

PITCH COMPOSITIONS AND METHODS RELATED THERETO

FIELD OF THE INVENTION

[0001] The present disclosure relates to pitch compositions, and more particularly to controlled
5 pitch composition properties and methods for their production and use.

BACKGROUND OF THE INVENTION

[0002] Pitch is a carbon-containing feedstock which can be classified as an isotropic pitch, or
a mesophase pitch. Both isotropic and mesophase pitch can be complex mixtures of aromatic
molecules; however, the aromatic molecules in an isotropic pitch are randomly oriented, whereas
10 in a mesophase pitch, at least a portion of these aromatic molecules are ordered. A mesophase
pitch may have a heterogeneous two-phase structure comprising the said ordered aromatic
molecules (*e.g.*, anisotropic region), and an isotropic region. In general, an isotropic pitch
formation precedes a mesophase pitch formation. Both types of pitches will be collectively
referred to herein as “pitch,” unless otherwise indicated.

15 [0003] Pitch can be produced from petroleum, coal tar, biomass tar, or from an acid-catalyzed
oligomerization of small molecules (*e.g.*, naphthalene) feedstocks, for example. Typical chemical
components of pitch include, but are not limited to from alkanes, cycloalkanes, aromatics,
hydroaromatics, phenols, alkenes, ketones, carboxylic acids, sulfur-containing compounds,
oxygen-containing compounds, and nitrogen-containing compounds. These components depend
20 on the starting feedstock and process conditions.

[0004] Pitch is used in a number of product applications, such as carbon fiber, binder pitch,
impregnation pitch, and the like. Major markets for pitch include, but are not limited to, pitch for
high-performance and general purpose carbon fiber, refractories, carbon/carbon composites,
synthetic graphite, and graphite parts; binder and impregnated pitch for electrodes; binder and
25 impregnated aluminum production anodes and cathodes; impregnated pitch for steel electric arc
furnace electrodes; mesocarbon microbeads for anodes for lithium ion batteries; carbon foam for
heat transfer applications^{12, 13} and sound absorbers; roofing products; lubricants; consumer
products (*e.g.*, cosmetics); and the like.

[0005] Given the wide chemical diversity of pitch, pitch properties are at least dependent upon,
30 but not limited to, its feedstock, production (*e.g.*, pyrolysis), and separation (*e.g.*, distillation)
conditions. Depending on the particular end-use, different pitch properties are specified and have
its own unique range of acceptable specification values, such as, but not limited to, value ranges
for softening point, microcarbon residue, percent (%) mesophase, and other applicable properties.
However, there is no current method of predicting and controlling these properties and the typical

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means of obtaining suitable pitch property specifications for a particular end-use is merely based on trial-and-error and past experience, requiring significant costs at least in terms of manufacturing time and raw materials (*e.g.*, pitch material). Indeed, such trial-and-error approaches require many sets of experiments on multiple different conditions and product properties before arriving at the desired pitch properties. Tremendous research and development effort has been expended to identify appropriate feeds and processes to make certain commercial pitches, such as ASHLAND A240, as well as suitable pitch blends, such as for binder pitch, which prove untenable when pitch feedstock is invariant. Moreover, this trial-and-error approach fails to consider pitch composition and is only effective if pitch composition remains nearly invariant. If large volume markets are desired for new pitch products, such as carbon fiber composites for infrastructure applications, feedstock variability is inevitable and thus pitch composition is consistently variant, making the trial-and-error approach even more objectionable.

[0006] Accordingly, a method enabling controlled pitch composition production with tailored and reproducible properties is highly desired.

SUMMARY

[0007] In nonlimiting aspects of the present disclosure, a composition including a pitch composition having one or both of an A-Factor in the range of about 0.4 to about 0.8 and/or an Aromaticity in the range of about 0.3 to about 1.3.

[0008] In nonlimiting aspects of the present disclosure, a method is provided including pyrolyzing at least a first pitch composition from a first pitch feed and a second pitch composition from a second pitch feed; wherein the pyrolyzing of the first pitch composition and the second pitch composition are performed separately. A first infrared spectrum is obtained of the at least first pitch composition and selecting at least one first infrared parameter based on (1) the first infrared spectrum and a calibration curve or (2) the first infrared spectrum and chemometric modeling. A second infrared spectrum is obtained of the at least second pitch composition and selecting at least one second infrared parameter based on (1) the second infrared spectrum and a calibration curve or (2) the second infrared spectrum and chemometric modeling. The selected first and second infrared parameters are at least one or both of an A-Factor in a range of about 0.4 to about 0.8 and/or an Aromaticity in a range of about 0.3 to about 1.3 and the first and second pitch compositions are blended in a ratio to achieve the selected first and second infrared parameters, thereby forming a blended pitch composition.

[0009] In nonlimiting aspects of the present disclosure, a method is provided including extruding a pitch composition to produce a green carbon fiber and thereafter, stabilizing the extruded pitch composition. The stabilizing comprises obtaining an infrared spectrum of the

extruded pitch composition and selecting at least one infrared parameter based on (1) the first infrared spectrum and a calibration curve or (2) the first infrared spectrum and chemometric modeling, wherein the at least one infrared parameter is at least an A-Factor and an Aromaticity. Stabilization is ceased based upon the at least one infrared parameter.

- 5 [0010] These and other features and attributes of the disclosed methods for producing pitch compositions having tailored and reproducible properties of the present disclosure and their advantageous applications and/or uses will be apparent from the detailed description which follows.

BRIEF DESCRIPTION OF THE DRAWINGS

- 10 [0011] To assist those of ordinary skill in the relevant art in making and using the subject matter hereof, reference is made to the appended drawings. The following figures are included to illustrate certain aspects of the disclosure, and 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
15 of this disclosure.

[0012] FIGS. 1A-1D shows diffuse reflectance infrared Fourier transform (DRIFT) spectra of pitch samples, according to one or more aspects of the present disclosure.

- [0013] FIGS. 2A-2D show trend charts for infrared parameters based on DRIFT spectra of pitch samples as they change upon pyrolysis, according to one or more aspects of the present
20 disclosure.

[0014] FIGS. 3A-3D show correlation charts between infrared parameters based on DRIFT spectra and pitch properties of pitch samples, according to one or more aspects of the present disclosure.

- [0015] FIGS. 4A-4D show parity plots for predicted pitch properties based on DRIFT structural correlations to experimental values in FIGS. 3A-3D, according to one or more aspects
25 of the present disclosure.

[0016] FIG. 5 shows a partial least squares (PLS) modeled correlation chart for a representative pitch property of pitch samples, according to one or more aspects of the present disclosure.

- [0017] FIGS. 6A-6D show parity plots for predicted pitch properties using the PLS modeled correlation to experimentally determined pitch properties, according to one or more aspects of the
30 present disclosure.

[0018] FIGS. 7A-7D show prediction charts for pitch properties of pitch samples using least squares analysis (LSA) modeled correlation, according to one or more aspects of the present disclosure.

DETAILED DESCRIPTION

[0019] The present disclosure relates to pitch compositions, and more particularly to controlled pitch composition properties and methods for their production and use.

[0020] There is a need for a methodology for the production of pitch compositions having
5 tailored and reproducible properties, which will be suitable for one or more particular end-uses. The present disclosure provides a methodology that employs compositional details to permit the rapid identification of pitch properties. In particular, disclosed herein is a method for tailoring pitch properties based on infrared structural parameters specific to pitch composition. The method described herein may be particularly suitable for, among other things, development of pitch
10 blending rules, optimization of carbon fiber spinning, informing reaction operations, and enabling scale-up of pitch-based carbon material production.

[0021] As provided hereinabove, methods of the present disclosure produce pitch compositions with tailored pitch properties; these properties include softening point, microcarbon residue, hydrogen to carbon ratio, and percent pitch volatiles. Predicting these properties can aid
15 in, among other things, end-use optimization of the production of spinnable pitches for carbon fibers, matrixes for carbon/carbon composites, and other pitch-derived carbon products, such as those described hereinabove.

[0022] The methods of the present disclosure to produce tailored pitch properties are advantageously derived based on compositional-based modeling of pitch: (1) correlations
20 (predictions) of IR parameters (*e.g.*, ratios of infrared spectroscopic absorbance bands that correlate with pitch properties), without regard to the particular pitch-producing reaction (*e.g.*, pyrolysis, air-oxidation, and the like) and (2) multivariate analysis of infrared spectra.

[0023] In other aspects, the methods of the present disclosure to produce tailored pitch properties are advantageously derived based on chemometric compositional-based modeling of
25 pitch: (1) correlations (predictions) of IR parameters (*e.g.*, ratios of infrared spectroscopic absorbance bands that correlate with pitch properties), without regard to the particular pitch type, (2) multivariate analysis of infrared spectra, and (3) partial least squares (PLS) modeling and analysis. As such, the particular correlation developed can be considered agnostic, or universal, for any particular pitch composition.

[0024] Using the methodologies of the present disclosure, properties of starting pitch compositions may be used to inform a composition of a blended pitch in order to satisfy a particular
30 desired pitch value or range. In particular, infrared spectra are added together from various pitch compositions to generate a pitch blend with the particular desired property or properties, or a PLS model can be used. Because the pitch blend ratio is dependent upon the starting pitch blend

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composition, it will be appreciated that multiple solutions, using multiple starting pitch compositions, may be advantageously used to achieve the desired, ultimate pitch properties. As such, the methods of the present disclosure, and compositions produced therefrom, are capable of substantial customization and rapid identification of suitable (and unsuitable) starting pitch compositions and blends, without the traditional trial-and-error method involving substantial resources.

Definitions and Test Methods

[0025] 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 or “RT”) is about 25°C.

[0026] As used in the present disclosure and claims, the singular forms “a,” “an,” and “the” include plural forms unless the context clearly dictates otherwise.

[0027] 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.”

[0028] For the purposes of the present disclosure and the claims thereto, the following definitions shall be used.

[0029] As used herein, the term “pitch,” or “pitch composition,” and grammatical variants thereof, includes petroleum pitch, coal tar pitch, natural asphalt, biomass pitch, pitch produced from oligomerization and/or polymerization of aromatics, and pitch obtained as a by-product in the naphtha cracking industry.

[0030] The term “pyrolysis” or “pyrolysing,” and grammatical variants thereof, refers to thermal reactions induced by high temperatures (*e.g.*, dehydrogenation, cyclization, cracking, condensation, and the like).

[0031] The term “softening point” or “SP,” and grammatical variants, as used herein, refers to a temperature or a range of temperatures at which a substance softens. Herein, the softening point is measured using a METTLER TOLEDO dropping point instrument, such as METTLER TOLEDO DP70, according to a procedure analogous to the American Society for Testing and Materials (ASTM) ASTM D3104-14a.

[0032] As used herein, the term “microcarbon residue” or “MCR,” and grammatical variants thereof, refers to an amount of carbonaceous residue formed after evaporation and pyrolysis of petroleum materials under particular conditions. The term “microcarbon residue test” or “MCRT,” and grammatical variants thereof, as used herein, refers to a standard method for the determination of MCR and is measured according to ASTM D4530 (2020).

[0033] As used herein, the term “mesocarbon microbead,” refers to a porous graphite carbon material wherein an inner core is composed of amorphous carbon while an outer shell is composed of graphitic carbon. Both the inner core and the outer shell are porous. The mesocarbon microbeads have an diameter ranging from 10 microns to 100 microns.

5 **[0034]** As used herein, the term “hydrogen to carbon ratio” or “H/C Ratio,” and grammatical variants thereof, refers to an amount of elemental hydrogen to elemental carbon within a pitch composition. The H/C Ratio is measured according to ASTM D5291-21.

[0035] The term “percent pitch volatiles” or “%PV,” and grammatical variants thereof, refers to the amount of volatile substances, which may be airborne, within a pitch composition upon
10 heating, such as pyrene, phenanthrene, acridine, chrysene, anthracene, and benzo(a)pyrene. The %PV is measured by recording the mass loss after a given pyrolysis reaction. The %PV varies with each experiment because the temperatures and times used vary with each experiment. When measured by weight, the percent pitch volatiles is measured by weight, it is referred to herein as “wt%PV.”

15 **[0036]** The H/C Ratio may be referred to herein as “elemental analysis.”

[0037] The term “infrared parameter” or “IR structural parameter,” or simply “IR parameter,” and grammatical variants thereof, as used herein, refers to Methyl-to-Methylene Ratio, A-Factor, Aromaticity, and Degree of Condensation as determined from an infrared spectrum.

[0038] As used herein, the term “Diffuse Reflectance Infrared Fourier Transform (DRIFT)
20 spectra” or “DRIFT spectroscopy,” and grammatical variants thereof refers to an FTIR spectrometer equipped with a DRIFT accessory. DRIFT spectra can provide both chemical and structural information about a measured sample. The FTIR used in the Examples described herein was a Thermo Fisher Scientific Inc. NICOLET™ 3700 FTIR spectrometer (Waltham, MA) and the DRIFT accessory used in the Examples described herein was a Pike Technologies
25 DIFFUSIR™ (Madison, WI). The FTIR spectrometer was further equipped with a Thermo Fisher Scientific Inc. deuterated triglycine sulfate (DGTS) detector

[0039] The term “Methyl-to-Methylene Ratio” or “CH₃/CH₂ Ratio,” as used herein, and grammatical variants thereof, refers to an infrared parameter in which the asymmetric stretch of CH₃ is divided by the asymmetric stretch of CH₂ of a sample based on an infrared spectrum. The
30 CH₃/CH₂ Ratio provides an indicator of aliphatic chain length and/or the degree of branching of aliphatic moieties approximated by the CH₃ and CH₂ asymmetric stretching vibrations. Infrared absorbance band heights (intensities) or integrated areas may be used to develop calculated ratios. For example, based on center of integration in wavenumber space, the CH₃/CH₂ Ratio = I₂₉₆₀ ÷ I₂₉₁₈.

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[0040] As used herein, the term “A-Factor,” and grammatical variants thereof refers to an infrared parameter correlating aliphatic and aromatic content of a sample based on an infrared spectrum. The A-factor expresses changes in the integrated intensities of absorbance from aliphatic CH₂ relative to aromatic C=C ring stretching vibrations of a sample. Based on center of
5 integration in wavenumber space, the A-Factor = $[I_{2850} + I_{2918}] \div [I_{2850} + I_{2918} + I_{1600}]$.

[0041] As used herein, the term “Aromaticity,” and grammatical variants thereof refers to an infrared parameter representative of the ratio of aromatic C-H stretching to the absorbance from CH₃ and CH₂ vibrations of a sample based on an infrared spectrum. The Aromaticity is an indicator of the relative amount of aromatic versus aliphatic carbon content in a sample. Based on center of
10 integration in wavenumber space, the Aromaticity = $I_{3000} / [I_{2960} + I_{2918} + I_{2870} + I_{2850}]$.

[0042] The term “Degree of Condensation” or “DoC,” and grammatical variants thereof, as used herein, refers to the ratio of aromatic C-H stretching to aromatic C=C ring stretching of a sample based on an infrared spectrum. The DoC represents the number of hydrogens directly bonded to ring structures, indicative of the degree of aromatic substitution versus ring condensation
15 of a sample. Based on center of integration in wavenumber space, the DoC = I_{3000} / I_{1600} .

[0043] The center of integration in wavenumber space term “I₂₉₆₀” is representative of the asymmetric stretch of CH₃, and is herein calculated, for example, but not limited to, from 2941 cm⁻¹ to 2991 cm⁻¹.

[0044] The center of integration in wavenumber space term “I₂₉₁₈” is representative of the asymmetric stretch of CH₂, and is herein calculated, for example, but not limited to, from 2902 cm⁻¹ to 2941 cm⁻¹.
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[0045] The center of integration in wavenumber space term “I₂₈₅₀” is representative of the symmetric stretch of CH₂, and is herein calculated, for example, but not limited to, from 2819 to 2864 cm⁻¹.

[0046] The center of integration in wavenumber space term “I₁₆₀₀” is representative of the aromatic C=C ring stretch, and is herein calculated, for example, but not limited to, from 1570 to 1632 cm⁻¹.
25

[0047] The center of integration in wavenumber space term “I₃₀₀₀” is representative of the aromatic C-H stretch, and is herein calculated, for example, but not limited to, from 2991 cm⁻¹ to 3101 cm⁻¹.
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[0048] The center of integration in wavenumber space term “I₂₈₇₀” is representative of the symmetric stretch of CH₃, and is herein calculated, for example, but not limited to, from 2864 cm⁻¹ to 2889 cm⁻¹.

Methods of Making Pitch Compositions

[0049] The present disclosure provides a method comprising blending two or more prepared pitch compositions, measuring their infrared structural parameters, and selecting at least one final structural IR parameter based upon a calibration curve or chemometric modeling. The two or more
5 prepared pitch compositions are thereafter blended to achieve a resultant blended pitch composition having the desired final infrared structural parameter(s).

[0050] Pitch is prepared by (or otherwise the residual product of) pyrolysis of various feedstock sources, such as petroleum, coal tar, biomass tar, or from an acid-catalyzed oligomerization of small molecules (*e.g.*, naphthalene), as described above, and is itself an intermediate product. The
10 pyrolysis of the pitch for use in the various methods described herein is performed in a pyrolysis reactor at a temperature in the range of about 200°C to about 600°C, encompassing any value and subset therebetween, such as about 200°C to about 500°C, or about 200°C to about 400°C, or about 200°C to about 300°C, or about 300°C to about 600°C, or about 400°C to about 500°C, or about 500°C to about 600°C. A gas may be present in the reactor, which may include one or more or all
15 of hydrogen, air, oxygen, hydrogen peroxide, carbon monoxide, carbon dioxide, formic acid, nitrogen dioxide, and/or ozone, for example. Other suitable pyrolysis gases may also be suitable, without departing from the scope of the present disclosure. Further, the pyrolysis reactor is operated at a pressure ranging from about 0.3 to 2,500 pounds per square inch (psi), or about from 0.3 to about 100 psi, or about 1 to about 75 psi, or about 5 to about 50 psi, or about 10 to about 25
20 psi, or about 50 to about 2,000 psi, or about 100 to about 1,500 psi, or about 200 to about 1,000 psi, or about 400 to about 1,000 psi, or about 500 to about 1,000 psi. After pyrolysis, a resultant pitch effluent may be further separated to obtain the desired pitch, such as by distillation separation, deasphalting separation, membrane separation, and any combination thereof. Accordingly, the present disclosure provides for preparation of pitch compositions as described herein for further
25 analysis to determine pitch properties and suitable blending ratios based on desired structural parameters.

[0051] In one or more aspects of the present disclosure, the pyrolysis reaction may be used to tailor a pitch composition having one or more undesirable structural properties, as described herein below. That is, a particular pitch feed (also referred to herein as “feedstock” interchangeably) may
30 have certain undesirable IR parameter(s) and the feed pyrolyzed to achieve the desired IR parameters (and resultant pitch properties) by adjusting the pyrolysis reaction conditions. For example, in one or more aspects, a desired pitch may preferably have one or both of an A-Factor in the range of about 0.6 to about 0.8 and/or an Aromaticity in the range of about 0.3 to about 0.6 but the pitch feed has dissimilar IR parameters; or a desired pitch may preferably have one or both

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of an A-Factor in the range of about 0.4 to about 0.6 and/or an Aromaticity in the range of about 0.5 to about 0.8 but the pitch feed has dissimilar IR parameters. In each case, the feed may be fed into a pyrolysis reactor at a temperature in the range of about 200°C to about 600°C and a pressure above about 0.3 psi to achieve the particular desired pitch IR parameters (and thus structural properties). Thereafter, the pitch effluent may be separated, as described herein. When at least two pitch compositions are blended, two pyrolysis reactions are conducted on separate pitch feeds, two optional separations performed separately, two infrared spectrums measured separately, and two selections of desired IR parameter(s) performed separately prior to the blending.

[0052] Moreover, the structural properties of the present disclosure may be measured (using DRIFT or other IR technique, or other techniques with the ability to measure or approximate the intensities of the vibrational bands described above, such techniques as Raman, photothermal, photoacoustic, Multivariate optical computing, spectrophotometers, filter photometers, and the like) after the prepared pitch compositions exit the reactor, including in-line with a carbon fiber (e.g., green carbon fiber) manufacturing process wherein the infrared spectrum is measured (using DRIFT or other IR technique) and IR parameters selected after the carbon fiber exits an extrusion die and is undergoing stabilization in a carbon fiber stabilization process including contacting the carbon fiber with a reactive gas (*i.e.*, reaction zone), termed air-stabilization or air-oxidation. The IR parameters can be utilized to cease stabilization once desired IR parameters are reached, as described herein below. The reactive gas may include any of those listed hereinabove that are oxidizing gases, as well as hydrogen peroxide and nitrogen dioxide, without limitation and in any combination.

[0053] The spinning zone may be a spinneret that operates in the temperature range relative to the softening point of the pitch of about $T_{sp} - 10^{\circ}\text{C}$ to about $T_{sp} + 50^{\circ}\text{C}$, typically from about 50°C to about 500°C, or in some instances 350°C, encompassing any value and subset therebetween, under an inert environment. A spinneret is a type of die for extruding carbon fiber filaments, such as through small holes. In some embodiments, the pitch composition may be blown through an extrusion die, such as a spinneret or other suitable die. After the filament, or extruded product, has been formed, it can be oxidized in a reaction zone. The reaction zone may be an oven, such as a batch oven or continuous oven that is able to heat the fiber or molded product to a temperature in the range of about -5°C to about 50°C, encompassing any value and subset therebetween, in the presence of the reactive gases. In one or more aspects, the extruded pitch composition for forming the carbon fiber may be spooled prior to contact with the reactive gas.

[0054] Significant reactions can occur as a result of the pyrolysis, based on thermal reactions proceeding by radical reactions initiated by homolytic bond scission, which can alter the

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composition and/or properties of the pitch; such reactions may include, but are not limited to, dealkylation (*e.g.*, demethylization), dehydrogenation, cyclization, condensation reactions, and the like, and combinations thereof. If these pyrolysis reactions permit off-gassing, then separation of low molecular weight species from the higher molecular weight compounds can occur, as well. In order to account for these potential significant changes, the present disclosure uses infrared spectroscopy and multivariate analysis to blend pitch compositions together to achieve desired compositional and structural properties.

[0055] The type of infrared spectroscopy for acquiring pitch composition infrared spectra of the present disclosure may preferably be multivariate FTIR, including a FTIR spectrometer coupled to a gas handling system (*e.g.*, N₂, air, vacuum, and the like), but it is to be appreciated that dispersive infrared spectroscopy may also be used, without departing from the scope of the present disclosure. In one or more aspects, a FTIR spectrometer may be further equipped with a Diffuse Reflectance Infrared Fourier Transform (DRIFT) accessory. The DRIFT accessory permits temperature control of samples up to 1000°C. DRIFT spectra can provide both chemical and structural information about a measured sample, which is diluted in potassium bromide (KBr), although other DRIFT spectroscopy compatible diluents may be used, without departing from the scope of the present disclosure.

[0056] In one or more aspects of the present disclosure, for DRIFT spectroscopy analysis, the sample may be diluted in KBr in the range of about 0.1 weight percent (wt%) to about 10 wt%, encompassing any value and subset therebetween, such as about 0.1 wt% to about 1 wt%, or about 0.1 wt% to about 2 wt%, or about 0.2 wt% to about 1 wt%, or about 1 wt% to about 5 wt%, or about 5 wt% to about 10 wt%.

[0057] The DRIFT spectra for use in the present disclosure may be in the range of about 200 cm⁻¹ to about 6000 cm⁻¹, encompassing any value and subset therebetween, such as in the range of about 200 cm⁻¹ to about 4000 cm⁻¹, or about 400 cm⁻¹ to about 4000 cm⁻¹, or about 400 cm⁻¹ to about 2000 cm⁻¹, or about 1000 cm⁻¹ to about 6000 cm⁻¹.

[0058] In one or more aspects of the present disclosure, acquired pitch DRIFT spectra are evaluated to determine certain structural IR parameters. These IR parameters include, but are not limited to, methyl-to-methylene ratio ("CH₃/CH₂ ratio"); A-Factor; Aromaticity; and Degree of Condensation (DoC).

[0059] It is noted that as a pitch feed is pyrolyzed, the alkyl side chains crack off and are removed from the pyrolysis system. Often, a methyl group is left on the aromatic where an alkyl group was present due to the weaker C—C bond adjacent to an aromatic ring. In general, the CH₃/CH₂ ratio increases at least due to the loss of these CH₂ units from the alkyl side chains;

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however, this is not the case for all feeds. For example, in some instances, highly aromatic steam cracker tar (*e.g.*, SOP2 samples in the Examples below) and isotropic pitch (*e.g.*, M50 samples in the Examples below) show a generally opposite trend in the CH₃/CH₂ ratio with increased pyrolysis times. Additionally, the loss in alkyl sidechains during pyrolysis generally results in a decrease in the A-Factor since this is a measure of the size of the alkyl side chains on an aromatic core and as the cracking proceeds, the chain length decreases. However, Aromaticity generally increases due to the removal of these aliphatic side chains and dehydrogenation reactions of the hydroaromatics that can occur. As pyrolysis increases, the DoC decreases due to the increase in aromaticity from cyclization, dehydrogenation, and condensation reactions. These correlations can be seen in the results of the Examples provided hereinbelow.

[0060] Further, it is observed that the prediction of pitch properties from structural IR parameters are best when using pitch specific correlations. As described with reference to the Examples hereinbelow, pitch property and the A-Factor and Aromaticity were noted to be particularly correlated.

[0061] Accordingly, the present disclosure provides methods for determining pitch properties by obtaining an infrared spectrum of a pitch composition (prepared as described herein) and correlating the obtained infrared spectrum with at least one structural IR parameter using a calibration curve. In additional aspects, the present disclosure provides methods for tailoring one or more pitch properties by obtaining a first infrared spectrum of a first pitch composition (prepared as described herein) and obtaining at least a second infrared spectrum of a second pitch composition (prepared as described herein), correlating the obtained infrared spectra with at least one structural IR parameter using a calibration curve, and blending the first and second pitch compositions in a ratio to obtain blended pitch composition having at least one desired pitch property.

[0062] As provided above, chemometric modeling of the infrared spectrum to correlate (predict) structural IR parameters may be used in accordance with the present disclosure, such as by use of multivariate statistical analysis techniques, such as, but not limited to, Partial Least Squares (PLS). It is to be appreciated, however, that other chemometric modeling types may be used without departing from the scope of the present disclosure. The chemometric approach may be particularly useful, for example, in understanding and predicting pitch properties from samples undergoing air-oxidation. Air-oxidation is an important process used in the stabilization of green carbon fibers and the air-blowing process (encompassing any reactive gas described herein) used to increase the SP of pitches. In the stabilization of green fibers, the objective is to produce an infusible solid that will not flow or stick to neighboring fibers during subsequent carbonization and

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graphitization (referred to as carbon fiber processing herein). Air-blowing's objective is to raise the SP of the pitch, but to still produce a pitch that can soften and flow at a reasonable temperature. Due to these differing objectives and processes, the resulting pitch composition is completely different. Accordingly, the chemometric approach may be particularly useful for predicting pitch composition properties, including blended pitch compositions, during stabilization of green carbon fibers, although the IR parameter methodology provided herein above can also be used for blended pitch compositions.

[0063] Accordingly, the present disclosure provides methods for determining pitch properties by obtaining an infrared spectrum of a pitch composition (prepared as described herein) and inputting the spectrum into chemometric modeling, such as PLS or other modeling technique. In additional aspects, the present disclosure provides methods for tailoring one or more pitch properties by obtaining a first infrared spectrum of a first pitch composition (prepared as described herein) and obtaining at least a second infrared spectrum of a second pitch composition (prepared as described herein), modeling at least one structural IR parameter using the infrared spectra using chemometric modeling, and blending the first and second pitch compositions in a ratio to obtain blended pitch composition having at least one desired pitch property.

Pitch Compositions

[0064] The present disclosure provides various compositions of pitch compositions, which may comprise two or more pitch compositions that have been blended in a particular ratio, according to the methods described herein, to obtain desired structural properties thereof. A singular pitch (unblended) may also be evaluated according to the methodologies of the present disclosure, without limitation.

[0065] In one or more aspects, the pitch composition or blended pitch composition comprise a A-Factor in the range of about 0.4 to about 0.8, encompassing any value and subset therebetween, such as about 0.4 to 0.7, or about 0.4 to 0.6, or about 0.4 to about 0.5, or about 0.5 to about 0.8, or about 0.6 to about 0.8, or about 0.7 to about 0.8.

[0066] In various aspects of the present disclosure, the pitch composition or blended pitch composition comprise an Aromaticity in the range of about 0.3 to about 0.9, encompassing any value and subset therebetween, such as about 0.3 to about 0.8, or about 0.3 to about 0.7, or about 0.3 to about 0.6, or about 0.3 to about 0.5, or about 0.4 to about 0.8, or about 0.5 to about 0.8, or about 0.6 to about 0.8, or about 0.7 to about 0.8, or about 0.8 to about 0.9.

[0067] In certain particular aspects, the pitch composition or blended pitch composition comprise an A-Factor in the range of about 0.6 to about 0.8, encompassing any value or subset therebetween, or an Aromaticity in the range of about 0.3 to about 0.6, encompassing any value

and subset thereof. In other certain particular aspects, the pitch composition or blended pitch composition comprise an A-Factor in the range of about 0.4 to about 0.6, encompassing any value or subset therebetween, or an Aromaticity in the range of about 0.5 to about 0.8, encompassing any value and subset thereof.

5 **[0068]** The pitch composition or blended pitch composition of the present disclosure may comprise a SP in the range of about 90°C to about 350°C, encompassing any value and subset therebetween, such as 90°C to about 300°C, or about 90°C to about 250°C, or about 90°C to about 200°C, or about 90°C to about 150°C, or about 150°C to about 350°C, or about 200°C to about 300°C.

10 **[0069]** In various aspects, the pitch compositions and blending pitch composition of the present disclosure may comprise an SP of less than 150°C, such as between 90°C and 150°C, encompassing any value and subset therebetween, and a mesophase volume (vol%) of less than about 20 vol% (including 0%), encompassing any value and subset therebetween. In other various aspects, the pitch compositions and blending pitch composition of the present disclosure may
15 comprise an SP of about 150°C to about 350°C, encompassing any value and subset therebetween, and a mesophase vol% of greater than 50% (including 100%), encompassing any value and subset therebetween.

[0070] In certain particular aspects, the pitch composition or blended pitch composition comprise (1) an A-Factor in the range of about 0.4 to about 0.8, encompassing any value or subset
20 therebetween, or an Aromaticity in the range of about 0.3 to about 1.3, encompassing any value and subset thereof, and (2) a SP in the range of about 90°C to about 150°C, encompassing any value and subset therebetween, and (3) a mesophase vol% of less than about 20% (including 0%), encompassing any value and subset therebetween. In various other particular aspects, the pitch composition or blended pitch composition comprise (1) an A-Factor in the range of about 0.4 to
25 about 0.6, encompassing any value or subset therebetween, or an Aromaticity in the range of about 0.5 to about 0.8, encompassing any value and subset thereof, and (2) a SP in the range of about 250°C to about 350°C, encompassing any value and subset therebetween, and (3) a mesophase vol% of greater than about 30% (including 100%), encompassing any value and subset therebetween.

30 **[0071]** In various aspects of the present disclosure, a pitch composition or blended pitch composition has an MCR in the range of about 45 wt% to about 100 wt%, encompassing any value and subset therebetween, such as in the range of about 55 wt% to about 95 wt%, or about 60 wt% to about 90 wt%, or about 65 wt% to about 85 wt%, or about 70 wt% to about 80 wt%.

[0072] The present disclosure, in one or more aspects, provides a pitch composition or blended pitch composition having a wt%PV of less than about 70 wt%, such as in the range of 0 wt% to about 70 wt%, encompassing any value and subset therebetween, such as 5 wt% to about 65 wt%, or 10 wt% to about 60 wt%, or 15 wt% to about 55 wt%, or about 20 wt% to about 50 wt%.

5 [0073] In one or more aspects of the present disclosure, a pitch or blended pitch composition has an H/C Ratio in the range of about 0.5 to about 1.0, encompassing any value and subset therebetween, such as about 0.5 to about 0.9, or about 0.5 to about 0.8, or about 0.5 to about 0.7, or about 0.5 to about 0.6, or about 0.6 to about 0.7, or about 0.7 to about 0.8, or about 0.8 to about 0.9, or about 0.9 to about 1.0.

10 [0074] It is to be appreciated that any combination of the SP, MCR, wt%PV, and H/C Ratio values may be applicable to a particular pitch based on the values and ranges provided herein, without limitation. That is, a pitch composition or blended pitch composition according to the present disclosure may have one more or all of an SP in the range of about 90°C to about 350°C, a MRC in the range of about 5°C to about 100°C, a wt%PV of less than about 90 wt%, and an H/C
15 Ratio in the range of about 0.5 to about 1.0.

Carbon Fiber Application

[0075] The present disclosure also relates to methods for making carbon fiber, including green carbon fiber, comprising combining one or more carbon fibers derived from the pitch compositions or blended pitch compositions prepared according to the present disclosure. In some instances, the
20 carbon fiber derived from the pitch may be combined with a thermoset polymer (*e.g.*, cyclopentadiene, dicyclopentadiene, epoxy, pitch, phenolic resins, vinylester, polyimide and polyesters), a thermoplastic polymer (*e.g.*, a thermoplastic polymer including one or more of: polyethylene, polypropylene, high-density polyethylene, linear low-density polyethylene, low-density polyethylene, polyamides, polyvinylchloride, polyetheretherketone,
25 polyetherketoneketone, polyaryletherketone, polyetherimide and polyphenylene sulfide), cement, concrete, ceramic, metal, metal alloy, or any combination thereof. In other instances, the pitch itself can be used as a matrix and/or binder for producing a carbon fiber, thus enabling production of carbon-carbon composites.

[0076] In addition to carbon fibers, other suitable products can also be prepared from the pitch
30 composition or blended pitch compositions in accordance with the present disclosure. For example, mesocarbon microbeads, graphite, and/or needle coke, among others, may be produced from the pitch composition or blended pitch compositions. Any suitable technique may be used for production of mesocarbon microbeads includes a condensation process that may include thermal

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polycondensation of the pitch or blended pitch composition. Additional techniques for production of mesocarbon microbeads may include emulsion or suspension processes.

[0077] Accordingly, the present disclosure provides two methods using IR spectroscopy, as described herein, for predicting pitch properties using structural IR parameters. The first approach examines the structural IR parameters for predicting pitch properties from a given pitch feedstock, whereas the second method uses a wide variety of different feedstocks and IR parameters to develop a feed agnostic model for predicting pitch properties.

Example Embodiments

[0078] Nonlimiting example embodiments of the present disclosure include:

[0079] Embodiment A: A composition comprising: a pitch composition having one or both of an A-Factor in the range of about 0.4 to about 0.8 and/or an Aromaticity in the range of about 0.3 to about 1.3.

[0080] Nonlimiting example embodiment A may include one or more of the following elements:

[0081] Element 1: Wherein the A-Factor is in the range of about 0.6 to about 0.8 and the Aromaticity is in the range of about 0.3 to about 0.6.

[0082] Element 2: Further comprising a softening point in the range of about 90°C to about 150°C and a mesophase by volume of less than about 20%.

[0083] Element 3: Wherein the A-Factor is in the range of about 0.4 to about 0.6 and the Aromaticity is in the range of about 0.5 to about 0.8.

[0084] Element 4: Further comprising a softening point in the range of about 250°C to about 350°C and a mesophase by volume of greater than about 30%.

[0085] Element 5: Further comprising a softening point in the range of about 150°C to about 350°C and a mesophase by volume of greater than about 50%.

[0086] Element 6: Wherein the pitch composition is composed of a blend of pitches comprised of at least a first pitch composition and a second pitch composition.

[0087] By way of non-limiting example, exemplary combinations applicable to embodiment A include: A with 1 and 2; A with 1 and 4; A with 1 and 5; A with 1 and 6; A with 1, 2, and 6; A with 1, 4, and 6; A with 1, 5, and 6; A with 2 and 3; A with 2 and 6; A with 2, 3, and 6; A with 3 and 4; A with 3 and 5; A with 3 and 6; A with 3, 4, and 6; A with 4 and 6; A with 5 and 6.

[0088] Embodiment B: A method comprising: pyrolyzing at least a first pitch composition from a first pitch feed and a second pitch composition from a second pitch feed; wherein the pyrolyzing of the first pitch composition and the second pitch composition are performed separately; obtaining a first infrared spectrum of the at least first pitch composition and selecting at least one first infrared parameter based on (1) the first infrared spectrum and a calibration curve or (2) the first infrared

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spectrum and chemometric modeling; obtaining a second infrared spectrum of the at least second pitch composition and selecting at least one second infrared parameter based on (1) the second infrared spectrum and a calibration curve or (2) the second infrared spectrum and chemometric modeling; and wherein the selected first and second infrared parameters are at least one or both of an A-Factor in a range of about 0.4 to about 0.8 and/or an Aromaticity in a range of about 0.3 to about 1.3; and blending the first and second pitch compositions in a ratio to achieve the selected first and second infrared parameters, thereby forming a blended pitch composition.

[0089] Nonlimiting example embodiments A, B, C, or D may include one or more of the following elements:

[0090] Element 7: Wherein the selected first and second infrared parameters further include a softening point in the range of about 90°C to about 150°C and a mesophase by volume of less than about 20%.

[0091] Element 8: Wherein the selected first and second infrared parameters further include a softening point in the range of about 250°C to about 350°C and a mesophase by volume of greater than about 30%.

[0092] Element 9: Wherein the selected first and second infrared parameters further include a softening point in the range of about 150°C to about 350°C and a mesophase by volume of greater than about 50%.

[0093] Element 10: Further comprising spinning or producing one or both of a carbon fiber and/or a carbon fiber composite with the blended pitch.

[0094] Element 11: Further comprising producing one or more of mesocarbon microbeads, graphite, and/or needle coke with the blended pitch.

[0095] Element 12: Further comprising: prior to the pyrolyzing: obtaining a first initial infrared spectrum of the first pitch feed and selecting at least one first initial infrared parameter based on (1) the first initial infrared spectrum and a calibration curve or (2) the first initial infrared spectrum and chemometric modeling; obtaining a second initial infrared spectrum of the second pitch feed and selecting at least one second initial infrared parameter based on (1) the second initial infrared spectrum and a calibration curve or (2) the second initial infrared spectrum and chemometric modeling; and wherein the selected first and second initial infrared parameters are one or both of an initial A-Factor outside of a range of about 0.4 to about 0.8 and/or an initial Aromaticity outside of a range of about 0.3 to about 1.3.

[0096] Element 13: Wherein the pyrolyzing further comprises contacting the first and the second pitch feeds with a reactive gas, at a temperature in the range of about 200°C to about 600°C, and

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at a pressure greater than 0.3 psi, thereby producing a first pitch effluent comprising the first pitch composition and a second pitch effluent comprising the second pitch composition.

[0097] Element 14: After the pyrolyzing: separating the first pitch composition from the first pitch effluent and separating the second pitch composition from the second pitch effluent, wherein
5 the separating is selected from distillation separating, deasphalting separation, membrane separation, or any combination thereof.

[0098] Element 15: Wherein the reactive gas is selected from the group consisting of hydrogen, air, oxygen, ozone, hydrogen peroxide, carbon monoxide, carbon dioxide, formic acid, nitrogen dioxide, and any combination thereof.

[0099] By way of non-limiting example, exemplary combinations applicable to embodiment B
10 include: B with 7 and 10; B with 7 and 11; B with 7, 10, and 12; B with 7, 11, and 12; B with 7, 12, and 13; B with 7, 10, 12, and 13; B with 7, 11, 12, and 13; B with 7, 12, 13, and 14; B with 7, 10, 12, 13, and 14; B with 7, 11, 12, 13, and 14; B with 7, 12, 13, 14, and 15; B with 7, 10, 12, 13, 14, and 15; B with 7, 11, 12, 13, 14, and 15; B with 7, 10, 12, 13, and 15; B with 7, 11, 12, 13, and 15; B with 7, 12, 13, and 15; B with 8 and 10; B with 8 and 11; B with 8, 10, and 12; B with 8, 11, and 12; B with 8, 12, and 13; B with 8, 10, 12, and 13; B with 8, 11, 12, and 13; B with 8, 12, 13, and 14; B with 8, 10, 12, 13, and 14; B with 8, 11, 12, 13, and 14; B with 8, 12, 13, 14, and 15; B with 8, 10, 12, 13, 14, and 15; B with 8, 11, 12, 13, 14, and 15; B with 8, 10, 12, 13, and 15; B with 8, 11, 12, 13, and 15; B with 8, 12, 13, and 15; B with 9 and 10; B with 9 and 11; B with 9, 10, and 12; B with 9, 11, and 12; B with 9, 12, and 13; B with 9, 10, 12, and 13; B with 9, 10, 11, 12, and 13; B with 9, 12, 13, and 14; B with 9, 10, 12, 13, and 14; B with 9, 11, 12, 13, and 14; B with 9, 12, 13, 14, and 15; B with 9, 10, 12, 13, 14, and 15; B with 9, 11, 12, 13, 14, and 15; B with 9, 10, 12, 13, and 15; B with 9, 11, 12, 13, and 15; B with 9, 12, 13, and 15; B with 10 and 12; B with 11 and 12; B with 10, 12, and 13; B with 11, 12, and 13; B with 10, 12, 13, and 14; B with 11, 12, 13, and 14; B with 10, 12, 13, and 14; B with 11, 12, 13, and 14; B with 10, 12, 13, 14, and 15; B with 11, 12, 13, 14, and 15; B with 10, 12, 13, and 15; B with 11, 12, 13, and 15; B with 12, 13, and 15; B with 12 and 13; B with 12 and 15; B with 12, 13, and 14; B with 12, 13, 14, and 15.
20 25

[0100] Embodiment C: A method comprising: extruding a pitch composition to produce a green carbon fiber; and thereafter, stabilizing the extruded pitch composition; wherein the stabilizing
30 comprises obtaining an infrared spectrum of the extruded pitch composition and selecting at least one infrared parameter based on (1) the first infrared spectrum and a calibration curve or (2) the first infrared spectrum and chemometric modeling, wherein the at least one infrared parameter is at least an A-Factor and an Aromaticity; and ceasing stabilizing based upon the at least one infrared parameter.

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[0101] By way of non-limiting example, exemplary combinations applicable to embodiment C include:

[0102] Element 15: Wherein the pitch composition is extruded through a spinneret and the method further comprises spooling the extruded pitch composition prior to the stabilizing, wherein
5 the stabilizing is performed with a reactive gas.

[0103] Element 16: Wherein the extruding comprising blowing the pitch composition through an extrusion die.

[0104] Element 17: Wherein the reactive gas is selected from the group consisting of hydrogen, air, oxygen, ozone, nitrogen dioxide, hydrogen peroxide, carbon monoxide, carbon dioxide, formic
10 acid, and any combination thereof.

[0105] Element 18: Wherein the selected at least one infrared parameter is at least one or both of an A-Factor and an Aromaticity, and the stabilizing is ceased when the A-Factor is in a range of about 0.4 to about 0.8 and/or the Aromaticity in a range of about 0.3 to about 1.3.

[0106] By way of non-limiting example, exemplary combinations applicable to embodiment C
15 include: C with 15 and 17; C with 16 and 17; C with 15 and 18; C with 16 and 18; C with 15, 17, and 18; ; C with 16, 17, and 18; C with 17 and 18.

[0107] Embodiment D: A method comprising: pyrolyzing a pitch composition from a pitch feed; obtaining an infrared spectrum of the first pitch composition and selecting at least one infrared parameter based on (1) the infrared spectrum and a calibration curve or (2) the infrared spectrum
20 and chemometric modeling; wherein the selected at least one infrared parameter is at least one or both of an A-Factor in a range of about 0.4 to about 0.8 and/or an Aromaticity in a range of about 0.3 to about 1.3.

[0108] By way of non-limiting example, exemplary combinations applicable to embodiment D include:

[0109] Element 18: Wherein the selected at least one infrared parameter further include a
25 softening point in the range of about 90°C to about 150°C and a mesophase by volume of less than about 20%.

[0110] Element 19: Wherein the selected at least one infrared parameter further include a softening point in the range of about 250°C to about 350°C and a mesophase by volume of greater
30 than about 30%.

[0111] Element 20: Wherein the selected at least one infrared parameter further include a softening point in the range of about 150°C to about 350°C and a mesophase by volume of greater than about 50%.

[0112] Element 21: Further comprising spinning or producing one or both of a carbon fiber and/or a carbon fiber composite with the pitch composition.

[0113] Element 22: Further comprising: prior to the pyrolyzing: obtaining an initial infrared spectrum of the pitch feed and selecting at least one initial infrared parameter based on (1) the
5 initial infrared spectrum and a calibration curve or (2) the initial infrared spectrum and chemometric modeling; wherein the selected at least one initial infrared parameter is one or both of an initial A-Factor outside of a range of about 0.4 to about 0.8 and/or an initial Aromaticity outside of a range of about 0.3 to about 1.3.

[0114] Element 23: Wherein the pyrolyzing further comprises contacting the pitch feed with a
10 reactive gas, at a temperature in the range of about 200°C to about 600°C, and at a pressure greater than 0.3 psi, thereby producing a pitch effluent comprising the pitch composition.

[0115] Element 24: Further comprising: after the pyrolyzing: separating the pitch composition from the pitch effluent, wherein the separating is selected from distillation separating, deasphalting separation, membrane separation, or any combination thereof.

[0116] Element 25: Wherein the reactive gas is selected from the group consisting of hydrogen, air, oxygen, ozone, hydrogen peroxide, carbon monoxide, carbon dioxide, formic acid, nitrogen
15 dioxide, and any combination thereof.

[0117] By way of non-limiting example, exemplary combinations applicable to embodiment D include: D with 18 and 21; D with 18 and 22; D with 18, 21, and 22; D with 18, 22, and 23; D with
20 18, 21, 22, and 23; D with 18, 22, 23, and 24; D with 18, 21, 22, 23, and 24; D with 18, 21, 22, 23, 24, and 25; D with 18, 21, 22, 23, 24, and 25; D with 19 and 21; D with 19 and 22; D with 19, 21, and 22; D with 19, 22, and 23; D with 19, 21, 22, and 23; D with 19, 22, 23, and 24; D with 19, 21, 22, 23, and 24; D with 19, 21, 22, 23, 24, and 25; D with 19, 21, 22, 23, 24, and 25; D with 18 and 21; D with 18 and 22; D with 18, 21, and 22; D with 18, 22, and 23; D with 18, 21, 22, and 23; D
25 with 18, 22, 23, and 24; D with 18, 21, 22, 23, and 24; D with 18, 21, 22, 23, 24, and 25; D with 18, 21, 22, 23, 24, and 25; D with 21 and 22; D with 21, 22, and 23; D with 21, 22, 23, and 24; D with 21, 22, 23, and 25; D with 22 and 23; D with 22, 23, and 24; D with 22, 23, and 25; D with 22, 23, 24, and 25.

[0118] To facilitate a better understanding of the embodiments of the present invention, the
30 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

[0119] In the following nonlimiting Examples, representative methodologies of the present disclosure for tailoring pitch properties are provided.

BACKGROUND INFRARED SPECTRA – FOR EXAMPLES 1 AND 2

[0120] Infrared spectra of various prepared pitch compositions were obtained using DRIFT. The pitch samples were prepared by loading approximately 2 grams (g) of a feedstock described below into a glass vial and placed in a PAC™ Micro Carbon Residue Tester. Therein, the samples were heated to 100°C for 10 minutes (min) under a flow of nitrogen gas (600 mL min⁻¹). Immediately thereafter, the samples were heated to 400°C using a 30°C min⁻¹ ramp rate and 600 mL min⁻¹ nitrogen flow rate. Upon reaching 400°C, the flow rate was decreased to 150 mL min⁻¹, and the samples held at 400°C for a specified time between zero (0) to six (6) hours (hr). After the heat soak for the specified time, the samples were cooled to RT under nitrogen gas at a 600 mL min⁻¹ flow rate over the course of several hours in the oven.

[0121] The results and pyrolysis parameters—heating time (hr) and temperature (°C)—are provided in Table 1 below. The sample pitch compositions were derived from feedstock of: (1) Solvent Assisted Tar Conversion (SATC) bottoms stream samples, labeled SATC-1 through SATC-8; (2) “seeded” SATC PDU bottoms stream samples formed from mixing 0 hour, non-heat treated SATC bottoms stream (SATC-1) with 5 hour treated SATC bottom stream (SATC-6), labeled sSATC-1 through s-SATC-8; (3) tar derived from steam cracker, labeled SOP2-1 through SOP2-5; (4) heavy vacuum gas oil pitch (bottoms streams of temperature 986°F-1038°F, or 524°C-559°C), labeled HVGO-1 and HVGO-2; (5) Kearn-derived bitumen pitch, labeled KB-1 through KB-6; (6) hydrotreated mesocarbon microbeads pitch, labeled MCB-1 and MC-2; and (8) isotropic petroleum pitch M-50, available from Marathon Oil Corporation (Findlay, OH), labeled M50-1 through M50-4.

[0122] The SP, MCR, and elemental analysis of H/C ratio and %PVs were measured as defined hereinabove. Entry of “N/A” in Table 1 indicates that the particular pitch property was not measured or an unknown measurement error occurred. Provision of a “*” superscript in Table 1 indicates that the value represents a lower limit because the instrument errored out at the applicable temperature and the material had not fully softened.

TABLE 1

Sample No.	Treatment Conditions	MCR (°C)	SP (°C)	H/C Ratio	wt%PV
SATC-1	0 hr, RT	38.65	180	0.959	0
SATC-2	1 hr, 400°C	53.51	153.3	0.836	25.62
SATC-3	2 hr, 400°C	68.68	185.8	0.820	38.16
SATC-4	3 hr, 400°C	83.96	200.8	0.666	41.42

SATC-5	4 hr, 400°C	89.83	228.9	0.634	44.85
SATC-6	5 hr, 400°C	81.94	248.6	0.613	48.98
SATC-8	5 hr, 400°C	N/A	248.6	N/A	45.98
SATC-8	6 hr, 400°C	86.32	313.2	0.594	48.62
sSATC-1	0 hr, RT	40.1	181.9	0.954	0
sSATC-2	1 hr, 400°C	62.32	163.2	0.815	25.51
sSATC-3	2 hr, 400°C	69.11	183.9	0.804	36.28
sSATC-4	3 hr, 400°C	85.85	206.8	0.658	40.03
sSATC-5	4 hr, 400°C	80.82	240.2	0.623	43.46
sSATC-6	5 hr, 400°C	85.05	N/A	0.604	46.22
sSATC-8	6 hr, 400°C	86.86	323.2	0.569	46.02
SOP2-1	0 hr, RT	25.8	N/A	N/A	N/A
SOP2-2	2 hr, 400°C	83.8	308.9	0.61	65.9
SOP2-3	3 hr, 400°C	93.3	380	0.51	69.1
SOP2-4	4 hr, 400°C	91.4	>382*	0.56	68.4
SOP2-5	6 hr, 400°C	94	>382*	0.51	68.9
HVGO-1	0 hr, RT	6.6	84.9	1.05	N/A
HVGO-2	6 hr, 400°C	68.4	182.1	0.63	85.3
KB-1	0 hr, RT	10.4	N/A	NA	N/A
KB-2	0 hr, RT	68	285	0.994	N/A
KB-3	2 hr, 400°C	80.9	351	0.81	83
KB-4	3 hr, 400°C	92.8	>385*	0.6	85
KB-5	4 hr, 400°C	93.8	>390*	0.6	85
KB-6	6 hr, 400°C	96.3	>390*	0.58	85.3
MCB-1	0 hr, RT	53.9	158.3	1.03	N/A
MCB-2	4.5 hr, 400°C	83.1	209	0.6	65.2
M50-1	0 hr, RT	52.5	128	0.88	N/A
M50-2	2 hr, 400°C	86.9	218.3	0.6	30.9
M50-3	4 hr, 400°C	88.8	321.6	0.6	39.5
M50-4	6 hr, 400°C	84.6	388.8	0.56	42

[0123] Each sample from Table 1 was diluted in potassium bromide (KBr) at 2 wt% pitch sample loading and their respective DRIFT spectra (using an FT-IR spectrometer equipped with a

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DRIFT accessory and detector, as provided hereinabove) measured at RT. The DRIFT data were collected in a spectral range from 400 to 4000 cm^{-1} and were converted to absorbance using Thermo Fisher Scientific Inc. OMNICTM software, version 9 using a ratio of the sample spectra to a room temperature spectrum of KBr. The measurements were obtained using 256 scans per sample at a resolution of 4 cm^{-1} using a Happ-Genzel apodization function.

[0124] Representative results are shown in FIGS. 1A-1D. FIG. 1A shows the DRIFT spectra for samples HVGO-1 and HVGO-2; FIG. 1B shows the DRIFT spectra for samples KB-1 through KB-6; FIG. 1C shows the DRIFT spectra for samples MCB-1 and MCB-2; FIG. 1D shows the DRIFT spectra for samples M50-1 through M50-4.

[0125] As shown in FIGS. 1A-1D, the DRIFT spectra show spectral changes associated with increasing aromatic C-H stretching (in the approximate 2991-3100 cm^{-1} range) concurrent with decreasing aliphatic C-H stretching (in the approximate 2820-3000 cm^{-1} range) as the thermal treatment progressed (*i.e.*, a longer period of time at 400°C). Similar results were observed in the DRIFT spectra for the remaining samples in Table 1.

EXAMPLE 1 – DRIFT SPECTRAL ANALYSIS + INFRARED PARAMETERS

[0126] Representative DRIFT spectra were obtained as provided above for samples SATC-1 to SATC-6 and SATC-8 (represented by diamond labeling); and samples sSATC-1 through sSATC-8 (represented by circle labeling). Thereafter, based on the DRIFT spectra obtained, the infrared structural parameters of CH_3/CH_2 Ratio, A-Factor, Aromaticity, and DoC, as defined above, were measured. FIG. 2A shows the measured results of the infrared parameter CH_3/CH_2 Ratio; FIG. 2B shows the measured results of the infrared parameter A-Factor; FIG. 2C shows the measured results of the infrared parameter Aromaticity; FIG. 2D shows the measured results of the infrared parameter DoC.

[0127] As shown in FIGS. 2A-2D, CH_3/CH_2 Ratio and Aromaticity increase with increasing pyrolysis time (at 400°C in this Example), whereas A-Factor and DoC decrease with increasing pyrolysis time. The decrease in DoC as thermal conversion time increases is indicative of an increase in ring condensation. Similar results were observed in the infrared parameters for the remaining samples in Table 1 (not shown).

[0128] As provided above, for each of the samples listed in Table 1, a DRIFT spectra was obtained and infrared parameters measured (each of CH_3/CH_2 Ratio, A-Factor, Aromaticity, and DoC). Thereafter, correlation was made between each of the infrared parameters and each of the pitch properties (SP, MCR, H/C ratio, and %PV). The infrared parameters are intended to track various key structural changes occurring during the pyrolysis of pitch.

[0129] Based on correlations developed between the infrared parameters and the structural properties of pitch, it was observed that the best fit correlations were based on the A-Factor and Aromaticity. FIGS. 3A-3D show representative correlation charts, for each of the samples in Table 1, between A-Factor and MCR (FIG. 3A); A-Factor and SP (FIG. 3B); Aromaticity and MCR (FIG. 3C); and Aromaticity and SP. As shown in FIGS. 3A-3D, the infrared parameters and pitch properties correlate, but vary with pitch type, and thus this example is dependent upon pitch type. As provided above, the average of the A-Factor and/or Aromaticity is used to predict a particular structural pitch property.

[0130] Based on the determined average A-Factor and average Aromaticity, parity plots were established for each of the pitch properties MCR (%), SP (°C), H/C Ratio, and %PV between the A-Factor and Aromaticity property predictions and the actual measured predictions. Representative samples were selected that included sufficient data and sufficient reference (actual) data. The parity plot results are shown in FIGS. 4A-4D, where FIG. 4A shows the parity plot for MCR; FIG. 4B shows the parity plot for SP (note the dashed line indicates a limitation of the measurement instrument above 380°C); FIG. 4C shows the parity plot for H/C Ratio; and FIG. 4D shows the parity plot for %PV. As can be observed, significant parity exists between the predicted pitch property and the actual pitch property for all infrared parameters.

[0131] Accordingly, this Example demonstrates the methodology of the present disclosure to use a correlation between DRIFT infrared parameters and pitch type prediction of structural properties thereof.

EXAMPLE 2 – DRIFT SPECTRAL ANALYSIS + CHEMOMETRIC ANALYSIS

[0132] In this Example, chemometric modeling was used to predict pitch properties based on the DRIFT spectra and based on Table 1 and representative FIGS. 1A-1B. The chemometric methodology permits pitch property predictions independent of pitch type (an “agnostic” pitch model), as described hereinabove.

[0133] Each of the four (4) pitch properties described herein (MCR, SP, H/C Ratio, %PV) were evaluated using aforementioned PLS modeling technique.

[0134] Referring now to FIG. 5, illustrated is a PLS modeled correlation chart for the representative pitch property MCR, wherein the MCR was predicted based on PLS and compared to the actual MCR values in Table 1. As shown in FIG. 5, significant correlation exists between the PLS predicted MCR and the actual MCR values.

[0135] As with Example 1, parity plots were prepared for this Example and the parity plot results are shown in FIGS. 6A-6D, where FIG. 6A shows the parity plot for MCR; FIG. 6B shows the parity plot for SP; FIG. 6C shows the parity plot for H/C Ratio; and FIG. 6D shows the parity

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plot for %PV. As can be observed, significant parity exists between the predicted pitch property and the actual pitch property for all infrared parameters.

[0136] FIGS. 7A-7D show predictions of pitch properties based on the chemometric approach of this Example for SATC-1, SATC-4, SATC-8, sSATC-1, sSATC-4, sSATC-8 samples of Table 1 using an IR structural parameter least squares analysis (LSA) (polynomial order 2). As shown, and as compared to the Table 1 values, the predictions are within the measured actual ranges for each sample.

[0137] 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.

[0138] 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.

[0139] 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-

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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.

[0140] One or more illustrative embodiments 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 of the present disclosure, 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 one of ordinary skill in the art and having benefit of this disclosure.

[0141] 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 composition comprising:
 - 5 a pitch composition having one or both of an A-Factor in the range of about 0.4 to about 0.8 and/or an Aromaticity in the range of about 0.3 to about 1.3.
2. The composition of claim 1, wherein the A-Factor is in the range of about 0.6 to about 0.8 and the Aromaticity is in the range of about 0.3 to about 0.6.
- 10 3. The composition of claim 1 or claim 2, further comprising a softening point in the range of about 90°C to about 150°C and a mesophase by volume of less than about 20%.
4. The composition of claim 1, wherein the A-Factor is in the range of about 0.4 to about 0.6 and the Aromaticity is in the range of about 0.5 to about 0.8.
- 15 5. The composition of any one of claims 1, 2, or 4, further comprising a softening point in the range of about 250°C to about 350°C and a mesophase by volume of greater than about 30%.
- 20 6. The composition of any one of claims 1, 2, or 4, further comprising a softening point in the range of about 150°C to about 350°C and a mesophase by volume of greater than about 50%.
7. The composition of claim 1, wherein the pitch composition is composed of a blend of pitches comprised of at least a first pitch composition and a second pitch composition.
- 25 8. A method comprising:
 - pyrolyzing at least a first pitch composition from a first pitch feed and a second pitch composition from a second pitch feed;
 - wherein the pyrolyzing of the first pitch composition and the second pitch
 - 30 composition are performed separately;
 - obtaining a first infrared spectrum of the at least first pitch composition and selecting at least one first infrared parameter based on (1) the first infrared spectrum and a calibration curve or (2) the first infrared spectrum and chemometric modeling;
 - obtaining a second infrared spectrum of the at least second pitch composition and selecting

at least one second infrared parameter based on (1) the second infrared spectrum and a calibration curve or (2) the second infrared spectrum and chemometric modeling; and

wherein the selected first and second infrared parameters are at least one or both of an A-Factor in a range of about 0.4 to about 0.8 and/or an Aromaticity in a range of about 0.3 to about 1.3; and

blending the first and second pitch compositions in a ratio to achieve the selected first and second infrared parameters, thereby forming a blended pitch composition.

9. The method of claim 8, wherein the selected first and second infrared parameters further include a softening point in the range of about 90°C to about 150°C and a mesophase by volume of less than about 20%.

10. The method of claim 8, wherein the selected first and second infrared parameters further include a softening point in the range of about 250°C to about 350°C and a mesophase by volume of greater than about 30%.

11. The method of claim 8, wherein the selected first and second infrared parameters further include a softening point in the range of about 150°C to about 350°C and a mesophase by volume of greater than about 50%.

12. The method of any one of claims 8-11, further comprising spinning or producing one or both of a carbon fiber and/or a carbon fiber composite with the blended pitch.

13. The method of any one of claims 8-11, further comprising producing one or more of mesocarbon microbeads, graphite, and/or needle coke with the blended pitch.

14. The method of claim 8, further comprising:
prior to the pyrolyzing:
obtaining a first initial infrared spectrum of the first pitch feed and selecting at least one first initial infrared parameter based on (1) the first initial infrared spectrum and a calibration curve or (2) the first initial infrared spectrum and chemometric modeling;
obtaining a second initial infrared spectrum of the second pitch feed and selecting at least one second initial infrared parameter based on (1) the second initial infrared spectrum and a calibration curve or (2) the second initial infrared spectrum and chemometric modeling; and

wherein the selected first and second initial infrared parameters are one or both of an initial A-Factor outside of a range of about 0.4 to about 0.8 and/or an initial Aromaticity outside of a range of about 0.3 to about 1.3.

5 15. The method of claim 14, wherein the pyrolyzing further comprises contacting the first and the second pitch feeds with a reactive gas, at a temperature in the range of about 200°C to about 600°C, and at a pressure greater than 0.3 psi, thereby producing a first pitch effluent comprising the first pitch composition and a second pitch effluent comprising the second pitch composition.

10 16. The method of claim 15, further comprising:
after the pyrolyzing:

separating the first pitch composition from the first pitch effluent and separating the second pitch composition from the second pitch effluent, wherein the separating is selected from distillation separating, deasphalting separation, membrane separation, or any combination thereof.

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17. The method of claim 15 or claim 16, wherein the reactive gas is selected from the group consisting of hydrogen, air, oxygen, ozone, hydrogen peroxide, carbon monoxide, carbon dioxide, formic acid, nitrogen dioxide, and any combination thereof.

20 18. A method comprising:

extruding a pitch composition to produce a green carbon fiber; and
thereafter, stabilizing the extruded pitch composition;

wherein the stabilizing comprises obtaining an infrared spectrum of the extruded pitch composition and selecting at least one infrared parameter based on (1) the first infrared spectrum and a calibration curve or (2) the first infrared spectrum and chemometric modeling,

25 wherein the at least one infrared parameter is at least an A-Factor and an Aromaticity;
and

ceasing stabilizing based upon the at least one infrared parameter.

30 19. The method of claim 18, wherein the pitch composition is extruded through a spinneret and the method further comprises spooling the extruded pitch composition prior to the stabilizing, wherein the stabilizing is performed with a reactive gas.

20. The method of claim 18, wherein the extruding comprising blowing the pitch composition

through an extrusion die.

21. The method of any one of claims 18-20, wherein the reactive gas is selected from the group consisting of hydrogen, air, oxygen, ozone, nitrogen dioxide, hydrogen peroxide, carbon monoxide,
5 carbon dioxide, formic acid, and any combination thereof.

22. The method of any one of claims 18-21, wherein the selected at least one infrared parameter is at least one or both of an A-Factor and an Aromaticity, and the stabilizing is ceased when the A-Factor is in a range of about 0.4 to about 0.8 and/or the Aromaticity in a range of about 0.3 to about
10 1.3.