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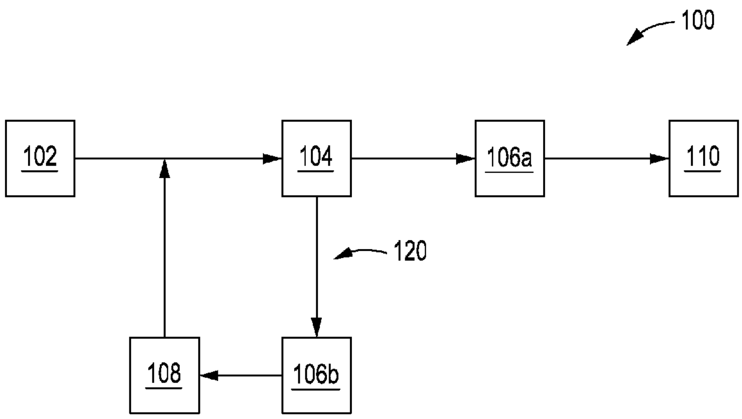

FIGURE

(57) Abstract: Pitch particles may be produced by a grinding process, in which pitch fines may be recovered and recycled to a grinding apparatus as a pitch melt. Such methods may comprise: providing a petroleum pitch having a first softening temperature; grinding the petroleum pitch in a grinding apparatus below the first softening temperature to produce a plurality of pitch particles and a plurality of pitch fines; separating the pitch particles from the pitch fines; heating the pitch fines at a temperature above the first softening temperature to produce a pitch melt; and combining the pitch melt with the petroleum pitch in the grinding apparatus. The pitch melt hardens in the grinding apparatus and is reground. The pitch particles may be further stabilized by heating at a treatment temperature below the first softening temperature in an environment comprising about 1 mol% to about 20 mol% oxygen to form stabilized pitch particles.

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METHODS FOR PRODUCTION OF PITCH PARTICLES WITH REPROCESSING OF PITCH FINES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of priority to U.S. Provisional Application No. 63/508,392 filed June 15, 2023, the disclosure of which is incorporated by reference in its entirety.

FIELD

[0002] The present disclosure relates to processing of petroleum pitch to produce pitch particles and, more particularly, to processes that may increase recovery of pitch particles from a pitch source.

BACKGROUND

[0003] Petroleum pitch ("pitch") is a carbon-rich viscoelastic material originating from petroleum and having properties similar to a thermoplastic polymer by virtue of having a softening temperature. Petroleum pitch comprises a complex mixture of aromatic molecules that may be at least partially ordered and coalesced into a liquid crystalline phase. The liquid crystalline phase may be referred to as "mesophase pitch," which may comprise a majority or all of a pitch sample in some cases. Petroleum pitch may be produced as a byproduct of thermal or catalytic conversion of a hydrocarbon feedstock (*e.g.*, a highly aromatic hydrocarbon feedstock) or recovered from a source material, such as petroleum. In the disclosure herein, the term "petroleum pitch" is used to refer to such pitch materials, regardless of the source from which a given pitch is obtained.

[0004] Pitch is an excellent precursor for a wide range of amorphous carbon or graphitic materials, such as pitch-based carbon fibers, binders, carbon microbeads, solid lubricants, carbon-carbon composites, activated carbon fibers, battery anodes, carbon foams, carbon-based molecular sieves, and the like. Such carbonaceous materials are used ubiquitously in industries and applications such as oil and gas processing, automotive components, aerospace components, marine components, sporting goods, construction materials, energy production, electrodes for electric arc furnaces, and the like.

[0005] In many cases, it may be desirable for a petroleum pitch to be in the form of pitch particles before being converted into amorphous carbon and subsequently graphite. Although pitch particles may be produced readily through grinding and similar pulverization processes, significant material losses (up to 50% mass loss in some cases) may occur due to formation of pitch fines that are too small to handle during subsequent carbonization and graphitization. The pitch fines become a high-volume waste material that has to be disposed of. Another difficulty of using petroleum pitch as a precursor to amorphous carbon and graphite arises due to its thermoplastic nature, wherein the petroleum pitch becomes deformable at its softening temperature. Namely, a shaped pitch material, such as pitch particles in a mold, may deform prior to undergoing carbonization or graphitization, which may be unsuitable for producing objects having strict size or shape tolerances. Since there may be a large difference between the softening temperature and the temperature at which carbonization takes place, there is often a wide temperature window over which deformation of the pitch particles may occur.

SUMMARY

[0006] In one or more aspects, the present disclosure provides methods for processing pitch fines. The methods comprise: providing a petroleum pitch having a first softening temperature; grinding the petroleum pitch in a grinding apparatus below the first softening temperature to produce a plurality of pitch particles and a plurality of pitch fines; separating the pitch particles from the pitch fines; heating the pitch fines at a temperature above the first softening temperature to produce a pitch melt; and combining the pitch melt with the petroleum pitch in the grinding apparatus; wherein the pitch melt hardens in the grinding apparatus and is reground.

[0007] In some or other aspects, the present disclosure provides methods for processing pitch fines and upgrading pitch particles. The methods comprise: providing a petroleum pitch having a first softening temperature of about 180°C to about 500°C; grinding the petroleum pitch in a grinding apparatus below the first softening temperature to produce a plurality of pitch particles and a plurality of pitch fines; separating the pitch particles from the pitch fines; heating the pitch fines at a temperature above the first softening temperature to produce a pitch melt; combining the pitch melt with the petroleum pitch in the grinding apparatus; wherein the pitch melt hardens in the grinding apparatus and is reground; and heating the pitch particles at a treatment temperature below the first softening temperature in an environment comprising about 1 mol% to about 20 mol% oxygen to form stabilized pitch particles; wherein the stabilized pitch particles have second softening temperature that is higher than the first softening temperature.

[0008] These and other features and attributes of the disclosed compositions and methods 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

[0009] To assist one of ordinary skill in the relevant art in making and using the subject matter hereof, reference is made to the appended drawing. The following figure is included to illustrate certain aspects of the disclosure, and should not be viewed as an exclusive configuration. 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.

[0010] The FIGURE is a block diagram of an illustrative system and method for processing petroleum pitch according to the present disclosure.

DETAILED DESCRIPTION

[0011] The present disclosure relates to processing of petroleum pitch to produce pitch particles and, more particularly, to processes that may increase recovery of pitch particles from a pitch source.

[0012] It is to be understood that the terms “pitch” and “petroleum pitch” are used interchangeably herein. Moreover, it is to be understood that the “pitch particles” described herein contain petroleum pitch.

[0013] Although petroleum pitch is a versatile material for forming amorphous carbon and graphite, particularly when processed into a particle form, there are difficulties in doing so. One difficulty is excessive production and subsequent loss of pitch fines when producing pitch particles through pulverization and similar grinding processes. In addition, the softening temperature of petroleum pitch is problematic in terms of leading to deformation when carbonizing or graphitizing a petroleum pitch.

[0014] To address the foregoing issues, the present disclosure utilizes a recycling loop to recover pitch fines generated during production of pitch particles, followed by melting of the pitch fines and subsequent re-solidification thereof. Namely, a petroleum pitch sample may be ground below a softening temperature of the petroleum pitch, followed by separation of pitch particles having a desired size from pitch fines having an undesired size, and then recycling the pitch fines to a grinding apparatus as a pitch melt above the softening temperature. By cooling and re-solidifying the pitch melt in the grinding apparatus, a petroleum pitch sample may be exhaustively processed into pitch particles, such that all or nearly all of the petroleum pitch sample is converted into pitch particles having a desired size range. Up to 100% conversion of a petroleum pitch sample into pitch particles may be realized through application of the disclosure herein, which may decrease overall costs associated with production and use of the pitch particles.

[0015] In addition to the benefits afforded by recovering an increased percentage of the petroleum pitch in the form of pitch particles through recycling of pitch fines, the present disclosure may further facilitate upgrading the petroleum pitch within the pitch particles, once the pitch particles have been separated from the pitch fines. In particular, once the pitch particles have been separated from the pitch fines, the petroleum pitch within the pitch particles may be stabilized by increasing the softening temperature of the petroleum pitch from a first softening temperature to a second softening temperature. The foregoing may be accomplished by heating the pitch particles in a low-oxygen environment (*e.g.*, about 0.1 mol% oxygen to about 20 mol% oxygen) at an elevated temperature below the first (initial) softening temperature of the petroleum pitch. Without being bound by theory or mechanism, the increased softening temperature is believed to arise through crosslinking of the petroleum pitch in the presence of oxygen at the elevated temperature, which may correspond to an onset of oxidation temperature. By increasing the softening temperature in the foregoing manner, the petroleum pitch within the pitch particles may maintain its initial form (shape) more readily as the pitch particles are heated in the course of undergoing carbonization in a no-oxygen or very low-oxygen environment (*e.g.*, less than about 0.1 mol% oxygen). The increased softening temperature of the upgraded petroleum pitch decreases the temperature window (and decreases the amount of time) during which the petroleum pitch is in a softened state prior to undergoing conversion into amorphous carbon, thereby lessening the propensity toward deformation. Additionally, heat treating the petroleum pitch in the foregoing manner may encourage diffusion of impurities out of the petroleum pitch, thereby improving the quality of amorphous carbon and graphite resulting from the pitch particles.

[0016] Accordingly, methods of the present disclosure may comprise: providing a petroleum pitch having a first softening temperature; grinding the petroleum pitch in a grinding apparatus below the first softening temperature to produce a plurality of pitch particles and a plurality of pitch fines; separating the pitch particles from the pitch fines; heating the pitch fines at a temperature above the first softening temperature to produce a pitch melt; and combining the pitch melt with the petroleum pitch in the grinding apparatus. To facilitate the production of pitch particles, the petroleum pitch may be maintained at a temperature below the first softening temperature in the grinding apparatus. By keeping the petroleum pitch below the first softening temperature, the pitch melt may then harden in the grinding apparatus and be reground.

[0017] Grinding processes (also referred to herein as "grinding") may be utilized to facilitate preparation of the pitch particles herein. Any suitable grinding apparatus or technique may be used to facilitate production of pitch particles through pulverization of a petroleum pitch sample. The terms “grinding” and “pulverizing,” as well as grammatical variants thereof, are to be considered equivalent herein. Suitable grinding processes may employ a grinding apparatus that may be operated in a batchwise manner or a continuous manner. Batchwise grinding apparatuses may employ, for example, ball milling, jet milling, impact milling, and like techniques. Continuous grinding apparatuses may employ, for example, jet milling, Wiley milling, extrusion, and related techniques. In particular examples, grinding in the disclosure herein may be performed by jet milling. Jet milling may be especially desirable since it typically produces narrow particle size distributions. Moreover, because jet milling equipment lacks blades and other direct grinding structures, there is a lower likelihood of introducing contaminants from the mill (*e.g.*, due to microabrasion of the milling equipment) compared to other types of grinding processes.

[0018] It is to be appreciated that two or more grinding apparatuses may be used in combination with one another in implementing the embodiments of the present disclosure. For example, two or more jet mills or extruders in series may be utilized to achieve a desired particle size and/or two or more jet mills or extruders in parallel may be utilized to increase throughput.

[0019] Grinding of the petroleum pitch may produce pitch particles and pitch fines. Pitch fines may include pitch particles having a particle size of about 5 microns or below or about 1 micron or below, including pitch fines having a size residing in a nanoparticle size range of about 500 nm or below or about 100 nm or below. Pitch particles may have a size ranging from about 1 micron to about 100 microns, or about 1 micron to about 50 microns, or about 5 microns to about 100 microns, or about 5 microns to about 50 microns, or about 5 microns to about 25 microns, or about 1 micron to about 25 microns, or about 10 microns to about 30 microns, or about 15 microns to about 50 microns. The ratio of pitch fines to pitch particles may range from about 1:1 to about 1:9, or about 1:1 to about 1:99, or about 1:3 to about 1:9 on a mass basis. Alternately, pitch fines may be produced in preference to pitch particles in the grinding process in a ratio ranging from about 9:1 to about 1:1, or about 8:1 to about 1:1, or about 7:1 to about 1:1, or about 6:1 to about 1:1. Desirably, the pitch fines that are produced may be recovered and re-processed into pitch particles having a desired size range according to the disclosure herein.

[0020] In addition, pitch particles that are not within a desired size range may be rejected by a size separation, such as sieving, and the rejected pitch particles may be recycled in a similar manner to the pitch fines, preferably with the rejected pitch particles being combined with the pitch fines to form the pitch melt. Accordingly, the present disclosure may facilitate a tight sizing (narrow particle size distribution) of the pitch particles but without suffering from excessive mass loss of the petroleum pitch sample in doing so.

[0021] The petroleum pitch used in the present disclosure may be obtained from any source or process, provided that the petroleum pitch does not contain components that might be detrimental to an intended application following carbonization or graphitization of the pitch particles. In some examples, at least a majority of the petroleum pitch may comprise a mesophase pitch. Once carbonized and converted to graphite, the highly aligned structure of mesophase pitch may promote enhanced electrical conductivity of the graphite. In non-limiting examples, the petroleum pitch used herein may have a mesophase pitch content of about 50 wt% or greater, or about 60 wt% or greater, or about 70 wt% or greater, or about 80 wt% or greater, or about 90 wt% or greater, or about 95 wt% or greater, or about 99 wt% or greater, or about 99.9 wt% or greater, such as about 80 wt% to about 99.9 wt%, or about 90 wt% to about 99.9 wt%, or about 95 wt% to about 99.9 wt%, or even 100 wt%, each based on a total mass of the petroleum pitch.

[0022] Prior to undergoing stabilization through heating of the pitch particles, the petroleum pitch being processed according to the disclosure herein may have a first softening temperature of about 500°C or below, or about 450°C or below, or about 400°C or below, or about 350°C or below, or about 300°C or below. In non-limiting examples, the first softening temperature may reside within a range of about 180°C to about 500°C, or about 250°C to about 500°C, or about 280°C to about 400°C, or about 180°C to about 400°C, or about 250°C to about 330°C, or about 300°C to about 340°C.

[0023] During recycling, the pitch fines may be heated at a temperature above the first softening temperature to form a pitch melt that is then returned to the grinding apparatus and re-solidified through cooling before being re-ground to form additional pitch particles. In non-limiting examples, the pitch fines may be heated at a temperature at least about 5°C above the first softening temperature, or at least about 10°C above the first softening temperature, or at least about 20°C above the first softening temperature, or at least about 30°C above the first softening temperature, or at least about 40°C above the first softening temperature, or at least about 50°C above the first softening temperature. Preferably, the pitch fines being recycled to the grinding apparatus may be heated in a no-oxygen or low-oxygen environment having an oxygen content of about 0.1 mol% or below to minimize a reaction of the petroleum pitch with oxygen.

[0024] The grinding apparatus may be operated at any temperature that maintains the petroleum pitch in a hardened state (and re-solidifies the pitch melt returned to the grinding apparatus) to promote particle formation therefrom. Such temperatures are below the first softening temperature of the petroleum pitch, such as at least about 5°C below the first softening temperature, or at least about 10°C below the first softening temperature, or at least about 25°C below the first softening temperature, or at least about 50°C below the first softening temperature, or about 100°C below the first softening temperature, or about 150°C below the first softening temperature, or about 200°C below the first softening temperature, or about 250°C below the first softening temperature, or about 300°C below the first softening temperature, or about 350°C below the first softening temperature. In some examples, grinding of the petroleum pitch may be conducted with the grinding apparatus cooled to a temperature below room temperature (23°C), such as from about -10°C to about 5°C or from about 0°C to about 15°C. Such "cold grinding" processes may render the petroleum pitch brittle to facilitate particle formation during grinding and keep the risk of oxidative degradation very low.

[0025] Another feature of the present disclosure is that one or more additives may be incorporated within the pitch particles by introducing the additive(s) to the pitch fines. By blending the additive(s) into the pitch melt, at least a portion of the pitch particles subsequently produced therefrom in the grinding apparatus may contain the additive. Additives that may be incorporated in the foregoing manner include, but are not limited to, graphite, carbon black, carbon nanotubes, polymers, inorganic materials (*e.g.*, iron oxide and chromium oxide), metal-containing compounds (*e.g.*, compounds containing sodium, potassium, calcium, iron, nickel, tungsten, cobalt, lithium, magnesium, titanium, vanadium, chromium, copper, zinc, zirconium, molybdenum, aluminum, or any combination thereof), graphitization catalysts, or any combination thereof. The additives may provide reinforcement to the petroleum pitch, increase bulk volume or density of the petroleum pitch, modify the reactivity of the petroleum pitch toward stabilization, carbonization, graphitization, or any combination thereof. When included, additives may be introduced to the pitch melt in an amount up to about 50 vol% of the pitch melt, such as at a vol% ranging from about 0.1 vol% to about 50 vol%, or about 1 vol% to about 25 vol%, or about 1 vol% to about 10 vol%, or about 5 vol% to about 20 vol%.

[0026] As an alternative to recycling the pitch fines containing the additive in the form of a pitch melt, as described herein, the pitch melt may instead be provided to a second grinding apparatus to produce a second pitch product comprising pitch particles containing the additive. By processing the pitch melt in a second grinding apparatus to produce a second pitch product, concentration variance of the additive in the pitch particles obtained from each grinding apparatus may be better managed.

[0027] The one or more additives may alternately be introduced to the petroleum pitch at similar loading values before grinding to produce the pitch particles. In one example, the additive(s) may be melt blended with the petroleum pitch, and after cooling the melt blend and grinding, the additive(s) may be contained within the pitch particles. In another example, the additive(s) may remain external to the petroleum pitch before grinding, and after separation of the pitch fines from the pitch particles, the additive(s) may remain external to the pitch particles. When added to the petroleum pitch from the outset, the pitch fines may be recycled without introducing further additive(s) to the pitch fines, or additional additive(s) may be added to the pitch fines to adjust the amount of additive(s) present in the pitch particles.

[0028] In addition to recycling the pitch fines in the foregoing manner, the pitch particles may be further stabilized through heating conducted at a treatment temperature below the first softening temperature and in a low-oxygen environment comprising about 0.1 mol% to about 20 mol% oxygen to form stabilized pitch particles. In more specific examples, the low-oxygen environment may have an oxygen concentration ranging from about 1 mol% to about 20 mol%, or about 1 mol% to about 15 mol%, or about 1 mol% to about 10 mol%, or about 1 mol% to about 5 mol%, or less than about 5 mol%, or less than about 1 mol%.

[0029] As discussed in brief above, such heating at the treatment temperature may facilitate stabilization of the petroleum pitch by promoting at least partial crosslinking thereof. In non-limiting examples, the treatment temperature may be at least about 5°C below the first softening temperature, or at least about 10°C below the first softening temperature, or at least about 15°C below the first softening temperature, or at least about 20°C below the first softening temperature, or at least about 25°C below the first softening temperature, or at least about 50°C below the first softening temperature, or at least about 75°C below the first softening temperature, or at least about 100°C below the first softening temperature, or at least about 150°C below the first softening temperature, such as within a range of about 150°C to about 250°C, or about 200°C to about 250°C, or about 250°C to about 300°C, or about 200°C to about 300°C, or about 200°C to about 450°C. Heating at the treatment temperature may take place over a time period of about 10 minutes to about 24 hours, or about 10 minutes to about 6 hours, or about 30 minutes to about 20 hours, or about 1 hour to about 18 hours, or about 30 minutes to about 2 hours, or about 2 hours to about 6 hours.

[0030] The treatment temperature of the pitch particles may correspond to an onset of oxidation temperature (OOT) associated with the petroleum pitch. The OOT may be characterized by a rapid exothermic release of heat upon reacting the petroleum pitch with oxygen. Maintaining the treatment temperature at the OOT for a specified hold time may be desirable for promoting stabilization of the petroleum pitch.

[0031] The at least partial crosslinking occurring at the treatment temperature may increase the softening temperature of the petroleum pitch from the first softening temperature to a second softening temperature that is higher than the first softening temperature, which may encourage the petroleum pitch to maintain its shape upon being further heated during carbonization or graphitization. In non-limiting examples, the second softening temperature may be at least about 5°C higher than the first softening temperature, or at least about 10°C higher than the first softening temperature, or least about 20°C higher than the first softening temperature, or least about 30°C higher than the first softening temperature, or least about 40°C higher than the first softening temperature, or least about 50°C higher than the first softening temperature. In some or other non-limiting examples, the second softening temperature may range from about 300°C to about 500°C, or about 320°C to about 450°C, or about 340°C to about 400°C, or about 380°C to about 480°C.

[0032] The foregoing pitch particles may further undergo carbonization in the disclosure herein to convert at least a portion of the petroleum pitch into amorphous carbon. Amorphous carbon may be formed upon heating the pitch particles at a carbonization temperature in a no-oxygen or very low-oxygen environment comprising about 0.1 mol% oxygen or below, preferably in the presence of an inert gas environment. The carbonization temperature may range from about 700°C to about 1800°C, or about 900°C to about 1800°C, or about 900°C to about 1500°C, or about 1000°C to about 1500°C, or about 900°C to about 1400°C. Preferably, the amorphous carbon may remain in predominantly particle form upon carbonizing the pitch particles, although a small amount of particle consolidation may take place during carbonization in some cases.

[0033] A small amount of mass loss may occur when carbonizing the pitch particles to form amorphous carbon. Without being limited by theory or mechanism, the mass loss is believed to result from various reactions of the petroleum pitch that form gaseous products. Such reactions may include, for instance, dehydrogenation, polymerization with side chain loss and/or hydrogen production, condensation of aromatic rings, and decomposition of oxygen-containing groups. Gaseous products may include, for example, carbon monoxide, carbon dioxide, water vapor, hydrocarbon vapor, methane, and the like. Up to about 20 wt% mass loss may occur during carbonization due to such reactions. Preferably, the amount of mass loss is about 10 wt% or less, or about 5 wt% or less, or about 2 wt% or less.

[0034] After converting the petroleum pitch to amorphous carbon, graphitization of amorphous carbon may then occur through further heating in the no-oxygen or low-oxygen environment. Thus, in further non-limiting examples, after carbonization, the pitch particles may be heated at a graphitization temperature in a no-oxygen or low-oxygen environment comprising about 0.1 mol% oxygen or below, preferably in the presence of an inert gas environment. In non-limiting examples, the graphitization temperature may range from about 2000°C to about 3500°C, or about 2000°C to about 3400°C, or about 2500°C to about 3400°C, or about 2800°C to about 3400°C.

[0035] The present disclosure will now be described with further reference to the drawing. The FIGURE is a block diagram of an illustrative system and method for processing petroleum pitch according to the present disclosure. In system and method **100**, petroleum pitch **102** is provided and introduced to grinder **104**, such as a jet mill or other suitable grinding apparatus. A portion of petroleum pitch **102** is ground to pitch particles **106a** having a desired size, and the remainder of petroleum pitch **102** is converted to pitch fines **106b** having a size below the desired size. Pitch particles **106a** may be stabilized through heating in an environment comprising about 0.1 mol% to about 20 mol% oxygen to produce stabilized pitch particles **110**, which have a softening temperature higher than that of pitch particles **102**. Pitch fines **106b** are processed in recycle loop **120** by heating above the softening temperature of petroleum pitch **102** to form pitch melt **108**. Pitch melt **108** is then combined with petroleum pitch **102** and reintroduced to grinder **104**, from which additional pitch particles **106a** and pitch fines **106b** may be produced. Although shown in the FIGURE as being introduced to a line carrying petroleum pitch **102** to grinder **104**, it is to be appreciated that pitch melt **108** may be introduced directly to grinder **104** and separately from petroleum pitch **102**.

[0036] Accordingly, more specific example methods of the present disclosure may comprise: providing a petroleum pitch having a first softening temperature of about 180°C to about 500°C (or about 180°C to about 400°C); grinding the petroleum pitch in a grinding apparatus below the first softening temperature to produce a plurality of pitch particles and a plurality of pitch fines; separating the pitch particles from the pitch fines; heating the pitch fines at a temperature above the first softening temperature to produce a pitch melt; combining the pitch melt with the petroleum pitch in the grinding apparatus, in which the pitch melt hardens in the grinding apparatus and is reground; and heating the pitch particles at a treatment temperature below the first softening temperature in an environment comprising about 1 mol% to about 20 mol% oxygen to form stabilized pitch particles having a second softening temperature that is higher than the first softening temperature.

[0037] Embodiments disclosed herein include:

[0038] A. Methods for recycling pitch fines. The methods comprise: providing a petroleum pitch having a first softening temperature; grinding the petroleum pitch in a grinding apparatus below the first softening temperature to produce a plurality of pitch particles and a plurality of pitch fines; separating the pitch particles from the pitch fines; heating the pitch fines at a temperature above the first softening temperature to produce a pitch melt; and combining the pitch melt with the petroleum pitch in the grinding apparatus; wherein the pitch melt hardens in the grinding apparatus and is reground.

[0039] B. Methods for stabilizing pitch particles with recycling of pitch fines. The methods comprise: providing a petroleum pitch having a first softening temperature of about 180°C to about 500°C; grinding the petroleum pitch in a grinding apparatus below the first softening temperature to produce a plurality of pitch particles and a plurality of pitch fines; separating the pitch particles from the pitch fines; heating the pitch fines at a temperature above the first softening temperature to produce a pitch melt; combining the pitch melt with the petroleum pitch in the grinding apparatus; wherein the pitch melt hardens in the grinding apparatus and is reground; and heating the pitch particles at a treatment temperature below the first softening temperature in an environment comprising about 1 mol% to about 20 mol% oxygen to form stabilized pitch particles; wherein the stabilized pitch particles have second softening temperature that is higher than the first softening temperature.

[0040] Embodiments A and B may have one or more of the following additional elements in any combination:

[0041] Element 1: wherein the first softening temperature ranges from about 180°C to about 500°C.

[0042] Element 2: wherein the pitch particles having a particle size ranging from about 1 micron to about 25 microns.

[0043] Element 3: wherein the grinding is performed using a jet mill.

[0044] Element 4: wherein the method further comprises heating the pitch particles at a treatment temperature below the first softening temperature in an environment comprising about 1 mol% to about 20 mol% oxygen to form stabilized pitch particles; wherein the stabilized pitch particles have second softening temperature that is higher than the first softening temperature.

[0045] Element 5: wherein the treatment temperature is at least about 5°C below the first softening temperature.

[0046] Element 6: wherein heating is conducted over a time period of about 10 minutes to about 6 hours.

[0047] Element 7: wherein the method further comprises heating the pitch particles at a carbonization temperature in an environment comprising about 0.1 mol% oxygen or below.

[0048] Element 8: wherein the carbonization temperature ranges from about 700°C to about 1800°C.

[0049] Element 9: wherein the method further comprises heating the pitch particles at a graphitization temperature in an environment comprising about 0.1 mol% oxygen or below.

[0050] Element 10: wherein the graphitization temperature ranges from about 2000°C to about 3400°C.

[0051] Element 11: wherein the method further comprises introducing one or more additives to the pitch melt.

[0052] Element 12: wherein the petroleum pitch comprises about 50 wt% or greater mesophase pitch.

[0053] Element 13: wherein the pitch fines have a particle size of about 1 micron or less.

[0054] Element 14: wherein the method further comprises performing a size separation of the pitch particles after separating the pitch particles from the pitch fines; wherein rejected pitch particles are removed in the size separation; and combining the rejected pitch particles with the pitch fines to form the pitch melt.

[0055] By way of non-limiting example, exemplary combinations applicable to A-B include, but are not limited to, 1 and 2; 1 and 3; 1 and 4; 1 and 5; 1, 5 and 6; 1 and 7; 1, 7 and 8; 1 and 9; 1, 9 and 10; 1 and 12; 1 and 13; 1 and 14; 2 and 3; 2 and 4; 2 and 5; 2, 5 and 6; 2 and 7; 2, 7 and 8; 2 and 9; 2, 9 and 10; 2 and 12; 2 and 13; 2 and 14; 3 and 4; 3 and 5; 3, 5 and 6; 3 and 7; 3, 7 and 8; 3 and 9; 3, 9 and 10; 3 and 12; 3 and 13; 3 and 14; 4 and 5; 4 and optionally 5, and 6; 4 and optionally 5, and 7; 4 and optionally 5, 7 and 8; 4 and optionally 5, and 9; 4 and optionally 5, 9 and 10; 4 and optionally 5, and 12; 4 and optionally 5, and 13; 4 and optionally 5, and 14; 7 and 8; 7 and optionally 8, and 9; 7 and optionally 8, 9 and 10; 7 and optionally 8, and 12; 7 and optionally 8, and 13; 7 and optionally 8, and 14; 9 and 10; 9 and optionally 10, and 12; 9 and optionally 10, and 13; 9 and optionally 10, and 14; 12 and 13; 12 and 14; 12-14; and 13 and 14.

[0056] Additional embodiments disclosed herein include:

[0057] Embodiment 1. A method comprising:

providing a petroleum pitch having a first softening temperature;

grinding the petroleum pitch in a grinding apparatus below the first softening temperature to produce a plurality of pitch particles and a plurality of pitch fines;

separating the pitch particles from the pitch fines;

heating the pitch fines at a temperature above the first softening temperature to produce a pitch melt; and

combining the pitch melt with the petroleum pitch in the grinding apparatus;

wherein the pitch melt hardens in the grinding apparatus and is reground.

[0058] Embodiment 2. The method of embodiment 1, wherein the first softening temperature ranges from about 180°C to about 500°C.

[0059] Embodiment 3. The method of embodiment 1 or embodiment 2, wherein the pitch particles having a particle size ranging from about 1 micron to about 25 microns.

[0060] Embodiment 4. The method of any one of embodiments 1-3, wherein the grinding is performed using a jet mill.

[0061] Embodiment 5. The method of any one of embodiments 1-4, further comprising:

heating the pitch particles at a treatment temperature below the first softening temperature in an environment comprising about 1 mol% to about 20 mol% oxygen to form stabilized pitch particles;

wherein the stabilized pitch particles have second softening temperature that is higher than the first softening temperature.

[0062] Embodiment 6. The method of embodiment 5, wherein the treatment temperature is at least about 5°C below the first softening temperature.

[0063] Embodiment 7. The method of embodiment 5 or embodiment 6, wherein heating is conducted over a time period of about 10 minutes to about 6 hours.

[0064] Embodiment 8. The method of any one of embodiments 1-7, further comprising:

heating the pitch particles at a carbonization temperature in an environment comprising about 0.1 mol% oxygen or below.

[0065] Embodiment 9. The method of embodiment 8, wherein the carbonization temperature ranges from about 700°C to about 1800°C.

[0066] Embodiment 10. The method of embodiment 8 or embodiment 9, further comprising:

heating the pitch particles at a graphitization temperature in an environment comprising about 0.1 mol% oxygen or below.

[0067] Embodiment 11. The method of embodiment 10, wherein the graphitization temperature ranges from about 2000°C to about 3400°C.

[0068] Embodiment 12. The method of any one of embodiments 1-11, further comprising:

introducing one or more additives to the pitch melt.

[0069] Embodiment 13. The method of any one of embodiments 1-12, wherein the petroleum pitch comprises about 50 wt% or greater mesophase pitch.

[0070] Embodiment 14. The method of any one of embodiments 1-13, wherein the pitch fines have a particle size of about 1 micron or less.

[0071] Embodiment 15. The method of any one of embodiments 1-14, further comprising:

performing a size separation of the pitch particles after separating the pitch particles from the pitch fines;

wherein rejected pitch particles are removed in the size separation; and

combining the rejected pitch particles with the pitch fines to form the pitch melt.

[0072] Embodiment 16. A method comprising:

providing a petroleum pitch having a first softening temperature of about 180°C to about 500°C;

grinding the petroleum pitch in a grinding apparatus below the first softening temperature to produce a plurality of pitch particles and a plurality of pitch fines;

separating the pitch particles from the pitch fines;

heating the pitch fines at a temperature above the first softening temperature to produce a pitch melt;

combining the pitch melt with the petroleum pitch in the grinding apparatus;

wherein the pitch melt hardens in the grinding apparatus and is reground; and

heating the pitch particles at a treatment temperature below the first softening temperature in an environment comprising about 1 mol% to about 20 mol% oxygen to form stabilized pitch particles;

wherein the stabilized pitch particles have second softening temperature that is higher than the first softening temperature.

[0073] Embodiment 17. The method of embodiment 16, wherein the treatment temperature is at least about 5°C below the first softening temperature.

[0074] Embodiment 18. The method of embodiment 16 or embodiment 17, wherein the pitch particles having a particle size ranging from about 1 micron to about 25 microns.

[0075] Embodiment 19. The method of any one of embodiments 16-18, wherein the grinding is performed using a jet mill.

[0076] Embodiment 20. The method of any one of embodiments 16-19, further comprising:

performing a size separation of the pitch particles after separating the pitch particles from the pitch fines;

wherein rejected pitch particles are removed in the size separation; and

combining the rejected pitch particles with the pitch fines to form the pitch melt.

[0077] Any alterations, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description without departing from the spirit or scope of the present disclosure and that when numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

[0078] 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 that 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 may 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.

[0079] 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 disclosure. 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.

[0080] 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. 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.

[0081] All numerical values within the detailed description herein are modified by “about” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0082] 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.

[0083] While compositions and methods are described herein in terms of “comprising” or "having" various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and steps.

[0084] 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:

providing a petroleum pitch having a first softening temperature;

grinding the petroleum pitch in a grinding apparatus below the first softening temperature to produce a plurality of pitch particles and a plurality of pitch fines;

separating the pitch particles from the pitch fines;

heating the pitch fines at a temperature above the first softening temperature to produce a pitch melt; and

combining the pitch melt with the petroleum pitch in the grinding apparatus,

wherein the pitch melt hardens in or before the grinding apparatus and is reground.

2. The method of claim 1, wherein the first softening temperature is in a range from about 180°C to about 500°C.

3. The method of claim 1, wherein the pitch particles having a particle size ranging from about 1 micron to about 25 microns.

4. The method of claim 1, wherein the grinding is performed using a jet, impact, or ball mill.

5. The method of claim 1, further comprising:

heating the pitch particles at a treatment temperature below the first softening temperature in an environment comprising about 1 mol% to about 20 mol% oxygen to form stabilized pitch particles,

wherein the stabilized pitch particles have second softening temperature that is higher than the first softening temperature.

6. The method of claim 5, wherein the treatment temperature is at least about 5°C below the first softening temperature.

7. The method of claim 5, wherein heating is conducted over a time period of about 10 minutes to about 6 hours.

8. The method of claim 1, further comprising:

heating the pitch particles at a carbonization temperature in an environment comprising about 0.1 mol% oxygen or below.

9. The method of claim 8, wherein the carbonization temperature is in a range of from about 700°C to about 1800°C.

10. The method of claim 8, further comprising:

heating the pitch particles at a graphitization temperature in an environment comprising about 0.1 mol% oxygen or below.

11. The method of claim 10, wherein the graphitization temperature is in a range of from about 2000°C to about 3400°C.

12. The method of claim 1, further comprising:

introducing one or more additives to the pitch melt.

13. The method of claim 1, wherein the petroleum pitch comprises about 50 wt% or greater mesophase pitch.

14. The method of claim 1, wherein the pitch fines have a particle size of about 1 micron or less.

15. The method of claim 1, further comprising:

performing a size separation of the pitch particles after separating the pitch particles from the pitch fines;

wherein rejected pitch particles are removed in the size separation; and

combining the rejected pitch particles with the pitch fines to form the pitch melt.

16. A method comprising:

providing a petroleum pitch having a first softening temperature of about 180°C to about 500°C;

grinding the petroleum pitch in a grinding apparatus below the first softening temperature to produce a plurality of pitch particles and a plurality of pitch fines;

separating the pitch particles from the pitch fines;

heating the pitch fines at a temperature above the first softening temperature to produce a pitch melt;

combining the pitch melt with the petroleum pitch in the grinding apparatus;

wherein the pitch melt hardens in or before the grinding apparatus and is reground; and

heating the pitch particles at a treatment temperature below the first softening temperature in an environment comprising about 1 mol% to about 20 mol% oxygen to form stabilized pitch particles,

wherein the stabilized pitch particles have second softening temperature that is higher than the first softening temperature.

17. The method of claim 16, wherein the treatment temperature is at least about 5°C below the first softening temperature.

18. The method of claim 16, wherein the pitch particles having a particle size ranging from about 1 microns to about 25 microns.

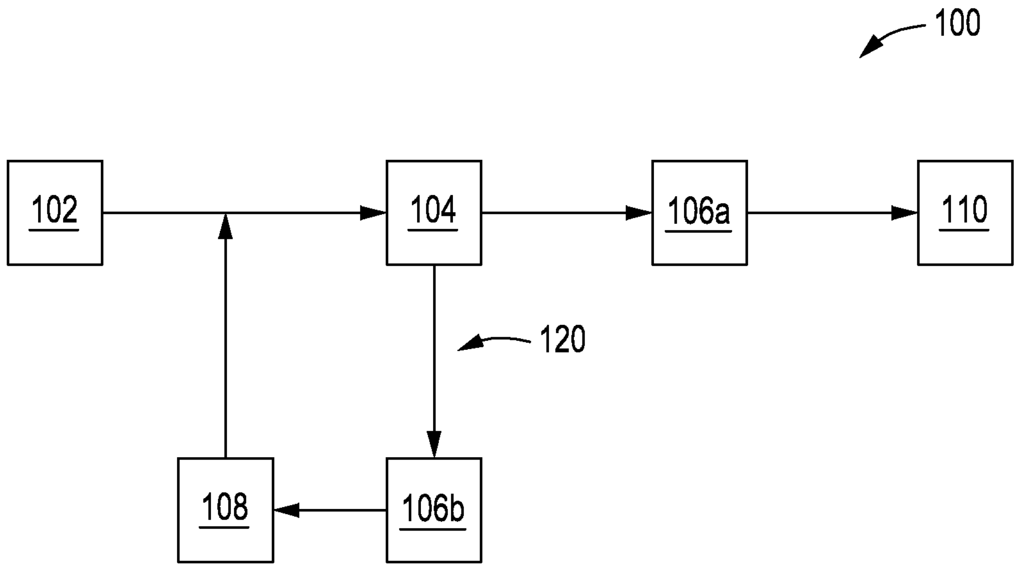
19. The method of claim 16, wherein the grinding is performed using a jet, impact, or ball mill.

20. The method of claim 16, further comprising:

performing a size separation of the pitch particles after separating the pitch particles from the pitch fines;

wherein rejected pitch particles are removed in the size separation; and

combining the rejected pitch particles with the pitch fines to form the pitch melt.



FIGURE

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/027446

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G31/06 C10C3/00
ADD.

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

B. FIELDS SEARCHED

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

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2020/002169 A1 (BASEL RICHARD [US] ET AL) 2 January 2020 (2020-01-02) paragraphs [0046], [0055] - [0057], [0063], [0086], [0088], [0092], [0093], [0100], [0131]; figure 1 -----	1-20
A	US 2 681 318 A (MAYER PERRY E) 15 June 1954 (1954-06-15) column 4, line 10 - line 26; figure 1 -----	1-20

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

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

"P" document published prior to the international filing date but later than the priority date claimed

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

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 August 2024	21/08/2024

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2024/027446

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2020002169 A1	02-01-2020	CN 110536863 A	03-12-2019
		EP 3580169 A2	18-12-2019
		US 2020002169 A1	02-01-2020
		WO 2018146080 A2	16-08-2018
US 2681318 A	15-06-1954	NONE	