



(51) International Patent Classification:
C10G 21/06 (2006.01) *C10G 29/06* (2006.01)

(21) International Application Number:
PCT/US2010/032473

(22) International Filing Date:
27 April 2010 (27.04.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
12/430,696 27 April 2009 (27.04.2009) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

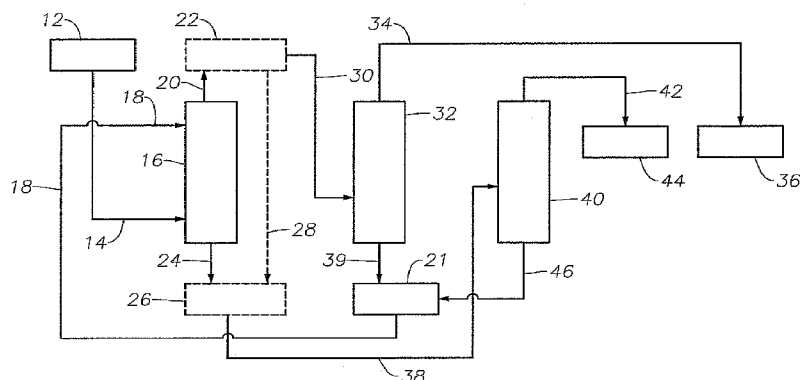
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: DESULFURIZATION AND DENITROGENATION WITH IONIC LIQUIDS AND METAL ION SYSTEMS

Fig. 1



DESULFURIZATION AND DENTROGENATION WITH IONIC LIQUIDS AND METAL ION SYSTEMS

BACKGROUND OF THE INVENTION

Technical Field of the Invention

[0001] This invention generally relates to the field of the upgrading of hydrocarbons. In particular, the invention is directed to a process for the improved removal of sulfur and nitrogen from petroleum based hydrocarbon feeds.

Description of the Prior Art

[0002] In the petroleum industry, it is common for gas oils, particularly middle distillate petroleum fuels, to contain sulfur and nitrogen species. Engines utilizing sulfur-containing petroleum based fuels produce emissions of nitrogen oxide, sulfur oxide and particulate matter. Government regulations have become more stringent in recent years with respect to allowable levels of these potentially harmful emissions.

[0003] Currently, many countries around the world limit allowable sulfur content in gasoline fuels to less than 50 ppm, and in some cases as low as 10 ppm or less. Thus, catalysts and processes for the production of gasoline fuels having a sulfur content of 10 ppm or less are of great interest.

[0004] Gasoline is typically produced as a blend of multiple components, from refining processes that use a variety of equipment, such as for example, distillation columns, catalytic crackers (FCC), hydro-crackers, and cokers. The sulfur content of the gasoline component from an FCC can be as high as 1000 to 5000 ppm, thus requiring extensive treatment to meet the current regulations by reducing the sulfur content to an acceptable level for use in automobile engines. Although several different methods can be employed, most commonly the FCC feed is pre-treated prior to being supplied to the FCC unit, or the gasoline component from the FCC is treated before being used as a fuel.

[0005] Conventional pre-treatment of an FCC feed can include hydrotreating of the feed to reduce the content of sulfur, nitrogen and metals, hydrofinishing all or a portion of the FCC naphtha, and hydrotreating the straight run kerosene and distillate, coker distillate and light cycle oil.

[0006] Post treatment processes can include hydrotreating all or a portion of an FCC naphtha, and hydrotreatment of the straight run kerosene and distillate, coker distillate and FCC light cycle oil.

[0007] In addition, products from straight run distillation columns can be hydrotreated to reduce the sulfur, nitrogen and metal content in finished products.

[0008] Post-treatment of the FCC naphtha is the least costly route to desulfurization. However, conventional FCC naphtha hydrotreating processes are expensive because they are not selective. In the process of removing sulfur, the hydrotreating process also results in saturation of essentially all of the olefins present in FCC naphtha. This in turn leads to substantial loss of research octane number (RON) (up to 10 octane numbers), as well as high hydrogen consumption, thus accounting for the high cost of conventional hydrotreating.

[0009] Furthermore, the reactivity of various organosulfur compounds over traditional hydrodesulfurization catalysts can depend on a variety of factors, including the molecular structures of the sulfur containing compounds. Aliphatic organosulfur compounds are typically highly reactive in conventional hydrotreating processes, and in general, are completely removed from fuels and feedstocks with little difficulty. In contrast, aromatic sulfur compounds, which can include thiophenes, dibenzothiophenes and alkylated dibenzothiophenes, are generally more difficult to remove over traditional hydrodesulfurization catalysts.

[0010] There are also other disadvantages associated with previously proposed desulfurization methods. For example, hydrodesulfurization in catalytic reactors requires that the reactors operate under relatively severe reaction conditions; i.e., low flow rates, high temperatures, high pressures and hydrogen consumption conditions. The relatively severe reaction conditions are necessary to overcome strong inhibition of refractory sulfur and nitrogen compounds against hydrodesulfurization. Therefore, strict conditions are also imposed on a process design, thereby typically incurring high construction costs.

[0011] Other methods for the removal of sulfur and nitrogen containing compounds can include various oxidative methods, which are typically followed by extraction of polar oxidized species, reactive adsorption, and fixed bed metal ion complexation methods. The main disadvantage to oxidative/extraction technologies are disposal of the oxidized sulfur

species, difficulties associated with separation of the oxidizing media, and oxidant selectivity. Generally, while fixed bed metal complexation technologies offer a relatively simple route to the removal of sulfur containing compounds from motor fuels, when compared with oxidation/extraction technologies, fixed bed metal complexation technologies frequently suffer from metal leaching. In addition, fixed bed technologies can be limited by liquid-solid diffusion and progressive deterioration of the catalyst bed.

[0012] The present invention described herein can achieve sulfur removal of nearly 100% yield of the original feed stream. Additionally, the processes described herein typically do not create light compounds, which can increase the vapor pressure of the effluent. Because the methods described herein are not a hydrotreating technique, high hydrogen consumption, hydrogen purity, and the associated operating costs are not an issue.

SUMMARY OF THE INVENTION

[0013] In one embodiment, a method for upgrading a hydrocarbon feed having one or more contaminants is provided. The method includes the steps of: contacting the hydrocarbon feed with an extracting stream, the extracting stream including at least one metal salt and at least one ionic liquid, to create a mixed stream. During the step of contacting the feed stream and the extracting stream, the metal ion of the metal salt binds with at least one contaminant contained in the feed stream, such that a significant amount of the at least one contaminant is removed from the hydrocarbon feed and bound to the metal. The mixed stream is separated into a contaminant-lean hydrocarbon stream and a contaminant-rich stream; and the contaminant-lean hydrocarbon stream is collected as a product stream.

[0014] In certain embodiments, the ionic liquid includes an ion selected from the group consisting of an imidazolium ion, a pyridinium ion, an ammonium ion and a phosphonium ion. In certain preferred embodiments, the cation of the ionic liquid is selected from 1-butyl-4-methylpyridinium ion and 1-butyl-3-methylimidazolium ion. The metal salt can be a salt of a Group IB, IIB, VIB, or VIIIB metal. In certain embodiments the metal salt is a salt of copper, nickel, zinc, cobalt, molybdenum, silver or palladium. In certain preferred embodiments, the metal salt is a salt of copper(II) or palladium(II).

[0015] In certain embodiments, the method further includes the steps of: supplying the contaminant-lean hydrocarbon stream to a distillation column; separating the contaminant-lean hydrocarbon stream into a vapor stream and a liquid stream; and collecting the vapor stream as a purified product stream. In certain embodiments, the method further includes:

supplying the contaminant-lean hydrocarbon stream to a phase separator to remove a residual extracting stream, and combining the residual extracting stream with the contaminant-rich stream; wherein the phase separator is positioned downstream of the contacting step and upstream of the distillation column. In certain embodiments, the method further includes: supplying the contaminant-lean hydrocarbon stream to a phase separator to remove a residual extracting stream, and combining the residual extracting stream with the contaminant-rich stream; wherein the phase separator is positioned downstream of the contacting step and upstream of the distillation column. In certain embodiments, the method further includes recycling the liquid stream to the extraction stream.

[0016] In another embodiment, a process for upgrading of a hydrocarbon feed, wherein the hydrocarbon feed includes one or more contaminants, is provided. The process includes the steps of: mixing the hydrocarbon feed and an adsorbent containing solution in a mixing vessel, wherein the adsorbent containing solution includes at least one ionic liquid and at least one metal salt; and wherein during the step of mixing the hydrocarbon feed and the adsorbent containing solution, the metal ion of the metal salt can bind to and remove one or more contaminants present in the hydrocarbon feed. The method further includes separating the mixture into a contaminant-lean hydrocarbon product stream and a contaminant-rich stream; and supplying the contaminant-lean hydrocarbon stream to a first distillation column and separating residual extracting solution to produce a hydrocarbon product stream having a reduced contaminant concentration relative to the hydrocarbon feed stream. The contaminant-rich stream is supplied to a second distillation column to produce a top stream and a bottom stream, wherein the top stream includes a contaminant-rich stream and the bottom stream includes ionic liquid. Finally, the process includes recycling the ionic liquid to the mixing vessel.

[0017] In certain embodiments, the ionic liquid includes an ion selected from the group consisting of an imidazolium ion, a pyridinium ion, an ammonium ion and a phosphonium ion. In certain other embodiments, the metal salt can be a salt of a Group IB, IIB, VIB, or VIIIB metal, preferably selected from copper, nickel, zinc, cobalt, molybdenum, silver or palladium.

[0018] In certain embodiments, the at least one contaminant in the hydrocarbon feed stream includes sulfur containing compounds. In other embodiments, the at least one contaminant in the hydrocarbon feed stream includes nitrogen containing compounds.

Brief Description of the Drawings

[0019] So that the manner in which the features, advantages and objects of the invention, as well as others that will become apparent, can be understood in more detail, more particular description of the invention briefly summarized above can be had by reference to the embodiment thereof which is illustrated in the appended drawings, which form a part of this specification. It is to be noted, however, that the drawings illustrate only a preferred embodiment of the invention and is therefore not to be considered limiting of the invention's scope as it can admit to other equally effective embodiments.

[0020] Figure 1 depicts a schematic of one embodiment of a process of producing desulfurized and/or denitrogenated hydrocarbons according to one of the invention.

[0021] Figure 2 is an expanded stacked chromatogram showing an untreated Arabian Light fraction 400-600°F (top), an Arabian Light fraction 400-600°F treated with 1-ethyl-3-methylimidazolium tosylate/copper mixture (second from top), an Arabian Light fraction 400-600°F treated with 1-butyl-4-methylpyridinium tetrafluoroborate/copper mixture (third from top), and an Arabian Light fraction 400-600°F treated with 1-butyl-3-methylimidazolium octyl sulfate/copper mixture (bottom).

[0022] Figure 3 is an expanded stacked chromatogram for an untreated Arabian Light fraction 400-600°F (top) and an Arabian Light fraction 400-600°F treated with 1-ethyl-3-methylimidazolium tosylate/copper mixture (bottom).

[0023] Figure 4 is an expanded stacked chromatogram for an untreated Arabian Light fraction 400-600°F (top) and an Arabian Light fraction 400-600°F treated with 1-butyl-4-methylpyridinium tetrafluoroborate/copper mixture (bottom).

[0024] Figure 5 is an expanded stacked chromatogram for an untreated Arabian Light fraction 400-600°F (top) and an Arabian Light fraction 400-600°F treated with 1-butyl-3-methylimidazolium octyl sulfate/copper mixture (bottom).

[0025] Figure 6 is an expanded stacked chromatogram showing an untreated Arabian Light fraction 400-600°F (top), an Arabian Light fraction 400-600°F treated with 1-ethyl-3-methylimidazolium tosylate/palladium mixture (second from top), an Arabian Light fraction 400-600°F treated with 1-butyl-4-methylpyridinium tetrafluoroborate/palladium mixture (third from top), and an Arabian Light fraction 400-600°F treated with 1-butyl-3-methylimidazolium octyl sulfate/palladium mixture (bottom).

[0026] Figure 7 is an expanded stacked chromatogram for an untreated Arabian Light fraction 400-600°F (top) and an Arabian Light fraction 400-600°F treated with 1-ethyl-3-methylimidazolium tosylate/ palladium mixture (bottom).

[0027] Figure 8 is an expanded stacked chromatogram for an untreated Arabian Light fraction 400-600°F (top) and an Arabian Light fraction 400-600°F treated with 1-butyl-4-methylpyridinium tetrafluoroborate/ palladium mixture (bottom).

[0028] Figure 9 is an expanded stacked chromatogram for an untreated Arabian Light fraction 400-600°F (top) and an Arabian Light fraction 400-600°F treated with 1-butyl-3-methylimidazolium octyl sulfate/ palladium mixture (bottom).

DETAILED DESCRIPTION OF THE INVENTION

[0029] Methods for the removal of contaminants from petroleum based hydrocarbon feeds are provided. Specifically, a solution operable as an extracting media for the selective removal of sulfur and/or nitrogen, and a method for the same, are provided. The extracting media, also called the extracting stream, can include an ionic liquid and a metal salt. Removal of sulfur and/or nitrogen from petroleum based hydrocarbon feeds utilizing the extracting media and methods does not result in a substantial loss of research octane number (RON).

[0030] As used herein, the terms “adsorption” and “complexation” are used to describe the complexation of metal ions with sulfur and/or nitrogen species.

[0031] As used herein, the term “adsorbent” is used to describe the sulfur or nitrogen complexing metal ions, alone or dissolved, suspended or dispersed in ionic liquids.

[0032] As used herein, the term “top” is used to describe the portion of a process stream which is collected from the top of a vessel during a fractionating process.

[0033] As used herein, the term “bottoms” is used to describe the portion of a process stream which collects in the bottom of a vessel during a fractionating process.

[0034] As used herein, the terms “Group IB metal”, “Group IIB metal”, “Group VIB metal” and “Group VIIIB metal” are used to describe elements from Group IB, Group IIB, Group VIB and Group VIIIB (IUPAC Notation) of the periodic table of elements, respectively.

[0035] Hydrocarbon Feed

[0036] The hydrocarbon feed can be any petroleum based feed stream that includes sulfur and/or nitrogen. In certain embodiments, the feed stream can include gas oils, kerosenes, cat naphtha, diesel, vacuum gas oils, and the like. In certain embodiments, the hydrocarbon feed

employed in the method described herein have been previously treated by one or more processes designed to remove at least a portion of the sulfur and/or nitrogen present in the feed stream.

[0037] Sulfur species present in the feed stream can be present as aliphatic organosulfur compounds (sulfides) and both substituted and unsubstituted thiophenes, benzothiophenes, dibenzothiophenes and higher thiophene ring systems. Preferably, the hydrocarbon feed is free of mercaptans and hydrogen sulfide, as both mercaptans and hydrogen sulfide can react with free metal ion to form metal mercaptides and metal sulfides, respectively. Thus, to limit undesired side reactions, the mercaptans and hydrogen sulfide are preferably removed from the hydrocarbon feed stream prior to the contacting step.

[0038] Nitrogen species which can be present in the petroleum based feed can include pyrroles, carbazoles, benzocarbazoles, and higher nitrogen containing ring analogs, in addition to basic nitrogen containing compounds and polyhetero compounds. The nitrogen containing compound can be acidic, basic or neutral. Frequently, nitrogen containing species are present in naphtha, kerosene and gas oil fractions of petroleum based feeds.

[0039] Ionic Liquids

[0040] Ionic liquids are organic salts, which can be liquids at room temperature. Because of their ionic nature, ionic liquids are frequently very good solvents for ionic or polar compounds.

[0041] Ionic liquids without metals have been previously used for extractive desulfurization, wherein sulfur is removed from petroleum based hydrocarbon feeds at ambient conditions. However, as noted previously, the selectivity between aromatic hydrocarbons and sulfur containing molecules is generally poor. The prior methods typically do not include the use of metal salts and can be achieved without the need for special equipment.

[0042] Ionic liquids containing metal functionality can be used for deep desulfurization of diesel fuel. Typically, diesel is desulfurized by hydrotreatment, which can eliminate aliphatic and cyclic sulfur compounds. Generally, not all dibenzothiophenes and alkyl-substituted dibenzothiophenes are removed by this process. The use of ionic liquids removes aliphatic and cyclic compounds but also these difficult sulfur compounds, this being defined as deep desulfurization.

[0043] Ionic liquids have a variety of desirable properties, including but not limited to, low melting temperature, extremely low vapor pressure, high temperature stability, high heat capacity, high density, high thermal conductivity, and non-flammability. Additionally, because of the many variations in composition that are possible, ionic liquids can be fine-

tuned to have specific desired properties based upon the large number of cation and anion combinations that are possible. For several years, ionic liquids have been specifically studied as potential replacements for conventional organic solvents which are frequently toxic, flammable and/or volatile.

[0044] Ionic liquids include a cation and an anion.

[0045] Cations of ionic liquids generally include a combination of substituted and unsubstituted organic cations having nitrogen or phosphorous. In certain embodiments, the ionic liquid includes an imidazolium ion, a pyridinium ion, a pyrrolium, a quaternary ammonium ion, or a phosphonium ion. Exemplary cations useful in the invention include, but are not limited to, alkyl-imidazolium anions (for example, 1-butyl-3-methyl-imidazolium 1-octyl-3-methylimidazolium, ethyl-3-methyl-1-imidazolium, hexyl-3-methyl-1-imidazolium, or butyl-3-dimethyl-1,2-imidazolium) or alkoxy-imidazolium salts (for example, 1-Hexyloxymethyl-3-methyl-imidazolium or 1-hexyloxymethyl-3-methyl-imidazolium), alkyl-pyridinium salts (for example, N-butyl-N-methylpyrrolidinium, N-butylpyridinium, N-ethylpyridinium, or pyridinium), quaternary ammonium (for example, trimethylphenyl-ammonium) or phosphonium ions (for example, tetrabutylphosphonium, or tributyl-tetradecyl-phosphonium).

[0046] In certain embodiments, the anions can include a variety of alkyl substituents (e.g., methyl, ethyl, butyl, etc.). Exemplary inorganic anions can include, but are not limited to, halo or alkyl-sulfates, halo or alkyl-sulfonates, halides, hydroxide, perchlorate, borates, halo-borates, nitrates, sulfates, phosphates, acetates, haloacetates, triflate (i.e., CF_3SO_3^-), bis(triflyl)imide [$(\text{CF}_3\text{SO}_2)_2\text{N}^-$], halo-aluminates, tetrafluoroborate, halo-phosphates, halo-antimonates halo-sulfonates, alkyl sulfonates (for example, methyl sulfonate), halo-alkyl sulfonates (for example, trifluoromethyl sulfonate), sulfonyls, halo-sulfonyl amides (for example, bis(trifluoromethanesulfonyl) amide, and bis(trifluoromethylsulfonyl) imide), tris-trifluoromethanesulfonyl methyllide (having the formula $\text{C}(\text{CF}_3\text{SO}_2)^3^-$), arenesulfonates, optionally substituted by halogen or haloalkyl groups, and tetraphenylborates and tetraphenylborates having substituted aromatic cores.

[0047] Exemplary salts that can be used include, but are not limited to, 1-ethyl-3-methylimidazolium tosylate, N-butyl-pyridinium hexafluorophosphate, 1-butyl-4-methylpyridinium hexafluorophosphate, 1-butyl-4-methylpyridinium tetrafluoroborate, N-ethyl-pyridinium tetrafluoroborate, pyridinium fluorosulfonate, 1-butyl-3-methyl-imidazolium tetrafluoroborate, 1-butyl-3-methyl-imidazolium octyl sulfate, 1-butyl-3-methyl-imidazolium bis-trifluoromethane-sulfonyl amide, triethylsulfonium bis-trifluoromethane-

sulfonyl amide, butyl-3-methyl-1-imidazolium hexafluoro-antimonate, butyl-3-methyl-1-imidazolium hexafluorophosphate, butyl-3-methyl-1-imidazolium trifluoroacetate, butyl-3-methyl-1-imidazolium trifluoromethylsulfonate, butyl-3-methyl-1-imidazolium bis(trifluoromethylsulfonyl)-amide, trimethyl-phenylammonium hexafluorophosphate, and tetrabutylphosphonium tetrafluoroborate. These salts can be used alone or in a mixture.

[0048] Additional examples of ionic liquids and their properties are described, for example, in *J. Chem. Tech. Biotechnol.*, 68:351-356 (1997); *Chem. Ind.*, 68:249-263 (1996); and *J. Phys. Condensed Matter*, 5 :(supp 34B):B99-B106 (1993), *Chemical and Engineering News*, Mar. 30, 1998, 32-37; *J. Mater. Chem.*, 8:2627-2636 (1998); and *Chem. Rev.*, 99:2071-2084 (1999), the contents of which are hereby incorporated by reference in their entirety.

[0049] In certain embodiments, the ionic liquids can be dried under reduced pressure to remove water prior to use. Most ionic liquids are hygroscopic, and in certain instances, the presence of water can change their properties. In certain instances, the presence of water can negatively effect the removal of sulfur, nitrogen and/or other contaminants. Thus, in certain embodiments, substantially all water is removed.

[0050] In certain embodiments, ionic liquids show selectivity for the separation of aromatic hydrocarbons from a mixture of aromatic and non-aromatic hydrocarbons. Cation choice can also play a role in selectivity during separations. For example, substituted pyridinium ions have more aromatic character than imidazolium based ionic liquids, and thus may exhibit higher aromatic selectivity than imidazolium based ionic liquids. Generally, it is believed that ionic liquids based on alkyl imidazolium ions having shorter alkyl chains can be favorable for aromatic/aliphatic selectivity. Thus, ionic liquids having short chain alkyl imidazolium ions can show improved removal of aromatic sulfur species from hydrocarbon feeds. As would be expected, aromatic selectivity with quaternary phosphonium and ammonium ionic liquids are generally low. The use of such ionic liquids that can include substituted pyridinium ions can be useful for the removal of aromatic sulfur species.

[0051] Metal Salt

[0052] The ionic liquids can be mixed with one or more metal salt to form an extracting media. Preferably, the metal ion of the metal salt is capable of bonding to sulfur and nitrogen species. In certain embodiments, the metal salt can include a metal selected from Groups IB, IIB, VIB and VIIIB of the periodic table. In certain embodiments, the metal salt can include one or more of copper, nickel, zinc, cobalt, molybdenum, silver and palladium. In certain exemplary embodiments, the metal salt can include copper(II). In certain other exemplary

embodiments, the metal salt can include palladium(II). Anions for the metal salt can include any organic or inorganic anion.

[0053] Without being bound by a specific theory, it is believed that the metals present in the metal salts can form complexes with sulfur and/or nitrogen containing compounds present in hydrocarbon feeds by coordinating to the free electron pair present in sulfur and nitrogen. Copper, nickel, zinc, cobalt, molybdenum, silver and palladium are believed to be particularly effective in coordinating to the various aromatic and non-aromatic sulfur compounds.

[0054] Extraction of sulfur and/or nitrogen with an extracting media that includes an ionic liquid and a metal salt can be accomplished at any temperature at which the ionic salt is present as a liquid. In certain embodiments, the extraction can occur at a temperature of greater than 0°C. In certain other embodiments, the extraction can occur at room temperature. Preferably, the extraction occurs at a temperature between 0°C and 100°C. Preferably, the extraction temperature is lower than the decomposition temperature of the metal-sulfur complex or the metal-nitrogen complex.

[0055] Extraction

[0056] The process for removing sulfur and/or nitrogen from hydrocarbon feed streams includes the steps of contacting a hydrocarbon stream that includes one or more contaminants (e.g., sulfur and/or nitrogen containing compounds) in a mixing vessel with an extracting media or extracting stream that can include at least one ionic liquid and at least one metal salt. In certain embodiments, the extracting media can include two or more metal salts. In certain other embodiments, the extracting media can include two or more ionic liquids. In yet other embodiments, the extracting media can include two or more ionic solvents and two or more metal salts.

[0057] As noted above, the extracting media consists of an ionic liquid and a metal salt. Typically, the concentration of the metal salt in the ionic liquid is maximized to maximize the efficiency of the process. Thus, in certain embodiments, when possible, a saturated solution of the metal salt and ionic liquid is preferred. However, solutions having lower concentrations of the metal salt can also be used for the desulfurization and denitrogenation of hydrocarbon feed streams. In certain instances, when solubility of the metal salt is relatively low, the extracting media can be in the form of a suspension of the metal salt in an ionic liquid.

[0058] In preferred embodiments, the hydrocarbon stream and extracting media are combined in a mixing vessel, to which they can be supplied in a counter-current flow. The

reaction between the extracting media and the sulfur and/or nitrogen containing compounds is relatively quick, thus, in certain embodiments, long contact and/or residence times are not required for substantial removal of sulfur and/or nitrogen. In certain embodiments, the mixing vessel can include trays or baffles which are designed to increase the contact between the hydrocarbon feed stream and the extracting media. In other embodiments, the mixing vessel can include mechanical stirring means or other means of mixing the contents to ensure adequate mixing between the extracting media and the hydrocarbon stream.

[0059] Preferably, the hydrocarbon stream and extracting media are contacted for up to one hour. More preferably, the hydrocarbon stream and extracting media are contacted for less than 30 minutes. Even more preferably, the hydrocarbon stream and the extracting media are contacted for less than 15 minutes.

[0060] The extraction is preferably conducted at a temperature of between 0°C and 100°C. Preferably the temperature is ambient temperature. Generally, the complexation equilibrium between the sulfur compound and the metal ion is temperature sensitive, and extraction of sulfur compounds is favored at lower temperatures. Preferably, the extraction process is performed at the lowest temperature possible, while still maintaining good fluid flow and good fluid mixing. In certain preferred embodiments, the extraction is performed at room temperature.

[0061] During the extraction process, the ratio of the hydrocarbon feed to the extracting media can be between about 0.1:1 and about 100:1. In certain embodiments, the ratio can be between about 0.25:1 and about 50:1. In preferred embodiments, the ratio of the hydrocarbon feed to extracting media is between about 0.5:1 and about 10:1.

[0062] In certain embodiments, the hydrocarbon is supplied to the mixing vessel as a gas. Preferably, the hydrocarbon feed stream is supplied to the mixing vessel as a liquid.

[0063] As noted previously, it is believed that the metal ion in the extracting media form complexes with the free electron pair of sulfur and/or nitrogen present in the hydrocarbon feed stream. The metal-sulfur complex and/or metal-nitrogen complex are preferably soluble in the ionic liquid, thus allowing the complexes to be easily removed from the mixing vessel. In certain embodiments, the metal-sulfur complex and/or metal-nitrogen complex can be removed from the mixing vessel as a bottom stream.

[0064] Referring to Figure 1, which demonstrates a process for the removal of sulfur and nitrogen from a hydrocarbon feed stream based on liquid-liquid extraction, combined with distillation, to recover a contaminant-free petroleum stream from residual extracting media, and a contaminant-containing petroleum stream from the extracting media.

[0065] As used herein, petroleum stream refers to hydrocarbons derived from natural or synthetic crude oil. The petroleum stream preferably has a final boiling point temperature lower than the decomposition temperature of the extracting media phase. Also, petroleum stream is preferably substantially free of hydrogen sulfide and mercaptans.

[0066] A petroleum stream feed is delivered from the feed tank 12 via line 14 to the bottom of the counter current extraction column 16. The extracting media is delivered via line 18, from the recycle tank 21, to the top of the counter current extraction column 16. The flow through the counter current extraction column is gravity assisted due to the difference between the gravity of the feed and the extracting media. Optionally, pumps can be connected to the petroleum feed line 14 and the extracting media line 18 to control the respective velocities through the counter current extraction column 16.

[0067] A contaminant-free petroleum stream 20 is collected from the top of the counter current extraction column 16 in optional first settling tank 22. The contaminant-rich petroleum stream 24 containing sulfur and/or nitrogen dissolved in the extracting media, may be drawn from the bottom of the counter current extraction column into optional second settling tank 26, to facilitate separation of the contaminant-free petroleum from residual the extracting media. Separated residual extracting media, from the bottom of the first settling tank 22, flows by gravity flow via line 28 into second settling tank 26. The extracting media may include at least one ionic liquid and at least one metal salt. The first and second settling tanks 22 and 26 can, in certain embodiments, be integrated into a single unit with counter current extraction column 16.

[0068] The contaminant-free petroleum stream 30 is directed from optional first settling tank 22 to first distillation column 32, to separate entrained and dissolved extracting media in the contaminant free petroleum stream into an extracting media stream 39. The bottom stream 39 from the first distillation column 32, which includes ionic extracting media, is returned to the extracting media recycle tank 21. A purified contaminant-free petroleum stream 34 is collected in the tank 36, or may optionally be supplied to an integrated plant process.

[0069] A contaminant-rich petroleum stream 38 is directed from settling tank 26 to second distillation column 40, to recover sulfur and nitrogen contaminants that were present in the petroleum stream feed. The contaminant-rich petroleum stream 42 collected from the top of the second distillation column 40 is delivered to tank 44 via line 42. The extracting media recovered from the second distillation column 40 is returned to the extracting media recycle tank 21 via line 46. The extracting media recovered in the extracting media recycle tank 21 can be resupplied to the process via line 18. Optionally, fresh extracting media can be

supplied to the counter current extraction column 16, instead of or in combination with the recycled extracting media from recycle tank 21.

[0070] In certain embodiments, the process for the removal of sulfur and/or nitrogen from petroleum stream using ionic liquid/metal ion (extracting media) can include other separation methods based on membrane, supported membrane, solvent extraction, and adsorption schemes, and the like.

[0071] In certain embodiments, both the mixing and separation steps are performed in the same vessel. This is due, in part, to the fact that the extracting media is denser than the hydrocarbon feed stream, thus allowing for a counter-current flow to be designed and used. Thus, the extracting media is preferably supplied to the top of the mixing vessel and the less dense hydrocarbon supplied to the bottom of the mixing vessel. Gravity separation can facilitate recovery of a sulfur and/or nitrogen lean hydrocarbon stream from the upper section of the vessel and a sulfur and/or nitrogen rich stream, which includes extracting media, from the lower section of the vessel. In other embodiments, a second vessel, such as for example, a settling tank, can be used to receive the mixture from the mixing vessel and for separation into a sulfur and/or nitrogen lean stream and a stream that includes sulfur and/or nitrogen compounds.

[0072] In certain embodiments, hydrocarbons in the sulfur and/or nitrogen-lean stream and hydrocarbons present in the sulfur and/or nitrogen-rich stream can be recovered in two separate distillation processes.

[0073] A first distillation column can be supplied with the sulfur and/or nitrogen-lean hydrocarbon stream to produce a hydrocarbon product stream of increased purity relative to the initial feed. Residual extracting media that can be present in the sulfur and/or nitrogen lean hydrocarbon stream can be removed as a bottom stream from the first distillation column.

[0074] Alternatively, the separation of the residual extracting media from the sulfur and/or nitrogen lean hydrocarbon stream can be accomplished by solvent extraction, membrane separation, or a combination of solvent extraction and membrane separation.

[0075] In the case of heavy hydrocarbon fractions (i.e., petroleum fractions having a final boiling point greater than the decomposition temperature of the applied ionic liquid solvent), residual extracting media dissolved in the hydrocarbon can be removed by solvent extraction with a polar solvent, preferably a polar organic solvent, such as for example, an alcohol or ketone.

[0076] The sulfur and/or nitrogen-rich stream can be supplied from the mixing vessel to a second distillation column. The sulfur and/or nitrogen-rich stream can include extracting media, and sulfur and nitrogen components dissolved in the extracting media and residual hydrocarbon feed. Elevated temperatures applied during a distillation process can decompose complexes formed between the metal ions and sulfur and/or nitrogen compounds. The second distillation column can be operated to produce a top stream that primarily includes sulfur and nitrogen containing compounds and a bottom stream that can include the extracting media.

[0077] As noted above, the extracting media has a very low vapor pressure (particularly in comparison to the hydrocarbon streams), thus separation by distillation can be employed. However, distillation temperatures (i.e., the final boiling point of the hydrocarbon feed) are typically maintained below the decomposition temperature of the ionic liquid. In certain embodiments, separation of the extracting media from the sulfur and/or nitrogen rich hydrocarbon stream can be achieved by flash distillation.

[0078] Alternatively, the separation of the residual hydrocarbons from the extracting media carried out by the second distillation column can be accomplished by solvent extraction, membrane separation, or a combination of solvent extraction and membrane separation.

[0079] The desulfurization and denitrogenation methods, as disclosed herein, are effective to reduce the sulfur and/or nitrogen content of the hydrocarbon feed stream by at least 10%, 25%, 50%, 75% or 90%. In certain embodiments, the desulfurization and denitrogenation methods disclosed herein can reduce the sulfur and nitrogen content of a hydrocarbon feed stream by at least 95%. In instances of sufficient contact time between the hydrocarbon stream and the extracting media, essentially 100% of the sulfur and nitrogen containing species can be removed. In certain embodiments, a hydrocarbon stream that includes sulfur and/or nitrogen can be contacted with the extracting media having at least one ionic liquid and at least one metal salt to produce a hydrocarbon stream having a sulfur content of less than 100 ppm, 50 ppm, 30 ppm, 20 ppm or 10 ppm. In certain instances, the resulting hydrocarbon stream may have a sulfur content of less than 5 ppm. Optionally, for increased removal of sulfur and/or nitrogen, the hydrocarbon feed stream can be contacted with the extracting media multiple times.

[0080] In an alternate embodiment, the extraction method can also include the step of regenerating the ionic liquid by removing the sulfur compounds. The step of removing the sulfur compound from the ionic liquid can include heating the ionic liquid to vaporize the sulfur compound, extraction of the sulfur compound from the ionic liquid with another

solvent, gas stripping, vaporization at a reduced pressure, and combinations of the foregoing techniques.

[0081] It is understood that there are other possible process options for the removal of sulfur and/or nitrogen from petroleum stream using ionic liquid/metal ion extracting media, and thus the present invention should not be limited to this example. In certain embodiments, the process can include one or more other separation techniques, such as for example, the use of membranes, supported membranes, solvent extraction, adsorption schemes, and the like.

[0082] While the desulfurization and/or denitrogenation process has been described herein as a batch process, it is understood that one of skill in the art can make modification to the process and operate the desulfurization and/or denitrogenation as a continuous process.

[0083] Examples

[0084] Examples 1-3 are directed to ionic liquid/metal salt extracting media combinations for the desulfurization of petroleum hydrocarbons.

[0085] Example 1

[0086] One mass unit of 1-butyl-4-methylpyridinium tetrafluoroborate was mixed with 0.2 mass units of copper(II) nitrate hemipentahydrate at room temperature. The resulting mixture was contacted with a gas oil fraction at a ratio of 4:6 (extracting media to gas oil fraction), followed by vigorous mixing for approximately 2 minutes. The gas oil fraction consists of a 1:1 ratio by volume of Arabian Light crude having boiling points of 400-500°F and 500-600°F and a sulfur content of 9,639 ppm.

[0087] The hydrocarbon phase was decanted from the mixture and washed with distilled water to remove residual extracting media. Analysis of a single extraction step yielded partially desulfurized gas oil having 7,744 ppm sulfur, a 19.7% reduction of sulfur.

[0088] Example 2

[0089] One mass unit of 1-butyl-3-methylimidazolium octyl sulfate was mixed with 0.2 mass units of copper(II) nitrate hemipentahydrate at room temperature. The mixture was contacted with a gas oil fraction at a ratio of 4:6 (extracting media to gas oil fraction), followed by vigorous mixing for approximately 2 minutes. The gas oil fraction consists of a 1:1 ratio by volume of Arabian Light crude having boiling points of 400-500°F and 500-600°F and a sulfur content of 9,639 ppm.

[0090] The hydrocarbon phase was decanted from the mixture and washed with distilled water to remove residual extracting media. Analysis of a single extraction step yielded partially desulfurized gas oil having 8,457 ppm sulfur, a 12.3% reduction in sulfur content.

[0091] Example 3

[0092] One mass unit of 1-butyl-4-methylpyridinium tetrafluoroborate was mixed with 0.2 mass units of palladium(II) nitrate hydrate at room temperature. The mixture was contacted with a gas oil fraction at a ratio of 4:6 (extracting media to gas oil fraction), followed by vigorous mixing for approximately 2 minutes. The gas oil fraction consists of a 1:1 ratio by volume of Arabian Light crude having boiling points of 400-500°F and 500-600°F and a sulfur content of 9,639 ppm.

[0093] The hydrocarbon phase was decanted from the mixture and washed with distilled water to remove residual extracting media. Analysis of a single extraction step yielded partially desulfurized gas oil having 5,212 ppm sulfur, a 45.9% reduction in sulfur content.

[0094] Examples 4-9

[0095] Examples 4-9 were prepared and tested for a variety of properties.

[0096] Example 4

[0097] A sample was prepared by combining 1-ethyl-3-methylimidazolium tosylate and palladium(II) nitrate hydrate in a 5:1 ratio.

[0098] Example 5

[0099] A sample was prepared by combining 1-butyl-4-methylpyridinium tetrafluoroborate and copper(II) nitrate hemipentahydrate in a 5:1 ratio.

[00100] Example 6

[00101] A sample was prepared by combining 1-butyl-3-methylimidazolium octyl sulfate and palladium(II) nitrate in a 5:1 ratio.

[00102] Example 7

[00103] A sample was prepared by combining 1-ethyl-3-methylimidazolium tosylate and copper(II) nitrate hemipentahydrate in a 5:1 ratio.

[00104] Example 8

[00105] A sample was prepared by combining 1-butyl-4-methylpyridinium tetrafluoroborate and palladium(II) nitrate in a 5:1 ratio.

[00106] Example 9

[00107] A sample was prepared by combining 1-butyl-3-methylimidazolium octyl sulfate and copper(II) nitrate hemipentahydrate in a 5:1 ratio.

Metal Solubility in Ionic Liquid

[00108] As shown in Table 1, metal solubility in the ionic liquid was tested by combining the ionic liquid and metal salt in a vial in a 5:1 weight ratio. In certain

embodiments, the samples were heated to approximately 80°C and cooled to room temperature to induce solubility.

[00109] Of the three ionic liquids, 1-butyl-4-methylpyridinium tetrafluoroborate demonstrated the highest solubility for both copper(II) nitrate and palladium(II) nitrate. The palladium and copper metals exhibited solubility of between 2 weight% and 20 weight%. Additionally, as shown, palladium(II) nitrate hydrate exhibited greater solubility in the ionic liquid than copper(II) nitrate hemipentahydrate. Tests were not conducted to determine if palladium(II) nitrate was soluble in an amount greater than 20% by weight.

Table 1

Example	Ionic Liquid	Metal Salt	Estimated Solubility of Ionic Liquid [wt%]	Comments
4	1-ethyl-3-methylimidazolium tosylate	Palladium (II) nitrate hydrate	12	Dark brown color (CT complex)
5	1-ethyl-3-methylimidazolium tosylate	Copper (II) nitrate hemipentahydrate	2	Transparent light blue
6	1-butyl-4-methylpyridinium tetrafluoroborate	Palladium (II) nitrate hydrate	20	Dark red (CT complex)
7	1-butyl-4-methylpyridinium tetrafluoroborate	Copper (II) nitrate hemipentahydrate	12	Dark purple (CT complex)
8	1-butyl-3-methylimidazolium octyl sulfate	Palladium (II) nitrate hydrate	12	Dark brown (CT complex)
9	1-butyl-3-methylimidazolium octyl sulfate	Copper (II) nitrate hemipentahydrate	4	Cloudy blue

Gas Oil Solubility in Ionic Liquids

[00110] The solubility of the light gas oil fraction (Arabian Light crude, 400°F – 500°F fraction) in the three ionic liquid samples were also tested. A sample of the light gas oil fraction was added to a sample of the ionic liquid. The sample was allowed to separate and settle, and the ionic liquid phase was removed, dried under nitrogen gas and the samples were weighed to measure the amount of gas oil adsorbed by the ionic liquid.

[00111] As shown in Table 2, solubility of the gas oil fraction was low in the sampled ionic liquids, and ranged between 2.3 and 4 weight%.

Table 2

Ionic Liquid	Gas Oil	Solubility in Ionic Liquid [wt%]
1-ethyl-3-methylimidazolium tosylate	Fraction boiling between 400-500°F	3.2
1-butyl-4-methylpyridinium tetrafluoroborate	Fraction boiling between 400-500°F	2.3
1-butyl-3-methylimidazolium octyl sulfate	Fraction boiling between 400-500°F	4.0

Desulfurization

[00112] Desulfurization of sulfur containing samples was also tested and the results are shown in Table 3. A gas oil mixture that includes equal volumes of a first fraction having a boiling range between 400°F – 500°F and a second fraction having a boiling range between 500°F – 600°F was contacted with various ionic liquids and ionic liquid/metal salts.

[00113] Sulfur concentration was determined by a Varian Pulsed Flame Photometric Detector (PFPD) installed on a Varian 3400 CX instrument having a DB-1 column installed for separation of hydrocarbons. The chromatographic conditions were as follows: Injector Parameters: injector temperature of 300°C; split mode of 1/80 or 1/50; injection volume between 0.2 and 1 µL; Column Parameters: column length of 30m, having a 0.25 mm ID and a 250µm film; initial column temperature of 40°C; ramp to 300°C at a rate of 10°C/min; hold time at 300°C for 5 min.; pressure of 17 psi; column flow rate of 1.2 mL/min at 40°C; and Detector Parameters: temperature 300°C; hydrogen flow rate of 35 mL/min and air flow rate of 400 mL/min. Benzothiophene was used as the internal standard due to the low concentration that occurs naturally relative to the alkylated benzothiophene species and lower boiling point.

[00114] Desulfurization with copper resulted in desulfurization of between 4.1% and 19.7%, whereas desulfurization with palladium resulted in desulfurization of between 15.4% and 45.9%. As noted above with respect to solubility, the palladium metal salt achieved higher desulfurization than copper in the ionic solvent. For example, palladium in 1-butyl-4-methylpyridinium tetrafluoroborate removed 2.3 times more sulfur than copper in the same solvent.

[00115] Additionally, the desulfurization capacity of the ionic liquid/metal salt solutions increases in those systems where the solubility of the metal salt is higher, and in those solutions that tend to form strong charge transfer complexes.

[00116] Referring to Figure 2, stacked chromatograms are provided for the desulfurization of an Arabian Light fraction (400-600°F) gas oil by extraction with ionic liquid/copper metal salt extracting media. From top to bottom the figure provides the chromatogram for untreated gas oil and, gas oil extracted with 1-ethyl-3-methylimidazolium tosylate/copper mixture (third from bottom), 1-butyl-4-methylpyridinium tetrafluoroborate/copper mixture (second from bottom), and 1-butyl-3-methylimidazolium octyl sulfate/copper mixture (bottom). Individual chromatograms for each of ionic liquid/copper metal salt examples 5, 7 and 9 are provided in Figures 3, 4 and 5, respectively. Specifically, Figure 3 corresponds to Example 5 and provides a comparison of the chromatogram of an untreated gas oil with the chromatogram of a gas oil fraction extracted with 1-ethyl-3-methylimidazolium tosylate/copper mixture. Similarly, Figure 4 corresponds to Example 7 and provides a comparison for the chromatogram of an untreated gas oil with the chromatogram of a gas oil fraction extracted with 1-butyl-4-methylpyridinium tetrafluoroborate/copper mixture. Finally, Figure 5 corresponds to Example 9 and provides a comparison of the chromatogram of an untreated gas oil and the chromatogram of a gas oil that has been extracted with 1-butyl-3-methylimidazolium octyl sulfate/copper mixture. Comparing the relative peak intensity for components having a retention time above and below 18 minutes (relating to dibenzothiophenes and benzothiophenes, respectively) demonstrates that each of the ionic liquid/metal salt systems from Examples 5, 7 and 9 have higher selectivity to removal of dibenzothiophenes than benzothiophenes.

[00117] Referring now to Figure 6, stacked chromatograms are provided for the desulfurization of an Arabian Light fraction (400-600°F) gas oil by extraction with ionic liquid/palladium metal salt extracting media. From top to bottom the figure provides the chromatogram for untreated gas oil and, gas oil extracted with 1-ethyl-3-methylimidazolium tosylate/palladium mixture (third from bottom), 1-butyl-4-methylpyridinium tetrafluoroborate/palladium mixture (second from bottom), and 1-butyl-3-methylimidazolium octyl sulfate/palladium mixture (bottom). Individual chromatograms for each of the ionic liquid/palladium metal salt provided in Examples 4, 6 and 8 are provided in Figures 7, 8 and 9, respectively. Specifically, Figure 7 corresponds to Example 4 and provides a comparison of the chromatogram of an untreated gas oil with the chromatogram of a gas oil extracted with 1-ethyl-3-methylimidazolium tosylate/palladium mixture. Figure 8 corresponds to

Example 6 and provides a comparison of the chromatogram of an untreated gas oil and the chromatogram of a gas oil extracted with 1-butyl-4-methylpyridinium tetrafluoroborate/palladium mixture. Finally, Figure 9 corresponds to Example 8 and provides a comparison of the chromatogram of an untreated gas oil and the chromatogram of a gas oil extracted with 1-butyl-3-methylimidazolium octyl sulfate/palladium mixture. As demonstrated with the copper systems, the ionic liquid/palladium systems show higher selectivity to removal of dibenzothiophenes than benzothiophenes.

Table 3

Example	Measured Sample	Sulfur concentration (ppm)	Percent Desulfurization
--	Gas Oil Feed*	9639	
--	Gas Oil Feed + 1-ethyl-3-methylimidazolium tosylate	9780	-1.5
--	Gas Oil Feed + 1-butyl-4-methylpyridinium tetrafluoroborate	9362	2.9
--	Gas Oil Feed + 1-butyl-3-methylimidazolium octyl sulfate	9715	-0.08
5	Gas Oil Feed + 1-ethyl-3-methylimidazolium tosylate/Cu	9239	4.1
7	Gas Oil Feed + 1-butyl-4-methylpyridinium tetrafluoroborate/Cu	7744	19.7
9	Gas Oil Feed + 1-butyl-3-methylimidazolium octyl sulfate/Cu	8457	12.3
4	Gas Oil Feed + 1-ethyl-3-methylimidazolium tosylate/Pd	8152	15.4
6	Gas Oil Feed + 1-butyl-4-methylpyridinium tetrafluoroborate/Pd	5212	45.9
8	Gas Oil Feed + 1-butyl-3-methylimidazolium octyl sulfate/Pd	6916	28.2

* Gas oil feed is 1:1 mixtures by weight of two separate cuts from Arabian Light crude (a 400°F – 500°F fraction, and a 500°F – 600°F fraction).

[00118] As used herein, the terms about and approximately should be interpreted to include any values which are within 5% of the recited value. Furthermore, recitation of the term about and approximately with respect to a range of values should be interpreted to include both the upper and lower end of the recited range.

[00119] Although the following detailed description contains many specific details for purposes of illustration, one of ordinary skill in the art will appreciate that many variations and alterations to the following details are within the scope and spirit of the invention. Accordingly, the exemplary embodiments of the invention described herein are set forth without any loss of generality to, and without imposing limitations thereon, the present invention.

[00120] As used herein, optional or optionally means that the subsequently described event or circumstances may or may not occur. The description includes instances where the event or circumstance occurs and instances where it does not occur.

[00121] As used herein, recitation of the term about and approximately with respect to a range of values should be interpreted to include both the upper and lower end of the recited range. Ranges may be expressed herein as from about one particular value, and/or to about another particular value. When such a range is expressed, it is to be understood that another embodiment is from the one particular value and/or to the other particular value, along with all combinations within said range.

[00122] As used in the specification and claims, the singular form "a", "an" and "the" may include plural references, unless the context clearly dictates the singular form.

[00123] Throughout this application, where patents or publications are referenced, the disclosures of these references in their entireties are intended to be incorporated by reference into this application, in order to more fully describe the state of the art to which the invention pertains, except when these reference contradict the statements made herein.

We claim:

1. A method for upgrading a hydrocarbon feed **14**, the hydrocarbon feed comprising one or more contaminants, the method of upgrading the hydrocarbon stream comprising the steps of:

contacting the hydrocarbon feed **14** with an extracting stream **18**, the extracting stream **18** comprising at least one metal salt and at least one ionic liquid, to create a mixed stream **16**,

wherein during the step of contacting the feed stream and the extracting stream, the metal ion of the metal salt binds with at least one contaminant contained in the feed stream such that a significant amount of the at least one contaminant is removed from the hydrocarbon feed and bound to the metal;

separating the mixed stream **16** into a contaminant-lean hydrocarbon stream **20** and a contaminant-rich stream **24**; and

collecting the contaminant-lean hydrocarbon stream as a product stream **36**.

2. The method of claim 1 wherein the ionic liquid comprises at least one cation and at least one anion,

wherein the cation is selected from the group consisting of an imidazolium ion, a pyridinium ion, a pyrrolium, a quaternary ammonium ion, and a phosphonium ion; and

wherein the anion is selected from the group consisting of halo or alkyl-sulfates, halo or alkyl-sulfonates, halides, hydroxide, perchlorate, borates, halo-borates, nitrates, sulfates, phosphates, acetates, haloacetates, triflate, bis(triflyl)imide, halo-aluminates, tetrafluoroborate, halo-phosphates, halo-antimonates halo-sulfonates, alkyl sulfonates, halo-alkyl sulfonates sulfonyls, halo-sulfonyl amides, tris-trifluoromethanesulfonyl methylide, arenesulfonates, optionally substituted by halogen or haloalkyl groups, and tetraphenylborates.

3. The method of any of the preceding claims wherein the ionic liquid comprises an ion selected from the group consisting of an imidazolium ion, a pyridinium ion, an ammonium ion and a phosphonium ion.
4. The method of any of the preceding claims wherein the cation of the ionic liquid is selected from 1-butyl-4-methylpyridinium ion and 1-butyl-3-methylimidazolium ion.
5. The method of any of the preceding claims wherein the metal salt is a salt of a Group IB, IIB, VIB, or VIIIB metal.
6. The method of any of the preceding claims wherein the metal salt is a salt of copper, nickel, zinc, cobalt, molybdenum, silver or palladium.
7. The method of any of the preceding claims wherein the metal salt is a salt of copper(II) or palladium(II).
8. The method of any of the preceding claims wherein the hydrocarbon feed stream **14** and extracting stream **18** are contacted in a counter-current flow **16**.
9. The method of any of the preceding claims wherein the hydrocarbon feed stream **14** and the extracting stream **18** are contacted in a mixing vessel **16** and the contaminant-lean hydrocarbon stream **20** is removed from the top of the mixing vessel and the contaminant-rich stream **24** is removed from the bottom of the mixing vessel **16**.
10. The method of any of the preceding claims wherein the contaminant-rich stream **24** includes a significant amount of the ionic liquid.
11. The method of any of the preceding claims wherein the ratio of hydrocarbon feed to extracting stream is between 0.5:1 and 100:1.
12. The method of any of the preceding claims further comprising the steps of:

supplying the contaminant-lean hydrocarbon stream **20** to a distillation column **32**;

separating the contaminant-lean hydrocarbon stream **30** into a vapor stream **34** and a liquid stream **39**; and

collecting the vapor stream as a purified product stream **34**.

13. The method of claim 12 further comprising:

supplying the contaminant-lean hydrocarbon stream **20** to a phase separator **22** to remove a residual extracting stream **28**, and

combining the residual extracting stream **28** with the contaminant-rich stream **24**;

wherein the phase separator **22** is positioned downstream of the contacting step and upstream of the distillation column **32**.
14. The method of any of claims 12 and 13 further comprising the step of:

recycling the liquid stream **39** to the extracting stream **18**.
15. The method of any of the preceding claims further comprising the steps of:

feeding the contaminant-rich stream **24** to a distillation column **40**;

separating the contaminant-rich stream **24** into a vapor stream **42** and a liquid stream **46**; and

recycling the liquid stream **46** to the extracting stream **18**.
16. The method of any of the preceding claims wherein the hydrocarbon feed stream is a liquid.
17. The method of any of the preceding claims wherein the at least one contaminant in the hydrocarbon feed stream **14** comprises sulfur containing compounds.
18. The method of any of the preceding claims wherein the at least one contaminant in the hydrocarbon feed stream **14** comprises thiophene.
19. The method of any of the preceding claims wherein the at least one contaminant in the hydrocarbon feed stream **14** comprises nitrogen containing compounds.
20. The method of any of the preceding claims wherein the metal ion of the metal salt reacts with the contaminant contained in the feed stream **14** to form a metal-contaminant complex such that a significant amount of contaminant is removed from the hydrocarbon feed.

21. The method of any of the preceding claims wherein the metal ion of the metal salt reacts with the sulfur contained in the feed stream **14** to form a metal-sulfur complex such that a significant amount of sulfur is removed from the hydrocarbon feed.

22. The method of any of the preceding claims wherein the metal ion of the metal salt reacts with the nitrogen contained in the feed stream **14** to form a metal-nitrogen complex such that a significant amount of nitrogen is removed from the hydrocarbon feed.

23. The method of any of the preceding claims wherein the at least one contaminant comprises sulfur containing compounds and nitrogen containing compounds, and wherein the step of contacting the contaminants with the extracting stream comprises forming metal-sulfur and metal-nitrogen complexes and wherein the sulfur-lean product stream **20** has a reduced concentration of nitrogen compounds.

24. A process for upgrading of a hydrocarbon feed **14**, wherein said hydrocarbon feed includes one or more contaminants, the process comprising the steps of:

mixing the hydrocarbon feed **14** and an adsorbent containing solution **18** in a mixing vessel **16**, wherein the adsorbent containing solution **18** comprises at least one ionic liquid and at least one metal salt;

wherein during the step of mixing the hydrocarbon feed **14** and the adsorbent containing solution **18**, the metal ion of the metal salt can bind to and remove one or more contaminants present in the hydrocarbon feed **14**;

separating the mixture into a contaminant-lean hydrocarbon product stream **20** and a contaminant-rich stream **24**;

supplying the contaminant-lean **20** hydrocarbon stream to a first distillation column **32** and separating residual extracting solution to produce a hydrocarbon product stream **34** having a reduced contaminant concentration relative to the hydrocarbon feed stream **14**;

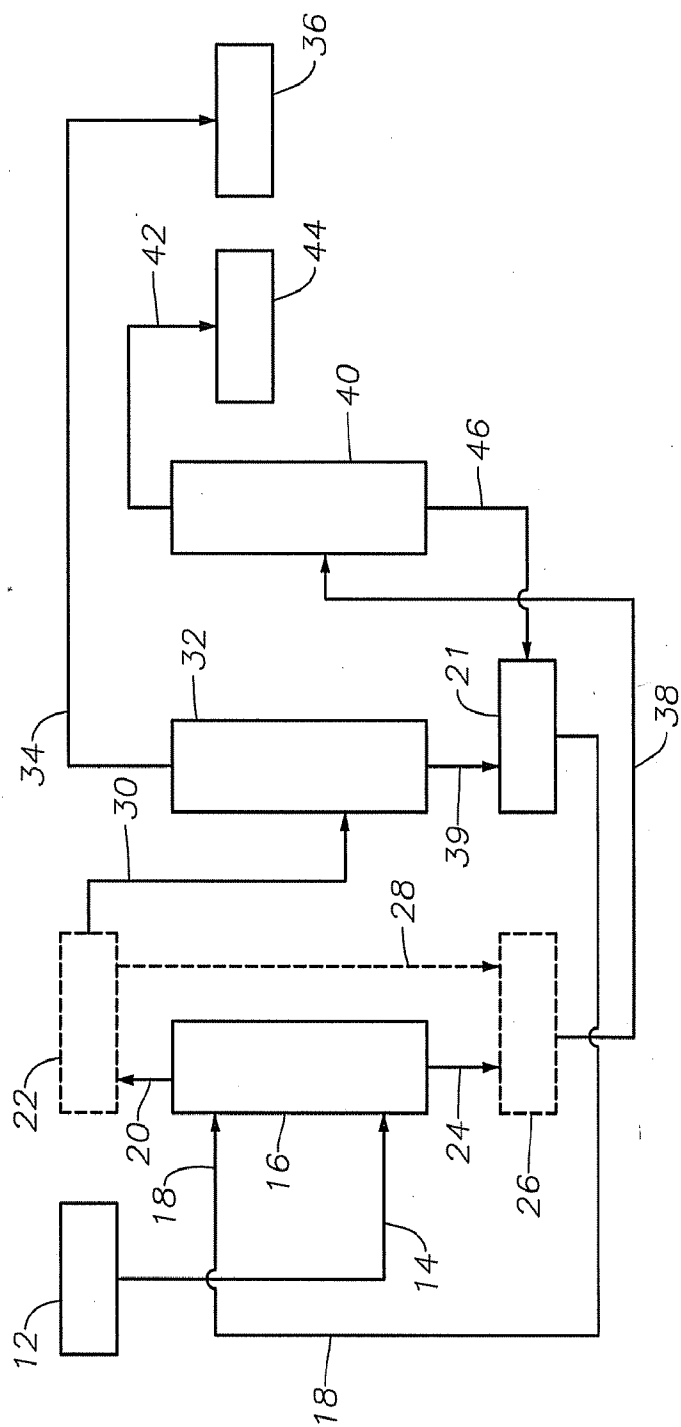
supplying the contaminant-rich stream **24** to a second distillation column **40** to produce a top stream **42** and a bottom stream **46**, wherein the top stream **42** comprises a contaminant-rich stream and the bottom stream **46** comprises ionic liquid; and

recycling the ionic liquid **18** to the mixing vessel **16**.

25. The process of claim 38 further comprising the step of supplying the recovered ionic liquid streams to a feed tank **21** comprising ionic liquid and metal salts.

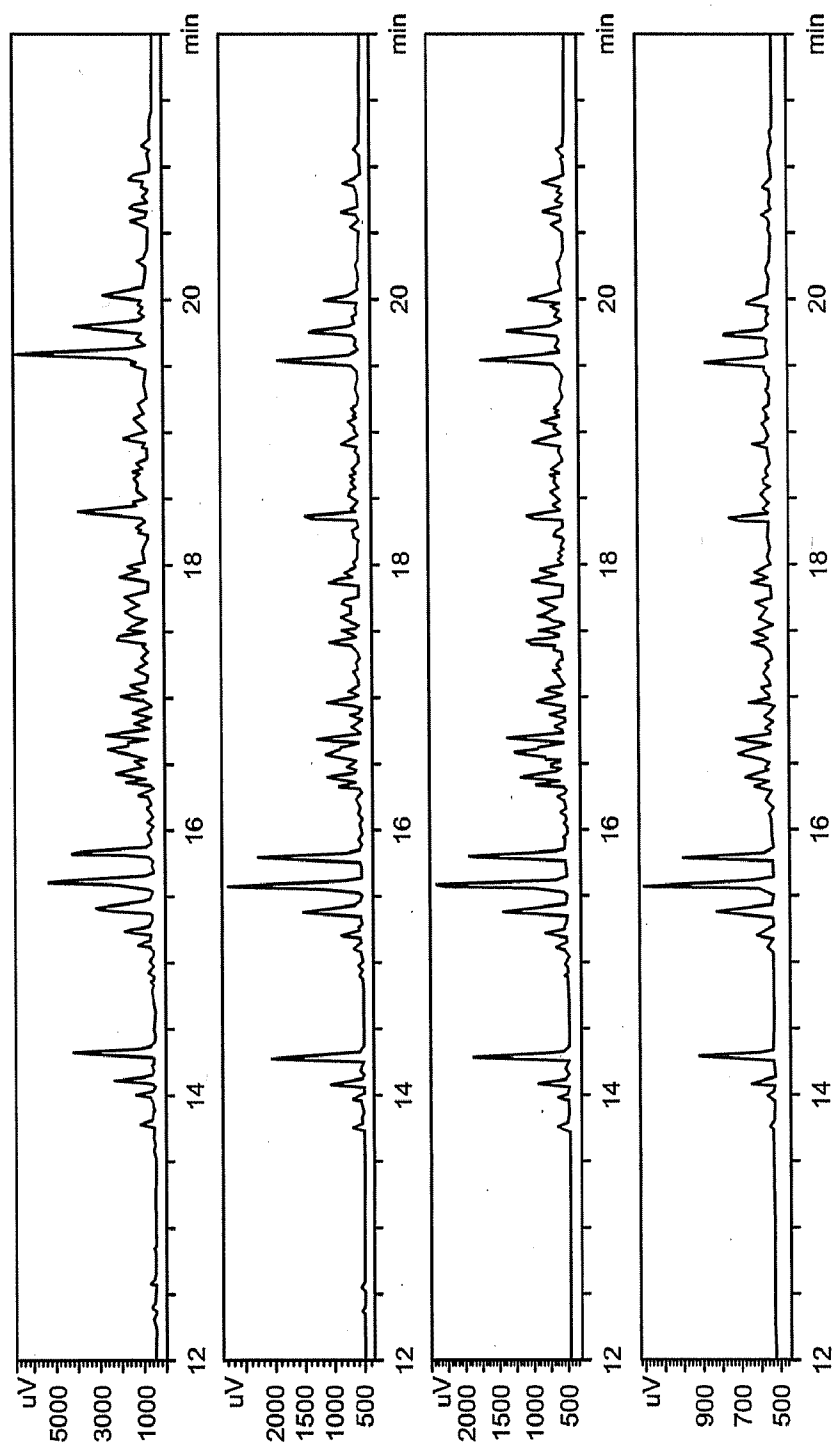
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Fig. 1



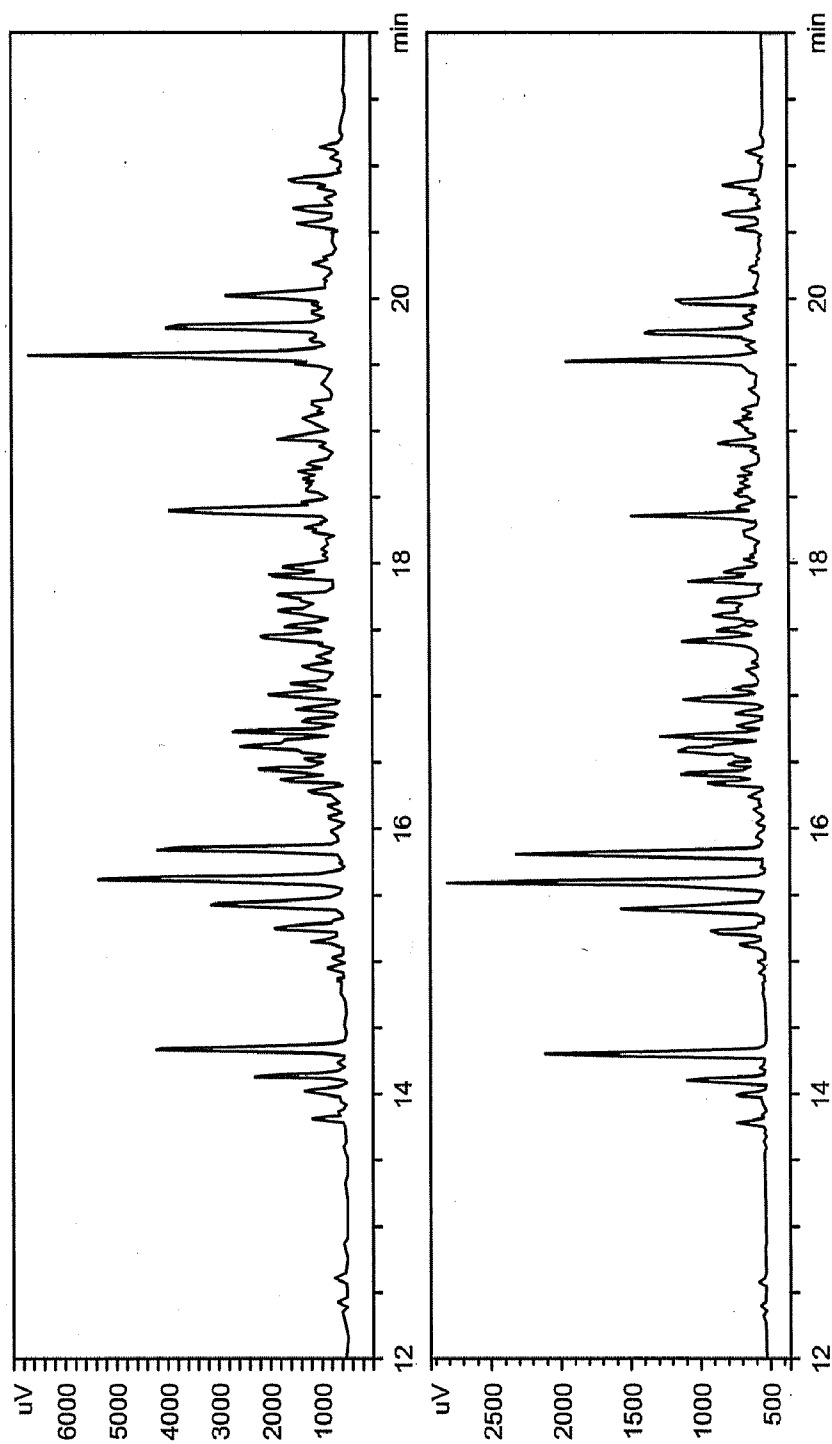
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Fig. 2



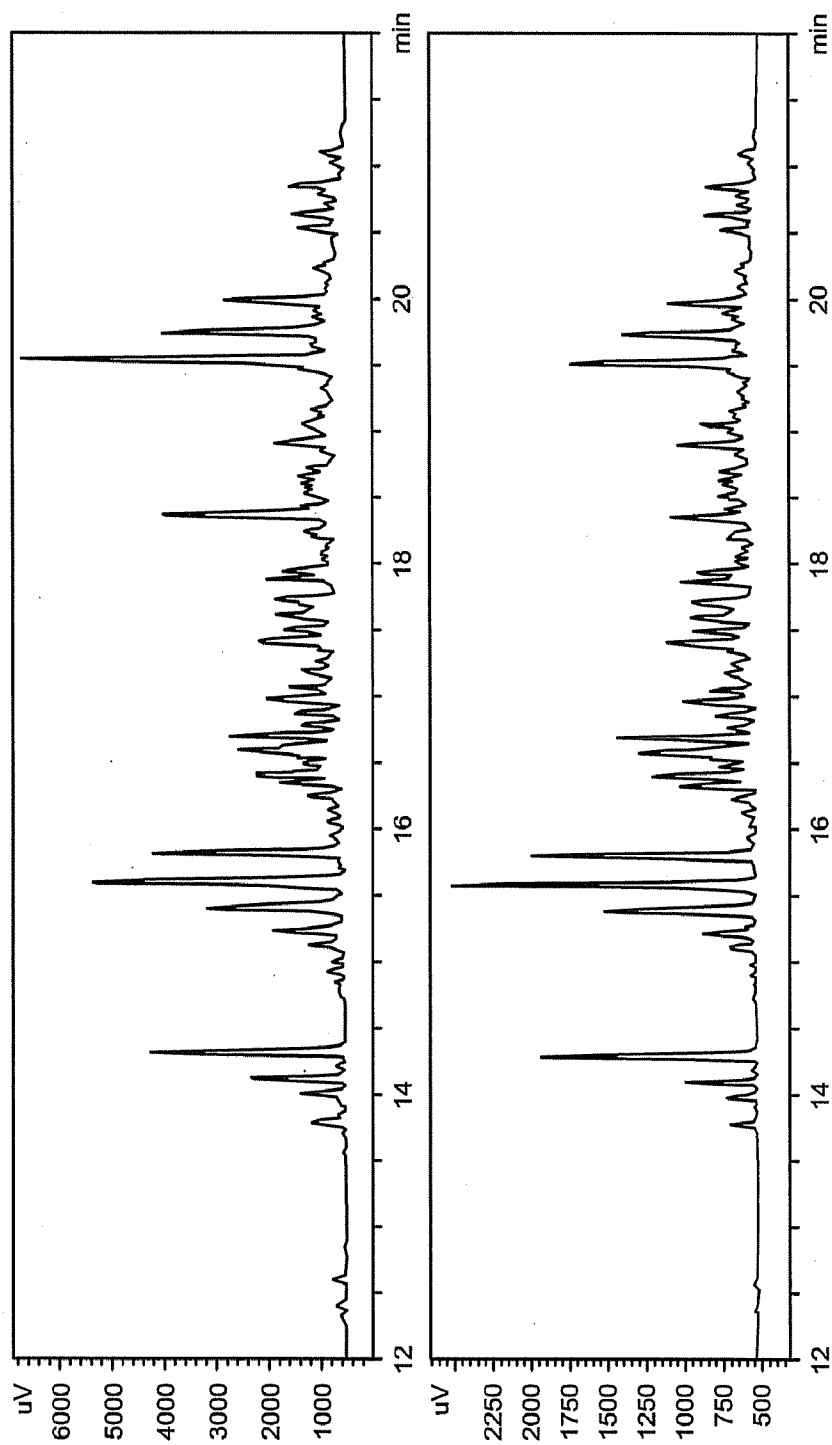
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Fig. 3



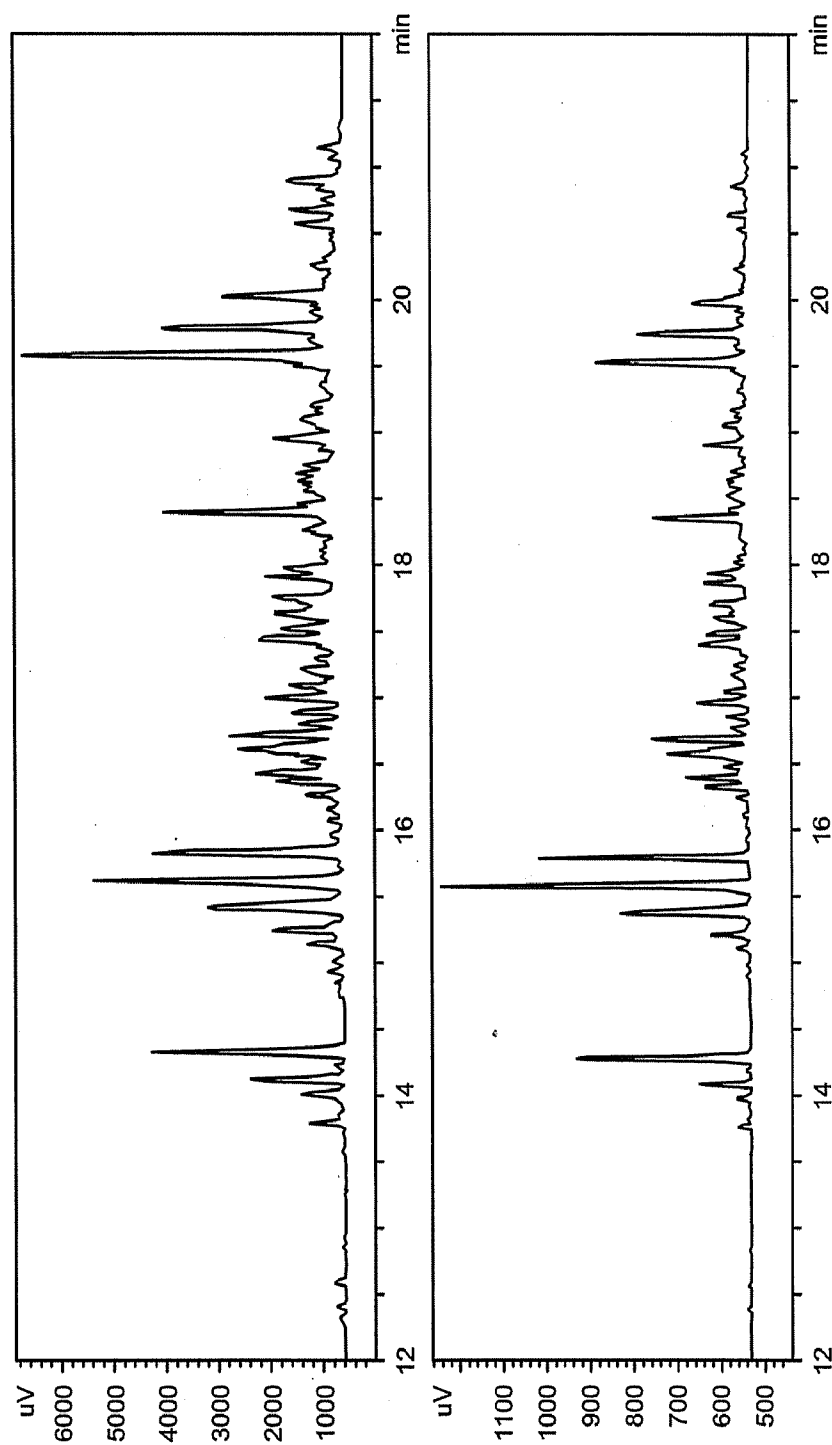
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Fig. 4



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Fig. 5



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Fig. 6

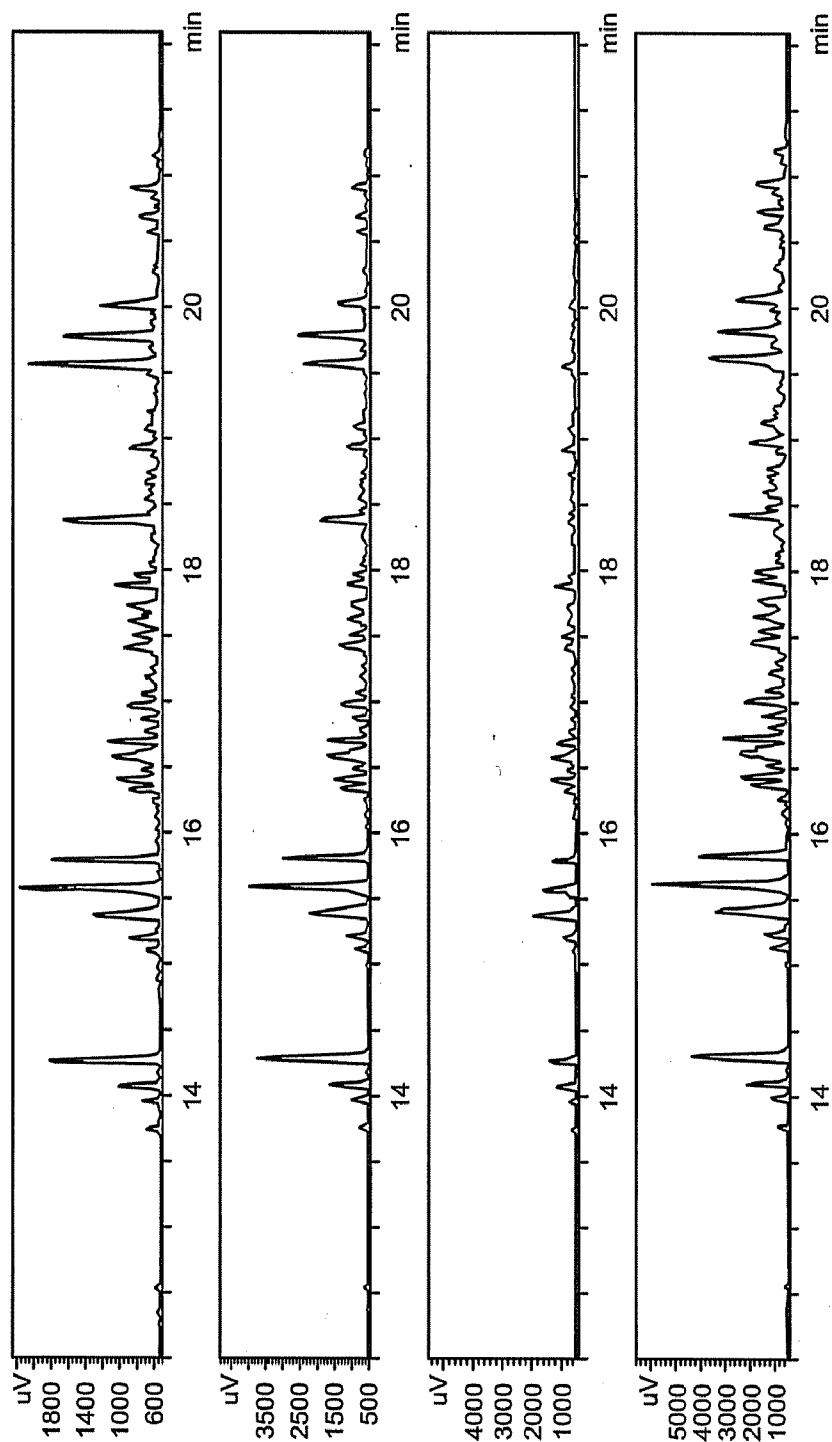
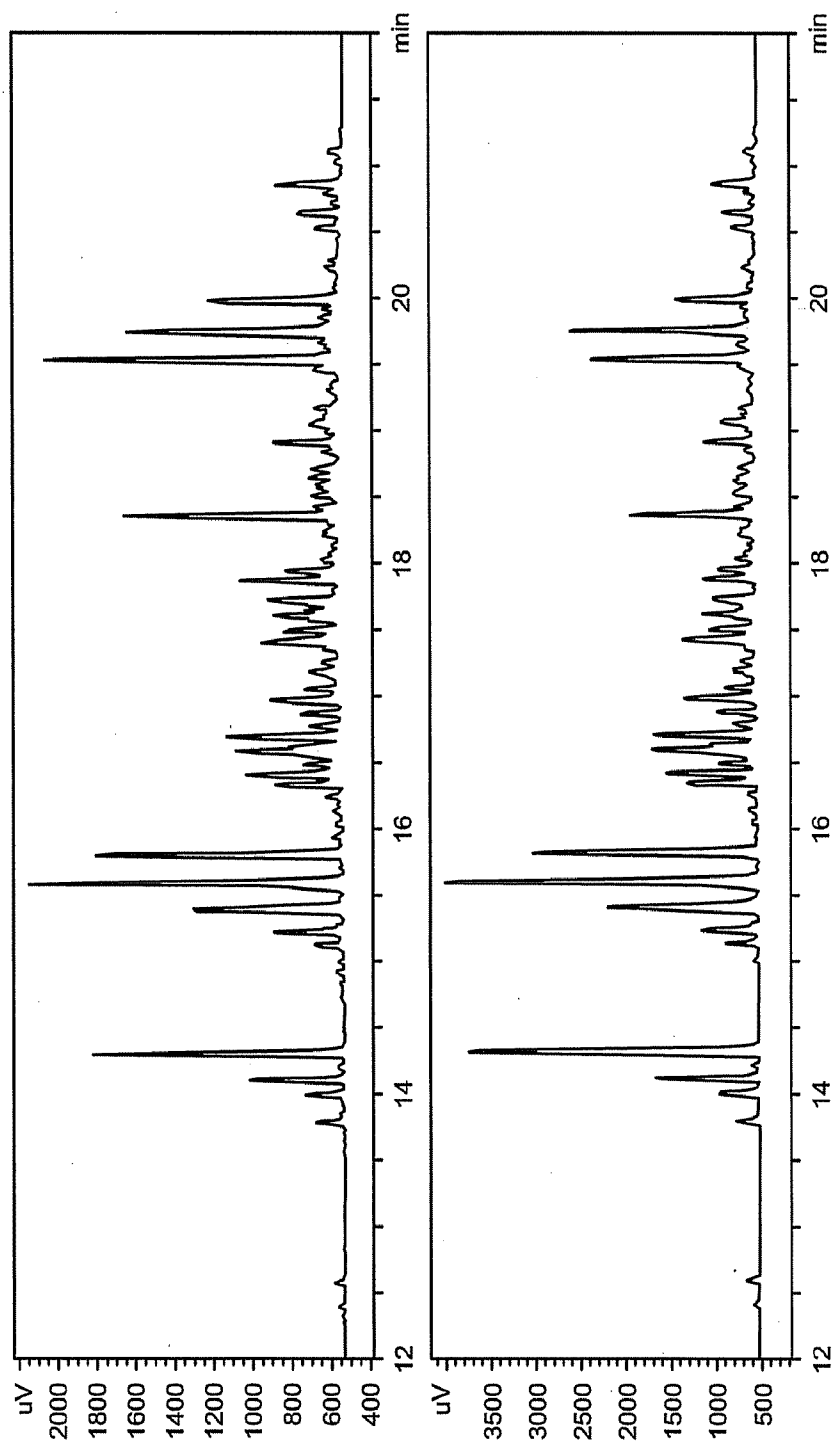


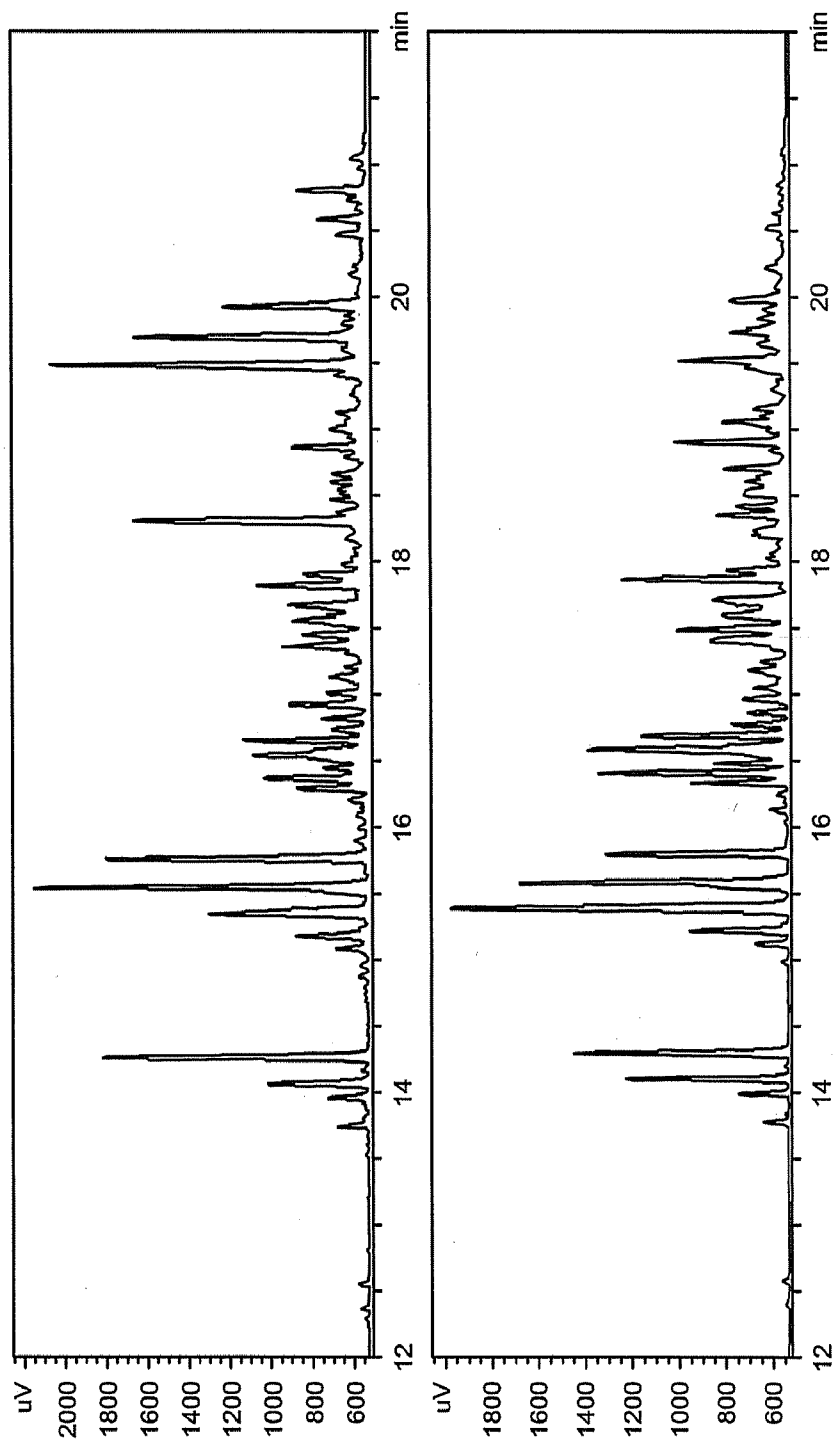
Fig. 7



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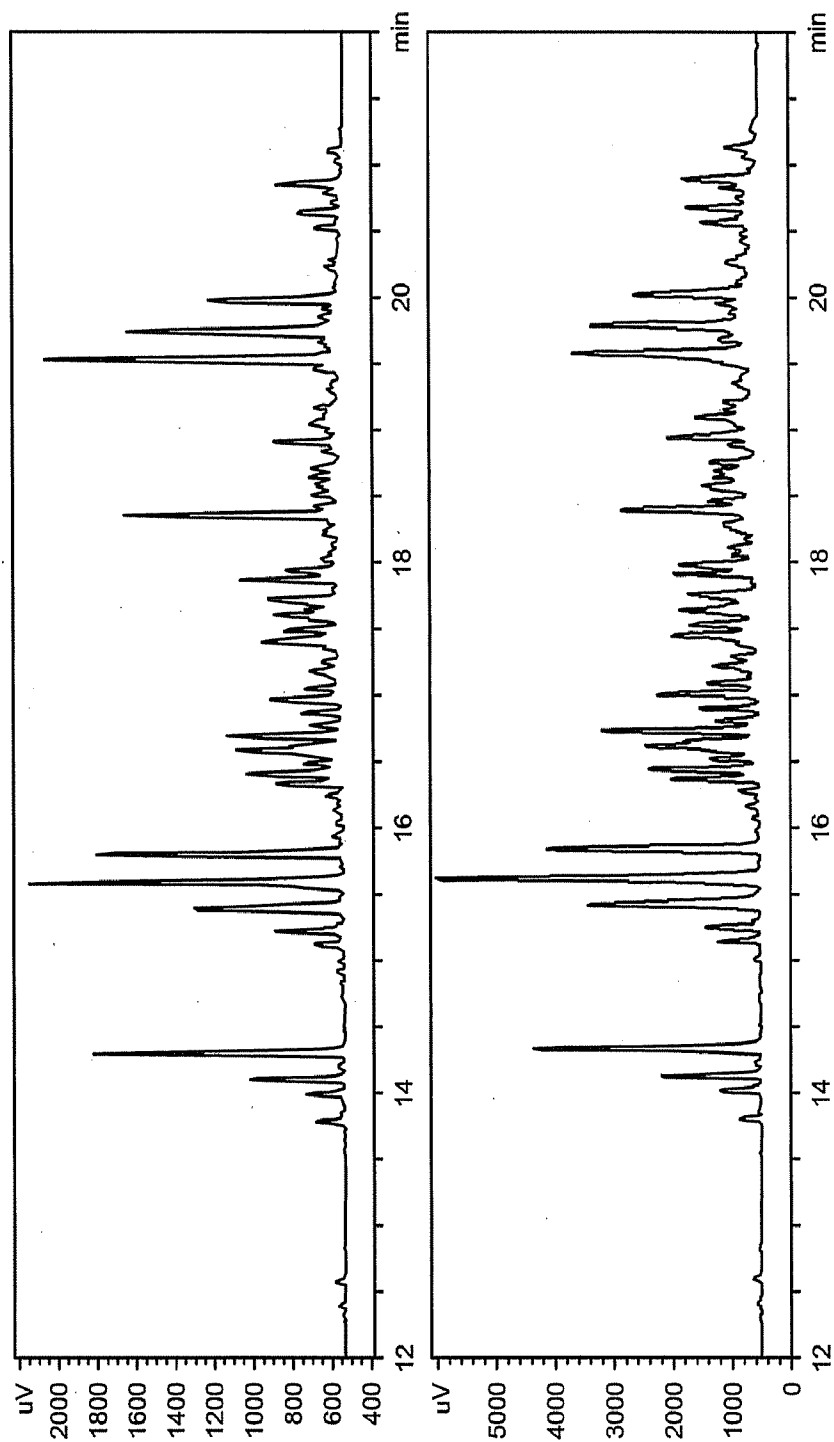
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Fig. 8



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Fig. 9



INTERNATIONAL SEARCH REPORT

International application No

PCT/US2010/032473

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G21/06 C10G29/06

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10G

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 practical, search terms used)

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FAN H F ET AL: "Experimental study on using ionic liquids to upgrade heavy oil" JOURNAL OF FUEL CHEMISTRY AND TECHNOLOGY,, vol. 35, no. 1, 1 February 2007 (2007-02-01), pages 32-35, XP022937052 ISSN: 1872-5813 [retrieved on 2007-02-01] * abstract page 32, right-hand column, paragraph 3 - page 33, left-hand column, paragraph 1 page 34, right-hand column, paragraph 2 - page 35, left-hand column, paragraph 1; table 2 ----- -/--	1-18,20, 21,24

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents :

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"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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Date of the actual completion of the international search

30 August 2010

Date of mailing of the international search report

09/09/2010

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/032473

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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