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(54) **Title:** MULTI-STAGE SUPERCRITICAL WATER UPGRADING OF ASPHALTENES FOR THE PRODUCTION OF HIGH-QUALITY MESOPHASE PITCH

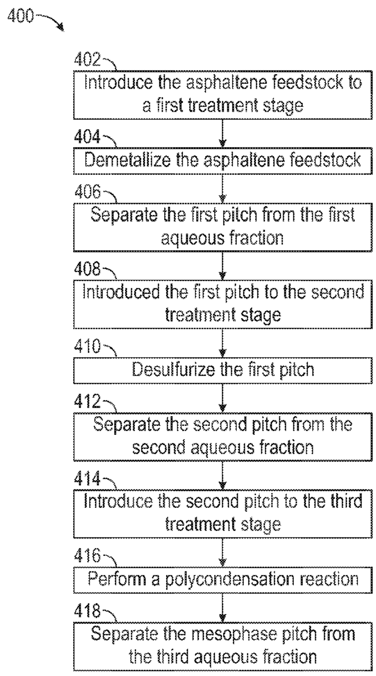

FIG. 4

(57) **Abstract:** A system for upgrading asphaltenes includes an asphaltene treatment line 111, a series of asphaltene upgrade units, a series of carbon fiber production units, an aqueous collection unit 140, and a gaseous collection unit 130. The series of asphaltene upgrade units includes a demetallizing unit that includes a first supercritical water (SCW) treatment unit 110 and a first centrifugation unit 112, a desulfurizing unit that includes a second SCW treatment unit 114 and a second centrifugation unit 116, and a polycondensation unit that includes a third SCW treatment unit 118 and a third centrifugation unit 120. A method for mesophase pitch production from an asphaltene feedstock and a method for manufacturing carbon fibers from asphaltene feedstock are also described.

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MULTI-STAGE SUPERCRITICAL WATER UPGRADING OF ASPHALTENES FOR THE PRODUCTION OF HIGH-QUALITY MESOPHASE PITCH

BACKGROUND

[0001] Pitch is a viscoelastic material that is composed of aromatic hydrocarbons. Pitch is produced via the distillation of carbon-based materials, such as plants, crude oil, and coal. Pitch is isotropic but can be made anisotropic through the use of heat treatments. Mesophase pitch, which has a higher molecular weight than pitch, is a useful precursor for making carbon fibers. It is not typically economical to produce mesophase pitch from purer chemicals, such as naphthalene or anthracene. Mesophase pitch can be prepared from pitch through several methods. In general, a crude feedstock is treated via removal of volatile compounds followed by a pyrolytic heat-treatment to obtain mesophase pitch. The pyrolytic heat-treatment promotes conversion of an isotropic pitch to an anisotropic pitch, which plays an important role in the development of carbon fiber microstructure.

[0002] One method of making mesophase pitch includes using a rapid gas blowing method. However, a drawback to this approach is the long treatment time required to ensure removal of volatile compounds and/or non-mesogen compounds. Non-mesogen compounds are those that cannot be converted to mesophase pitch due to their low molecular weights. In addition, this method can take more than 40 hours to complete, and the rapid gas blowing method can induce excessive condensation, which increases the softening point of the resulting mesophase pitch. The formation of mesophase pitch is often optimized to control the viscosity, the molecular weight distribution, and the softening point. In particular, the softening point must be balanced to allow a stable spinning, favorable at low value, as well as a sufficient stabilization reactivity, favorable at high value. The increased softening point of the mesophase pitch requires increased temperature for spinning to produce fibers, but such increased temperature can induce pyrolytic degradation, or cutting of the fiber during spinning. Accordingly, there exists a need for efficient processes to access mesophase pitch from various sources of pitch feedstock.

SUMMARY

[0003] This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used as an aid in limiting the scope of the claimed subject matter.

[0004] In one aspect, embodiments disclosed herein relate to a system for upgrading asphaltenes. The system includes an asphaltene treatment line, a series of asphaltene upgrade units, a series of carbon fiber production units, an aqueous collection unit, and a a gaseous collection unit. The series of carbon fiber production unit includes a demetallizing unit that includes a first supercritical water (SCW) treatment unit and a first centrifugation unit, a desulfurizing unit that includes a second SCW treatment unit and a second centrifugation unit, and a polycondensation unit that includes a third SCW treatment unit and a third centrifugation unit.

[0005] In another aspect, embodiments disclosed herein relate to a method for mesophase pitch production from an asphaltene feedstock. The method includes introducing the asphaltene feedstock to an asphaltene treatment line, introducing the asphaltene feedstock to a first SCW treatment unit of a demetallizing unit, demetallizing the asphaltene feedstock, thereby producing a first mixture and a first reaction gas stream. The first mixture includes a first aqueous fraction and a first pitch. The method then includes separating the first aqueous fraction from the first pitch, introducing the first pitch to a second SCW treatment unit of a desulfurizing unit, desulfurizing the first pitch, thereby forming a second mixture and a second reaction gas stream. The second mixture includes a second aqueous fraction and a second pitch. The method further includes separating the second aqueous fraction from the second pitch, introducing the second pitch to a third SCW treatment unit of a polycondensation stage, performing a polycondensation reaction in the third SCW treatment unit, thereby forming a third reaction gas stream and a third mixture. The third mixture includes a third aqueous fraction and the mesophase pitch. The method then includes separating the third aqueous fraction from the mesophase pitch, thereby producing the mesophase pitch.

[0006] In another aspect, embodiments disclosed herein also relate to a method for manufacturing carbon fibers from asphaltene feedstock. The method includes introducing the asphaltene feedstock to an asphaltene treatment line, introducing the asphaltene feedstock to a first SCW treatment unit of a demetallizing unit, demetallizing the asphaltene feedstock, thereby producing a first mixture and a first reaction gas stream. The method further includes separating a first aqueous fraction from a first pitch, introducing the first pitch to a second SCW treatment unit of a desulfurizing unit, desulfurizing the first pitch, thereby forming a second mixture and a second reaction gas stream. The method then includes separating the second aqueous fraction from the second pitch, introducing the second pitch to a third SCW treatment unit of a polycondensation stage, performing a polycondensation reaction in the third SCW treatment unit, thereby forming a third reaction gas stream and a third mixture, separating the third aqueous fraction from the mesophase pitch, producing the mesophase pitch, introducing the mesophase pitch fraction to a series of carbon fiber production units, thereby producing carbon fibers.

[0007] Other aspects and advantages of the claimed subject matter will be apparent from the following description and the appended claims.

BRIEF DESCRIPTION OF DRAWINGS

[0008] FIGs. 1A and 1B are schematics of a system for upgrading asphaltenes in accordance with one or more embodiments.

[0009] FIG. 1C is a schematic of a mesophase enrichment system in accordance with one or more embodiments.

[0010] FIG. 2 is a schematic of a series of carbon fiber production units in accordance with one or more embodiments.

[0011] FIG. 3A is a schematic of a supercritical reactor unit in accordance with one or more embodiments.

[0012] FIG. 3B is a schematic of a supercritical reactor unit with a demetallizing agent injection unit in accordance with one or more embodiments.

[0013] FIG. 4 is a block flow diagram of a method for upgrading asphaltenes in accordance with one or more embodiments.

[0014] FIG. 5 is a block flow diagram of a method for producing carbon fibers in accordance with one or more embodiments.

DETAILED DESCRIPTION

[0015] Asphaltenes, also a component of crude oil, are comprised of the highest amount of aromatic residues in petroleum pitches, which increases the complexity of processing (or “upgrading”) methods to advanced materials. The aromatic residues of asphaltenes include polycyclic aromatic hydrocarbons substituted with alkyl side chains in the presence of heteroatoms, such as nitrogen, sulfur, oxygen, and metals. In particular, asphaltenes are rich in heavy metal impurities in the form of petroporphyrins, which exist predominantly as vanadyl- and nickel-chelated compounds. The presence of these metallo-porphyrins within the networks of asphaltene form agglomerates of high molecular weight compounds, which present difficulties upon treatment and/or separation using common crude oil processing techniques. Often, asphaltenes present detrimental effects for upgrading to mesophase pitch as a result of high agglomeration tendencies of metal containing compounds.

[0016] Similarly, sulfur present in asphaltenes, such as thiophenic and sulfidic species, can affect the upgrading process of a crude asphaltene feedstock. In particular, these sulfur-based impurities can affect the upgrading of a crude feedstock to mesophase pitch, which can alter the production quality and efficiency of advanced material manufacturing, such as carbon fiber manufacturing, Thus, to upgrade an asphaltene feedstock to obtain a valuable mesophase pitch, impurities such as metal containing compounds, sulfur containing compounds, and other impurities must be reduced and/or removed from an asphaltene feedstock.

[0017] Thus, in one or more embodiments, the systems and methods of the present disclosure include a multi-stage supercritical water (SCW) treatment system to upgrade a crude pitch feedstock. One or more embodiments of the present disclosure relate to methods of carbon fiber production from a crude pitch feedstock. The crude pitch feedstock of one or more embodiments include tar of wood, coal, and hydrocarbons, as well as asphaltenes. In other embodiments, the present disclosure relates to systems and methods to upgrade asphaltenes to a mesophase pitch. Processes of one or more embodiments described herein allow for the control of mesophase pitch viscosity, molecular weight distribution, and softening point as obtained from a crude asphaltene feedstock.

[0018] In one or more particular embodiments, the crude pitch feedstock is an asphaltene feedstock. The term "asphaltene" refers to asphaltenes isolated from crude petroleum source or a crude oil source that includes an amount of asphaltenes. The systems and processes herein are advantageous over conventional crude feedstock upgrading methods as asphaltenes may be utilized in the upgrading process, where asphaltenes are a class of material with known detrimental effects to crude feedstock upgrading methods that require lengthy and resource-intensive separation in such conventional upgrading methods. In addition, the systems and processes herein describe the upgrading of asphaltenes with more eco-friendly supercritical treatments including water.

[0019] In one aspect, embodiments disclosed herein relate to systems and methods to upgrade the high aromatic content of an asphaltene feedstock to a mesophase pitch. Mesophase pitch is generally obtained by removing volatile compounds followed by a pyrolytic heat-treatment for a polycondensation reaction, which promotes a free-radical reaction of small aromatics to form polyaromatic molecules. Such processes convert isotropic pitch to anisotropic pitch, which can affect the development of advanced material microstructure, such as carbon fiber microstructure.

[0020] DEFINITIONS

[0021] The term "isotropic pitch" refers to the IUPAC gold books definition of a residue from pyrolysis of petroleum which is solid at room temperature, consisting of a complex mixture of numerous, essentially aromatic hydrocarbons and heterocyclic compounds. Isotropic pitch is a pitch having optical isotropic nature, meaning no regular structure.

[0022] The term "upgrade" refers to at least one of increasing American Petroleum Institute (API) gravity, decreasing the amount of heteroatoms, decreasing the amount of metal-containing compounds, decreasing the amount of the atmospheric fraction, increasing the amount of light fractions, and decreasing the viscosity. One of skill in the art understands that upgrade can have a relative meaning such that a stream may be upgraded in comparison to another stream but can still contain undesirable components, such as heteroatoms. The term "upgrade" may refer to the increase of the anisotropic ratio of a feedstock, such as a crude feedstock, a first pitch, a second pitch, a mesophase pitch, or combinations thereof, of a treatment stage of one or more embodiments.

[0023] The term "anisotropic ratio" refers to a ratio of an anisotropic content of a feedstock to an isotropic content of the feedstock. The feedstock may include a crude asphaltene feedstock, a first pitch, a second pitch, a mesophase pitch, or combinations thereof.

[0024] The term "pitch" refers to an intermediate component in the upgrading process. Pitch can contain aliphatic, naphthenic, and aromatic compounds. Pitch can include heteroatoms, including sulfur compounds, nitrogen compounds, organometallic compounds, and combinations of the same. Pitch may have a softening point range from about 50 °C to about 180 °C. The softening point range may depend upon the origin of the crude feedstock material (i.e., crude oil, asphaltenes, among other crude feedstock material). As used throughout, references to "pitch" do not include mesophase pitch. Pitch does not include coke and processes that produce coke do not produce pitch.

[0025] The term "mesophase pitch" refers to a pitch having optical anisotropic nature with a liquid crystalline nature and a short range orientational residue-end carbon materials. The evaporation of volatile compounds and removal of impurities is important to minimize chemical impurity interference with the formation of mesophase pitch. Mesophase pitch can be prepared by heat treatment of pitch at temperatures in the range between 300 °C and 500 °C. Mesophase pitch produced from the pitch produced in the polycondensation stage described herein can include a toluene insoluble fraction less than 70 wt% and alternately less than 60 wt%.

[0026] The water described in the present disclosure may be distilled water, deionized water, tap water, fresh water from surface or subsurface sources, production water, formation water, natural and synthetic brines, brackish water, natural and synthetic sea water, black water, brown water, gray water, blue water, potable water, non-potable water, other waters, and combinations thereof. In one or more embodiments, the water used may naturally contain contaminants, such as salts, ions, minerals, organics, and combinations thereof, as long as the contaminants do not interfere with the upgrading of the asphaltene feedstock, such as the removal of metal containing compounds, removal of heteroatoms, transformation from an isotropic pitch to anisotropic pitch, or combinations thereof.

[0027] The term “supercritical water” refers to water at a temperature at or greater than the critical temperature of water and at a pressure at or greater than the critical pressure of water. The critical temperature of water is 373.946 °C. The critical pressure of water is 22.06 megapascals (MPa). Supercritical water has unique properties making it suitable for use as a petroleum reaction medium where the reaction objectives can include conversion reactions, desulfurization reactions, denitrogenation reactions, and demetallization reactions. Advantageously, the supercritical water acts as both a hydrogen source and a solvent (diluent) in conversion reactions. In some embodiments, a catalyst may not be required for demetallization of an asphaltene feedstock, desulfurization of a pitch, or both. Hydrogen from the water molecules is transferred to the hydrocarbons through direct transfer or through indirect transfer, such as the water-gas shift reaction. In the water-gas shift reaction, carbon monoxide and water react to produce carbon dioxide and hydrogen. The resulting hydrogen can be transferred to hydrocarbons in conversion desulfurization reactions, demetallization reactions, denitrogenation reactions, and combinations thereof.

[0028] The term “residence time” refers to the time a material has spent inside a reactor. The residence time of the material may be calculated by subtracting the time the material enters the reaction from the time at which the material leaves the reactor. The residence time may also be calculated by dividing a volume of the reactor by the flow rate of the material. The flow rate of the material may be the rate of flow of the material entering the reactor or the rate of flow of the material out of the reactor. In embodiments in which the upgrade system is in equilibrium, such as in continuous flow systems, the rate of flow in and out of the reactor may be equal.

[0029] The term “liquid hourly space velocity” refers to the ratio of flow rate into a reactor to the internal reactor volume, having units per hour (h^{-1}).

SYSTEM FOR UPGRADING CRUDE ASPHALTENES

[0030] As mentioned above, one or more embodiments of the present disclosure relate to a system for upgrading asphaltene feedstock. The systems of such embodiments may upgrade the asphaltene feedstock to a mesophase pitch. An asphaltene may include a crude (or "untreated") asphaltene feedstock, a treated asphaltene feedstock, or both. The treated asphaltene feedstock may include asphaltenes that have been processed to undergo demetallization and/or desulfurization via extraction, hydrocracking, hydrotreating, among other processes. The crude asphaltene feedstock may be an asphaltene isolated from a crude petroleum source, a crude oil that includes asphaltenes, or combinations thereof.

[0031] The crude asphaltene may include a heavy oil stream, such as a heavy residue stream, a decant oil from a fluid catalytic cracking (FCC) unit, pyrolysis fuel oil, atmospheric residue streams from distillation of crude oil, vacuum residue streams from distillation of crude oil, vacuum gas oil from vacuum distillation unit, visbreaker bottoms, and combinations of the same. Heavy residue streams can have a 5 mass percentage thermal degradation value (T5%) greater than 600 °F (or 315 °C), an aromatic content greater than 60 wt% (weight percent) and alternately greater than 70 wt%, as measured using a high-performance liquid chromatograph (HPLC) method.

[0032] In one or more embodiments, the crude feedstock is a heterogenous mixture such that the mixture does not have a measurable anisotropic ratio. The crude feedstock may be upgraded in one or more embodiments (e.g., via one or more refinery processes, such as treating pitch) to obtain an upgraded product with an enriched anisotropic ratio. In some embodiments, the crude oil can include a mixture of different crude oil grades (e.g., different ratios of one or more of heavy, middle, and light hydrocarbon cuts (or "fractions)). As one of ordinary skill may appreciate, heavy hydrocarbon cuts, middle hydrocarbon cuts, and light hydrocarbon cuts may refer to hydrocarbons having a boiling point above 490 °C, boiling point selected from a range from 160 °C to 490 °C, and a boiling point of 160 °C or less, respectively.

[0033] A non-limiting example of a system 100 for upgrading asphaltene feedstock may be as described in FIG. 1A. The system 100 includes a series of asphaltene upgrade units 108 in fluid communication on an asphaltene treatment line 111. The asphaltene upgrade units 108 include a series of supercritical water treatment stages to upgrade a crude asphaltene feedstock on the asphaltene treatment line 111, such as a first treatment stage 102, a second treatment stage 104 downstream of the first treatment stage 102, and a third treatment stage 106 downstream of the second treatment stage 104. In one or more embodiments, the first treatment stage 102 may be a demetallization stage, the second treatment stage 104 may be a desulfurization stage, and the third treatment stage 106 may be a polycondensation phase. The third treatment stage 106 is in fluid communication with a mesophase pitch outlet line 128.

[0034] FIG. 1B shows a schematic of the subunits of the asphaltene upgrade system 100. As shown in FIG. 1B, the first treatment stage 102, second treatment stage 104, and the third treatment stage 106 include treatment subunits (110, 112, 114, 116, 118, and 120).

[0035] The SCW treatment units (110, 114, and 118) of the asphaltene upgrade system 100 of FIG. 1B, the supercritical carbon dioxide unit 152 (FIG. 1B), or combinations thereof can be vertically oriented or horizontally oriented. The supercritical water treatment reactors of one or more embodiments can independently have operating conditions, such as a supercritical water reaction temperature, a reaction pressure, and a reaction residence time. In one or more embodiments, the supercritical water reaction temperature may be in a range with a lower limit of any one of about 300 °C, about 310 °C, about 320 °C, about 350 °C, about 370 °C, about 400 °C, and about 450 °C and an upper limit of any one of about 380 °C, about 385 °C, about 390 °C, about 395 °C, about 400 °C, about 410°C, about 420 °C, about 450 °C, about 475 °C, and about 500 °C, where any lower limit can be paired with any mathematically compatible upper limit. The reaction pressure in supercritical water treatment reactor (or "supercritical water treatment unit") may be in a range with a lower limit of any one of about 22 MPa, about 23 MPa, about 24 MPa, and about 25 MPa and an upper limit of any one of about 24 MPa, about 25 MPa, about 26 MPa and about 27 MPa, where any lower limit can be paired with any mathematically compatible upper limit.

[0036] The residence time of an asphaltene or pitch sample in a supercritical water (SCW) treatment unit of treatment stages 102, 104, and 106 may be in a range with a lower limit of any one of about 1 min (minutes), about 5 min, about 10 min, about 15 min, about 20 min, about 25 min, about 30 min, about 40 min, and about 45 min (minutes) and an upper limit of any one of about 15 min, about 20 min, about 25 min, about 30 min, about 40 min, about 50 min, about 60 min, about 12 hours, about 24 hours, about 2 days, about 3 days, about 4 days, about 5 days, about 6 days, and about 1 week, where any upper limit can be paired with any mathematically compatible upper limit. Residence time of SCW treatment units can be calculated by assuming the density of the fluid in SCW treatment unit has the density of water at reaction conditions. In some embodiments, the residence time of an asphaltene or pitch feed in a SCW treatment unit depends on the type of feedstock, metal concentrations of the feedstock, sulfur concentrations of the feedstock, the supercritical temperature and pressure of the SCW treatment unit, and combinations thereof.

[0037] The liquid hourly space velocity (LHSV) in one or more SCW treatment units may be in a range with a lower limit of any one of about 1 h^{-1}, about 2.5 h^{-1}, about 5 h^{-1}, about 10 h^{-1}, about 15 h^{-1}, about 20 h^{-1}, about 25 h^{-1}, about 30 h^{-1}, about 35 h^{-1}, and about 45 h^{-1} and an upper limit of any one of about 15 h^{-1}, about 20 h^{-1}, about 25 h^{-1}, about 30 h^{-1}, about 35 h^{-1}, about 40 h^{-1}, about 45 h^{-1}, about 50 h^{-1} and about 60 h^{-1}, where any lower limit can be paired with any mathematically compatible upper limit.

[0038] The supercritical carbon dioxide treatment reactor (or "supercritical CO_2 treatment unit") of one or more embodiments can have operating conditions, such as a CO_2 reaction temperature, a CO_2 reaction pressure, and a CO_2 reaction residence time. The reaction temperature in the supercritical CO_2 reactor can be in the range between about 25 °C and about 50 °C, between about 25 °C and about 40 °C, or between about 30 °C and about 40 °C. In one or more embodiments, the reaction temperature may be in a range with a lower limit of any one of about 25 °C, about 26 °C, about 27 °C, about 30 °C, about 32 °C, and about 35 °C and an upper limit of any one of about 30 °C, about 31 °C, about 32 °C, about 35 °C, about 37 °C, about 40 °C, about 45 °C, and about 50 °C, where any lower limit can be paired with any mathematically compatible upper limit. The reaction pressure in supercritical CO_2 treatment unit (or "supercritical CO_2 treatment unit") may be in a range with a lower limit of any one of about 5 MPa, about 6 MPa, about 7 MPa, and about 8 MPa and an upper limit of any one of about 7 MPa, about 8 MPa, about 9 MPa and about 10 MPa, where any lower limit can be paired with any mathematically compatible upper limit.

[0039] The residence time in a supercritical CO_2 treatment unit may be in a range with a lower limit of any one of about 1 min (minutes), about 5 min, about 10 min, about 15 min, about 20 min, about 25 min, about 30 min, about 40 min, and about 45 min (minutes) and an upper limit of any one of about 15 min, about 20 min, about 25 min, about 30 min, about 40 min, about 50 min, about 60 min, about 12 hours, about 24 hours, about 2 days, about 3 days, about 4 days, about 5 days, about 6 days, and about

1 week, where any lower limit can be paired with any mathematically compatible upper limit. Residence time of supercritical CO_2 treatment unit can be calculated by assuming the density of the fluid in supercritical CO_2 treatment unit treatment unit has the density of carbon dioxide at reaction conditions.

[0040] The LHSV in a supercritical CO_2 treatment unit may be in a range with a lower limit of any one of about 1 h^{-1}, about 2.5 h^{-1}, about 5 h^{-1}, about 10 h^{-1}, about 15 h^{-1}, about 20 h^{-1}, about 25 h^{-1}, about 30 h^{-1}, about 35 h^{-1}, and about 45 h^{-1} and an upper limit of any one of about 15 h^{-1}, about 20 h^{-1}, about 25 h^{-1}, about 30 h^{-1}, about 35 h^{-1}, about 40 h^{-1}, about 45 h^{-1}, about 50 h^{-1} and 60 h^{-1}, where any lower limit can be paired with any mathematically compatible upper limit.

[0041] In one or more embodiments, a crude asphaltene feedstock is injected in the treatment line upstream of the first treatment stage. The injection of the one or more asphaltene feedstocks may be maintained in a suspension. The asphaltene feedstock may be passed to a first treatment stage 102 as shown in FIG. 1B that includes a first supercritical water treatment (SCW) unit 110 and a first centrifugation unit 112 for the demetallization of the crude feedstock. In one or more embodiments, the crude asphaltene feedstock is injected directly into the first SCW treatment unit 110. The crude asphaltene feedstock may be continuously injected in the first SCW treatment unit 110. The crude asphaltene feedstock may be kept in suspension as a result of the supercritical conditions of the first SCW treatment unit 110.

[0042] Water may then be injected to the asphaltene feedstock to form a crude feedstock solution when the crude asphaltene feedstock is present in the first SCW treatment unit. Water may be injected into a supercritical water treatment unit of one or more embodiments using a high-pressure metering pump and/or a high-pressure dosing pump. Water may be injected at the supercritical point of water, described above. The water may be distilled water, deionized water, tap water, fresh water from surface or subsurface sources, production water, formation water, natural and synthetic brines, brackish water, natural and synthetic sea water, and combinations thereof.

[0043] Water may be injected to the first SCW treatment unit such that the asphaltene feedstock is in a mass ratio with water in a range from about 1:1 to 1:100 asphaltene feedstock to water. In one or more particular embodiments, the mass ratio may have a lower limit of any one of about 1:1 asphaltene feedstock to water, about 1:2 asphaltene feedstock to water, about 1:5 asphaltene feedstock to water, about 1:10 asphaltene feedstock to water, about 1:25 asphaltene feedstock to water, and about 1:50 asphaltene feedstock to water and an upper limit of any one of about 1:25 asphaltene feedstock to water, about 1:40 asphaltene feedstock to water, about 1:50 asphaltene feedstock to water, about 1:75 asphaltene feedstock to water, and about 1:100 asphaltene feedstock to water, where any lower limit may be combined with any mathematically compatible upper limit.

[0044] The first SCW treatment unit 110 treats the asphaltene feedstock received from asphaltene treatment line 111 with supercritical water to form a first pitch and a first aqueous fraction.

[0045] After the water is added to the first SCW treatment unit 110, a demetallizing agent is then added to the asphaltene feedstock and water mixture in the first SCW treatment unit 110. The demetallizing agent may be any agent that removes a metal atom from a compound. Examples of the demetallizing agent include, but are not limited to, phosphorous compounds, mineral acids, fatty acids, boron trifluoride diethyl etherate, sodium hypochlorite, peroxyacetic acid, or combinations thereof.

[0046] In one or more embodiments, a molar ratio of demetallizing agent to the molar amount of metal to be removed is above a 1:1 ratio. In one or more embodiments, the molar ratio of the demetallizing agent to the metal to be removed from the asphaltene feedstock is at least about a 1:1 ratio.

[0047] The first SCW treatment unit may be operated such that the temperature and pressure increase to a supercritical water range as described above. For example, operating the first SCW treatment unit at about the supercritical point of water may be performed. Such operations may include a residence time of the first SCW treatment unit for a time between 1 to 70 min. The residence time of crude feedstock in the first SCW treatment unit 110 may be in a range with a lower limit of any one of about 1 min (minutes), about 5 min, about 10 min, about 15 min, about 20 min, about 25 min, about 30 min, about 40 min, and about 45 min (minutes) and an upper limit of any one of about 15 min, about 20 min, about 25 min, about 30 min, about 40 min, about 50 min, about 60 min, about 65 min, and about 70 min. The residence time of the crude feedstock in the first SCW treatment unit 110 is in a range from 1 min to 70 min. In one or more particular embodiments, the residence time of the crude feedstock in the first SCW treatment unit 110 is in a range from 10 min to 60 min.

[0048] The liquid hourly space velocity (LHSV) in the first SCW treatment unit 110 may be in a range with a lower limit of any one of about 0.1 h^{-1}, about 0.15 h^{-1}, about 0.2 h^{-1}, about 1 h^{-1}, and about 2.5 $h^{-1}$and an upper limit of any one of about 3.5 h^{-1}, about 4 h^{-1}, about 4.5 h^{-1}, and about 5 h^{-1}, where any lower limit can be paired with any mathematically compatible upper limit.

[0049] In some embodiments, the first SCW treatment unit 110 has operation parameters similar to a hydrotreating unit, a hydrocracking unit, or a combination thereof. The first SCW treatment of the asphaltene feedstock may produce a first mixture stream and a first reaction gas stream. The first SCW treatment of an asphaltene feedstock may produce a mixture of a first organic fraction (or a "first pitch") and a first aqueous fraction.

[0050] In one or more embodiments, the first SCW treatment unit 110 includes a gaseous outlet line 132 that may be in fluid communication with a gaseous collection unit 130. The first reaction gas stream may be released via gaseous outlet line 132 and may be passed to a gaseous collection unit 130. The first reaction gas stream may include low molecular weight hydrocarbons and/or volatile organic compounds of the asphaltene feedstock, volatile reaction products from the first SCW treatment of the asphaltene feedstock, or both.

[0051] The gases collected in the gaseous collection unit 130 may be discarded. In one or more embodiments, the gases collected in the gaseous collection unit 130 are directed away from the asphaltene upgrade system 100. The gases directed away from the asphaltene upgrade system 100 may be used in other refining processes. For example, the low molecular weight hydrocarbons and/or volatile organic compounds from the first reaction gas stream may be collected for any purpose, such as refining, that may require light gaseous hydrocarbons and/or volatile organic compounds as feedstock.

[0052] After the SCW treatment including demetallization, the mixture of the first pitch and the aqueous fraction may be passed to the first centrifugation unit 112. The first centrifugation unit 112 may be any unit that separates a mixture of components based on centrifugal force.

[0053] The centrifugation unit is operated to separate the aqueous fraction from the first pitch. The first pitch may include a lower concentration of metals as compared to the asphaltene feedstock. The separated first aqueous fraction is then removed from the first centrifugation unit. The first centrifugation unit 112 includes an aqueous fraction outlet line 122 in fluid communication with an aqueous fraction collection unit 140. The first aqueous fraction may be removed via an aqueous fraction outlet line 122, and the first aqueous fraction may be passed through the aqueous fraction outlet line 122 to an aqueous fraction collection unit 140. The first pitch is then passed to the second treatment stage 104 on the asphaltene treatment line 111.

[0054] In one or more embodiments, an anisotropic ratio of the first pitch is in a range with a lower limit of one of about 0:1, about 0.1:0.9, about 0.15:0.85, about 0.25:0.75, about 0.35:0.65, about 0.5:0.5, about 0.65:0.35, about 0.75:0.25, and about 0.85:0.15 with an upper limit of one of about 0.1:1, about 0.15:0.85, about 0.25:0.75, about 0.35:0.65, about 0.5:0.5, about 0.65:0.35, about 0.75:0.25, and about 0.85:0.15, about 0.90:0.1, about 0.95:0.05, about 0.99:0.01, and about 1:0, where any lower limit can be paired with any mathematically compatible upper limit.

[0055] The anisotropic ratio of the first pitch can be measured using one or more analytical techniques including, but not limited to, optical microscopy (e.g., with polarized light), X-ray diffraction (XRD), nuclear magnetic resonance (NMR), small angle X-ray scattering (SAXS), among others.

[0056] The second treatment stage (or the “desulfurization unit”) 104 includes a second SCW treatment unit 114 and a second centrifugation unit 116. The first pitch may be passed to the second SCW treatment the second SCW treatment unit 114, which treats the first pitch with supercritical water. In such embodiments, water may be injected to the first pitch within the second SCW treatment unit. Water may be injected to such that the first pitch in a mass ratio with water in a range from about 1:1 to 1:100 first pitch to water. In one or more particular embodiments, the mass ratio may have a lower limit of any one of 1:1 first pitch to water, 1:2 first pitch to water, 1:5 first pitch to water, 1:10 first pitch to water, 1:25 first pitch to water, and 1:50 first pitch to water and an upper limit of any one of 1:25 first pitch to water, 1:40 first pitch to water, 1:50 first pitch to water, 1:75 first pitch to water, and 1:100 first pitch to water, where any lower limit may be combined with any mathematically compatible upper limit.

[0057] In one or more embodiments, the second SCW treatment unit including the first pitch and water operates at a supercritical water range of parameters, such as temperature and pressure as described above. For example, operating the second SCW treatment unit operating the unit at about the supercritical point of water for a designated period of time. Such operations may include a residence time of the second SCW treatment unit for a time between 1 to 70 min. The residence time of the first pitch in the second SCW treatment unit 114 may be in a range with a lower limit of any one of about 1 min (minutes), about 5 min, about 10 min, about 15 min, about 20 min, about 25 min, about 30 min, about 40 min, and about 45 min (minutes) and an upper limit of any one of about 15 min, about 20 min, about 25 min, about 30 min, about 40 min, about 50 min, about 60 min, about 65 min, and about 70 min. The residence time of the first pitch in the second SCW treatment unit 114 is in a range from 1 min to 70 min. In one or more particular embodiments, the residence time of the first pitch in the second SCW treatment unit 114 is in a range from 10 min to 60 min.

[0058] The liquid hourly space velocity (LHSV) in the second SCW treatment unit 114 may be in a range with a lower limit of any one of about 0.1 h^{-1}, about 0.15 h^{-1}, about 0.2 h^{-1}, about 1 h^{-1}, and about 2.5 $h^{-1}$and an upper limit of any one of about 3.5 h^{-1}, about 4 h^{-1}, about 4.5 h^{-1}, and about 5 h^{-1}, where any lower limit can be paired with any mathematically compatible upper limit.

[0059] In some embodiments, the second SCW treatment unit 114 has operation parameters similar to a hydrotreating unit, a hydrocracking unit, or a combination thereof. the second SCW treatment of the first pitch may produce a second treatment mixture and a second reaction gas stream.

[0060] The second reaction gas stream may include gaseous sulfur-containing productions, such as hydrogen sulfide, volatile organic compounds produced from the second SCW treatment, low molecular weight hydrocarbons, or combinations thereof. The second SCW treatment unit 114 has a gaseous outlet line 134 configured to release gaseous products, such as hydrogen sulfide, that may be generated during the second

SCW treatment. The second reaction gas stream may be passed through the gaseous outlet line 134 may be in fluid communication with the gaseous collection unit 130.

[0061] In one or more particular embodiments, the desulfurization of the first pitch is performed in the presence of supercritical water without additives. As described above, hydrogen donation from the supercritical water to sulfur containing compounds promote formation of gaseous sulfur containing compounds, such as hydrogen sulfide, and volatile sulfur containing compounds. The second SCW treatment includes removal of sulfur-containing compounds from the first pitch to form a second mixture that includes a second pitch and a second aqueous fraction.

[0062] The second mixture is passed (or “introduced”) to a centrifugation unit 116 of the second SCW treatment stage (or “the second centrifugation unit”). The second centrifugation unit 116 may be a centrifugation unit as described above in which the second pitch and the second aqueous fraction are separated. The second centrifugation unit 116 has an aqueous fraction outlet line 124 that is in fluid communication with the aqueous fraction collection unit 140. In one or more embodiments, the second aqueous fraction is passed through the aqueous fraction outlet line 124 to the aqueous fraction collection unit 140.

[0063] The second pitch may include a lower sulfur concentration as compared to the crude asphaltene feedstock and the first pitch. In one or more embodiments, an anisotropic ratio of the second pitch is in a range with a lower limit of one of about 0:1, about 0.1:0.9, about 0.15:0.85, about 0.25:0.75, about 0.35:0.65, about 0.5:0.5, about 0.65:0.35, about 0.75:0.25, and about 0.85:0.15 with an upper limit of one of about 0.1:1, about 0.15:0.85, about 0.25:0.75, about 0.35:0.65, about 0.5:0.5, about 0.65:0.35, about 0.75:0.25, and about 0.85:0.15, about 0.90:0.1, about 0.95:0.05, about 0.99:0.01, and about 1:0, where any lower limit can be paired with any mathematically compatible upper limit.

[0064] The anisotropic ratio of the second pitch can be measured using one or more analytical techniques including, but not limited to, optical microscopy (e.g., with polarized light), X-ray diffraction (XRD), nuclear magnetic resonance (NMR), small angle X-ray scattering (SAXS), among others.

[0065] The second pitch may be passed to the third treatment stage 106 (or the "polycondensation unit"), which includes a third SCW treatment unit 118 and a third centrifugation unit 120 in fluid communication with a mesophase pitch outlet line 128.

[0066] The third SCW treatment unit 118 may upgrade the second pitch to a third mixture of a mesophase pitch and an aqueous fraction with supercritical water. For example, water may then be injected to the second pitch in the third SCW treatment unit. Water may be injected to such that the second pitch in a mass ratio with water in a range from about 1:1 to 1:100 of second pitch to water. In one or more particular embodiments, the mass ratio may have a lower limit of any one of 1:1 second pitch to water, 1:2 second pitch to water, 1:5 second pitch to water, 1:10 second pitch to water, 1:25 second pitch to water, and 1:50 second pitch to water and an upper limit of any one of 1:25 second pitch to water, 1:40 second pitch to water, 1:50 second pitch to water, 1:75 second pitch to water, and 1:100 second pitch to water, where any lower limit may be combined with any mathematically compatible upper limit.

[0067] Operating the third SCW treatment unit 118 includes operating at about the supercritical point of water. Such operations may include a residence time of the third SCW treatment unit 118 for a time between 60 minutes to several days. The residence time of the second pitch in the third SCW treatment unit 118 may be a time in a range with a lower limit of any one of about 60 min (minutes), about 2 hours, about 5 hours, about 12 hours, about 24 hours, about 2 days, and about 3 days and an upper limit of any one of about 24 hours, about 2 days, about 3 days, about 4 days, about 5 days, about 6 days, about 1 week, and about 2 weeks. The residence time of the second pitch in the third SCW treatment unit 118 is in a range from 60 min to 2 weeks. In one or more particular embodiments, the residence time of the second pitch in the third SCW treatment unit 118 is in a range from 5 hours to 5 days.

[0068] The transformation time of the isotropic nature of the second pitch to an anisotropic mesophase may take several hours up to several days. In such embodiments, the transformation time can depend on the heating rate, composition of the second pitch, the maximum temperature selected for the treatment process, or any combination thereof. The longer residence time of the second pitch in the third SCW treatment unit 118 as compared to the residence time of the crude feedstock in the first SCW treatment unit 110 and the first pitch in the second SCW treatment unit 114 is a result of the complex molecular reorganization to upgrade the second pitch. Transforming the isotropic nature of the second pitch includes initializing mesophase domains, coalescing the mesophase domains, merging of these viscous liquid crystalline domains inducing some sort of diffusion limitations. The coalescence of the mesophase domains is a physical step that requires the movement of the mesophase domains.

[0069] The liquid hourly space velocity (LHSV) in the third SCW treatment unit 118 may be in a range from 5 h^{-1} to 65 h^{-1}. The liquid hourly space velocity (LHSV) in the third SCW treatment unit 118 may be in a range with a lower limit of any one of about 5 h^{-1}, about 7.5 h^{-1}, about 10 h^{-1}, about 12 h^{-1}, and about 15 $h^{-1}$and an upper limit of any one of about 35 h^{-1}, about 40 h^{-1}, about 45 h^{-1}, about 50 h^{-1}, about 60 h^{-1}, and about 65 h^{-1}, where any lower limit can be paired with any mathematically compatible upper limit.

[0070] The third SCW treatment of the second pitch forms a mesophase pitch and a third reaction gas stream. The third SCW treatment includes upgrading the second pitch to the mesophase pitch. The second pitch upgrade to the mesophase pitch includes promoting conversion of an isotropic nature of the second pitch to an anisotropic mesophase pitch.

[0071] In some embodiments, the mesophase pitch is isotropic. In one or more embodiments, an anisotropic ratio of the mesophase pitch is in a range with a lower limit of one of about 0.50:0.50, about 0.55:0.45, about 0.60:0.40, about 0.65:0.35, about 0.70:0.30, about 0.75:0.25, about 0.77:0.23, about 0.79:0.21, about 0.80:0.20, about 0.90:0.1, about 0.92:0.08, about 0.95:0.05, and about 0.98:0.02, with an upper limit of one of about 0.80:0.20, about 0.82:0.18, about 0.85:0.15, about 0.90:0.1, about 0.92:0.08, about 0.95:0.05, and about 0.98:0.02, about 0.99:0.01, and about 1:0, where any lower limit may be combined with any mathematically compatible upper limit.

[0072] In one or more particular embodiments, the third SCW treatment includes promoting a polycondensation reaction. The third SCW treatment may be as described in U.S. Patent Application No. 16/877,820, which is incorporated by reference herein in its entirety. The supercritical water treatment of the polycondensation unit may promote the abstraction of hydrogen molecules from the second pitch and promote the condensation of aromatic molecules to polyaromatic molecules.

[0073] Volatile and/or gaseous compounds may be produced in the third SCW treatment that may be removed and/or collected. The third SCW treatment unit 118 may include a gaseous outlet line 136 that may be in fluid communication with the gaseous collection unit 130. Volatile and/or gaseous compounds may be passed through outlet line 136 and collected in the gaseous collection unit 130.

[0074] The third mixture of the mesophase pitch and the third aqueous fraction may be separated by the third centrifugation unit 120 as described previously. An aqueous outlet line 126 of the third centrifugation unit 120 may be in fluid communication with aqueous fraction collection unit 140. The third separated aqueous fraction may be removed from the mesophase pitch via aqueous outlet line 126 and may be collected by the aqueous fraction collection unit 140. The mesophase pitch may be collected via the mesophase pitch outlet line 128.

[0075] In one or more particular embodiments, the desulfurization and the polycondensation reaction may be performed in the same treatment unit. In such embodiments, an asphaltene upgrade system may include two treatment stages. The first treatment stage may be as described above to promote demetallization of an asphaltene feedstock. The second treatment stage may be operated at supercritical water conditions to desulfurize and provide polycondensation reaction conditions in the same stage.

[0076] The asphaltene upgrade system 100 of one or more embodiments may optionally include a mesophase pitch enrichment system 150 as presented in FIG. 1C downstream of the third treatment stage 106. In such embodiments, the mesophase pitch enrichment system 150 may be in fluid communication with the mesophase pitch outlet line 128 via a three-way valve 144. The three-way valve 144 can direct an output of mesophase pitch to an enrichment system inlet line 158 or to an upgraded organic outlet line 138. The upgraded organic line 138 transfers the mesophase pitch from the third treatment stage 106, the enriched mesophase pitch from the mesophase pitch enrichment system 150, or combinations thereof to an advanced material processing system, such as a series of carbon fiber production units described below.

[0077] In one or more embodiments, the mesophase pitch is introduced to the mesophase pitch enrichment system 150 based on the anisotropic ratio of the mesophase pitch from the third treatment phase. The mesophase pitch introduced to the mesophase pitch enrichment system 150 may be further upgraded to increase the amount of anisotropy in the sample. The mesophase pitch enrichment system 150 sequentially includes a supercritical carbon dioxide unit 152, an inert gas bubbling unit 154, and a fourth centrifugation unit 156. The mesophase pitch enrichment system 150 may upgrade the mesophase pitch to an enriched mesophase pitch.

[0078] The mesophase pitch may be introduced to the supercritical carbon dioxide unit 152, in which the mesophase pitch may be treated under supercritical carbon dioxide conditions. For example, operating the supercritical carbon dioxide unit 152 includes operating the unit at the supercritical point of carbon dioxide as described above. Such operations may include a residence time of the supercritical carbon dioxide unit 152 for a time between 60 minutes to several days. The residence time of the mesophase pitch in the supercritical carbon dioxide unit 152 may be a time in a range with a lower limit of any one of about 60 min (minutes), about 2 hours, about 5 hours, about 12 hours, about 24 hours, about 2 days, and about 3 days and an upper limit of any one of about 24 hours, about 2 days, about 3 days, about 4 days, about 5 days, about 6 days, about 1 week, and about 2 weeks. The residence time of the mesophase pitch in the supercritical carbon dioxide unit 152 may be in a range from 60 min to 2 weeks. In one or more particular embodiments, the residence time of the mesophase pitch in the supercritical carbon dioxide unit 152 is in a range from 5 hours to 5 days.

[0079] The transformation time of the isotropic nature of the mesophase pitch to an enriched anisotropic mesophase may take several hours up to several days. In such embodiments, the transformation time can depend on the heating rate, composition of the second pitch, the maximum temperature selected for the treatment process, or any combination thereof. The longer residence time of the mesophase pitch in the supercritical carbon dioxide unit 152 as compared to the residence time of the crude feedstock in the first SCW treatment unit 110 and the first pitch in the second SCW treatment unit 114 is a result of the complex molecular reorganization to enrich the anisotropic nature of the mesophase pitch. Transforming the isotropic nature of the mesophase pitch includes initializing mesophase domains, coalescing the mesophase domains, merging of these viscous liquid crystalline domains, and inducing some sort of diffusion limitations. The coalescence of the mesophase domains is a physical step that requires the movement of the mesophase domains to enrich the mesophase pitch.

[0080] The liquid hourly space velocity (LHSV) in the third SCW treatment unit 118 may be in a range from 5 h^{-1} to 65 h^{-1}. The liquid hourly space velocity (LHSV) in the third SCW treatment unit 118 may be in a range with a lower limit of any one of about 5 h^{-1}, about 7.5 h^{-1}, about 10 h^{-1}, about 12 h^{-1}, and about 15 $h^{-1}$and an upper limit of any one of about 35 h^{-1}, about 40 h^{-1}, about 45 h^{-1}, about 50 h^{-1}, about 60 h^{-1}, and about 65 h^{-1}, where any lower limit can be paired with any mathematically compatible upper limit.

[0081] The supercritical carbon dioxide treatment of the mesophase pitch may form a fourth mixture, which includes an enriched mesophase pitch and a second aqueous fraction, and a fourth reaction gas stream.

[0082] The fourth mixture and the fourth reaction gas stream may be passed through the inert gas bubbling unit 154. The inert gas bubbling unit 154 may provide an inert gas stream to remove volatile and/or gaseous compounds from the fourth mixture. The fourth reaction gas stream, volatile compounds, and the inert gas may be removed from the fourth mixture via gaseous outlet line 160.

[0083] In one or more embodiments, the anisotropic ratio of the enriched mesophase pitch may be in a range with a lower limit of one of about 0.50:0.50, about 0.55:0.45, about 0.60:0.40, about 0.65:0.35, about 0.70:0.30, about 0.75:0.25, about 0.77:0.23, about 0.79:0.21, about 0.80:0.20, about 0.90:0.1, about 0.92:0.08, about 0.95:0.05, and about 0.98:0.02, with an upper limit of one of about 0.80:0.20, about 0.82:0.18, about 0.85:0.15, about 0.90:0.1, about 0.92:0.08, about 0.95:0.05, and about 0.98:0.02, about 0.99:0.01, and about 1:0, where any lower limit may be combined with any mathematically compatible upper limit.

[0084] In one or more embodiments, the isotropic content of the mesophase pitch is completely converted to the anisotropic phase via treatment with the supercritical carbon dioxide unit, the inert gas bubbling unit, or both.

[0085] In one or more particular embodiments, the fourth mixture may contain a residual aqueous fraction. The fourth mixture may be passed to a fourth centrifugation unit 156 of the mesophase pitch enrichment system 150. The fourth centrifugation unit 156 may include an aqueous outlet line 142. In some embodiments the aqueous outlet line 142 may be in fluid communication with the aqueous fraction collection unit 140. The enriched mesophase pitch may be produced via an enrichment outlet line 148 from the mesophase pitch enrichment system 150. The enrichment outlet line 148 is in fluid communication with the upgraded organic outlet line 138.

[0086] The asphaltene upgrade system 100 of one or more embodiments may include a series of carbon fiber production units 200, as shown in FIG. 2. The series of carbon fiber production units is in fluid communication with the upgraded organic outlet line 138 of the asphaltene upgrade system of one or more embodiments. The series of carbon fiber production units 200 includes a melt-spinning unit 202, an oxidative stabilization unit 204, a carbonization unit 206, a surface treatment unit 208, a sizing chamber 210, and a winding unit 212. The melt-spinning unit 202 may include a screw-extruder with a gear pump, a multi-filament spinneret, and a wind-up device. The oxidative stabilization unit 204 includes an oven and atmospheric air. The series of carbon fiber production units 200 produce carbon fibers that exit the system via a carbon fiber output line 218.

[0087] In one or more particular embodiments, the SCW treatment units (110, 114, and 118) and the supercritical carbon dioxide unit 152 are continuous supercritical reactors. The SCW treatment units (110, 114, and 118) of the asphaltene upgrade system are configured to operate at the supercritical point of water as described above, such as an autoclave vessel reactor, a pressure-vessel type reactor, or a pressure tube type reactor. The supercritical carbon dioxide unit 152 of the mesophase pitch enrichment system 150 is configured to operate at the supercritical point of carbon dioxide as described above.

[0088] An example schematic of a SCW treatment unit (e.g., 110, 114, and 118) or a supercritical carbon dioxide unit 152 may be a supercritical reactor unit 300 as shown in FIG. 3A or the supercritical reactor unit 308 as shown in FIG. 3B.

[0089] The supercritical reactor unit 300 may include an organic inlet 302. The organic inlet 302 may be in fluid communication on the asphaltene treatment line 111 of the first treatment stage 102, the second treatment stage 104, the third treatment stage 106, or combinations thereof. The organic inlet 302 may pass the asphaltene feedstock, a pitch generated in one of the stages above, the mesophase pitch, or combinations thereof to the next sequential treatment stage. The supercritical reactor unit 300 may include a pump on the organic inlet 302. Optionally, a heat exchanger 306 may be downstream of the pump 304 and upstream of a supercritical reactor unit 308. A second optional heat exchanger 310 may be downstream of the supercritical reactor unit 308. A backpressure regulator 312 may be downstream of the second optional heat exchanger and upstream of a vapor-liquid separator 314. Volatile and/or gaseous compounds are passed to a gaseous outlet line 316 that is in fluid communication with the gaseous collection unit 130. The gaseous outlet lines 132, 134, 136 may independently be represented by the gaseous outlet line 316. Aqueous mixtures of upgraded asphaltenes, such as the first mixture, the second mixture, the third mixture, or the fourth mixture, may be passed from the reactor unit via an organic outlet line 318 of the supercritical reactor unit. In such embodiments, the reaction temperature of the SCW treatment units and/or the supercritical carbon dioxide unit may be measured at the outlet 360 of supercritical reactor unit 300.

[0090] In one or more embodiments, an internal pressure of the supercritical reactor unit is controlled. The internal pressure of the supercritical reactor unit may be controlled with one or more autoclave pressure relief valves, which may be similar to safety valves. The one or more autoclave pressure relief valves may control the internal pressure of a supercritical reactor unit such that excess internal pressure is released via the one or more valves.

[0091] A temperature of the supercritical reactor unit may be controlled. As one of ordinary skill may appreciate, the temperature of the supercritical reactor units may be controlled via electronic communication with internal heating elements and/or with proportional-integral-derivative controller.

[0092] In some embodiments, the first SCW treatment unit 110 may be a supercritical reactor unit 350 as shown in FIG. 3B. The supercritical reactor unit 350 may be as described above and may also include a demetallizing agent injection port 320. The demetallizing agent injection port 320 may be in fluid communication with a demetallizing agent source 330 via injection line 322. The demetallizing agent injection port may include a high-pressure metering and dosing pump (not shown).

METHOD OF UPGRADING ASHPALTENES TO MESOPHASE PITCH

[0093] One or more embodiments relate to a method for mesophase pitch production from an asphaltene feedstock. In such embodiments, the method 400 (FIG. 4) may include a method to upgrade an asphaltene feedstock for mesophase pitch production. In one or more particular embodiments, the method of upgrading asphaltenes to a mesophase pitch is a continuous process.

[0094] In one or more embodiments, the method includes introducing the asphaltene feedstock to a first treatment stage (step 402), introducing the asphaltene feedstock to a first SCW treatment unit of a demetallizing unit, and demetallizing the asphaltene feedstock (step 404) in the first SCW treatment unit. The demetallization step includes decreasing the amount of metal containing compounds, increasing the amount of anisotropic characteristics (or “phase”) of the asphaltene feedstock, or both.

[0095] In one or more embodiments, decreasing the amount of metal containing compounds includes reacting metals of the asphaltenes with demetallizing agents as described above to produce decomplexed metals. In such embodiments, the method includes solvating the decomplexed metals such that a first pitch is produced and has a decreased metal content compared to the asphaltene feedstock. In such embodiments, demetallizing the asphaltene feedstock produces a first mixture and a first reaction gas stream, wherein the first mixture comprises a first aqueous fraction and a first pitch. The first mixture is then passed (or “introduced”) to the first centrifugation unit to separate the first aqueous fraction from the first pitch in step 406.

[0096] In step 408, the first pitch is introduced to the second treatment stage and desulfurizing the first pitch (step 410) in the second SCW treatment unit, producing the second mixture as described above. The desulfurization step includes removing sulfur containing compounds from the first pitch. The removed sulfur compounds may be as described above. The second mixture formed in the desulfurizing step includes a second pitch and a second aqueous fraction. The second mixture may be introduced to the second centrifugation unit. The second aqueous fraction may be separated from the second pitch in the second centrifugation unit in step 412.

[0097] In step 414, the second pitch is introduced to the third treatment stage. The introducing the second pitch to the third treatment stage includes passing the second pitch to the third SCW treatment unit. Then, a polycondensation reaction may be performed (step 416) with the second pitch in the third SCW treatment unit. Performing the polycondensation reaction with the second treatment includes increasing the isotropic to anisotropic conversion of the second pitch, thereby forming a mesophase pitch, a third aqueous fraction and a third reaction gas stream. In one or more embodiments, the third reaction gas stream may be removed as described above. The mesophase pitch may be introduced to the third centrifugation unit, where it may be separated from the third aqueous fraction in step 418, thereby producing a mesophase pitch.

[0098] The asphaltene upgrade system of one or more embodiments may remove sulfur and/or metallic compounds to significantly decrease the sulfur and/or metallic compounds content of an intermediary pitch relative to a crude asphaltene feedstock. The asphaltene upgrade system may completely remove sulfur and/or metallic compounds from a crude feedstock.

[0099] In one or more particular embodiments, the generated mesophase pitch is introduced to a mesophase enrichment system as described above. In such embodiments, the mesophase pitch introduced to the mesophase enrichment system increases the anisotropic content of the mesophase pitch to provide 100% conversion to the anisotropic phase, reduces the low molecular weight compounds of the mesophase pitch, removes volatile and/or gaseous components, or combinations thereof. The treatments of the mesophase enrichment system may provide a fourth mixture and a fourth reaction gas stream. The fourth reaction gas stream may be separated from the fourth mixture and collected via a gaseous outlet line as previously described. The fourth mixture includes an enriched mesophase pitch and a fourth aqueous fraction. The fourth centrifuge unit separates the fourth aqueous fraction from the enriched mesophase pitch.

[00100] In one or more embodiments, the mesophase pitch, the enriched mesophase pitch, or combinations thereof may be directed to a series of carbon fiber production units to produce carbon fibers. The method to produce carbon fibers of one or more particular embodiments includes the method 500 as shown in FIG. 5. The method to produce carbon fibers includes steps as described above (i.e., steps 502, 504, 506 508, 510, 512, 514, 516, and 518) with an additional step 520 of introducing the mesophase pitch, the enriched mesophase pitch, or combinations thereof to a series of carbon fiber production units. The softening point of the mesophase pitch, the softening point of the enriched mesophase pitch, or combinations thereof is balanced to promote stable spinning from the melt-spinning unit to produce melt-spun fibers as mentioned above. The melt-spun fibers may then be introduced to an oxidative stabilization unit, a carbonization unit, a surface treatment unit, a sizing chamber, and a winding unit to produce carbon fibers.

[00101] In some embodiments, one or more analytical methods can be used to analyze the metal and sulfur content before and after each stage of the asphaltene upgrade system 100. The one or more analytical methods may include, but are not limited to, Fourier-transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), optical microscopy (e.g., with polarized light), X-ray diffraction (XRD), nuclear magnetic resonance (NMR), small angle X-ray scattering (SAXS), inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS), X-ray fluorescence (XRF), flame photometry, among others. A concentration of sulfur in a sample may be detected using FTIR spectroscopy. Additionally, metals of the sample may include heavy atoms, which can be detected by X-ray photoelectron spectroscopy (XPS), inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS), X-ray fluorescence (XRF), flame photometry, or combinations thereof. As one of ordinary skill may appreciate, the above analytical methods each include a concentration resolution limit. A combination of two or more analytical methods may have the capability of measuring resolution to a concentration on the parts per million (ppm) scale. In one or more embodiments, two or more analytical methods can be used to analyze the crude feedstock, the product of each processing step (e.g., the first pitch, the second pitch, the mesophase pitch, an enriched mesophase pitch), or combinations thereof.

[00102] Embodiments of the present disclosure may provide at least one of the following advantages. In one or more embodiments, asphaltene feedstock may be upgraded to a mesophase pitch, an enriched mesophase pitch, or combinations thereof. The system and methods of one or more embodiments may allow for an increased isotropic to anisotropic conversion of the mesophase pitch. In addition, the system and processes of one or more embodiments may remove trace metals, sulfur-containing compounds, volatile organic compounds, and combinations thereof from an asphaltene feedstock.

[00103] Although only a few example embodiments have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the example embodiments without materially departing from this invention. Accordingly, all such modifications are intended to be included within the scope of this disclosure as defined in the following claims.

CLAIMS

What is claimed:

1. A system for upgrading asphaltenes, the system comprising:
   an asphaltene treatment line;
   a series of asphaltene upgrade units, the series comprising:
      a demetallizing unit, wherein the demetallizing unit comprises a first supercritical water (SCW) treatment unit and a first centrifugation unit;
      a desulfurizing unit, wherein the desulfurizing unit comprises a second SCW treatment unit and a second centrifugation unit; and
      a polycondensation unit, wherein the polycondensation unit comprises a third SCW treatment unit and a third centrifugation unit;
   a series of carbon fiber production units;
   an aqueous collection unit; and
   a gaseous collection unit.

2. The system of claim 1, wherein the demetallizing unit comprises a demetallizing agent injection port.

3. The system of claim 1 or 2, wherein the series of asphaltene upgrade units further comprises a mesophase pitch enrichment unit downstream of the polycondensation unit and upstream of the series of carbon fiber production units.

4. The system of claim 3, wherein the mesophase pitch enrichment unit comprises a supercritical carbon dioxide treatment unit, an inert gas bubbling chamber, and a fourth centrifugation unit.

5. The system of claim 2 or 4, wherein the demetallizing agent is selected from the group consisting of mineral acids, fatty acids, boron trifluoride ether, sodium hypochlorite, peroxyacetic acid, phosphorous compounds, and combinations thereof.

6. The system of any one claims 1 to 5, wherein the series of carbon fiber production units comprises:

a mesophase pitch inlet line in fluid communication with the series of asphaltene upgrade units;

a melt-spinning unit;

an oxidative stabilization unit;

a carbonization unit;

a surface treatment unit;

a sizing chamber; and

a winding unit.

7. A method for mesophase pitch production from an asphaltene feedstock, the method comprising:

introducing the asphaltene feedstock to an asphaltene treatment line;

introducing the asphaltene feedstock to a first SCW treatment unit of a demetallizing unit;

demetallizing the asphaltene feedstock, thereby producing a first mixture and a first reaction gas stream, wherein the first mixture comprises a first aqueous fraction and a first pitch;

separating the first aqueous fraction from the first pitch;

introducing the first pitch to a second SCW treatment unit of a desulfurizing unit;

desulfurizing the first pitch, thereby forming a second mixture and a second reaction gas stream, wherein the second mixture comprises a second aqueous fraction and a second pitch;

separating the second aqueous fraction from the second pitch;

introducing the second pitch to a third SCW treatment unit of a polycondensation stage;

performing a polycondensation reaction in the third SCW treatment unit, thereby forming a third reaction gas stream and a third mixture, wherein the third mixture comprises a third aqueous fraction and the mesophase pitch; and

separating the third aqueous fraction from the mesophase pitch, thereby producing the mesophase pitch.

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8. The method of claim 7, wherein the asphaltene feedstock, the first pitch, and the second pitch independently comprises an anisotropic ratio in a range from about 0:1 to about 1:0.

9. The method of claim 7 or 8, wherein the mesophase pitch comprises an anisotropic ratio from about 0.75:0.25 to about 1:0.

10. The method of any one of claims 7 to 9, further comprising introducing a decomplexing agent into the first SCW treatment unit prior to demetallizing the asphaltene feedstock.

11. The method according to claim 10, wherein the decomplexing agent is selected from the group consisting of mineral acids, fatty acids, boron trifluoride ether, sodium hypochlorite, peroxyacetic acid, phosphorous compounds, and combinations thereof.

12. The method of any one of claims 7 to 11, further comprising, prior to producing the mesophase pitch:

introducing the mesophase pitch to a mesophase enrichment unit downstream of the polycondensation stage, wherein the mesophase enrichment unit comprises a supercritical carbon dioxide treatment unit, an inert gas bubbling unit, and a fourth centrifugation unit;

introducing the mesophase pitch to the supercritical carbon dioxide treatment unit of the mesophase enrichment unit;

operating the fourth treatment unit, thereby forming a fourth mixture and a fourth reaction gas stream, wherein the fourth mixture comprises an enriched mesophase pitch and a fourth aqueous fraction;

introducing the fourth mixture to the inert gas bubbling unit of the mesophase enrichment unit;

introducing an inert gas to the fourth treatment mixture;

removing the fourth gas stream from the enriched mesophase pitch and the fourth aqueous fraction;

introducing the enriched mesophase pitch and the fourth aqueous fraction to the fourth centrifugation unit; and

separating the fourth aqueous fraction from the enriched mesophase pitch, thereby producing the enriched mesophase pitch.

13. The method of claim 12, wherein the inert gas is nitrogen gas.

14. A method for manufacturing carbon fibers from asphaltene feedstock, the method comprising:

introducing the asphaltene feedstock to an asphaltene treatment line;

introducing the asphaltene feedstock to a first SCW treatment unit of a demetallizing unit;

demetallizing the asphaltene feedstock, thereby producing a first mixture and a first reaction gas stream, wherein the first mixture comprises a first aqueous fraction and a first pitch;

separating the first aqueous fraction from the first pitch;

introducing the first pitch to a second SCW treatment unit of a desulfurizing unit;

desulfurizing the first pitch, thereby forming a second mixture and a second reaction gas stream, wherein the second treatment mixture comprises a second aqueous fraction and a second pitch;

separating the second aqueous fraction from the second pitch;

introducing the second pitch to a third SCW treatment unit of a polycondensation stage;

performing a polycondensation reaction in the third SCW treatment unit, thereby forming a third reaction gas stream and a third mixture, wherein the third mixture comprises a third aqueous fraction and a mesophase pitch;

separating the third aqueous fraction from the mesophase pitch;

producing the mesophase pitch; and

introducing the mesophase pitch fraction to a series of carbon fiber production units, thereby producing carbon fibers.

15. The method according to claim 14, further comprising:

introducing the mesophase pitch to a mesophase enrichment unit downstream of the polycondensation stage, wherein the mesophase enrichment unit comprises a supercritical carbon dioxide treatment unit, an inert gas bubbling unit, and a fourth centrifugation unit;

introducing the mesophase pitch to the fourth treatment unit of the mesophase enrichment unit;

operating the fourth treatment unit, thereby forming a fourth mixture and a fourth reaction gas stream, wherein the fourth mixture comprises an enriched mesophase pitch and a fourth aqueous fraction;

introducing the fourth treatment mixture to the inert gas bubbling unit of the mesophase enrichment unit;

introducing an inert gas to the fourth treatment mixture;

removing the fourth gas stream from the enriched mesophase pitch and the fourth aqueous fraction;

introducing the enriched mesophase pitch and the fourth aqueous fraction to the fourth centrifugation unit;

separating the fourth aqueous fraction from the enriched mesophase pitch; and

producing the enriched mesophase pitch.

16. The method of claim 15, further comprising introducing a decomplexing agent into the first SCW treatment unit prior to demetallizing the asphaltene feedstock.

17. The method of claim 16, wherein the decomplexing agent is compound selected from the group consisting of mineral acids, fatty acids, boron trifluoride ether, sodium hypochlorite, peroxyacetic acid, phosphorous compounds, and combinations thereof.

18. The method of any one of claims 15 to 17, wherein the series of carbon fiber production units comprises:

a screw-extruder comprising a gear pump, a multi-filament spinneret, and a wind-up device;

an oxidative stabilization unit;

a carbonization unit;

a sizing unit; and

a winding unit.

19. The method any one of claims 15 to 18, wherein the enriched mesophase pitch has an anisotropic ratio from about 0.85:0.15 to about 1:0.

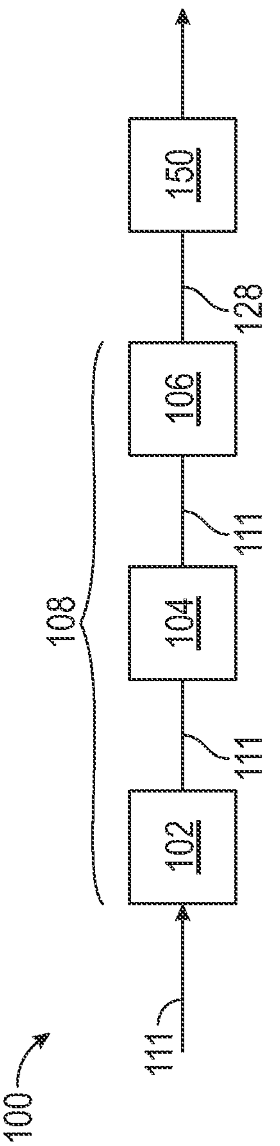
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FIG. 1A

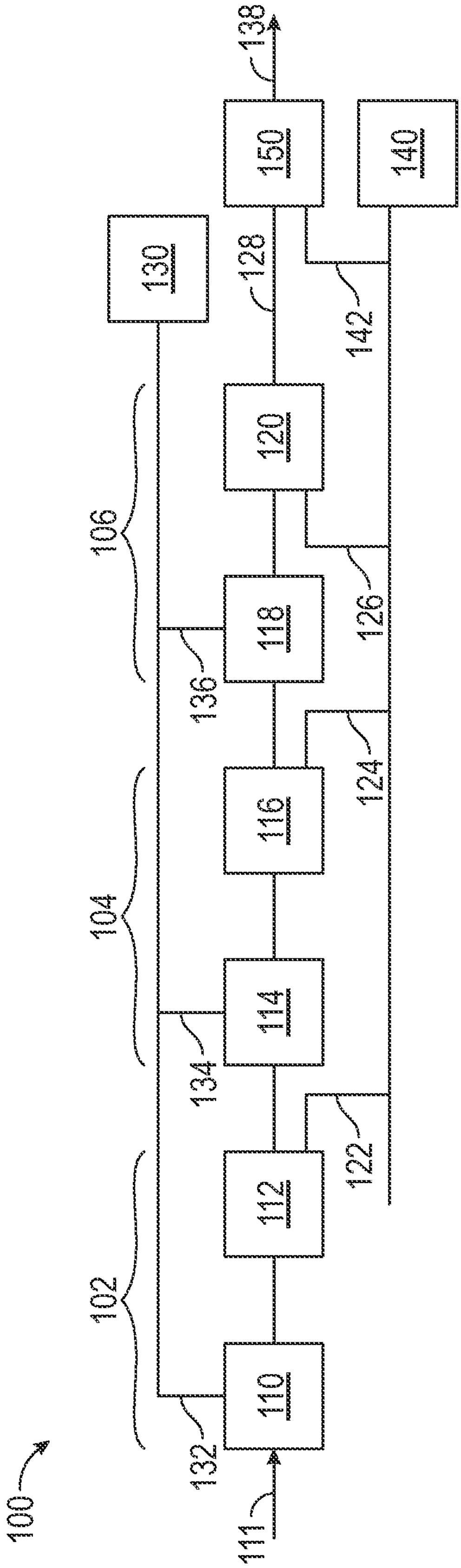
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FIG. 1B

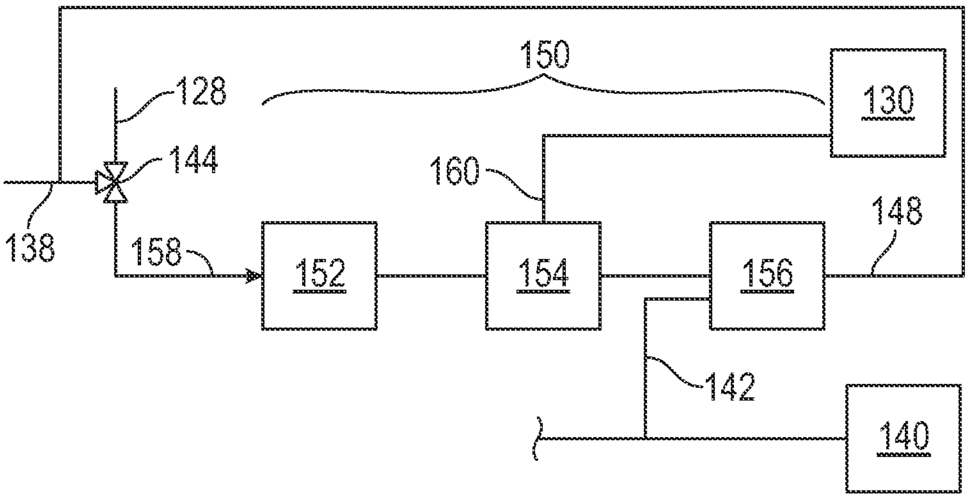
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FIG. 1C

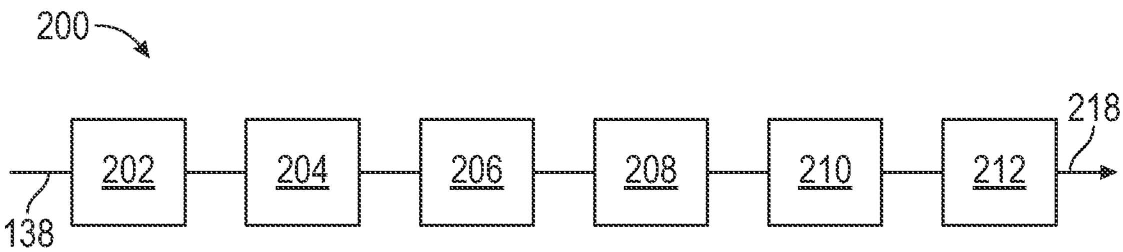
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FIG. 2

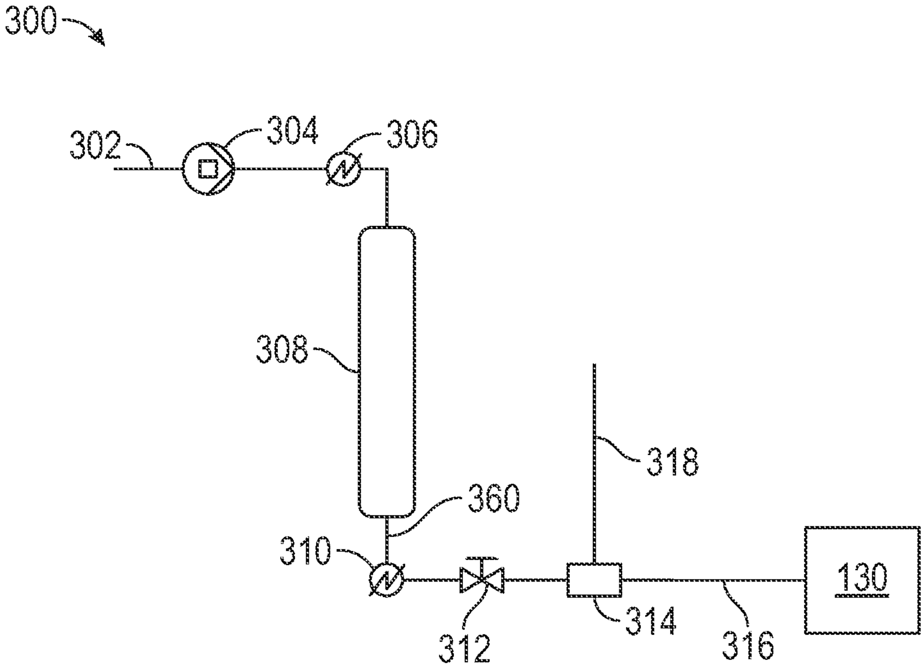
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FIG. 3A

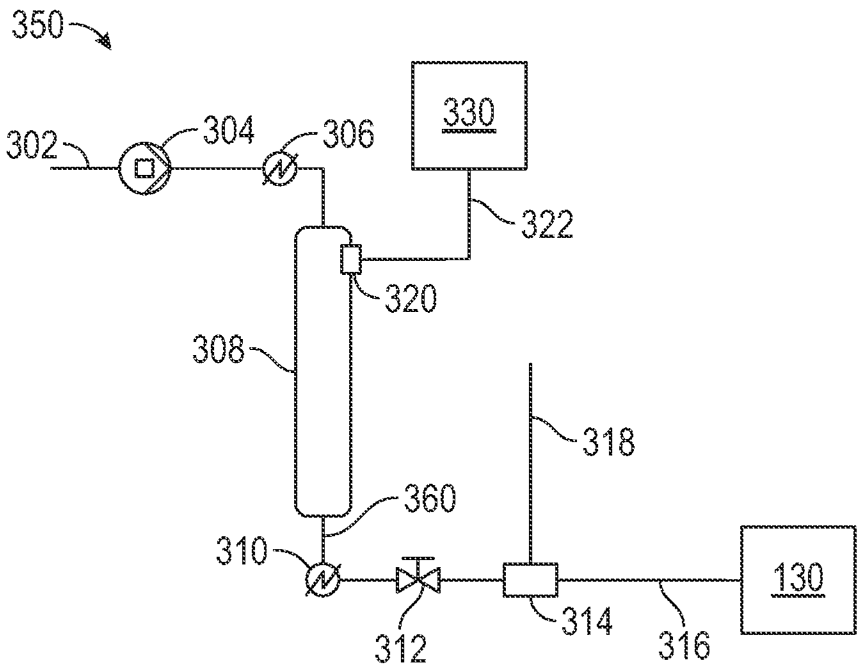
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FIG. 3B

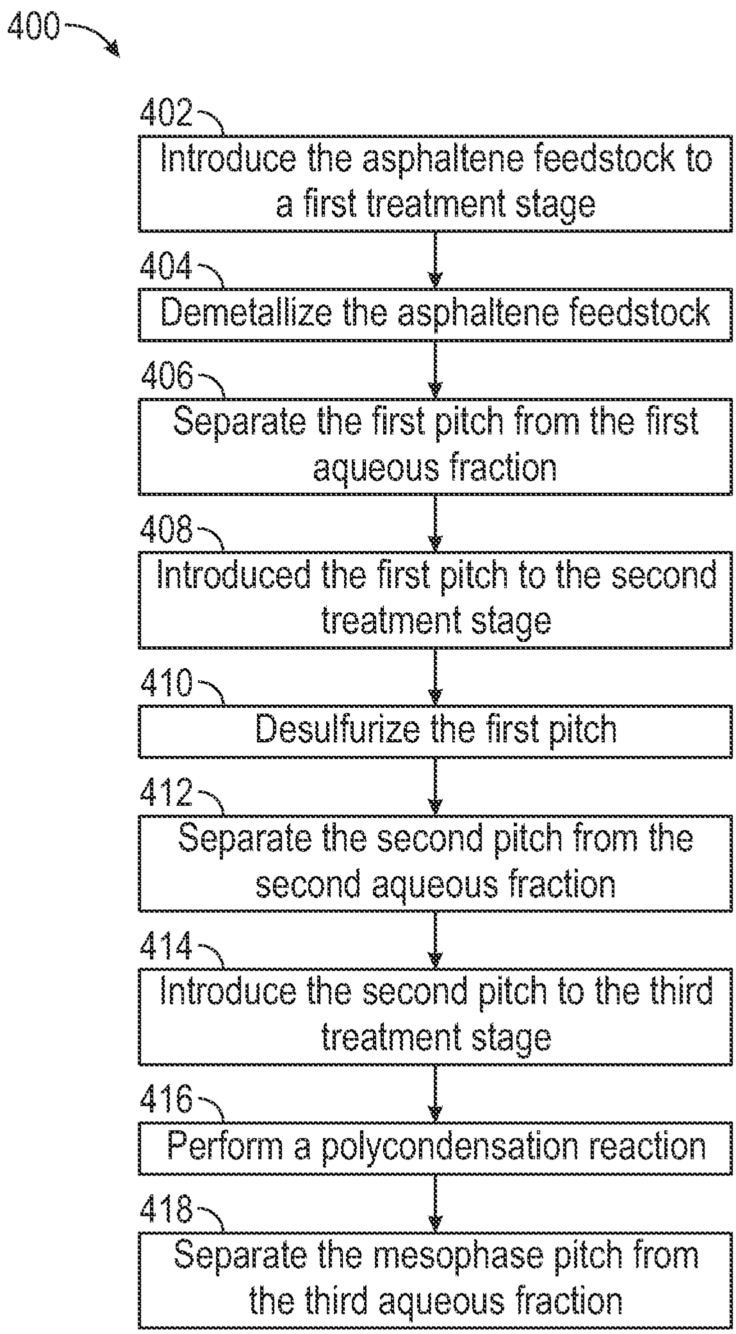
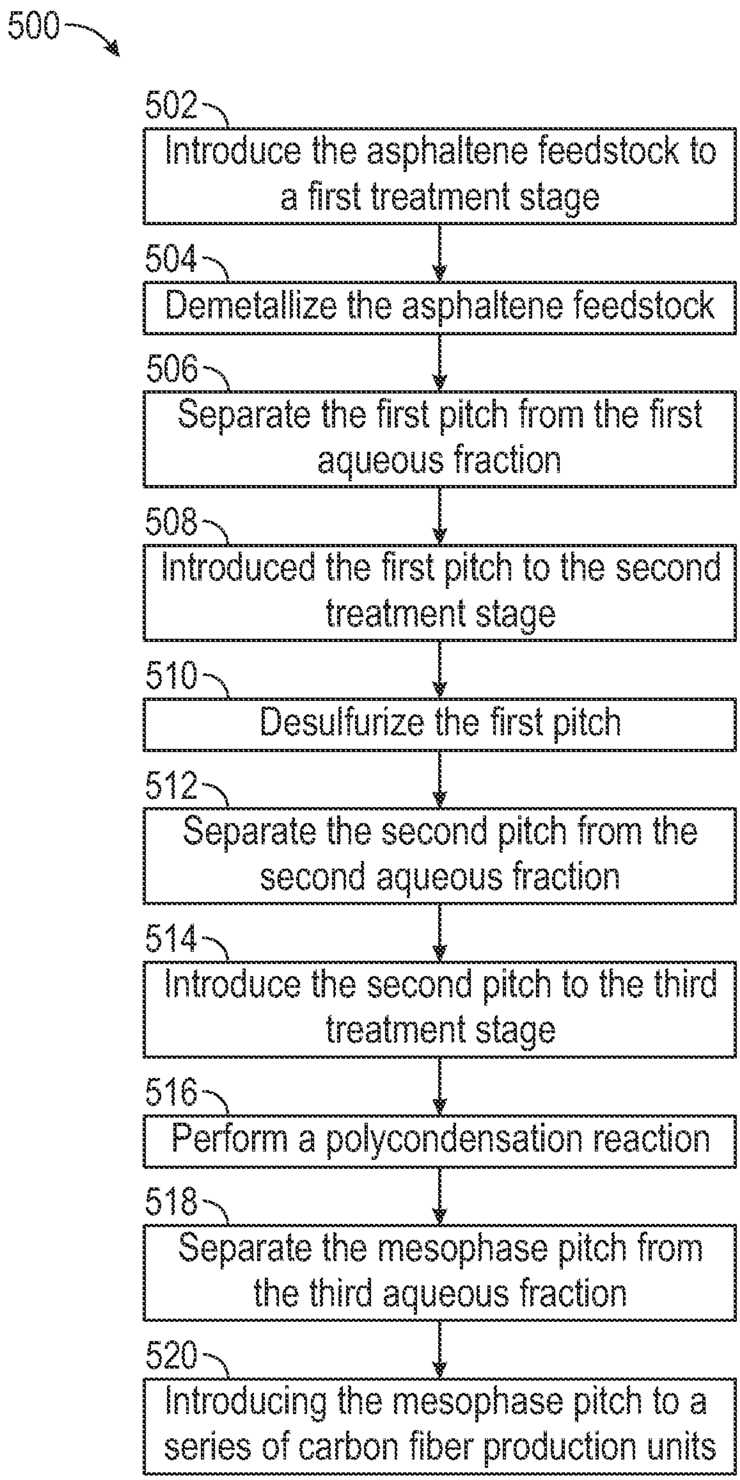

400
402
Introduce the asphaltene feedstock to a first treatment stage
404
Demetallize the asphaltene feedstock
406
Separate the first pitch from the first aqueous fraction
408
Introduced the first pitch to the second treatment stage
410
Desulfurize the first pitch
412
Separate the second pitch from the second aqueous fraction
414
Introduce the second pitch to the third treatment stage
416
Perform a polycondensation reaction
418
Separate the mesophase pitch from the third aqueous fraction

FIG. 4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502
Introduce the asphaltene feedstock to a first treatment stage
504
Demetallize the asphaltene feedstock
506
Separate the first pitch from the first aqueous fraction
508
Introduced the first pitch to the second treatment stage
510
Desulfurize the first pitch
512
Separate the second pitch from the second aqueous fraction
514
Introduce the second pitch to the third treatment stage
516
Perform a polycondensation reaction
518
Separate the mesophase pitch from the third aqueous fraction
520
Introducing the mesophase pitch to a series of carbon fiber production units

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/079396

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G31/08 C10C3/00 C10G53/02 D01F9/145
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G C10H D01F C10C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2021/363428 A1 (CHOI KI-HYOUK [SA] ET AL) 25 November 2021 (2021-11-25) paragraphs [0023], [0026], [0035], [0055], [0067]; figure 3 -----	1-19
A	CN 113 817 501 A (CNOOC TIANJIN CHEMICAL RES & DESIGN INST CO LTD ET AL.) 21 December 2021 (2021-12-21) claim 1 -----	1-19
A	US 2018/187093 A1 (CHOI KI-HYOUK [SA] ET AL) 5 July 2018 (2018-07-05) paragraphs [0015], [0016], [0018], [0034], [0035], [0047], [0088] -----	1-19

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 February 2024	23/02/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Chau, Thoi Dai

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2023/079396

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			SG 10201913319P	A	27-02-2020
			US 2018187093	A1	05-07-2018
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