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(54) **PROCESS FOR REGENERATING IONIC LIQUIDS BY ADDING LIGHT HYDROCARBON STREAM**

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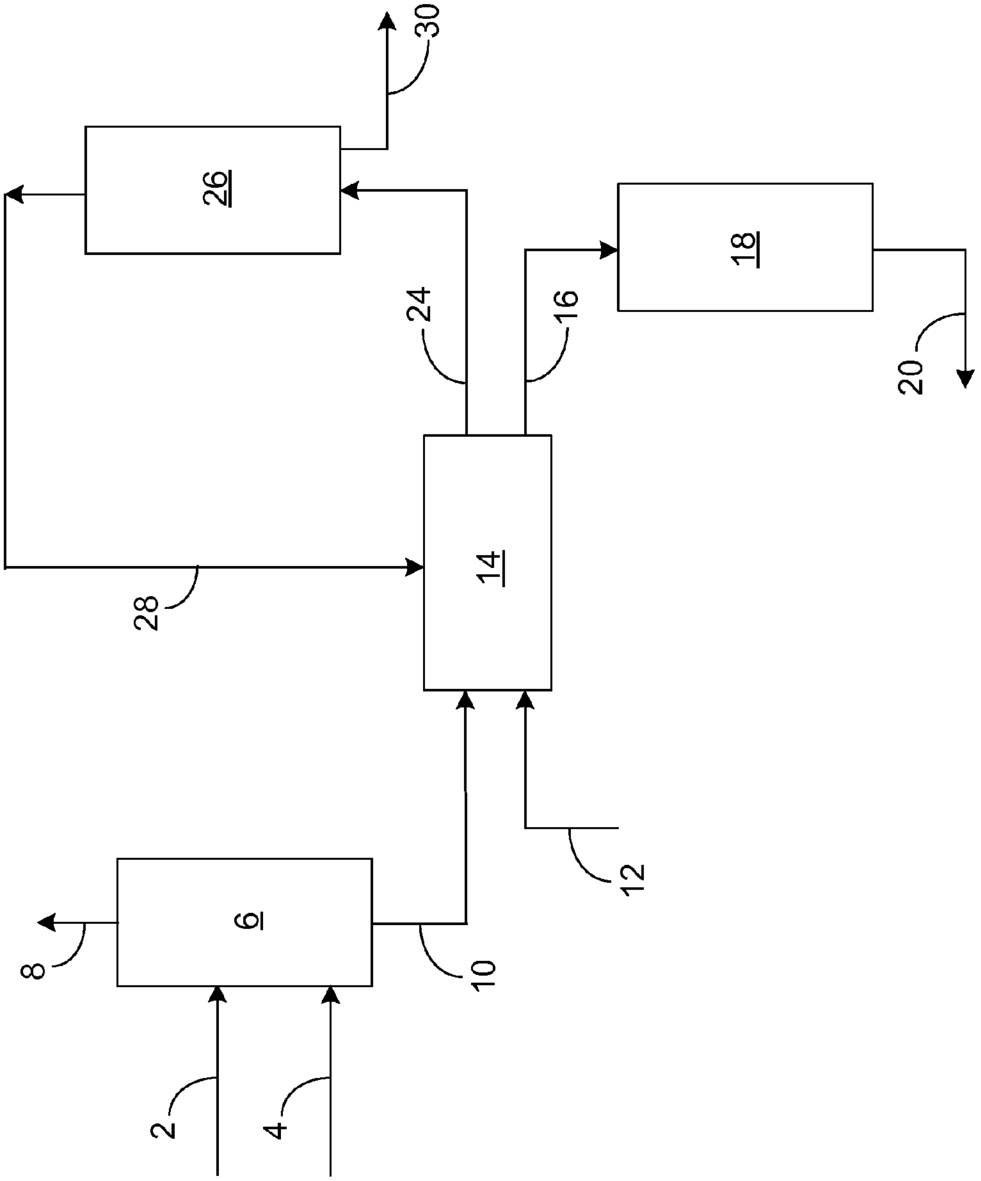
(57) **ABSTRACT**

A process for removing at least one impurity from a hydrocarbon feed such as vacuum gas oil in which the process includes the steps of contacting the feed with a hydrocarbon-immiscible phosphonium ionic liquid to produce a hydrocarbon and hydrocarbon-immiscible phosphonium ionic liquid mixture, and separating the mixture to produce a hydrocarbon effluent having a reduced impurity content relative to the hydrocarbon feed.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PROCESS FOR REGENERATING IONIC LIQUIDS BY ADDING LIGHT HYDROCARBON STREAM

BACKGROUND OF THE INVENTION

[0001] This invention relates to processes for regenerating ionic liquids that are used in decontamination of hydrocarbon streams. More particularly, the invention relates to process conditions where the hydrocarbon stream has a density that is close to the density of an ionic liquid/water mixture and the use of a lower density hydrocarbon to facilitate the removal of contaminants from the ionic liquid/water mixture.

[0002] Ionic liquids have many different applications in the refining industry. For example, they can be used as a solvent to decontaminate a hydrocarbon stream that feeds into reactors such as a fluidized catalytic cracking unit (FCC), a hydroprocessing unit or a hydrocracking unit. During the decontamination process, the ionic liquid extracts the contaminants and forms two phases—a clean hydrocarbon phase and a dirty ionic liquid phase comprising ionic liquid plus contaminants that are mostly hydrocarbons such as nitrogen, sulfur, or metal containing hydrocarbons and certain aromatic compounds. Since ionic liquids are usually expensive to replace, they need to be regenerated for recycling back to the extraction or contaminant removal step. To separate ionic liquids from the hydrocarbon impurities, water at typically a 1:1 ionic liquid/water ratio is added to the mixture. Ionic liquid has more affinity towards water than the hydrocarbon impurities so that the ionic liquid rejects the hydrocarbon impurities and forms a separate phase with water. The hydrocarbon impurities are then separated from the ionic liquid/water phase as the hydrocarbon impurity stream and the water is boiled off to regenerate the ionic liquid. However, it has now been found that, if the density of the hydrocarbon impurity stream is close to the density of the ionic liquid/water phase then the separation of the hydrocarbon impurity stream from the ionic liquid/water phase becomes difficult.

[0003] Hydrocarbon streams may be converted into higher value hydrocarbon fractions such as diesel fuel, jet fuel, naphtha, gasoline, and other lower boiling fractions in refining processes such as hydrocracking and fluid catalytic cracking (FCC). However, hydrocarbon streams having higher amounts of nitrogen are more difficult to convert. For example, the degree of conversion, product yields, catalyst deactivation, and/or ability to meet product quality specifications may be adversely affected by the nitrogen content of the feed stream. It is known to reduce the nitrogen content of vacuum gas oil (VGO) by catalytic hydrogenation reactions such as in a hydrotreating process unit. The nitrogen that is removed is often part of a hydrocarbon.

[0004] There are other hydrocarbons and mixtures of hydrocarbons that have a similar need to remove nitrogen content and other impurities such as sulfur compounds, or metals. Treatment of such other hydrocarbons with ionic liquids is within the scope of the present invention.

[0005] Various processes using ionic liquids to remove sulfur and nitrogen compounds from hydrocarbon fractions are also known. U.S. Pat. No. 7,001,504 B2 discloses a process for the removal of organosulfur compounds from hydrocarbon materials which includes contacting an ionic liquid with a hydrocarbon material to extract sulfur containing compounds into the ionic liquid. U.S. Pat. No. 7,553,406 B2 discloses a process for removing polarizable impurities from hydrocarbons and mixtures of hydrocarbons using ionic liquids as an extraction medium. U.S. Pat. No. 7,553,406 B2 also discloses that different ionic liquids show different extractive properties for different polarizable compounds.

[0006] This invention is related to regenerating the ionic liquid from the ionic liquid/hydrocarbon mixture by adding water and a light hydrocarbon stream to assist with the removal of hydrocarbon impurities from the ionic liquid.

SUMMARY OF THE INVENTION

[0007] Water and a light hydrocarbon stream such as naphtha/kerosene/LCO or any other hydrocarbon which is miscible with the hydrocarbon feed and/or the extracted hydrocarbon impurities and has a density lower than water or the ionic liquid is added to the ionic liquid/hydrocarbon impurities mixture to regenerate the ionic liquid from the ionic liquid/hydrocarbon impurities mixture and to also increase the density difference between the ionic liquid phase and the hydrocarbon phase. In an embodiment water is added to the ionic liquid/extracted hydrocarbon mixture before the light hydrocarbon stream is added. The density difference between the hydrocarbon and ionic liquid phase will help in the separation of the ionic liquid phase in a conventional mixer-settler. The hydrocarbon phase (lighter phase) can be sent to an evaporator or other well known operations such as a steam stripping column to separate the light hydrocarbon from the hydrocarbon impurities and the separated light hydrocarbon can be recycled back to the regeneration step.

[0008] In an embodiment, the invention is a process for removing nitrogen compounds and other impurities from a hydrocarbon feed comprising contacting the hydrocarbon with a hydrocarbon-immiscible phosphonium ionic liquid to produce a hydrocarbon and hydrocarbon—immiscible phosphonium ionic liquid mixture, and separating the mixture to produce a hydrocarbon effluent and a hydrocarbon-immiscible phosphonium ionic liquid effluent comprising the nitrogen compound. The hydrocarbon-immiscible phosphonium ionic liquid effluent is mixed with water to separate the hydrocarbon containing impurities from the ionic liquid. In addition, a light hydrocarbon such as naphtha, light cycle oil, kerosene or benzene is added to this mixture to separate the hydrocarbon containing impurities from the ionic liquid since such separations are difficult to achieve when the ionic liquid, water and hydrocarbon containing impurities have essentially the same density. The light hydrocarbon that is added has a lower density than water, the ionic liquid or mixtures thereof.

[0009] In an embodiment, the hydrocarbon-immiscible phosphonium ionic liquid comprises at least one ionic liquid from at least one of tetraalkylphosphonium dialkylphosphates, tetraalkylphosphonium dialkyl phosphinates, tetraalkylphosphonium phosphates, tetraalkylphosphonium tosylates, tetraalkylphosphonium sulfates, tetraalkylphosphonium sulfonates, tetraalkylphosphonium carbonates, tetraalkylphosphonium metalates, oxometalates, tetraalkylphosphonium mixed metalates, tetraalkylphosphonium polyoxometalates, and tetraalkylphosphonium halides. In another embodiment, the hydrocarbon-immiscible phosphonium ionic liquid comprises at least one of trihexyl(tetradecyl)phosphonium chloride, trihexyl(tetradecyl)phosphonium bromide, tributyl(methyl)phosphonium bromide, tributyl(methyl)phosphonium chloride, tributyl(hexyl)phosphonium bromide, tributyl(hexyl)phosphonium chloride, tributyl(octyl)phosphonium bromide, tributyl(octyl)phosphonium chloride, tributyl(decyl)phosphonium bromide, tributyl(decyl) phosphonium chloride, tetrabutylphosphonium bromide, tetrabutylphosphonium chloride, triisobutyl(methyl)phosphonium tosylate, tributyl(methyl)phosphonium methylsulfate, tributyl(ethyl)phosphonium diethylphosphate, and tetrabutylphosphonium methanesulfonate.

BRIEF DESCRIPTION OF THE DRAWING

[0010] The FIGURE shows the flow scheme of the present invention in which a light hydrocarbon stream is employed to separate hydrocarbon wastes from ionic liquid/water.

DETAILED DESCRIPTION OF THE INVENTION

[0011] In general, the invention may be used to remove a nitrogen or sulfur compound or other hydrocarbon containing impurity from a hydrocarbon fraction through use of a hydrocarbon-immiscible phosphonium ionic liquid.

[0012] The terms “vacuum gas oil”, “VGO”, “VGO phase” and similar terms relating to vacuum gas oil as used herein are to be interpreted broadly to receive not only their ordinary meanings as used by those skilled in the art of producing and converting such hydrocarbon fractions, but also in a broad manner to account for the application of our processes to hydrocarbon fractions exhibiting VGO-like characteristics. Thus, the terms encompass straight run VGO as may be produced in a crude fractionation section of an oil refinery, as well as, VGO product cuts, fractions, or streams that may be produced, for example, by coker, deasphalting, and visbreaking processing units, or which may be produced by blending various hydrocarbons. In addition to the processing of vacuum gas oils, it is contemplated that the processing of certain other hydrocarbons would benefit from the regeneration process of the present invention.

[0013] In general, the hydrocarbon feed has a specific gravity from about 0.8 to 1.2. The hydrocarbon feed may be a VGO which comprises petroleum hydrocarbon components boiling in the range of from about 100° to about 720° C. In an embodiment the VGO boils from about 250° to about 650° C. and has a specific gravity in the range of from about 0.8 to about 0.95. The nitrogen content may be determined using ASTM method D4629-02, Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection. The sulfur content may be determined using ASTM method D5453-00, Ultraviolet Fluorescence; and the metals content may be determined by UOP389-09, Trace Metals in Oils by Wet Ashing and ICP-OES. Unless otherwise noted, the analytical methods used herein such as ASTM D5453-00 and UOP389-09 are available from ASTM International, 100 Barr Harbor Drive, West Conshohocken, Pa., USA.

[0014] Processes according to the invention remove nitrogen compounds and other impurities from a hydrocarbon. That is, the invention removes at least one type of impurity from hydrocarbons. It is understood that the hydrocarbon will usually comprise a plurality of nitrogen compounds of different types in various amounts. Thus, the process removes at least a portion of at least one type of nitrogen compound from the hydrocarbon. Other compounds such as sulfur compounds may also be removed from the hydrocarbon. These compounds are defined as “hydrocarbon impurities” to differentiate them from the hydrocarbon feed and from the light hydrocarbons that are used in the regeneration of the ionic liquids.

[0015] One or more ionic liquids are used to extract one or more hydrocarbon impurities from the hydrocarbon. Generally, ionic liquids are non-aqueous, organic salts composed of ions where the positive ion is charge balanced with negative ion. These materials have low melting points, often below 100° C., undetectable vapor pressure and good chemical and thermal stability. The cationic charge of the salt is localized over hetero atoms, such as nitrogen, phosphorous, sulfur, arsenic, boron, antimony, and aluminum, and the anions may be any inorganic, organic, or organometallic species.

[0016] Ionic liquids suitable for use in the instant invention are hydrocarbon-immiscible phosphonium ionic liquids. As used herein the term “hydrocarbon-immiscible phosphonium ionic liquid” means an ionic liquid having a cation comprising at least one phosphorous atom and which is capable of forming a separate phase from the hydrocarbon under operating conditions of the process. Ionic liquids that are miscible with the hydrocarbon at the process conditions will be completely soluble with the hydrocarbon; therefore, no phase separation will be feasible. Thus, hydrocarbon-immiscible phosphonium ionic liquids may be insoluble with or partially soluble with the hydrocarbon under operating conditions. A phosphonium ionic liquid capable of forming a separate phase from the hydrocarbon under the operating conditions is considered to be hydrocarbon-immiscible. Ionic liquids according to the invention may be insoluble, partially soluble, or completely soluble (miscible) with water.

[0017] In an embodiment, the hydrocarbon-immiscible phosphonium ionic liquid comprises at least one ionic liquid from at least one of the following groups of ionic liquids: tetraalkylphosphonium dialkylphosphates, tetraalkylphosphonium dialkyl phosphinates, tetraalkylphosphonium phosphates, tetraalkylphosphonium tosylates, tetraalkylphosphonium sulfates, tetraalkylphosphonium sulfonates, tetraalkylphosphonium carbonates, tetraalkylphosphonium metalates, oxometalates, tetraalkylphosphonium mixed metalates, tetraalkylphosphonium polyoxometalates, and tetraalkylphosphonium halides. In another embodiment, the hydrocarbon-immiscible phosphonium ionic liquid comprises at least one of trihexyl(tetradecyl)phosphonium chloride, trihexyl(tetradecyl)phosphonium bromide, tributyl(methyl)phosphonium bromide, tributyl(methyl)phosphonium chloride, tributyl(hexyl)phosphonium bromide, tributyl (hexyl)phosphonium chloride, tributyl(octyl)phosphonium bromide, tributyl(octyl)phosphonium chloride, tributyl(decyl)phosphonium bromide, tributyl(decyl)phosphonium chloride, tetrabutylphosphonium bromide, tetrabutylphosphonium chloride, triisobutyl(methyl)phosphonium tosylate, tributyl(methyl)phosphonium methylsulfate, tributyl(ethyl) phosphonium diethylphosphate, and tetrabutylphosphonium methanesulfonate. In a further embodiment, the hydrocarbon-immiscible phosphonium ionic liquid is selected from the group consisting of trihexyl(tetradecyl)phosphonium chloride, trihexyl(tetradecyl)phosphonium bromide, tributyl (methyl)phosphonium bromide, tributyl(methyl)phosphonium chloride, tributyl(hexyl)phosphonium bromide, tributyl (hexyl)phosphonium chloride, tributyl(octyl)phosphonium bromide, tributyl(octyl)phosphonium chloride, tributyl(decyl)phosphonium bromide, tributyl(decyl)phosphonium chloride, tetrabutylphosphonium bromide, tetrabutylphosphonium chloride, triisobutyl(methyl)phosphonium tosylate, tributyl(methyl)phosphonium methylsulfate, tributyl(ethyl) phosphonium diethylphosphate, tetrabutylphosphonium methanesulfonate, and combinations thereof. The hydrocarbon-immiscible phosphonium ionic liquid may be selected from the group consisting of trihexyl(tetradecyl)phosphonium halides, tetraalkylphosphonium dialkylphosphates, tetraalkylphosphonium tosylates, tetraalkylphosphonium sulfonates, tetraalkylphosphonium halides, and combinations thereof. The hydrocarbon-immiscible phosphonium ionic liquid may comprise at least one ionic liquid from at least one of the following groups of ionic liquids trihexyl(tetradecyl) phosphonium halides, tetraalkylphosphonium dialkylphosphates, tetraalkylphosphonium tosylates, tetraalkylphosphonium sulfonates, and tetraalkylphosphonium halides.

[0018] In an embodiment, the invention is a process for removing impurities including nitrogen and sulfur compounds from a hydrocarbon stream comprising a contacting step, a separating step and a regenerating step. In the contacting step, vacuum gas oil comprising impurities and a hydrocarbon-immiscible phosphonium ionic liquid are contacted or mixed. The contacting may facilitate transfer or extraction of the one or more impurities from the hydrocarbon to the ionic liquid. Although a hydrocarbon-immiscible phosphonium ionic liquid that is partially soluble in hydrocarbon may facilitate transfer of the impurities from the hydrocarbon to the ionic liquid, partial solubility is not required. Insoluble hydrocarbon/ionic liquid mixtures may have sufficient interfacial surface area between the hydrocarbon and ionic liquid to be useful. In the separation step, the mixture of hydrocarbon and ionic liquid settles or forms two phases, a hydrocarbon phase and an ionic liquid phase, which is separated to produce a hydrocarbon-immiscible phosphonium ionic liquid effluent and a hydrocarbon effluent. In the regeneration phase, water and a light hydrocarbon are added to the mixture of hydrocarbon-immiscible phosphonium ionic liquid effluent. This facilitates the separation of the hydrocarbon phase (both the hydrocarbon containing impurities and the added light hydrocarbon from the ionic liquid. Then the water can be removed from the ionic liquid by the water being boiled off.

[0019] The process may be conducted in various equipment which are well known in the art and are suitable for batch or continuous operation. For example, in a small scale form of the invention, hydrocarbon and a hydrocarbon-immiscible phosphonium ionic liquid may be mixed in a beaker, flask, or other vessel, e.g., by stirring, shaking, use of a mixer, or a magnetic stirrer. The mixing or agitation is stopped and the mixture forms a hydrocarbon phase and an ionic liquid phase which can be separated, for example, by decanting, centrifugation, or use of a pipette to produce a hydrocarbon effluent having a lower impurities content relative to the hydrocarbon. The process also produces a hydrocarbon-immiscible phosphonium ionic liquid effluent comprising the one or more impurities.

[0020] The contacting and separating steps may be repeated for example when the impurities content of the hydrocarbon effluent is to be reduced further to obtain a desired impurities level in the ultimate hydrocarbon product stream from the process. Each set, group, or pair of contacting and separating steps may be referred to as a nitrogen removal step. Thus, the invention encompasses single and multiple impurities removal steps. A impurities removal zone may be used to perform a impurities removal step. As used herein, the term "zone" can refer to one or more equipment items and/or one or more sub-zones. Equipment items may include, for example, one or more vessels, heaters, separators, exchangers, conduits, pumps, compressors, and controllers. Additionally, an equipment item can further include one or more zones or sub-zones. The impurities removal process or step may be conducted in a similar manner and with similar equipment as is used to conduct other liquid-liquid wash and extraction operations. Suitable equipment includes, for example, columns with: trays, packing, rotating discs or plates, and static mixers. Pulse columns and mixing/settling tanks may also be used.

[0021] The invention can employ an impurities removal or extraction zone that comprises a multi-stage, counter-current extraction column wherein hydrocarbon and hydrocarbon-immiscible phosphonium ionic liquid are contacted and hydrocarbon containing impurities separated. The hydrocarbon or hydrocarbon feed stream and a lean ionic liquid stream enter an extraction column and then a hydrocarbon effluent and a hydrocarbon-immiscible phosphonium ionic liquid effluent including the impurities are removed from the hydrocarbon feed.

[0022] Consistent with common terms of art, the ionic liquid introduced to the nitrogen removal step may be referred to as a "lean ionic liquid" generally meaning a hydrocarbon-immiscible phosphonium ionic liquid that is not saturated with one or more extracted hydrocarbon impurities. Lean ionic liquid may include one or both of fresh and regenerated ionic liquid and is suitable for accepting or extracting nitrogen from the hydrocarbon feed. Likewise, the ionic liquid effluent may be referred to as "rich ionic liquid", which generally means a hydrocarbon-immiscible phosphonium ionic liquid effluent produced by an impurities removal step or process or otherwise including a greater amount of extracted impurities than the amount of extracted impurities included in the lean ionic liquid. A rich ionic liquid may require regeneration or dilution, e.g. with fresh ionic liquid, before recycling the rich ionic liquid to the same or another nitrogen removal step of the process.

[0023] Static in-line mixers that are well known in the art may be used for contacting the hydrocarbon feed stream with the lean ionic liquid stream. These mixers may include a conduit with fixed internals such as baffles, fins, and channels that mix the fluid as it flows through the conduit. In other embodiments, not illustrated, lean ionic liquid stream may be introduced into the hydrocarbon feed stream, or the lean ionic liquid stream and hydrocarbon feed stream may be combined such as through a "Y" conduit. In another embodiment, the lean ionic liquid stream and hydrocarbon feed stream are separately introduced into the static in-line mixer. In other embodiments, the streams may be mixed by any method well know in the art including stirred tank and blending operations. The mixture comprising hydrocarbon and ionic liquid is transferred to a separation zone which may comprise a separation vessel wherein the two phases are allowed to separate into a rich ionic liquid phase which is withdrawn from a lower portion of the separation vessel and the hydrocarbon phase which is withdrawn from an upper portion of separation vessel via a hydrocarbon effluent conduit. The separation vessel may comprise a boot, not illustrated, from which rich ionic liquid is withdrawn.

[0024] The separation vessel may contain a solid media and/or other coalescing devices which facilitate the phase separation. In other embodiments the separation zone may comprise multiple vessels which may be arranged in series, parallel, or a combination thereof. The separation vessels may be of any shape and configuration to facilitate the separation, collection, and removal of the two phases. In a further embodiment, the nitrogen removal zone may include a single vessel wherein the lean ionic liquid stream and hydrocarbon feed stream are mixed, then remain in the vessel to settle into the hydrocarbon effluent and rich ionic liquid phases. In an embodiment the process comprises at least two impurities removal steps. For example, the hydrocarbon effluent from one impurities removal step may be passed directly as the hydrocarbon feed to a second impurities removal step. In another embodiment, the hydrocarbon effluent from one nitrogen removal step may be treated or processed before being introduced as the hydrocarbon feed to the second impurities removal step. There is no requirement that each impurities removal zone comprises the same type of equipment. Different equipment and conditions may be used in different nitrogen removal zones.

[0025] The impurities removal step may be conducted under nitrogen removal conditions including temperatures and pressures sufficient to keep the hydrocarbon-immiscible phosphonium ionic liquid and hydrocarbon feeds and effluents as liquids. For example, the impurities removal step temperature may range between about 10° C. and less than the decomposition temperature of the phosphonium ionic liquid; and the pressure may range between about atmospheric pressure and about 700 kPa(g). When the hydrocarbon-immiscible ionic liquid comprises more than one ionic liquid component, the decomposition temperature of the ionic liquid is the lowest temperature at which any of the ionic liquid components decompose. The nitrogen removal step may be conducted at a uniform temperature and pressure or the contacting and separating steps of the nitrogen removal step may be operated at different temperatures and/or pressures. In an embodiment, the contacting step is conducted at a first temperature, and the separating step is conducted at a temperature at least 5° C. lower than the first temperature. In a non limiting example, the first temperature is about 80° C. Such temperature differences may facilitate separation of the hydrocarbon and ionic liquid phases.

[0026] The above and other nitrogen removal step conditions such as the contacting or mixing time, the separation or settling time, and the ratio of hydrocarbon feed to hydrocarbon-immiscible phosphonium ionic liquid (lean ionic liquid) may vary greatly based, for example, on the specific ionic liquid or liquids employed, the nature of the hydrocarbon feed (straight run or previously processed), the impurities content of the hydrocarbon feed, the degree of impurities removal required, the number of impurities removal steps employed, and the specific equipment used. In general it is expected that contacting time may range from less than one minute to about two hours; settling time may range from about one minute to about eight hours; and the weight ratio of hydrocarbon feed to lean ionic liquid introduced to the impurities removal step may range from 1:10,000 to 10,000:1. In an embodiment, the weight ratio of hydrocarbon feed to lean ionic liquid may range from about 1:1,000 to about 1,000:1; and the weight ratio of hydrocarbon feed to lean ionic liquid may range from about 1:100 to about 100:1. In an embodiment the weight of hydrocarbon feed is greater than the weight of ionic liquid introduced to the nitrogen removal step.

[0027] In an embodiment, a single impurities removal step reduces the impurities content of the hydrocarbon by more than about 40 wt-%. In another embodiment, more than about 50% of the impurities by weight is extracted or removed from the hydrocarbon feed in a single impurities removal step; and more than about 60% of the nitrogen by weight may be extracted or removed from the hydrocarbon feed in a single impurities removal step. As discussed herein the invention encompasses multiple impurities removal steps to provide the desired amount of impurities removal. The degree of phase separation between the hydrocarbon and ionic liquid phases is another factor to consider as it affects recovery of the ionic liquid and hydrocarbon. The degree of impurities removed and the recovery of the hydrocarbon and ionic liquids may be affected differently by the nature of the hydrocarbon feed, the specific ionic liquid or liquids, the equipment, and the impurities removal conditions such as those discussed above.

[0028] The amount of water present in the hydrocarbon/hydrocarbon-immiscible phosphonium ionic liquid mixture during the impurities removal step may also affect the amount of hydrocarbon removed and/or the degree of phase separation, i.e., recovery of the hydrocarbon and ionic liquid. In an embodiment, the hydrocarbon/hydrocarbon-immiscible phosphonium ionic liquid mixture has a water content of less than about 10% relative to the weight of the ionic liquid. In another embodiment, the water content of the hydrocarbon/hydrocarbon-immiscible phosphonium ionic liquid mixture is less than about 5% relative to the weight of the ionic liquid; and the water content of the hydrocarbon/hydrocarbon-immiscible phosphonium ionic liquid mixture may be less than about 2% relative to the weight of the ionic liquid. In a further embodiment, the hydrocarbon/hydrocarbon-immiscible phosphonium ionic liquid mixture is water free, i.e., the mixture does not contain water.

[0029] After the ionic liquid contacts the hydrocarbon stream to remove the impurities, a hydrocarbon washing step is used to recover ionic liquid that is entrained or otherwise remains in the hydrocarbon effluent stream by using water to wash or extract the ionic liquid from the hydrocarbon effluent. Various hydrocarbon washing step equipment and conditions such as temperature, pressure, times, and solvent to feed ratio may be the same as or different from the nitrogen removal zone equipment and conditions. In general, the hydrocarbon washing step conditions will fall within the same ranges as given above for the impurities removal step conditions. A portion or all of the washed hydrocarbon stream may be passed to a hydrocarbon conversion zone.

[0030] An ionic liquid regeneration step is used to regenerate the ionic liquid by removing the hydrocarbon impurities from the ionic liquid, i.e. reducing the nitrogen content of the rich ionic liquid. In an embodiment, a portion or all of a hydrocarbon-immiscible phosphonium ionic liquid effluent stream (as feed) comprising the hydrocarbon impurities and a regeneration solvent stream are introduced to an ionic liquid regeneration zone. The hydrocarbon-immiscible phosphonium ionic liquid effluent and regeneration solvent streams are mixed and separated to produce an extract stream comprising the hydrocarbon impurities, and a regenerated ionic liquid stream. The ionic liquid regeneration step may be conducted in a similar manner and with similar equipment as used to conduct other liquid-liquid wash and extraction operations as discussed above. Various ionic liquid regeneration step conditions such as temperature, pressure, times, and solvent to feed may be the same as or different from the nitrogen removal conditions. In general, the ionic liquid regeneration step conditions will fall within the same ranges as given above for the nitrogen removal step conditions.

[0031] In an embodiment, the regeneration solvent stream comprises a mixture of water and a light hydrocarbon which is immiscible with the phosphonium ionic liquid and water. In an embodiment, the light hydrocarbon has a lower average boiling point than the hydrocarbon feed. The light hydrocarbon fraction may consist of a single hydrocarbon compound or may comprise a mixture of hydrocarbons. In an embodiment, the light hydrocarbon fraction comprises at least one of a naphtha, gasoline, diesel, kerosene, light cycle oil (LCO), toluene, benzene and light coker gas oil (LCGO) hydrocarbon fraction. In an embodiment, this light hydrocarbon fraction may be the hydrocarbon feed itself or it may be any other hydrocarbon with a specific gravity lower than that of the hydrocarbon feed. The light hydrocarbon fraction may comprise straight run fractions and/or products from conversion processes such as hydrocracking, hydrotreating, fluid catalytic cracking (FCC), reforming, coking, and visbreaking In this embodiment, the extract stream comprises the light hydrocarbon fraction of the regeneration solvent and the hydrocarbon impurities. A portion or the entire regenerated hydrocarbon-immiscible phosphonium ionic liquid stream may be recycled to the impurities removal step via a conduit not shown consistent with other operating conditions of the process. For example, a constraint on the water content of the hydrocarbon-immiscible phosphonium ionic liquid stream or the ionic liquid/hydrocarbon mixture in the impurities removal zone may be met by controlling the proportion and water content of fresh and recycled ionic liquid streams. In an embodiment, the water fraction of the regeneration solvent stream is added to the hydrocarbon-immiscible phosphonium ionic liquid stream, and the light hydrocarbon fraction is added to achieve countercurrent flow to the hydrocarbon-immiscible phosphonium ionic liquid stream.

[0032] The ionic liquid drying step may be employed to reduce the water content of one or more of the streams comprising ionic liquid to control the water content of the nitrogen removal step as described above. In the embodiment of the invention, a portion or all of regenerated hydrocarbon-immiscible phosphonium ionic liquid stream is introduced to a drying zone. Although not shown, other streams comprising ionic liquid such as the fresh ionic liquid stream, hydrocarbon-immiscible phosphonium ionic liquid effluent stream, and spent water stream, may also be dried in any combination in the drying zone. To dry the ionic liquid stream or streams, water may be removed by one or more various well known methods including distillation, flash distillation, multistage evaporation, and using a dry inert gas to strip water. Generally, the drying temperature may range from about 100° C. to less than the decomposition temperature of the ionic liquid, usually less than about 300° C. The pressure may range from about 35 to about 350 kPa. The drying step produces a dried hydrocarbon-immiscible phosphonium ionic liquid stream and a drying zone water effluent stream. Although not illustrated, a portion or all of dried hydrocarbon-immiscible phosphonium ionic liquid stream may be recycled or passed to provide all or a portion of the hydrocarbon-immiscible phosphonium ionic liquid introduced to impurities removal zone. A portion or all of drying zone water effluent stream may be recycled or passed to provide all or a portion of the water introduced into hydrocarbon washing zone and/or ionic liquid regeneration zone.

[0033] The FIGURE shows a simplified flow scheme in which a hydrocarbon feed stream **2** is sent to an extraction unit **6** containing ionic liquid which is shown in line **4** entering the extraction unit **6**. The ionic liquid removes impurities with the clean hydrocarbon exiting in line **8** and the ionic liquid containing the impurities is sent in line **10** to regenerator unit **14**. Water enters regenerator **14** through line **12** and a light hydrocarbon such as naphtha, kerosene or benzene enters regenerator **14** through line **28**. A stream comprising the light hydrocarbon and the impurities is shown in line **24** going to an evaporator **26** in which the hydrocarbon is vaporized and is sent in line **28** to return to the regenerator **14**. The impurities exit evaporator **26** through line **30**. The ionic liquid and water from regenerator **14** are sent through line **16** to a second evaporator **18** with the ionic liquid flowing out the bottom of the unit in line **20** to be recycled to the ionic liquid in line **4**. The water is (not shown) being evaporated from evaporator **18**.

[0034] Unless otherwise stated, the exact connection point of various inlet and effluent streams within the zones is not essential to the invention. For example, it is well known in the art that a stream to a distillation zone may be sent directly to the column, or the stream may first be sent to other equipment within the zone such as heat exchangers, to adjust temperature, and/or pumps to adjust the pressure. Likewise, streams entering and leaving impurities removal, washing, and regeneration zones may pass through ancillary equipment such as heat exchanges within the zones. Streams, including recycle streams, introduced to washing or extraction zones may be introduced individually or combined prior to or within such zones.

[0035] The invention encompasses a variety of flow scheme embodiments including optional destinations of streams, splitting streams to send the same composition, i.e. aliquot portions, to more than one destination, and recycling various streams within the process. Examples include: various streams comprising ionic liquid and water may be dried and/or passed to other zones to provide all or a portion of the water and/or ionic liquid required by the destination zone. The various process steps may be operated continuously and/or intermittently as needed for a given embodiment e.g. based on the quantities and properties of the streams to be processed in such steps. As discussed above the invention encompasses multiple nitrogen removal steps, which may be performed in parallel, sequentially, or a combination thereof. Multiple nitrogen removal steps may be performed within the same nitrogen removal zone and/or multiple nitrogen removal zones may be employed with or without intervening washing, regeneration and/or drying zones.

[0036] The following examples are illustrative of the present invention in showing the advantages to the use of naphtha or kerosene as the light hydrocarbon to separate the impurities from the water/ionic liquid mixture.

COMPARATIVE EXAMPLE

[0037] A sample of triisobutylmethylphosphonium tosylate (ionic liquid) with a specific gravity of 1.05 and vacuum gas oil (VGO) with a specific gravity of 0.9271 were combined in a beaker at ratio of 10:1 VGO:ionic liquid. The beaker was placed onto a heated stir plate and stirred at 80° C. for 30 minutes. After 30 minutes, the stirring was stopped and the ionic liquid mixture was allowed to settle for 30 minutes. A pipette was used to draw off the extracted VGO from the ionic liquid. The specific gravity of the extracted VGO was 0.909. The resulting triisobutylmethylphosphonium tosylate and extract from the VGO had a specific gravity of 1.033. Water was added to mixture of triisobutylmethylphosphonium tosylate and extract at a ratio of 1:1 mixture:water. The triisobutylmethylphosphonium tosylate preferentially combined with the water and the extract was freed from the mixture. The combined water and ionic liquid had a specific gravity of 1.017 and the extract had a specific gravity of

1.016. Because the specific gravities of the two phases were very similar a clean separation did not occur.

EXAMPLE 1

[0038] A sample of triisobutylmethylphosphonium tosylate with a specific gravity of 1.05 and vacuum gas oil (VGO) with a specific gravity of 0.9271 were combined in a beaker at ratio of 10:1 VGO:ionic liquid. The beaker was placed onto a heated stir plate and stirred at 80° C. for 30 minutes. After 30 minutes, the stirring was stopped and the ionic liquid mixture was allowed to settle for 30 minutes. A pipette was used to draw off the extracted VGO from the ionic liquid. The specific gravity of the extracted VGO was 0.909. The resulting triisobutylmethylphosphonium tosylate and extract from the VGO had a specific gravity of 1.033. Water and naphtha were added to a mixture of triisobutylmethylphosphonium tosylate and extract at a ratio of 1:1:0.2 mixture:water:naphtha. The naphtha had a specific gravity of 0.6637. The triisobutylmethylphosphonium tosylate preferentially combined with the water and the naphtha combined with the extract. The density of the naphtha combined with the extract was less than 1.017, the specific gravity of the ionic liquid plus water, as a result, the extract floated.

EXAMPLE 2

[0039] A sample of tributylethylphosphonium diethylphosphate with a specific gravity of 0.996 and vacuum gas oil (VGO) with a specific gravity of 0.9271 were combined in a beaker at ratio of 10:1 VGO:ionic liquid. The beaker was placed onto a heated stir plate and stirred at 80° C. for 30 minutes. After 30 minutes, the stirring was stopped and the ionic liquid mixture was allowed to settle for 30 minutes. A pipette was used to draw off the extracted VGO from the ionic liquid. The specific gravity of the extracted VGO was 0.9236. Water and naphtha were added to mixture of tributylethylphosphonium diethylphosphate and extract at a ratio of 1:1:0.2 mixture:water:naphtha. The naphtha had a specific gravity of 0.6637. The tributylethylphosphonium diethylphosphate preferentially combined with the water and the naphtha combined with the extract. The density of the naphtha combined with the extract was less than **0.98**, the specific gravity of the ionic liquid plus water, as a result, the extract floated.

EXAMPLE 3

[0040] A sample of triisobutylmethylphosphonium tosylate with a specific gravity of 1.05 and vacuum gas oil (VGO) with a specific gravity of 0.9271 were combined in a beaker at ratio of 10:1 VGO:ionic liquid. The beaker was placed onto a heated stir plate and stirred at 80° C. for 30 minutes. After 30 minutes, the stirring was stopped and the ionic liquid mixture was allowed to settle for 30 minutes. A pipette was used to draw off the extracted VGO from the ionic liquid. The specific gravity of the extracted VGO was 0.924. The resulting triisobutylmethylphosphonium tosylate and extract from the VGO had a specific gravity of 1.033. Water and kerosene were added to the mixture of triisobutylmethylphosphonium tosylate and extract at a ratio of 1:1:0.2 mixture:water:kerosene. The kerosene had a specific gravity of 0.8112 The triisobutylmethylphosphonium tosylate preferentially combined with the water and the kerosene combined with the extract. The density of the kerosene combined with the extract was less than 1.017, the specific gravity of the ionic liquid plus water, as a result, the extract floated.

1. A process for removing at least one impurity from a hydrocarbon stream comprising:

(a) contacting a hydrocarbon stream with a hydrocarbon-immiscible phosphonium ionic liquid to produce a mixture comprising the hydrocarbon and the hydrocarbon-immiscible phosphonium ionic liquid;

(b) separating the mixture to produce a hydrocarbon product and a hydrocarbon-immiscible phosphonium ionic liquid effluent, the hydrocarbon-immiscible phosphonium ionic liquid effluent comprising at least one hydrocarbon impurity; and

(c) contacting the hydrocarbon-immiscible phosphonium ionic liquid effluent with water and with a light hydrocarbon stream, separating said hydrocarbon-immiscible phosphonium ionic liquid and said water from the light hydrocarbon stream and the at least one hydrocarbon impurity to produce an extract stream comprising the light hydrocarbon stream and the at least one hydrocarbon impurity and a separate stream comprising said hydrocarbon-immiscible phosphonium ionic liquid and water.

2. The process of claim **1** wherein the hydrocarbon stream has a specific gravity from about 0.8 to 1.2.

3. The process of claim **1** wherein said light hydrocarbon stream is selected from the group of hydrocarbons having a density lower than the water or the ionic liquid.

4. The process of claim **1** wherein said hydrocarbon stream is selected from the group consisting of consisting of naphtha, diesel, light cycle oil, benzene, kerosene, and toluene.

5. The process of claim **1** wherein the extract stream comprising the light hydrocarbon stream and the at least one hydrocarbon impurity has a specific gravity difference of at least 0.01 than a mixture of said hydrocarbon-immiscible phosphonium ionic liquid and said water.

6. The process of claim **1** wherein the hydrocarbon stream comprises a vacuum gas oil.

7. The process of claim **1** wherein the hydrocarbon-immiscible phosphonium ionic liquid comprises at least one ionic liquid from at least one of tetraalkylphosphonium dialkylphosphates, tetraalkylphosphonium dialkyl phosphinates, tetraalkylphosphonium phosphates, tetraalkylphosphonium tosylates, tetraalkylphosphonium sulfates, tetraalkylphosphonium sulfonates, tetraalkylphosphonium carbonates, tetraalkylphosphonium metalates, oxometalates, tetraalkylphosphonium mixed metalates, tetraalkylphosphonium polyoxometalates, and tetraalkylphosphonium halides.

8. The process of claim **1** wherein the hydrocarbon-immiscible phosphonium ionic liquid comprises at least one of trihexyl(tetradecyl)phosphonium chloride, trihexyl(tetradecyl)phosphonium bromide, tributyl(methyl)phosphonium bromide, tributyl(methyl)phosphonium chloride, tributyl (hexyl)phosphonium bromide, tributyl(hexyl)phosphonium chloride, tributyl(octyl)phosphonium bromide, tributyl(octyl)phosphonium chloride, tributyl(decyl)phosphonium bromide, tributyl(decyl)phosphonium chloride, tetrabutylphosphonium bromide, tetrabutylphosphonium chloride, triisobutyl(methyl)phosphonium tosylate, tributyl(methyl) phosphonium methylsulfate, tributyl(ethyl)phosphonium diethylphosphate, and tetrabutylphosphonium methanesulfonate.

9. The process of claim **1** further comprising separating said hydrocarbon-immiscible phosphonium ionic liquid and water.

10. The process of claim **1** further comprising separating said light hydrocarbon stream and said at least one hydrocarbon impurity

11. The process of claim **1** wherein the ratio of the hydrocarbon stream to the hydrocarbon-immiscible phosphonium ionic liquid in the mixture ranges from about 1:1000 to about 1000:1 on a weight basis.

12. A process for regenerating an ionic liquid comprising sending a mixture of an ionic liquid, water and a hydrocarbon extract containing impurities to a regeneration unit, adding a quantity of a light hydrocarbon having a lower specific gravity than said mixture, and removing said light hydrocarbon together with said hydrocarbon extract containing impurities.

13. The process of claim **12** wherein said light hydrocarbon is selected from the group consisting of naphtha, kerosene, light cycle oil, benzene and toluene.

14. The process of claim **12** wherein the hydrocarbon stream comprises a vacuum gas oil.

15. The process of claim **12** wherein the hydrocarbon-immiscible phosphonium ionic liquid comprises at least one ionic liquid from at least one of tetraalkylphosphonium dialkylphosphates, tetraalkylphosphonium dialkyl phosphinates, tetraalkylphosphonium phosphates, tetraalkylphosphonium tosylates, tetraalkylphosphonium sulfates, tetraalkylphosphonium sulfonates, tetraalkylphosphonium carbonates, tetraalkylphosphonium metalates, oxometalates, tetraalkylphosphonium mixed metalates, tetraalkylphosphonium polyoxometalates, and tetraalkylphosphonium halides.

16. The process of claim **12** wherein the hydrocarbon-immiscible phosphonium ionic liquid comprises at least one of trihexyl(tetradecyl)phosphonium chloride, trihexyl(tetradecyl)phosphonium bromide, tributyl(methyl)phosphonium bromide, tributyl(methyl)phosphonium chloride, tributyl(hexyl)phosphonium bromide, tributyl(hexyl) phosphonium chloride, tributyl(octyl)phosphonium bromide, tributyl(octyl)phosphonium chloride, tributyl(decyl)phosphonium bromide, tributyl(decyl)phosphonium chloride, tetrabutylphosphonium bromide, tetrabutylphosphonium chloride, triisobutyl(methyl)phosphonium tosylate, tributyl(methyl)phosphonium methylsulfate, tributyl(ethyl) phosphonium diethylphosphate, and tetrabutylphosphonium methanesulfonate.

17. The process of claim **12** further comprising separating said hydrocarbon-immiscible phosphonium ionic liquid and water.

18. The process of claim **12** further comprising separating said light hydrocarbon stream and said at least one hydrocarbon impurity.

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