

**MESOPHASE PITCH COMPOSITIONS FROM AROMATIC FEEDSTOCKS,
METHODS OF MAKING THE SAME, AND USES THEREOF**

CROSS REFERENCE TO RELATED APPLICATIONS

5 [0001] This application claims the benefit of and priority to US Provisional Application No. 63/167319 filed March 29, 2021, the disclosure of which is incorporated herein by reference.

[0002] This application is related to concurrently filed USSN 63/167,354, a provisional patent application entitled “Isotropic Pitch Compositions from Aromatic Feedstocks, Methods
10 of Making the same, and Uses Thereof”.

FIELD

[0003] The present disclosure relates to mesophase pitch compositions produced from synthetic isotropic pitch compositions from aromatic hydrocarbon feedstocks, methods of making the same, and uses thereof.

15 **BACKGROUND**

[0004] Carbon fibers market has grown significantly over the past decade, which can be attributed to the increasing demand from a wide range of industries such as automotive (*e.g.*, body parts such as deck lids, hoods, front end, bumpers, doors, chassis, suspension systems such as leaf springs, drive shafts), aerospace (such as aircraft and space systems), high
20 performance aquatic vessels (such as yachts and rowing shells), airplanes, sports equipment (*e.g.*, golf club, tennis racket, ski boards, snowboards, helmets, rowing or water skiing equipment), construction (non-structural and structural systems), military (*e.g.*, flying drones, armor, armored vehicles, military aircraft), wind energy industries, energy storage applications, fireproof materials, carbon-carbon composites, carbon fibers, and in many insulating and
25 sealing materials used in construction and road building (*e.g.*, concrete), turbine blades, light weight cylinders and pressure vessels, off-shore tethers and drilling risers, medical, for example. The non-limiting properties of the carbon fibers make such material suitable for high-performance applications: high bulk modulus and tensile modulus (depending on the morphology of the carbon fiber), high electrical and thermal conductivities, high specific
30 density, etc. However, the high cost of carbon fiber limits its applications and widespread use, in spite of the remarkable properties exhibited by such material. Hence, developing low-cost technologies to produce carbon fibers has been a major challenge for researchers and key manufacturers.

[0005] A reliable and low cost process of producing liquid crystalline, or mesophase pitches from heavy petroleum bottoms suitable for manufacturing carbon fibers has been a difficult challenge in the petrochemical industry, requiring harsh reaction condition such as high temperature and pressure, long residence time. In addition, unselective reaction tends to
5 create, in addition to pitch, a broad spectrum of undesirable products such as lights and coke.

[0006] Particularly, the stringent requirements on product quality and purity for carbon fiber remain difficult to achieve. To qualify for carbon fiber production, the mesophase pitch must exhibit very low sulfur and low solid fine contents, both of which are extremely challenging to remove from petroleum bottoms. Highly oriented carbon fibers with excellent
10 mechanical properties from pitch precursors has been a long-standing goal in the petrochemical industry. The ultrahigh tensile modulus of mesophase pitch-based carbon fibers are attributable to the highly oriented aromatic molecules with planar liquid crystal structure in the parent mesophase pitches. Petroleum byproducts with abundant aromatic fractions have been commonly used to produce mesophase pitch. However, oftentimes, such production process
15 requires toxic and aggressive conditions such as the use of super-acids (*e.g.*, HF/BF₃ or AlCl₃). Moreover, the harsh acidic conditions and difficulties to produce highly pure pitch materials limit the wide application of the current processes. Further, the mechanical properties of pitch-based carbon fibers depend on the orientation and uniformity of precursor pitch fibers and the purity of the pitch itself.

[0007] Factors that may dictate the suitability of a pitch composition precursor for an intended application (*e.g.*, mesophase pitch production, carbon fibers manufacture, etc.), include, for example, softening point, molecular weight, viscosity, density, melting point, as well as secondary performance factors influenced by these parameters. Although pitch compositions having a wide range of physical properties may be desirable for use in various
25 types of applications, there is not presently a ready way of producing high-quality synthetic mesotrophic pitch compositions, particularly with the ability to tune structural and other physical properties needed for addressing certain application-specific needs.

SUMMARY

[0008] In some embodiments, the present disclosure provides methods for making
30 mesophase pitch composition. The methods comprise: heat treating an isotropic pitch composition comprising two or more aromatic classes linked with at least one methylene bridge between each aromatic classes, at a temperature of about 300°C to about 500°C to produce a mesophase pitch composition having a weight average molecular weight (Mw) of about 300 g/mol to about 2,000 g/mol, a softening point (T_{sp}) of about 100°C or greater, a mesophase

content of about 0.01 vol% to 100 vol%, based on the total volume of the mesophase pitch composition, and a micro carbon residue (MCR) of about 25 wt% or greater, based on the total weight of the mesophase pitch composition; wherein heat treating induces cyclization between at least two of the two or more aromatic classes to form one or more 5-membered rings and/or
5 6-membered rings.

[0009] In some embodiments, the present disclosure provides mesophase pitch compositions. The mesophase pitch compositions comprise: a weight average molecular weight (Mw) of about 300 g/mol to about 2,000 g/mol, a softening point (T_{sp}) of about 100°C or greater, a mesophase content of about 0.01 vol% to 100 vol%, based on the total volume of
10 the mesophase pitch composition, and a micro carbon residue (MCR) of about 25 wt% or greater, based on the total weight of the mesophase pitch composition; wherein the mesophase pitch composition is produced from an isotropic pitch composition having two or more aromatic classes linked with at least one methylene bridge between each aromatic classes; and wherein the isotropic pitch composition has a weight average molecular weight (Mw) of about
15 300 g/mol to about 2,000 g/mol, a softening point (T_{sp}) of 50°C or greater, and a micro carbon residue (MCR) of about 15 wt% or greater, based on the total weight of the isotropic pitch composition.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The following figures are included to illustrate certain aspects of the disclosure, and
20 should not be viewed as exclusive configurations. The subject matter disclosed is capable of considerable modifications, alterations, combinations, and equivalents in form and function, as will occur to those skilled in the art and having the benefit of this disclosure.

[0011] FIG. 1 is a laser desorption/ionization mass spectrometry (LDI-MS) of an isotropic pitch composition of the present disclosure, and its proposed structures based on the LDI-MS
25 spectra.

[0012] FIG. 2 is a laser desorption/ionization mass spectrometry (LDI-MS) of an isotropic pitch composition its corresponding mesotrophic pitch compositions after heat soaking treatment.

[0013] FIG. 3 is a graph depicting the distribution of the oligomers comprised in the
30 mesophase pitch compositions.

[0014] FIGS. 4A and 4B depict the mass spectrometry of an isotropic pitch composition its corresponding mesotrophic pitch compositions after heat soaking treatment.

[0015] FIG. 5 is a mass spectrometry depicting the C32 assignments of a mesotrophic pitch composition after heat soaking treatment, and its proposed structures based on the LDI-MS spectra.

[0016] FIG. 6 a mass spectrometry of an isotropic pitch composition its corresponding mesotrophic pitch composition after heat soaking treatment, and its proposed structures based on the LDI-MS spectra.

[0017] FIG. 7 is a polarized light microscopy of a mesophase pitch composition of the present disclosure.

[0018] FIG. 8 is a laser desorption/ionization mass spectrometry (LDI-MS) of a mesophase pitch composition of the present disclosure.

[0019] FIG. 9 is a polarized light microscopy of a mesophase pitch composition of the present disclosure.

DETAILED DESCRIPTION

[0020] The present disclosure relates to mesophase pitch compositions produced from synthetic isotropic pitch compositions from aromatic hydrocarbon feedstocks, methods of making the same, and uses thereof. Particularly, present disclosure relates to acid-mediated production of the said isotropic pitch compositions from aromatic hydrocarbon feedstocks, methods of making the same, and uses thereof (*e.g.*, conversion into mesophase pitches for carbon fiber manufacture).

[0021] As discussed above, there is growing demand for pitches in a variety of industries, especially high-quality pitches, such as those suitable for making carbon fibers, for example. At present, there are no synthetic options available for producing high-quality mesophase pitch compositions, particularly with the ability to tune their structural, physical, and mechanical properties of the pitch compositions to meet particular application-specific needs.

[0022] The present disclosure demonstrates that certain abundant products of the chemical and petroleum industries (*e.g.*, aromatic feedstocks) may be suitable precursors for forming high-quality mesophase pitch compositions thereof. More specifically, the present disclosure utilizes aromatics as a feed for producing isotropic pitch compositions comprising oligomers (*e.g.*, dimer, trimer, tetramer, pentamer, hexamer, heptamer, etc.), which may be further subjected to thermal treatment under mild reaction conditions (*e.g.*, at a temperature of about 300°C to about 500°C; ambient pressure), thus leading to cyclization within each oligomers of the isotropic pitch compositions and forming the corresponding mesophase pitch compositions. In some instances, the said mesophase pitch compositions may be dehydrogenated or partially

hydrogenated to form the corresponding mesophase pitch compositions with higher aromaticity as a reaction product.

- [0023]** Surprisingly and advantageously, mesophase pitch compositions with tunable properties and controlled molecular weight distribution (MWD) may be formed through mild thermal treatment (*e.g.*, thermal treatment at a temperature range of about 300°C to about 500°C) of well-defined and highly pure isotropic pitch compositions (*e.g.*, about 80% isolated yield or greater, such as about 90% isolated yield or greater, such as 100% isolated yield). Without being bound by any theory or mechanism, it is believed that narrow MWD materials may yield mesophase pitches with higher quality compared to broader MWD materials.
- Further, the mild thermal treatment significantly prevents coke formation, thus reducing fouling concerns. Particularly, the mild thermal treatment of the isolated oligomers (*i.e.*, well-defined and highly pure isotropic pitch compositions) may induce cyclization and, in some cases, aromatization of the pitch compositions at temperature range significantly lower than conventional pitch production (*e.g.*, typically ranging from about 450°C to about 550°C).
- Additionally, mesophase pitch compositions produced through the said mild thermal treatment can be further processed to concentrate the mesophase molecules using a solvent with high solubility blending number (SBN) (*e.g.*, typically 80 or higher, such as 100 or higher) (*e.g.*, toluene) is believed to produce mesophases with higher purity and yield, when compared to lower SBN (less than 80).
- [0024]** The present disclosure provides a method comprising: heat treating an isotropic pitch composition comprising two or more aromatic classes linked with at least one methylene bridge between each aromatic classes, at a temperature of about 300°C to about 500°C to produce a mesophase pitch composition having a weight average molecular weight (Mw) of about 300 g/mol to about 2,000 g/mol, a softening point (T_{sp}) of about 100°C or greater, a mesophase content of about 0.01 vol% to 100 vol%, based on the total volume of the mesophase pitch composition, and a micro carbon residue (MCR) of about 25 wt% or greater, based on the total weight of the mesophase pitch composition; wherein heat treating induces cyclization between at least two of the two or more aromatic classes to form one or more 5-membered rings and/or 6-membered rings. Cyclization between at least two of the two or more aromatic classes to form one or more 6-membered rings may be followed by dehydrogenative aromatization to produce a highly aromatic mesophase pitch composition.

[0025] The aromatic classes may be unsubstituted aromatics and/or substituted aromatics selected from the group consisting of 1-membered ring aromatics (ARC1), 2-membered ring aromatics (ARC2), 3-membered ring aromatics (ARC3), 4-membered aromatics (ARC4),

5-membered ring aromatics (ARC5), 6-membered ring aromatics (ARC6), 7-membered ring aromatics (ARC7), 8-membered ring aromatics (ARC8), 9-membered ring aromatics (ARC9), 10 or more-membered ring aromatics (ARC10+), and any combination thereof.

- [0026] The isotropic pitch composition may have a weight average molecular weight (Mw) of about 300 g/mol to about 2,000 g/mol, a softening point (T_{sp}) of 50°C or greater, and a micro carbon residue (MCR) of about 15 wt% or greater, based on the total weight of the isotropic pitch composition.

Definitions and Test Methods

- [0027] All numerical values within the detailed description and the claims herein are modified by “about” or “approximately” with respect to the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art. Unless otherwise indicated, ambient temperature (room temperature) is about 25°C.

- [0028] As used in the present disclosure and claims, the singular forms “a,” “an,” and “the” include plural forms unless the context clearly dictates otherwise.

[0029] The term “and/or” as used in a phrase such as “A and/or B” herein is intended to include “A and B,” “A or B,” “A,” and “B.”

[0030] For the purposes of the present disclosure and the claims thereto, the following definitions shall be used.

- [0031] Unless otherwise specified, the term “C_n” means hydrocarbon(s) having n carbon atom(s) per molecule, wherein n is a positive integer.

- [0032] The term “C_n” group or compound refers to a group or a compound comprising carbon atoms at total number thereof of n. Thus, a “C_m-C_n” group or compound refers to a group or compound comprising carbon atoms at a total number thereof in the range from m to n. Thus, a C₁-C₅₀ alkyl group refers to an alkyl group comprising carbon atoms at a total number thereof in the range from 1 to 50.

[0033] The terms “group,” “radical,” and “substituent” may be used interchangeably.

- [0034] The terms “hydrocarbyl radical,” “hydrocarbyl group,” or “hydrocarbyl” may be used interchangeably and are defined to mean a group consisting of hydrogen and carbon atoms only. Preferred hydrocarbyls are C₁-C₁₀₀ radicals that may be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic. Examples of such radicals include, but are not limited to, alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, iso-amyl, hexyl, octyl cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like, aryl groups, such as phenyl, benzyl naphthalenyl, and the like.

[0035] Unless otherwise indicated, (*e.g.*, the definition of "substituted hydrocarbyl", etc.), the term "substituted" means that at least one hydrogen atom has been replaced with at least one non-hydrogen group, such as a hydrocarbyl group.

[0036] The term "aryl" or "aryl group" means an aromatic ring (typically made of 6 carbon atoms) and the substituted variants thereof, such as phenyl, 2-methyl-phenyl, xylyl, 4-bromo-xylyl, for example.

[0037] The term "substituted aromatic," means an aromatic group having 1 or more hydrogen groups replaced by a hydrocarbyl, or substituted hydrocarbyl.

[0038] The term "ring atom" means an atom that is part of a cyclic ring structure. By this definition, a benzyl group has six ring atoms and tetrahydrofuran has 5 ring atoms.

[0039] Where isomers of a named alkyl, alkenyl, alkoxide, or aryl group exist (*e.g.*, *n*-butyl, iso-butyl, sec-butyl, and tert-butyl) reference to one member of the group (*e.g.*, *n*-butyl) shall expressly disclose the remaining isomers (*e.g.*, iso-butyl, sec-butyl, and tert-butyl) in the family. Likewise, reference to an alkyl, alkenyl, alkoxide, or aryl group without specifying a particular isomer (*e.g.*, butyl) expressly discloses all isomers (*e.g.*, *n*-butyl, iso-butyl, sec-butyl, and tert-butyl).

[0040] The terms "linear" or "linear hydrocarbon" refer to a hydrocarbon or hydrocarbyl group having a continuous carbon chain without side chain branching, in which the continuous carbon chain may be optionally substituted.

[0041] The terms "cyclic" or "cyclic hydrocarbon" refer to a hydrocarbon or hydrocarbyl group having a closed carbon ring, which may be optionally substituted. The term "carbocyclic" may also synonymously refer to such a hydrocarbon or hydrocarbyl group.

[0042] The terms "branched" or "branched hydrocarbon" refer to a hydrocarbon or hydrocarbyl group having a linear carbon chain or a closed carbon ring, in which a hydrocarbyl side chain extends from the linear carbon chain or the closed carbon ring. Optional substitution may be present in the linear carbon chain, the closed carbon ring, and/or the hydrocarbyl side chain.

[0043] The terms "aromatic" or "aromatic hydrocarbon" refer to a hydrocarbon or hydrocarbyl group having a cyclic arrangement of conjugated pi-electrons that satisfies the Hückel rule.

[0044] The term "independently," when referenced to selection of multiple items from within a given Markush group, means that the selected choice for a first item does not necessarily influence the choice of any second or subsequent item. That is, independent

selection of multiple items within a given Markush group means that the individual items may be the same or different from one another.

[0045] Examples of saturated hydrocarbyl groups include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, iso-amyl (isopentyl),
5 neopentyl, hexyl, octyl cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like, including their substituted analogues. Examples of unsaturated hydrocarbyl groups include, but are not limited to, ethenyl, propenyl, allyl, 1,4-butadienyl, cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, cyclooctenyl and the like, including their substituted analogues.

10 [0046] Examples of aromatic hydrocarbyl groups include, but are not limited to, phenyl, tolyl, xylyl, naphthyl, and the like. Polynuclear aryl groups may include, but are not limited to, naphthalenyl, anthracenyl, indanyl, indenyl, and tetralinyl.

[0047] Unless specified otherwise, the term “substantially free of” with respect to a particular component means the concentration of that component in the relevant composition
15 is no greater than 5 mol% (such as no greater than 3 mol%, no greater than 1 mol%, or about 0%, within the bounds of the relevant measurement framework), based on the total quantity of the relevant composition.

[0048] The term “isolated” refers to the condition of a substance being obtained in a state substantially free of solvent and/or precursors to the given substance.

20 [0049] As used herein, Mw is weight average molecular weight, wt% is weight percent, and mol% is mole percent. Unless otherwise noted, molecular weight unit (*e.g.*, Mw) is g/mol.

[0050] Unless otherwise indicated, the term “room temperature”, also referred to as “ambient temperature”, is approximately 23°C.

[0051] The “microcarbon residue test”, also referred to as “MCRT”, is a standard test
25 method for the determination of carbon residue (micro method). The carbon residue value of the various petroleum materials serves as an approximation of the tendency of the material to form carbonaceous type deposits under degradation conditions similar to those used in the test method, and can be useful as a guide in manufacture of certain stocks. However, care needs to be exercised in interpreting the results. This test method covers the determination of the
30 amount of carbon residue formed after evaporation and pyrolysis of petroleum materials under certain conditions and is intended to provide some indication of the relative coke forming tendency of such materials. Herein, the MCRT is measured according to the ASTM D4530-15 standard test method.

[0052] The term “Solvent Blending Number” (SBN) refers to a parameter relating to the compatibility of a material (*e.g.*, an oil, a pitch, etc.) with different proportions of a model solvent (*e.g.*, toluene) or solvent mixture (*e.g.*, toluene/n-heptane).

[0053] The “softening point” refers to a temperature or a range of temperatures at which a substance softens. Herein, the softening point (SP) is measured using a METTLER TOLEDO dropping point instrument, such as METTLER TOLEDO DP70, according to a procedure analogous to ASTM D36.

[0054] The following abbreviations may be used through the present disclosure and claims: “MCRT” is microcarbon residue test, “equiv” is molar equivalent, “ppm” is parts per million, and “T_{sp}” is softening point temperature.

Isotropic Pitch Compositions.

[0055] Methods of the present disclosure are a non-dehydrogenative synthetic route which provides a pathway for the production of pitch precursors for the manufacturing of advanced carbon products. Further, methods of the present disclosure provide a way of producing high-quality synthetic isotropic pitch compositions, particularly with the ability to tune structural and other physical properties needed for addressing certain application-specific needs. The isotropic pitch compositions of the present disclosure may be used as precursors of mesophase pitches for carbon fiber manufacture to improve the production of highly oriented carbon fibers with excellent mechanical properties, as well as normal paraffin hydrocarbons, or tackifiers.

[0056] Embodiments of the present disclosure include isotropic pitch compositions comprising: two or more aromatic classes linked with at least one methylene bridge between each aromatic classes, wherein the isotropic pitch composition has a weight average molecular weight (M_w) of about 300 g/mol to about 2,000 g/mol, a softening point (T_{sp}) of 50°C or greater, and a micro carbon residue (MCR) of about 15 wt% or greater, based on the total weight of the pitch composition. The isotropic pitch compositions of the present disclosure are methylene-bridged aromatic oligomers produced by reacting aromatic feedstocks with formaldehyde and/or paraformaldehyde in the presence of acetic acid and sulfuric acid.

[0057] Herein, the aromatic classes may comprise: unsubstituted aromatics and/or substituted aromatics selected from the group consisting of 1-membered ring aromatics (ARC1), 2-membered ring aromatics (ARC2), 3-membered ring aromatics (ARC3), 4-membered aromatics (ARC4), 5-membered ring aromatics (ARC5), 6-membered ring aromatics (ARC6), 7-membered ring aromatics (ARC7), 8-membered ring aromatics (ARC8), 9-membered ring aromatics (ARC9), 10 or more-membered ring aromatics (ARC10+), and any combination thereof. The substituted aromatics can be selected from the group consisting of

C₁ to C₂₀ hydrocarbyl monosubstituted aromatics, C₁ to C₂₀ hydrocarbyl disubstituted aromatics, C₁ to C₂₀ hydrocarbyl trisubstituted aromatics, and any combination thereof. In at least one embodiment, the substituted aromatics can be selected from the group consisting of C₁ to C₅ hydrocarbyl monosubstituted aromatics, C₁ to C₅ hydrocarbyl disubstituted aromatics, C₁ to C₅ hydrocarbyl trisubstituted aromatics, and any combination thereof. The isotropic pitch compositions can be produced from well-defined, highly pure, and cost-effective substituted and/or non-substituted single-ring aromatic feedstocks, substituted and/or non-substituted polycyclic aromatic hydrocarbon (PAH) feedstocks, and any combination thereof. PAH may include two-ring aromatic feedstocks or multi-ring aromatic feedstocks (*e.g.*, three ring aromatic feedstocks or greater).

[0058] The one or more aromatic classes may also comprise partially hydrogenated aromatic rings, such as tetralin (also referred to as “1,2,3,4-tetrahydronaphthalene”) or indene, for example.

[0059] The isotropic pitch composition of the present disclosure may be produced by: mixing an aromatic feedstock comprising the one or more aromatic classes with acetic acid and sulfuric acid, at ambient temperature to produce a first mixture; heating the first mixture at a temperature of about 40°C to about 400°C; adding formaldehyde and/or paraformaldehyde to the first mixture at a temperature of about 40°C to about 400°C to produce a second mixture comprising a reaction products composition, wherein the reaction products composition comprises or consists essentially of oligomer products (*e.g.*, dimers, trimers, tetramers, pentamers, etc.); filtering the second mixture; and isolating the isotropic pitch composition.

[0060] The isotropic pitch composition of the present disclosure may be in a continuous mode, such as in a continuous stirred tank reactor (CSTR) or a tubular reactor, which may be compatible with continuous production line processes. Other suitable reactors for conducting the production of isotropic pitch compositions according to the disclosure herein may include CSTRs or CSTRs in series, stirred tank reactors (STRs) or STRs in series, tubular reactors, staged bubble column reactors, tubular reactors with co-current gas/liquid flows, tubular reactors with periodic gas/liquid separation, and the like.

[0061] The isotropic pitch composition of the present disclosure may be carried out at a temperature ranging from about 40°C to about 400°C, and/or a residence time ranging from less than a minute to about 48 hours, such as 36 hours or less, such as 24 hours or less, such as 12 hours or less, such as 6 hours or less.

[0062] Another aspect of the present disclosure relates to the methods for making the isotropic pitch compositions comprising: mixing an aromatic feedstock comprising one or more

- aromatic classes with paraformaldehyde, in the presence of acetic acid at ambient temperature to produce a first mixture; heating the first mixture at a temperature of about 40°C to about 100°C; and mixing a second mixture comprising sulfuric acid and acetic acid to the first mixture at a temperature of about 40°C to about 100°C to form a mix comprising an isotropic pitch composition, wherein the isotropic pitch composition comprises: one or more aromatic classes linked with at least one methylene bridge between each aromatic classes, wherein the isotropic pitch composition has a weight average molecular weight (Mw) of about 300 g/mol to about 2,000 g/mol, a softening point (T_{sp}) of 50°C or greater, and a micro carbon residue (MCR) of about 15 wt% or greater, based on the total weight of the isotropic pitch composition.
- 5 [0063] The reaction conditions of the methods herein are critical for the molecular weight distribution and the softening point of the isotropic pitch compositions. Advantageously, methods of the present disclosure enable control over both the molecular weight distribution and the softening point by tuning the molar ratio of acetic acid, sulfuric acid, and/or paraformaldehyde. The softening points of the isotropic pitch compositions can increase
- 15 particularly based on the amount of sulfuric acid and paraformaldehyde. Acetic acid may be used at least partially as a solvent. Further, any residual acids can be easily removed by filtration after washing the residue comprising the isotropic pitch composition with water and a dilute base solution (e.g., NaOH or NH_4OH), thus facilitating the isolation of the said isotropic pitch composition as a highly pure material (i.e., starting materials quantitatively
- 20 consumed, confirmed by mass spectrometry (e.g., Fourier-transform ion cyclotron resonance (FTICR)), 1H NMR, and ^{13}C NMR spectra).
- [0064] Nonlimiting examples of aromatic feedstocks may comprise benzene, toluene, xylenes (e.g., ortho-, meta-, para-substituted xylene), naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 3-methylnaphthalene, 2,6-dimethylnaphthalene, 1-ethylnaphthalene,
- 25 2-ethylnaphthalene, 1,7-diisopropylnaphthalene, 2,3-diisopropylnaphthalene, 2,6-diisopropylnaphthalene, 2,7-diisopropylnaphthalene, 1-butylnaphthalene, 2-butylnaphthalene, 1-tert-butylnaphthalene, 2-tert-butylnaphthalene, anthracene, 1-methylanthracene, 2-methylanthracene, 9-methylanthracene, 9,10-dimethylanthracene, 9,10-diphenylanthracene, phenanthrene, 1-methylphenanthrene, 1-ethylphenanthrene,
- 30 2-methylphenanthrene, 1-phenylphenanthrene, 2,7-diphenylphenanthrene, pyrene, 1-propylpyrene, 4-propylpyrene, 1,2,3-trimethylpyrenebenzopyrene, picenecoronene, chrysene, tetracene, pentacene, triphenylene, corannulene, fluorine, benzo[j]fluoranthene, Benzo[c]fluorene, perylene, benzo-perylene, ovalene, AROMATIC-200™, acenaphthene, and any isomers thereof, and any combination thereof.

[0065] Suitable aromatic hydrocarbons compounds may comprise 1 to 3 rings and may be substituted by alkyl groups containing 1 to 6 carbon atoms, phenyl group, or aralkyl groups containing 7 to 9 carbon atoms. Herein, an aromatic hydrocarbon is advantageously selected from xylene, naphthalene, methylnaphthalene, dimethylnaphthalene, biphenyl, anthracene, phenanthrene, pyrene and their derivatives substituted with alkyl groups containing 1 to 6 carbon atoms. More preferable are polycyclic aromatic hydrocarbons such as naphthalene, methylnaphthalene and dimethylnaphthalene and mixtures of these polycyclic aromatic hydrocarbons such as aromatic oils.

[0066] In the cases where a polycyclic aromatic compound is used as a reactant, the compound, for example, may be an aromatic hydrocarbon oil containing 90 wt% or more of naphthalene, high-purity naphthalene or an aromatic hydrocarbon oil mainly containing naphthalene. Available as such hydrocarbon oils are the naphthalene oil fraction, methylnaphthalene oil fraction and intermediate oil fraction derived from coal tar or the intermediate products and residual oils obtained by recovering the principal components of these fractions by distillation, extraction and the like. The said naphthalene- or methylnaphthalene-containing oils often occur as mixtures of the principal components and polycyclic aromatic hydrocarbons whose boiling points are close to each other. An aromatic hydrocarbon to be used in the reaction can be a mixture unless a pure raw material is used.

[0067] A naphthalene-containing aromatic hydrocarbon oil naturally contains aromatic hydrocarbons as main components and may additionally contain aromatic compounds having functional groups containing inert aliphatic hydrocarbons. An aromatic hydrocarbon oil containing 90 wt% or more of naphthalene may be refined naphthalene, but a preferred example is 95% grade naphthalene. This particular material contains benzothiophene, methylnaphthalene and the like in addition to naphthalene.

[0068] Formaldehyde to be used in the methods of the present disclosure may be formaldehyde itself or a compound which is capable of generating formaldehyde in the reaction system and formaldehyde, formalin, paraformaldehyde and the like can be used. In some cases, paraformaldehyde may be used neat or in an alkaline solution (*e.g.*, NaOH or KOH).

[0069] Nonlimiting examples of acids may comprise sulfuric acid, hydrochloric acid, nitric acid, acetic acid, phosphoric acid, citric acid, carbonic acid, oxalic acid, aromatic sulfonic acid. Acids of the present disclosure may be used as solvent.

[0070] The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC1, 0.1 wt% to 100 wt% ARC2, 0.1 wt% to 100 wt% ARC3, 0.1 wt% to 100 wt% ARC4, 0.1 wt% to 100 wt% ARC5, 0.1 wt% to 100 wt% ARC6, 0.1 wt% to 100 wt%

ARC7, 0.1 wt% to 100 wt% ARC8, 0.1 wt% to 100 wt% ARC9, 0.1 wt% to 100 wt% ARC10+, based on the total weight of the isotropic pitch composition.

5 **[0071]** The isotropic pitch composition of the present disclosure may comprise 0.1 wt% to 100 wt% ARC1 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

10 **[0072]** The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC2 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%,
15 or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

20 **[0073]** The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC3 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

25 **[0074]** The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC4 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic
30 pitch composition.

30 **[0075]** The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC5 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to

50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

[0076] The isotropic pitch composition of the present disclosure may comprise: 0.1 wt%
5 to 100 wt% ARC6 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt%
to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to
60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to
50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to
30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic
10 pitch composition.

[0077] The isotropic pitch composition of the present disclosure may comprise: 0.1 wt%
to 100 wt% ARC7 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt%
to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to
60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to
15 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to
30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic
pitch composition.

[0078] The isotropic pitch composition of the present disclosure may comprise: 0.1 wt%
to 100 wt% ARC8 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt%
20 to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to
60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to
50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to
30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic
pitch composition.

[0079] The isotropic pitch composition of the present disclosure may comprise: 0.1 wt%
to 100 wt% ARC9 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt%
to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to
60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to
50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to
30 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic
pitch composition.

[0080] The isotropic pitch composition of the present disclosure may comprise: 0.1 wt%
to 100 wt% ARC10+ (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or
5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt%

to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

5 **[0081]** The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC1, 0.1 wt% to 100 wt% ARC2, 0.1 wt% to 80 wt% ARC3, 0.1 wt% to 50 wt% ARC4, 0.1 wt% to 50 wt% ARC5, 0.1 wt% to 25 wt% ARC6, 0.1 wt% to 25 wt% ARC7, 0 wt% to 10 wt% ARC8, 0 wt% to 10 wt% ARC9, 0 wt% to 5 wt% ARC10+, based on the total weight of the isotropic pitch composition.

10 **[0082]** Further, the isotropic pitch composition may have a T_{sp} of about 500°C or less (or from about 90°C to about 500°C, or from about 100°C to about 490°C, or from about 110°C to about 480°C, or from about 120°C to about 470°C, or from about 130°C to about 460°C, or from about 140°C to about 450°C, or from about 150°C to about 440°C, or from about 160°C to about 430°C, or from about 170°C to about 420°C, or from about 180°C to about 410°C, or
15 from about 200°C to about 400°C). The isotropic pitch composition may have a T_{sp} of about 100°C or greater.

20 **[0083]** The isotropic pitch composition may have an MCR of about 40 wt% or less (or 35 wt% or less, or 30 wt% or less, or 25 wt% or less, or 20 wt% or less, or 15 wt% or less), based on the total weight of the isotropic pitch composition. The isotropic pitch composition may
25 have an MCR of from about 15 wt% to about 40 wt%, based on the total weight of the isotropic pitch composition.

30 **[0084]** The isotropic pitch composition may have an Mw of about 300 g/mol to about 2,000 g/mol (or about 400 g/mol to about 2,000 g/mol, or about 500 g/mol to about 1,500 g/mol, or about 600 g/mol to about 800 g/mol, or about 300 g/mol to about 1,000 g/mol, or about 300 g/mol to about 500 g/mol). Alternately, the isotropic pitch composition may have an Mw of
35 about 500 g/mol or less (or about 100 g/mol to about 500 g/mol, or about 150 g/mol to about 400 g/mol, or about 200 g/mol to about 350 g/mol, or about 250 g/mol to about 300 g/mol, or about 100 g/mol to about 250 g/mol, or about 250 g/mol to about 500 g/mol).

40 **[0085]** Methods for making the isotropic pitch compositions described above may
45 comprise: mixing an aromatic feedstock comprising one or more aromatic classes with paraformaldehyde, in the presence of acetic acid at ambient temperature to produce a first mixture; heating the first mixture at a temperature of about 40°C to about 100°C; and mixing a second mixture comprising sulfuric acid and acetic acid to the first mixture at a temperature of about 40°C to about 100°C to form a mix comprising an isotropic pitch composition, wherein

the isotropic pitch composition comprises: one or more aromatic classes linked with at least one methylene bridge between each aromatic classes, wherein the isotropic pitch composition has a weight average molecular weight (M_w) of 300 g/mol to 2,000 g/mol, a softening point (T_{sp}) of 90°C or greater, and a micro carbon residue (MCR) of about 25 wt% or greater, based on the total weight of the isotropic pitch composition. Without being bound by any theory, it is believed that the reaction may be initiated via Friedel-Craft acylation reaction, followed by condensation reactions.

[0086] Mixing the aromatic feedstock and paraformaldehyde can be carried out at a molar ratio aromatic feedstock: formaldehyde equivalence of from about 10:1 to about 1:10 (or about 1:1.5 to about 1:9, or about 1:2 to about 1:8, or about 1:2.5 to about 1:7, or about 1:3 to about 1:6, or about 1:4 to about 1:5). In some cases, the molar ratio aromatic feedstock: formaldehyde equivalence is 1:3. In some other cases, the molar ratio aromatic feedstock: formaldehyde equivalence is 1:1.

[0087] Further, the addition of sulfuric acid can be carried out at a molar ratio aromatic feedstock: sulfuric acid of from about 1:0.001 to about 1:20 (or about 1:0.01 to about 1:19, or about 1:0.1 to about 1:18, or about 1:0.5 to about 1:17, or about 1:1 to about 1:16, or about 1:1.5 to about 1:15, or about 1:2 to about 1:14, or about 1:2.5 to about 1:13, or about 1:3 to about 1:12, or about 1:3.5 to about 1:11, or about 1:4 to about 1:10). In at least one embodiment, the molar ratio aromatic feedstock: sulfuric acid is 1:2.

[0088] The mixing of the second mixture comprising sulfuric acid and acetic acid to the first mixture may be carried out at a temperature of about 40°C to about 100°C, such as about 50°C to about 90°C, such as about 60°C to about 80°C, such as about 40°C to about 60°C, such as about 60°C to about 90°C, for a time period of about 5 hours or less (or about 5 minutes to about 5 hours, or about 10 minutes to about 4 hours, or about 15 minutes to about 3 hours, or about 20 minutes to about 2 hours, or about 25 minutes to about 1 hours, or about 30 minutes, for example), although the conditions may vary with the raw materials and acids in use.

[0089] Separating the isotropic pitch composition from any remaining paraformaldehyde, sulfuric acid and/or acetic acid can performed by filtration of the reaction mixture, using alkalis to wash the residue and neutralize the acids.

[0090] Suitable examples of alkalis can be water-soluble alkalis such as sodium hydroxide, potassium hydroxide, ammonium hydroxide and sodium carbonate. "Water-soluble" means that not only alkalis themselves are water-soluble but also the salts to be formed by their reaction with acids are water-soluble. Moreover, "alkali" means a substance which can neutralize an acid and its examples are hydroxides and weak acid salts such as carbonates of

alkali metals and alkaline earth metals. For example, sodium hydroxide can be used during the filtration process as it is readily available and soluble in many acids.

[0091] Methods of the present disclosure may further comprise: cooling the mix comprising the isotropic pitch composition to ambient temperature; and separating the isotropic pitch composition from any remaining paraformaldehyde, sulfuric acid and/or acetic acid.

[0092] In some instances, mixing the second mixture comprising sulfuric acid and acetic acid to the first mixture may be carried out at ambient pressure.

Mesophase Pitch Compositions and Method for making the same.

[0093] The present disclosure provides herein a method comprising: heat treating an isotropic pitch composition (described above) comprising two or more aromatic classes linked with at least one methylene bridge between each aromatic classes, at a temperature of about 300°C to about 500°C to produce a mesophase pitch composition having a weight average molecular weight (Mw) of about 300 g/mol to about 2,000 g/mol, a softening point (T_{sp}) of about 100°C or greater, a mesophase content of about 0.01 vol% to 100 vol%, based on the total volume of the mesophase pitch composition, and a micro carbon residue (MCR) of about 25 wt% or greater, based on the total weight of the mesophase pitch composition; wherein heat treating induces cyclization between at least two of the two or more aromatic classes to form one or more 5-membered rings and/or 6-membered rings. In some cases, the cyclization between at least two of the two or more aromatic classes to form one or more 6-membered rings may be followed by dehydrogenative aromatization to produce a highly aromatic mesophase pitch composition.

[0094] The mesophase pitch may be produced in a batch reactor, preferably in a continuous flow reactor. In at least one embodiment, the mesophase pitch is produced in a continuous tubular reactor, at a temperature ranging from of about 300°C to about 500°C, at a residence time ranging from less than a minute to 48 hours (or 36 hours or less, or 24 hours or less, or 20 hours or less, or 15 hours or less, or 10 hours or less, or 5 hours or less, or 2.5 hours or less, or 1 hour or less).

[0095] As described above, the two or more aromatic classes can be unsubstituted aromatics and/or substituted aromatics selected from the group consisting of 1-membered ring aromatics (ARC1), 2-membered ring aromatics (ARC2), 3-membered ring aromatics (ARC3), 4-membered aromatics (ARC4), 5-membered ring aromatics (ARC5), 6-membered ring aromatics (ARC6), 7-membered ring aromatics (ARC7), 8-membered ring aromatics (ARC8), 9-membered ring aromatics (ARC9), 10 or more-membered ring aromatics (ARC10+), and any combination thereof.

[0096] The mesophase pitch composition may comprise: 0.1 wt% to 100 wt% ARC1, 0.1 wt% to 100 wt% ARC2, 0.1 wt% to 100 wt% ARC3, 0.1 wt% to 100 wt% ARC4, 0.1 wt% to 100 wt% ARC5, 0.1 wt% to 100 wt% ARC6, 0.1 wt% to 100 wt% ARC7, 0.1 wt% to 100 wt% ARC8, 0.1 wt% to 100 wt% ARC9, 0.1 wt% to 100 wt% ARC10+, based on the total weight of the isotropic pitch composition.

[0097] The isotropic pitch composition of the present disclosure may comprise 0.1 wt% to 100 wt% ARC1 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

[0098] The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC2 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

[0099] The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC3 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

[0100] The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC4 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

[0101] The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC5 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

[0102] The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC6 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

[0103] The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC7 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

[0104] The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC8 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

[0105] The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC9 (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

5 **[0106]** The isotropic pitch composition of the present disclosure may comprise: 0.1 wt% to 100 wt% ARC10+ (0.1 wt% to 95 wt%, or 0.5 wt% to 90 wt%, or 1 wt% to 85 wt%, or 5 wt% to 80 wt%, or 10 wt% to 75 wt%, or 15 wt% to 70 wt%, or 20 wt% to 65 wt%, or 25 wt% to 60 wt%, or 30 wt% to 55 wt%, or 35 wt% to 50 wt%, or 40 wt% to 45 wt%, or 0.1 wt% to 50 wt%, or 0.5 wt% to 45 wt%, or 1 wt% to 40 wt%, or 1.5 wt% to 35 wt%, or 2 wt% to 30 wt%, or 2.5 wt% to 25 wt%, or 3 wt% to 20 wt%), based on the total weight of the isotropic pitch composition.

10 **[0107]** The mesophase pitch composition may comprise: 0.1 wt% to 100 wt% ARC1, 0.1 wt% to 100 wt% ARC2, 0.1 wt% to 80 wt% ARC3, 0.1 wt% to 50 wt% ARC4, 0.1 wt% to 50 wt% ARC5, 0.1 wt% to 25 wt% ARC6, 0.1 wt% to 25 wt% ARC7, 0 wt% to 10 wt% ARC8, 0 wt% to 10 wt% ARC9, 0 wt% to 5 wt% ARC10+, based on the total weight of the isotropic pitch composition.

15 **[0108]** Herein, the heat treating may be heat soaking and/or deasphalting. The heat treating may be carried out at a pressure ranging from ambient pressure to 1,000 psi (or from about 1 psi to about 500 psi, or from about 10 psi to about 450 psi, or from about 50 psi to about 400 psi, or from about 100 psi to about 350, such as 300 psi, for example).

20 **[0109]** Deasphalting may be carried out at a temperature ranging from room temperature to 280°C, at a pressure ranging from ambient pressure to 700 psi, and/or at a reaction time ranging from about 1 hour to 3 hours. Nonlimiting example of solvents used for deasphalting may be selected from the group consisting of: toluene, heptane, or combination of the two at various ratios.

25 **[0110]** The mesophase pitch composition of the present disclosure may have a mesophase content ranging from about 40 vol% to about 100% (or from about 45 vol% to about 95 vol%, or from about 50 vol% to about 90 vol%, or from about 55 vol% to about 85 vol%, or from about 60 vol% to about 80 vol%), based on the total volume of the mesophase pitch composition.

30 **[0111]** The mesophase pitch composition may have a softening point (T_{sp}) of about 100°C or greater (or about 150°C or greater, or about 200°C or greater, or about 250°C or greater, or about 300°C or greater, or about 350°C or greater, or about 400°C or greater). The mesophase pitch composition may have a softening point (T_{sp}) from about 100°C to about 500, such as about 150°C to about 475°C, such as about 200°C to about 450°C.

[0112] The mesophase pitch composition may have a micro carbon residue (MCR) of about 25 wt% or greater (or from about 25 wt% to about 95 wt%, or from about 30 wt% to about 90 wt%, or from about 35 wt% to about 85 wt%, or from about 40 wt% to about 80 wt%), based on the total weight of the mesophase pitch composition.

- 5 [0113] The mesophase pitch composition of the present disclosure may be used for the production of one or more of: fiber, oxidized fiber, carbonized fiber, graphitized fiber, fiber web, oxidized fiber web, carbonized fiber web, or graphitized fiber web.

End Uses

- 10 [0114] Mesophase pitch compositions of the present disclosure may be used as a precursor for the production of carbon fiber manufacture to improve the production of highly oriented carbon fibers with excellent mechanical properties, as well as fibers, oxidized fibers, carbonized fibers, graphitized fibers, fiber webs, oxidized fiber webs, carbonized fiber webs, or graphitized fiber webs.

- 15 [0115] In some instances, methods of the present disclosure may comprise: heat treating an isotropic pitch composition comprising two or more aromatic classes linked with at least one methylene bridge between each aromatic classes, at a temperature of about 300°C to about 500°C to produce a mesophase pitch composition suitable for spinning into carbon fibers, wherein the mesophase pitch composition has a weight average molecular weight (Mw) of about 300 g/mol to about 2,000 g/mol, a softening point (T_{sp}) of about 100°C or greater, a
20 mesophase content of about 0.01 vol% to 100 vol%, based on the total volume of the mesophase pitch composition, and a micro carbon residue (MCR) of about 25 wt% or greater, based on the total weight of the mesophase pitch composition; wherein heat treating induces cyclization between at least two of the two or more aromatic classes to form one or more 5-membered rings and/or 6-membered rings.

- 25 [0116] Embodiments disclosed herein include:

- [0117] A. Methods for making mesophase pitch composition. The methods comprise: heat treating an isotropic pitch composition comprising two or more aromatic classes linked with at least one methylene bridge between each aromatic classes, at a temperature of about 300°C to about 500°C to produce a mesophase pitch composition having a weight average molecular
30 weight (Mw) of about 300 g/mol to about 2,000 g/mol, a softening point (T_{sp}) of about 100°C or greater, a mesophase content of about 0.01 vol% to 100 vol%, based on the total volume of the mesophase pitch composition, and a micro carbon residue (MCR) of about 25 wt% or greater, based on the total weight of the mesophase pitch composition; wherein heat treating

induces cyclization between at least two of the two or more aromatic classes to form one or more 5-membered rings and/or 6-membered rings.

[0118] B. Mesophase pitch compositions. The mesophase pitch compositions comprise: a weight average molecular weight (Mw) of about 300 g/mol to about 2,000 g/mol, a softening point (T_{sp}) of about 100°C or greater, a mesophase content of about 0.01 vol% to 100 vol%, based on the total volume of the mesophase pitch composition, and a micro carbon residue (MCR) of about 25 wt% or greater, based on the total weight of the mesophase pitch composition; wherein the mesophase pitch composition is produced from an isotropic pitch composition having two or more aromatic classes linked with at least one methylene bridge between each aromatic classes; and wherein the isotropic pitch composition has a weight average molecular weight (Mw) of about 300 g/mol to about 2,000 g/mol, a softening point (T_{sp}) of 50°C or greater, and a micro carbon residue (MCR) of about 15 wt% or greater, based on the total weight of the isotropic pitch composition.

[0119] Embodiments A and B may have one or more of the following elements in any combination:

[0120] Element 1: wherein each one of the two or more aromatic classes are unsubstituted aromatics and/or substituted aromatics selected from the group consisting of 1-membered ring aromatics (ARC1), 2-membered ring aromatics (ARC2), 3-membered ring aromatics (ARC3), 4-membered aromatics (ARC4), 5-membered ring aromatics (ARC5), 6-membered ring aromatics (ARC6), 7-membered ring aromatics (ARC7), 8-membered ring aromatics (ARC8), 9-membered ring aromatics (ARC9), 10 or more-membered ring aromatics (ARC10+), and any combination thereof.

[0121] Element 2: wherein the substituted aromatics are selected from the group consisting of C₁ to C₂₀ hydrocarbyl monosubstituted aromatics, C₁ to C₂₀ hydrocarbyl disubstituted aromatics, C₁ to C₂₀ hydrocarbyl trisubstituted aromatics, and any combination thereof.

[0122] Element 3: wherein cyclization between at least two of the two or more aromatic classes to form one or more 6-membered rings is followed by dehydrogenative aromatization to produce a highly aromatic mesophase pitch composition.

[0123] Element 4: wherein the isotropic pitch composition is produced by: mixing an aromatic feedstock comprising the one or more aromatic classes with acetic acid and sulfuric acid, to produce a first mixture; heating the first mixture at a temperature of about 40°C to about 400°C; adding formaldehyde and/or paraformaldehyde to the first mixture at a temperature of about 40°C to about 400°C to produce a second mixture comprising a reaction

products composition; filtering the second mixture; and isolating the isotropic pitch composition.

5 [0124] Element 5: wherein the isotropic pitch composition has a weight average molecular weight (Mw) of about 300 g/mol to about 2,000 g/mol, a softening point (T_{sp}) of 50°C or greater, and a micro carbon residue (MCR) of about 15 wt% or greater, based on the total weight of the isotropic pitch composition.

[0125] Element 6: wherein each one of the two or more aromatic classes comprise partially hydrogenated aromatic rings.

10 [0126] Element 7: wherein each one of the two or more aromatic classes are selected from the group consisting of benzene, toluene, xylenes (such as ortho-, meta-, para-xylene), naphthalene, 1-methyl naphthalene, 2-methyl naphthalene, anthracene, phenanthrene, pyrene, benzopyrene, picenecoronene, chrysene, tetracene, pentacene, triphenylene, corannulene, benzo[j]fluoranthene, Benzo[c]fluorene, perylene, benzo-perylene, ovalene, AROMATIC-200™, and any combination thereof.

15 [0127] Element 8: wherein the molar ratio aromatic feedstock: formaldehyde equivalence is from about 10:1 to about 1:10.

[0128] Element 9: wherein the molar ratio aromatic feedstock: formaldehyde equivalence is 1:3.

20 [0129] Element 10: wherein the molar ratio aromatic feedstock: sulfuric acid is from about 1:0.001 to about 1:20.

[0130] Element 11: wherein the molar ratio aromatic feedstock: sulfuric acid is 1:2.

25 [0131] Element 12: wherein the isotropic pitch composition comprises: 0.1 wt% to 100 wt% ARC1, 0.1 wt% to 100 wt% ARC2, 0.1 wt% to 100 wt% ARC3, 0.1 wt% to 100 wt% ARC4, 0.1 wt% to 100 wt% ARC5, 0.1 wt% to 100 wt% ARC6, 0.1 wt% to 100 wt% ARC7, 0.1 wt% to 100 wt% ARC8, 0.1 wt% to 100 wt% ARC9, 0.1 wt% to 100 wt% ARC10+, based on the total weight of the isotropic pitch composition.

30 [0132] Element 13: wherein the isotropic pitch composition comprises: 0.1 wt% to 100 wt% ARC1, 0.1 wt% to 100 wt% ARC2, 0.1 wt% to 80 wt% ARC3, 0.1 wt% to 50 wt% ARC4, 0.1 wt% to 50 wt% ARC5, 0.1 wt% to 25 wt% ARC6, 0.1 wt% to 25 wt% ARC7, 0 wt% to 10 wt% ARC8, 0 wt% to 10 wt% ARC9, 0 wt% to 5 wt% ARC10+, based on the total weight of the isotropic pitch composition.

[0133] Element 14: wherein heat treating is heat soaking and/or deasphalting.

[0134] Element 15: wherein deasphalting is carried out at a temperature ranging from room temperature to 280°C, at a pressure ranging from ambient pressure to 700 psi, and/or at a reaction time ranging from about 1 hour to 3 hours.

5 [0135] Element 16: wherein solvent used for deasphalting is selected from the group consisting of: toluene, heptane, or combination of the two at various ratios.

[0136] Element 17: wherein heat treating is carried out at a pressure ranging from ambient pressure to 1,000 psi.

10 [0137] Element 18: wherein the mesophase pitch composition has a mesophase content ranging from about 40 vol% to about 100 vol%, based on the total volume of the mesophase pitch composition.

[0138] Element 19: A fiber, an oxidized fiber, carbonized fiber, graphitized fiber, fiber web, oxidized fiber web, carbonized fiber web, or graphitized fiber web prepared using the mesophase pitch composition of any of the preceding elements.

15 [0139] By way of non-limiting example, exemplary combinations applicable to A include, but are not limited to: 1 or 2, and 3; 1 or 2, and 4; 1 or 2, and 5; 1 or 2, and 6; 1 or 2, and 7; 1 or 2, and 8; 1 or 2, and 9; 1 or 2, and 10; 1 or 2, and 11; 1 or 2, and 12; 1 or 2, and 13; 1 or 2, and 14; 1 or 2, and 15; 1 or 2, and 16; 1 or 2, and 17; 1 or 2, and 18; 1 or 2, and 19; 1 or 2, and 6 and 7; 1 or 2, and 13 and 14; 15 and 16.

20 [0140] By way of non-limiting example, exemplary combinations applicable to B include, but are not limited to: 1 or 2, and 3; 1 or 2, and 4; 1 or 2, and 5; 1 or 2, and 6; 1 or 2, and 7; 1 or 2, and 8; 1 or 2, and 9; 1 or 2, and 10; 1 or 2, and 11; 1 or 2, and 12; 1 or 2, and 13; 1 or 2, and 14; 1 or 2, and 15; 1 or 2, and 16; 1 or 2, and 17; 1 or 2, and 18; 1 or 2, and 19; 1 or 2, and 6 and 7; 1 or 2, and 13 and 14; 15 and 16; 1 or 2, and 18 and 19.

25 [0141] To facilitate a better understanding of the embodiments of the present disclosure, the following examples of preferred or representative embodiments are given. In no way should the following examples be read to limit, or to define, the scope of the invention.

EXAMPLES

30 [0142] All solvents and reagents with the exception of AROMATIC-200™ Fluid were purchased from Sigma Aldrich or Fisher Scientific and used as received without further purification. Unless otherwise specified, all reactions were carried out under standards N₂ atmosphere. AROMATIC-200™ Fluid (“naphthalene-free” grade), also referred to as AR-200™ (e.g., SOLVESSO™ 200 Fluid) was obtained from ExxonMobil Chemical Company and used as received.

[0143] General Procedure for the Synthesis of the Isotropic Pitch Compositions: To a 3-neck round bottom flask was added aromatic molecules (1 molar equivalent), 18M sulfuric acid (2 molar equivalent), and acetic acid (make up to 200 mL total volume). A dropper funnel containing a solution of formaldehyde (3 molar equivalent, 35 wt% in water, or paraformaldehyde pre-dissolved in dilute NaOH) was attached to the 3-neck round bottom flask. Under rapid stirring (either with a large stir bar or with a mechanical stirrer, depending on reaction scale), the mixture is heated to 100°C. When temperature reached 60°C, the solution of formaldehyde was added dropwise very slowly to the mixture over a period of 2.5 hours to 3 hours, while the reaction mixture continued to heat up and maintained at a temperature ranging from 90°C to 100°C. Upon complete addition, the mixture was further heated at 100°C for an additional 1 hour to 3 hours, after which the mixture was cooled to room temperature. Water was added and the slurry mixture was filtered, and the solid content washed thoroughly with dilute ammonia or sodium hydroxide, and finally with water to obtain either a gel like or a powdery residue (depending on reaction condition and aromatic starting material used).

[0144] Table 1 illustrates the reaction conditions and properties of the isotropic pitch compositions. Example 1 used a 1:10:3 naphthalene to sulfuric acid to formaldehyde ratio, using paraformaldehyde. Example 2 used a 1:2:3 naphthalene to sulfuric acid to formaldehyde ratio, with 35% formaldehyde solution. Example 3 used a 1:2:3 naphthalene to sulfuric acid to formaldehyde ratio, with formaldehyde solution prepared from paraformaldehyde in a dilute solution of NaOH.

Table 1.

Example	Aromatic Feedstock	Sulfur (wt%, residual sulfates)	MCR (wt%)	Softening Point, T _{sp} (°C)
1	Naphthalene	N/D	29	252
2	Naphthalene	N/D	20	145
3	Naphthalene	0.51	23	86
4	AROMATIC-200™	0.55	25	170
5	Toluene	N/D	34	Gel-like at room temperature
6	m-xylene	0.22	18	Gel-like at room temperature
7	o-xylene	0.25	21	125
8	o-/m-/p-xylenes (in 1:2:1 molar ratio)	0.51	24	130

[0145] FIG. 1 is a laser desorption/ionization mass spectrometry (LDI-MS) of isotropic pitch composition (Example 2) showing the presence of five oligomer species including dimer, trimer, tetramer, pentamer, and hexamer. The mass spectrometry analysis of the isotropic pitch composition formed from naphthalene (Example 2) showed distribution of a range of oligomers from dimers up to hexamers (MW of 200 g/mol to 900 g/mol), with dominant species being in the trimer to pentamer range (MW of 400 g/mol to 700 g/mol).

[0146] A mild thermal treatment of the synthesized isotropic pitch compositions (Examples 1-8) led to the formation of their corresponding mesophase pitch compositions. The thermal treatment was performed at a temperature sufficient to induce dehydrogenative-cyclization within each oligomer of the isotropic pitch composition, and not high enough in order to prevent thermal cracking. The reaction conditions and properties of the pitch compositions are illustrated in Table 2.

[0147] Each methylene-linkage between aromatic molecules served as a mean of cyclization. The thermal treatment (*e.g.*, heat soaking) was carried out at a temperature ranging from 300°C to 420°C, which is well below conventional thermal conversion processes (*i.e.*; typically ranging from 420°C to 550°C) for pitch production. Table 2 shows the results of the mesophase pitch compositions (Examples 9-11) obtained from the thermal treatment of the isotropic pitch composition (Example 2) comprising naphthalene based oligomers, at a temperature ranging from 300°C to 350°C. MCR values for the mesophase pitch compositions (Examples 9-11) were higher than the MCR value of the isotropic pitch composition (Example 2). T_{sp} values for the mesophase pitch compositions (Examples 9-11) were higher than the T_{sp} value of the isotropic pitch composition (Example 2), noting that, as the temperature of the thermal treatment increased, T_{sp} of the mesophase pitch composition decreased. Examples 9-11 did not contain any mesophase. Results obtained for Examples 9-11 highlight the minimum temperature requirements for mesophase formation.

Table 2.

Example	Heat Soak Time (Hours)	Temperature (°C)	Pressure (psi)	Starting MCR (wt%)	Ending MCR (wt%)
9	2	300	ambient	20%	31%
10	2	325	ambient	20%	27%
11	2	350	ambient	20%	28%

Table 2 (continued).

Example	Starting Softening Point, T _{sp} (°C)	Ending Softening Point, T _{sp} (°C)	Mesophase content (vol%)
9	145	175	0
10	145	172	0
11	145	160	0

[0148] FIG. 2 is a laser desorption/ionization mass spectrometry (LDI-MS) of Example 2
 5 its corresponding mesotrophic pitch compositions (Examples 9-11) after heat soaking treatment. Significantly condensed molecules were observed for Examples 9 and 10.

[0149] FIG. 3 is a graph depicting the distribution of the oligomers comprised in the mesophase pitch compositions (Examples 9-11). Fig. 3 shows that tetramer was the major product obtained after heat soaking of Example 2.

10 [0150] Mass spectroscopy analysis revealed that the thermally treated isotropic pitch compositions underwent dehydrogenative cyclization reactions to result in new molecules of very little carbon number change, with mild to severe hydrogen deficiency. FIGS. 4A and 4B depict the mass spectrometry of isotropic pitch composition (Example 2) and its corresponding mesotrophic pitch compositions (Examples 9-11) after heat soaking treatment. Broadband
 15 spectra revealed the extent of the condensation as the temperature of the heat treatment increased. Condensed molecules with increased heat were observed (see FIG. 4B). For species of the same carbon number, a loss of up to 8 hydrogen atoms was observed in the treated samples, this not only indicates cyclization but it is also evidence for extensive aromatization reactions. The resulting species are thought to be highly conjugated aromatic species which
 20 are desirable molecules for high quality pitches.

[0151] FIG. 5 is a mass spectrometry depicting the C32 assignments of the mesotrophic pitch composition (Example 10) after heat soaking treatment.

[0152] FIG. 6 a mass spectrometry of the isotropic pitch composition (Example 2) and its corresponding mesotrophic pitch composition (Example 10) after heat soaking treatment,
 25 depicting the reaction mechanism for the formation of the mesophase and the carbon number redistribution.

[0153] Table 3 illustrates the conditions and the results obtained after thermal treatment of an AROMATIC-200™-based isotropic pitch composition (mesophase pitch compositions Examples 12 and 13). The thermal treatment was carried out in an autoclave for 3 hours, at

420°C, at a pressure of 300 psi, as follow: AROMATIC-200™ was first loaded in a scintillation vial, and the vial was then inserted open ended into the autoclave pre-loaded with quartz sand. The entire set up stimulated an “open” thermal treatment at pressure, where gaseous materials were allowed to escape from the vial during the reaction, but not necessarily recovered inside the vial at the end of the reaction.

[0154] FIG. 7 is a polarized light microscopy of Example 12 depicting large mesophase domains, thus showing that the resulting solid residue (20% isolated recovery) exhibited large mesophase domains (i.e., the white domains showed in FIG. 7).

[0155] FIG. 8 is a laser desorption/ionization mass spectrometry (LDI-MS) of mesophase pitch composition Example 12.

Table 3.

Example	Heat Soak Time (hours)	Temperature (°C)	Pressure (psi)	Starting MCR (wt%)	Ending MCR (wt%)
12	3	420	300	25%	87%
13	3	420	300	24%	100%

Table 3 (continued).

Example	Starting Softening Point T _{sp} (°C)	Ending Softening Point T _{sp} (°C)	Mesophase content (vol%)
12	170	>400	>80
13	130	>400	>80

[0156] Table 4 illustrates the conditions and the results obtained after thermal treatment of an 1-methylnaphthalene-formaldehyde based isotropic pitch composition. Example 14 was performed in a reactor (conventional autoclave) at 300 psi where light molecules were allowed to condense back into product residue after reaction. The recovered residue had a low melting point of about 50°C and no mesophase. The recovered residue was further treated via deasphalting, using a solvent mixture of heptane/toluene (70:30, v/v), at a solvent to sample ratio of 10, thus yielding the production of mesophase (60% mesophase). FIG. 9 is a polarized light microscopy of Example 15 depicting large mesophase domains. (i.e., the white domains showed in FIG. 9).

Table 4.

Example	Heat Soak Time (hours)	Temperature (°C)	Pressure (psi)
14	2	450	300
15	1	280	700

Table 4 (continued).

Example	Starting Softening Point T_{sp} (°C)	Starting MCR (wt%)	Ending MCR (wt%)	Mesophase content (vol%)
14	180	29	60	0
15		60	76	60

5 **[0157]** All documents described herein are incorporated by reference herein for purposes of all jurisdictions where such practice is allowed, including any priority documents and/or testing procedures to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while forms of the disclosure have been illustrated and described, various modifications can be made without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the disclosure be limited thereby. For example, the compositions described herein may be free of any component, or composition not expressly recited or disclosed herein. Any method may lack any step not recited or disclosed herein. Likewise, the term “comprising” is considered synonymous with the term “including.” Whenever a method, composition, element or group of elements is preceded with the transitional phrase “comprising,” it is understood that we also contemplate the same composition or group of elements with transitional phrases “consisting essentially of,” “consisting of,” “selected from the group of consisting of,” or “is” preceding the recitation of the composition, element, or elements and vice versa.

15 **[0158]** One or more illustrative incarnations incorporating one or more invention elements are presented herein. Not all features of a physical implementation are described or shown in this application for the sake of clarity. It is understood that in the development of a physical embodiment incorporating one or more elements of the present invention, numerous implementation-specific decisions must be made to achieve the developer's goals, such as compliance with system-related, business-related, government-related and other constraints, which vary by implementation and from time to time. While a developer's efforts might be

time-consuming, such efforts would be, nevertheless, a routine undertaking for those of ordinary skill in the art and having benefit of this disclosure.

[0159] Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth used in the present specification and associated claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the embodiments of the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claim, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0160] Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed, including the lower limit and upper limit. In particular, every range of values (of the form, “from about a to about b,” or, equivalently, “from approximately a to b,” or, equivalently, “from approximately a-b”) disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles “a” or “an,” as used in the claims, are defined herein to mean one or more than one of the element that it introduces.

[0161] Therefore, the present disclosure is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present disclosure may be modified and practiced in different but equivalent manners apparent to one having ordinary skill in the art and having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered, combined, or modified and all such variations are considered within the scope and spirit of the present disclosure. The embodiments illustratively disclosed herein suitably may be practiced in the absence of any element that is not specifically disclosed herein and/or any optional element disclosed herein.

CLAIMS

What is claimed is:

1. A method comprising:

heat treating an isotropic pitch composition comprising two or more unsubstituted aromatics and/or substituted aromatics linked with at least one methylene bridge between each unsubstituted aromatics and/or substituted aromatics, at a temperature of 300°C to 500°C to produce a mesophase pitch composition having a weight average molecular weight (Mw) of 300 g/mol to 2,000 g/mol, a softening point (T_{sp}) of 100°C or greater, a mesophase content of 0.01 vol% to 100 vol%, based on the total volume of the mesophase pitch composition, and a micro carbon residue (MCR) of 25 wt% or greater, based on the total weight of the mesophase pitch composition;

wherein heat treating induces cyclization between at least two of the two or more unsubstituted aromatics and/or substituted aromatics to form one or more 5-membered rings and/or 6-membered rings.

2. The method of claim 1, wherein each one of the two or more unsubstituted aromatics and/or substituted aromatics is selected from the group consisting of 1-membered ring aromatics (ARC1), 2-membered ring aromatics (ARC2), 3-membered ring aromatics (ARC3), 4-membered aromatics (ARC4), 5-membered ring aromatics (ARC5), 6-membered ring aromatics (ARC6), 7-membered ring aromatics (ARC7), 8-membered ring aromatics (ARC8), 9-membered ring aromatics (ARC9), 10 or more-membered ring aromatics (ARC10+), and any combination thereof.

3. The method of claim 2, wherein the substituted aromatics are selected from the group consisting of C_1 to C_{20} hydrocarbyl monosubstituted aromatics, C_1 to C_{20} hydrocarbyl disubstituted aromatics, C_1 to C_{20} hydrocarbyl trisubstituted aromatics, and any combination thereof.

4. The method of claim 1, wherein cyclization between at least two of the two or more unsubstituted aromatics and/or substituted aromatics to form one or more 6-membered rings is followed by dehydrogenative aromatization to produce a highly aromatic mesophase pitch composition.

5. The method of claim 1, wherein the isotropic pitch composition is produced by: mixing an aromatic feedstock comprising the two or more unsubstituted aromatics and/or substituted aromatics with acetic acid and sulfuric acid, to produce a first mixture;

heating the first mixture at a temperature of 40°C to 400°C;

5 adding formaldehyde and/or paraformaldehyde to the first mixture at a temperature of 40°C to 400°C to produce a second mixture comprising a reaction products composition;

filtering the second mixture; and

isolating the isotropic pitch composition.

10 6. The method of claim 1, wherein the isotropic pitch composition has a weight average molecular weight (Mw) of 300 g/mol to 2,000 g/mol, a softening point (T_{sp}) of 50°C or greater, and a micro carbon residue (MCR) of 15 wt% or greater, based on the total weight of the isotropic pitch composition.

15 7. The method of claim 1, wherein each one of the two or more unsubstituted aromatics and/or substituted aromatics comprise partially hydrogenated aromatic rings.

8. The method of claim 1, wherein each one of the two or more unsubstituted aromatics and/or substituted aromatics are selected from the group consisting of benzene, toluene,
20 xylenes (such as ortho-, meta-, para-xylene), naphthalene, 1-methyl naphthalene, 2-methyl naphthalene, anthracene, phenanthrene, pyrene, benzopyrene, picenecoronene, chrysene, tetracene, pentacene, triphenylene, corannulene, benzo[j]fluoranthene, Benzo[c]fluorene, perylene, benzo-perylene, ovalene, AROMATIC-200™, and any combination thereof.

25 9. The method of claim 5, wherein the molar ratio aromatic feedstock: formaldehyde equivalence is from 10:1 to 1:10.

10. The method of claim 5, wherein the molar ratio aromatic feedstock: formaldehyde equivalence is 1:3.

30

11. The method of claim 5, wherein the molar ratio aromatic feedstock: sulfuric acid is from 1:0.001 to 1:20.

12. The method of claim 5, wherein the molar ratio aromatic feedstock: sulfuric acid is 1:2.

35

13. The methods of claim 1, wherein the isotropic pitch composition comprises: 0.1 wt% to 100 wt% ARC1, 0.1 wt% to 100 wt% ARC2, 0.1 wt% to 100 wt% ARC3, 0.1 wt% to

100 wt% ARC4, 0.1 wt% to 100 wt% ARC5, 0.1 wt% to 100 wt% ARC6, 0.1 wt% to 100 wt% ARC7, 0.1 wt% to 100 wt% ARC8, 0.1 wt% to 100 wt% ARC9, 0.1 wt% to 100 wt% ARC10+, based on the total weight of the isotropic pitch composition.

5 14. The methods of claim 1, wherein the isotropic pitch composition comprises: 0.1 wt% to 100 wt% ARC1, 0.1 wt% to 100 wt% ARC2, 0.1 wt% to 80 wt% ARC3, 0.1 wt% to 50 wt% ARC4, 0.1 wt% to 50 wt% ARC5, 0.1 wt% to 25 wt% ARC6, 0.1 wt% to 25 wt% ARC7, 0 wt% to 10 wt% ARC8, 0 wt% to 10 wt% ARC9, 0 wt% to 5 wt% ARC10+, based on the total weight of the isotropic pitch composition.

10 15. The methods of claim 1, wherein heat treating is heat soaking and/or deasphalting that is carried out at a temperature ranging from room temperature to 280°C, at a pressure ranging from ambient pressure to 700 psi, and/or at a reaction time ranging from 1 hour to 3 hours, wherein solvent used for deasphalting is selected from the group consisting of: toluene,
15 heptane, or combination of the two at various ratios, and wherein heat treating is carried out at a pressure ranging from ambient pressure to 1,000 psi.

16. The methods of claim 12, wherein the mesophase pitch composition has a mesophase content ranging from 40 vol% to 100 vol%, based on the total volume of the mesophase pitch
20 composition.

17. A fiber, an oxidized fiber, carbonized fiber, graphitized fiber, fiber web, oxidized fiber web, carbonized fiber web, or graphitized fiber web prepared using the mesophase pitch composition of claim 1.

25 18. A mesophase pitch composition comprising:
a weight average molecular weight (M_w) of 300 g/mol to 2,000 g/mol, a softening point (T_{sp}) of 100°C or greater, a mesophase content of 0.01 vol% to 100 vol%, based on the total volume of the mesophase pitch composition, and a micro carbon residue (MCR) of 25 wt% or
30 greater, based on the total weight of the mesophase pitch composition;

wherein the mesophase pitch composition is produced from an isotropic pitch composition having two or more unsubstituted aromatics and/or substituted aromatics linked with at least one methylene bridge between each unsubstituted aromatics and/or substituted aromatics; and

35 wherein the isotropic pitch composition has a weight average molecular weight (M_w) of 300 g/mol to 2,000 g/mol, a softening point (T_{sp}) of 50°C or greater, and a micro carbon

residue (MCR) of 15 wt% or greater, based on the total weight of the isotropic pitch composition.

19. The mesophase pitch composition of claim 18, wherein each one of the two or more
5 unsubstituted aromatics and/or substituted aromatics is selected from the group consisting of
1-membered ring aromatics (ARC1), 2-membered ring aromatics (ARC2), 3-membered ring
aromatics (ARC3), 4-membered aromatics (ARC4), 5-membered ring aromatics (ARC5), 6-
membered ring aromatics (ARC6), 7-membered ring aromatics (ARC7), 8-membered ring
aromatics (ARC8), 9-membered ring aromatics (ARC9), 10 or more-membered ring aromatics
10 (ARC10+), and any combination thereof.

20. The mesophase pitch composition of claim 18, wherein the isotropic pitch composition
comprises: 0.1 wt% to 100 wt% ARC1, 0.1 wt% to 100 wt% ARC2, 0.1 wt% to 80 wt% ARC3,
0.1 wt% to 50 wt% ARC4, 0.1 wt% to 50 wt% ARC5, 0.1 wt% to 25 wt% ARC6, 0.1 wt% to
15 25 wt% ARC7, 0 wt% to 10 wt% ARC8, 0 wt% to 10 wt% ARC9, 0 wt% to 5 wt% ARC10+,
based on the total weight of the isotropic pitch composition.