
29 preferably silver salts. A preferred silver salt is silver tetrafluoroborate,
30 although Pd salts may be preferred for separating olefins higher than C₈.
31 Preferred ionic liquids are those which form stable solutions, suspensions or
32 dispersions of the metal salts, which do not dissolve unwanted non-olefins,
33 and which do not isomerize the mono- or di-olefins.

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2 The olefins may be recovered from the ionic liquids by a number of
3 regeneration options including any combination of thermal regeneration
4 (increasing the solution temperature to reverse the complexation) and
5 pressure swing regeneration (reducing the pressure to reverse the
6 complexation). Sweep gases may also be used in the regeneration step.

7

8 In one embodiment, the method involves selectively complexing di-olefins in
9 the presence of mono-olefins, and separating the non-complexed mono-
10 olefins from the complexed di-olefins. The selective complexation is
11 performed by adjusting the equivalents of the metal salt in the ionic liquid
12 such that essentially only di-olefins are complexed. If non-olefins are present
13 and it is desired to separate them from the mono-olefins, the mono-olefins
14 can be complexed and then the non-complexed non-olefins are separated
15 from the olefins. The separation can be effected by distillation, decantation or
16 other means known to those of skill in the art.

17

18 In another embodiment, both mono- and di-olefins are complexed, and any
19 non-olefins can be separated, for example via distillation or decantation. The
20 complexed mono- and di-olefins are separated by staged desorption. Mono-
21 olefins are not as tightly bound to the complexing agent as the di-olefins,
22 and can be desorbed more readily. The desorption conditions typically
23 involve distillation under vacuum. After the mono-olefins are desorbed, the
24 di-olefins can then be desorbed, generally at high temperatures and/or lower
25 pressures than the mono-olefins.

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27 In one embodiment, the mono- and di-olefin-containing mixture can be in the
28 gas phase or in the liquid phase. In the liquid phase, conventional liquid/liquid
29 extraction equipment, such as mixer-settlers, can be used. The flow of the
30 mono- and di-olefin-containing mixture over/through the ionic liquid can be,
31 for example, co-current, counter-current, or staged in stirred tanks, with
32 counter current being preferred.

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1 Silver complexes may be poisoned by various compounds, including sulfur
2 compounds, cyanides and acetylides. Silver acetylides also pose potential
3 risk of explosion. Accordingly, these compounds should be removed before
4 the mixtures are brought into contact with the ionic liquids. Methods for
5 removing such contaminants are well known to those of skill in the art.

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7 In a first aspect of this invention, there is provided a method for separating
8 mono-olefins from a mixture including mono-olefins and di-olefins wherein
9 the mixture is contacted with an ionic liquid solution, suspension or
10 dispersion of an olefin-complexing metal salt capable of selectively
11 complexing the di-olefin over the mono-olefin. The mixture is maintained in
12 contact with the ionic liquid solution for sufficient time to selectively complex
13 the di-olefin over the mono-olefin to form a metal salt/olefin complex. The
14 non-complexed mono-olefin is then separated from the overall mixture. The
15 di-olefin may then be desorbed from the metal salt/olefin complex.

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17 In a second aspect of this invention, there is provided a method for
18 separating mono-olefins from a mixture comprising di-olefins and mono-
19 olefins contacted with an olefin-complexing metal salt dissolved, dispersed,
20 or suspended in an ionic liquid. The mixture is maintained in contact with the
21 olefin-complexing metal salt for sufficient time to complex the mono-olefins
22 and di-olefins with the olefin-complexing metal salt to form a metal salt/olefin
23 complex. The mono-olefins are then selectively desorbed from the metal
24 salt/olefin complex. The di-olefin may then be desorbed from the metal
25 salt/olefin complex.

26 In a third aspect of this invention, there is provided a method for separating
27 mono-olefins and/or di-olefins from a mixture including mono-olefins, di-
28 olefins and non-olefins. The mixture, comprising a di-olefin, a mono-olefin
29 and a non-olefin, is contacted with an ionic liquid solution, suspension or
30 dispersion of an olefin-complexing metal salt capable of selectively
31 complexing the di-olefin over the mono-olefin. The mixture is maintained in
32 contact with the ionic liquid solution for sufficient time to complex the mono-
33 olefins and di-olefins with the olefin-complexing metal salt to form a metal

1 salt/olefin complex. The non-complexed non-olefins are separated, and then
2 the mono-olefin is selectively desorbed from the metal salt/olefin complex.
3 The di-olefin may then be desorbed from the metal salt/olefin complex.
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5 In a fourth aspect of this invention, there is provided a method for separating
6 mono-olefins and/or di-olefins from a mixture comprising di-olefins, mono-
7 olefins and non-olefins contacted with an olefin-complexing metal salt
8 dissolved, dispersed or suspended in an ionic liquid. The mixture is
9 maintained in contact with the olefin-complexing metal salt for sufficient time
10 to selectively complex the di-olefins over the mono-olefins to form a first metal
11 salt/olefin complex. The non-complexed mono-olefins and non-olefins are
12 separated. Then, the di/olefins may be desorbed from the first metal
13 salt/olefin complex. Next, the non-complexed mono-olefins and non-olefins
14 are contacted with the olefin-complexing metal salt and maintained in contact
15 with such olefin-complexing metal salt for sufficient time to complex the
16 mono-olefins to form a second metal salt/olefin complex. Then, the non-
17 complexed non-olefins are separated. The mono-olefins may then be
18 desorbed from the metal salt/olefin complex.
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30 DETAILED DESCRIPTION OF THE INVENTION

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32 The present invention is directed to methods for separating di-olefins from
33 mono-olefins, and olefins from non-olefins. The compositions include ionic

1 liquid solutions, suspensions or dispersions of metal salts which complex
2 mono- and di-olefins. The di-olefins can be selectively complexed in the
3 presence of mono-olefins, or both di-olefins and mono-olefins can be
4 complexed, and the mono-olefins selectively decomplexed in the presence of
5 complexed di-olefins. Non-olefins, which are not complexed, tend to be
6 immiscible in the ionic liquids and can be separated from any olefins, which
7 are complexed. The complexed olefins tend to be either present in solution in
8 the ionic liquids or precipitate out of solution and can be isolated, for example,
9 via filtration.

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DEFINITIONS

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13 As used herein, the terms "adsorption" and "complexation" are used to
14 describe the complexation of metal salts with olefinic species such as mono-
15 and di-olefins. The term "desorption" is used to describe the decomplexation
16 of the olefin from the olefin/metal salt complex. The term "adsorbents" is
17 used to describe the olefin-complexing metal salts, alone or dissolved,
18 suspended or dispersed in ionic liquids. The term "bottoms" is used to
19 describe the portion of a process stream which collects in the bottom of a
20 vessel during a fractionating process. The term "Group IB metal" is used to
21 describe elements from Group IB (IUPAC Notation) of the periodic table of
22 elements.

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MONO-OLEFINS

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27 The mono-olefins to be separated are preferably C₂₋₅₀ mono-olefins, more
28 preferably C₂₋₂₀ mono-olefins. They may include other functional groups,
29 such as hydroxy groups, carboxylic acid groups, heteroatoms, and the like,
30 provided that such groups do not react with either the olefin-complexing salt
31 or the ionic liquid so as to prevent an effective separation.

32 The mono-olefins can be used commercially to form a wide variety of
33 products. For example, the mono-olefins can be used to form polyethylene,
34 polypropylenes, polyisobutylene and other polymers, alcohols, vinyl chloride

1 monomer, acrylonitrile, methyl tertiary butyl ether and other petrochemicals,
2 and a variety of rubbers such as butyl rubber.

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SOURCES OF MONO- AND DI-OLEFINS

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8 Mono- and di-olefin mixtures can be derived from a variety of sources. One
9 source of mono-olefin/di-olefin mixtures is from the dehydrogenation of
10 paraffins over a suitable dehydrogenation catalyst. Other commercial
11 sources of mono- and/or di-olefins include wax hydrocracking; ethylene and
12 propylene derived from ethane, ethane/propane (EP) and flexi-crackers; fluid
13 catalytic cracking (FCC) crackers; naptha crackers; ethenolysis of heavier
14 internal olefins; and ethylene oligomerization. Olefins may also be produced
15 in a Fischer-Tropsch process.

16

17 Catalysts and conditions for performing Fischer-Tropsch synthesis are
18 well known to those of skill in the art, and are described, for example, in EP 0
19 921 184 A1, the contents of which are hereby incorporated by reference in
20 their entirety. In the Fischer-Tropsch synthesis process, liquid and gaseous
21 hydrocarbons are formed by contacting a synthesis gas (syngas) comprising
22 a mixture of H₂ and CO with a Fischer-Tropsch catalyst under suitable
23 temperature and pressure reactive conditions. The Fischer-Tropsch reaction
24 is typically conducted at temperatures of about from 300° to 700°F (149 to
25 371°C) preferably about from 400° to 550°F (204° to 228°C); pressures of
26 about from 10 to 600 psia (0.7 to 41 bars), preferably 30 to 300 psia (2 to 21
27 bars), and catalyst space velocities of about from 100 to 10,000 cc/g/hr.,
28 preferably 300 to 3,000 cc/g/hr.

29 The Fischer-Tropsch products may range from C₁ to C₂₀₀₊ with a
30 majority in the C₅-C₁₀₀₊ range. The reaction can be conducted in a variety of
31 reactor types for example, fixed bed reactors containing one or more catalyst
32 beds, slurry reactors, fluidized bed reactors, or a combination of different type
33 reactors. Such reaction processes and reactors are well known and

1 documented in the literature. Slurry Fischer-Tropsch processes utilize
2 superior heat (and mass) transfer characteristics for the strongly exothermic
3 synthesis reaction and are able to produce relatively high molecular weight,
4 paraffinic hydrocarbons.

5 Fischer-Tropsch chemistry tends to provide a variety of gaseous and
6 liquid products, including unreacted synthesis gas, methane, and C₂₋₄
7 hydrocarbons (a mixture of olefins and paraffins). These gases are typically
8 separated from the liquid products. The methane and other light paraffins
9 can be recycled through an upstream synthesis gas generator. However, the
10 light olefins tend to coke the catalysts, and need to be removed before the
11 recycle gas is sent to the synthesis gas generator. The olefins are typically
12 removed via cryogenic separation. The current invention allows for the
13 removal of the olefins at ambient temperatures using ionic liquids.

14 Typically, about 75% of the C₂₋₈ products from Fischer-Tropsch
15 synthesis are normal alpha-olefins (NAOs). Separation of the NAOs may be
16 accomplished using conventional distillation. However, as noted above, there
17 is only a small difference in relative volatility between an olefin and its
18 corresponding di-olefin and corresponding paraffin with the same number of
19 carbons. Therefore, distillation requires a large number of stages and/or high
20 reflux ratios, and, as a result, is very expensive. The present invention
21 provides an inexpensive method of separating mono-olefins, di-olefins and
22 non-olefins using ionic liquids.

23

24 Other sources of olefins include processes for converting hydrocarbons at
25 high temperature, including steam-cracking, catalytic cracking or deep
26 catalytic cracking to produce relatively high yields of unsaturated
27 hydrocarbons, for example ethylene, propylene, and butenes, are well known
28 in the art. See, for example, U.S. Patent No. 3,407,789 to Hallee et al., U.S.
29 Patent No. 3,820,955 to Woebcke, U.S. Patent No. 4,499,055 to
30 DiNicolantonio, U.S. Patent No. 4,814,067 to Gartside et al., U.S. Patent No.
31 4,828,679 to Cormier, Jr. et al., U.S. Patent No. 3,647,682 to Rabo et al.,
32 U.S. Patent No. 3,758,403 to Rosinski et al., U.S. Patent No. 4,814,067 to
33 Gartside et al., U.S. Patent No. 4,980,053 to Li et al. and U.S. Patent No.
34 5,326,465 to Yongqing et al., the contents of which are hereby incorporated

1 by reference. Many of these also produce mono-olefins and di-olefins, which
2 can be advantageously separated from the mono-olefins according to this
3 invention.

4

5 Steam cracking is a petrochemical process sometimes used in refineries to
6 produce olefinic raw materials (e.g. ethylene) from various feedstock for
7 petrochemical manufacture. The feedstock range from ethane to vacuum
8 gas oil, with heavier feeds giving higher yields of by-products such as
9 naphtha. The most common feeds are ethane, butane, and naphtha. Steam
10 cracking is carried out at temperatures of 1,500 – 1,600 ° F, and at pressures
11 slightly above atmospheric.

12

13 In the cracking reaction of conventional fluid catalytic cracking (FCC) units of
14 petroleum refineries, a hydrocarbon feedstock may be catalytically converted
15 into a variety of products commonly known as slurry oil, heavy cycle oil, light
16 cycle oil, naphtha, and various components lighter than naphtha, including
17 paraffins and olefins. Of course, the particular products from any particular
18 cat cracker unit depend on a variety of factors including the design and needs
19 of the petroleum refinery. The products that include naphtha and lighter
20 components are separated into various product streams. The products from
21 the gas plant vary depending on the particular refinery design but commonly
22 include naphtha, C₄s (butylenes and butanes), propane, propylene, and a
23 stream (commonly referred to as "fuel gas") that contains ethane and lighter
24 components (C₂ and lighter), including light olefinic components such as
25 ethylene and propylene.

26

27 The product yields from a conventional FCC unit vary depending on a wide
28 range of design and operating parameters, such as feedstock quality, the
29 amount of regenerated catalyst supplied to the riser reactor per volume or
30 mass unit of feed, the temperature at which the cracking reaction takes place,
31 the residence time of the feed in the riser reactor, and the like. The
32 conventional fluid catalytic cracking unit may process one or more feedstocks.
33 Typical feedstocks may include atmospheric gas oils, heavier feedstocks from

1 vacuum distillation units, and streams from other units such as cokers,
2 visbreakers, hydrotreaters, and hydrocrackers.

3

4 NON-OLEFINS

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6 Non-olefins present in the mono-olefin and di-olefin mixtures of this invention
7 include paraffins, oxygenates, and/or aromatics, as well as hydrogen, water,
8 carbon monoxide, carbon dioxide, acetylenics, sulfur and nitrogen-containing
9 impurities and a wide variety of other materials which may be present in such
10 mixtures.

11

12 Non-olefins such as paraffins and aromatics are often desirable products,
13 particularly for use in distillate fuel compositions. However, it is often
14 desirable to separate them from mono- and/or di-olefins, particularly if the
15 mono- and/or di-olefins are desired products themselves.

16

17 Sulfur impurities are preferably removed from the feedstocks before they are
18 added to the ionic liquid/metal salt solution, suspension or dispersion. This
19 can be accomplished by hydrotreatment or other means well known to those
20 of skill in the art.

21

22 Acetylene impurities are potentially undesirable, as they can form potentially
23 explosive salts with various metals. Acetylene impurities are commonly
24 removed by selective hydrogenation. The hydrogenation system may employ
25 any of the catalysts well known to selectively hydrogenate acetylenics and
26 dienes, for example acetylene, methyl acetylene and propadiene, as used, for
27 example, in ethane crackers. Group VIII metal hydrogenation catalysts are
28 the most commonly used and are preferred. Group VIII metal hydrogenation
29 catalysts are ordinarily associated with a support, such as alumina. One
30 preferred catalyst is a low surface area granular alumina impregnated with
31 about 0.1 weight percent palladium. Examples of other catalysts which can
32 be used include Raney nickel, ruthenium-on-aluminum, nickel
33 arsenide-on-aluminum, and mixtures thereof. The catalysts ordinarily contain
34 a Group VIII metal in an amount ranging from about 0.01 to about 1 percent

1 by weight of the total catalyst. These and other catalysts are well known to
2 those of skill in the art, and are described, for example, in U.S. Patent
3 No. 3,679,762 to La Hue et al., U.S. Patent No. 4,571,442 to Cosyns et al.,
4 U.S. Patent No. 4,347,392 to Cosyns et al. U.S. Patent No. 4,128,595 to
5 Montgomery, U.S. Patent No. 5,059,732 to Cosyns et al., and U.S. Patent
6 No. 4,762,956 to Liu et al., the contents of which are hereby incorporated by
7 reference.

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9

METAL SALTS

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11 The metal salts useful according to this invention are selected from heavy
12 metal ions which form chemical complexes with olefins, e.g., copper(I),
13 silver(I), gold(I), nickel(II), platinum(II) and palladium(II). Silver (I) salts are
14 particularly preferred, although Pd salts may be preferred for separating
15 olefins higher than C₈. Useful silver(I) salts include silver acetate, silver
16 nitrate, silver fluoride, silver tetrafluoroborate, and mixtures thereof. Silver
17 tetrafluoroborate is particularly preferred.

18

19 Copper salts include copper halide salts, and can be buffered with a soluble
20 organic nitrogen ligand, such as pyridine, piperidine, hydroxypropionitrile,
21 diethylene triamine, acetonitrile, formamide and acetamide, derivatives
22 thereof and mixtures thereof. Pyridine and/or hydroxypropionitrile are
23 particularly preferred.

24

25 Salts such as iron (II), cobalt (II) and nickel (II) salts can also be used,
26 provided they are effective at complexing the olefins.

27 The concentration of metal salt in the ionic liquid is typically at least about 0.5
28 moles of salt per liter of solvent, and preferably at least about 2 moles of salt
29 per liter of solvent.

30

31 It does not matter whether the salts are dissolved or merely suspended or
32 dispersed in the ionic liquids for them to function as intended. Further, it
33 tends not to matter whether the salts dissolve in, or are reacted with, the ionic

1 liquids. For example, it appears that silver salts tend to dissolve in the ionic
2 liquids, and copper salts tend to react with the ionic liquids, and both tend to
3 complex the desired olefins.

4

5 The salts are able to complex the olefins at a variety of concentrations. At
6 relatively high concentrations, the olefin/metal salt complex may precipitate
7 from solution. If this precipitation is not desirable, more dilute
8 solutions/dispersions should be used. However, this precipitation may be
9 desirable and allow one to separate various olefins by precipitation and
10 subsequent filtration.

11

12 Metal salts such as Ag^+ salts are believed to form complexes with di-olefins in
13 which two double bonds from a first diolefin and a single double bond from a
14 second di-olefin complex with a single Ag^+ ion, and the second double bond
15 from the second di-olefin and two double bonds from a third di-olefin form a
16 complex with a second Ag^+ ion.

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18 IONIC LIQUIDS

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20 Ionic liquids are a category of compounds which are made up entirely of ions
21 and are liquid at or below process temperatures. Usually, such compounds
22 produce solids with high melting points, for example, above 450°C . These
23 solids are commonly known as 'molten salts'. An example of a common
24 'molten salt' is NaCl , with a melting point of 800°C . Ionic liquids differ from
25 'molten salts', in that they have low melting points, for example, from -100°C
26 to 200°C . They tend to be liquid over a very wide temperature range, with a
27 liquid range of up to about 500°C . Ionic liquids are generally non-volatile,
28 with no effective vapor pressure. Most are air and water stable, and are good
29 solvents for a wide variety of inorganic, organic, and polymeric materials.
30 They are used herein to dissolve, suspend or disperse the olefin-complexing
31 metal salts.

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33 The properties of ionic liquids can be tailored by varying the cation and anion

1 pairing. Ionic liquids and their commercial applications are described, for
2 example, in J. Chem. Tech. Biotechnol., 68:351-356 (1997), Chem. Ind.,
3 68:249-263 (1996), J. Phys. Condensed Matter, 5:(supp 34B):B99-B106
4 (1993); Chemical and Engineering News, March 30, 1998, 32-37; J. Mater.
5 Chem., *:2627-2636 (1998); and Chem. Rev., 99:2071-2084 (1999), the
6 contents of which are hereby incorporated by reference.

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8 Many ionic liquids are formed by reacting a nitrogen-containing heterocyclic
9 ring, preferably a heteroaromatic ring, with an alkylating agent (for example,
10 an alkyl halide) to form a quaternary ammonium salt, and performing ion
11 exchange or other suitable reactions with various Lewis acids or their
12 conjugate bases to form ionic liquids. Examples of suitable heteroaromatic
13 rings include pyridine, substituted pyridines, imidazole, substituted imidazoles,
14 pyrrole and substituted pyrroles. These rings can be alkylated with virtually
15 any straight, branched or cyclic C₁₋₂₀ alkyl group, but preferably the alkyl
16 groups are C₁₋₁₂ groups, since groups larger than this tend to produce low
17 melting solids rather than ionic liquids. Various quaternary phosphonium
18 compounds, thioethers, and cyclic and non-cyclic quaternary ammonium salts
19 have also been used.

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21 Counterions which have been used include chloroaluminate, bromoaluminate,
22 gallium chloride, tetrafluoroborate, tetrachloroborate, hexafluorophosphate,
23 nitrate, trifluoromethane sulfonate, methylsulfonate, *p*-toluenesulfonate,
24 hexafluoroantimonate, hexafluoroarsenate, tetrachloroaluminate,
25 tetrabromoaluminate, perchlorate, hydroxide anion, copper dichloride anion,
26 iron trichloride anion, antimony hexafluoride, copper dichloride anion, zinc
27 trichloride anion, as well as various lanthanum, potassium, lithium, nickel,
28 cobalt, manganese, and other metal ions.

29

30 The ionic liquids can be neutral, basic or acidic. Neutral ionic liquids should
31 be used if the desired mono- or di- olefins are not to be isomerized. If it does
32 not matter whether the olefins are isomerized (and if the non-olefins are not
33 acid-sensitive), either neutral or acidic ionic liquids can be used. Acidic ionic

1 liquids can be used, for example, when the desired goal is to remove olefins
2 and provide a paraffinic hydrocarbon stream, and when the olefins are
3 unlikely to isomerize.

4

5 In one embodiment, a library of ionic liquids is prepared, for example by
6 preparing various alkyl derivatives of the quaternary ammonium cation, and/or
7 varying the associated anions. The acidity of the ionic liquids can be
8 adjusted, for example, by varying the molar equivalents, types and
9 combinations of Lewis and Bronsted acidic components.

10

11 METHODS FOR SEPARATING OLEFINS FROM NON-OLEFINS

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13 Mono-olefins, di-olefins and mixtures thereof can be selectively removed from
14 mixtures including the olefins and non-olefins, such as paraffins, oxygenates
15 and aromatics. The olefins are brought into contact with olefin-complexing
16 metal salts to form a metal salt/olefin complex. In one embodiment, di-olefins
17 are selectively complexed over mono-olefins and non-olefins, with olefin-
18 complexing metals salts which are dissolved, dispersed or suspended in an
19 ionic liquid. The mono-olefins and non-olefins can then be separated from
20 the complexed di-olefins, for example by decantation or distillation. Then, the
21 mono-olefins can be complexed, and the non-complexed non-olefins
22 separated from the complexed mono-olefins. Both, the di-olefins and mono-
23 olefins, may be recovered from the metal salt/olefin complex by desorption.

24

25 In another embodiment, the mono- and di-olefins are both complexed, and
26 the non-olefins are removed. Then, the mono-olefins can be selectively
27 desorbed, separating them from the complexed di-olefins. Finally, the
28 complexed di-olefins can be desorbed, typically at higher temperatures and/or
29 lower pressures than those at which the mono-olefins are desorbed.

30

31 The flow of olefin-containing mixtures over/through the ionic liquid can be, for
32 example, co-current, counter-current, or staged in stirred tanks.

33 Countercurrent is preferred as it is the most efficient.

1

2 METHODS FOR SELECTIVELY COMPLEXING DI-OLEFINS OVER MONO-
3 OLEFINS

4

5 According to this invention, metal salts selectively complex di-olefins over
6 mono-olefins. This selective complexation can be exploited to selectively
7 remove di-olefins from a mixture including di-olefins and mono-olefins. Since
8 both mono-olefins and di-olefins complex with the metal salts, where di-
9 olefins are to be complexed with a high selectivity, it will be important to
10 adjust the equivalents of the metal salt to essentially complex only the di-
11 olefins. Mixtures containing di-olefins and mono-olefins can be contacted
12 with a solution, suspension or dispersion of an olefin-complexing metal salt in
13 an ionic liquid, for example by direct addition, and the di-olefin can be
14 selectively complexed by maintaining the olefin mixture in contact with the
15 ionic liquid solution, suspension or dispersion, with or without agitation, for
16 sufficient residence time to permit the complexation of the di-olefin, for
17 example from about 1 minute to about 24 hours, or preferably about 10
18 minutes to about 8 hours. The di-olefin/metal salt complex tends to be either
19 dissolved or suspended in the ionic liquid, or precipitate out. When the
20 complex forms a precipitate, it can be removed, for example by filtration.
21 When the complex is dissolved, dispersed or suspended in the ionic liquid,
22 the non-complexed mono-olefin can be separated, for example by
23 decantation or distillation. The complexed di-olefins can be isolated, for
24 example by desorption. When the di-olefin has been removed, the enriched
25 mono-olefin can be further purified or used directly, depending on whether
26 there are additional contaminants.

27

28 According to one embodiment, the method of this invention can be carried out
29 via an extractive distillation process. A mono-olefin/di-olefin containing
30 mixture is added to a solution, suspension or dispersion of an olefin-
31 complexing metal salt in an ionic liquid in a first distillation apparatus (10),
32 and the di-olefin is maintained in contact with the ionic liquid for sufficient
33 time to complex with the metal salt, for example from about 1

1 minute to about 24 hours, or preferably about 10 minutes to about 8 hours.
2 After the complexation is essentially complete, for example after about 8
3 hours, the non-complexed mono-olefin is isolated via distillation (20). Then,
4 the di-olefin/metal salt complex and ionic liquid are sent to a second
5 distillation apparatus (30), where the di-olefin is desorbed and isolated via
6 distillation (40). The bottoms from the second distillation apparatus, including
7 the ionic liquid - metal salt solution, suspension or dispersion is then sent
8 back to the first distillation apparatus.

9
10 The method can also be carried out via a liquid-liquid extraction process. A
11 mono-olefin/di-olefin mixture is added to a solution, suspension or dispersion
12 of an olefin-complexing metal salt in an ionic liquid in a first liquid mixer (50),
13 and can be passed through a series of mixers (60 and 70), during which time
14 the di-olefin is permitted to complex with the metal salt. After the
15 complexation is essentially complete, for example after about 8 hours, the
16 mixing is stopped, and the non-complexed mono-olefin is isolated via
17 decantation. Then, the di-olefin/metal salt complex and ionic liquid are
18 sent to a regeneration apparatus (80), where the di-olefin is desorbed and
19 isolated via distillation. The bottoms from the regeneration apparatus,
20 including the ionic liquid/metal salt solution, suspension or dispersion is then
21 sent back to the series of mixers.

22
23 Non-complexed non-olefins, if present, can be removed from complexed
24 olefins, for example by decantation or distillation. After di-olefins are
25 removed, it may be desirable to complex the remaining mono-olefins and
26 then remove any non-complexed non-olefins.

27

28 METHODS FOR DESORBING OLEFINS FROM THE METAL SALT- 29 COMPLEXES

30

31 According to the present invention, desorption is effected, preferably in a
32 packed tower or flash drum, by dissociating the olefins from the olefin/metal
33 salt complexes using a combination of increased temperature and lower

1 pressure. At temperatures ranging from about 65°C to about 110°C,
2 preferably from about 70°C to about 85°C, and pressures ranging from about
3 5 psig to about 50 psig, the mono-olefins readily dissociate from the metal
4 salt complexes. Inexpensive quench water can conveniently be used as the
5 heating medium for olefin stripper temperatures in the lower end of the range,
6 as well as any other heating means known to those of ordinary skill in the art.

7 The olefin stripper is preferably equipped with a water wash section in the top
8 of the stripper to prevent entrainment of the scrubbing solution with the
9 desorbed gases.

10

11 According to one embodiment, the olefin stripper or flash drum may include
12 multi-stage stripping or flashing for increased energy efficiency. In such
13 systems, the olefin-rich solution is flashed and stripped at progressively
14 higher temperatures and/or lower pressures. The design of such systems is
15 well known to those skilled in the art.

16

17 Once the mono-olefins are stripped from the ionic liquid solution, the di-
18 olefins may then be desorbed in a reclaimer or regenerator. The stripped
19 ionic liquid solution can be removed from the olefin stripper for reclaiming and
20 recycling (regeneration). The reclaimer typically operates at a higher
21 temperature than the olefin stripper. Typically, the temperature in the
22 reclaimer ranges from about 100°C to about 150°C, preferably from about
23 120°C to about 140°C. The pressure ranges from about 5 psig to about 50
24 psig, preferably from about 10 psig to about 30 psig. The heating duty may
25 be supplied by steam or any other means known to those skilled in the art. At
26 these higher temperatures, di-olefins are dissociated from the metal salt
27 complexes.

28

29 METHODS FOR SELECTIVELY DESORBING MONO-OLEFINS OVER 30 DI-OLEFINS

31

32 According to this invention, the complexed mono-olefins selectively desorb
33 over complexed di-olefins. This selective desorption can be exploited to

1 selectively remove mono-olefins from a mixture including di-olefins and mono-
2 olefins. Since both mono-olefins and di-olefins complex with the metal salts,
3 the equivalents of the metal salt should be sufficient to complex both the
4 mono- and di-olefins. Mixtures containing di-olefins and mono-olefins can be
5 contacted with a solution, suspension or dispersion of an olefin-complexing
6 metal salt in an ionic liquid, for example by direct addition, and the olefins can
7 be complexed by maintaining the olefin mixture in contact with the ionic liquid
8 solution, suspension or dispersion, with or without agitation, for sufficient
9 residence time to permit the complexation of the olefins, for example from
10 about 1 minute to about 24 hours, or preferably about 10 minutes to about 8
11 hours. Since the complexed olefins tend to be dissolved or suspended in the
12 ionic liquid, any non-complexed non-olefins can be separated, for example by
13 decantation or distillation.

14

15 After any non-olefins are separated, the complexed mono-olefins can be
16 selectively desorbed from the metal salts. Mono-olefins are not as tightly
17 bound as di-olefins, and when subjected to conditions of elevated
18 temperature and reduced pressure, tend to desorb faster than diolefins. After
19 the mono-olefins have desorbed from the metal salts, the temperature can be
20 raised and/or the pressure decreased, and the di-olefins desorbed.

21

22 In one embodiment, a mixture includes di-olefins, mono-olefins and non-
23 olefins such as paraffins and aromatics. The di-olefins can be selectively
24 complexed and separated from this mixture as described above. Then, the
25 mono-olefins can be complexed and separated from the non-olefins in a
26 similar manner. Finally, both the mono- and di-olefins may be desorbed and
27 recovered as described above.

28

29

COMMERCIAL APPLICATIONS

30

31 There are many commercial applications for the separation technology
32 described herein. For example, the technology can be used in ethane,
33 ethane/propane and flexi-crackers to separate propadiene and propylene
34 from propane, and then to separate propylene from propadiene.

1 Commercially, this is typically done using expensive distillation facilities.
2 Such facilities are expensive because the boiling point difference between
3 propylene and propadiene is small, and the separation must be done at very
4 low temperatures and/or at very high pressures. The present separation
5 method can be performed at room temperature and atmospheric pressure,
6 using simple agitation. The major cost is due to the silver ions, which are
7 recycled and reused.

8
9 Another commercial use is in the alkylation of aromatics, particularly where
10 paraffins are dehydrogenated to form mixtures of mono- and di-olefins, and
11 which also tend to include unreacted paraffins. The current technology for
12 removing the di-olefins from the mono-olefins involves selective
13 hydrogenation. The present methodology merely involves complexing the di-
14 olefins with the metal ions in the ionic liquid. A preferred way to do this
15 involves bubbling the olefin-containing stream, in the form of a gas rather
16 than a liquid, through the ionic liquid.

17
18 Yet another commercial use is in olefin oligomerization, for example ethylene
19 and propylene oligomerization. Such oligomerization reactions are commonly
20 performed in normal alpha-olefin synthesis, and the separation methods can
21 be used to upgrade the product stream to remove di-olefins.

22 A potential advantage of the methods described herein are that the di-olefins
23 are not converted to mono-olefins, and can be purified and used in
24 commercial applications where di-olefins are required, for example in Diels-
25 Alder and similar chemistry.

26

27 COMBINATORIAL CHEMISTRY APPROACHES

28

29 Because of the wide applicability of this invention to a broad variety of
30 separations, a combinatorial approach can be used to identify optimum ionic
31 liquids and/or metal salts for separating the di-olefins from mono-olefins and
32 non-olefins. An advantage to the combinatorial approach is that the choice of
33 ionic liquid, metal salt and the like can be tailored to specific applications.

1

2 The scale of the separations in combinatorial chemistry is preferably in the
3 range of about 1 mg to 200 g, more preferably between one mg and 10 g,
4 although the scale can be modified as desired depending on the equipment
5 used. Those of skill in the art can readily determine appropriate sets of
6 reactions and reaction conditions to generate and/or evaluate the libraries of
7 interest.

8

9 The ionic liquids can be laid out in a logical fashion in multi-tube arrays or
10 multi-well plates in the form of arrays of ionic liquids. Preferably, the ionic
11 liquids all have a central core structure, and have various modifications which
12 permit the identification of structure-activity relationships with which to
13 determine optimum compounds for a particular use. The metal salts or
14 combinations thereof can also be laid out in a logical fashion, for example in
15 arrays. In a preferred embodiment, an A x B array is prepared, with various
16 combinations of ionic liquids and metal salts. However, it is also possible to
17 evaluate a single ionic liquid with a plurality of metal salts, optionally at
18 different concentrations, and then repeat the process as desired with a
19 plurality of different ionic liquids.

20

21 The ability of the particular combination of ionic liquid and metal salt at
22 performing a desired separation can be measured and correlated to specific
23 combinations. The array can be ordered in such a fashion as to expedite
24 synthesis and/or evaluation, to maximize the informational content obtained
25 from the testing and to facilitate the rapid evaluation of that data. Methods for
26 organizing libraries of compounds are well known to those of skill in the art,
27 and are described, for example, in U.S. Patent No. 5,712,171 to
28 Zambias et al. Such methods can readily be adapted for use with the ionic
29 liquids and metal salts described herein.

30

31 By screening multiple synthetic variations of a core molecule, the selection of
32 the optimal candidate is more a function of the data collection method than
33 the "rational" basis for selecting a useful ionic liquid and/or metal salt. The

1 desired physical and chemical properties for the ionic liquid, when used as a
2 solvent or dispersing agent for a particular metal salt, and for separating a
3 particular product mixture, can be rapidly optimized, and directly correlated
4 with the structural changes within a particular array or sub-array.

5

6 The ionic liquids are typically formed by first forming a desired (cyclic or non-
7 cyclic) quaternary ammonium salt, and then combining the salt with an
8 appropriate anion precursor (typically a metal salt such as aluminum chloride,
9 zinc chloride, sodium hexafluorophosphate, sodium tetrafluoroborate,
10 hexafluorophosphoric acid, tetrafluoroboric acid and the like). Side product
11 salts can be removed, for example, by filtration. In cases where the anion
12 precursor was an acid, the acid side product such as HCl can be removed by
13 extraction or by gently heating the ionic liquid under vacuum.

14

15 The separations using the ionic liquids/metal salts in the libraries generally
16 involve contacting appropriate mixtures of mono- and di-olefins to the tubes
17 or wells in the multi-tube rack or multi-well plate, and allowing the olefin-
18 complexation reactions to take place. Where a stoichiometric amount of
19 metal complexing agent is used to selectively complex the di-olefins, the
20 olefin layer can be analyzed, for example by gas chromatography (GC), for di-
21 olefin concentration. Alternatively, where both mono-olefins and di-olefins are
22 complexed, the complexed mixture can be subjected to conditions of
23 relatively high temperature and low pressure, and as the olefins become
24 desorbed from the metal salts, the products can be monitored as they are
25 desorbed and the appearance of di-olefins monitored. Ideal results would be
26 those in which mono-olefins are desorbed first, and where little or no mono-
27 olefins are still being desorbed under conditions where the di-olefins begin
28 desorbing. Here the desired separation involves selectively separating di-
29 olefins, mono-olefins and non-olefins, the presence or absence of these
30 components can be evaluated, for example using GC, to determine the
31 success of the particular combination of ionic liquid and olefin-complexing
32 metal salt.

33

1 Robotic arms and multi-pipet devices are commonly used to add appropriate
2 reagents to the appropriate tubes in multi-tube racks, or wells in multi-well
3 plates. When appropriate, the chemistry can be performed in an inert
4 atmosphere. The tubes can each be covered with a rubber septum to avoid
5 contamination, and the reagents added via injection.

6

7 In one embodiment, the separations are carried out via computer control.
8 The identity of each of the ionic liquids and metal salts can be stored in a
9 computer in a "memory map" or other means for correlating the data
10 regarding the chemical reactions to the ionic liquids in the multi-tube racks or
11 multi-well plates.

12

13 Alternatively, the chemistry can be performed manually, preferably in multi-
14 tube racks or multi-well plates, and the information stored, for example on a
15 computer.

16

17 Any type of multi-well plate or multi-tube array commonly used in
18 combinatorial chemistry can be used. Preferably, the number of wells or
19 tubes is in excess of 30, and there is a tube in at least 60 percent of the
20 positions in each multi-tube array. The shape of the rack is not important, but
21 preferably, the rack is square or rectangular. The tubes can be made, for
22 example, from plastic, polymers, glass or metal, such as stainless steel,
23 depending on the type of anions used in the ionic liquid or in the metal salt.
24 Any type of liquid handler that can add reagents to, or remove reagents from,
25 the wells and/or tubes can be used. Many involve the use of robotic arms
26 and robotic devices. Suitable devices are well known to those of skill in the
27 art of combinatorial chemistry.

28

29 Any device that can take samples from the individual wells and/or tubes and
30 analyze the resulting hydrocarbon phase can be used. Preferably, the device
31 is a chromatographic device, such as an analytical or preparative scale high
32 performance liquid chromatography (HPLC), GC or column chromatography,
33 although other devices can be envisioned, depending on the chemistry

1 performed. Since the ionic liquid is non-volatile, the sample is preferably
2 taken from the hydrocarbon phase, which is immiscible with the ionic liquid.
3
4 Preferably, in those embodiments in which a chromatographic column (HPLC,
5 GC or column chromatography) is used, the device has the ability to identify
6 when the compound of interest is eluting from the column. Various means
7 have commonly been used to identify when compounds of interest are eluting
8 from a column, including ultra-violet (UV), infra-red (IR), thin layer
9 chromatography (TLC), gas chromatography-mass spectrometry (GC-MS),
10 free induction decay (FID), nuclear magnetic resonance (NMR), evaporative
11 light scattering detector (ELSD), nitrogen detection and the like. Any of these
12 means, and others known to those of skill in the art, can be used, alone or in
13 combination. However, when petroleum chemistry is being evaluated, the
14 product stream often does not include UV-active compounds. In this type of
15 embodiment, the analytical equipment preferably includes an ELSD detector.
16
17 The entire eluent from the chromatographic columns described above can be
18 sent through an appropriate detector and then to a mass spectrometer.
19 When sample collection is desired, it can begin when the UV or mass
20 spectrometry signal indicates the presence of the eluting compound, and can
21 end when the UV signal indicates that the compound has finished eluting
22 from the column. Mass spectrometry can verify that the eluted compound is
23 really the compound of interest. Particularly when mono-olefins, di-olefins,
24 oxygenates and paraffins are evaluated using the library, a combination of
25 GC and MS is used, particularly since mono- and di-olefins may elute from
26 the GC column at similar rates.
27
28 The device preferably includes a computer system capable of storing
29 information regarding the identity of the ionic liquids, metal salts and the
30 product streams obtained when combinations of ionic liquids and metal salts
31 are used to separate the mono- and di-olefins from each other and optionally
32 from non-olefins. Software for managing the data is stored on the computer.
33

1 Relational database software can be used to correlate the identity of the ionic
2 liquids, the metal salts, and the analytical data from each product stream.
3 Numerous commercially available relational database software programs are
4 available.

5
6 Relational database software is a preferred type of software for managing the
7 data obtained during the processes described herein. However, any software
8 that is able to create a "memory map" of the ionic liquids in the tubes and
9 correlate that information with the information obtained from the chemical
10 reactions can be used. This type of software is well known to those of skill in
11 the art.

12
13 The present invention will be better understood with reference to the following
14 non-limiting examples.

15
16 Example 1: Synthesis of Neutral Ionic Liquids

17
18 A variety of quaternary amine ionic liquid precursors were prepared as
19 follows. 1-Methylimidazole was measured into a stainless-steel autoclave
20 along with a slight molar excess of 1-chlorobutane. The autoclave was
21 sealed, pressurized with 75 psig of nitrogen, and heated to 90°C for 18 h.
22 The autoclave was then cooled to room temperature and the contents were
23 placed on a rotary evaporator at 95°C for several hours to remove any
24 unreacted chlorobutane and 1-methylimidazole. A ^1H NMR of the product
25 indicated the formation of 1-butyl-3-methylimidazolium chloride (bmim^+Cl^-).
26 The reaction was repeated with 1-chlorohexane to give 1-hexyl-3-
27 methylimidazolium chloride (hmim^+Cl^-). This general procedure was repeated
28 with pyridine to give the ionic liquid precursors N-butylpyridinium chloride
29 ($\text{butpyr}^+\text{Cl}^-$) and N-hexylpyridinium chloride ($\text{hexpyr}^+\text{Cl}^-$), although a higher
30 reaction temperature (130°C) was required to achieve high yields.

31
32 Two different procedures were used for conducting an anion exchange
33 reaction to give a neutral ionic liquid. In one procedure, the precursor is

1 dissolved in acetone and reacted with the sodium salt of the desired anion
 2 (NaBF_4 or NaPF_6). In the other procedure, the precursor is dissolved in water
 3 and reacted with the acid form of the anion (HBF_4 or HPF_6). The precursor
 4 hmim^+Cl^- was used make the ionic liquid $\text{hmim}^+\text{PF}_6^-$ by both procedures. The
 5 miscibility of the resulting ionic liquid with water was greatly influenced by the
 6 route of synthesis. The ionic liquid made by the acid route was immiscible
 7 with water, while the ionic liquid made using the sodium salt was miscible with
 8 water. While not wishing to be bound to a particular theory, it is believed that
 9 this change in miscibility with water is due to the presence of residual NaCl in
 10 the liquid made via the salt route.

11

12 The acid procedure was then used to generate a variety of ionic liquids using
 13 the precursors synthesized above, as well as additional precursors purchased
 14 from commercial suppliers. These reactions are summarized in Table 1.

15

16 Table 1. Ionic Liquids

17

Ionic Liquid Precursor	Anion Source	Ionic Liquid
Bmim^+Cl^-	HBF_4	$\text{Bmim}^+\text{BF}_4^-$
Bmim^+Cl^-	HPF_6	$\text{Bmim}^+\text{PF}_6^-$
Hmim^+Cl^-	NaBF_4	$\text{Hmim}^+\text{BF}_4^-$
Hmim^+Cl^-	HBF_4	$\text{Hmim}^+\text{BF}_4^-$
Hmim^+Cl^-	NaPF_6	$\text{Hmim}^+\text{PF}_6^-$
Hmim^+Cl^-	HPF_6	$\text{Hmim}^+\text{PF}_6^-$
$\text{Hexpyr}^+\text{Cl}^-$	HBF_4	$\text{Hexpyr}^+\text{BF}_4^-$

Hexpyr ⁺ Cl ⁻	HPF ₆	Hexpyr ⁺ PF ₆ ⁻ (mp = 38.7 °C)
(C ₈ H ₁₇) ₃ MeN ⁺ Cl ⁻	HBf ₄	(C ₈ H ₁₇) ₃ MeN ⁺ BF ₄ ⁻ (mp = 58.8°C)
(C ₈ H ₁₇) ₃ MeN ⁺ Cl ⁻	HPF ₆	(C ₈ H ₁₇) ₃ MeN ⁺ PF ₆ ⁻
Me ₃ NH ⁺ Cl ⁻	HBf ₄	Me ₃ NH ⁺ BF ₄ ⁻ (mp = 183°C)
Bu ₂ Me ₂ N ⁺ Cl ⁻	HPF ₆	Bu ₂ Me ₂ N ⁺ PF ₆ ⁻ (mp = 154.5°C)
(C ₁₆ H ₃₃)Me ₃ N ⁺ Cl ⁻	HPF ₆	(C ₁₆ H ₃₃)Me ₃ N ⁺ PF ₆ ⁻ (mp = 131.7°C)
Bu ₂ Me ₂ N ⁺ Cl ⁻	HBf ₄	Bu ₂ Me ₂ N ⁺ BF ₄ ⁻ (mp = 75.1 °C)

1 bmim = 1-butyl-3-methylimidazolium

2 hexpyr = N-hexylpyridinium

3 hmim = 1-hexyl-3-methylimidazolium

4

5 Example 2: Solubility of Cu and Ag complexes in Ionic Liquids

6 The present example investigated the possibility of immobilizing Ag and Cu
 7 ions in an ionic liquid. The Ag(I) and Cu(I) compounds have been proposed
 8 for use in the selective complexation of dienes over mono-olefins. The
 9 immobilization of these ions can be accomplished by either dissolving Ag and
 10 Cu salts in an existing ionic liquid or by reacting an ionic liquid precursor with
 11 a Ag or Cu complex to create a new ionic liquid.

12 Several screening reactions were conducted to determine whether Ag and
 13 Cu complexes were soluble in ionic liquids. The results are summarized in
 14 Table 2.

1 Table 2. Solubility of Ag and Cu ion in ionic liquids

2

Ionic Liquid or Precursor	Salt	Soluble?
Bmim ⁺ BF ₄ ⁻	AgBF ₄	Yes
Bmim ⁺ PF ₆ ⁻	AgPF ₆	No
Bmim ⁺ Cl ⁻	AgCl	No
Hmim ⁺ Cl ⁻	AgCl	No
Hexpyr ⁺ Cl ⁻	AgCl	No
Bmim ⁺ Cl ⁻	CuCl	Yes
Hmim ⁺ Cl ⁻	CuCl	Yes
Hexpyr ⁺ Cl ⁻	CuCl	Yes

3

4 As shown above, an attempt was made to dissolve the Ag salts in ionic liquids
5 that contained the same anions. For example, AgBF₄ was combined with
6 bmim⁺BF₄⁻ and AgPF₆ was combined with bmim⁺PF₆⁻. AgBF₄ was soluble in
7 the ionic liquid. Neither AgPF₆ nor AgCl dissolved in the ionic liquids that
8 were tested. Attempts were made to dissolve CuCl in a couple of different
9 ionic liquids and ionic liquid precursors. The CuCl dissolved in bmim⁺Cl⁻,
10 hmim⁺Cl⁻, and hexpyr⁺Cl⁻. It is believed that the CuCl participated in a
11 complexation reaction to give new ionic liquids with CuCl₂⁻ anions.

Example 3: Use of Ionic Liquids Containing Ag(I) and Cu(I) Salts for
Diene Coordination

This example evaluated the use of Ag(I) and Cu(I) compounds immobilized in ionic liquids for the selective complexation of dienes. The adsorption of 1-butene gas by the ionic liquid samples was measured and is summarized in Table 3. The ionic liquid samples containing varying amounts of dissolved AgBF_4 showed reversible absorption of the butene gas while the ionic liquids containing the CuCl_2^- anion did not show any appreciable absorption. For the Ag-containing ionic liquids, the ratio of butene absorbed to Ag was slightly higher than 1. This suggests that the Ag coordinates more than one olefin at a time which would make an Ag-diene complex more thermodynamically stable. Therefore, these Ag-containing ionic liquids are able to selectively coordinate dienes over mono-enes.

As a control experiment, the Ag-containing ionic liquids were also tested for butane absorption. No appreciable absorption was detected. This again suggests that the Ag is forming a complex with the olefin and that the gases are not merely dissolving in the ionic liquid.

1 Table 3. Gas Absorption by Ionic Liquids Containing Ag(I) and Cu(I) salts.

2

Ionic Liquid	Salt	Gas	Wt% Gas Absorbed	Mols Gas/mols M(I)
Bmim ⁺ BF ₄ ⁻	5% AgBF ₄	1 – butene	1.45	1.32
Bmim ⁺ BF ₄ ⁻	10% AgBF ₄	1- butene	1.89	0.87
Bmim ⁺ BF ₄ ⁻	25% AgBF ₄	1- butene	7.69	1.30
Bmim ⁺ Cl ⁻	1.0 equiv CuCl	1- butene	0.03	Nc
Bmim ⁺ Cl ⁻	2.0 equiv CuCl	1- butene	0.15	Nc
Hexpyr ⁺ Cl ⁻	1.0 equiv CuCl	1- butene	0.60	Nc
Bmim ⁺ BF ₄ ⁻	5% AgBF ₄	Butane	0.13	0.10
Bmim ⁺ BF ₄ ⁻	10% AgBF ₄	Butane	0	0
Bmim ⁺ BF ₄ ⁻	25% AgBF ₄	Butane	2.56	0.35

3

4 bmim = 1-butyl-3-methylimidazolium;

5 hexpyr = N-hexylpyridium;

6 nc = not calculated

1 Next, a mixture of hexene and 1,5 hexadiene was mixed in n-decane and
 2 exposed to four ionic liquid solutions. The ionic liquid solutions were 1-butyl-
 3 3-methyl-imidazolium tetrafluoroborate ($\text{Bmim}^+\text{BF}_4^-$) mixed with 0%, 5%,
 4 10%, and 25% AgBF_4 to form silver containing ionic liquids. The results
 5 showed a preference for adsorbing the 1,5 hexadiene over the hexene. The
 6 results are shown in Table 4.

8 Table 4. Selective Absorption of dienes over mono-olefins

	Mol Hexene/mol Ag^+	Mol Hexadiene/mol Ag^+	Hexadiene/hexene
0% AgBF_4	N/A	N/A	1.66
5% AgBF_4	0	1.4	N/A
10% AgBF_4	0.27	1.1	4.0
25% AgBF_4	0.42	1.1	2.6

10
 11 The ionic liquids also show an affinity for adsorption of dienes over alpha
 12 olefins, and alpha olefins over paraffins. The same ionic liquids were run in a
 13 TGA (total gas adsorption) system to measure the uptake of butane, butene,
 14 and 1,3 butadiene. The liquids show very little uptake of the butane because
 15 it contains no double bonds to interact with the Ag^+ . Higher uptakes of the
 16 olefins showed the ability of metal infused ionic liquids to serve as
 17 adsorbents. The results are shown below in Table 5.

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1 Table 5. Selective Absorption of dienes over mono-olefins over paraffins

2

	Mol butane/mol Ag ⁺	Mol butene/mol Ag ⁺	Mol 1,3-butadiene/mol Ag ⁺
5% AgBF ₄	0.1	1.3	3.7
10% AgBF ₄	0	0.8	2.3
25% AgBF ₄	0.2	1.3	1.3

3

4 Next, a mixture of hexene and 1,5 hexadiene was mixed in n-decane and
 5 exposed to an ionic liquid solution containing a copper triflate. The ionic
 6 liquid solution was 1-butyl-3-methyl-imidazolium/copper
 7 trifluoromethanesulfonate (Bmim/CuOTf). The results showed a preference
 8 for adsorbing the 1,5 hexadiene over the hexene. The results are shown in
 9 Table 6.

10

11 Table 6. Selective Absorption of dienes over mono-olefins

12

	Mol hexene/mol Cu ⁺	Mol hexadiene/mol Cu ⁺	Mol hexadiene/mol hexene
10% CuOTf	0.072	0.367	5.13

13

14 Next, a mixture of hexene and 1,5 hexadiene was mixed in n-decane and
 15 exposed to Bmim/CuOTf wherein the triflate had been slightly air exposed.
 16 Two samples were run, both with and without hydrogen exposure. The
 17 results again showed a preference for adsorbing the 1,5 hexadiene over the
 18 hexene. Furthermore, there was no decrease in diene loading or selectivity in
 19 the hydrogen exposed sample. The results are shown in Table 7.

1 Table 7. Selective Absorption of dienes over mono-olefins

2

	Mol hexene/mol Cu ⁺	Mol hexadiene/mol Cu ⁺	Mol hexadiene/mol hexene
No H ₂ Exposure 10% CuOTf	0.073	0.284	3.91
H ₂ Exposure 10% CuOTf	0.077	0.291	3.80

3

4 While not wishing to be bound to any particular theory, it is believed that the
5 decrease in diene loading in the air exposed sample (compared with the non-
6 air exposed sample) is due to partial deactivation of the Cu due to O₂
7 exposure. Notably, no decrease was observed due to H₂ exposure. It is also
8 believed that the lack of appreciable uptake of diene by the ionic liquids
9 containing copper salts shown in Table 3 was due to the formation of a new
10 ionic liquid, Bmim⁺CuCl₂⁻, wherein the copper is tied up in the anion and, as
11 such, not available for complexation.

12

13 Additionally, TGA adsorption experiments were conducted on each of the
14 ionic liquids described above with butane and 1-butene under the following
15 test conditions: sample size: approximately 20 mg; C₄ flow rate: 50 cc/min;
16 temperature: isothermal at -24°C. The TGA recorded the sample weight until
17 a plateau was reached in the sample weight versus time plot. Three of the
18 samples displayed significant amounts of butane and 1-butene adsorption
19 and were further tested with 1,3-butadiene. Additional adsorption
20 experiments were conducted using 1,7 octadiene, 1-octene, and
21 1,9 decadiene. The C₈-diolefin and C₁₀-diolefin runs were done with a new
22 batch of 10% AgBF₄ imidazolium ionic liquid, so a C₈-diolefin was run for
23 comparison with previous results. The results show that the ionic liquids
24 selectively adsorb out the alpha-omega diene over the paraffin and normal
25 alpha olefins (NAOs).

26

1 A mixture of 1,7 octadiene and 1-octene (about 3.2wt% each in n-decane)
2 was evaluated. The resulting liquid after 24 hours in mixing contact with the
3 ionic liquid contained the same amount of 1-octene, but only 1.4 wt % of the
4 1,7 octadiene. This corresponds to an adsorption of 0.72 moles
5 C₈-diene/mole Ag⁺, slightly lower than previous experiments showed for
6 C₆-diene, and demonstrates that the C₈-diene is preferentially adsorbed over
7 the C₈-mono-olefin.

8
9 A mixture of C₁₀-diolefin in decane (4.2 wt%) was also run and showed a
10 decrease to 0.7 wt% after 24 hours. This corresponds to an adsorption ratio
11 of 1.2 mol C₁₀-diolefin /mol Ag⁺.

12
13 A mixture of a C₆-diolefin, a C₈-diolefin and a C₁₀-diolefin was subjected to
14 the same conditions. The C₆-diolefin was preferentially adsorbed over the
15 C₈-diolefin and the C₁₀-diolefin. While not wishing to be bound to a particular
16 theory, it is believed that the differential adsorption is due to differences in
17 solubility.

18
19 Ionic liquids can be used to improve the separation of diolefins (alpha-omega
20 olefins) from normal alpha olefins (NAOs). The ionic liquids which have been
21 tested are mixtures that contain an organic amine and a transition metal
22 compound. Because ionic liquids readily separate from hydrocarbons and
23 are thermally stable over a wide temperature range, they can be used in an
24 extractive distillation or liquid-liquid extraction separation process. The
25 process can therefore be used to purify large amounts of NAOs, which are
26 typically used as chemical precursors for the synthesis of polyethylenes,
27 surfactants, synthetic lubricants and additives, etc.

28
29 It will be apparent to those skilled in the art of chemical separations that the
30 process of this invention can be applied to a wide variety of mixtures of
31 mono-olefins, di-olefins, and/or non-olefins, and the forgoing examples are
32 intended to be illustrative and non-limiting. Those skilled in the art of
33 chemical separations can readily determine the operative and optimal ionic

WO 03/059483

PCT/US02/41739

- 1 liquids, metal salt and conditions for carrying out the processes and process
- 2 steps of this invention for any specific separation of mono-olefins, di-olefins
- 3 and/or non-olefins using the combinational chemistry approaches herein and
- 4 other techniques known in the art.

1 WHAT IS CLAIMED IS:

2

3 1. A method for separating mono-olefins comprising:

4 a) contacting a mixture comprising di-olefins and mono-olefins with an
5 olefin-complexing metal salt dissolved, dispersed, or suspended in an
6 ionic liquid;7 b) maintaining such mixture in contact with such olefin-complexing metal
8 salt for sufficient time to selectively complex the di-olefins over the
9 mono-olefins to form a metal salt/olefin complex; and

10 c) separating the non-complexed mono-olefins.

11

12 2. The method of claim 1, further comprising desorbing the di-olefins from
13 the metal salt/olefin complex.

14

15 3. The method of claim 2, wherein said ionic liquid is capable of forming a
16 solution, suspension or dispersion with said olefin-complexing metal salt.

17

18 4. The method of claim 3, wherein the amount of said olefin-complexing
19 metal salt is adjusted so as to complex essentially only the di-olefins.

20

21 5. The method of claim 1, wherein the metal salt comprises a Group IB
22 metal.

23

24 6. The method of claim 5, wherein the metal salt is a copper salt.

25

26 7. The method of claim 6, wherein the metal salt is CuOTf.

27

28 8. The method of claim 5, wherein the metal salt is a silver salt.

29

30 9. The method of claim 8, wherein the metal salt is AgBF₄.

31

32 10. The method of claim 1, wherein the mono-olefin and di-olefin-containing
33 mixture is a gaseous olefin-containing stream.

1

2 11. The method of claim 1, wherein said mixture is contacted with said olefin-
3 complexing metal salt in a distillation apparatus.

4

5 12. The method of claim 11, further comprising separating said non-
6 complexed mono-olefins by distillation in said distillation apparatus.

7

8 13. The method of claim 12, further comprising desorbing said di-olefins from
9 said metal salt/olefin complex by distillation in said distillation apparatus.

10

11 14. The method of claim 1, wherein said mixture is contacted with said
12 olefin-complexing metal salt in a system of one or more liquid mixers.

13

14 15. The method of claim 14, further comprising separating said non-
15 complexed mono-olefins from said metal salt/olefin complex by
16 decantation.

17

18 16. The method of claim 15, further comprising desorbing said di-olefins from
19 said metal salt/olefin complex in a regeneration apparatus.

20

21 17. The method of claim 16, further comprising sending the bottoms from
22 said regeneration apparatus to said system of liquid mixers.

23

24 18. The method of claim 1, wherein the mixture of mono- and di-olefins is
25 derived from wax hydrocracking, paraffin dehydrogenation, or
26 combinations thereof.

27

28 19. The method of claim 1, further comprising subjecting the mixture to
29 partial hydrogenation prior to the contacting step.

30

31 20. A method for separating mono-olefins comprising:

32 a) contacting a mixture comprising di-olefins and mono-olefins with an
33 olefin-complexing metal salt dissolved, dispersed, or suspended in an

- 1 ionic liquid;
- 2 b) maintaining such mixture in contact with such olefin-complexing metal
- 3 salt for sufficient time to complex the mono-olefins and di-olefins with
- 4 the olefin-complexing metal salt to form a metal salt/olefin complex; and
- 5 c) selectively desorbing the mono-olefins from the metal salt/olefin
- 6 complex.
- 7
- 8 21. The method of claim 20, further comprising desorbing the di-olefins from
- 9 the metal salt/olefin complex.
- 10
- 11 22. A method for separating mono-olefins and/or di-olefins comprising:
- 12 a) contacting a mixture comprising di-olefins, mono-olefins and non-olefins
- 13 with an olefin-complexing metal salt dissolved, dispersed or suspended
- 14 in an ionic liquid;
- 15 b) maintaining such mixture in contact with such olefin-complexing metal
- 16 salt for sufficient time to complex the mono-olefins and di-olefins with the
- 17 olefin-complexing metal salt to form a metal salt/olefin complex;
- 18 c) separating the non-complexed non-olefins; and
- 19 d) selectively desorbing the mono-olefins from the metal salt/olefin
- 20 complex.
- 21
- 22 23. The method of claim 22, further comprising desorbing the di-olefins from
- 23 the metal salt/olefin complex.
- 24
- 25 24. The method of claim 23, wherein said ionic liquid is capable of forming a
- 26 solution, suspension or dispersion with said olefin-complexing metal salt.
- 27
- 28 25. The method of claim 22, wherein the metal salt comprises a Group IB
- 29 metal.
- 30
- 31 26. The method of claim 25, wherein the metal salt is a copper salt.
- 32
- 33 27. The method of claim 26, wherein the metal salt is CuOTf.

1

2 28. The method of claim 25, wherein the metal salt is a silver salt.

3

4 29. The method of claim 28, wherein the metal salt is AgBF_4 .

5

6 30. The method of claim 22, wherein the non-olefins comprise at least one of
7 paraffins, oxygenates, aromatics, or mixtures and combinations thereof.

8

9 31. The method of claim 30, wherein the paraffins comprise cycloparaffins.

10

11 32. The method of claim 22, wherein the mono-olefins comprise at least one
12 of ethylene, propylene, or mixtures and combinations thereof.

13

14 33. The method of claim 32, wherein the ethylene is produced in an ethylene
15 cracker, an EP cracker, a naphtha cracker, or combinations thereof.

16

17 34. The method of claim 22, wherein the olefins are produced in an
18 apparatus selected from the group consisting of an FCC unit, naphtha
19 hydrotreater, catalytic reformer, distillate hydrotreater, hydrocracker, coker,
20 RFCC unit, RDS unit and combinations thereof.

21

22 35. The method of claim 22, wherein the olefins are derived from paraffin
23 dehydrogenation, ethylene oligomerization, wax hydrocracking, or
24 combinations thereof.

25

26 36. The method of claim 22, wherein the olefins are produced in a Fischer-
27 Tropsch synthesis.

28

29 37. The method of claim 22, wherein the mono-olefins are normal alpha
30 olefins derived from the ethenolysis of heavier internal olefins.

31

32 38. The method of claim 22, wherein the olefins are separated from a recycle
33 stream in a Fischer-Tropsch synthesis to reduce the amount of olefins

- 1 recycled from a Fischer-Tropsch unit to an upstream methane reformer.
2
- 3 39. The method of claim 22, wherein the olefin-containing mixture is a
4 gaseous olefin-containing stream.
5
- 6 40. The method of claim 22, wherein said mixture is contacted with said
7 olefin-complexing metal salt in a distillation apparatus.
8
- 9 41. The method of claim 40, further comprising separating said non-
10 complexed non-olefins from said metal salt/olefin complex by distillation.
11
- 12 42. The method of claim 41, further comprising desorbing said mono-olefins
13 from said metal salt/olefin complex by distillation in said distillation
14 apparatus.
15
- 16 43. The method of claim 42, further comprising desorbing said di-olefins from
17 said metal salt/olefin complex by distillation in said distillation apparatus.
18
- 19 44. The method of claim 22, wherein said mixture is contacted with said
20 olefin-complexing metal salt in a system of one or more liquid mixers.
21
- 22 45. The method of claim 44, further comprising separating said non-
23 complexed non-olefins from said metal salt/olefin complex by decantation.
24
- 25 46. The method of claim 45, further comprising desorbing said mono-olefins
26 from said metal salt/olefin complex in a regeneration apparatus.
27
- 28 47. The method of claim 46, further comprising desorbing said di-olefins from
29 said metal salt/olefin complex in said regeneration apparatus.
30
- 31 48. The method of claim 47, further comprising sending the bottoms from
32 said regeneration apparatus to said system of liquid mixers.
33

1 49. The method of claim 22, further comprising purifying the olefin-containing
2 mixture before the contacting step to remove sulfur, acetylenics,
3 oxygenates, and other heteroatoms.
4

5 50. A method for separating mono-olefins and/or di-olefins comprising:

- 6 a) contacting a mixture comprising di-olefins, mono-olefins and non-
7 olefins with an olefin-complexing metal salt dissolved, dispersed or
8 suspended in an ionic liquid;
- 9 b) maintaining such mixture in contact with such olefin-complexing metal
10 salt for sufficient time to selectively complex the di-olefins over the
11 mono-olefins to form a first metal salt/olefin complex;
- 12 c) separating the non-complexed mono-olefins and non-olefins;
- 13 d) desorbing the di-olefins from the first metal salt/olefin complex;
- 14 e) contacting the non-complexed mono-olefins and non-olefins with the
15 olefin-complexing metal salt;
- 16 f) maintaining such non-complexed mono-olefins and non-olefins in
17 contact with such olefin-complexing metal salt for sufficient time to
18 complex the mono-olefins to form a second metal salt/olefin complex;
19 and
- 20 g) separating the non-complexed non-olefins.
21

22 51. The method of claim 50 further comprising desorbing the mono-olefins
23 from the second metal salt/olefin complex.
24

25 52. The method of claim 51, wherein the amount of said olefin-complexing
26 metal salt is adjusted so as to complex essentially only the di-olefins.
27

28 53. The method of claim 1, wherein said ionic liquid is comprised of anions
29 and cations, wherein;

30 said anions are selected from the group consisting of halide salts,
31 metal anions, chloroaluminate, bromoaluminate, gallium chloride,
32 tetrafluoroborate, tetrachloroborate, hexafluorophosphate, nitrate,
33 trifluoromethane sulfonate, methylsulfonate, *p*-toluenesulfonate,

1 hexafluoroantimonate, hexafluoroarsenate, tetrachloroaluminate,
2 tetrabromoaluminate, perchlorate, hydroxide anion, copper dichloride
3 anion, iron trichloride anion, antimony hexafluoride, copper dichloride
4 anion, zinc trichloride anion, lanthanum anion, potassium anion, lithium
5 anion, nickel anion, cobalt anion, manganese anion, and combinations
6 and mixtures thereof; and

7 said cations are selected from the group consisting of cyclic and non-
8 cyclic quaternary ammonium cations, alkylammoniums, pyridiniums,
9 substituted pyridiniums, N-alkylpyridiniums, imidazoliums, substituted
10 imidazoliums, N,N'-dialkylimidazoliums, pyrroliniums, substituted
11 pyrroliniums, phosphoniums, alkylphosphoniums, arylphosphoniums, 1-
12 butyl-3-methylimidazolium, N-hexylpyridinium, 1-hexyl-3-
13 methylimidazolium, $(C_8H_{17})_3MeN$, Bu_2Me_2N , and mixtures and
14 combinations thereof.

15

16 54. The method of claim 22, wherein said ionic liquid is comprised of anions
17 and cations, wherein;

18 said anions are selected from the group consisting of halide salts,
19 metal anions, chloroaluminate, bromoaluminate, gallium chloride,
20 tetrafluoroborate, tetrachloroborate, hexafluorophosphate, nitrate,
21 trifluoromethane sulfonate, methylsulfonate, *p*-toluenesulfonate,
22 hexafluoroantimonate, hexafluoroarsenate, tetrachloroaluminate,
23 tetrabromoaluminate, perchlorate, hydroxide anion, copper dichloride
24 anion, iron trichloride anion, antimony hexafluoride, copper dichloride
25 anion, zinc trichloride anion, lanthanum anion, potassium anion, lithium
26 anion, nickel anion, cobalt anion, manganese anion, and combinations
27 and mixtures thereof; and

28 said cations are selected from the group consisting of cyclic and non-
29 cyclic quaternary ammonium cations, alkylammoniums, pyridiniums,
30 substituted pyridiniums, N-alkylpyridiniums, imidazoliums, substituted
31 imidazoliums, N,N'-dialkylimidazoliums, pyrroliniums, substituted
32 pyrroliniums, phosphoniums, alkylphosphoniums, arylphosphoniums, 1-
33 butyl-3-methylimidazolium, N-hexylpyridinium, 1-hexyl-3-

1 methylimidazolium, $(C_8H_{17})_3MeN$, Bu_2Me_2N , and mixtures and
2 combinations thereof.

3

4 55. A method for optimizing the method of claim 1, comprising preparing a
5 combinatorial library including a plurality of combinations of ionic liquids
6 and olefin-complexing metal salts, and evaluating the library for its ability
7 to separate di-olefins from a mixture comprising mono-olefins and di-
8 olefins.

9

10 56. A method for optimizing the method of claim 20, comprising preparing
11 a combinatorial library including a plurality of combinations of ionic
12 liquids and olefin-complexing metal salts, and evaluating the library for
13 its ability to separate olefins from a mixture comprising olefins and non-
14 olefins.