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METHODS FOR RECOVERING ORGANIC HETEROATOM COMPOUNDS FROM HYDROCARBON FEEDSTOCKS

BACKGROUND

FIELD

[0001] The present specification generally relates to recovery of organic heteroatom compounds from hydrocarbon feedstocks. More particularly, the present specification is directed to methods for separating heteroatom compounds from hydrocarbons using a tunable/switchable/reversible solvent.

TECHNICAL BACKGROUND

[0002] Organic heteroatom-containing compounds such as sulfur compounds, nitrogen compounds, and organometallic compounds, have numerous uses and applications as starting materials or feedstocks in technologies such as solar energy harvesting, organic photovoltaic and solar cell manufacturing, organic LED manufacturing, organic thin-film transistor manufacturing, and pharmaceutical manufacturing. These compounds have high abundance in crude oils, particularly in heavy crude oils, but are typically removed from the crude oils by hydrotreatment (HDT) or oxidative desulfurization or denitrogenation to meet environmental regulations with regard to fuel sulfur and nitrogen content. During the HDT, oxidative desulfurization, or denitrogenation processes, the organic heteroatom-containing compounds typically undergo molecular transformations and not retain their molecular structure, thereby rendering them useless to further applications.

[0003] Accordingly, systems and methods that enable recovery of organic heteroatom compounds from hydrocarbons are desirable.

SUMMARY

[0004] According to some embodiments, methods for recovering organic heteroatom compounds from a hydrocarbon feedstock may include feeding a hydrocarbon feedstock

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into a contactor, the hydrocarbon feedstock comprising at least one hydrocarbon and at least one organic heteroatom compound. An aqueous solvent may be fed into the contactor to form an extraction mixture of the aqueous solvent with the hydrocarbon feedstock, the aqueous solvent comprising an ionic liquid formed from pressurized carbon dioxide and water. A contactor pressure and a contactor temperature of the extraction mixture in the contactor may be established that together tune the aqueous solvent to selectively form a solvent complex with the at least one organic heteroatom compound. Then, the solvent complex may be extracted to a recovery vessel from the extraction mixture in the contactor. By adjustment of a recovery temperature of the recovery vessel, a recovery pressure of the recovery vessel, or both, the solvent complex may be decomposed/dissociated in the recovery vessel into carbon dioxide, water molecule and the at least one organic heteroatom compound. Then, the at least one organic heteroatom compound may be recovered from the recovery vessel.

[0005] According to other embodiments, methods for recovering organic heteroatom compounds from a hydrocarbon feedstock may include feeding a hydrocarbon feedstock into a contactor. The hydrocarbon feedstock may include crude oil or a crude oil fraction and at least one organic heteroatom compound. The organic heteroatom may be chosen from nitrogen-containing heterocyclic compounds, sulfur-containing heterocyclic compounds, porphyrins, such as vanadyl and nickel porphyrin, and other organometallic compounds, and combinations thereof. According to embodiments, organometallic compound includes compounds that can form a complex with an aqueous solvent, such as those described below, and include, for example, porphyrins, nitrogen-containing organometallic compounds, and sulfur-containing organometallic compounds. An aqueous solvent may be fed into the contactor to form an extraction mixture of the aqueous solvent with the hydrocarbon feedstock. The aqueous solvent may include an ionic liquid formed from pressurized carbon dioxide and water. A contactor pressure and a contactor temperature of the extraction mixture may be established in the contactor that together tune the aqueous solvent to selectively form a solvent complex with the at least one organic heteroatom compound. Then, the solvent complex may be extracted to a recovery vessel from the extraction mixture in the contactor. The solvent complex in the recovery vessel may be depressurized to decompose/dissociate the solvent complex

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into carbon dioxide and the at least one organic heteroatom compound. Then, the at least one organic heteroatom compound may be recovered from the recovery vessel.

[0006] Additional features and advantages will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the embodiments described herein, including the detailed description which follows, the claims, as well as the appended drawings.

[0007] It is to be understood that both the foregoing general description and the following detailed description describe various embodiments and are intended to provide an overview or framework for understanding the nature and character of the claimed subject matter. The accompanying drawings are included to provide a further understanding of the various embodiments, and are incorporated into and constitute a part of this specification. The drawings illustrate the various embodiments described herein, and together with the description serve to explain the principles and operations of the claimed subject matter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1 schematically depicts components of a system for separating organic heteroatom compounds from a hydrocarbon feedstock according to embodiments described herein;

[0009] FIG. 2 schematically depicts phases within a contactor according to embodiments described herein;

[0010] FIG. 3 depicts formation of complexes between organic heteroatom compounds and the solvent according to embodiments described herein; and

[0011] FIG. 4 schematically depicts electrical plates for aligning particles according to embodiments described herein.

DETAILED DESCRIPTION

[0012] Removing refractory organic heteroatom compounds, such as, for example, sulfur compounds, nitrogen compounds, and organometallic compounds, from hydrocarbon feedstocks, such as, for example, crude oil or crude oil fractions, can be a difficult process because of the stubborn behavior of these compounds to transform during HDT, e.g., desulfurization and/or denitrogenation processes. Therefore, separating the organic heteroatom compounds from the hydrocarbon feedstocks can be both energy and cost prohibitive. In addition, using desulfurization and/or denitrogenation it can be difficult to control side reactions that can impede the separation process or introduce further impurities into the hydrocarbon feedstocks. Moreover, HDT processes may typically result in decomposition of the organic heteroatom compounds, rendering these components (which have many valuable uses, e.g. as synthetic building blocks for the chemical manufacturing processes) useless for such applications.

[0013] Some embodiments herein include methods for separating and recovering organic heteroatom compounds from a hydrocarbon feedstock using a reversible/switchable/tunable solvent (hereinafter referred to as “tunable solvent”). As used in any embodiment described herein, the tunable solvent is preferably an aqueous solvent. In embodiments, the aqueous solvent comprises an ionic liquid formed from pressurized carbon dioxide and water. The carbon dioxide may be present in a supercritical state, a subcritical state, or both. In some embodiments, the tunable solvent comprises supercritical carbon dioxide and water.

[0014] As used in any embodiment discussed herein, the term “organic heteroatom compound” refers to an organic compound that contains at least one atom other than carbon and hydrogen. In some embodiments, the heteroatom compound may be a compound containing at least one heteroatom that can act as an electron donor, preferably wherein the heteroatom is sulfur or nitrogen. More preferably, the organic heteroatom compound is a heterocyclic compound containing at least a sulfur or nitrogen atom forming part of the heterocyclic ring, wherein the ring is unsaturated. Particularly, the organic heteroatom compound comprises a heterocyclic aromatic portion. The organic heteroatom compound can be monocyclic or polycyclic. Examples of organic

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heteroatom compounds include organosulfur compounds such as sulfur-containing heterocyclic compounds, organonitrogen compounds such as nitrogen-containing heterocyclic compounds, and organometallic compounds such as porphyrins. In some embodiments, the organic heteroatom compound comprises pyrrole, pyridine, quinoline, carbazole, indole, nickel-tetraphenyl-porphyrin, vanadyl-tetraphenyl-porphyrin, thiophene, benzothiophene, dibenzothiophene, and 7,8,9,10-tetrahydro-benzo[b]naphtho[2,3-d]thiophene, pehnol, furan, benzofuran, isoquinoline, acridine, benzocarbazole, and combinations thereof. In some embodiments, the heteroatom compound may comprise non-aromatic sulfur compounds, such as dimethyl sulfide, dimethyldisulfide, or thiocyclohexane. In some embodiments, the organic heteroatom compounds may be natural impurities found in a hydrocarbon feedstock such as crude oil or a crude oil fraction, for example. The tunable solvent allows the organic heteroatom compounds to maintain their physical and chemical properties upon separation from the hydrocarbon feedstock. Thus, in contrast to HDT, the present process advantageously enables the organic heteroatom compound to be removed from the hydrocarbon feedstock in a non-destructive manner. The organic heteroatom compound can then be employed in other chemical manufacturing processes.

[0015] In some embodiments, the tunable solvent may be an ionic liquid, a gas expanded ionic liquid, or another solvent that selectively attracts the organic heteroatom compounds. The tunable solvent may form a reversible complex with the organic heteroatom compounds. In some embodiments, various properties of the tunable solvent can be controlled so that the tunable solvent becomes more ionic or less ionic in nature and, thus, may be selectively attracted to or selectively form reversible complexes with one or more chosen organic heteroatom compounds.

[0016] Different hydrocarbon feedstocks, particularly those derived from crude oil or crude oil fractions, can contain different types of organic heteroatom compounds. By adjusting the solubility parameters of the target organic heteroatom compound, such as, for example, exploiting the polarity of any target organic heteroatom compound, impurities in the hydrocarbon feedstock may be selectively separated from the hydrocarbon feedstocks using the tunable solvent. In some embodiments, the tunable solvent may be modified by adjusting the pressure, temperature, and/or pH of the solvent

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system so that the target organic heteroatom compound is maintained as a solute in the solvent system, for example, by the formation of a reversible solvent complex. Once the organic heteroatom compound is solvated, further adjustment of the pressure, temperature, and/or pH of the solvent system may reverse the solvation, whereby the organic heteroatom compound can be easily recovered as an aggregate, a precipitate, a liquid, an oil, or the like.

[0017] In some embodiments, the tunable solvent may be modified by, for example, adjusting the pressure of the solvent system, such as, for example, by adjusting the pressure in the contactor, so that the solvent is tuned to attract or complex with a target organic heteroatom compound that has a certain polarity. By using such a selective solvent, interference from impurities that are not the target organic heteroatom compound may be less likely than in other separation processes. For example, separation processes that separate impurities based on, for example, the boiling point and condensation point of impurities may be likely to separate impurities other than the target organic heteroatom compound, particularly ones that have a similar boiling point as the target organic heteroatom compound. In contrast, tunable solvents according to embodiments herein may be precisely tuned so that they selectively separate only the target organic heteroatom compound or compounds. In other embodiments, the tunable solvent may be modified, such as by adjusting the pressure of the solvent system, so that the tunable solvent separates the organic heteroatom compounds from the hydrocarbons. For example, in some embodiments, the tunable solvent may be modified to attract or complex with the most polar organic heteroatom compound as a solute in the solvent system. In other embodiments, the tunable solvent may be modified to attract organic heteroatom compounds having even weak polarity, such as, for example, weak dipole moments. In addition to pressure, temperature may be used, in embodiments, to modify the equilibrium of the solvent system.

[0018] In any embodiment, suitable pressures may vary according to the tunable solvent that is used and the target organic heteroatom compound(s). In some embodiments, the pressure may be from about 2 bar to about 300 bar, such as from about 20 bar to about 275 bar, from about 50 bar to about 250 bar, or from about 75 bar to about 225 bar. In any embodiment of the present invention, the pressure may be from

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about 100 bar to about 200 bar. In still other embodiments, the pressure in the contactor may be from about 125 bar to about 175 bar, such as about 150 bar. It should be understood that the above ranges are intended to include each point between the disclosed endpoints, and that each pressure point between 2 bar and 300 bar is envisioned in this disclosure.

[0019] Moreover, temperature may be used to affect the solubility of the organic heterocyclic molecules. Increased solubility of the organic heterocyclic molecules may increase the extraction and selectivity of the solvent system and, thereby, temperature may be used to fine-tune the tunable solvent. Thus, the temperature at which the tunable solvent and hydrocarbon feedstock are mixed may vary according to the tunable solvent that is used and the target organic heteroatom compounds. In any embodiment in which carbon dioxide is the tunable solvent, the temperature in the contactor may be greater than or equal to the critical temperature of carbon dioxide, such as about 20 °C greater than the critical temperature of carbon dioxide. In some embodiments, the temperature in the contactor is greater than or equal to 40 °C above the critical temperature of carbon dioxide, such as about 60 °C above the critical temperature of carbon dioxide. In embodiments, the temperature in the contactor may be less than or equal to about 100 °C above the critical temperature of carbon dioxide, such as less than or equal to about 80 °C above the critical temperature of carbon dioxide. In embodiments, the temperature in the contractor is from greater than or equal to about 20 °C above the critical temperature of carbon dioxide to less than or equal to about 100 °C above the critical temperature of carbon dioxide, such as from greater than or equal to about 40 °C above the critical temperature of carbon dioxide to less than or equal to about 80 °C above the critical temperature of carbon dioxide, such as from greater than or equal to about 50 °C above the critical temperature of carbon dioxide to less than or equal to about 70 °C above the critical temperature of carbon dioxide.

[0020] In preferred embodiments of the present invention, the pressure in the contactor is in the range of from about 2 bar to about 300 bar and the temperature is in the range of from greater than or equal to about 20 °C above the critical temperature of carbon dioxide to less than or equal to about 100 °C above the critical temperature of carbon dioxide, more preferably, the pressure in the contractor is in the range of about 50

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bar to about 250 bar and the temperature is in the range of from greater than or equal to about 50 °C above the critical temperature of carbon dioxide to less than or equal to about 70 °C above the critical temperature of carbon dioxide, and particularly preferred the pressure in the contactor is in the range of about 20 bar to about 275 bar and the temperature is in the range of from greater than or equal to about 40 °C above the critical temperature of carbon dioxide to less than or equal to about 80 °C above the critical temperature of carbon dioxide

[0021] In the methods for recovering organic heteroatom compounds from a hydrocarbon feedstock according to some embodiments, the hydrocarbon feedstock, such as, for example, crude oil or crude oil fraction, may be contacted with a tunable solvent that is capable of being modified, or tuned, to attract one or more organic heteroatom compounds into the solvent system as a solute. Preferably, the tunable solvent is an aqueous solvent. Contacting of the hydrocarbon feedstock with the tunable solvent may include feeding the hydrocarbon feedstock into a contactor, and feeding the aqueous solvent into the contactor to form an extraction mixture of the aqueous solvent with the hydrocarbon feedstock. The tunable solvent may be formed from pressurized carbon dioxide, water, and optional modifiers, such as viscosity modifiers. Changes in pressure of the solvent system can be used to tune the tunable solvent to attract specific organic heteroatom compounds into the solvent system as a solute. Accordingly, the methods may include establishing a contactor pressure and a contactor temperature of the extraction mixture in the contactor that together tune the aqueous solvent to selectively form a solvent complex with the at least one organic heteroatom compound.

[0022] In some embodiments, the aqueous solvent includes supercritical carbon dioxide. In some embodiments, the aqueous solvent includes subcritical carbon dioxide. In other embodiments, the aqueous solvent comprises both supercritical and subcritical carbon dioxide. In any embodiment as described herein, the tunable solvent is an aqueous solvent. Particularly, the aqueous solvent is a mixture comprising water and carbon dioxide, wherein the carbon dioxide is subcritical, supercritical, or both. Preferably in any embodiment, the aqueous solvent is a mixture consisting essentially of water and carbon dioxide, wherein the carbon dioxide is supercritical, subcritical or both.

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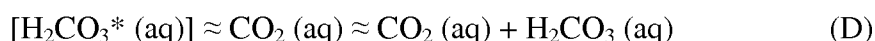
[0023] Without intent to be bound by theory, characteristics of the solvent system applicable to embodiments of methods for recovering organic heteroatom compounds will now be described using the equations and description below. In the following equations, gaseous carbon dioxide is denoted by “CO₂ (g)” and may have a partial pressure P_{CO_2} , dissolved carbon dioxide is denoted by “CO₂ (aq)”, and dissolved carbonic acid is denoted by “H₂CO₃ (aq)”. In some embodiments, dissolved carbon dioxide may account for greater than or equal to about 90.0 mol% of the dissolved components, such as greater than or equal to about 95.0% of the dissolved components. In other embodiments, dissolved carbon dioxide, particularly dissolved carbon dioxide gas may account for greater than or equal to about 97.0 mol% of the dissolved components, such as greater than or equal to about 99.0 mol% of the dissolved components. In some embodiments, dissolved carbon dioxide may account for 99.85 mol% of the dissolved components, and dissolved carbonic acid may account for 0.15 mol% of the dissolved components. The dissolved components in the solvent system may be denoted as H₂CO₃^{*}, as shown in equation (A) below.



[0024] With respect to pressure, gaseous carbon dioxide may be in equilibrium with dissolved carbonic acid in accordance with formulas (B) and (C) below.



[0025] Thus, the dissolved carbon dioxide and dissolved carbonic acid may have the relationship shown in equation (D).



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[0026] Gaseous carbon dioxide may be in equilibrium with the carbon dioxide in an aqueous phase in the contactor according to Henry's law, as denoted in equation (E), where Henry's law constant is denoted as k_H (mole/(kg·atm)).

$$CO_2 (aq) = P_{CO_2} / k_H \quad (E)$$

[0027] Thus, the solubility of carbon dioxide in the aqueous phase may increase with respect to increasing pressure of the solvent system employed in the methods according to some embodiments. In addition, the solubility of gaseous carbon dioxide in water or aqueous phase increases as the temperature of the solvent system decreases. However, to maintain supercritical behavior of carbon dioxide in the solvent system, according to embodiments, the temperature and the pressure of the solvent system may be maintained above the critical temperature and pressure of carbon dioxide. As a result, the combined effect of the carbon dioxide and water in the tunable solvent achieves unique properties that allow the solvent to be used to attract or complex with organic heteroatom compounds from hydrocarbon feedstocks into the solvent system as a solute.

[0028] Properties of the tunable solvent system included in various embodiments will be described in equations below, K_1 is the first dissociation constant and $a(j)$ is the activity of the involved species "j."

$$K_1 = \{a(H^+) a(HCO_3^-)\} / a(H_2CO_3) \quad (F)$$

Using commonly known definitions of pH and pK, equation (F) may be rewritten as equation (G):

$$pK_1 = pH + \log\{[H_2CO_3^*] / [HCO_3^-]\} - \log(\gamma_a) \quad (G)$$

In equation (G), γ_a is the activity coefficient of HCO_3^- . The activity coefficient of a neutral species may be assumed to be unity.

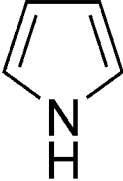
[0029] As shown by the above equations, the carbon dioxide in the solvent system according to embodiments herein may play multiple roles in the separation process.

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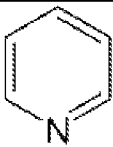
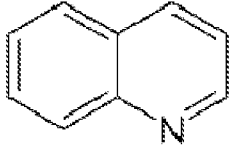
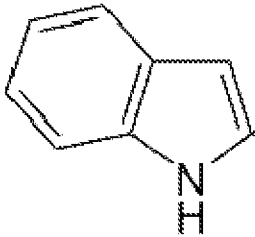
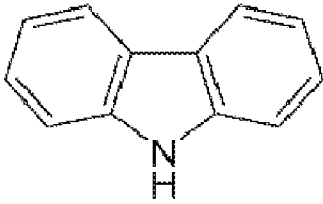
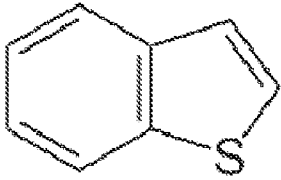
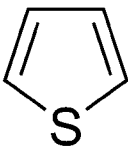
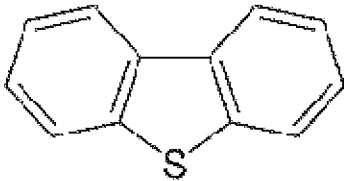
Supercritical carbon dioxide may diffuse through the hydrocarbon feedstock because it has good diffusivity and lower viscosity than other solvents, which allows the carbon dioxide to better initiate the mass transfer that attracts the organic heteroatom compounds into the solvent system as a solute. For example, in embodiments, the polar nature of refractory sulfur compounds, nitrogen compounds, and organometallic compounds may bring the organics into the reversible aqueous phase of the solvent. For example, the polar characteristics of the organic heteroatom compounds may be attracted by the HCO_3^- in the H_2CO_3^* (aq) phase.

[0030] In some embodiments, the temperature of the solvent system, the pressure of the solvent system, or both, may be adjusted to tune the solvent system to contain more or fewer ions, such as, for example, HCO_3^- , thereby making the solvent system more or less attractive to ionic refractory components or to tune the solvent system's ability to form complexes between the tunable solvent and the organic heteroatom compound. To remove target refractory components, such as, for example, target organic sulfur compounds, target organic nitrogen compounds, target organometallic compounds, or combinations thereof, properties such as boiling point, as well as the chemical structures of the target organic heteroatom compounds may affect temperature and pressure parameters that result in selectivity of the solvent system. Various organic sulfur compounds, organic nitrogen compounds, and organometallic compounds are shown in TABLE 1 as examples of the organic heteroatom compounds that may be removed from hydrocarbon feedstocks in various embodiments. It should be understood that the compounds listed below are only exemplary in nature and are not intended to be an exhaustive list of all organic heteroatom compounds that may be removed according to embodiments of this disclosure.

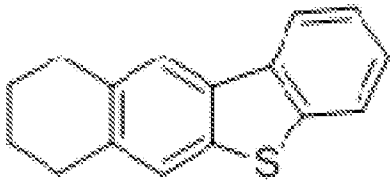
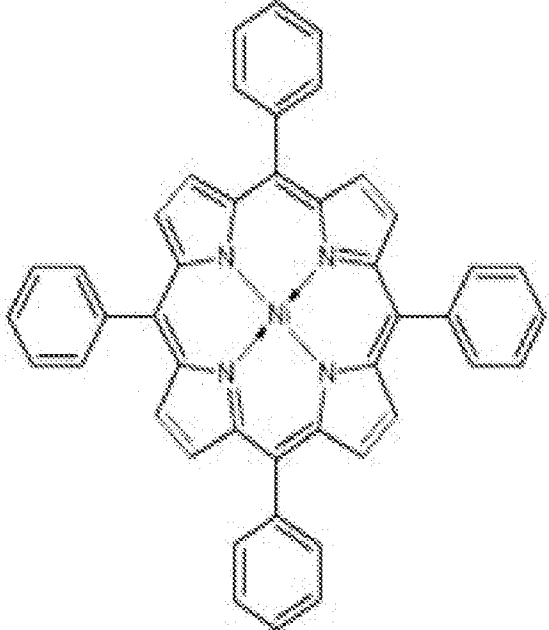
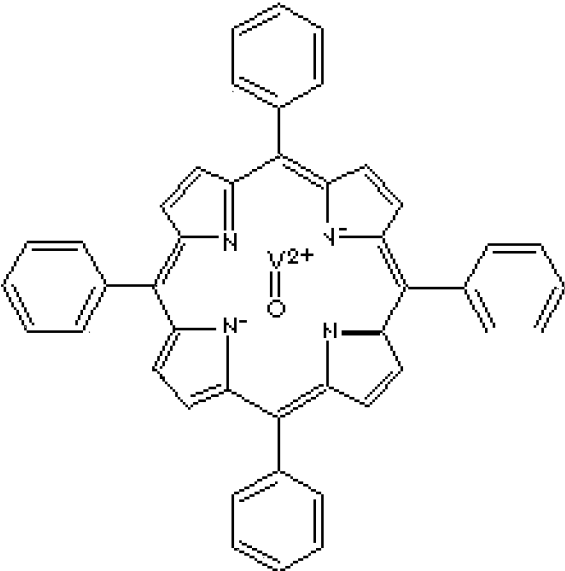
TABLE 1

pyrrole	
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pyridine	
quinoline	
indole	
carbazole	
benzothiophene	
thiophene	
dibenzothiophene	

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7,8,9,10-tetrahydro- benzo[b]naphtho[2,3-d]thiophene	
nickel-tetraphenyl-porphyrin	
vanadyl-tetraphenyl-porphyrin	

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[0031] As should be evident from the organic heteroatom compounds in TABLE 1, the compounds that may be removed from hydrocarbon feedstocks according to various embodiments may have varieties of chemical structures. Thus, the compounds that are to be removed from the hydrocarbon feedstocks will have an impact and can determine the appropriate amount of solvent tuning required, such as, for example, adjustments of the pressure and/or temperature of the solvent system. Additionally, in embodiments, the selection of a tunable solvent for the separation of a specific organic heteroatom compound from hydrocarbons may impact the mass transfer of the organic heteroatom compounds from a hydrocarbon phase to a solvent phase that result from phase separation of the extraction mixture.

[0032] Tunable solvents and organic heteroatom compounds to be removed from hydrocarbons, such as, for example, crude oil or crude oil fractions, according to embodiments of this disclosure have been described above. Below embodiments of methods and systems for using tunable solvents to separate organic heteroatom compounds are provided. It should be understood that the methods and systems described below are exemplary only and other methods and systems for separating organic heteroatom compounds from hydrocarbons using a tunable solvent are within the scope of this disclosure.

[0033] A single stream or a series of streams of tunable solvents may be used for selectively separating organic heteroatom compounds, such as, for example, organic sulfur compounds, organic nitrogen compounds, and/or organometallic compounds, from hydrocarbons. In embodiments, the separation may proceed by running the tunable solvent and the hydrocarbons in a series of cross-current or counter-current contactors, such as, for examples, packed bed contactors, fluidized bed contactors, and baffled contactors.

[0034] The method of any embodiment of the present the invention may be performed as a batch or continuous operation. Preferably, the method is performed as a continuous operation.

[0035] Referring to FIG. 1, a typical process set-up **100** is depicted. A hydrocarbon feedstock **131**, such as crude oil, may be dispersed from a hydrocarbon storage unit **130**

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into the bottom of contactor **110**, such as by bottom spray nozzles **112**. Similarly, a tunable solvent **150** may be formed by mixing carbon dioxide **121** from a carbon dioxide storage unit **120** and water **141** from a water storage unit **140**. The tunable solvent **150** may be dispersed into the top of the contactor **100**, such as by top spray nozzles **114**. Droplets and sprays of the hydrocarbon **131** may flow upward, such as by spray propulsion and by filling the bottom of the contactor **110** with the hydrocarbon **131**. Droplets and sprays of the tunable solvent **150** may flow downward in the contactor **110**, such as by spray propulsion and gravitational forces. Further, in embodiments, the hydrocarbon **131** and the tunable solvent **150** may be selected such that the density of the tunable solvent **150** is greater than the density of the hydrocarbon **131**. This difference in density may cause the tunable solvent **150** to contact the hydrocarbon **131** and traverse through the hydrocarbon phase. Thus, in embodiments, the hydrocarbon **131** and the tunable solvent **150** proceed in counter-flow contact, thereby increasing residence time of the contact between the hydrocarbon **131** and the tunable solvent **150**. Preferably, the hydrocarbon **131** is a hydrocarbon feedstock, and more preferably the hydrocarbon feedstock is a crude oil or crude oil fraction.

[0036] In some embodiments, the hydrocarbon **131** may optionally be premixed with supercritical carbon dioxide **122** before the hydrocarbon **131** is introduced into the contactor **110** to initiate separation of the target organic heteroatom compounds from the hydrocarbon **131** before it is fed into the contactor **110**. For example, supercritical carbon dioxide in any suitable form, such as supercritical carbon dioxide alone or as a component in a solvent, may be transmitted from the carbon dioxide storage unit **120** into the hydrocarbon **131**.

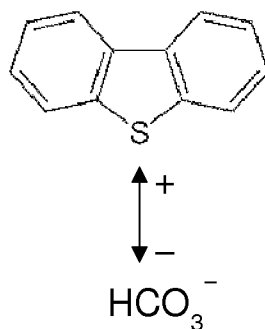
[0037] In some embodiments, droplets of both the hydrocarbon **131** and the tunable solvent **150** may coalesce to form separate homogeneous phases at their respective outlets of the contactor **110** (i.e., the bottom of the contactor **110** for the tunable solvent **150** and the top of the contactor **110** for the hydrocarbon **131**). In embodiments where the hydrocarbon **131** is more dense than the tunable solvent **150**, the flow of these components into the contactor may be reversed (i.e., the denser hydrocarbon **131** may be introduced into the top of the contactor **110**, and the tunable solvent **150** may be introduced into the bottom of the contactor **110**).

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[0038] In any embodiment, during contact between the hydrocarbon **131** and the tunable solvent **150**, organic heteroatom compounds may be attracted into the solvent phase of the tunable solvent **150** as solutes, for example, by forming complexes with the tunable solvent. Thus, after the hydrocarbon **131** and the tunable solvent **150** interact for a period of time, lean hydrocarbon **132** may be extracted from the middle of the contactor **110**. The solute-rich solvent **151**, which is rich with organic heteroatom compounds, may be removed from the bottom of the contactor **110**.

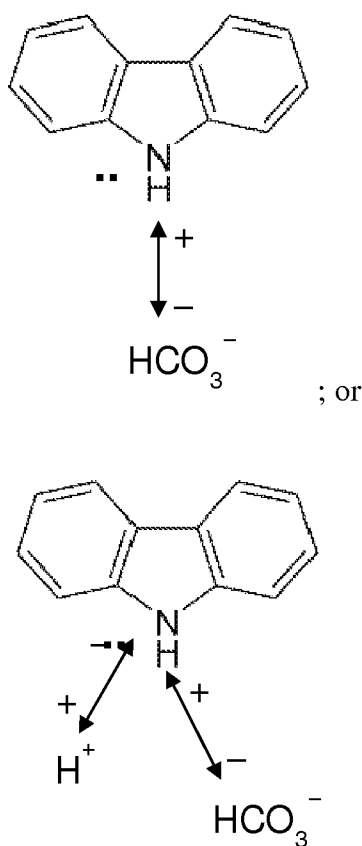
[0039] As discussed above, in embodiments, the pressure and/or temperature within the contactor may be modified to tune the solvent to have ions that attract polar components in the hydrocarbon feedstock. Target organic heteroatom compounds, such as, for example, organic sulfur compounds, organic nitrogen compounds, and organometallic compounds naturally have polarities in the molecular structures. For example, dibenzothiophene, shown in TABLE 1 above, has a sulfur atom that is more electropositive than its other, bonded carbon atoms. Particularly, the delocalized electrons of dibenzothiophene may be drawn inside of its ring structure and, thus, the sulfur atoms' outer shell may also be drawn inside toward the electrons. As a result, the sulfur atom attached to the rings becomes electropositive and provides the dibenzothiophene with polar properties.

[0040] Because various organic heteroatom compounds have polarities, such as the above-described dibenzothiophene, they can be separated from the hydrocarbon phase into the aqueous phase of the solvent by the HCO_3^- ions by forming a temporary complex between the polar organic heteroatom compound and the HCO_3^- ion. For example, a temporary complex that is formed between dibenzothiophene and HCO_3^- is shown below:



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[0041] Organic heteroatom compounds containing nitrogen may also have polar behavior. However, unlike organic sulfur compounds, HCO_3^- or H^+ may attract the organic nitrogen compounds because, in certain compounds, the nitrogen bond may have a positive or negative polarity. For example, in carbazole, the N—H bond may take on a positive or negative polarity and, thus, the following complexes may be formed between the tunable solvent and carbazole:



[0042] The above reaction mechanisms are exemplary only and are not intended to limit the scope of any embodiment herein. Similar reaction mechanism may occur with respect separation other organic heteroatom compounds, such as, for example, any of the compounds in TABLE 1.

[0043] Further explanation of the extraction mechanism according to embodiments may be made with reference to FIG. 2, which shows the phases in contactor 110 during the reaction between the tunable solvent and the hydrocarbon. FIG. 2 depicts an embodiment in which the density of the tunable solvent 150 is greater than the density of

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the hydrocarbon feedstock **131** and hence the tunable solvent is preferably fed to the top of the contactor and the hydrocarbon feedstock is fed to the bottom of the contactor. However, the following is also applicable to the embodiment wherein the density of the tunable solvent is less than the density of the hydrocarbon feedstock, and the tunable solvent is fed into the bottom of the contactor whilst the hydrocarbon feedstock is fed to the top of the contactor. In FIG. 2, the fluids in the contactor **110** are divided into four phase regions **210**, **220**, **230**, and **240**. Each phase region is separated from adjacent phase region(s) by a phase boundary (represented by dotted lines). According to some embodiments, the top of the contactor **110** may comprise phase **210** that includes supercritical and subcritical carbon dioxide. Below phase **210** is phase **220** that may include lean hydrocarbon and carbon dioxide. In embodiments, the lean hydrocarbon **132** extracted from the contactor **110** may be extracted from phase **220**. Below phase **220** is phase **230** that includes a mixture of aqueous carbon dioxide, water, hydrogen ions, carbonic acid, hydrocarbon, and supercritical carbon dioxide. The tunable solvent **150** and the hydrocarbon **131** are introduced into the contactor **110** in phase **220**, such as by spraying through spray nozzles **112** and **114**. At the bottom of the contactor is phase **240**, which may comprise aqueous carbon dioxide, hydrogen ions, water, carbonic acid, and solute rich solvent. The solute-rich solvent **151** that is extracted from the contactor may be extracted from phase **240**.

[0044] Using the phases in the contactor **110**, such as the phases shown in FIG. 2, the effect of pressure on the solvent system within the contactor **110** may be understood referring to equation (C) above. For example, complexes between organic heteroatom compounds and the solvent, such as the complexes shown above, may be driven by pressure increases in the solvent system. One example of how pressure drives complexes between organic heteroatom compounds and the solvent is shown in FIG. 3, which is exemplary only and does not limit the scope of any embodiment. FIG. 3 shows the formation of $\text{H}_2\text{CO}_3^*(\text{aq})$, $\text{H}^+(\text{aq})$, and $\text{HCO}_3^-(\text{aq})$ is promoted by increasing the pressure on the solvent system. In FIG. 3, a tunable solvent is signified by **310** and a heteroatom-bicarbonate ion complex is signified by **320**. In the mechanism shown in FIG. 3, $\text{H}_2\text{CO}_3^*(\text{aq})$, $\text{H}^+(\text{aq})$, and $\text{HCO}_3^-(\text{aq})$ constitute the tunable solvent. In addition, the solubility of carbon dioxide in water increases as the temperature of the solvent

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system decreases. However, formation of a complex between the HCO_3^- and the dibenzothiophene also promotes the forward reaction to form $\text{H}_2\text{CO}_3^*(\text{aq})$ in water, so that the concentration of $\text{HCO}_3^- (\text{aq})$ may be maintained. Thus, equilibrium is established immediately after a complex forms through the disassociation of an equivalent of $\text{H}_2\text{CO}_3^*(\text{aq})$ into $\text{H}^+(\text{aq})$, and $\text{HCO}_3^-(\text{aq})$. Accordingly, in embodiments, increasing the pressure in the contactor promotes the formation of the complex between one $\text{HCO}_3^-(\text{aq})$ ion and one molecule of the organic heteroatom compound. Similarly, a decrease in pressure will drive the above mechanism in the opposite direction and will decrease the formation of complexes between ions and organic heteroatom compounds or may decompose any complexes that already exist in solution. Thus, it should be apparent that the organic heteroatom compound may be ejected from the solvent or may be made to aggregate or precipitate out of the solvent by decreasing the pressure in the contactor, for example.

[0045] The pressure in the contactor may vary according to the tunable solvent **150** that is used and the target organic heteroatom compounds, such as varying the pressure to produce more or less HCO_3^- to attract various specific organic heteroatom compounds. However, in embodiments, the pressure in the contactor may be from about 2 bar to about 300 bar, such as from about 20 bar to about 275 bar. In some embodiments, the pressure in the contactor may be from about 50 bar to about 250 bar, such as from about 75 bar to about 225 bar. In yet other embodiments, the pressure in the contactor may be from about 100 bar to about 200 bar. In still other embodiments, the pressure in the contactor may be from about 125 bar to about 175 bar, such as about 150 bar. It should be understood that the above ranges are intended to include each point between the disclosed endpoints, and that each pressure point between 2 bar and 300 bar is envisioned in this disclosure.

[0046] The temperature in the contactor may vary according to the tunable solvent **150** that is used and the target organic heteroatom compounds. In embodiments in which aqueous carbon dioxide is the tunable solvent, the temperature in the contactor may be greater than or equal to the critical temperature of carbon dioxide, such as about 20 °C greater than the critical temperature of carbon dioxide. In some embodiments, the temperature in the contactor is greater than or equal to 40 °C above the critical

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temperature of carbon dioxide, such as about 60 °C greater than the critical temperature of carbon dioxide. In embodiments, the temperature in the contactor may be less than or equal to about 100 °C above the critical temperature of carbon dioxide, such as less than or equal to about 80 °C above the critical temperature of carbon dioxide. Accordingly, in embodiments, the temperature in the contactor may be from greater than or equal to about 40 °C above the critical temperature of carbon dioxide to less than or equal to about 100 °C above the critical temperature of carbon dioxide, such as from greater than or equal to about 60 °C above the critical temperature of carbon dioxide to less than or equal to about 80 °C above the critical temperature of carbon dioxide.

[0047] Referring again to FIG. 1, in embodiments, the lean hydrocarbon **132** that has been extracted from the middle of the contactor **110** is sent to a vessel **160** where the lean hydrocarbon **132** may be depressurized, causing a discharge stream **133** of any residual carbon dioxide and/or water to be separated from the lean hydrocarbon **132** and removed from the vessel **160**. The discharge stream **133** may be further treated to separate the carbon dioxide and water, which may be returned to the carbon dioxide storage unit **120** and the water storage unit **140**, respectively. In other embodiments, the discharge stream may be discarded.

[0048] In embodiments, the solute rich tunable solvent **151**, which may be extracted from the bottom of the contactor **110**, may be fed to recovery vessel **170** where it is depressurized to tune down the ionic properties of the solute rich solvent **151** and thereby eject the solute **171**, such as, for example, organic heteroatom compounds. The ejected solute **171** may then be stored and used in some other capacity. In some embodiments, the ejected solute **171** may be filtered out of the solute rich solvent **151**. In other embodiments, the ejected solute **171** may be removed from the solute rich solvent **151** by aromatic solvent extraction. In either embodiment (i.e., whether the solute is removed by filtering or aromatic extraction), carbon dioxide **123** [no label **123** in Figure 1], which has been released by lowering the pressure of the solute-rich solvent **151**, is repressurized and returned to the carbon dioxide storage unit **120** where it may be dispersed with water **141** into the contactor, or premixed with the hydrocarbon **131**.

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[0049] In embodiments where aromatic solvent extraction is used to separate the solute **171** from the solute rich solvent **151**, the solute rich aromatic solvent may be sent to an additional vessel where the aromatic solvent is evaporated off, such as by heating to the boiling point of the aromatic solvent, thus ejecting the solute **171**. The evaporated aromatic solvent may then be condensed and reused to extract further solute **171** from a solute rich solvent **151**, and the solute **171** may be stored and used in another capacity.

[0050] It should be understood that while FIG. 1 shows only one contactor **110**, in embodiments, multiple contactors may be used in series depending on the number and characteristics of the organic heteroatom compounds to be removed. For example, the tunable solvent in a first contactor may be tuned to separate a first organic heteroatom compound, and a second contactor may be used to tune a second tunable solvent to separate a second organic heteroatom compound, such as, for example, having a pressure or temperature in the second contactor that is different from the pressure in the first contactor. Similarly, although FIG. 1 shows only one recovery vessel **170** for ejecting a solute **171** from a solute rich solvent **151**, multiple vessels for ejected solute may be used. For example, where the solute rich solvent **151** includes multiple solutes with differing boiling points, multiple vessels may be used to eject the multiple solutes from the solute rich solvent **151**.

Electric Field Assisted Mass Transfer

[0051] Separation of organic heteroatom compounds from a hydrocarbon feedstock may be further enhanced using an electrical field. Referring to FIG. 4, in some embodiments, an electric field may be generated between two electrical plates **410** and **420** of a capacitor. This electric field may lead to alignment of ionic species within the electric field, thereby improving mass transfer between the ions. Particles **430** may be bipolar aqueous solvent particles, which are not aligned outside of the electric plates **410** and **420**. Particles **450** may be organic bipolar particles that are not aligned outside of the electric plates **410** and **420**. Between the electric plates may be heteroatom complexes, such as, for example, the complexes of tunable solvent and an organic heteroatom compound described above, that are aligned **440**. The residence time and contact between the tunable solvent and the hydrocarbon feedstock may be increased by

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having the ions aligned within the electric plates **410** and **420**. Further, using an electric field to align particles allows the tunable solvent to have a higher affinity toward the organic heteroatom compounds, and may facilitate mass transfer between the two plates by attracting polar ions.

[0052] In embodiments, the electrical plates may cause an alignment of organic heteroatom compounds from the hydrocarbon feedstock with respect to the electrical field and, thereby, facilitate their transfer toward the tunable solvent, where they are attracted into the aqueous phase of the solvent via the mechanisms discussed hereinabove. The outgoing tunable solvent, which is saturated with organic heteroatom compounds, may then be sent to a separate vessel where the organic heteroatom compounds may be removed from the tunable solvent by aromatic extraction of by reducing the pressure of the solvent system to allow the tunable solvent to eject the solute where the solute may be collected by, for example, filtration. After separation, the tunable solvent may be re-pressurized and returned to the contactor, and the organic heteroatom compound solutes may be stored and used in another capacity.

[0053] In embodiments, the electrical plates **410** and **420** may have through-holes to facilitate transfer of particles between the plates. In some embodiments, a bank of electrical plates may be used to form baffles or packing material within a contactor, such as contactor **110**. The bank of plates may be offset from one another.

[0054] Thus, various embodiments of methods for recovering organic heteroatom compounds from a hydrocarbon feedstock have been described. In the methods, an aqueous solvent system such as an ionic liquid formed from pressurized carbon dioxide and water, may be contacted with a hydrocarbon feedstock such as crude oil or a crude oil fraction. The contacting may occur in a contactor vessel at a pressure and temperature that tunes the aqueous solvent system to selectively form complexes with organic heteroatom compounds in the hydrocarbon feedstock. The complexes may then be transferred to a recovery vessel, in which pressure, temperature, or both, may be adjusted to cause the organic heteroatom compounds to come out of solution. Thereby, the organic heteroatom compounds may be used for further applications. Unlike with common denitrogenation or desulfurization processes used for hydrocarbon feedstocks

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such as crude oil, the organic heteroatom compounds maintain their chemical structure and can be utilized as a valuable byproduct of petroleum refining that previously would have been wasted.

[0055] It will be apparent to those skilled in the art that various modifications and variations can be made to the embodiments described herein without departing from the spirit and scope of the claimed subject matter. Thus it is intended that the specification cover the modifications and variations of the various embodiments described herein provided such modification and variations come within the scope of the appended claims and their equivalents.

CLAIMS

1. A method for recovering organic heteroatom compounds from a hydrocarbon feedstock, the method comprising:
- 5 feeding a hydrocarbon feedstock into a contactor, wherein the hydrocarbon feedstock comprises crude oil or a crude oil fraction and at least one organic heteroatom compound chosen from pyrrole, pyridine, quinoline, carbazole, indole, nickel-tetraphenyl-porphyrin, vanadyl-tetraphenyl-porphyrin, thiophene, benzothiophene, dibenzothiophene, and 7,8,9,10-tetrahydro-benzo[b]naphtho[2,3-d]thiophene, and
- 10 combinations thereof;
- feeding an aqueous solvent into the contactor to form an extraction mixture of the aqueous solvent with the hydrocarbon feedstock, the aqueous solvent comprising an ionic liquid formed from pressurized carbon dioxide and water;
- establishing a contactor pressure and a contactor temperature of the extraction
- 15 mixture in the contactor that together tune the aqueous solvent to selectively form a solvent complex with the at least one organic heteroatom compound;
- extracting the solvent complex to a recovery vessel from the extraction mixture in the contactor;
- adjusting a recovery temperature of the recovery vessel, a recovery pressure of
- 20 the recovery vessel, or both, to decompose the solvent complex in the recovery vessel into carbon dioxide and the at least one organic heteroatom compound; and
- recovering the at least one organic heteroatom compound from the recovery vessel.
- 25 2. The method of claim 1, wherein the pressurized carbon dioxide in the aqueous solvent comprises supercritical CO₂, subcritical CO₂, or both.
3. The method of claim 1, wherein the contactor pressure is from about 2 bar to about 300 bar.
- 30 4. The method of claim 3, wherein the contactor pressure is greater than or equal to the critical pressure of CO₂.

5. The method of claim 3, wherein adjusting a recovery temperature of the recovery vessel, a recovery pressure of the recovery vessel, or both comprises reducing the recovery pressure to less than the contactor pressure.

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6. The method of claim 1, wherein the contactor temperature is from greater than the critical temperature of carbon dioxide to about 100°C.

7. The method of claim 6, wherein adjusting a recovery temperature of the recovery vessel, a recovery pressure of the recovery vessel, or both comprises lowering the recovery temperature to less than the contactor temperature.

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8. The method of claim 1, wherein recovering the at least one organic heteroatom compound comprises mixing an aromatic solvent with the solvent complex.

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9. The method of claim 1, wherein:

feeding the hydrocarbon feedstock comprises spraying the hydrocarbon feedstock into a bottom of the contactor; and

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feeding the aqueous solvent comprises spraying the aqueous solvent into a top of the contactor.

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10. The method of claim 9, wherein the density of the aqueous solvent is greater than the density of the hydrocarbon feedstock, whereby the extraction mixture phase separates into at least an organic phase and an aqueous phase and at least a portion of the solvent complex migrates into the aqueous phase.

11. The method of claim 10, wherein extracting the solvent complex comprises removing the at least a portion of the solvent complex from the aqueous phase or from a CO₂ phase that forms above the aqueous phase in the contactor.

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12. The method of claim 1, further comprising mixing the hydrocarbon feedstock with supercritical CO₂ before feeding the hydrocarbon feedstock into the contactor.

5 13. The method of claim 1, wherein the contactor comprises electrical plates, the method further comprising activating the electrical plates to align ions of the ionic liquid and ions of the at least one organic heteroatom compound.

10 14. A method for recovering organic heteroatom compounds from a hydrocarbon feedstock, the method comprising:

 feeding a hydrocarbon feedstock into a contactor, the hydrocarbon feedstock comprising crude oil or a crude oil fraction and at least one organic heteroatom compound chosen from pyrrole, pyridine, quinoline, carbazole, indole, nickel-tetraphenyl-porphyrin, vanadyl-tetraphenyl-porphyrin, thiophene, benzothiophene, 15 dibenzothiophene, and 7,8,9,10-tetrahydro-benzo[b]naphtho[2,3-d]thiophene, and combinations thereof;

 feeding an aqueous solvent into the contactor to form an extraction mixture of the aqueous solvent with the hydrocarbon feedstock, the aqueous solvent comprising an ionic liquid formed from pressurized carbon dioxide and water;

20 establishing a contactor pressure and a contactor temperature of the extraction mixture in the contactor that together tune the aqueous solvent to selectively form a solvent complex with the at least one organic heteroatom compound;

 extracting the solvent complex to a recovery vessel from the extraction mixture in the contactor;

25 depressurizing the solvent complex in the recovery vessel to decompose the solvent complex into carbon dioxide and the at least one organic heteroatom compound; and

 recovering the at least one organic heteroatom compound from the recovery vessel.

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15. The method of claim 14, further comprising recycling at least a portion of the carbon dioxide released during the depressurizing of the solvent complex in the recovery vessel back to the contactor.