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(57) Abstract: Some variations provide a process for producing biocarbon pellets, comprising: pyrolyzing a biomass-containing feedstock in a first pyrolysis reactor to generate a first biogenic reagent and a pyrolysis vapor; introducing the pyrolysis vapor to a separation unit, to generate a pyrolysis precipitate in liquid or solid form; contacting the first biogenic reagent with the pyrolysis precipitate, thereby generating an intermediate material; pelletizing the intermediate material, to generate intermediate pellets; optionally, drying the intermediate pellets; separately pyrolyzing the intermediate pellets in a second pyrolysis reactor to generate a second biogenic reagent and a pyrolysis off-gas; and recovering the second biogenic reagent as biocarbon pellets. Some variations provide a similar process that utilizes a carbon-containing condensed-matter material, which is not necessarily a pyrolysis precipitate. The disclosure provides improved processes for producing biocarbon compositions, especially with respect to carbon yield and biocarbon properties, such as reactivity.

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# PROCESSES FOR PRODUCING BIOCARBON PELLETS WITH HIGH FIXED-CARBON CONTENT AND OPTIMIZED REACTIVITY, AND BIOCARBON PELLETS OBTAINED THEREFROM

## CROSS-REFERENCE TO RELATED APPLICATION(S)

**[0001]** This application claims the priority benefit of U.S. Provisional Patent Application No. 63/220,073, filed on July 9, 2021, which is incorporated by reference herein in its entirety.

## TECHNICAL FIELD

**[0002]** The present disclosure generally relates to pyrolysis processes for making high-yield biocarbon compositions, and biocarbon compositions produced therefrom.

## BACKGROUND

**[0003]** Carbon is a platform element in a wide variety of industries and has a vast number of chemical, material, and fuel uses. Carbon is used as fuel to produce energy, including electricity. Carbon also has chemical value for various commodities and advanced materials, including metals, metal alloys, composites, carbon fibers, electrodes, and catalyst supports. For metal making, carbon is useful as a reactant, for reducing metal oxides to metals during processing; as a fuel, to provide heat for processing; and as a component of a metal alloy.

**[0004]** Carbon can be produced from many sources of carbonaceous material. Carbonaceous materials commonly comprise fossil resources such as natural gas, petroleum, coal, and lignite; and renewable resources such as lignocellulosic biomass and various carbon-rich waste materials. It is preferable to utilize renewable biomass to produce carbon-based reagents because of the rising economic, environmental, and social costs associated with fossil resources.

## SUMMARY

**[0005]** The disclosed technology addresses the aforementioned needs in the art.

**[0006]** Some variations provide a process for producing a biocarbon pellet, the process comprising:

(a) pyrolyzing, in a first pyrolysis reactor, a biomass-containing feedstock, thereby generating a first biogenic reagent and a pyrolysis vapor;

(b) introducing, to a separation unit, the pyrolysis vapor, thereby generating a pyrolysis precipitate, wherein the pyrolysis precipitate is in liquid, solid, or slurry form;

(c) contacting the first biogenic reagent with the pyrolysis precipitate, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the pyrolysis precipitate;

(d) pelletizing the intermediate material, thereby generating an intermediate pellet;

(e) optionally, drying the intermediate pellet;

(f) separately from step (a), pyrolyzing, in a second pyrolysis reactor, the intermediate pellet, thereby generating a second biogenic reagent and a pyrolysis off-gas, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same reactor or distinct reactors; and

(g) recovering the second biogenic reagent as a biocarbon pellet,

wherein a fixed carbon content of the second biogenic reagent is greater than a fixed carbon content of the first biogenic reagent; and

wherein, according to a thermogravimetric analysis, an oxygen reactivity of the second biogenic reagent is less than an oxygen reactivity of the first biogenic reagent, wherein the thermogravimetric analysis is performed using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

**[0007]** In some embodiments, according to a TGA graph of weight loss versus time from the thermogravimetric analysis, the second biogenic reagent requires at least a 5% longer time to reach 99% carbon oxidation, compared to the first biogenic reagent. In certain embodiments, according to the TGA graph, the second biogenic reagent requires at least a 10% longer time to reach 99% carbon oxidation, compared to the first biogenic reagent.

**[0008]** In some embodiments, the TGA graph shows a first carbon-oxidation regime associated with oxidation of volatile carbon, which is succeeded by a second carbon-oxidation regime associated with oxidation of fixed carbon.

**[0009]** In some embodiments, a volatile-carbon oxidation time is defined from the onset of the first carbon-oxidation regime to the onset of the second carbon-oxidation regime. During the volatile-carbon oxidation time, a mass loss of the first biogenic reagent can be at least 25% or at least 50% greater than a mass loss of the second biogenic reagent.

**[0010]** In some embodiments, during the first carbon-oxidation regime, the thermogravimetric analysis shows that a mass loss rate of the first biogenic reagent is at least 25% or at least 50% greater than a mass loss rate of the second biogenic reagent during the first carbon-oxidation regime.

**[0011]** In some embodiments, the thermogravimetric analysis shows that the first biogenic reagent has at least 10% higher average rate of mass loss during the first carbon-oxidation regime compared to the second carbon-oxidation regime.

**[0012]** In some embodiments, the thermogravimetric analysis shows a first-derivative curve peak within the first carbon-oxidation regime for the second biogenic reagent at a temperature of at least about 500°C, and the thermogravimetric analysis shows a first-derivative curve peak within the first carbon-oxidation regime for the first biogenic reagent at a temperature from 200°C to 500°C.

**[0013]** The biomass-containing feedstock can be selected from softwood chips, hardwood chips, timber harvesting residue, tree branches, tree stumps, leaves, bark, sawdust, corn, corn stover, wheat, wheat straw, rice, rice straw, sugarcane, sugarcane bagasse, sugarcane straw, energy cane, sugar beets, sugar beet pulp, sunflowers, sorghum, canola, algae, miscanthus, alfalfa, switchgrass, fruits, fruit shells, fruit stalks, fruit peels, fruit pits, vegetables, vegetable shells, vegetable stalks, vegetable peels, vegetable pits, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, food waste, commercial waste, grass pellets, hay pellets, wood pellets, cardboard, paper, paper pulp, paper packaging, paper trimmings, food packaging, construction or demolition waste, railroad ties, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof.

**[0014]** In some embodiments, the separation unit comprises a condensing system. The condensing system can have multiple stages, in which case the pyrolysis precipitate can be a condensed product of a first condenser stage of the multiple stages.

The pyrolysis precipitate can be a condensed product of another condenser stage of the multiple stages.

**[0015]** In various embodiments, the separation unit comprises a condensing system, a liquid-vapor cyclone separator, a demister, a distillation unit, a filtration unit, a membrane unit, a scrubbing unit, a chemical precipitation unit, a liquid-liquid extraction unit, an electrostatic precipitation unit, or a combination thereof.

**[0016]** In some embodiments, the intermediate material comprises the pyrolysis precipitate adsorbed onto a surface of the first biogenic reagent. Alternatively, or additionally, the intermediate material can comprise the pyrolysis precipitate absorbed into a bulk phase of the first biogenic reagent.

**[0017]** The pyrolysis precipitate can be in liquid form, in solid form, or in slurry form (a slurry meaning a suspension of solids in liquid).

**[0018]** In some embodiments, steps (c) and (d) are integrated.

**[0019]** A binder can be introduced to the intermediate material. The binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, a derivative thereof, or a combination of any of the foregoing. In certain embodiments, the binder is selected from starch, thermoplastic starch, crosslinked starch, starch polymers, a derivative thereof, or a combination of any of the foregoing.

**[0020]** In some embodiments, no external binder is introduced to the intermediate material during the pelletizing. Note that the pyrolysis precipitate (from the process) itself can function as an *in situ* binder. An *in situ* binder is not an external binder.

**[0021]** In some embodiments, step (e) for the drying is conducted. In this case, steps (d) and (e) can be integrated. Additionally, or alternatively, steps (e) and (f) can be integrated.

**[0022]** In some embodiments, the first biogenic reagent is milled utilizing a first mechanical-treatment apparatus selected from a hammer mill, an extruder, an attrition mill, a disc mill, a pin mill, a ball mill, a cone crusher, a jaw crusher, or a combination thereof.

**[0023]** In some embodiments, the intermediate material is milled utilizing a second mechanical-treatment apparatus selected from a hammer mill, an extruder, an attrition mill, a disc mill, a pin mill, a ball mill, a cone crusher, a jaw crusher, or a combination thereof.

**[0024]** In some embodiments, step (d) utilizes a pelletizing apparatus selected from an extruder, a ring die pellet mill, a flat die pellet mill, a roll compactor, a roll briquetter, a wet agglomeration mill, a dry agglomeration mill, or a combination thereof.

**[0025]** The first pyrolysis reactor can be distinct from the second pyrolysis reactor. Alternatively, the first pyrolysis reactor and the second pyrolysis reactor can be the same unit, wherein steps (a) and (f) are conducted at different times, such as in a campaign mode of the process.

**[0026]** In some embodiments, the first biogenic reagent acts as a catalyst or reaction matrix for fixed-carbon formation reactions of the pyrolysis precipitate.

**[0027]** Step (a) can be conducted at a first pyrolysis temperature selected from about 250°C to about 700°C, for example. Step (a) can be conducted for a first pyrolysis time selected from about 1 minute to about 4 hours, for example.

**[0028]** Step (f) can be conducted at a second pyrolysis temperature selected from about 300°C to about 1250°C, for example. Step (f) can be conducted for a second pyrolysis time selected from about 1 minute to about 4 hours, for example.

**[0029]** In some embodiments, a pyrolysis non-precipitate is generated in the separation unit, wherein the pyrolysis non-precipitate is optionally recovered and at least partially oxidized to generate heat, and wherein the heat is optionally used within the process.

**[0030]** In some embodiments, some of the pyrolysis vapor is at least partially oxidized to generate heat, wherein the heat is optionally used within the process.

**[0031]** In some embodiments, the pyrolysis off-gas is at least partially oxidized to generate heat, wherein the heat is optionally used within the process.

**[0032]** The pyrolysis off-gas is optionally conveyed to the separation unit. Alternatively, or additionally, the pyrolysis off-gas can be conveyed to a second separation unit (different from the separation unit in step (b)) operated under effective precipitation conditions to generate a second pyrolysis precipitate, wherein the second pyrolysis precipitate is in liquid, solid, or slurry form. The process can further comprise contacting the second pyrolysis precipitate with the first biogenic reagent or with the second biogenic reagent.

**[0033]** The biocarbon pellet can comprise at least 60 wt% fixed carbon. In various embodiments, the biocarbon pellet comprises at least 70 wt% fixed carbon, at least 80 wt% fixed carbon, at least 85 wt% fixed carbon, or at least 90 wt% fixed carbon.

**[0034]** The biocarbon pellet can comprise at most 10 wt% ash. In various embodiments, the biocarbon pellet comprises at most 5 wt% ash, or at most 1 wt% ash.

**[0035]** The pyrolysis precipitate can itself comprise at most 1 wt% ash, at most 0.1 wt% ash, or essentially no ash. A low-ash pyrolysis precipitate is beneficial so that ash is not added to the first biogenic reagent, leading to a lower-ash final product.

**[0036]** In some embodiments, the biocarbon pellet comprises at most 20 wt% total volatile matter. In certain embodiments, the biocarbon pellet comprises at most 10 wt% total volatile matter.

**[0037]** In some embodiments, at least 10 wt% of carbon comprised in the pyrolysis precipitate is converted to fixed carbon in the biocarbon pellet. In various embodiments, at least 20 wt% or at least 50% of carbon comprised in the pyrolysis precipitate is converted to fixed carbon in the biocarbon pellet. In certain embodiments, from 30 wt% to 90 wt% of carbon comprised in the pyrolysis precipitate is converted to fixed carbon in the biocarbon pellet.

**[0038]** In some embodiments, from 1 wt% to 50 wt% of fixed carbon in the biocarbon pellet is derived from the pyrolysis precipitate. In certain embodiments, from

10 wt% to 40 wt% of fixed carbon in the biocarbon pellet is derived from the pyrolysis precipitate.

**[0039]** In some embodiments, the intermediate material further comprises additional pyrolysis precipitate that is not provided from step (b) of the process.

**[0040]** In step (c), less than all, or all, of the first biogenic reagent can be contacted with the pyrolysis precipitate. In step (c), less than all, or all, of the pyrolysis precipitate can be contacted with the first biogenic reagent.

**[0041]** In some embodiments, total carbon within the biocarbon pellet is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. Total carbon within the biocarbon pellet can be at least 90% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. Total carbon within the biocarbon pellet can be fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

**[0042]** The biocarbon pellet can be characterized by a Hardgrove Grindability Index of at least 30, for example.

**[0043]** The biocarbon pellet can be characterized by a bulk density of at least about 20 $lb/ft^3$ on a dry basis, for example.

**[0044]** The biocarbon pellet can have an average pellet size selected from about 1 mm to about 10 cm, calculated as effective diameter of the biocarbon pellet, for example.

**[0045]** The biocarbon pellet can have a pellet effective diameter that is within 10% or within 5% of the effective pellet diameter of the intermediate pellet. In other embodiments, the biocarbon pellet has an effective pellet diameter that is more than 110%, or less than 90%, of the effective pellet diameter of the intermediate pellet.

**[0046]** The biocarbon pellet can have a pellet shape selected from sphere, cylinder, cube, octagon, hexagon, honeycomb, oval, column, bar, pillow, lentil, random granular, or a combination thereof.

**[0047]** The biocarbon pellet can be characterized by a pellet compressive strength at 25°C of at least about 100 $lb_f/in^2$, or at least about 150 $lb_f/in^2$, for example.

**[0048]** The biocarbon pellet can be characterized by at most 20 wt% water uptake at 25°C after 24 hours of soaking in water.

**[0049]** The biocarbon pellet can be characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances."

**[0050]** The process can further comprise introducing an additive during the process. The additive can be selected from acids, bases, or salts thereof. Alternatively, or additionally, the additive can be selected from metals, metal oxides, metal hydroxides, metal halides, or a combination thereof. In some embodiments, the additive is selected from sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron halide, iron chloride, iron bromide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, titanium dioxide, or a combination thereof.

**[0051]** In some embodiments, the oxygen reactivity of the second biogenic reagent is reduced by addition of an additive to the second biogenic reagent.

**[0052]** An additive can be selected to adjust filtrate pH of the biocarbon pellet, wherein the filtrate pH is measured by combining 20 grams on a dry basis of the biocarbon pellet, or a powder form thereof, with 100 milliliters of distilled water, to form a mixture; filtering the mixture through filter paper; and measuring pH of the filtrate with a pH meter.

**[0053]** An additive can be added to the second biogenic reagent to adjust filtrate pH of the second biogenic reagent, wherein the filtrate pH is measured by combining 20 grams on a dry basis of the second biogenic reagent with 100 milliliters of distilled water, to form a mixture; filtering the mixture through filter paper; and measuring pH of the filtrate with a pH meter. In some embodiments, the additive is added to the second biogenic reagent to decrease filtrate pH of the second biogenic reagent. In other embodiments, the additive is added to the second biogenic reagent to increase filtrate pH of the second biogenic reagent.

**[0054]** In some embodiments, the process provides an overall carbon yield of at least 50%, calculated as carbon comprised in the biocarbon pellet as a percentage of carbon comprised in the biomass-containing feedstock. In various embodiments, the overall carbon yield is at least 60%, at least 70%, or at least 80%.

**[0055]** The process can be continuous or semi-continuous.

**[0056]** In some embodiments, the biocarbon pellet is mechanically treated to generate biocarbon powder. Alternatively, or additionally, the biocarbon pellet can be combined with another amount of the second biogenic reagent, to generate a biocarbon object. The other amount of second biogenic reagent can itself be in pellet form, or can be in powder form, for example.

**[0057]** Other variations provide a process for producing a biocarbon pellet, the process comprising:

(a) pyrolyzing, in a first pyrolysis reactor, a biomass-containing feedstock, thereby generating a first biogenic reagent and a pyrolysis vapor;

(b) providing a carbon-containing condensed-matter material, wherein the carbon-containing condensed-matter material is a liquid, a solid, or a slurry;

(c) contacting the first biogenic reagent with the carbon-containing condensed-matter material, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the carbon-containing condensed-matter material;

(d) pelletizing the intermediate material, thereby generating an intermediate pellet;

(e) optionally, drying the intermediate pellet;

(f) separately from step (a), pyrolyzing, in a second pyrolysis reactor, the intermediate pellet, thereby generating a second biogenic reagent and a pyrolysis off-gas, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same reactor or distinct reactors; and

(g) recovering the second biogenic reagent as a biocarbon pellet,

wherein a fixed carbon content of the second biogenic reagent is greater than a fixed carbon content of the first biogenic reagent; and

wherein the second biogenic reagent has lower oxygen reactivity than the first biogenic reagent according to a thermogravimetric analysis using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

**[0058]** In some embodiments, according to a TGA graph of weight loss versus time from the thermogravimetric analysis, the second biogenic reagent requires at least a 5% or at least 10% longer time to reach 99% oxidation, compared to the first biogenic reagent.

**[0059]** In some embodiments, the TGA graph shows a first carbon-oxidation regime associated with oxidation of volatile carbon, which is succeeded by a second carbon-oxidation regime associated with oxidation of fixed carbon.

**[0060]** In some embodiments, a volatile-carbon oxidation time is defined from the onset of the first carbon-oxidation regime to the onset of the second carbon-oxidation regime. During the volatile-carbon oxidation time, the first biogenic reagent can have at least 25% or at least 50% more mass loss compared to the second biogenic reagent.

**[0061]** In some embodiments, the thermogravimetric analysis shows that the first biogenic reagent has at least 25% or at least 50% higher rate of mass loss during the first carbon-oxidation regime than the rate of mass loss of the second biogenic reagent during the first carbon-oxidation regime.

**[0062]** In some embodiments, the thermogravimetric analysis shows that the first biogenic reagent has at least 10% higher average rate of mass loss during the first carbon-oxidation regime compared to the second carbon-oxidation regime.

**[0063]** In some embodiments, the thermogravimetric analysis shows a first-derivative curve peak within the first carbon-oxidation regime for the second biogenic reagent at a temperature of at least about 500°C, and wherein the thermogravimetric analysis shows a first-derivative curve peak within the first carbon-oxidation regime for the first biogenic reagent at a temperature from 200°C to 500°C.

**[0064]** The biomass-containing feedstock can be selected from softwood chips, hardwood chips, timber harvesting residues, tree branches, tree stumps, leaves, bark, sawdust, corn, corn stover, wheat, wheat straw, rice, rice straw, sugarcane, sugarcane bagasse, sugarcane straw, energy cane, sugar beets, sugar beet pulp, sunflowers, sorghum, canola, algae, miscanthus, alfalfa, switchgrass, fruits, fruit shells, fruit stalks,

fruit peels, fruit pits, vegetables, vegetable shells, vegetable stalks, vegetable peels, vegetable pits, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, food waste, commercial waste, grass pellets, hay pellets, wood pellets, cardboard, paper, paper pulp, paper packaging, paper trimmings, food packaging, construction or demolition waste, railroad ties, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof.

**[0065]** In some embodiments, the carbon-containing condensed-matter material is a pyrolysis precipitate derived from the pyrolysis vapor. In other embodiments, the carbon-containing condensed-matter material is a pyrolysis precipitate provided externally from a different process. The pyrolysis precipitate can also be a mixture of the foregoing.

**[0066]** In some embodiments, the carbon-containing condensed-matter material comprises aromatic species. For example, the carbon-containing condensed-matter material can be an off-spec or waste aromatics stream. In certain embodiments, the carbon-containing condensed-matter material comprises lignin.

**[0067]** In some embodiments, the carbon-containing condensed-matter material comprises a sugar or a sugar-degradation product.

**[0068]** In some embodiments, the carbon-containing condensed-matter material comprises a polymer or a polymer-degradation product.

**[0069]** In some embodiments, the carbon-containing condensed-matter material comprises liquid products produced by chemical reactions of syngas, and wherein the syngas is optionally obtained from the pyrolysis vapor or the pyrolysis off-gas.

**[0070]** In some embodiments, the carbon-containing condensed-matter material comprises at least 50%, at least 90%, or 100% (fully) renewable carbon as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio.

**[0071]** In some embodiments, the intermediate material comprises the carbon-containing condensed-matter material adsorbed onto a surface of the first biogenic reagent. Alternatively, or additionally, the intermediate material can comprise the carbon-containing condensed-matter material absorbed into a bulk phase of the first biogenic reagent.

**[0072]** In some embodiments, steps (c) and (d) are integrated.

**[0073]** In some embodiments, a binder is introduced to the intermediate material. The binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, a derivative thereof, or a combination of any of the foregoing. In certain embodiments, the binder is selected from starch, thermoplastic starch, crosslinked starch, starch polymers, a derivative thereof, or a combination of any of the foregoing.

**[0074]** In some embodiments, no external binder is introduced to the intermediate material during the pelletizing. Note that the pyrolysis precipitate (from the process) itself can function as an *in situ* binder. An *in situ* binder is not an external binder.

**[0075]** In some embodiments, step (e) for the drying is conducted. When step (e) is done, steps (d) and (e) can be integrated. Also, when step (e) is done, steps (e) and (f) can be integrated.

**[0076]** In some embodiments, the first biogenic reagent is milled utilizing a first mechanical-treatment apparatus selected from a hammer mill, an extruder, an attrition mill, a disc mill, a pin mill, a ball mill, a cone crusher, a jaw crusher, or a combination thereof.

**[0077]** In some embodiments, the intermediate material is milled utilizing a second mechanical-treatment apparatus selected from a hammer mill, an extruder, an attrition mill, a disc mill, a pin mill, a ball mill, a cone crusher, a jaw crusher, or a combination thereof.

**[0078]** In some embodiments, step (d) utilizes a pelletizing apparatus selected from an extruder, a ring die pellet mill, a flat die pellet mill, a roll compactor, a roll briquetter, a wet agglomeration mill, a dry agglomeration mill, or a combination thereof.

**[0079]** In some embodiments, the first pyrolysis reactor is distinct from the second pyrolysis reactor. Alternatively, the first pyrolysis reactor and the second pyrolysis reactor can be the same unit, wherein steps (a) and (f) are conducted at different times.

**[0080]** In some embodiments, the first biogenic reagent acts as a catalyst or reaction matrix for fixed-carbon formation reactions of the carbon-containing condensed-matter material.

**[0081]** In some embodiments, step (a) is conducted at a first pyrolysis temperature selected from about 250°C to about 700°C or for a first pyrolysis time selected from about 1 minute to about 4 hours.

**[0082]** In some embodiments, step (f) is conducted at a second pyrolysis temperature selected from about 300°C to about 1250°C or for a second pyrolysis time selected from about 1 minute to about 4 hours.

**[0083]** In some embodiments, the pyrolysis vapor is at least partially oxidized to generate heat, and wherein the heat is optionally used within the process.

**[0084]** In some embodiments, the pyrolysis off-gas is at least partially oxidized to generate heat, and wherein the heat is optionally used within the process.

**[0085]** In some embodiments, the pyrolysis off-gas is conveyed to a separation unit operated under effective precipitation conditions to generate a second pyrolysis precipitate, wherein the second pyrolysis precipitate is in liquid or solid form. In certain embodiments, the process further comprises contacting the first biogenic reagent with the second pyrolysis precipitate. In certain embodiments, the process further comprises contacting the second biogenic reagent with the second pyrolysis precipitate.

**[0086]** In some embodiments, the biocarbon pellet comprises at least 60 wt% fixed carbon. In certain embodiments, the biocarbon pellet comprises at least 70 wt%, at least 80 wt%, at least 85 wt%, or at least 90 wt% fixed carbon.

**[0087]** In some embodiments, the biocarbon pellet comprises at most 10 wt% ash. In certain embodiments, the biocarbon pellet comprises at most 5 wt% ash, or at most 1 wt% ash.

**[0088]** In some embodiments, the biocarbon pellet comprises at most 20 wt% total volatile matter, such as at most 10 wt% total volatile matter.

**[0089]** In some embodiments, at least 25 wt%, at least 50 wt%, or at least 75 wt% of carbon in the carbon-containing condensed-matter material is converted to fixed carbon in the biocarbon pellet.

**[0090]** In some embodiments, from 1 wt% to 50 wt% of fixed carbon in the biocarbon pellet is derived from the carbon-containing condensed-matter material. In certain embodiments, from 10 wt% to 40 wt% of fixed carbon in the biocarbon pellet is derived from the carbon-containing condensed-matter material.

**[0091]** In some embodiments, in step (c), less than all, or all, of the first biogenic reagent is contacted with the carbon-containing condensed-matter material.

**[0092]** In some embodiments, in step (c), less than all, or all, of the carbon-containing condensed-matter material is contacted with the first biogenic reagent.

**[0093]** In some embodiments, total carbon within the biocarbon pellet is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. In certain embodiments, total carbon within the biocarbon pellet is at least 90% renewable, or is fully renewable, as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

**[0094]** In some embodiments, the biocarbon pellet is characterized by a Hardgrove Grindability Index of at least 30.

**[0095]** In some embodiments, the biocarbon pellet is characterized by a bulk density of at least about 20 $lb/ft^3$ on a dry basis.

**[0096]** In some embodiments, the biocarbon pellet has an average pellet size selected from about 1 mm to about 10 cm, calculated as effective diameter of the biocarbon pellet.

**[0097]** The biocarbon pellet can have a pellet effective diameter that is within 10% or within 5% of the effective pellet diameter of the intermediate pellet. In other embodiments, the biocarbon pellet has an effective pellet diameter that is more than 110%, or less than 90%, of the effective pellet diameter of the intermediate pellet.

**[0098]** In some embodiments, the biocarbon pellet has a pellet shape selected from sphere, cylinder, cube, octagon, hexagon, honeycomb, oval, column, bar, pillow, lentil, random granular, or a combination thereof.

**[0099]** In some embodiments, the biocarbon pellet is characterized by a pellet compressive strength at 25°C of at least about 100 $lb_f/in^2$.

**[0100]** In some embodiments, the biocarbon pellet is characterized by a pellet compressive strength at 25°C of at least about 150 $lb_f/in^2$.

**[0101]** In some embodiments, the biocarbon pellet is characterized by at most 20 wt% water uptake at 25°C after 24 hours of soaking in water.

**[0102]** In some embodiments, the biocarbon pellet is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances."

**[0103]** In some embodiments, the process further comprises introducing an additive during the process. The additive can be selected from acids, bases, or salts thereof. The additive can be selected from metals, metal oxides, metal hydroxides, metal halides, or a combination thereof. For example, the additive can be selected from sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron halide, iron chloride, iron bromide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, titanium dioxide, or a combination thereof.

**[0104]** An additive can be selected to adjust filtrate pH of the biocarbon pellet, wherein the filtrate pH is measured by combining 20 grams on a dry basis of the biocarbon pellet, or a powder form thereof, with 100 milliliters of distilled water, to form a mixture; filtering the mixture through filter paper; and measuring pH of the filtrate with a pH meter.

**[0105]** An additive can be added to the second biogenic reagent to adjust filtrate pH of the second biogenic reagent, wherein the filtrate pH is measured by combining 20 grams on a dry basis of the second biogenic reagent with 100 milliliters of distilled water, to form a mixture; filtering the mixture through filter paper; and measuring pH of the filtrate with a pH meter. The additive can be added to the second biogenic reagent to decrease filtrate pH of the second biogenic reagent. Alternatively, the additive can

be added to the second biogenic reagent to increase filtrate pH of the second biogenic reagent. When an additive is added for a different reason that for pH adjustment, the additive added to the second biogenic reagent can cause no change to the filtrate pH of the second biogenic reagent.

**[0106]** In some embodiments, the oxygen reactivity of the second biogenic reagent is reduced by addition of the additive to the second biogenic reagent.

**[0107]** In some embodiments, the process provides an overall carbon yield of at least 50%, calculated as carbon comprised in the biocarbon pellet as a percentage of the sum of carbon in the biomass-containing feedstock plus carbon in the carbon-containing condensed-matter material. In certain embodiments, the overall carbon yield is at least 60%, at least 70%, or at least 80%.

**[0108]** The process can be continuous or semi-continuous.

**[0109]** Optionally, the biocarbon pellet, after it is formed, is mechanically treated to generate biocarbon powder.

**[0110]** Optionally, the biocarbon pellet is combined with another amount of the second biogenic reagent, to generate a biocarbon object.

**[0111]** Some variations provide a biocarbon pellet comprising fixed carbon with a fixed carbon content of at least 60 wt%, wherein the biocarbon pellet is characterized by a thermogravimetric analysis that measures the oxygen reactivity of the biocarbon pellet, wherein the thermogravimetric analysis is performed using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen, and wherein, according to a thermogravimetric analysis graph of weight loss versus time (a "TGA graph"), the biocarbon pellet requires at least 240 minutes to reach 99% carbon oxidation.

**[0112]** In some embodiments of biocarbon pellets, according to the TGA graph of weight loss versus time from the thermogravimetric analysis performed using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen, the biocarbon pellet requires at least 250, 260, 270, 280, 290, 300, 310, or 320 minutes to reach 99% carbon oxidation.

**[0113]** In some embodiments, the thermogravimetric analysis is performed on an anthracite control sample, wherein the anthracite control sample requires a control time

to reach 99% carbon oxidation, and wherein the time required for the biocarbon pellet to reach 99% carbon oxidation is from about 85% to about 100% of the control time. In various embodiments, the time required for the biocarbon pellet to reach 99% carbon oxidation is from about 90% to about 100%, such as from about 95% to about 98%, of the control time.

**[0114]** In some embodiments, the biocarbon pellet comprises volatile carbon, and the TGA graph shows a first carbon-oxidation regime associated with oxidation of volatile carbon, which is succeeded by a second carbon-oxidation regime associated with oxidation of fixed carbon. In certain embodiments, the thermogravimetric analysis shows a first-derivative curve peak within the first carbon-oxidation regime for the biocarbon pellet at a temperature of at least about 500°C.

**[0115]** In some embodiments, the biocarbon pellet comprises at least 60 wt% fixed carbon, at least 70 wt% fixed carbon, at least 80 wt% fixed carbon, at least 85 wt% fixed carbon, or at least 90 wt% fixed carbon.

**[0116]** In some embodiments, the biocarbon pellet comprises at most 10 wt% ash, at most 5 wt% ash, or at most 1 wt% ash.

**[0117]** In some embodiments, the biocarbon pellet comprises at most 20 wt% total volatile matter, or at most 10 wt% total volatile matter.

**[0118]** In some embodiments, the biocarbon pellet comprises a binder. The binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, a derivative thereof, or a combination of any of the foregoing. In certain embodiments, the binder is selected from starch, thermoplastic starch, crosslinked starch, starch polymers, a derivative thereof, or a combination of any of the foregoing.

**[0119]** In some embodiments, the biocarbon pellet does not comprise a binder. In some embodiments, the biocarbon pellet does not comprise a binder other than a pyrolysis precipitate.

**[0120]** In some embodiments, the biocarbon pellet comprises an additive. The additive can be selected from acids, bases, or salts thereof. The additive can be selected from metals, metal oxides, metal hydroxides, metal halides, or a combination thereof. In various embodiments, the additive is selected from sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron halide, iron chloride, iron bromide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, titanium dioxide, or a combination thereof.

**[0121]** In some embodiments, total carbon within the biocarbon pellet is at least 50%, at least 90%, or fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

**[0122]** In some embodiments, the biocarbon pellet is characterized by a Hardgrove Grindability Index of at least 30.

**[0123]** In some embodiments, the biocarbon pellet is characterized by a bulk density of at least about 20 $lb/ft^3$ on a dry basis.

**[0124]** In some embodiments, the biocarbon pellet has an average pellet size selected from about 1 mm to about 10 cm, calculated as effective diameter of the biocarbon pellet.

**[0125]** In some embodiments, the biocarbon pellet has a pellet shape selected from sphere, cylinder, cube, octagon, hexagon, honeycomb, oval, column, bar, pillow, lentil, random granular, or a combination thereof.

**[0126]** In some embodiments, the biocarbon pellet is characterized by a pellet compressive strength at 25°C of at least about 100 $lb_f/in^2$ or at least about 150 $lb_f/in^2$.

**[0127]** In some embodiments, the biocarbon pellet is characterized by at most 20 wt% water uptake at 25°C after 24 hours of soaking in water.

**[0128]** In some embodiments, the biocarbon pellet is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*,

Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances."

**[0129]** The biocarbon pellet can be produced by a process comprising:

(a) pyrolyzing, in a first pyrolysis reactor, a biomass-containing feedstock, thereby generating a first biogenic reagent and a pyrolysis vapor;

(b) introducing, to a separation unit, the pyrolysis vapor, thereby generating a pyrolysis precipitate, wherein the pyrolysis precipitate is in liquid, solid, or slurry form;

(c) contacting the first biogenic reagent with the pyrolysis precipitate, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the pyrolysis precipitate;

(d) pelletizing the intermediate material, thereby generating an intermediate pellet;

(e) optionally, drying the intermediate pellet;

(f) separately from step (a), pyrolyzing, in a second pyrolysis reactor, the intermediate pellet, thereby generating a second biogenic reagent and a pyrolysis off-gas, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same reactor or distinct reactors; and

(g) recovering the second biogenic reagent as the biocarbon pellet,

wherein a fixed carbon content of the second biogenic reagent is greater than a fixed carbon content of the first biogenic reagent; and

wherein, according to a thermogravimetric analysis, an oxygen reactivity of the second biogenic reagent is less than an oxygen reactivity of the first biogenic reagent, wherein the thermogravimetric analysis is performed using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

**[0130]** The biocarbon pellet can be produced by a process comprising:

(a) pyrolyzing, in a first pyrolysis reactor, a biomass-containing feedstock, thereby generating a first biogenic reagent and a pyrolysis vapor;

(b) providing a carbon-containing condensed-matter material, wherein the carbon-containing condensed-matter material is a liquid, a solid, or a slurry;

(c) contacting the first biogenic reagent with the carbon-containing condensed-matter material, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the carbon-containing condensed-matter material;

(d) pelletizing the intermediate material, thereby generating an intermediate pellet;

(e) optionally, drying the intermediate pellet;

(f) separately from step (a), pyrolyzing, in a second pyrolysis reactor, the intermediate pellet, thereby generating a second biogenic reagent and a pyrolysis off-gas, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same reactor or distinct reactors; and

(g) recovering the second biogenic reagent as the biocarbon pellet,

wherein a fixed carbon content of the second biogenic reagent is greater than a fixed carbon content of the first biogenic reagent; and

wherein the second biogenic reagent has lower oxygen reactivity than the first biogenic reagent according to a thermogravimetric analysis using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

**[0131]** Some variations provide a biocarbon composition comprising fixed carbon with a fixed carbon content of at least 60 wt%, wherein the biocarbon composition is characterized by a thermogravimetric analysis that measures the oxygen reactivity of the biocarbon pellet, wherein the thermogravimetric analysis is performed using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen, and wherein, according to a TGA graph of weight loss versus time from the thermogravimetric analysis, the biocarbon pellet requires at least 240 minutes to reach 99% carbon oxidation.

**[0132]** The biocarbon composition (e.g., powder) can be produced by a process comprising:

(a) pyrolyzing, in a first pyrolysis reactor, a biomass-containing feedstock, thereby generating a first biogenic reagent and a pyrolysis vapor;

(b) introducing, to a separation unit, the pyrolysis vapor, thereby generating a pyrolysis precipitate, wherein the pyrolysis precipitate is in liquid, solid, or slurry form;

(c) contacting the first biogenic reagent with the pyrolysis precipitate, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the pyrolysis precipitate;

(d) separately from step (a), pyrolyzing, in a second pyrolysis reactor, the intermediate material, thereby generating a second biogenic reagent and a pyrolysis off-gas, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same reactor or distinct reactors; and

(e) recovering the second biogenic reagent as the biocarbon composition,

wherein a fixed carbon content of the second biogenic reagent is greater than a fixed carbon content of the first biogenic reagent; and

wherein, according to a thermogravimetric analysis, an oxygen reactivity of the second biogenic reagent is less than an oxygen reactivity of the first biogenic reagent, wherein the thermogravimetric analysis is performed using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

**[0133]** The biocarbon composition (e.g., powder) can be produced by a process comprising:

(a) pyrolyzing, in a first pyrolysis reactor, a biomass-containing feedstock, thereby generating a first biogenic reagent and a pyrolysis vapor;

(b) providing a carbon-containing condensed-matter material, wherein the carbon-containing condensed-matter material is a liquid, a solid, or a slurry;

(c) contacting the first biogenic reagent with the carbon-containing condensed-matter material, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the carbon-containing condensed-matter material;

(d) separately from step (a), pyrolyzing, in a second pyrolysis reactor, the intermediate material, thereby generating a second biogenic reagent and a pyrolysis off-gas, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same reactor or distinct reactors; and

(e) recovering the second biogenic reagent as the biocarbon composition,

wherein a fixed carbon content of the second biogenic reagent is greater than a fixed carbon content of the first biogenic reagent; and

wherein the second biogenic reagent has lower oxygen reactivity than the first biogenic reagent according to a thermogravimetric analysis using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0134]** FIG. 1 depicts an exemplary block-flow diagram of a process and system in which biomass is pyrolyzed in a first pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor. The pyrolysis vapor is sent to a separation unit that generates a pyrolysis precipitate and a pyrolysis non-precipitate. A pyrolysis precipitate is fed to an optional mixing unit, into which is also fed the biogenic reagent. The combined material is sent to a pelletizing unit to generate intermediate pellets. Alternatively, there is no mixing unit, and the pyrolysis precipitate and the biogenic reagent are directly fed to a pelletizing unit. A binder is optionally added to the pelletizing unit. Pellets are then fed to a second pyrolysis reactor which generates a biocarbon product. The second pyrolysis reactor also generates a pyrolysis off-gas, which could be recycled (e.g., back to the separation unit) or otherwise processed (e.g., combusted). Dotted boxes and lines denote optional units and streams, respectively.

**[0135]** FIG. 2 depicts an exemplary block-flow diagram of a process and system in which biomass is pyrolyzed in a first pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor. A carbon-containing, condensed-matter material is fed to an optional mixing unit, into which is also fed the biogenic reagent. The combined material is sent to a pelletizing unit to generate intermediate pellets. Alternatively, there is no mixing unit, and the carbon-containing, condensed-matter material and the biogenic reagent are directly fed to a pelletizing unit. A binder is optionally added to the pelletizing unit. Pellets are then fed to a second pyrolysis reactor which generates a biocarbon product. Dotted boxes and lines denote optional units and streams, respectively.

**[0136]** FIG. 3 shows TGA results of the Example 1 biocarbon pellet with pyrolysis tar carbonization, compared to the profile of a biocarbon pellet without pyrolysis tar carbonization.

**[0137]** FIG. 4 shows TGA results of the Example 2 samples, to characterize their oxygen reactivity compared to an anthracite control sample.

DETAILED DESCRIPTION

**[0138]** Some variations are premised on the discovery that by pelletizing a biogenic reagent and simultaneously or sequentially adding pyrolysis precipitate that is derived from pyrolysis vapor, the pelletized solids enhance reactions that form fixed carbon, thereby significantly increasing the yield of fixed carbon. It has also been found that the biocarbon pellets produced have optimized reactivity, especially reduced oxygen reactivity, for many commercial applications.

**[0139]** Biomass is a term used to describe any biologically produced matter, or biogenic matter. The chemical energy comprised in biomass is derived from solar energy using the natural process of photosynthesis. Photosynthesis is the process by which plants take in carbon dioxide and water from their surroundings and, using energy from sunlight, convert them into sugars, starches, cellulose, hemicellulose, and lignin. Of all the renewable energy sources, biomass is unique in that it is, effectively, stored solar energy. Furthermore, biomass is the only renewable source of carbon.

**[0140]** There exist a variety of conversion technologies to turn biomass feedstocks into high-carbon materials. Pyrolysis is a process for thermal conversion of solid materials in the complete absence of oxidizing agent (air or oxygen), or with such limited supply that oxidation does not occur to any appreciable extent. Depending on process conditions and additives, biomass pyrolysis can be adjusted to produce widely varying amounts of gas, liquid, and solid. Lower process temperatures and longer vapor residence times favor the production of solids. High temperatures and longer residence times increase the biomass conversion to syngas, while moderate temperatures and short vapor residence times are generally optimum for producing liquids. Historically, slow pyrolysis of wood has been performed in large piles, in a simple batch process, with no emissions control. Traditional charcoal-making technologies are energy-inefficient as well as highly polluting.

**[0141]** There is a desire for improved or optimized processes for producing biocarbon compositions, especially with respect to carbon yield and biocarbon properties such as reactivity.

**[0142]** This description will enable one skilled in the art to make and use the invention, and it describes several embodiments, adaptations, variations, alternatives, and uses of the invention. These and other embodiments, features, and advantages of the present invention will become more apparent to those skilled in the art when taken with reference to the following detailed description of the invention in conjunction with the accompanying drawings.

**[0143]** For purposes of an enabling technical disclosure, various explanations, hypotheses, theories, speculations, assumptions, and so on are disclosed. The present invention does not rely on any of these being in fact true. None of the explanations, hypotheses, theories, speculations, or assumptions in this detailed description shall be construed to limit the scope of the invention in any way.

Definitions

**[0144]** As used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly indicates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as is commonly understood by one of ordinary skill in the art to which this invention belongs.

**[0145]** Unless otherwise indicated, all numbers expressing reaction conditions, stoichiometries, concentrations of components, and so forth used in the specification and 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 can vary depending at least upon a specific analytical technique.

**[0146]** As used herein, the term "about" means ± 20% of the indicated range, value, or structure, unless otherwise indicated.

**[0147]** As used herein, any concentration range, percentage range, ratio range, or integer range is to be understood to include the value of any integer within the recited range and, when appropriate, fractions thereof (such as one tenth and one-hundredth

of an integer), unless otherwise indicated. Also, any number range recited herein is to be understood to include any integer within the recited range, unless otherwise indicated.

**[0148]** As used herein, "in the range of from or in between about," for example, "in the range of from or in between about X, Y, or Z," includes "at least X to at most Z."

**[0149]** The term "comprising," which is synonymous with "including," "containing," or "characterized by" is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. "Comprising" is a term of art used in claim language which means that the named claim elements are essential, but other claim elements can be added and still form a construct within the scope of the claim.

**[0150]** As used herein, the phrase "consisting of" excludes any element, step, or ingredient not specified in the claim. When the phrase "consists of" (or variations thereof) appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole. As used herein, the phrase "consisting essentially of" limits the scope of a claim to the specified elements or method steps, plus those that do not materially affect the basis and novel characteristic(s) of the claimed subject matter.

**[0151]** With respect to the terms "comprising," "consisting of," and "consisting essentially of," where one of these three terms is used herein, the presently disclosed and claimed subject matter can include the use of either of the other two terms. Thus in some embodiments not otherwise explicitly recited, any instance of "comprising" can be replaced by "consisting of" or, alternatively, by "consisting essentially of."

**[0152]** As used herein, unless expressly stated to the contrary, "or" refers to an inclusive "or" and not to an exclusive "or." Unless the word "or" is expressly limited to mean only a single item exclusive from the other items in reference to a list of two or more items, then the use of "or" in such a list is to be interpreted as including (a) any single item in the list, (b) all of the items in the list, or (c) any combination of the items in the list. As used herein, the phrase "and/or" as in "A and/or B" refers to A alone, B alone, and both A and B. Where the context permits, singular or plural terms can also include the plural or singular term, respectively.

**[0153]** As used herein, "biogenic" is a material (whether a feedstock, product, or intermediate) that contains an element, such as carbon, that is renewable on time scales of months, years, or decades. Non-biogenic materials can be non-renewable, or can be renewable on time scales of centuries, thousands of years, millions of years, or even longer geologic time scales. For example, traditional fuel sources of coal and petroleum are non-renewable and non-biogenic. A biogenic material can consist essentially of biogenic sources. It will be understood by one skilled in the art that biogenic materials, as natural sources or derived from nature, can comprise an immaterial amount of non-biogenic material. Further, the processes disclosed herein can be used with non-biogenic material, though the beneficial environmental impact may not be as great.

**[0154]** There are three naturally occurring isotopes of carbon, $^{12}C$, $^{13}C$, and $^{14}C$. $^{12}C$ and $^{13}C$ are stable, occurring in a natural proportion of approximately 93:1. $^{14}C$ is produced by thermal neutrons from cosmic radiation in the upper atmosphere, and is transported down to earth to be absorbed by living biological material. Isotopically, $^{14}C$ constitutes a negligible part; but, since it is radioactive with a half-life of 5,700 years, it is radiometrically detectable. Dead tissue does not absorb $^{14}C$, so the amount of $^{14}C$ is one of the methods used for radiometric dating of biological material.

**[0155]** Plants take up $^{14}C$ by fixing atmospheric carbon through photosynthesis. Animals then take $^{14}C$ into their bodies when they consume plants or consume other animals that consume plants. Accordingly, living plants and animals have the same ratio of $^{14}C$ to $^{12}C$ as the atmospheric $CO_2$. Once an organism dies, it stops exchanging carbon with the atmosphere, and thus no longer takes up new $^{14}C$. Radioactive decay then gradually depletes the $^{14}C$ in the organism. This effect is the basis of radiocarbon dating.

**[0156]** Fossil fuels, such as coal, are made primarily of plant material that was deposited millions of years ago. This period of time equates to thousands of half-lives of $^{14}C$, so essentially all of the $^{14}C$ in fossil fuels has decayed. Fossil fuels also are depleted in $^{13}C$ relative to the atmosphere, because they were originally formed from living organisms. Therefore, the carbon from fossil fuels is depleted in both $^{13}C$ and $^{14}C$ compared to biogenic carbon.

**[0157]** This difference between the carbon isotopes of recently deceased organic matter, such as that from renewable resources, and the carbon isotopes of fossil fuels, such as coal, allows for a determination of the source of carbon in a composition. Specifically, whether the carbon in the composition was derived from a renewable resource or from a fossil fuel; in other words, whether a renewable resource or a fossil fuel was used in the production of the composition.

**[0158]** Biomass is a term used to describe any biologically produced matter, or biogenic matter. Biomass refers to the mass of living organisms, including plants, animals, and microorganisms, or, from a biochemical perspective, cellulose, lignin, sugars, fats, and proteins. Biomass includes both the above- and belowground tissues of plants, for example, leaves, twigs, branches, boles, as well as roots of trees and rhizomes of grasses. The chemical energy contained in biomass is derived from solar energy using the natural process of photosynthesis. This is the process by which plants take in carbon dioxide and water from their surroundings and, using energy from sunlight, convert them into sugars, starches, cellulose, hemicellulose, and lignin. Biomass is useful in that it is, effectively, stored solar energy. Biomass is the only renewable source of carbon.

**[0159]** As used herein, "total carbon" is fixed carbon plus non-fixed carbon that is present in volatile matter. In some embodiments, component weight percentages are on an absolute basis, which is assumed unless stated otherwise. In other embodiments, component weight percentages are on a moisture-free and ash-free basis.

**[0160]** As used herein, "zones" are regions of space within a single physical unit, physically separate units, or any combination thereof. For a continuous reactor, the demarcation of zones can relate to structure, such as the presence of flights within the reactor or distinct heating elements to provide heat to separate zones. Alternatively, or additionally, the demarcation of zones in a continuous reactor can relate to function, such as distinct temperatures, fluid flow patterns, solid flow patterns, or extent of reaction. In a single batch reactor, "zones" are operating regimes in time, rather than in space. There are not necessarily abrupt transitions from one zone to another zone. For example, the boundary between the preheating zone and pyrolysis zone can be somewhat arbitrary; some amount of pyrolysis can take place in a portion of the

preheating zone, and some amount of "preheating" can continue to take place in the pyrolysis zone. The temperature profile in the reactor is typically continuous, including at zone boundaries within the reactor.

**[0161]** For present purposes, "reagent" is intended to mean a material in its broadest sense; a reagent can be a fuel, a chemical, a material, a compound, an additive, a blend component, a solvent, and so on. A reagent is not necessarily a chemical reagent that causes or participates in a chemical reaction. A reagent can or can not be a chemical reactant; it can or can not be consumed in a reaction. A reagent can be a chemical catalyst for a particular reaction. A reagent can cause or participate in adjusting a mechanical, physical, or hydrodynamic property of a material to which the reagent can be added. For example, a reagent can be introduced to a metal to impart certain strength properties to the metal. A reagent can be a substance of sufficient purity (which, in the current context, is typically carbon purity) for use in chemical analysis or physical testing.

**[0162]** As used herein, a "derivative" is a compound, molecule, or ion that is derived from another substance by a chemical reaction. The substance from which the derivative is derived is an additive. A derivative is also an additive.

**[0163]** The terms "low fixed carbon" and "high fixed carbon" are used herein for practical purposes to describe materials that can be produced by processes and systems as disclosed, in various embodiments. Limitations as to carbon content, or any other concentrations, shall not be imputed from the term itself but rather only by reference to particular embodiments and equivalents thereof.

**[0164]** Some variations provide a process for producing a biocarbon pellet, the process comprising:

(a) pyrolyzing, in a first pyrolysis reactor, a biomass-containing feedstock, thereby generating a first biogenic reagent and a pyrolysis vapor;

(b) introducing, to a separation unit, the pyrolysis vapor, thereby generating a pyrolysis precipitate, wherein the pyrolysis precipitate is in liquid, solid, or slurry form;

(c) contacting the first biogenic reagent with the pyrolysis precipitate, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the pyrolysis precipitate;

(d) pelletizing the intermediate material, thereby generating an intermediate pellet;

(e) optionally, drying the intermediate pellet;

(f) separately from step (a), pyrolyzing, in a second pyrolysis reactor, the intermediate pellet, thereby generating a second biogenic reagent and a pyrolysis off-gas, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same reactor or distinct reactors; and

(g) recovering the second biogenic reagent as a biocarbon pellet,

wherein a fixed carbon content of the second biogenic reagent is greater than a fixed carbon content of the first biogenic reagent; and

wherein, according to a thermogravimetric analysis, an oxygen reactivity of the second biogenic reagent is less than an oxygen reactivity of the first biogenic reagent, wherein the thermogravimetric analysis is performed using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

**[0165]** Thermogravimetric analysis (TGA) is a well-known method of analysis in which the mass of a sample is measured over time as the temperature changes. In order to perform TGA on both the first biogenic reagent and the second biogenic reagent, a sample of the first biogenic reagent can be collected following its generation in step (a), while a sample of the second biogenic reagent is provided by step (g). The TGA measurements can be made simultaneously on both samples, as well as other samples (e.g., a control sample), using a commercial TGA instrument that accommodates many samples (e.g. see FIG. 4).

**[0166]** In some embodiments, according to a TGA graph of weight loss versus time from the thermogravimetric analysis, the second biogenic reagent requires at least a 5% longer time to reach 99% carbon oxidation, compared to the first biogenic reagent. In certain embodiments, according to the TGA graph, the second biogenic reagent requires at least a 10% longer time to reach 99% carbon oxidation, compared to the first biogenic reagent.

**[0167]** In some embodiments, the TGA graph shows a first carbon-oxidation regime associated with oxidation of volatile carbon, which is succeeded by a second carbon-oxidation regime associated with oxidation of fixed carbon.

**[0168]** In some embodiments, a volatile-carbon oxidation time is defined from the onset of the first carbon-oxidation regime to the onset of the second carbon-oxidation regime. During the volatile-carbon oxidation time, a mass loss of the first biogenic reagent can be at least 25% or at least 50% greater than a mass loss of the second biogenic reagent.

**[0169]** In some embodiments, during the first carbon-oxidation regime, the thermogravimetric analysis shows that a mass loss rate of the first biogenic reagent is at least 25% or at least 50% greater than a mass loss rate of the second biogenic reagent during the first carbon-oxidation regime.

**[0170]** In some embodiments, the thermogravimetric analysis shows that the first biogenic reagent has at least 10% higher average rate of mass loss during the first carbon-oxidation regime compared to the second carbon-oxidation regime.

**[0171]** In some embodiments, the thermogravimetric analysis shows a first-derivative curve peak within the first carbon-oxidation regime for the second biogenic reagent at a temperature of at least about 500°C, and the thermogravimetric analysis shows a first-derivative curve peak within the first carbon-oxidation regime for the first biogenic reagent at a temperature from 200°C to 500°C.

**[0172]** The biomass-containing feedstock can be selected from softwood chips, hardwood chips, timber harvesting residues, tree branches, tree stumps, leaves, bark, sawdust, corn, corn stover, wheat, wheat straw, rice, rice straw, sugarcane, sugarcane bagasse, sugarcane straw, energy cane, sugar beets, sugar beet pulp, sunflowers, sorghum, canola, algae, miscanthus, alfalfa, switchgrass, fruits, fruit shells, fruit stalks, fruit peels, fruit pits, vegetables, vegetable shells, vegetable stalks, vegetable peels, vegetable pits, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, food waste, commercial waste, grass pellets, hay pellets, wood pellets, cardboard, paper, paper pulp, paper packaging, paper trimmings, food packaging, construction or demolition waste, railroad ties, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof.

**[0173]** In some embodiments, the separation unit is or comprises a condensing system. In certain embodiments, the condensing system has multiple stages. The pyrolysis precipitate can be a condensed product of a first condenser stage of multiple stages, for example. Alternatively, or additionally, the pyrolysis precipitate can be a

condensed product of a second, third, or later condenser stage of multiple stages. The pyrolysis precipitate can be a condensed product that is the combination of multiple condensed products of a plurality of stages that can be equal to, or less than, the multiple stages present in the condensing system.

**[0174]** Separation in step (b) can generally utilize thermal means, chemical means, mechanical means, electrical/electrostatic means, or other means, or a combination thereof. When thermal means are utilized, there can be indirect heat exchange (e.g., heat exchange with air or oil on the opposite side of a separation-unit wall) or direct heat exchange (e.g., direct injection of water or cool pyrolysis precipitate). Chemical means can utilize adsorption, absorption, or extraction, for example. Mechanical means can utilize centrifugal forces or molecule-size exclusion, for example. Electrical/electrostatic means can utilize the presence of an electromagnetic field, for example.

**[0175]** In various embodiments, the separation unit is or comprises a condensing unit, a liquid-vapor cyclone separator, a demister, a distillation unit, a filtration unit, a membrane unit, a scrubbing unit, a chemical precipitation unit, a liquid-liquid extraction unit, an electrostatic precipitation unit, or a combination thereof.

**[0176]** When the separation unit comprises a condensing unit, the condensing unit can be a single-stage condenser or a multiple-stage condensing system as discussed above. Exemplary types of condensing units comprise liquid-cooled condensers (e.g., water-cooled condensers), gas-cooled condensers (e.g., air-cooled condensers), and evaporative condensers, for example. A condensing unit can be a direct-contact condenser or an indirect condenser (e.g., surface condenser, such as a shell-and-tube condenser).

**[0177]** When the separation unit comprises a liquid-vapor cyclone separator, exemplary types of liquid-vapor cyclone separators are known commercially (e.g., from Sulzer, Winterthur, Switzerland). A liquid-vapor cyclone separator utilizes a combination of centrifugal, buoyant, and drag forces to cause liquid-vapor separation, in particular when the centrifugal force is sufficient to overcome other forces. Exemplary centrifugal force are from about 10*g* to about 1000*g*, such as about 100-500*g*, where *g* is the gravitational force.

**[0178]** When the separation unit comprises a demister, exemplary types of demisters comprise mesh demisters, vane demisters, cyclone demisters, and fiber-bed demisters, for example.

**[0179]** When the separation unit comprises a distillation unit, exemplary types of distillation units comprise single-column units, multiple-column units, and reactive-distillation units, for example. The distillation unit can be vertical or horizontal, and can be operated in continuous or batch mode.

**[0180]** When the separation unit comprises a filtration unit, exemplary types of filtration units comprise gravity filters, vacuum filters, pressure filters, pneumatic-press filters, centrifugal filters, and crossflow filters, for example. The filtration media can be selected to separation components by molecular weight, particle size, or viscosity, for example.

**[0181]** When the separation unit comprises a membrane unit, exemplary types of membrane units comprise microfiltration units, ultrafiltration units, nanofiltration units, reverse-osmosis units, and electrodialysis units, for example.

**[0182]** When the separation unit comprises a scrubbing unit, exemplary types of scrubbing units comprise suction scrubbers and vent scrubbers, for example. In some embodiments, scrubbing utilizes recovered/recycled pyrolysis precipitate.

**[0183]** When the separation unit comprises a chemical precipitation unit, the chemical precipitation can be catalyzed or assisted using a solvent, an acid, or a base to induce precipitation of pyrolysis vapor components from vapor to liquid or solid, for example.

**[0184]** When the separation unit comprises a liquid-liquid extraction unit, exemplary types of liquid-liquid extraction units comprise mixer-settlers, centrifugal extractors, static extraction columns, agitated extraction columns, and multistage countercurrent extraction units, for example. The liquid-liquid extraction can use an extraction solvent that is or comprises aromatic hydrocarbons, for example. In some embodiments, the extraction solvent is recovered pyrolysis precipitate. The liquid-liquid extraction unit can operate in continuous or batch mode.

**[0185]** When the separation unit comprises an electrostatic precipitation unit, exemplary types of electrostatic precipitation units comprise electrostatic precipitators,

electrostatic separators, electrodynamic separators, capacitor-based separators, and other means or apparatus employing the principles of separating by electrical forces. Electrostatic precipitation units can be designed to collect liquid droplets using electric field forces. Electrostatic precipitators work by charging particles (e.g., liquid droplets), then collecting the charged particles in an electric field. Charging occurs by two mechanisms: diffusion charging and field charging. In diffusion charging, ions in the gas bounce around due to Brownian motion, bump into a particle, and transfer their charge to it. Field charging occurs when a particle is located within an electric field that comprises ions. Electrostatic precipitators use a high-voltage power supply to create an electrical potential difference between discharge electrodes and collecting electrodes in order to capture charged or polarized liquid droplets.

**[0186]** In some embodiments, an electrostatic precipitator comprises one or more tubes, channels, or ducts that the material flows through, acting as an electrical ground and collection surface for the liquid droplets. A discharge electrode can be suspended in the center of the pipe, acting as the high voltage (e.g., ±10-100 kV DC) electrode. The high voltage applied to the electrode causes an electrostatic field to be formed between the electrode and the grounding channel. This field projects a force on any particle that passes through it. As the particle passes through the field, it moves towards the ground wall and thus collects on the wall. Gravity forces collected liquids to flow down the electrostatic precipitator to be recovered. The electrostatic precipitator uses a positive or negative polarity power supply.

**[0187]** Combinations of separation units are possible. For example, a separation unit could comprise a single-stage condenser as a first sub-unit for creating a primary pyrolysis precipitate, and a fractional condensation or distillation as a second sub-unit for fractionating the primary pyrolysis precipitate into multiple fractions of precipitates. In another example, a separation unit could comprise a liquid-vapor cyclone separator as a first sub-unit for creating a liquid stream and a vapor stream, a liquid-liquid extraction unit as a second sub-unit for recovering a portion of the liquid stream as a pyrolysis precipitate, and a filtration unit for recovering a portion of the vapor stream as an additional pyrolysis precipitate. Other embodiments utilize a combination of a condensing unit and an electrostatic precipitator to collect individual liquid products.

**[0188]** In some embodiments, the intermediate material comprises the pyrolysis precipitate adsorbed onto a surface of the first biogenic reagent. In these or other embodiments, the intermediate material can comprise the pyrolysis precipitate absorbed into a bulk phase of the first biogenic reagent.

**[0189]** The pyrolysis precipitate can be in liquid form (one or more liquid phases), solid form (one or more solid phases), or a combination (e.g., a slurry) of one or more liquid phases and one or more solid phases. Solid phases can vary widely in viscosity and density. For example, a solid phase, or a combined solid-liquid material, can be a gel-like material, a tacky material, or a rubber-like material.

**[0190]** The ratio of pyrolysis precipitate to first biogenic reagent can be varied to achieve various properties of the final pellets (e.g., reactivity). Varying the ratio can be accomplished by diverting some of the first biogenic reagent and blending the remaining portion of the first biogenic reagent with the pyrolysis precipitate. Alternatively, or additionally, two pyrolysis reactors can be operated in parallel, with pyrolysis precipitate collected from a first pyrolysis reactor diverted to a second pyrolysis reactor. In one scenario, one pyrolysis reactor produces a lower-reactivity product incorporating the additional pyrolysis of a double portion of pyrolysis precipitate, while the other pyrolysis reactor produces a higher-reactivity product without additional pyrolysis of the pyrolysis precipitate.

**[0191]** In some embodiments, steps (c) and (d) are integrated. For example, the pyrolysis precipitate can be contacted with the first biogenic reagent within a pelletizing unit.

**[0192]** A binder can be introduced to the intermediate material. The binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, a derivative thereof, or a combination

of the foregoing. In certain embodiments, a binder is selected from starch, thermoplastic starch, crosslinked starch, starch polymers, a derivative thereof, or a combination of the foregoing.

**[0193]** In other embodiments, no external binder is introduced to the intermediate material during the pelletizing. Certain components within the intermediate material—in particular, for example, the pyrolysis precipitate itself or a component comprised therein—can function as a binder.

**[0194]** In some processes, step (e) for drying is conducted. Steps (d) and (e) can be integrated, such that drying occurs along with pelletizing. Also, steps (e) and (f) can be integrated, such that pyrolysis and drying of the intermediate pellets both occur. In certain embodiments, steps (d), (e), and (f) are all integrated.

**[0195]** In some embodiments, the first biogenic reagent is milled utilizing a mechanical-treatment apparatus selected from a hammer mill, an extruder, an attrition mill, a disc mill, a pin mill, a ball mill, a cone crusher, a jaw crusher, or a combination thereof. In these or other embodiments, the intermediate material can be milled utilizing a mechanical-treatment apparatus selected from a hammer mill, an extruder, an attrition mill, a disc mill, a pin mill, a ball mill, a cone crusher, a jaw crusher, or a combination thereof. The intermediate material can be milled rather than the first biogenic reagent, or in addition to the first biogenic reagent being milled.

**[0196]** In some embodiments, step (d) utilizes a pelletizing apparatus selected from an extruder, a ring die pellet mill, a flat die pellet mill, a roll compactor, a roll briquetter, a wet agglomeration mill, a dry agglomeration mill, or a combination thereof.

**[0197]** In some processes, the first pyrolysis reactor is distinct from the second pyrolysis reactor. Alternatively, the first pyrolysis reactor and the second pyrolysis reactor can be the same unit, with steps (a) and (f) conducted at different times.

**[0198]** In some embodiments, step (a) is conducted at a first pyrolysis temperature selected from about 250°C to about 1250°C, such as from about 300°C to about 700°C. In these or other embodiments, step (f) is conducted at a second pyrolysis temperature selected from about 250°C to about 1250°C, such as from about 400°C to about 1000°C. The second pyrolysis temperature can be of at least about the first pyrolysis temperature, although that is not necessary.

**[0199]** In some embodiments, step (a) is conducted for a first pyrolysis time selected from about 10 seconds to about 24 hours, such as from about 1 minute to about 4 hours. In these or other embodiments, step (f) is conducted for a second pyrolysis time selected from about 10 seconds to about 24 hours, such as from about 1 minute to about 4 hours. The second pyrolysis time can be longer than the first pyrolysis time, although that is not necessary.

**[0200]** In the process, such as during step (f), the first biogenic reagent can act as a catalyst or reaction matrix for fixed-carbon formation reactions of the pyrolysis precipitate.

**[0201]** A pyrolysis non-precipitate is typically generated in the separation unit. The pyrolysis non-precipitate is typically a vapor stream and can be purged from the process. A purge stream from the separation unit is not necessarily a vapor phase, depending on the selection of the separation unit. For example, a purge stream can be a liquid stream such as a liquid-liquid extraction solvent, or a vapor stream that comprises entrained liquids or solids. In some embodiments, the pyrolysis non-precipitate is recovered and at least partially oxidized to generate heat, which is optionally used within the process.

**[0202]** In some embodiments, the pyrolysis off-gas (from the second pyrolysis reactor) is at least partially oxidized to generate heat, which is optionally used within the process. Optionally, at least some of the pyrolysis off-gas is conveyed back to the separation unit. Recycling pyrolysis off-gas in this way can give the carbon atoms (in the pyrolysis off-gas) another chance to end up in the final biocarbon pellets as fixed carbon.

**[0203]** Alternatively, or additionally, the pyrolysis off-gas can be conveyed to a second separation unit (different from the separation unit in step (b)) operated under effective precipitation conditions to generate a second pyrolysis precipitate, wherein the second pyrolysis precipitate is in liquid, solid, or slurry form. The process can further comprise contacting the second pyrolysis precipitate with the first biogenic reagent or with the second biogenic reagent.

**[0204]** The biocarbon pellets, recovered in step (g), can comprise at least 60 wt% fixed carbon, at least 70 wt% fixed carbon, at least 80 wt% fixed carbon, at least 85 wt% fixed carbon, or at least 90 wt% fixed carbon, for example. The biocarbon pellets can

comprise less than 10 wt% ash, less than 5 wt% ash, or less than 1 wt% ash, for example.

**[0205]** In some processes, the pyrolysis precipitate comprises less than 1 wt% ash, less than 0.1 wt% ash, or essentially no ash. A low-ash pyrolysis precipitate is beneficial so that ash is not added to the first biogenic reagent, leading to a lower-ash final product.

**[0206]** In some embodiments, the biocarbon pellets comprise less than 20 wt% total volatile matter or less than 10 wt% total volatile matter.

**[0207]** In some embodiments, at least 10 wt% of carbon comprised in the pyrolysis precipitate is converted to fixed carbon in the biocarbon pellets. In various embodiments, at least 20 wt%, at least 30 wt%, at least 40 wt%, at least 50 wt%, or from 30 wt% to 90 wt% of carbon comprised in the pyrolysis precipitate is converted to fixed carbon in the biocarbon pellets.

**[0208]** In some embodiments, from about 1 wt% to about 50 wt% of fixed carbon in the biocarbon pellets is derived from the pyrolysis precipitate. In certain embodiments, from about 10 wt% to about 40 wt% of fixed carbon in the biocarbon pellets is derived from the pyrolysis precipitate.

**[0209]** Optionally, the intermediate material further comprises additional pyrolysis precipitate that is not provided from step (b) of the process. For example, the additional pyrolysis precipitate can be provided by a pyrolysis process conducted using (i) a different biomass-containing feedstock and (ii) a different time or place.

**[0210]** In step (c), less than all, or all, of the first biogenic reagent can be contacted with the pyrolysis precipitate. In step (c), less than all, or all, of the pyrolysis precipitate can be contacted with the first biogenic reagent.

**[0211]** The total carbon within the biocarbon pellets can be at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. The total carbon within the biocarbon pellets can be at least 90% renewable, or fully (about 100%) renewable, as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

**[0212]** In some embodiments, the biocarbon pellets are characterized by a Hardgrove Grindability Index of at least 30, or at least 50.

**[0213]** In some embodiments, the biocarbon pellets are characterized by a bulk density of at least about 25 lb/ft$^3$, at least about 30 lb/ft$^3$, at least about 35 lb/ft$^3$, at least about 40 lb/ft$^3$, or at least about 45 lb/ft$^3$, on a dry basis.

**[0214]** The biocarbon pellet can have a pellet effective diameter that is within 10% or within 5% of the effective pellet diameter of the intermediate pellet. In these embodiments, the pyrolysis in the second pyrolysis reactor does not does not significantly change the pellet size; alternatively, an additional process step is conducted to increase or decrease pellet size back to the size, or within 10% of the size, of the intermediate pellets. In other embodiments, the biocarbon pellet has an effective pellet diameter that is more than 110%, or less than 90%, of the effective pellet diameter of the intermediate pellet. In these embodiments, the pyrolysis in the second pyrolysis reactor does significantly change the pellet size; alternatively, an additional process step is conducted to increase or decrease pellet size.

**[0215]** In some embodiments, the biocarbon pellet has a pellet shape selected from sphere, cylinder, cube, octagon, hexagon, honeycomb, oval, column, bar, pillow, lentil, random granular, or a combination thereof.

**[0216]** In some embodiments, the biocarbon pellet is characterized by a pellet compressive strength at 25°C of at least about 100 lb$_f$/in$^2$. In certain embodiments, the biocarbon pellet is characterized by a pellet compressive strength at 25°C of at least about 150 lb$_f$/in$^2$. In various embodiments, the biocarbon pellet is characterized by a pellet compressive strength at 25°C of about, or at least about, 25, 50, 75, 100, 125, 150, 175, or 200 lb$_f$/in$^2$, including any intervening ranges.

**[0217]** In some embodiments, the biocarbon pellets are hydrophobic. In some embodiments, the biocarbon pellet is characterized by at most 20 wt% water uptake at 25°C after 24 hours of soaking in water. In certain embodiments, the biocarbon pellet is characterized by at most 15 wt%, 10 wt%, or 5 wt% water uptake at 25°C after 24 hours of soaking in water.

**[0218]** In some embodiments, the biocarbon pellets are characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances."

**[0219]** In some embodiments, the biocarbon pellets are characterized by an oxygen reactivity substantially as shown in the thermogravimetric analysis of FIG. 3 or FIG. 4 (see Examples 1 and 2 below). The biocarbon pellets are less reactive with oxygen, at temperatures of about 750–950°C, compared to biocarbon pellets produced by an otherwise-equivalent pyrolysis process but without carbon recapture in step (c).

**[0220]** The biocarbon pellets can be characterized by a "coke reactivity index" or CRI value. The CRI can be determined according to ASTM D5341, Coke Reactivity Index. When coke lumps descend in a blast furnace, they are subjected to reaction with countercurrent $CO_2$ and to abrasion as the lumps rub together and against the walls of the furnace. The process flow physically weakens and chemically reacts the coke lumps, producing an excess of fines that can decrease permeability and result in increased coke rates and lost hot metal production. The CRI test method is designed to measure indirectly this behavior of coke, or alternatively biocarbon, in a blast furnace. Note that the chemical reaction that is explicitly considered by the CRI value is not carbon oxidation, but rather the reverse Boudouard reaction, $C + CO_2 \rightarrow 2\ CO$. In certain embodiments, the CRI value is measured by placing a sample of 200 grams with a particle size between 19–22.5 mm in a reactor and heating to 1100°C in inert atmosphere. Subsequently, the carbon is degassed isothermally for two hours in 100% $CO_2$ gas atmosphere and then cooled with nitrogen gas. After cooling, the carbon is weighed and tumbled for 600 revolutions in an I-drum followed by sieving the material through screens with mesh sizes of +10 and –0.5 mm. The weight loss of carbon represents the Coke Reactivity Index, CRI, and the remaining carbon on the +10 mm sieve represents the Coke Strength after Reaction, CSR. In some embodiments, the CRI of the biocarbon pellets is from about 20% to about 80%, such as about, or at most about, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, or 80%.

**[0221]** The process can provide an overall carbon yield of at least 50%, calculated as carbon comprised in the biocarbon pellets as a percentage of carbon comprised in the biomass-containing feedstock. In some embodiments, the overall carbon yield is at least 60%, at least 70%, or at least 80%.

**[0222]** The process can provide an overall *fixed-carbon* yield of at least 50%, calculated as fixed carbon comprised in the biocarbon pellets as a percentage of total carbon comprised in the biomass-containing feedstock. In some embodiments, the

overall fixed-carbon yield is at least 60%, at least 70%, or at least 80%. The fixed-carbon yield cannot be of at least about the carbon yield. In some embodiments, due to additional pyrolysis conducted in the second pyrolysis reactor, most or all of the carbon is fixed carbon in the final biocarbon pellets, resulting in a fixed-carbon yield that is close to or even about the same as the carbon yield.

**[0223]** In some embodiments, the process further comprises introducing an additive during the process. The additive can be selected from acids, bases, or salts thereof. The additive can be selected from metals, metal oxides, metal hydroxides, metal halides, or a combination thereof. For example, the additive can be selected from sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron halide, iron chloride, iron bromide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, titanium dioxide, or a combination thereof.

**[0224]** An additive can be selected to adjust filtrate pH of the biocarbon pellet, wherein the filtrate pH is measured by combining 20 grams on a dry basis of the biocarbon pellet, or a powder form thereof, with 100 milliliters of distilled water, to form a mixture; filtering the mixture through filter paper; and measuring pH of the filtrate with a pH meter.

**[0225]** An additive can be added to the second biogenic reagent to adjust filtrate pH of the second biogenic reagent, wherein the filtrate pH is measured by combining 20 grams on a dry basis of the second biogenic reagent with 100 milliliters of distilled water, to form a mixture; filtering the mixture through filter paper; and measuring pH of the filtrate with a pH meter. The additive can be added to the second biogenic reagent to decrease filtrate pH of the second biogenic reagent. Alternatively, the additive can be added to the second biogenic reagent to increase filtrate pH of the second biogenic reagent. When an additive is added for a different reason that for pH adjustment, the additive added to the second biogenic reagent can cause no change to the filtrate pH of the second biogenic reagent.

**[0226]** In some embodiments, the oxygen reactivity of the second biogenic reagent is reduced by addition of the additive to the second biogenic reagent. An additive can

be added to the second biogenic reagent after it is formed, or an additive can be fed to the second pyrolysis reactor, to the first pyrolysis reactor, or to a pelletizing unit, for example. Additives can be introduced at multiple locations within a process.

**[0227]** In some embodiments, the process provides an overall carbon yield of at least 50%, calculated as carbon comprised in the biocarbon pellet as a percentage of the sum of carbon in the biomass-containing feedstock plus carbon in the carbon-containing condensed-matter material. In certain embodiments, the overall carbon yield is at least 60%, at least 70%, or at least 80%.

**[0228]** The process can be continuous or semi-continuous.

**[0229]** Optionally, the biocarbon pellet, after it is formed, is mechanically treated to generate biocarbon powder. For example, biocarbon pellets can be produced and shipped to another location. At a site of use, the pellets can be powderized and fed to a reactor, such as for combustion, gasification, for metal-ore reduction, for example.

**[0230]** Optionally, the biocarbon pellet is combined with another amount of the second biogenic reagent, to generate a biocarbon object. The other amount of second biogenic reagent can be in pellet, powder, or other form. In some embodiments, multiple pellets are mechanically pressed together to form a biocarbon object, which for example can be a structural carbon element for a metal-making furnace.

**[0231]** Other variations provide a process for producing a biocarbon pellet, the process comprising:

(a) pyrolyzing, in a first pyrolysis reactor, a biomass-containing feedstock, thereby generating a first biogenic reagent and a pyrolysis vapor;

(b) providing a carbon-containing condensed-matter material, wherein the carbon-containing condensed-matter material is a liquid, a solid, or a slurry;

(c) contacting the first biogenic reagent with the carbon-containing condensed-matter material, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the carbon-containing condensed-matter material;

(d) pelletizing the intermediate material, thereby generating an intermediate pellet;

(e) optionally, drying the intermediate pellet;

(f) separately from step (a), pyrolyzing, in a second pyrolysis reactor, the intermediate pellet, thereby generating a second biogenic reagent and a pyrolysis off-gas, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same reactor or distinct reactors; and

(g) recovering the second biogenic reagent as a biocarbon pellet,

wherein a fixed carbon content of the second biogenic reagent is greater than a fixed carbon content of the first biogenic reagent,

and wherein the second biogenic reagent has lower oxygen reactivity than the first biogenic reagent according to a thermogravimetric analysis using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

**[0232]** In some embodiments, according to a TGA graph of weight loss versus time from the thermogravimetric analysis, the second biogenic reagent requires at least a 5% or at least 10% longer time to reach 99% oxidation, compared to the first biogenic reagent.

**[0233]** In some embodiments, the TGA graph shows a first carbon-oxidation regime associated with oxidation of volatile carbon, which is succeeded by a second carbon-oxidation regime associated with oxidation of fixed carbon.

**[0234]** In some embodiments, a volatile-carbon oxidation time is defined from the onset of the first carbon-oxidation regime to the onset of the second carbon-oxidation regime. During the volatile-carbon oxidation time, the first biogenic reagent can have at least 25% or at least 50% more mass loss compared to the second biogenic reagent.

**[0235]** In some embodiments, the thermogravimetric analysis shows that the first biogenic reagent has at least 25% or at least 50% higher rate of mass loss during the first carbon-oxidation regime than the rate of mass loss of the second biogenic reagent during the first carbon-oxidation regime.

**[0236]** In some embodiments, the thermogravimetric analysis shows that the first biogenic reagent has at least 10% higher average rate of mass loss during the first carbon-oxidation regime compared to the second carbon-oxidation regime.

**[0237]** In some embodiments, the thermogravimetric analysis shows a first-derivative curve peak within the first carbon-oxidation regime for the second biogenic reagent at a temperature of at least about 500°C, and wherein the thermogravimetric analysis shows a first-derivative curve peak within the first carbon-oxidation regime for the first biogenic reagent at a temperature from 200°C to 500°C.

**[0238]** The biomass-containing feedstock can be selected from softwood chips, hardwood chips, timber harvesting residues, tree branches, tree stumps, leaves, bark, sawdust, corn, corn stover, wheat, wheat straw, rice, rice straw, sugarcane, sugarcane bagasse, sugarcane straw, energy cane, sugar beets, sugar beet pulp, sunflowers, sorghum, canola, algae, miscanthus, alfalfa, switchgrass, fruits, fruit shells, fruit stalks, fruit peels, fruit pits, vegetables, vegetable shells, vegetable stalks, vegetable peels, vegetable pits, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, food waste, commercial waste, grass pellets, hay pellets, wood pellets, cardboard, paper, paper pulp, paper packaging, paper trimmings, food packaging, construction or demolition waste, railroad ties, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof.

**[0239]** The "carbon-containing condensed-matter material" refers to a material that comprises at least one phase of condensed matter that comprises carbon. In this specification, a condensed-matter phase is solid, liquid, or a combination thereof (and is not purely vapor or plasma states of matter) at a temperature of 25°C and a pressure of 1 bar. In various embodiments, the carbon-containing condensed-matter material is in solid or liquid form at a temperature of about 25°C or less, about 50°C or less, about 75°C or less, about 100°C or less, about 125°C or less, about 150°C or less, about 175°C or less, about 200°C or less, about 225°C or less, about 250°C or less, about 275°C or less, or about 300°C or less, where these temperatures all refer to the form of condensed-matter material at atmospheric pressure of 1 bar.

**[0240]** To give an example, toluene is a carbon-containing condensed-matter material that is in liquid form at a temperature between about –95°C and 111°C, and is a vapor above 111°C, at a pressure of 1 bar. Toluene can therefore be a carbon-containing condensed-matter material in the disclosed process. As a comparative example, methane has a boiling point of –162°C at a pressure of 1 bar and therefore

is not a preferred carbon-containing condensed-matter material in the disclosed process.

**[0241]** Any carbon-containing condensed-matter material will generally vaporize at some point, i.e. at high enough temperature (and influenced by pressure). The fact that a carbon-containing material might be present in the process in a vapor phase does not disqualify its use as a carbon-containing condensed-matter material, as long as that material is eventually condensed to a liquid (or solid). In some embodiments, the carbon-containing material condenses to a liquid (or solid) during mixing with the first biogenic reagent in step (c).

**[0242]** The carbon-containing condensed-matter material can be in solid or liquid form at a temperature that is about the temperature in the contacting unit employed for contacting the first biogenic reagent with the carbon-containing condensed-matter material, which is typically either a mixing unit or a pelletizing unit. For example, if the contacting unit is operated at about 100°C, then the carbon-containing condensed-matter material should be in a solid or liquid phase, not solely a vapor phase, at 100°C. Essentially, the boiling point of the carbon-containing condensed-matter material should be the same as, or greater than, the temperature of the contacting unit (the boiling point here is calculated at the pressure of the contacting unit). If the contacting unit is operated at very low (e.g., cryogenic) temperatures, then ordinarily vapor carbon-containing materials can be employed if those carbon-containing materials are actually in a condensed-matter phase.

**[0243]** The carbon-containing condensed-matter material can be a liquid, a solid, a slurry of liquid and solid, a gas-liquid material (e.g. with bubbles dissolved in liquid, or a vapor with entrained liquid droplets), a gas-liquid-solid material, a gel, a plastic, a rubber-like material, a tacky material, or a gooey material. The phase and characteristics (e.g., rheological properties) of the carbon-containing condensed-matter material will depend to some extent on the type of separation unit.

**[0244]** In some embodiments, the carbon-containing condensed-matter material is a pyrolysis precipitate derived from the pyrolysis vapor. In other embodiments, the carbon-containing condensed-matter material is a pyrolysis precipitate provided externally from a different process. In some embodiments, the carbon-containing

condensed-matter material is not a pyrolysis precipitate but rather some other liquid or solid material.

**[0245]** In some embodiments, the carbon-containing condensed-matter material comprises aromatic species. For example, the carbon-containing condensed-matter material can be an off-spec or waste aromatics stream (e.g., a benzene/toluene/xylenes stream).

**[0246]** In some embodiments, the carbon-containing condensed-matter material is or comprises lignin. The lignin can be native lignin with high molecular weight, such as a lignin polymer obtained from lignocellulosic biomass. Alternatively, the lignin can be depolymerized lignin that has reduced molecular weight compared to native lignin.

**[0247]** In some embodiments, the carbon-containing condensed-matter material is or comprises one or more sugars or one or more sugar-degradation products. Sugars can be $C_5$ sugars (e.g., xylose), $C_6$ sugars (e.g., glucose), $C_{12}$ sugars (e.g., sucrose), or sugar oligomers (e.g., xylans), for example. Sugar-degradation products can comprise furfural, hydroxymethylfurfural, levulinic acid, or formic acid, for example. The carbon-containing condensed-matter material can be, or comprise, biomass-derived materials other than sugars or lignin—such as acetic acid, proteins, or decomposed proteins, for example.

**[0248]** In certain embodiments, the carbon-containing condensed-matter material is or comprises a non-biogenic material such as coal tars, coal-liquefaction products, petroleum tars, or crude oil. However, such non-biogenic materials reduce the renewable carbon content of the final biocarbon pellets.

**[0249]** In some embodiments, the carbon-containing condensed-matter material is or comprises one or more polymers or one or more polymer-degradation products. For example, the carbon-containing condensed-matter material can be polyethylene, polyethylene terephthalate, rubber (e.g., natural or synthetic rubber in recycled tires), or a thermally treated form thereof. In the case of recycled tires, carbon from the polyisoprene or styrene-butadiene rubber, as well as carbon from the carbon black, can be incorporated into biocarbon pellets.

**[0250]** In some embodiments, the carbon-containing condensed-matter material comprises liquid products produced by chemical reactions of syngas, wherein the syngas is optionally obtained from the pyrolysis vapor or the pyrolysis off-gas.

**[0251]** The carbon-containing condensed-matter material can comprise at least 50% renewable carbon as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio. The carbon-containing condensed-matter material can comprise at least 90%, at least 95%, at least 99%, or about 100% renewable carbon, as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio.

**[0252]** The intermediate material can comprise the carbon-containing condensed-matter material adsorbed onto a surface of the first biogenic reagent. Alternatively, or additionally, the intermediate material can comprise the carbon-containing condensed-matter material absorbed into a bulk phase of the first biogenic reagent.

**[0253]** In some processes utilizing a carbon-containing condensed-matter material, steps (c) and (d) are integrated.

**[0254]** A binder can be introduced to the intermediate material. The binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, a derivative thereof, or a combination of any of the foregoing. In certain embodiments, the binder is selected from starch, thermoplastic starch, crosslinked starch, starch polymers, a derivative thereof, or a combination of any of the foregoing.

**[0255]** In other processes, no external binder is introduced to the intermediate material during pelletizing. Binding can still occur. For example, the carbon-containing condensed-matter material can itself function as a pellet binder.

**[0256]** In some embodiments for which drying is desired, step (e) is conducted.

**[0257]** In some processes, steps (d) and (e) are integrated. In some processes, steps (e) and (f) are integrated. In certain processes, steps (d), (e), and (f) are all integrated.

**[0258]** The first biogenic reagent can be milled utilizing a mechanical-treatment apparatus selected from a hammer mill, an extruder, an attrition mill, a disc mill, a pin mill, a ball mill, a cone crusher, a jaw crusher, or a combination thereof. Alternatively, or additionally, the intermediate material can be milled utilizing a mechanical-treatment apparatus selected from a hammer mill, an extruder, an attrition mill, a disc mill, a pin mill, a ball mill, a cone crusher, a jaw crusher, or a combination thereof.

**[0259]** In some processes, step (d) utilizes a pelletizing apparatus selected from an extruder, a ring die pellet mill, a flat die pellet mill, a roll compactor, a roll briquetter, a wet agglomeration mill, a dry agglomeration mill, or a combination thereof.

**[0260]** The first pyrolysis reactor can be distinct from the second pyrolysis reactor. Alternatively, the first pyrolysis reactor and the second pyrolysis reactor can be the same unit, with steps (a) and (f) conducted at different times.

**[0261]** In some processes, step (a) is conducted at a first pyrolysis temperature selected from about 250°C to about 1250°C, such as from about 300°C to about 700°C. In some processes, step (f) is conducted at a second pyrolysis temperature selected from about 250°C to about 1250°C, such as from about 400°C to about 1000°C.

**[0262]** In some processes, step (a) is conducted for a first pyrolysis time selected from about 10 seconds to about 24 hours, such as from about 1 minute to about 4 hours. In some processes, step (f) is conducted for a second pyrolysis time selected from about 10 seconds to about 24 hours, such as from about 1 minute to about 4 hours.

**[0263]** During step (f), or potentially prior to that step, the first biogenic reagent can act as a catalyst or reaction matrix for fixed-carbon formation reactions of the carbon-containing condensed-matter material.

**[0264]** In some embodiments, the pyrolysis vapor is at least partially oxidized to generate heat, which is optionally used within the process. In these or other embodiments, the pyrolysis off-gas is at least partially oxidized to generate heat, which is optionally used within the process.

**[0265]** The biocarbon pellets can comprise at least 60 wt%, at least 70 wt%, at least 80 wt%, at least 85 wt%, or at least 90 wt% fixed carbon. The biocarbon pellets can comprise less than 10 wt%, less than 5 wt%, or less than 1 wt% ash. The biocarbon pellets can comprise less than 20 wt% or less than 10 wt% total volatile matter.

**[0266]** In some processes, at least 25 wt% of carbon in the carbon-containing condensed-matter material is converted to fixed carbon in the biocarbon pellets. In certain processes, at least 50 wt% of carbon in the carbon-containing condensed-matter material is converted to fixed carbon in the biocarbon pellets. In certain processes, at least 75 wt% of carbon in the carbon-containing condensed-matter material is converted to fixed carbon in the biocarbon pellets.

**[0267]** In some embodiments, from about 1 wt% to about 50 wt% of fixed carbon in the biocarbon pellets is derived from the carbon-containing condensed-matter material. In certain embodiments, from about 10 wt% to about 40 wt% of fixed carbon in the biocarbon pellets is derived from the carbon-containing condensed-matter material.

**[0268]** In step (c), less than all of the first biogenic reagent is contacted with the carbon-containing condensed-matter material. In step (c), less than all of the carbon-containing condensed-matter material is contacted with the first biogenic reagent.

**[0269]** The total carbon within the biocarbon pellets can be at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. The total carbon within the biocarbon pellets can be at least 90%, at least 95%, or fully (about 100%) renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

**[0270]** The biocarbon pellets can be characterized by a Hardgrove Grindability Index of at least 30 or at least 50.

**[0271]** The biocarbon pellets can be characterized by a bulk density of at least about 25, 30, 35, 40, or 45 $lb/ft^3$ on a dry basis.

**[0272]** In some embodiments, the biocarbon pellet has an average pellet size selected from about 1 mm to about 10 cm, calculated as effective diameter of the biocarbon pellet.

**[0273]** The biocarbon pellet can have a pellet effective diameter that is within 10% or within 5% of the effective pellet diameter of the intermediate pellet. In other embodiments, the biocarbon pellet has an effective pellet diameter that is more than 110%, or less than 90%, of the effective pellet diameter of the intermediate pellet.

**[0274]** In some embodiments, the biocarbon pellet has a pellet shape selected from sphere, cylinder, cube, octagon, hexagon, honeycomb, oval, column, bar, pillow, lentil, random granular, or a combination thereof.

**[0275]** In some embodiments, the biocarbon pellet is characterized by a pellet compressive strength at 25°C of at least about 100 $lb_f/in^2$, such as at least about 150 $lb_f/in^2$.

**[0276]** The biocarbon pellets can be hydrophobic or partially hydrophobic. In some embodiments, the biocarbon pellet is characterized by at most 20 wt% water uptake at 25°C after 24 hours of soaking in water.

**[0277]** In some embodiments, the biocarbon pellet is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances."

**[0278]** In some embodiments, the process further comprises introducing an additive during the process. The additive can be selected from acids, bases, or salts thereof. The additive can be selected from metals, metal oxides, metal hydroxides, metal halides, or a combination thereof. For example, the additive can be selected from sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron halide, iron chloride, iron bromide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, titanium dioxide, or a combination thereof.

**[0279]** An additive can be selected to adjust filtrate pH of the biocarbon pellet, wherein the filtrate pH is measured by combining 20 grams on a dry basis of the biocarbon pellet, or a powder form thereof, with 100 milliliters of distilled water, to form

a mixture; filtering the mixture through filter paper; and measuring pH of the filtrate with a pH meter.

**[0280]** An additive can be added to the second biogenic reagent to adjust filtrate pH of the second biogenic reagent, wherein the filtrate pH is measured by combining 20 grams on a dry basis of the second biogenic reagent with 100 milliliters of distilled water, to form a mixture; filtering the mixture through filter paper; and measuring pH of the filtrate with a pH meter. The additive can be added to the second biogenic reagent to decrease filtrate pH of the second biogenic reagent. Alternatively, the additive can be added to the second biogenic reagent to increase filtrate pH of the second biogenic reagent. When an additive is added for a different reason that for pH adjustment, the additive added to the second biogenic reagent can cause no change to the filtrate pH of the second biogenic reagent.

**[0281]** In some embodiments, the oxygen reactivity of the second biogenic reagent is reduced by addition of the additive to the second biogenic reagent.

**[0282]** The biocarbon pellets can be characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances."

**[0283]** In some embodiments, the process provides an overall carbon yield of at least 50%, calculated as carbon comprised in the biocarbon pellets as a percentage of the sum of carbon in the biomass-containing feedstock plus carbon in the carbon-containing condensed-matter material. The overall carbon yield can be at least 60%, at least 70%, or at least 80%.

**[0284]** The present technology also provides a biocarbon pellet produced by any of the disclosed processes.

**[0285]** Some variations provide a biocarbon pellet comprising fixed carbon with a fixed carbon content of at least 60 wt%, wherein the biocarbon pellet is characterized by a thermogravimetric analysis that measures the oxygen reactivity of the biocarbon pellet, wherein the thermogravimetric analysis is performed using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen, and wherein, according to a TGA graph of weight loss versus time from the thermogravimetric

analysis, the biocarbon pellet requires at least 240 minutes to reach 99% carbon oxidation.

**[0286]** In some embodiments of biocarbon pellets, according to the TGA graph of weight loss versus time from the thermogravimetric analysis performed using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen, the biocarbon pellet requires at least 250, 260, 270, 280, 290, 300, 310, or 320 minutes to reach 99% carbon oxidation.

**[0287]** In some embodiments, the thermogravimetric analysis is performed on an anthracite control sample, wherein the anthracite control sample requires a control time to reach 99% carbon oxidation, and wherein the time required for the biocarbon pellet to reach 99% carbon oxidation is from about 85% to about 100% of the control time. In various embodiments, the time required for the biocarbon pellet to reach 99% carbon oxidation is from about 90% to about 100%, such as from about 95% to about 98%, of the control time.

**[0288]** In some embodiments, the biocarbon pellet comprises volatile carbon, and the TGA graph shows a first carbon-oxidation regime associated with oxidation of volatile carbon, which is succeeded by a second carbon-oxidation regime associated with oxidation of fixed carbon. In certain embodiments, the thermogravimetric analysis shows a first-derivative curve peak within the first carbon-oxidation regime for the biocarbon pellet at a temperature of at least about 500°C.

**[0289]** In some embodiments, the biocarbon pellet comprises at least 60 wt% fixed carbon, at least 70 wt% fixed carbon, at least 80 wt% fixed carbon, at least 85 wt% fixed carbon, or at least 90 wt% fixed carbon.

**[0290]** In some embodiments, the biocarbon pellet comprises at most 10 wt% ash, at most 5 wt% ash, or at most 1 wt% ash.

**[0291]** In some embodiments, the biocarbon pellet comprises at most 20 wt% total volatile matter, or at most 10 wt% total volatile matter.

**[0292]** In some embodiments, the biocarbon pellet comprises a binder. The binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn

flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, a derivative thereof, or a combination of any of the foregoing. In certain embodiments, the binder is selected from starch, thermoplastic starch, crosslinked starch, starch polymers, a derivative thereof, or a combination of any of the foregoing.

**[0293]** In some embodiments, the biocarbon pellet does not comprise a binder. In some embodiments, the biocarbon pellet does not comprise a binder other than a pyrolysis precipitate.

**[0294]** In some embodiments, the biocarbon pellet comprises an additive. The additive can be selected from acids, bases, or salts thereof. The additive can be selected from metals, metal oxides, metal hydroxides, metal halides, or a combination thereof. In various embodiments, the additive is selected from sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron halide, iron chloride, iron bromide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, titanium dioxide, or a combination thereof.

**[0295]** In some embodiments, total carbon within the biocarbon pellet is at least 50%, at least 90%, or fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

**[0296]** In some embodiments, the biocarbon pellet is characterized by a Hardgrove Grindability Index of at least 30.

**[0297]** In some embodiments, the biocarbon pellet is characterized by a bulk density of at least about 20 $lb/ft^3$ on a dry basis.

**[0298]** In some embodiments, the biocarbon pellet has an average pellet size selected from about 1 mm to about 10 cm, calculated as effective diameter of the biocarbon pellet.

**[0299]** In some embodiments, the biocarbon pellet has a pellet shape selected from sphere, cylinder, cube, octagon, hexagon, honeycomb, oval, column, bar, pillow, lentil, random granular, or a combination thereof.

**[0300]** In some embodiments, the biocarbon pellet is characterized by a pellet compressive strength at 25°C of at least about 100 $lb_f/in^2$ or at least about 150 $lb_f/in^2$.

**[0301]** In some embodiments, the biocarbon pellet is characterized by at most 20 wt% water uptake at 25°C after 24 hours of soaking in water.

**[0302]** In some embodiments, the biocarbon pellet is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances."

**[0303]** The biocarbon pellet can be produced by a process comprising:

(a) pyrolyzing, in a first pyrolysis reactor, a biomass-containing feedstock, thereby generating a first biogenic reagent and a pyrolysis vapor;

(b) introducing, to a separation unit, the pyrolysis vapor, thereby generating a pyrolysis precipitate, wherein the pyrolysis precipitate is in liquid, solid, or slurry form;

(c) contacting the first biogenic reagent with the pyrolysis precipitate, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the pyrolysis precipitate;

(d) pelletizing the intermediate material, thereby generating an intermediate pellet;

(e) optionally, drying the intermediate pellet;

(f) separately from step (a), pyrolyzing, in a second pyrolysis reactor, the intermediate pellet, thereby generating a second biogenic reagent and a pyrolysis off-gas, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same reactor or distinct reactors; and

(g) recovering the second biogenic reagent as the biocarbon pellet,

wherein a fixed carbon content of the second biogenic reagent is greater than a fixed carbon content of the first biogenic reagent; and

wherein, according to a thermogravimetric analysis, an oxygen reactivity of the second biogenic reagent is less than an oxygen reactivity of the first biogenic reagent, wherein the thermogravimetric analysis is performed using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

**[0304]** The biocarbon pellet can be produced by a process comprising:

(a) pyrolyzing, in a first pyrolysis reactor, a biomass-containing feedstock, thereby generating a first biogenic reagent and a pyrolysis vapor;

(b) providing a carbon-containing condensed-matter material, wherein the carbon-containing condensed-matter material is a liquid, a solid, or a slurry;

(c) contacting the first biogenic reagent with the carbon-containing condensed-matter material, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the carbon-containing condensed-matter material;

(d) pelletizing the intermediate material, thereby generating an intermediate pellet;

(e) optionally, drying the intermediate pellet;

(f) separately from step (a), pyrolyzing, in a second pyrolysis reactor, the intermediate pellet, thereby generating a second biogenic reagent and a pyrolysis off-gas, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same reactor or distinct reactors; and

(g) recovering the second biogenic reagent as the biocarbon pellet,

wherein a fixed carbon content of the second biogenic reagent is greater than a fixed carbon content of the first biogenic reagent,

and wherein the second biogenic reagent has lower oxygen reactivity than the first biogenic reagent according to a thermogravimetric analysis using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

**[0305]** Some variations are premised on the recognition that while biocarbon pellets are beneficial in a wide range of embodiments, there are other embodiments in which the final biocarbon composition is not in pellet form, but rather another form, such as powders or films.

**[0306]** Some variations provide a biocarbon composition comprising fixed carbon with a fixed carbon content of at least 60 wt%, wherein the biocarbon composition is characterized by a thermogravimetric analysis that measures the oxygen reactivity of the biocarbon pellet, wherein the thermogravimetric analysis is performed using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen, and wherein, according to a TGA graph of weight loss versus time from the thermogravimetric analysis, the biocarbon pellet requires at least 240 minutes to reach 99% carbon oxidation.

**[0307]** The biocarbon composition can be produced by a process comprising:

(a) pyrolyzing, in a first pyrolysis reactor, a biomass-containing feedstock, thereby generating a first biogenic reagent and a pyrolysis vapor;

(b) introducing, to a separation unit, the pyrolysis vapor, thereby generating a pyrolysis precipitate, wherein the pyrolysis precipitate is in liquid, solid, or slurry form;

(c) contacting the first biogenic reagent with the pyrolysis precipitate, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the pyrolysis precipitate;

(d) separately from step (a), pyrolyzing, in a second pyrolysis reactor, the intermediate material, thereby generating a second biogenic reagent and a pyrolysis off-gas, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same reactor or distinct reactors; and

(e) recovering the second biogenic reagent as the biocarbon composition,

wherein a fixed carbon content of the second biogenic reagent is greater than a fixed carbon content of the first biogenic reagent; and

wherein, according to a thermogravimetric analysis, an oxygen reactivity of the second biogenic reagent is less than an oxygen reactivity of the first biogenic reagent, wherein the thermogravimetric analysis is performed using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

**[0308]** The biocarbon composition can be produced by a process comprising:

(a) pyrolyzing, in a first pyrolysis reactor, a biomass-containing feedstock, thereby generating a first biogenic reagent and a pyrolysis vapor;

(b) providing a carbon-containing condensed-matter material, wherein the carbon-containing condensed-matter material is a liquid, a solid, or a slurry;

(c) contacting the first biogenic reagent with the carbon-containing condensed-matter material, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the carbon-containing condensed-matter material;

(d) separately from step (a), pyrolyzing, in a second pyrolysis reactor, the intermediate material, thereby generating a second biogenic reagent and a pyrolysis off-gas, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same reactor or distinct reactors; and

(e) recovering the second biogenic reagent as the biocarbon composition,

wherein a fixed carbon content of the second biogenic reagent is greater than a fixed carbon content of the first biogenic reagent; and

wherein the second biogenic reagent has lower oxygen reactivity than the first biogenic reagent according to a thermogravimetric analysis using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

**[0309]** Certain embodiments provide a process for producing a biocarbon composition, the process comprising:

(a) pyrolyzing a biomass-containing feedstock in a first pyrolysis reactor to generate a first biogenic reagent and a first pyrolysis vapor;

(b) introducing at least some of the first pyrolysis vapor to a condensing system to generate a condenser liquid and a condenser vapor;

(c) contacting at least some of the first biogenic reagent with the condenser liquid, thereby generating an intermediate material comprising the first biogenic reagent and the condenser liquid;

(d) optionally, pelletizing the intermediate material;

(e) optionally, separately from step (a), further pyrolyzing the intermediate material in a second pyrolysis reactor to generate a second biogenic reagent and a second pyrolysis vapor;

(f) optionally, drying the second biogenic reagent; and

(g) recovering the second biogenic reagent as a biocarbon composition.

**[0310]** In some embodiments employing step (d), steps (c) and (d) are integrated. In some embodiments, step (d) is performed in a pelletizing unit, and step (c) is also conducted in the pelletizing unit. In other embodiments employing step (d), step (d) follows step (c).

**[0311]** When step (d) is performed, at least some of the intermediate material is pelletized. Optionally, the first biogenic reagent is pelletized, before or after contacting with condenser liquid.

**[0312]** In some embodiments for which intermediate material is pelletized, a binder is introduced to the intermediate material. A binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, a derivative thereof, or a combination of any of the foregoing. In certain embodiments, a binder is selected from starch, thermoplastic starch, crosslinked starch, starch polymers, a derivative thereof, or a combination of any of the foregoing.

**[0313]** In other embodiments for which intermediate material is pelletized, no external binder is introduced to the intermediate material during the pelletizing. In these cases, the condenser liquid can act as a binder for the pellets.

**[0314]** In some embodiments, a carbon recapture unit is disposed upstream of the second pyrolysis reactor. In other embodiments, a carbon recapture unit is a first stage of the second pyrolysis reactor. The carbon recapture unit can be configured to form a coating of condenser liquid onto pellets, for example.

**[0315]** In some processes employing step (e), steps (c) and (e) integrated.

**[0316]** The condensing system can comprise multiple condenser stages. In some embodiments, the condenser liquid is a condensed product of a first stage of the condensing system having multiple condenser stages.

**[0317]** In some embodiments, at least some of the second pyrolysis vapor is also conveyed to the condensing system.

**[0318]** The intermediate material can comprise condenser liquid adsorbed onto a surface of the first biogenic reagent. Alternatively, or additionally, the intermediate material can comprise condenser liquid absorbed into a bulk phase of the first biogenic reagent.

**[0319]** In some embodiments with step (e), the first pyrolysis reactor is distinct from the second pyrolysis reactor. In other embodiments, the first pyrolysis reactor and the second pyrolysis reactor are the same unit, wherein steps (a) and (e) are conducted at different times.

**[0320]** The first biogenic reagent can act as a catalyst or reaction matrix for fixed-carbon formation reactions of the condenser liquid.

**[0321]** In some embodiments, at least 25 wt% of total carbon comprised in the condenser liquid is converted to fixed carbon in the second biogenic reagent. In various embodiments, about, at least about, or at most about 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%, 80 wt%, or 90 wt% (including all intervening ranges) of total carbon comprised in the condenser liquid is converted to fixed carbon in the second biogenic reagent.

**[0322]** In some embodiments, from about 10 wt% to about 80 wt% of fixed carbon in the second biogenic reagent is derived from the first condenser liquid. In certain embodiments, from about 20 wt% to about 60 wt% of fixed carbon in the second biogenic reagent is derived from the first condenser liquid. In various embodiments, about, at least about, or at most about 1 wt%, 2 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%, 75 wt%, or 80 wt% (including all intervening ranges) of fixed carbon in the second biogenic reagent is derived from the first condenser liquid.

**[0323]** In some processes, step (a) is conducted at a first pyrolysis temperature selected from about 250°C to about 1250°C, such as from about 300°C to about 700°C.

In these or other processes, step (e) is conducted at a second pyrolysis temperature selected from about 300°C to about 1350°C, such as from about 350°C to about 800°C. The first pyrolysis temperature can be less than, equal, or greater than the second pyrolysis temperature. In some embodiments, the second pyrolysis temperature is of at least about the first pyrolysis temperature to enable effective pyrolysis of compounds that did not form fixed carbon in the first pyrolysis reactor. In such embodiments, the second pyrolysis temperature can be about 5°C, 10°C, 25°C, 50°C, 100°C, 150°C, or 200°C of at least about the first pyrolysis temperature, for example.

**[0324]** In some processes, step (a) is conducted for a first pyrolysis time selected from about 10 seconds to about 24 hours, such as from about 10 minutes to about 4 hours. In these or other processes, step (e) is conducted at a second pyrolysis time selected from about 10 seconds to about 24 hours, such as from about 15 minutes to about 5 hours. The first pyrolysis time can be less than, equal, or greater than the second pyrolysis time. In some embodiments, the second pyrolysis time is longer than the first pyrolysis time to enable effective pyrolysis of compounds that did not form fixed carbon in the first pyrolysis reactor. In such embodiments, the second pyrolysis time can be about 5, 10, 15, 20, 30, 40, 50, 60, 90, or 120 minutes longer than the first pyrolysis time, for example.

**[0325]** In some embodiments, some or all of the condenser vapor is at least partially oxidized to generate heat, wherein the heat is optionally used within the process. In these or other embodiments, some or all of the second pyrolysis vapor is at least partially oxidized (together with the condenser vapor, or separately) to generate heat, wherein the heat is optionally used within the process.

**[0326]** In certain embodiments, a pyrolysis off-gas or a condenser vapor is at least partially oxidized to generate a reducing gas comprising hydrogen or carbon monoxide. Such partial oxidation still generates useful heat but also produces a reducing gas that can be converted into other chemicals (e.g., methanol or Fischer-Tropsch hydrocarbons) if desired.

**[0327]** In some embodiments, the first biogenic reagent is milled utilizing a mechanical-treatment apparatus selected from a hammer mill, an extruder, an attrition mill, a disc mill, a pin mill, a ball mill, a cone crusher, a jaw crusher, or a combination thereof. In these or other embodiments, the intermediate material can be milled utilizing

a mechanical-treatment apparatus selected from a hammer mill, an extruder, an attrition mill, a disc mill, a pin mill, a ball mill, a cone crusher, a jaw crusher, or a combination thereof.

**[0328]** In embodiments employing step (d), step (d) can utilize a pelletizing apparatus selected from an extruder, a ring die pellet mill, a flat die pellet mill, a roll compactor, a roll briquetter, a wet agglomeration mill, a dry agglomeration mill, or a combination thereof.

**[0329]** In some processes, carbon-containing fines are generated in the second pyrolysis reactor. Optionally, the carbon-containing fines are recycled to step (c). When step (d) is conducted, carbon-containing fines generated in the second pyrolysis reactor can be recycled to step (d) instead of, or in addition to, recycling to step (c). Alternatively, or additionally, carbon-containing fines can be combusted to generate energy or used for other purposes.

**[0330]** In some embodiments, the biocarbon composition is in the form of powder. In some embodiments, the biocarbon composition is in the form of pellets. In some embodiments, the biocarbon composition is in the form of a film or coating.

**[0331]** The biocarbon composition can comprise at least 50 wt% fixed carbon, at least 60 wt% fixed carbon, at least 70 wt% fixed carbon, at least 75 wt% fixed carbon, at least 80 wt% fixed carbon, at least 85 wt% fixed carbon, or at least 90 wt% fixed carbon. In various embodiments, the biocarbon composition comprises about, at least about, or at most about 55, 60, 65, 70, 75, 80, 85, or 90 wt% fixed carbon.

**[0332]** The biocarbon composition can comprise at least 55 wt% total carbon, at least 60 wt% total carbon, at least 70 wt% total carbon, at least 75 wt% total carbon, at least 80 wt% total carbon, at least 85 wt% total carbon, at least 90 wt% total carbon, or at least 95 wt% total carbon. In various embodiments, the biocarbon composition comprises about, at least about, or at most about 60, 65, 70, 75, 80, 85, 90, or 95 wt% total carbon, including all intervening ranges.

**[0333]** In some embodiments, the biocarbon composition comprises less than 10 wt% ash, less than 5 wt% ash, less than 2 wt% ash, or less than 1 wt% ash. In various embodiments, the biocarbon composition comprises about, or at most about, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, 0.5, 0.2, or 0.1 wt% ash, including all intervening ranges.

**[0334]** The ash content of the biocarbon composition benefits (i.e., is lower) when condenser liquid with relatively low ash is incorporated into the material in the second pyrolysis reactor. In some embodiments, the first condenser liquid comprises less than 1 wt% ash, less than 0.1 wt% ash, or essentially no ash. In various embodiments, the first condenser liquid comprises about, or at most about, 5, 4, 3, 2, 1, 0.5, 0.2, 0.1, 0.05, 0.02, or 0.01 wt% ash, including all intervening ranges.

**[0335]** The total carbon within the biocarbon composition can be at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. In some embodiments, total carbon within the biocarbon composition is at least 90% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. Total carbon within the biocarbon composition can be fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

**[0336]** In some processes, the second biogenic reagent is pelletized in step (f), in step (g), or after step (g). The final biocarbon composition can therefore be in the form of pellets.

**[0337]** In some processes, the biocarbon composition is characterized by a Hardgrove Grindability Index of at least 30 or at least 50. In various embodiments, the biocarbon composition is characterized by a Hardgrove Grindability Index of about, at least about, or at most about 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, or 100, including all intervening ranges.

**[0338]** In some processes, the biocarbon composition is characterized by a bulk density of at least about 35 $lb/ft^3$ on a dry basis, or at least about 45 $lb/ft^3$ on a dry basis. In various embodiments, the bulk density of the biocarbon composition is about, or at least about, 25, 30, 35, 40, 45, or 50 $lb/ft^3$ on a dry basis, including all intervening ranges.

**[0339]** In some processes, the biocarbon composition is characterized as hydrophobic biocarbon or partially hydrophobic biocarbon.

**[0340]** In some processes, the biocarbon composition is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances."

**[0341]** In some processes, the biocarbon composition is characterized by a lack of odor generation at 25°C for 24 hours. In some embodiments, the biocarbon composition is characterized by a lack of odor generation at 50°C for 24 hours. In some embodiments, the biocarbon composition is characterized by a lack of odor generation at 25°C for 48 hours. Odor generation in this context refers to organic molecules being vaporized from the biocarbon composition, wherein such organic molecules are ordinarily detectible by humans. Examples comprise formaldehyde, acetic acid, ethanol, methanol, or mercaptan.

**[0342]** Some variations provide a method of making a high-fixed-carbon material comprising pyrolyzing biomass to generate intermediate solids and a pyrolysis vapor; condensing a portion of the pyrolysis vapor to generate pyrolysis liquid; introducing the pyrolysis liquid to the intermediate solids, to generate a solid-liquid mixture; optionally pelletizing to produce pellets compriseing the solid-liquid mixture; and optionally further pyrolyzing the solid-liquid mixture to generate a high-yield, high-fixed-carbon material.

**[0343]** In some methods, the method comprises pelletizing to produce pellets compriseing the solid-liquid mixture. In some embodiments, pelletizing does not utilize a binder other than the pyrolysis liquid. In other embodiments, pelletizing utilizes a binder other than the pyrolysis liquid. The step of further pyrolyzing the solid-liquid mixture can be enhanced by the pelletizing, such as when carbon comprised in the solid-liquid mixture acts as a catalyst or reaction matrix for forming additional fixed carbon.

**[0344]** In some methods, at least 60 wt% of total carbon comprised in the biomass forms fixed carbon in the high-fixed-carbon material. In certain methods, at least 70 wt%, at least 80 wt%, at least 90 wt%, or at least 95 wt% of total carbon comprised in the biomass forms fixed carbon in the high-fixed-carbon material.

**[0345]** Some variations provide a high-fixed-carbon material produced by a process comprising a method of making a high-fixed-carbon material comprising pyrolyzing biomass to generate intermediate solids and a pyrolysis vapor; condensing a portion of the pyrolysis vapor to generate pyrolysis liquid; introducing the pyrolysis liquid to the intermediate solids, to generate a solid-liquid mixture; optionally pelletizing to produce pellets compriseing the solid-liquid mixture; and optionally further pyrolyzing the solid-liquid mixture to generate a high-yield, high-fixed-carbon material.

**[0346]** Other variations provide a process for producing a biocarbon composition, the process comprising:

(a) pyrolyzing a biomass-containing feedstock in a first pyrolysis reactor to generate first pyrolysis solids and a first pyrolysis vapor;

(b) introducing at least some of the first pyrolysis vapor to a condensing system to generate a condenser liquid and a condenser vapor;

(c) separately from step (a), pyrolyzing the condenser liquid in a second pyrolysis reactor to generate second pyrolysis solids and a second pyrolysis vapor;

(d) blending the first pyrolysis solids with the second pyrolysis solids, thereby generating a biogenic reagent;

(e) optionally, pelletizing the biogenic reagent;

(f) optionally, drying or thermally treating the biogenic reagent; and

(g) recovering the biogenic reagent as a biocarbon composition.

**[0347]** In some processes, the biomass-containing feedstock is selected from softwood chips, hardwood chips, timber harvesting residues, tree branches, tree stumps, leaves, bark, sawdust, corn, corn stover, wheat, wheat straw, rice, rice straw, sugarcane, sugarcane bagasse, sugarcane straw, energy cane, sugar beets, sugar beet pulp, sunflowers, sorghum, canola, algae, miscanthus, alfalfa, switchgrass, fruits, fruit shells, fruit stalks, fruit peels, fruit pits, vegetables, vegetable shells, vegetable stalks, vegetable peels, vegetable pits, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, food waste, commercial waste, grass pellets, hay pellets, wood pellets, cardboard, paper, paper pulp, paper packaging, paper trimmings, food packaging, construction or demolition waste, railroad ties, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof.

**[0348]** In some processes, step (e) is performed, such that the biogenic reagent is pelletized. Step (e) can be integrated with step (d), with step (f), or with both of these steps.

**[0349]** In some embodiments employing step (e), a binder is introduced to the biogenic reagent. The binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose,

methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, a derivative thereof, or a combination of any of the foregoing. In certain embodiments, the binder is selected from starch, thermoplastic starch, crosslinked starch, starch polymers, a derivative thereof, or a combination of any of the foregoing.

**[0350]** In some embodiments employing step (e), no external binder is introduced to the biogenic reagent during the pelletizing.

**[0351]** In some processes, the condensing system comprises multiple condenser stages. The condenser liquid can be a condensed product of a first stage of multiple condenser stages.

**[0352]** In some embodiments, at least some of the second pyrolysis vapor is also conveyed to the same condensing system that condenses the first pyrolysis vapor, or to a distinct condensing system.

**[0353]** The first pyrolysis reactor is typically distinct from the second pyrolysis reactor, i.e., they are physically different units. In some embodiments, the first pyrolysis reactor and the second pyrolysis reactor are the same unit, and steps (a) and (c) are conducted at different times.

**[0354]** In some processes, at least 25 wt% of total carbon comprised in the condenser liquid is converted to fixed carbon in the second pyrolysis solids. In certain processes, at least 50 wt% of total carbon comprised in the condenser liquid is converted to fixed carbon in the second pyrolysis solids. In various embodiments, about, at least about, or at most about 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, or 90 wt% (including all intervening ranges) total carbon comprised in the condenser liquid is converted to fixed carbon in the second pyrolysis solids.

**[0355]** In some processes incorporating blending of first and second pyrolysis solids, the second pyrolysis solids form at least 5 wt% of the biogenic reagent on an

absolute basis. In certain processes, the second pyrolysis solids form at least 10 wt% or at least 20 wt% of the biogenic reagent on an absolute basis.

**[0356]** In some processes, from about 10 wt% to about 80 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid. In certain processes, from about 20 wt% to about 60 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid. In various embodiments, about, at least about, or at most about 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, or 90 wt% (including all intervening ranges) of fixed carbon in the biogenic reagent is derived from the condenser liquid.

**[0357]** Step (a) can be conducted at a first pyrolysis temperature selected from about 250°C to about 1250°C. Optionally, the first pyrolysis temperature is selected from about 300°C to about 700°C. Step (c) can be independently conducted at a second pyrolysis temperature selected from about 250°C to about 1250°C. Optionally, the second pyrolysis temperature is selected from about 300°C to about 700°C. The second pyrolysis temperature can be lower or of at least about the first pyrolysis temperature, or they could potentially be the same.

**[0358]** Step (a) can be conducted for a first pyrolysis time selected from about 10 seconds to about 24 hours. Step (c) can be independently conducted for a second pyrolysis time selected from about 10 seconds to about 24 hours. The second pyrolysis time can be shorter or longer than the first pyrolysis time, or they could potentially be the same.

**[0359]** In some processes, the condenser vapor is at least partially oxidized to generate heat, wherein the heat is optionally used within the process. In these or other processes, the second pyrolysis vapor is at least partially oxidized to generate heat, wherein the heat is optionally used within the process.

**[0360]** The biogenic reagent can be milled utilizing, for example, a mechanical-treatment apparatus selected from a hammer mill, an extruder, an attrition mill, a disc mill, a pin mill, a ball mill, a cone crusher, a jaw crusher, or a combination thereof.

**[0361]** When step (e) is conducted, it can utilize a pelletizing apparatus selected from an extruder, a ring die pellet mill, a flat die pellet mill, a roll compactor, a roll

briquetter, a wet agglomeration mill, a dry agglomeration mill, or a combination thereof, for example.

**[0362]** The biocarbon composition can be in the form of powder, pellets, or another geometry.

**[0363]** The biocarbon composition can comprise at least 50 wt% fixed carbon, at least 60 wt% fixed carbon, at least 70 wt% fixed carbon, at least 80 wt% fixed carbon, or at least 90 wt% fixed carbon. Other fixed carbon contents have been described previously and apply to these process embodiments (and other processes disclosed herein) as well.

**[0364]** The biocarbon composition can comprise less than 10 wt% ash, less than 5 wt% ash, less than 2 wt% ash, or less than 1 wt% ash. Other ash contents have been described previously and apply to these process embodiments (and other processes disclosed herein) as well.

**[0365]** In some embodiments, the condenser liquid comprises less than 1 wt% ash, less than 0.1 wt% ash, or essentially no ash. Low ash content of the condenser liquid reduces the final ash content of the biocarbon composition. Other condenser-liquid ash contents have been described previously and apply to these process embodiments (and other processes disclosed herein) as well.

**[0366]** In some processes, total carbon within the biocarbon composition is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. Total carbon within the biocarbon composition can be at least 90% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. Total carbon within the biocarbon composition can be fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

**[0367]** Some variations provide a process for producing a biocarbon composition, the process comprising:

(a) pyrolyzing a biomass-containing feedstock in a pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor;

(b) introducing at least some of the pyrolysis vapor to a condensing system to generate a condenser liquid and a condenser vapor;

(c) contacting a starting biomass feedstock with at least a portion of the condenser liquid, thereby generating the biomass-containing feedstock compriseing the starting biomass feedstock and at least a portion of the condenser liquid;

(d) optionally, pelletizing the biogenic reagent;

(e) optionally, drying the biogenic reagent; and

(f) recovering the biogenic reagent as a biocarbon composition.

**[0368]** The starting biomass feedstock can be selected from softwood chips, hardwood chips, timber harvesting residues, tree branches, tree stumps, leaves, bark, sawdust, corn, corn stover, wheat, wheat straw, rice, rice straw, sugarcane, sugarcane bagasse, sugarcane straw, energy cane, sugar beets, sugar beet pulp, sunflowers, sorghum, canola, algae, miscanthus, alfalfa, switchgrass, fruits, fruit shells, fruit stalks, fruit peels, fruit pits, vegetables, vegetable shells, vegetable stalks, vegetable peels, vegetable pits, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, food waste, commercial waste, grass pellets, hay pellets, wood pellets, cardboard, paper, paper pulp, paper packaging, paper trimmings, food packaging, construction or demolition waste, railroad ties, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof.

**[0369]** In some embodiments, step (c) utilizes spraying at least a portion of the condenser liquid onto the starting biomass feedstock. The biomass-containing feedstock can comprise condenser liquid adsorbed onto a surface of the starting biomass feedstock. Alternatively, or additionally, the biomass-containing feedstock comprises condenser liquid absorbed into a bulk phase of the starting biomass feedstock.

**[0370]** When step (d) is conducted, a binder can be introduced to the biogenic reagent. The binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland

cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, a derivative thereof, or a combination of any of the foregoing. In certain embodiments, the binder is selected from starch, thermoplastic starch, crosslinked starch, starch polymers, a derivative thereof, or a combination of any of the foregoing.

**[0371]** When step (d) is conducted, alternatively no external binder is introduced to the biogenic reagent during the pelletizing.

**[0372]** In some processes, steps (c) and (d) integrated and both performed in a pelletizing unit. In some processes, steps (d) and (e) are both conducted and are integrated.

**[0373]** The condensing system can comprise multiple condenser stages. The condenser liquid can be a condensed product of an individual stage (e.g., a first stage) of the multiple condenser stages.

**[0374]** In some processes, at least 25 wt% of total carbon comprised in the condenser liquid is converted to fixed carbon in the biogenic reagent. In certain processes, at least 50 wt% of total carbon comprised in the condenser liquid is converted to fixed carbon in the biogenic reagent.

**[0375]** In some processes, from about 10 wt% to about 80 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid. In certain processes, from about 20 wt% to about 60 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid.

**[0376]** Step (a) can be conducted at a pyrolysis temperature selected from about 250°C to about 1250°C, such as from about 300°C to about 700°C. Step (a) can be conducted for a first pyrolysis time selected from about 10 seconds to about 24 hours.

**[0377]** In some processes, some or all of the condenser vapor is at least partially oxidized to generate heat, wherein the heat is optionally used within the process.

**[0378]** The biogenic reagent can be milled utilizing a mechanical-treatment apparatus selected from a hammer mill, an extruder, an attrition mill, a disc mill, a pin mill, a ball mill, a cone crusher, a jaw crusher, or a combination thereof.

**[0379]** In processes employing step (d), that step can utilize a pelletizing apparatus selected from an extruder, a ring die pellet mill, a flat die pellet mill, a roll

compactor, a roll briquetter, a wet agglomeration mill, a dry agglomeration mill, or a combination thereof.

**[0380]** The final biocarbon composition can be in the form of powder or pellets, for example.

**[0381]** In some embodiments, the biocarbon composition comprises at least 50 wt% fixed carbon, at least 60 wt% fixed carbon, at least 70 wt% fixed carbon, at least 80 wt% fixed carbon, or at least 90 wt% fixed carbon.

**[0382]** In some embodiments, the biocarbon composition comprises less than 10 wt% ash, less than 5 wt% ash, less than 2 wt% ash, or less than 1 wt% ash.

**[0383]** In some embodiments, the condenser liquid comprises less than 1 wt% ash, less than 0.1 wt% ash, or essentially no ash.

**[0384]** The total carbon within the biocarbon composition can be at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. The total carbon within the biocarbon composition can be at least 90% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. The total carbon within the biocarbon composition can be fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

**[0385]** The low-fixed-carbon material and the high-fixed-carbon material can form distinct phases that do not dissolve into each other at equilibrium and at relatively low temperatures. In some embodiments, the low-fixed-carbon material and the high-fixed-carbon material can have high equilibrium (thermodynamic) solubilities in each other, but nevertheless remain kinetically frozen in the composition such that distinct materials are observable. The distinct materials can be observable by measuring compositions, densities, particle sizes, reactivities, or other physical or chemical properties. During final use of the biocarbon composition, it is possible (e.g., at elevated temperatures or during carbon oxidation) for the material distinction to be lost.

**[0386]** In one technique to demonstrate that a given biocarbon composition comprises both a low-fixed-carbon material and a distinct high-fixed-carbon material, thermogravimetric analysis (TGA) of oxidation (combustion) of a biocarbon composition test sample is performed. In some embodiments, the resulting TGA thermal curve has two peaks characteristic of distinct mass-loss events that correlate with the low-fixed-

carbon material and the high-fixed-carbon material. This can be compared against a control sample of a biocarbon composition that comprises a single material having a known uniform fixed-carbon concentration, to show a TGA thermal curve with a single peak characteristic of one mass-loss event for the material. In similar embodiments, the TGA thermal curve for the test sample has three or more peaks, while the TGA thermal curve for the control sample has at least one less peak than for the test sample.

**[0387]** Another technique to demonstrate that a given biocarbon composition comprises both a low-fixed-carbon material and a distinct high-fixed-carbon material is a particle-size analysis. This is a viable approach when the particle sizes associated with the low-fixed-carbon material and the high-fixed-carbon material are different, or when the particle-size distributions associated with the low-fixed-carbon material and the high-fixed-carbon material are different. In some embodiments, the high-fixed-carbon material tends to have smaller particles compared to the low-fixed-carbon material. In some embodiments, a bimodal particle-size distribution arising from the presence of both a low-fixed-carbon material and a high-fixed-carbon material, in contrast to a control sample that has a unimodal particle-size distribution characteristic of a uniform material. In similar embodiments, the test sample can have a particle-size distribution with at least one more mode than the control-sample particle-size distribution. It is possible, for example, for each of the low-fixed-carbon material and the high-fixed-carbon material to have bimodal particle-size distributions (with peaks centered at different sizes) and the control sample to also have a bimodal particle-size distribution, depending on how the control sample was produced.

**[0388]** Particle sizes can be measured by a variety of techniques, including dynamic light scattering, laser diffraction, image analysis, or sieve separation, for example. Dynamic light scattering is a non-invasive, well-established technique for measuring the size and size distribution of particles typically in the submicron region, and with the latest technology down to 1 nanometer. Laser diffraction is a widely used particle-sizing technique for materials ranging from hundreds of nanometers up to several millimeters in size. Exemplary dynamic light scattering instruments and laser diffraction instruments for measuring particle sizes are available from Malvern Instruments Ltd., Worcestershire, UK. Image analysis to estimate particle sizes and distributions can be done directly on photomicrographs, scanning electron micrographs,

or other images. Finally, sieving is a conventional technique of separating particles by size.

**[0389]** Imaging techniques can alternatively, or additionally, be utilized to demonstrate that a given biocarbon composition comprises both a low-fixed-carbon material and a distinct high-fixed-carbon material. Imaging techniques comprise, but are not limited to, optical microscopy; dark-field microscopy; scanning electron microscopy (SEM); transmission electron microscopy (TEM); and X-ray tomography (XRT), for example. An imaging technique can be used to demonstrate distinct materials in a blend, rather than a homogeneous material, for example. Or, an imaging technique can be used to select subsamples for further analysis. Further analysis can be compositional analysis to show three-dimensional variations in fixed carbon content. Further analysis can be property analysis to show three-dimensional variations in chemical or physical properties, such as density, particle size, or reactivity, for example.

**[0390]** Spectroscopy techniques can alternatively, or additionally, be utilized to demonstrate that a given biocarbon composition comprises both a low-fixed-carbon material and a distinct high-fixed-carbon material. Spectroscopy techniques comprise, but are not limited to, energy dispersive X-ray spectroscopy (EDS), X-ray fluorescence (XRF), infrared (IR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy, for example.

**[0391]** In some embodiments, the biocarbon composition comprises from about 10 wt% to about 90 wt% of a low-fixed-carbon material. In some embodiments, the biocarbon composition comprises from about 10 wt% to about 90 wt% of a high-fixed-carbon material. The weight ratio of the low-fixed-carbon material to the high-fixed-carbon material can be selected from about 0.1 to about 10, such as from about 0.2 to about 5, from about 0.5 to about 2, or from about 0.8 to about 1.2.

**[0392]** In some embodiments, the first fixed-carbon concentration is from about 20 wt% to about 40 wt%, or from about 25 wt% to about 50 wt%, or from about 30 wt% to about 55 wt%, for example.

**[0393]** In some embodiments, the second fixed-carbon concentration is from about 80 wt% to about 100 wt%, or from about 70 wt% to about 95 wt%, or from about 60 wt% to about 90 wt%, for example.

**[0394]** In some embodiments, the unweighted average of the first fixed-carbon concentration and the second fixed-carbon concentration is from about 30 wt% to about 90 wt%, such as from about 40 wt% to about 80 wt%.

**[0395]** The biocarbon composition can comprise an overall fixed-carbon concentration from about 25 wt% to about 95 wt% on an absolute basis. In some embodiments, the biocarbon composition comprises an overall fixed-carbon concentration from about 35 wt% to about 85 wt% on an absolute basis.

**[0396]** The low-fixed-carbon material can comprise from about 45 wt% to about 80 wt% volatile carbon on an absolute basis (i.e., including ash and moisture). In various embodiments, the low-fixed-carbon material can comprise about, at least about, or at most about 45, 50, 55, 60, 65, 70, 75, or 80 wt% volatile carbon on an absolute basis. The low-fixed-carbon material can comprise from about 1 wt% to about 20 wt% oxygen on an absolute basis, for example. The low-fixed-carbon material can comprise from about 0.1 wt% to about 10 wt% hydrogen on an absolute basis, for example.

**[0397]** The high-fixed-carbon material can comprise from about 0 to about 50 wt% volatile carbon on an absolute basis. In various embodiments, the high-fixed-carbon material can comprise about, at least about, or at most about 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, or 50 wt% volatile carbon on an absolute basis. The high-fixed-carbon material can comprise from about 1 wt% to about 20 wt% oxygen on an absolute basis, for example. The high-fixed-carbon material can comprise from about 0.1 wt% to about 10 wt% hydrogen on an absolute basis, for example.

**[0398]** The "biocarbon composition" is generally synonymous with "biocarbon product" when reference is to the final composition of a process. In some embodiments, the biocarbon composition comprises from about 0.1 wt% to about 20 wt% moisture. In various embodiments, the biocarbon composition comprises about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 wt% moisture, including all intervening ranges. The low-fixed-carbon material can comprise from 0 to about 50 wt% moisture, such as about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 wt% moisture, including all intervening ranges. Independently, the high-fixed-carbon material can comprise from 0 to about 50 wt% moisture, such as about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17,

18, 19, or 20 wt% moisture, including all intervening ranges. Drying can be employed at one or more points in the process.

**[0399]** In some embodiments, the biocarbon composition comprises from about 0.1 wt% to about 10 wt% ash. In various embodiments, the biocarbon composition comprises about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 wt% ash, including all intervening ranges. The low-fixed-carbon material can comprise from 0 to about 25 wt% ash, such as about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25 wt% ash, including all intervening ranges. Independently, the high-fixed-carbon material can comprise from 0 to about 50 wt% ash, such as about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25 wt% ash, including all intervening ranges.

**[0400]** In some embodiments, the biocarbon composition comprises from about 0.1 wt% to about 10 wt% of one or more additives. In some embodiments, the biocarbon composition comprises from about 1 wt% to about 15 wt% of one or more additives. In some embodiments, the biocarbon composition comprises from about 3 wt% to about 18 wt% of one or more additives. In various embodiments, the biocarbon composition comprises about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 wt% additive(s), including all intervening ranges.

**[0401]** The low-fixed-carbon material can comprise from 0 to about 20 wt% additives, such as about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 wt% additive(s), including all intervening ranges. Independently, the high-fixed-carbon material can comprise from 0 to about 50 wt% additives, such as about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 wt% additive(s), including all intervening ranges.

**[0402]** The additives can comprise an organic additive or an inorganic additive. In some embodiments, one or more additives comprise a renewable material. In some embodiments, one or more additives comprise a material that is capable of being partially oxidized or combusted.

**[0403]** In some embodiments, one or more additives comprise (or are) a binder. A binder can be selected from starch, thermoplastic starch, crosslinked starch, starch

polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, a derivative thereof, or a combination of any of the foregoing.

**[0404]** In certain embodiments, a binder is selected from starch, thermoplastic starch, crosslinked starch, starch polymers, a derivative thereof, or a combination of any of the foregoing. A binder can be a thermoplastic starch that is optionally crosslinked. The thermoplastic starch can be a reaction product of starch and a polyol, which can be selected from ethylene glycol, propylene glycol, glycerol, butanediols, butanetriols, erythritol, xylitol, sorbitol, or a combination thereof. The reaction product can be formed from a reaction that is catalyzed by an acid, which can be selected from formic acid, acetic acid, lactic acid, citric acid, oxalic acid, uronic acids, glucuronic acids, or a combination thereof. Alternatively, the reaction product can be formed from a reaction that is catalyzed by a base.

**[0405]** One or more additives can reduce the reactivity of the biocarbon composition compared to an otherwise-equivalent biocarbon composition without the one or more additives. The reactivity can be thermal reactivity. For example, the biocarbon composition with one or more additives can have a lower self-heating compared to the otherwise-equivalent biocarbon composition without the one or more additives. Alternatively, or additionally, the reactivity is chemical reactivity with oxygen, water, hydrogen, carbon monoxide, or metals (e.g., iron).

**[0406]** When additives are employed, the additives do not need to be uniformly distributed throughout the biomass composition. The additives can be present within one of the low-fixed-carbon material or high-fixed-carbon material, or even solely present within one of those materials. For example, a binder can be present in the overall biomass composition at 5 wt%, but of that amount, 4 percentage points are disposed within the low-fixed-carbon material and 1 percentage point is disposed within

the high-fixed-carbon material (i.e., 80% of the binder is placed within the low-fixed-carbon material). In various embodiments, the percentage of total additives disposed within the low-fixed-carbon material can be about, at least about, or at most about 0, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or 100%; the percentage of total additives disposed within the high-fixed-carbon material can be about, at least about, or at most about 0, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or 100%; and the percentage of total additives disposed within neither the low-fixed-carbon material nor the high-fixed-carbon material, but elsewhere within the biocarbon composition (e.g., as a separate additive phase) can be about, at least about, or at most about 0, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or 100%.

**[0407]** When the one or more additives are present, some or all of the additives can be pore-filling within the low-fixed-carbon material. When the one or more additives are present, some or all of the additives can be pore-filling within the high-fixed-carbon material. In some embodiments, one or more additives are present and are pore-filling within both of the low-fixed-carbon material and the high-fixed-carbon material.

**[0408]** Alternatively, or additionally, one or more additives can be disposed on an outer surface of the biocarbon composition (e.g., an outer surface of pellets or powder particles).

**[0409]** In some embodiments, the biocarbon composition is in the form of powder.

**[0410]** In some embodiments, the biocarbon composition is in the form of pellets. When the form is pellets, one or more additives can comprise a binder for the pellets. Alternatively, or additionally, pellets can utilize the low-fixed-carbon material itself as a binder within the pellets.

**[0411]** When one or more additives are present, the additive(s) can be located within one of the low-fixed-carbon material or the high-fixed-carbon material. Alternatively, the additive(s) can be uniformly distributed such that the additive(s) have the same average concentration within the low-fixed-carbon material and the high-fixed-carbon material.

**[0412]** In some embodiments, the biocarbon composition is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4:

"Test method for self-heating substances", which is hereby incorporated by reference herein.

**[0413]** The fixed-carbon concentration is an important parameter for the biocarbon composition. The present disclosure allows fixed-carbon concentration to be maximized, or optimized but not necessarily maximized, in various embodiments.

**[0414]** In some embodiments, the fixed-carbon concentration, and optionally the additive type or concentration, are selected to optimize energy content associated with the biocarbon composition.

**[0415]** In some embodiments, the fixed-carbon concentration, and optionally the additive type or concentration, are selected to optimize bulk density associated with the biocarbon composition.

**[0416]** In some embodiments, the fixed-carbon concentration, and optionally the additive type or concentration, are selected to optimize hydrophobicity associated with the biocarbon composition.

**[0417]** In some embodiments, the fixed-carbon concentration, and optionally the additive type or concentration, are selected to optimize pore sizes associated with the biocarbon composition.

**[0418]** In some embodiments, the fixed-carbon concentration, and optionally the additive type or concentration, are selected to optimize ratios of pore sizes associated with the biocarbon composition.

**[0419]** In some embodiments, the fixed-carbon concentration, and optionally the additive type or concentration, are selected to optimize surface area associated with the biocarbon composition.

**[0420]** In some embodiments, the fixed-carbon concentration, and optionally the additive type or concentration, are selected to optimize reactivity associated with the biocarbon composition.

**[0421]** In some embodiments, the fixed-carbon concentration, and optionally the additive type or concentration, are selected to optimize ion-exchange capacity associated with the biocarbon composition.

**[0422]** In some embodiments, the biocarbon composition is in the form of pellets, and the fixed-carbon concentration, and optionally the additive type or concentration, are selected to optimize Hardgrove Grindability Index associated with the pellets.

**[0423]** In some embodiments, the biocarbon composition is in the form of pellets, and the fixed-carbon concentration, and optionally the additive type or concentration, are selected to optimize Pellet Durability Index associated with the pellets.

**[0424]** The total carbon within the biocarbon composition can be at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. In some embodiments, the total carbon is at least 90% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. In certain embodiments, the total carbon is fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

**[0425]** It is important to note that while renewable biocarbon compositions are preferred, the principles of the disclosure can be applied to non-renewable materials. In certain embodiments, a biomass-containing feedstock comprises biomass (such as a biomass source recited herein) as well as a non-renewable feedstock, such as coal. Thus, a biomass-coal mixture can be utilized as biomass-containing feedstock—which can replace "biomass" in any of FIGS. 1 to 6, for example. Other non-biomass feedstocks that can be used in feedstock mixtures comprise pyrolyzed coal, coke, petroleum coke, metallurgical coke, activated carbon, carbon black, graphite, graphene, pyrolyzed polymers, or combinations thereof, for example.

**[0426]** In some processes, two or more distinct pyrolysis reactors are employed. The pyrolysis reactors are typically all conducted continuously or all conducted in batch, but in principle, a mixture of reaction modes can be used. Also, when distinct pyrolysis reactors are employed, they can be at a common site or at different sites.

**[0427]** In other embodiments, a process is conducted in a common pyrolysis reactor at different times, such as in distinct production campaigns. When a single pyrolysis reactor is used, it can be operated in batch mode with distinct batches of low-fixed-carbon material and high-fixed-carbon material, for example, or using different pyrolysis conditions. Alternatively, a single pyrolysis reactor can be operated continuously or semi-continuously, such that a first material is produced for a first period

of time and then a second material is produced for a second period of time, after which the reactor can be switched back to producing the first material or something else.

**[0428]** In some process embodiments, a first pyrolysis reactor is operated at a first pyrolysis temperature selected from about 250°C to about 1250°C, such as from about 300°C to about 700°C. A second pyrolysis reactor can be operated at a second pyrolysis temperature selected from about 250°C to about 1250°C, such as from about 300°C to about 700°C. The second pyrolysis temperature can be the same as, or different than, the first pyrolysis temperature.

**[0429]** In some embodiments, a first pyrolysis reactor is operated for a first pyrolysis time selected from about 10 seconds to about 24 hours. In these or other embodiments, a second pyrolysis reactor is operated for a second pyrolysis time selected from about 10 seconds to about 24 hours. The second pyrolysis time can be the same as, or different than, the first pyrolysis time.

**[0430]** Some embodiments are predicated on optimized pyrolysis of biomass along with carbon recapture—using principles taught herein—to generate a carbon substrate, mechanical size reduction of the carbon substrate, and use of a binder to agglomerate the carbon substrate to form biocarbon pellets. The carbon substrate can be or comprise a blend of low-fixed-carbon material and high-fixed-carbon material.

**[0431]** Hardgrove Grindability Index ("HGI") is a measure of the grindability of a material, such as biomass or coal. The HGI parameter for coal is important in power applications, such as pulverized coal boilers where coal is pulverized and burned in suspension, and in iron making, such as in pulverized coal injection where pulverized coal is injected through a lance into a blast furnace where pulverized coal can displace coke to reduce iron ores to metallic iron.

**[0432]** In some embodiments, varying the fixed-carbon content enables optimization of HGI. The incorporation of binders or other additives also can enable HGI adjustability.

**[0433]** The ability to adjust the HGI of biocarbon pellets is beneficial because downstream applications (e.g., replacement of coal in boilers) that utilize biocarbon pellets have varying HGI requirements. HGI adjustability addresses to well-known problems industrially: the difficulty to grind raw biomass, and the difficulty to grind

pellets. Furthermore, because there are so many downstream uses of biocarbon pellets, each having its own requirements, it is highly advantageous to be able to adjust the grindability of the pellets. It is desirable to be able to adjust HGI to suit a particular application, such as combustion in boilers, metal-making, or gasification to make syngas.

**[0434]** For many applications, pellets are preferred over powders (isolated biomass particles) due to advantages in shipping, storage, safety. Ultimately, the pellets can need to be converted back to powders, or at least smaller objects, at some point. Grindability of the pellets is thus often an important parameter that impacts operating costs and capital costs.

**[0435]** In some cases, pellets need to be ground or pulverized to a powder, such as when the boiler or gasifier utilizes a fluidized bed or a suspension of carbon particles. Another example is pulverized carbon injection into a blast furnace, for reducing metal ores to metals. In these cases, high grindability of the pellets is desired, but not too high such that the pellets fall apart during shipping and handling. In other cases, it is desired to feed pellets themselves to a process, such as a metal-making process. In these cases, lower grindability can be desirable since some pellet strength can be necessary to support a material bed in the reactor. Different technologies have different pellet grindability requirements.

**[0436]** The Hardgrove Grindability Index of the biocarbon pellet can be at least 30, at least 40, at least 50, at least 60, at least 70, at least 80, at least 90, or at least 100. In some embodiments, the Hardgrove Grindability Index is from about 30 to about 50 or from about 50 to about 70. ASTM-Standard D 409/D 409M for "Standard Test Method for Grindability of Coal by the Hardgrove-Machine Method" is hereby incorporated by reference herein in its entirety. Unless otherwise indicated, all references in this disclosure to Hardgrove Grindability Index or HGI are in reference to ASTM-Standard D 409/D 409M.

**[0437]** In various embodiments, the Hardgrove Grindability Index is about, at least about, or at most about 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82,

83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, including all intervening ranges (e.g., 25–40, 30–60, etc.).

**[0438]** The biocarbon pellet can be characterized by a Pellet Durability Index of at least 80%, at least 85%, at least 90%, at least 95%, or at least 99%. The biocarbon pellet can be characterized by a Pellet Durability Index less than 99%, less than 95%, less than 90%, less than 85%, or less than 80%. Unless otherwise indicated, all references in this disclosure to Pellet Durability Index are in reference to ISO 17831-1:2015 "Solid biofuels — Determination of mechanical durability of pellets and briquettes — Part 1: Pellets", which is hereby incorporated by reference herein in its entirety.

**[0439]** In some embodiments, the biocarbon pellets are utilized as a starting material to make smaller objects, which can also be referred to as biocarbon pellets since "pellet" does not limit the geometry. For example, initial biocarbon pellets that are 10 mm in average pellet diameter can be fabricated. Then, these initial biocarbon pellets can be crushed using various mechanical means (e.g., using a hammer mill). The crushed pellets can be separated according to size, such as by screening. In this manner, smaller biocarbon pellets can be produced, with an average pellet diameter of about, at least about, or at most about 50, 100, 150, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1500, 2000, 3000, 4000, or 5000 microns, for example. In certain embodiments, the average pellet diameter of the smaller biocarbon pellets is preferably larger than the average particle diameter of the initial carbon-containing particles that were used to make the pellets with the binder.

**[0440]** When the biocarbon pellets are crushed to generate smaller biocarbon pellets, a step of crushing (and optionally screening) can be integrated with another process step, including potentially at a site of industrial use. The optional step to generate smaller biocarbon pellets can utilize a crushing apparatus selected from a hammer mill, an attrition mill, a disc mill, a pin mill, a ball mill, a cone crusher, a jaw crusher, a rock crusher, or a combination thereof.

**[0441]** In various process embodiments, the Hardgrove Grindability Index is at least 40, at least 50, at least 60, at least 70, at least 80, at least 90, or at least 100. For example, the Hardgrove Grindability Index can be from about 30 to about 50 or from about 50 to about 70.

**[0442]** In various processes, the process conditions are selected and optimized to generate a final biocarbon pellet with a Hardgrove Grindability Index of about, at least about, or at most about 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, including all intervening ranges (e.g., 30–60, 33–47, etc.).

**[0443]** In some processes, the biocarbon pellet is characterized by a Pellet Durability Index of at least 80%, at least 90%, or at least 95%.

**[0444]** In some embodiments, the process comprises pre-selecting a Hardgrove Grindability Index, adjusting process conditions based on the pre-selected Hardgrove Grindability Index, and achieving within ±20% of the pre-selected Hardgrove Grindability Index for the biocarbon pellets, wherein the adjusting process conditions comprises adjusting one or more of pyrolysis temperature, pyrolysis time, mechanical-treatment conditions, pelletizing conditions, binder type, binder concentration, binding conditions, and drying. The process of certain embodiments can achieve within ±10%, or within ±5%, of the pre-selected Hardgrove Grindability Index for the biocarbon pellets.

**[0445]** The size and geometry of the biocarbon pellet can vary. By "pellet" as used herein, it is meant an agglomerated object rather than a loose powder. The pellet geometry is not limited to spherical or approximately spherical. Also, in this disclosure, "pellet" is synonymous with "briquette." The pellet geometry can be spherical (round or ball shape), cylindrical, cube (square), octagon, hexagon, honeycomb/beehive shape, oval shape, egg shape, column shape, bar shape, pillow shape, random shape, or a combination thereof. For convenience of disclosure, the term "pellet" will generally be used for any object compriseing a powder agglomerated with a binder. It is also reiterated that this technology is by no means limited to biocarbon compositions in the form of pellets. For example, after a pellet is produced using a disclosed process, the pellet can be powderized before use.

**[0446]** The biocarbon pellets can be characterized by an average pellet diameter, which is the true diameter in the case of a sphere or cylinder, or an equivalent diameter in the case of any other 3D geometry. The equivalent diameter of a non-spherical pellet is the diameter of a sphere of equivalent volume to the actual pellet. In some

embodiments, the average pellet diameter is about, or at least about, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 20, or 25 millimeters, including all intervening ranges. In some embodiments, the average pellet diameter is about, or at least about, 500, 1000, 1500, 2000, 2500, 3000, 3500, 4000, 4500, 5000, 5500, 6000, or 6500 microns, including all intervening ranges.

**[0447]** In some embodiments, there is a plurality of biocarbon pellets that is relatively uniform in size, such as a standard deviation of less than ±100%, less than ±50%, less than ±25%, less than ±10%, or less than ±5% of the average pellet diameter. In other embodiments, there is a wide range of sizes of biocarbon pellets, as this can be advantageous in some applications.

**[0448]** Biocarbon pellets can comprise moisture. The moisture present in a biocarbon pellet can be water that is chemically bound to carbon or binder, water that is physically bound (absorbed or adsorbed) to carbon or binder, free water present in an aqueous phase that is not chemically or physically bound to carbon or binder, or a combination thereof. When moisture is desired during the binding process, it is preferred that such moisture is chemically or physically bound to carbon or binder, rather than being free water.

**[0449]** Various moisture levels can be present. For example, the biocarbon pellet can comprise from about 1 wt% to about 30 wt% (e.g., 32 wt%) moisture, such as from about 5 wt% to about 15 wt% moisture, from about 2 wt% to about 10 wt% moisture, or from about 0.1 wt% to about 1 wt% moisture. In some embodiments, the biocarbon pellet comprises about 4–8 wt% moisture. In various embodiments, the biocarbon pellet comprises about, at least about, or at most about 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, or 35 wt% moisture, including all intervening ranges. Moisture levels of the biocarbon pellets can be optimized to vary the densification within the pellets.

**[0450]** For some market applications, such as in agriculture, higher moisture levels are desirable for dust control or other reasons. For other market applications, such as metallurgy, lower moisture levels can be desirable (e.g., 1 wt% moisture or even less). Note that although water is present during the process of making biocarbon pellets, those pellets are then optionally dried which means the final biocarbon pellets do not necessarily comprise moisture.

**[0451]** In some biocarbon pellets, the biocarbon pellet comprises from about 2 wt% to about 25 wt% of the binder, from about 5 wt% to about 20 wt% of the binder, or from about 1 wt% to about 5 wt% of the binder. In various embodiments, the biocarbon pellet comprises about, at least about, or at most about 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 20, 25, or 30 wt% binder, including all intervening ranges. In some embodiments, there is an inverse relationship between moisture content and binder concentration.

**[0452]** The binder can be pore-filling within the biogenic reagent of the biocarbon pellets. Alternatively, or additionally, the binder can be disposed on the surfaces of the biocarbon pellets.

**[0453]** The binder can be an organic binder or an inorganic binder. In some embodiments, the binder is or comprises a renewable material. In some embodiments, the binder is or comprises a biodegradable material. In some embodiments, the binder is capable of being partially oxidized or combusted.

**[0454]** In various embodiments, the binder is selected from starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, a derivative thereof, or a combination of any of the foregoing. The binder can be, or comprise, a grindable plasticizer.

**[0455]** In certain embodiments, the binder is selected from starch, thermoplastic starch, crosslinked starch, starch-based polymers (e.g., polymers based on amylose and amylopectin), a derivative thereof, or a combination of any of the foregoing. Starch can be non-ionic starch, anionic starch, cationic starch, or zwitterionic starch.

**[0456]** Starch is one of the most abundant biopolymers. It is completely biodegradable, inexpensive, renewable, and can be easily chemically modified. The cyclic structure of the starch molecules together with strong hydrogen bonding gives

starch a rigid structure and leads to highly ordered crystalline and granular regions. Starch in its granular state is generally unsuitable for thermoplastic processing. To obtain thermoplastic starch, the semi-crystalline starch granules can be broken down by thermal and mechanical forces. Since the melting point of pure starch is considerably of at least about its decomposition temperature, plasticizers such as water or glycols can be added. The natural crystallinity can then be disrupted by vigorous mixing (shearing) at elevated temperatures which yields thermoplastic starch. Starch can be plasticized (destructurized) by relatively low levels of molecules that are capable of hydrogen bonding with the starch hydroxyl groups, such as water, glycerol, or sorbitol.

**[0457]** Thermoplastic starch can be chemically modified or blended with other biopolymers to produce a tougher and more ductile and resilient bioplastic. For example, starch can be blended with natural and synthetic (biodegradable) polyesters such as polylactic acid, polycaprolactone, or polyhydroxybutyrate. To improve the compatibility of the starch/polyester blends, suitable compatibilizers such as poly(ethylene-co-vinyl alcohol) or polyvinyl alcohol can be added. The hydrophilic hydroxyl groups (–OH) of starch can be replaced with hydrophobic (reactive) groups, such as by esterification or etherification.

**[0458]** In some embodiments, a starch-containing binder is or comprises a crosslinked starch. Various methods for crosslinking starch are known in the art. A starch material can be crosslinked under acidic or alkaline conditions after dissolving or dispersing it in an aqueous medium, for example. Aldehydes (e.g., glutaraldehyde or formaldehyde) can be used to crosslink starch.

**[0459]** One example of a crosslinked starch is a reaction product of starch and glycerol or another polyol, such as (but not limited to) ethylene glycol, propylene glycol, glycerol, butanediols, butanetriols, erythritol, xylitol, sorbitol, or combinations thereof. The reaction product can be formed from a crosslinking reaction that is catalyzed by an acid, such as (but not limited to) formic acid, acetic acid, lactic acid, citric acid, oxalic acid, uronic acids, glucuronic acids, or combinations thereof. Inorganic acids, such as sulfuric acid, can also be utilized to catalyze the crosslinking reaction. In some embodiments, the thermoplasticizing or crosslinking reaction product can be formed

from a crosslinking reaction that is catalyzed instead by an base, such as (but not limited to) ammonia or sodium borate.

**[0460]** In some embodiments, a binder is designed to be a water-resistant binder. For example, in the case of starch, hydrophilic groups can be replaced by hydrophobic groups that better resist water.

**[0461]** In some embodiments, the binder serves other purposes, such as (but not limited to) water retention in the biocarbon pellet, a food source for microorganisms, etc.

**[0462]** In some embodiments, the binder reduces the reactivity of the biocarbon pellet compared to an otherwise-equivalent biocarbon pellet without the binder. Reactivity can refer to thermal reactivity or chemical reactivity (or both).

**[0463]** In the case of thermal reactivity, the biocarbon pellet can have lower self-heating compared to the otherwise-equivalent biocarbon pellet without the binder. "Self-heating" refers to biocarbon pellet undergoing spontaneous exothermic reactions, in absence of any external ignition, at relatively low temperatures and in an oxidative atmosphere, to cause the internal temperature of a biocarbon pellet to rise.

**[0464]** Chemical reactivity can be reactivity *with* oxygen, water, hydrogen, carbon monoxide, metals (e.g., iron), or combinations thereof. Chemical reactivity can be associated with reactions to CO, $CO_2$, $H_2O$, pyrolysis oils, and heat, for example.

**[0465]** Optionally, biocarbon pellets comprise one or more additives (that are not necessarily binders), such as inorganic bentonite clay, limestone, starch, cellulose, lignin, or acrylamides. When lignin is used as a binder or other additive, the lignin can be obtained from the same biomass feedstock as used in the pyrolysis process. For example, a starting biomass feedstock can be subjected to a lignin-extraction step, removing a quantity of lignin for use as a binder or additive.

**[0466]** Other possible additives including fluxing agents, such as inorganic chlorides, inorganic fluorides, or lime. In some embodiments, additives are selected from acids, bases, or salts thereof. In some embodiments, at least one additive is selected from a metal, a metal oxide, a metal hydroxide, a metal halide, or a combination thereof. For example, an additive can be selected from (but not limited to) the group consisting of sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, magnesium,

manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron halide, iron chloride, iron bromide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, or a combination thereof. Additives can be added before, during, or after any one or more steps of the process, including into the feedstock itself at any time, before or after it is harvested.

**[0467]** Biocarbon pellets disclosed herein have a wide variety of downstream uses. The biocarbon pellets can be stored, sold, shipped, and converted to other products. The biocarbon pellets can be pulverized for use in a boiler, to combust the carbon and generate electrical energy or heat. The biocarbon pellets can be pulverized, crushed, or milled for feeding into a furnace, such as a blast furnace in metal making. The biocarbon pellets can be fed directly into a furnace, such as a Tecnored furnace in metal making. The biocarbon pellets can be pulverized, crushed, or milled for feeding into a gasifier for purposes of making syngas from the biocarbon pellets.

**[0468]** In many embodiments, the biocarbon pellets are fed to a furnace, either directly or following a step to pulverize, crush, mill, or otherwise reduce particle size. A furnace can be a blast furnace, a top-gas recycling blast furnace, a shaft furnace, a reverberatory furnace (also known as an air furnace), a crucible furnace, a muffling furnace, a retort furnace, a flash furnace, a Tecnored furnace, an Ausmelt furnace, an ISASMELT furnace, a puddling furnace, a Bogie hearth furnace, a continuous chain furnace, a pusher furnace, a rotary hearth furnace, a walking beam furnace, an electric arc furnace, an induction furnace, a basic oxygen furnace, a puddling furnace, a Bessemer furnace, a direct-reduced-metal furnace, or a combination or derivative thereof.

**[0469]** Note that regardless of the Hardgrove Grindability Index of the biocarbon pellets, they are not necessarily later subjected to a grinding process. For example, the biocarbon pellets can be used directly in an agricultural application. As another example, the biocarbon pellets can be directly incorporated into an engineered structure, such as a landscaping wall. At the end-of-life of a structure compriseing biocarbon pellets, the pellets can then be ground, combusted, gasified, or otherwise reused or recycled.

*Pyrolysis Processes and Systems*

**[0470]** Processes and systems suitable for pyrolyzing a biomass feedstock, or a biogenic reagent together with condenser liquid, will now be further described in detail. Descriptions of a pyrolysis reactor (or reaction) will be understood as references to a reactor (or reaction) specifically for producing a high-fixed-carbon material in some instances.

**[0471]** "Pyrolysis" and "pyrolyze" generally refer to thermal decomposition of a carbonaceous material. In pyrolysis, less oxygen is present than is required for complete combustion of the material, such as less than 10%, 5%, 1%, 0.5%, 0.1%, or 0.01% of the oxygen ($O_2$ molar basis) that is required for complete combustion. In some embodiments, pyrolysis is performed in the absence of oxygen.

**[0472]** Exemplary changes that can occur during pyrolysis comprise any of the following: (i) heat transfer from a heat source increases the temperature inside the feedstock; (ii) the initiation of primary pyrolysis reactions at this higher temperature releases volatiles and forms a char; (iii) the flow of hot volatiles toward cooler solids results in heat transfer between hot volatiles and cooler unpyrolyzed feedstock; (iv) condensation of some of the volatiles in the cooler parts of the feedstock, followed by secondary reactions, can produce tar; (v) autocatalytic secondary pyrolysis reactions proceed while primary pyrolytic reactions simultaneously occur in competition; and (vi) further thermal decomposition, reforming, water-gas shift reactions, free-radical recombination, or dehydrations can also occur, which are a function of the residence time, temperature, and pressure profile.

**[0473]** Pyrolysis can at least partially dehydrate a starting feedstock (e.g., lignocellulosic biomass). In various embodiments, pyrolysis removes greater than about 50%, 75%, 90%, 95%, 99%, or more of the water from the starting feedstock.

**[0474]** In some embodiments, a starting biomass feedstock is selected from softwood chips, hardwood chips, timber harvesting residues, tree branches, tree stumps, leaves, bark, sawdust, corn, corn stover, wheat, wheat straw, rice, rice straw, sugarcane, sugarcane bagasse, sugarcane straw, energy cane, sugar beets, sugar beet pulp, sunflowers, sorghum, canola, algae, miscanthus, alfalfa, switchgrass, fruits, fruit shells, fruit stalks, fruit peels, fruit pits, vegetables, vegetable shells, vegetable stalks, vegetable peels, vegetable pits, grape pumice, almond shells, pecan shells,

coconut shells, coffee grounds, food waste, commercial waste, grass pellets, hay pellets, wood pellets, cardboard, paper, paper pulp, paper packaging, paper trimmings, food packaging, construction or demolition waste, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof. Note that typically a biomass feedstock comprises at least carbon, hydrogen, and oxygen.

**[0475]** The biogenic reagent can comprise at least about 50 wt%, at least about 75 wt%, or at least about 90 wt% total carbon. In various embodiments, the biogenic reagent comprises about, at least about, or at most about 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, or 99 wt% carbon. The total carbon is fixed carbon plus non-fixed carbon that is present in volatile matter. In some embodiments, component weight percentages are on an absolute basis, which is assumed unless stated otherwise. In other embodiments, component weight percentages are on a moisture-free and ash-free basis. Compositions of low-fixed-carbon materials and high-fixed-carbon materials have been discussed in detail above.

**[0476]** The pyrolysis conditions can be varied widely, depending on the desired compositions for the biogenic reagent and pyrolysis off-gas, the starting feedstock, the reactor configuration, and other factors.

**[0477]** In some embodiments, multiple reactor zones are designed and operated in a way that optimizes carbon yield and product quality from pyrolysis, while maintaining flexibility and adjustability for feedstock variations and product requirements.

**[0478]** In some non-limiting embodiments, the temperatures and residence times are selected to achieve relatively slow pyrolysis chemistry. The benefit is potentially the substantial preservation of cell walls comprised in the biomass structure, which means the final product can retain some, most, or all of the shape and strength of the starting biomass. In order to maximize this potential benefit, an apparatus that does not mechanically destroy the cell walls or otherwise convert the biomass particles into small fines can be used. Certain such reactor configurations are discussed following the process description below.

**[0479]** Additionally, if the feedstock is a milled or sized feedstock, such as wood chips or pellets, it can be desirable for the feedstock to be carefully milled or sized. Careful initial treatment will tend to preserve the strength and cell-wall integrity that is

present in the native feedstock source (e.g., trees). This can also be important when the final product should retain some, most, or all of the shape and strength of the starting biomass.

**[0480]** In some embodiments, a first zone of a pyrolysis reactor is configured for feeding biomass (or another carbon-containing feedstock) in a manner that does not "shock" the biomass, which would rupture the cell walls and initiate fast decomposition of the solid phase into vapors and gases. This first zone can be thought of as mild pyrolysis.

**[0481]** In some embodiments, a second zone of a pyrolysis reactor is configured as the primary reaction zone, in which preheated biomass undergoes pyrolysis chemistry to release gases and condensable vapors, leaving a significant amount of solid material which is a high-carbon reaction intermediate. Biomass components (primarily cellulose, hemicellulose, and lignin) decompose and create vapors, which escape by penetrating through pores or creating new nanopores. The latter effect contributes to the creation of porosity and surface area.

**[0482]** In some embodiments, a third zone of a pyrolysis reactor is configured for receiving the high-carbon reaction intermediate and cooling down the solids to some extent. Typically, the third zone will be a lower temperature than the second zone. In the third zone, the chemistry and mass transport can be surprisingly complex. Without being limited by any particular theory or proposed mechanisms, it is believed that secondary reactions can occur in the third zone. Essentially, carbon-containing components that are in the gas phase can decompose to form additional fixed carbon or become adsorbed onto the carbon. Thus, the final carbonaceous material can not simply be the solid, devolatilized residue of the processing steps, but rather can comprise additional carbon that has been deposited from the gas phase, such as by decomposition of organic vapors (e.g., tars) that can form carbon.

**[0483]** Certain embodiments extend the concept of additional carbon formation by including a separate unit in which cooled carbon is subjected to an environment including carbon-containing species, to enhance the carbon content of the final product. When the temperature of this unit is below pyrolysis temperatures, the additional carbon is expected to be in the form of adsorbed carbonaceous species, rather than additional fixed carbon.

**[0484]** There are a large number of options as to intermediate input and output (purge or probe) streams of one or more phases present in any particular zone, various mass and energy recycle schemes, various additives that can be introduced anywhere in the process, adjustability of process conditions including both reaction and separation conditions in order to tailor product distributions, and so on. Zone-specific input and output streams enable good process monitoring and control, such as through FTIR sampling and dynamic process adjustments.

**[0485]** Some embodiments do not employ fast pyrolysis, and some embodiments do not employ slow pyrolysis. Surprisingly high-quality carbon materials, including compositions with very high fractions of fixed carbon, can be obtained from the disclosed processes and systems.

**[0486]** In some embodiments, a pyrolysis process for producing a biogenic reagent comprises the following steps:

(a) providing a carbon-containing feedstock comprising biomass;

(b) optionally drying the feedstock to remove at least a portion of moisture comprised within the feedstock;

(c) optionally deaerating the feedstock to remove at least a portion of interstitial oxygen, if any, comprised with the feedstock;

(d) pyrolyzing the feedstock in the presence of a substantially inert gas phase for at least 10 minutes and with at least one temperature selected from about 250°C to about 700°C, to generate hot pyrolyzed solids, condensable vapors, and non-condensable gases;

(e) separating at least a portion of the condensable vapors and at least a portion of the non-condensable gases from the hot pyrolyzed solids;

(f) cooling the hot pyrolyzed solids to generate cooled pyrolyzed solids; and

(g) recovering a biogenic reagent comprising at least a portion of the cooled pyrolyzed solids.

**[0487]** "Biomass," for purposes of this disclosure, shall be construed as any biogenic feedstock or mixture of a biogenic and non-biogenic feedstocks. Elementally, biomass comprises at least carbon, hydrogen, and oxygen. The methods and

apparatus can accommodate a wide range of feedstocks of various types, sizes, and moisture contents.

**[0488]** Biomass comprises, for example, plant and plant-derived material, vegetation, agricultural waste, forestry waste, wood waste, paper waste, animal-derived waste, poultry-derived waste, and municipal solid waste. In various embodiments utilizing biomass, the biomass feedstock can comprise one or more materials selected from: timber harvesting residues, softwood chips, hardwood chips, tree branches, tree stumps, knots, leaves, bark, sawdust, off-spec paper pulp, cellulose, corn, corn stover, wheat straw, rice straw, sugarcane bagasse, switchgrass, miscanthus, animal manure, municipal garbage, municipal sewage, commercial waste, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, grass pellets, hay pellets, wood pellets, cardboard, paper, carbohydrates, plastic, and cloth. A person of ordinary skill in the art will readily appreciate that the feedstock options are virtually unlimited.

**[0489]** The present disclosure can also be used for carbon-containing feedstocks other than biomass, such as a fossil fuel (e.g., coal or petroleum coke), or any mixtures of biomass and fossil fuels (such as biomass/coal blends). In some embodiments, a biogenic feedstock is, or comprises, coal, oil shale, crude oil, asphalt, or solids from crude-oil processing (such as petcoke). Feedstocks can comprise waste tires, recycled plastics, recycled paper, construction waste, deconstruction waste, and other waste or recycled materials. For the avoidance of doubt, any method, apparatus, or system described herein can be used with any carbonaceous feedstock. Carbon-containing feedstocks can be transportable by any known means, such as by truck, train, ship, barge, tractor trailer, or any other vehicle or means of conveyance.

**[0490]** Selection of a particular feedstock or feedstocks is not regarded as technically critical, but is carried out in a manner that tends to favor an economical process. Typically, regardless of the feedstocks chosen, there can be (in some embodiments) screening to remove undesirable materials. The feedstock can optionally be dried prior to processing.

**[0491]** The feedstock employed can be provided or processed into a wide variety of particle sizes or shapes. For example, the feed material can be a fine powder, or a mixture of fine and coarse particles. The feed material can be in the form of large pieces of material, such as wood chips or other forms of wood (e.g., round, cylindrical, square,

etc.). In some embodiments, the feed material comprises pellets or other agglomerated forms of particles that have been pressed together or otherwise bound, such as with a binder.

**[0492]** It is noted that size reduction is a costly and energy-intensive process. Pyrolyzed material can be sized with significantly less energy input—that is, it can be preferred to reduce the particle size of the product, not the feedstock. This is an option because the process does not require a fine starting material, and there is not necessarily any significant particle-size reduction during processing. The ability to process very large pieces of feedstock is a significant economic advantage. Notably, some market applications of the high-carbon product actually require large sizes (e.g., on the order of centimeters), so that in some embodiments, large pieces are fed, produced, and sold.

**[0493]** When it is desired to produce a final carbonaceous biogenic reagent that has structural integrity, such as in the form of cylinders, there are at least two options in the context of this disclosure. First, the material produced from the process can be collected and then further process mechanically into the desired form. For example, the product can be pressed or pelletized, with a binder. The second option is to utilize feed materials that generally possess the desired size or shape for the final product, and employ processing steps that do not destroy the basic structure of the feed material. In some embodiments, the feed and product have similar geometrical shapes, such as spheres, cylinders, or cubes.

**[0494]** The ability to maintain the approximate size of feed material throughout the process is beneficial when product strength is important. Also, this avoids the difficulty and cost of pelletizing high fixed-carbon materials.

**[0495]** The starting feed material can be provided with a range of moisture levels, as will be appreciated. In some embodiments, the feed material can already be sufficiently dry that it need not be further dried before pyrolysis. Typically, it will be desirable to utilize commercial sources of biomass which will usually comprise moisture, and feed the biomass through a drying step before introduction into the pyrolysis reactor. However, in some embodiments a dried feedstock can be utilized.

**[0496]** It is usually desirable to provide a relatively low-oxygen environment in the pyrolysis reactor, such as about, or at most about, 10 mol%, 5 mol%, 4 mol%, 3 mol%,

2 mol%, 1.5 mol%, 1 mol%, 0.5 mol%, 0.2 mol%, 0.1 mol%, 0.05 mol%, 0.02 mol%, or 0.01 mol% $O_2$ in the gas phase. First, uncontrolled combustion should be avoided in the pyrolysis reactor, for safety reasons. Some amount of total carbon oxidation to $CO_2$ can occur, and the heat released from the exothermic oxidation can assist the endothermic pyrolysis chemistry. Large amounts of oxidation of carbon, including partial oxidation to syngas, will reduce the carbon yield to solids.

**[0497]** Practically speaking, it can be difficult to achieve a strictly oxygen-free environment in the reactor. This limit can be approached, and in some embodiments, the reactor is substantially free of molecular oxygen in the gas phase. To ensure that little or no oxygen is present in the pyrolysis reactor, it can be desirable to remove air from the feed material before it is introduced to the reactor. There are various ways to remove or reduce air in the feedstock.

**[0498]** In some embodiments, a deaeration unit is utilized in which feedstock, before or after drying, is conveyed in the presence of another gas which can remove adsorbed oxygen and penetrate the feedstock pores to remove oxygen from the pores. Essentially any gas that has lower than 21 vol% $O_2$ can be employed, at varying effectiveness. In some embodiments, nitrogen is employed. In some embodiments, CO or $CO_2$ is employed. Mixtures can be used, such as a mixture of nitrogen and a small amount of oxygen. Steam can be present in the deaeration gas, although adding significant moisture back to the feed should be avoided. The effluent from the deaeration unit can be purged (to the atmosphere or to an emissions treatment unit) or recycled.

**[0499]** In principle, the effluent (or a portion thereof) from the deaeration unit could be introduced into the pyrolysis reactor itself since the oxygen removed from the solids will now be highly diluted. In this embodiment, it can be advantageous to introduce the deaeration effluent gas to the last zone of the reactor, when it is operated in a countercurrent configuration.

**[0500]** Various types of deaeration units can be employed. If drying it to be performed, it can be preferable to dry and then deaerate since it can be inefficient to scrub soluble oxygen out of the moisture present. In certain embodiments, the drying and deaerating steps are combined into a single unit, or some amount of deaeration is achieved during drying, and so on.

**[0501]** The optionally dried and optionally deaerated feed material is introduced to a pyrolysis reactor or multiple reactors in series or parallel. The feed material can be introduced using any known means, including screw feeders or lock hoppers, for example. In some embodiments, a material feed system incorporates an air knife.

**[0502]** When a single reactor is employed, multiple zones can be present. Multiple zones, such as two, three, four, or more zones, can allow for the separate control of temperature, solids residence time, gas residence time, gas composition, flow pattern, or pressure in order to adjust the overall process performance.

**[0503]** References to "zones" shall be broadly construed to comprise regions of space within a single physical unit, physically separate units, or any combination thereof. For a continuous reactor, the demarcation of zones can relate to structure, such as the presence of flights within the reactor or distinct heating elements to provide heat to separate zones. Alternatively, or additionally, the demarcation of zones in a continuous reactor can relate to function, such as distinct temperatures, fluid flow patterns, solid flow patterns, extent of reaction, and so on. In a single batch reactor, "zones" are operating regimes in time, rather than in space. Multiple batch reactors can also be used.

**[0504]** It will be appreciated that there are not necessarily abrupt transitions from one zone to another zone. For example, the boundary between the preheating zone and pyrolysis zone can be somewhat arbitrary; some amount of pyrolysis can take place in a portion of the preheating zone, and some amount of "preheating" can continue to take place in the pyrolysis zone. The temperature profile in the reactor is typically continuous, including at zone boundaries within the reactor.

**[0505]** Some embodiments employ a first zone that is operated under conditions of preheating or mild pyrolysis. The temperature of the first zone can be selected from about 150°C to about 500°C, such as about 300°C to about 400°C. The temperature of the first zone is preferably not so high as to shock the biomass material which ruptures the cell walls and initiates fast decomposition of the solid phase into vapors and gases.

**[0506]** All references to zone temperatures in this specification should be construed in a non-limiting way to comprise temperatures that can apply to the bulk solids present, or the gas phase, or the reactor walls (on the process side). It will be

understood that there will be a temperature gradient in each zone, both axially and radially, as well as temporally (i.e., following start-up or due to transients). Thus, references to zone temperatures can be references to average temperatures or other effective temperatures that can influence the actual kinetics. Temperatures can be directly measured by thermocouples or other temperature probes, or indirectly measured or estimated by other means.

**[0507]** The second zone, or in general the primary pyrolysis zone, is operated under conditions of pyrolysis or carbonization. The temperature of the second zone can be selected from about 250°C to about 700°C, such as about, or at least about, or at most about 300°C, 350°C, 400°C, 450°C, 500°C, 550°C, 600°C, or 650°C. Within this zone, preheated biomass undergoes pyrolysis chemistry to release gases and condensable vapors, leaving a significant amount of solid material as a high-carbon reaction intermediate. Biomass components (primarily cellulose, hemicellulose, and lignin) decompose and create vapors, which escape by penetrating through pores or creating new pores. The preferred temperature will at least depend on the residence time of the second zone, as well as the nature of the feedstock and desired product properties.

**[0508]** The third zone, or cooling zone, is operated to cool down the high-carbon reaction intermediate to varying degrees. At a minimum, the temperature of the third zone should be a lower temperature than that of the second zone. The temperature of the third zone can be selected from about 100°C to about 550°C, such as about 150°C to about 350°C.

**[0509]** Chemical reactions can continue to occur in the cooling zone. Without being limited by any particular theory, it is believed that secondary pyrolysis reactions can be initiated in the third zone. Carbon-containing components that are in the gas phase can condense (due to the reduced temperature of the third zone). The temperature remains sufficiently high, however, to promote reactions that can form additional fixed carbon from the condensed liquids (secondary pyrolysis) or at least form bonds between adsorbed species and the fixed carbon. One exemplary reaction that can take place is the Boudouard reaction for conversion of carbon monoxide to carbon dioxide plus fixed carbon.

**[0510]** The residence times of the reactor zones can vary. There is an interplay of time and temperature, so that for a desired amount of pyrolysis, higher temperatures can allow for lower reaction times, and vice versa. The residence time in a continuous reactor (zone) is the volume divided by the volumetric flow rate. The residence time in a batch reactor is the batch reaction time, following heating to reaction temperature.

**[0511]** It should be recognized that in multiphase reactors, there are multiple residence times. In the present context, in each zone, there will be a residence time (and residence-time distribution) of both the solids phase and the vapor phase. For a given apparatus employing multiple zones, and with a given throughput, the residence times across the zones will generally be coupled on the solids side, but residence times can be uncoupled on the vapor side when multiple inlet and outlet ports are utilized in individual zones. The solids and vapor residence times are uncoupled.

**[0512]** The solids residence time of the preheating zone can be selected from about 5 min to about 60 min, such as about 10, 20, 30, 40, or 50 min. Depending on the temperature, sufficient time is desired to allow the biomass to reach a desired preheat temperature. The heat-transfer rate, which will depend on the particle type and size, the physical apparatus, and on the heating parameters, will dictate the minimum residence time necessary to allow the solids to reach a desired preheat temperature. Additional time can not be desirable as it would contribute to higher capital cost, unless some amount of mild pyrolysis is intended in the preheating zone.

**[0513]** The solids residence time of the pyrolysis zone can be selected from about 10 min to about 120 min, such as about 20, 30, 40, 50, 60, 70, 80, 90, or 100 min. Depending on the pyrolysis temperature in this zone, there should be sufficient time to allow the carbonization chemistry to take place, following the necessary heat transfer. For times below about 10 min, in order to remove high quantities of non-carbon elements, the temperature would need to be quite high, such as above 700°C. This temperature would promote fast pyrolysis and its generation of vapors and gases derived from the carbon itself, which is to be avoided when the intended product is solid carbon.

**[0514]** In a static system, there would be an equilibrium conversion that could be substantially reached at a certain time. When, as in certain embodiments, vapor is continuously flowing over solids with continuous volatiles removal, the equilibrium

constraint can be removed to allow for pyrolysis and devolatilization to continue until reaction rates approach zero. Longer times would not tend to substantially alter the remaining recalcitrant solids.

**[0515]** The solids residence time of the cooling zone can be selected from about 5 min to about 60 min, such as about 10, 20, 30, 40, or 50 min. Depending on the cooling temperature in this zone, there should be sufficient time to allow the carbon solids to cool to the desired temperature. The cooling rate and temperature will dictate the minimum residence time necessary to allow the carbon to be cooled. Additional time can not be desirable, unless some amount of secondary pyrolysis is desired.

**[0516]** As discussed above, the residence time of the vapor phase can be separately selected and controlled. The vapor residence time of the preheating zone can be selected from about 0.1 min to about 15 min, such as about 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 min. The vapor residence time of the pyrolysis zone can be selected from about 0.1 min to about 20 min, such as about 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15 min. The vapor residence time of the cooling zone can be selected from about 0.1 min to about 15 min, such as about 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 min. Short vapor residence times promote fast sweeping of volatiles out of the system, while longer vapor residence times promote reactions of components in the vapor phase with the solid phase.

**[0517]** The mode of operation for the reactor, and overall system, can be continuous, semi-continuous, batch, or any combination or variation of these. In some embodiments, the reactor is a continuous, countercurrent reactor in which solids and vapor flow substantially in opposite directions. The reactor can also be operated in batch but with simulated countercurrent flow of vapors, such as by periodically introducing and removing gas phases from the batch vessel.

**[0518]** Various flow patterns can be desired or observed. With chemical reactions and simultaneous separations involving multiple phases in multiple reactor zones, the fluid dynamics can be quite complex. Typically, the flow of solids can approach plug flow (well-mixed in the radial dimension) while the flow of vapor can approach fully mixed flow (fast transport in both radial and axial dimensions). Multiple inlet and outlet ports for vapor can contribute to overall mixing.

**[0519]** The pressure in each zone can be separately selected and controlled. The pressure of each zone can be independently selected from about 1 kPa to about 3000 kPa, such as about 101.3 kPa (normal atmospheric pressure). Independent zone control of pressure is possible when multiple gas inlets and outlets are used, including vacuum ports to withdraw gas when a zone pressure less than atmospheric is desired.

**[0520]** The process can conveniently be operated at atmospheric pressure, in some embodiments. There are many advantages associated with operation at atmospheric pressure, ranging from mechanical simplicity to enhanced safety. In certain embodiments, the pyrolysis zone is operated at a pressure of about 90 kPa, 95 kPa, 100 kPa, 101 kPa, 102 kPa, 105 kPa, or 110 kPa (absolute pressures).

**[0521]** Vacuum operation (e.g., 10-100 kPa) would promote fast sweeping of volatiles out of the system. Higher pressures (e.g., 100-1000 kPa) can be useful when the off-gases will be fed to a high-pressure operation. Elevated pressures can also be useful to promote heat transfer, chemistry, or separations.

**[0522]** The step of separating at least a portion of the condensable vapors and at least a portion of the non-condensable gases from the hot pyrolyzed solids can be accomplished in the reactor itself, or using a distinct separation unit. A substantially inert sweep gas can be introduced into one or more of the zones. Condensable vapors and non-condensable gases are then carried away from the zone(s) in the sweep gas, and out of the reactor.

**[0523]** The sweep gas can be $N_2$, Ar, CO, $CO_2$, $H_2$, $H_2O$, $CH_4$, other light hydrocarbons, or combinations thereof, for example. The sweep gas can first be preheated prior to introduction, or possibly cooled if it is obtained from a heated source.

**[0524]** The sweep gas more thoroughly removes volatile components, by getting them out of the system before they can condense or further react. The sweep gas allows volatiles to be removed at higher rates than would be attained merely from volatilization at a given process temperature. Or, use of the sweep gas allows milder temperatures to be used to remove a certain quantity of volatiles. The reason the sweep gas improves the volatiles removal is that the mechanism of separation is not merely relative volatility but rather liquid/vapor phase disengagement assisted by the sweep gas. The sweep gas can both reduce mass-transfer limitations of volatilization as well

as reduce thermodynamic limitations by continuously depleting a given volatile species, to cause more of it to vaporize to attain thermodynamic equilibrium.

**[0525]** Some embodiments remove gases laden with volatile organic carbon from subsequent processing stages, in order to produce a product with high fixed carbon. Without removal, the volatile carbon can adsorb or absorb onto the pyrolyzed solids, thereby requiring additional energy (cost) to achieve a purer form of carbon which can be desired. By removing vapors quickly, it is also speculated that porosity can be enhanced in the pyrolyzing solids. Higher porosity is desirable for some products.

**[0526]** In certain embodiments, the sweep gas in conjunction with a relatively low process pressure, such as atmospheric pressure, provides for fast vapor removal without large amounts of inert gas necessary.

**[0527]** In some embodiments, the sweep gas flows countercurrent to the flow direction of feedstock. In other embodiments, the sweep gas flows cocurrent to the flow direction of feedstock. In some embodiments, the flow pattern of solids approaches plug flow while the flow pattern of the sweep gas, and gas phase generally, approaches fully mixed flow in one or more zones.

**[0528]** The sweep can be performed in any one or more of the reactor zones. In some embodiments, the sweep gas is introduced into the cooling zone and extracted (along with volatiles produced) from the cooling or pyrolysis zones. In some embodiments, the sweep gas is introduced into the pyrolysis zone and extracted from the pyrolysis or preheating zones. In some embodiments, the sweep gas is introduced into the preheating zone and extracted from the pyrolysis zone. In these or other embodiments, the sweep gas can be introduced into each of the preheating, pyrolysis, and cooling zones and also extracted from each of the zones.

**[0529]** In some embodiments, the zone or zones in which separation is carried out is a physically separate unit from the reactor. The separation unit or zone can be disposed between reactor zones, if desired. For example, there can be a separation unit placed between pyrolysis and cooling units.

**[0530]** The sweep gas can be introduced continuously, especially when the solids flow is continuous. When the pyrolysis reaction is operated as a batch process, the sweep gas can be introduced after a certain amount of time, or periodically, to remove

volatiles. Even when the pyrolysis reaction is operated continuously, the sweep gas can be introduced semi-continuously or periodically, if desired, with suitable valves and controls.

**[0531]** The volatiles-containing sweep gas can exit from the one or more reactor zones, and can be combined if obtained from multiple zones. The resulting gas stream, compriseing various vapors, can then be fed to a thermal oxidizer for control of air emissions. Any known thermal-oxidation unit can be employed. In some embodiments, the thermal oxidizer is fed with natural gas and air, to reach sufficient temperatures for substantial destruction of volatiles comprised therein.

**[0532]** The effluent of the thermal oxidizer will be a hot gas stream comprising water, carbon dioxide, and nitrogen. This effluent stream can be purged directly to air emissions, if desired. Preferably, the energy content of the thermal oxidizer effluent is recovered, such as in a waste-heat recovery unit. The energy content can also be recovered by heat exchange with another stream (such as the sweep gas). The energy content can be utilized by directly or indirectly heating, or assisting with heating, a unit elsewhere in the process, such as the dryer or the reactor. In some embodiments, essentially all of the thermal oxidizer effluent is employed for indirect heating (utility side) of the dryer. The thermal oxidizer can employ other fuels than natural gas.

**[0533]** The yield of carbonaceous material can vary, depending on the above-described factors including type of feedstock and process conditions. In some embodiments, the net yield of solids as a percentage of the starting feedstock, on a dry basis, is at least 25%, 30%, 35%, 40%, 45%, 50%, or higher. The remainder will be split between condensable vapors, such as terpenes, tars, alcohols, acids, aldehydes, or ketones; and non-condensable gases, such as carbon monoxide, hydrogen, carbon dioxide, and methane. The relative amounts of condensable vapors compared to non-condensable gases will also depend on process conditions, including the water present.

**[0534]** In terms of the carbon balance, in some embodiments the net yield of carbon as a percentage of starting carbon in the feedstock is at least 25%, 30%, 40%, 50%, 60%, 65%, 70%, 75%, 80%, or higher. For example, the in some embodiments the carbonaceous material comprises between about 40% and about 70% of the carbon comprised in the starting feedstock. The rest of the carbon results in the formation of

methane, carbon monoxide, carbon dioxide, light hydrocarbons, aromatics, tars, terpenes, alcohols, acids, aldehydes, or ketones, to varying extents.

**[0535]** In alternative embodiments, some portion of these compounds is combined with the carbon-rich solids to enrich the carbon and energy content of the product. In these embodiments, some or all of the resulting gas stream from the reactor, compriseing various vapors, can be condensed, at least in part, and then passed over cooled pyrolyzed solids derived from the cooling zone or from the separate cooling unit. These embodiments are described in more detail below.

**[0536]** Following the reaction and cooling within the cooling zone (if present), the carbonaceous solids can be introduced into a distinct cooling unit. In some embodiments, solids are collected and simply allowed to cool at slow rates. If the carbonaceous solids are reactive or unstable in air, it can be desirable to maintain an inert atmosphere or rapidly cool the solids to, for example, a temperature less than 40°C, such as ambient temperature. In some embodiments, a water quench is employed for rapid cooling. In some embodiments, a fluidized-bed cooler is employed. A "cooling unit" should be broadly construed to also comprise compriseers, tanks, pipes, or portions thereof.

**[0537]** In some embodiments, the process further comprises operating the cooling unit to cool the warm pyrolyzed solids with steam, thereby generating the cool pyrolyzed solids and superheated steam; wherein the drying is carried out, at least in part, with the superheated steam derived from the cooling unit. Optionally, the cooling unit can be operated to first cool the warm pyrolyzed solids with steam to reach a first cooling-unit temperature, and then with air to reach a second cooling-unit temperature, wherein the second cooling-unit temperature is lower than the first cooling-unit temperature and is associated with a reduced combustion risk for the warm pyrolyzed solids in the presence of the air.

**[0538]** Following cooling to ambient conditions, the carbonaceous solids can be recovered and stored, conveyed to another site operation, transported to another site, or otherwise disposed, traded, or sold. The solids can be fed to a unit to reduce particle size. A variety of size-reduction units are known in the art, including crushers, shredders, grinders, pulverizers, jet mills, pin mills, and ball mills.

**[0539]** Screening or some other means for separation based on particle size can be comprised. The grinding can be upstream or downstream of grinding, if present. A portion of the screened material (e.g., large chunks) can be returned to the grinding unit. The small and large particles can be recovered for separate downstream uses. In some embodiments, cooled pyrolyzed solids are ground into a fine powder, such as a pulverized carbon or activated carbon product.

**[0540]** Various additives can be introduced throughout the process, before, during, or after any step disclosed herein. The additives can be broadly classified as process additives, selected to improve process performance such as carbon yield or pyrolysis time/temperature to achieve a desired carbon purity; and product additives, selected to improve one or more properties of the biogenic reagent, or a downstream product incorporating the reagent. Certain additives can provide enhanced process *and* product (biogenic reagents or products compriseing biogenic reagents) characteristics.

**[0541]** Additives can be added before, during, or after any one or more steps of the process, including into the feedstock itself at any time, before or after it is harvested. Additive treatment can be incorporated prior to, during, or after feedstock sizing, drying, or other preparation. Additives can be incorporated at or on feedstock supply facilities, transport trucks, unloading equipment, storage bins, conveyors (including open or closed conveyors), dryers, process heaters, or any other units. Additives can be added anywhere into the pyrolysis process itself, using suitable means for introducing additives. Additives can be added after carbonization, or even after pulverization, if desired.

**[0542]** In some embodiments, an additive is selected from a metal, a metal oxide, a metal hydroxide, or a combination thereof. For example an additive can be selected from, but is by no means limited to, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, magnesium oxide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, or a combination thereof.

**[0543]** In some embodiments, an additive is selected from an acid, a base, or a salt thereof. For example an additive can be selected from, but is by no means limited to, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, or combinations thereof.

**[0544]** In some embodiments, an additive is selected from a metal halide. Metal halides are compounds between metals and halogens (fluorine, chlorine, bromine, iodine, and astatine). The halogens can form many compounds with metals. Metal halides are generally obtained by direct combination, or more commonly, neutralization of basic metal salt with a hydrohalic acid. In some embodiments, an additive is selected from iron chloride ($FeCl_2$ or $FeCl_3$), iron bromide ($FeBr_2$ or $FeBr_3$), or hydrates thereof, and any combinations thereof.

**[0545]** Additives can result in a final product with higher energy content (energy density). An increase in energy content can result from an increase in total carbon, fixed carbon, volatile carbon, or even hydrogen. Alternatively or additionally, the increase in energy content can result from removal of non-combustible matter or of material having lower energy density than carbon. In some embodiments, additives reduce the extent of liquid formation, in favor of solid and gas formation, or in favor of solid formation.

**[0546]** Without being limited to any particular hypothesis, additives can chemically modify the starting biomass, or treated biomass prior to pyrolysis, to reduce rupture of cell walls for greater strength/integrity. In some embodiments, additives can increase fixed carbon content of biomass feedstock prior to pyrolysis.

**[0547]** Additives can result in a biogenic reagent with improved mechanical properties, such as yield strength, compressive strength, tensile strength, fatigue strength, impact strength, elastic modulus, bulk modulus, or shear modulus. Additives can improve mechanical properties by simply being present (e.g., the additive itself imparts strength to the mixture) or due to some transformation that takes place within the additive phase or within the resulting mixture. For example, reactions such as vitrification can occur within a portion of the biogenic reagent that comprises the additive, thereby improving the final strength.

**[0548]** Chemical additives can be applied to wet or dry biomass feedstocks. The additives can be applied as a solid powder, a spray, a mist, a liquid, or a vapor. In some embodiments, additives can be introduced through spraying of a liquid solution (such as an aqueous solution or in a solvent), or by soaking in tanks, bins, bags, or other compriseers.

**[0549]** In certain embodiments, dip pretreatment is employed wherein the solid feedstock is dipped into a bath comprising the additive, either batchwise or continuously, for a time sufficient to allow penetration of the additive into the solid feed material.

**[0550]** In some embodiments, additives applied to the feedstock can reduce energy requirements for the pyrolysis, or increase the yield of the carbonaceous product. In these or other embodiments, additives applied to the feedstock can provide functionality that is desired for the intended use of the carbonaceous product.

**[0551]** The throughput, or process capacity, can vary widely from small laboratory-scale units to full operations, including any pilot, demonstration, or semi-commercial scale. In various embodiments, the process capacity (for feedstocks, products, or both) is at least about 1 kg/day, 10 kg/day, 100 kg/day, 1 ton/day (all tons are metric tons), 10 tons/day, 100 tons/day, 500 tons/day, 1000 tons/day, 2000 tons/day, or higher.

**[0552]** In some embodiments, a portion of solids produced can be recycled to the front end of the process, i.e. to the drying or deaeration unit or directly to the reactor. By returning to the front end and passing through the process again, treated solids can become higher in fixed carbon. Solid, liquid, and gas streams produced or existing within the process can be independently recycled, passed to subsequent steps, or removed/purged from the process at any point.

**[0553]** In some embodiments, pyrolyzed material is recovered and then fed to a separate unit for further pyrolysis, to create a product with higher carbon purity (e.g., conversion of low-fixed-carbon material to high-fixed-carbon material). In some embodiments, the secondary process can be conducted in a simple compriseer, such as a steel drum, in which heated inert gas (such as heated $N_2$) is passed through. Other compriseers useful for this purpose comprise process tanks, barrels, bins, totes, sacks, and roll-offs. This secondary sweep gas with volatiles can be sent to the thermal oxidizer, or back to the main process reactor, for example. To cool the final product, another stream of inert gas, which is initially at ambient temperature for example, can be passed through the solids to cool the solids, and then returned to an inert gas preheat system.

**[0554]** Some variations utilize a biogenic reagent production system comprising:

(a) a feeder configured to introduce a carbon-containing feedstock;

(b) an optional dryer, disposed in operable communication with the feeder, configured to remove moisture comprised within a carbon-containing feedstock;

(c) a multiple-zone reactor, disposed in operable communication with the dryer, wherein the multiple-zone reactor comprises at least a pyrolysis zone disposed in operable communication with a spatially separated cooling zone, and wherein the multiple-zone reactor is configured with an outlet to remove condensable vapors and non-condensable gases from solids;

(d) a solids cooler, disposed in operable communication with the multiple-zone reactor; and

(e) a biogenic reagent recovery unit, disposed in operable communication with the solids cooler.

**[0555]** Some variations utilize a biogenic reagent production system comprising:

(a) a feeder configured to introduce a carbon-containing feedstock;

(b) an optional dryer, disposed in operable communication with the feeder, configured to remove moisture comprised within a carbon-containing feedstock;

(c) an optional preheater, disposed in operable communication with the dryer, configured to heat or mildly pyrolyze the feedstock;

(d) a pyrolysis reactor, disposed in operable communication with the preheater, configured to pyrolyze the feedstock;

(e) a cooler, disposed in operable communication with the pyrolysis reactor, configured to cool pyrolyzed solids; and

(f) a biogenic reagent recovery unit, disposed in operable communication with the cooler,

wherein the system is configured with at least one gas outlet to remove condensable vapors and non-condensable gases from solids.

**[0556]** The feeder can be physically integrated with the multiple-zone reactor, such as through the use of a screw feeder or auger mechanism to introduce feed solids into the first reaction zone.

**[0557]** In some embodiments, the system further comprises a preheating zone, disposed in operable communication with the pyrolysis zone. Each of the pyrolysis zone, cooling zone, and preheating zone (it present) can be located within a single unit, or can be located in separate units.

**[0558]** Optionally, the dryer can be configured as a drying zone within the multiple-zone reactor. Optionally, the solids cooler can be disposed within the multiple-zone reactor (i.e., configured as an additional cooling zone or integrated with the main cooling zone).

**[0559]** The system can comprise a purging means for removing oxygen from the system. For example, the purging means can comprise one or more inlets to introduce a substantially inert gas, and one or more outlets to remove the substantially inert gas and displaced oxygen from the system. In some embodiments, the purging means is a deaerater disposed in operable communication between the dryer and the multiple-zone reactor.

**[0560]** The multiple-zone reactor is preferably configured with at least a first gas inlet and a first gas outlet. The first gas inlet and the first gas outlet can be disposed in communication with different zones, or with the same zone.

**[0561]** In some embodiments, the multiple-zone reactor is configured with a second gas inlet or a second gas outlet. In some embodiments, the multiple-zone reactor is configured with a third gas inlet or a third gas outlet. In some embodiments, the multiple-zone reactor is configured with a fourth gas inlet or a fourth gas outlet. In some embodiments, each zone present in the multiple-zone reactor is configured with a gas inlet and a gas outlet.

**[0562]** Gas inlets and outlets allow not only introduction and withdrawal of vapor, but gas outlets (probes) in particular allow precise process monitoring and control across various stages of the process, up to and potentially including all stages of the process. Precise process monitoring would be expected to result in yield and efficiency improvements, both dynamically as well as over a period of time when operational history can be utilized to adjust process conditions.

**[0563]** In preferred embodiments, a reaction gas probe is disposed in operable communication with the pyrolysis zone. Such a reaction gas probe can be useful to

extract gases and analyze them, in order to determine extent of reaction, pyrolysis selectivity, or other process monitoring. Then, based on the measurement, the process can be controlled or adjusted in any number of ways, such as by adjusting feed rate, rate of inert gas sweep, temperature (of one or more zones), pressure (of one or more zones), additives, and so on.

**[0564]** As intended herein, "monitor and control" via reaction gas probes should be construed to comprise any one or more sample extractions via reaction gas probes, and optionally making process or equipment adjustments based on the measurements, if deemed necessary or desirable, using well-known principles of process control (feedback, feedforward, proportional-integral-derivative logic, etc.).

**[0565]** A reaction gas probe can be configured to withdraw gas samples in a number of ways. For example, a sampling line can have a lower pressure than the pyrolysis reactor pressure, so that when the sampling line is opened an amount of gas can readily be withdrawn from pyrolysis zone. The sampling line can be under vacuum, such as when the pyrolysis zone is near atmospheric pressure. Typically, a reaction gas probe will be associated with one gas output, or a portion thereof (e.g., a line split from a gas output line).

**[0566]** In some embodiments, both a gas input and a gas output are utilized as a reaction gas probe by periodically introducing an inert gas into a zone, and pulling the inert gas with a process sample out of the gas output ("sample sweep"). Such an arrangement could be used in a zone that does not otherwise have a gas inlet/outlet for the substantially inert gas for processing, or, the reaction gas probe could be associated with a separate gas inlet/outlet that is in addition to process inlets and outlets. A sampling inert gas that is introduced and withdrawn periodically for sampling (in embodiments that utilize sample sweeps) could even be different than the process inert gas, if desired, either for reasons of accuracy in analysis or to introduce an analytical tracer.

**[0567]** For example, acetic acid concentration in the gas phase of the pyrolysis zone can be measured using a gas probe to extract a sample, which is then analyzed using a suitable technique (such as gas chromatography, GC; mass spectroscopy, MS; GC-MS, or Fourier-Transform Infrared Spectroscopy, FTIR). CO or $CO_2$ concentration in the gas phase could be measured and used as an indication of the pyrolysis

selectivity toward gases/vapors, for example. Turpene concentration in the gas phase could be measured and used as an indication of the pyrolysis selectivity toward liquids, for example.

**[0568]** In some embodiments, the system further comprises at least one additional gas probe disposed in operable communication with the cooling zone, or with the drying zone (if present) or the preheating zone (if present).

**[0569]** A gas probe for the cooling zone could be useful to determine the extent of any additional chemistry taking place in the cooling zone, for example. A gas probe in the cooling zone could also be useful as an independent measurement of temperature (in addition, for example, to a thermocouple disposed in the cooling zone). This independent measurement can be a correlation of cooling temperature with a measured amount of a certain species. The correlation could be separately developed, or could be established after some period of process operation.

**[0570]** A gas probe for the drying zone could be useful to determine the extent of drying, by measuring water content, for example. A gas probe in the preheating zone could be useful to determine the extent of any mild pyrolysis taking place, for example.

**[0571]** In certain embodiments, the cooling zone is configured with a gas inlet, and the pyrolysis zone is configured with a gas outlet, to generate substantially countercurrent flow of the gas phase relative to the solid phase. Alternatively, or additionally, the preheating zone (when it is present) can be configured with a gas outlet, to generate substantially countercurrent flow of the gas phase relative to the solid phase. Alternatively, or additionally, the drying zone can be configured with a gas outlet, to generate substantially countercurrent flow.

**[0572]** The pyrolysis reactor or reactors can be selected from any suitable reactor configuration that is capable of carrying out the pyrolysis process. Exemplary reactor configurations comprise, but are not limited to, fixed-bed reactors, fluidized-bed reactors, entrained-flow reactors, augers, ablative reactors, rotating cones, rotary drum kilns, calciners, roasters, moving-bed reactors, transport-bed reactors, ablative reactors, rotating cones, or microwave-assisted pyrolysis reactors.

**[0573]** In some embodiments in which an auger is used, sand or another heat carrier can optionally be employed. For example, the feedstock and sand can be fed at

one end of a screw. The screw mixes the sand and feedstock and conveys them through the reactor. The screw can provide good control of the feedstock residence time and does not dilute the pyrolyzed products with a carrier or fluidizing gas. The sand can be reheated in a separate vessel.

**[0574]** In some embodiments in which an ablative process is used, the feedstock is moved at a high speed against a hot metal surface. Ablation of any char forming at surfaces can maintain a high rate of heat transfer. Such apparatus can prevent dilution of products. As an alternative, the feedstock particles can be suspended in a carrier gas and introduced at a high speed through a cyclone whose wall is heated.

**[0575]** In some embodiments in which a fluidized-bed reactor is used, the feedstock can be introduced into a bed of hot sand fluidized by a gas, which is typically a recirculated product gas. Reference herein to "sand" shall also comprise similar, substantially inert materials, such as glass particles, recovered ash particles, and the like. High heat-transfer rates from fluidized sand can result in rapid heating of the feedstock. There can be some ablation by attrition with the sand particles. Heat is usually provided by heat-exchanger tubes through which hot combustion gas flows.

**[0576]** Circulating fluidized-bed reactors can be employed, wherein gas, sand, and feedstock move together. Exemplary transport gases comprise recirculated product gases and combustion gases. High heat-transfer rates from the sand ensure rapid heating of the feedstock, and ablation is expected to be stronger than with regular fluidized beds. A separator can be employed to separate the product gases from the sand and char particles. The sand particles can be reheated in a fluidized burner vessel and recycled to the reactor.

**[0577]** In some embodiments, a multiple-zone reactor is a continuous reactor comprising a feedstock inlet, a plurality of spatially separated reaction zones configured for separately controlling the temperature and mixing within each of the reaction zones, and a carbonaceous-solids outlet, wherein one of the reaction zones is configured with a first gas inlet for introducing a substantially inert gas into the reactor, and wherein one of the reaction zones is configured with a first gas outlet.

**[0578]** In various embodiments the reactor comprises at least two, three, four, or more reaction zones. Each of the reaction zones is disposed in communication with separately adjustable heating means independently selected from electrical heat

transfer, steam heat transfer, hot-oil heat transfer, phase-change heat transfer, waste heat transfer, or a combination thereof. In some embodiments, at least one reactor zone is heated with an effluent stream from the thermal oxidizer, if present.

**[0579]** The reactor can be configured for separately adjusting gas-phase composition and gas-phase residence time of at least two reaction zones, up to and including all reaction zones present in the reactor.

**[0580]** The reactor can be equipped with a second gas inlet or a second gas outlet. In some embodiments, the reactor is configured with a gas inlet in each reaction zone. In these or other embodiments, the reactor is configured with a gas outlet in each reaction zone. The reactor can be a cocurrent or countercurrent reactor.

**[0581]** In some embodiments, the feedstock inlet comprises a screw or auger feed mechanism. In some embodiments, the carbonaceous-solids outlet comprises a screw or auger output mechanism.

**[0582]** Certain embodiments utilize a rotating calciner with a screw feeder. In these embodiments, the reactor is axially rotatable, i.e. it spins about its centerline axis. The speed of rotation will impact the solid flow pattern, and heat and mass transport. Each of the reaction zones can be configured with flights disposed on internal walls, to provide agitation of solids. The flights can be separately adjustable in each of the reaction zones.

**[0583]** Other means of agitating solids can be employed, such as augers, screws, or paddle conveyors. In some embodiments, the reactor comprises a single, continuous auger disposed throughout each of the reaction zones. In other embodiments, the reactor comprises twin screws disposed throughout each of the reaction zones.

**[0584]** Some systems are designed specifically with the capability to maintain the approximate size of feed material throughout the process—that is, to process the biomass feedstock without destroying or significantly damaging its structure. In some embodiments, the pyrolysis zone does not comprise augers, screws, or rakes that would tend to greatly reduce the size of feed material being pyrolyzed.

**[0585]** In some embodiments, the system further comprises a thermal oxidizer disposed in operable communication with the outlet at which condensable vapors and non-condensable gases are removed. The thermal oxidizer is preferably configured to

receive a separate fuel (such as natural gas) and an oxidant (such as air) into a combustion chamber, adapted for combustion of the fuel and at least a portion of the condensable vapors. Certain non-condensable gases can also be oxidized, such as CO or $CH_4$, to $CO_2$.

**[0586]** When a thermal oxidizer is employed, the system can comprise a heat exchanger disposed between the thermal oxidizer and the dryer, configured to utilize at least some of the heat of the combustion for the dryer. This embodiment can contribute significantly to the overall energy efficiency of the process.

**[0587]** In some embodiments, the system further comprises a carbon-enhancement unit, disposed in operable communication with the solids cooler, configured for combining condensable vapors, in at least partially condensed form, with the solids. The carbon-enhancement unit can increase the carbon content of the biogenic reagent obtained from the recovery unit.

**[0588]** The system can further comprise a separate pyrolysis unit adapted to further pyrolyze the biogenic reagent to further increase its carbon content. The separate pyrolysis unit can be a relatively simply compriseer, unit, or device, such as a tank, barrel, bin, drum, tote, sack, or roll-off.

**[0589]** The overall system can be at a fixed location, or it can be distributed at several locations. The system can be constructed using modules which can be simply duplicated for practical scale-up. The system can also be constructed using economy-of-scale principles, as is well-known in the process industries.

**[0590]** Some variations relating to carbon enhancement of solids will now be further described. In some embodiments, a process for producing a biogenic reagent comprises:

(a) providing a carbon-containing feedstock comprising biomass;

(b) optionally drying the feedstock to remove at least a portion of moisture comprised within the feedstock;

(c) optionally deaerating the feedstock to remove at least a portion of interstitial oxygen, if any, comprised with the feedstock;

(d) in a pyrolysis zone, pyrolyzing the feedstock in the presence of a substantially inert gas for at least 10 minutes and with a pyrolysis temperature selected from about

250°C to about 700°C, to generate hot pyrolyzed solids, condensable vapors, and non-condensable gases;

(e) separating at least a portion of the condensable vapors and at least a portion of the non-condensable gases from the hot pyrolyzed solids;

(f) in a cooling zone, cooling the hot pyrolyzed solids, in the presence of the substantially inert gas for at least 5 minutes and with a cooling temperature less than the pyrolysis temperature, to generate warm pyrolyzed solids;

(g) optionally cooling the warm pyrolyzed solids to generate cool pyrolyzed solids;

(h) subsequently passing at least a portion of the condensable vapors or at least a portion of the non-condensable gases from step (e) across the warm pyrolyzed solids or the cool pyrolyzed solids, to form enhanced pyrolyzed solids with increased carbon content; and

(i) recovering a biogenic reagent comprising at least a portion of the enhanced pyrolyzed solids.

**[0591]** In some embodiments, step (h) comprises passing at least a portion of the condensable vapors from step (e), in vapor or condensed form, across the warm pyrolyzed solids, to produce enhanced pyrolyzed solids with increased carbon content. In some embodiments, step (h) comprises passing at least a portion of the non-condensable gases from step (e) across the warm pyrolyzed solids, to produce enhanced pyrolyzed solids with increased carbon content.

**[0592]** Alternatively, or additionally, vapors or gases can be contacted with the cool pyrolyzed solids. In some embodiments, step (h) comprises passing at least a portion of the condensable vapors from step (e), in vapor or condensed form, across the cool pyrolyzed solids, to produce enhanced pyrolyzed solids with increased carbon content. In some embodiments, step (h) comprises passing at least a portion of the non-condensable gases from step (e) across the cool pyrolyzed solids, to produce enhanced pyrolyzed solids with increased carbon content.

**[0593]** In certain embodiments, step (h) comprises passing substantially all of the condensable vapors from step (e), in vapor or condensed form, across the cool pyrolyzed solids, to produce enhanced pyrolyzed solids with increased carbon content.

In certain embodiments, step (h) comprises passing substantially all of the non-condensable gases from step (e) across the cool pyrolyzed solids, to produce enhanced pyrolyzed solids with increased carbon content.

**[0594]** The process can comprise various methods of treating or separating the vapors or gases prior to using them for carbon enhancement. For example, an intermediate feed stream consisting of at least a portion of the condensable vapors and at least a portion of the non-condensable gases, obtained from step (e), can be fed to a separation unit configured to generate at least first and second output streams. In certain embodiments, the intermediate feed stream comprises all of the condensable vapors, all of the non-condensable gases, or both.

**[0595]** Separation techniques can comprise or use distillation columns, flash vessels, centrifuges, cyclones, membranes, filters, packed beds, capillary columns, and so on. Separation can be principally based, for example, on distillation, absorption, adsorption, or diffusion, and can utilize differences in vapor pressure, activity, molecular weight, density, viscosity, polarity, chemical functionality, affinity to a stationary phase, and any combinations thereof.

**[0596]** In some embodiments, the first and second output streams are separated from the intermediate feed stream based on relative volatility. For example, the separation unit can be a distillation column, a flash tank, or a condenser.

**[0597]** Thus in some embodiments, the first output stream comprises the condensable vapors, and the second output stream comprises the non-condensable gases. The condensable vapors can comprise at least one carbon-containing compound selected from terpenes, alcohols, acids, aldehydes, or ketones. The vapors from pyrolysis can comprise aromatic compounds such as benzene, toluene, ethylbenzene, and xylenes. Heavier aromatic compounds, such as refractory tars, can be present in the vapor. The non-condensable gases can comprise at least one carbon-containing molecule selected from carbon monoxide, carbon dioxide, and methane.

**[0598]** In some embodiments, the first and second output streams are separated intermediate feed stream based on relative polarity. For example, the separation unit can be a stripping column, a packed bed, a chromatography column, or membranes.

**[0599]** Thus in some embodiments, the first output stream comprises polar compounds, and the second output stream comprises non-polar compounds. The polar compounds can comprise at least one carbon-containing molecule selected from methanol, furfural, and acetic acid. The non-polar compounds can comprise at least one carbon-containing molecule selected from carbon monoxide, carbon dioxide, methane, a turpene, and a turpene derivative.

**[0600]** Step (h) can increase the total carbon content of the biogenic reagent, relative to an otherwise-identical process without step (h). The extent of increase in carbon content can be, for example, about 1%, 2%, 5%, 10%, 15%, 25%, or even higher, in various embodiments.

**[0601]** In some embodiments, step (h) increases the fixed carbon content of the biogenic reagent. In these or other embodiments, step (h) increases the volatile carbon content of the biogenic reagent. Volatile carbon content is the carbon attributed to volatile matter in the reagent. The volatile matter can be, but is not limited to, hydrocarbons including aliphatic or aromatic compounds (e.g., terpenes); oxygenates including alcohols, aldehydes, or ketones; and various tars. Volatile carbon will typically remain bound or adsorbed to the solids at ambient conditions but upon heating, will be released before the fixed carbon would be oxidized, gasified, or otherwise released as a vapor.

**[0602]** Depending on conditions associated with step (h), it is possible for some amount of volatile carbon to become fixed carbon (e.g., via Boudouard carbon formation from CO). Typically, the volatile matter will enter the micropores of the fixed carbon and will be present as condensed/adsorbed species, but remain relatively volatile. This residual volatility can be more advantageous for fuel applications, compared to product applications requiring high surface area and porosity.

**[0603]** Step (h) can increase the energy content (i.e., energy density) of the biogenic reagent. The increase in energy content can result from an increase in total carbon, fixed carbon, volatile carbon, or even hydrogen. The extent of increase in energy content can be, for example, about 1%, 2%, 5%, 10%, 15%, 25%, or even higher, in various embodiments.

**[0604]** Further separations can be employed to recover one or more non-condensable gases or condensable vapors, for use within the process or further

processing. For example, further processing can be comprised to produce refined carbon monoxide or hydrogen.

**[0605]** As another example, separation of acetic acid can be conducted, followed by reduction of the acetic acid into ethanol. The reduction of the acetic acid can be accomplished, at least in part, using hydrogen derived from the non-condensable gases produced.

**[0606]** Condensable vapors can be used for either energy in the process (such as by thermal oxidation) or in carbon enrichment, to increase the carbon content of the biogenic reagent. Certain non-condensable gases, such as CO or $CH_4$, can be utilized either for energy in the process, or as part of the substantially inert gas for the pyrolysis step. Combinations of any of the foregoing are also possible.

**[0607]** A potential benefit of including step (h) is that the gas stream is scrubbed, with the resulting gas stream being enriched in CO and $CO_2$. The resulting gas stream can be utilized for energy recovery, recycled for carbon enrichment of solids, or used as an inert gas in the reactor. Similarly, by separating non-condensable gases from condensable vapors, the $CO/CO_2$ stream is prepared for use as the inert gas in the reactor system or in the cooling system, for example.

**[0608]** Other variations are premised on the realization that the principles of the carbon-enhancement step can be applied to any feedstock in which it is desired to add carbon.

**[0609]** In some embodiments, a batch or continuous process for producing a biogenic reagent comprises:

(a) providing a solid stream comprising a carbon-containing material;

(b) providing a gas stream comprising condensable carbon-containing vapors, non-condensable carbon-containing gases, or a mixture of condensable carbon-containing vapors and non-condensable carbon-containing gases; and

(c) passing the gas stream across the solid stream under suitable conditions to form a carbon-containing product with increased carbon content relative to the carbon-containing material.

**[0610]** In some embodiments, the starting carbon-containing material is pyrolyzed biomass or torrefied biomass. The gas stream can be obtained during an integrated

process that provides the carbon-containing material. Or, the gas stream can be obtained from separate processing of the carbon-containing material. The gas stream, or a portion thereof, can be obtained from an external source (e.g., an oven at a lumber mill). Mixtures of gas streams, as well as mixtures of carbon-containing materials, from a variety of sources, are possible.

**[0611]** In some embodiments, the process further comprises recycling or reusing the gas stream for repeating the process to further increase carbon or energy content of the carbon-containing product. In some embodiments, the process further comprises recycling or reusing the gas stream for carrying out the process to increase carbon or energy content of another feedstock different from the carbon-containing material.

**[0612]** In some embodiments, the process further comprises introducing the gas stream to a separation unit configured to generate at least first and second output streams, wherein the gas stream comprises a mixture of condensable carbon-containing vapors and non-condensable carbon-containing gases. The first and second output streams can be separated based on relative volatility, relative polarity, or any other property. The gas stream can be obtained from separate processing of the carbon-containing material.

**[0613]** In some embodiments, the process further comprises recycling or reusing the gas stream for repeating the process to further increase carbon content of the carbon-containing product. In some embodiments, the process further comprises recycling or reusing the gas stream for carrying out the process to increase carbon content of another feedstock.

**[0614]** The carbon-containing product can have an increased total carbon content, a higher fixed carbon content, a higher volatile carbon content, a higher energy content, or any combination thereof, relative to the starting carbon-containing material.

**[0615]** In related variations, a biogenic reagent production system comprises:

(a) a feeder configured to introduce a carbon-containing feedstock;

(b) an optional dryer, disposed in operable communication with the feeder, configured to remove moisture comprised within a carbon-containing feedstock;

(c) a multiple-zone reactor, disposed in operable communication with the dryer, wherein the multiple-zone reactor comprises at least a pyrolysis zone disposed in

operable communication with a spatially separated cooling zone, and wherein the multiple-zone reactor is configured with an outlet to remove condensable vapors and non-condensable gases from solids;

(d) a solids cooler, disposed in operable communication with the multiple-zone reactor;

(e) a material-enrichment unit, disposed in operable communication with the solids cooler, configured to pass the condensable vapors or the non-condensable gases across the solids, to form enhanced solids with increased carbon content; and

(f) a biogenic reagent recovery unit, disposed in operable communication with the material-enrichment unit.

**[0616]** The system can further comprise a preheating zone, disposed in operable communication with the pyrolysis zone. In some embodiments, the dryer is configured as a drying zone within the multiple-zone reactor. Each of the zones can be located within a single unit or in separate units. Also, the solids cooler can be disposed within the multiple-zone reactor.

**[0617]** In some embodiments, the cooling zone is configured with a gas inlet, and the pyrolysis zone is configured with a gas outlet, to generate substantially countercurrent flow of the gas phase relative to the solid phase. In these or other embodiments, the preheating zone or the drying zone (or dryer) is configured with a gas outlet, to generate substantially countercurrent flow of the gas phase relative to the solid phase.

**[0618]** In particular embodiments, the system incorporates a material-enrichment unit that comprises:

(i) a housing with an upper portion and a lower portion;

(ii) an inlet at a bottom of the lower portion of the housing configured to carry the condensable vapors and non-condensable gases;

(iii) an outlet at a top of the upper portion of the housing configured to carry a concentrated gas stream derived from the condensable vapors and non-condensable gases;

(iv) a path defined between the upper portion and the lower portion of the housing; and

(v) a transport system following the path, the transport system configured to transport the solids, wherein the housing is shaped such that the solids adsorb at least some of the condensable vapors or at least some of the non-condensable gases.

**[0619]** The disclosed technology is capable of producing a variety of compositions useful as biogenic reagents, and products incorporating such reagents. In some variations, a biogenic reagent is produced by any process disclosed herein, such as a process comprising the steps of:

(a) providing a carbon-containing feedstock comprising biomass;

(b) optionally drying the feedstock to remove at least a portion of moisture comprised within the feedstock;

(c) optionally deaerating the feedstock to remove at least a portion of interstitial oxygen, if any, comprised with the feedstock;

(d) in a pyrolysis zone, pyrolyzing the feedstock in the presence of a substantially inert gas for at least 10 minutes and with a pyrolysis temperature selected from about 250°C to about 700°C, to generate hot pyrolyzed solids, condensable vapors, and non-condensable gases;

(e) separating at least a portion of the condensable vapors and at least a portion of the non-condensable gases from the hot pyrolyzed solids;

(f) in a cooling zone, cooling the hot pyrolyzed solids, in the presence of the substantially inert gas for at least 5 minutes and with a cooling temperature less than the pyrolysis temperature, to generate warm pyrolyzed solids;

(g) cooling the warm pyrolyzed solids to generate cool pyrolyzed solids; and

(h) recovering a biogenic reagent comprising at least a portion of the cool pyrolyzed solids.

**[0620]** In some embodiments, the reagent comprises about at least 70 wt%, at least 80 wt%, at least 90 wt%, or at least 95 wt% total carbon on a dry basis. The total carbon comprises at least fixed carbon, and can further comprise carbon from volatile matter. In some embodiments, carbon from volatile matter is about at least 5%, at least

10%, at least 25%, or at least 50% of the total carbon present in the biogenic reagent. Fixed carbon can be measured using ASTM D3172, while volatile carbon can be measured using ASTM D3175, for example.

**[0621]** The biogenic reagent can comprise about 10 wt% or less, such as about 5 wt% or less, hydrogen on a dry basis. The biogenic reagent can comprise about 1 wt% or less, such as about 0.5 wt% or less, nitrogen on a dry basis. The biogenic reagent can comprise about 0.5 wt% or less, such as about 0.2 wt% or less, phosphorus on a dry basis. The biogenic reagent can comprise about 0.2 wt% or less, such as about 0.1 wt% or less, sulfur on a dry basis.

**[0622]** Carbon, hydrogen, and nitrogen can be measured using ASTM D5373 for ultimate analysis, for example. Oxygen can be measured using ASTM D3176, for example. Sulfur can be measured using ASTM D3177, for example.

**[0623]** Certain embodiments provide reagents with little or essentially no hydrogen (except from any moisture that can be present), nitrogen, phosphorus, or sulfur, and are substantially carbon plus any ash and moisture present. Therefore, some embodiments provide a biogenic reagent with up to and including 100% carbon, on a dry/ash-free (DAF) basis.

**[0624]** Generally speaking, feedstocks such as biomass comprise non-volatile species, including silica and various metals, which are not readily released during pyrolysis. It is of course possible to utilize ash-free feedstocks, in which case there should not be substantial quantities of ash in the pyrolyzed solids. Ash can be measured using ASTM D3174, for example.

**[0625]** Various amounts of non-combustible matter, such as ash, can be present. The biogenic reagent can comprise about 10 wt% or less, such as about 5 wt%, about 2 wt%, about 1 wt% or less non-combustible matter on a dry basis. In certain embodiments, the reagent comprises little ash, or even essentially no ash or other non-combustible matter. Therefore, some embodiments provide essentially pure carbon, including 100% carbon, on a dry basis.

**[0626]** Various amounts of moisture can be present. On a total mass basis, the biogenic reagent can comprise at least 1 wt%, 2 wt%, 5 wt%, 10 wt%, 15 wt%, 25 wt%, 35 wt%, 50 wt%, or more moisture. As intended herein, "moisture" is to be construed

as including any form of water present in the biogenic reagent, including absorbed moisture, adsorbed water molecules, chemical hydrates, and physical hydrates. The equilibrium moisture content can vary at least with the local environment, such as the relative humidity. Also, moisture can vary during transportation, preparation for use, and other logistics. Moisture can be measured using ASTM D3173, for example.

**[0627]** The biogenic reagent can have various energy contents which for present purposes means the energy density based on the higher heating value associated with total combustion of the bone-dry reagent. For example, the biogenic reagent can possess an energy content of about at least 11,000 Btu/lb, at least 12,000 Btu/lb, at least 13,000 Btu/lb, at least 14,000 Btu/lb, or at least 15,000 Btu/lb. In certain embodiments, the energy content is between about 14,000-15,000 Btu/lb. The energy content can be measured using ASTM D5865, for example.

**[0628]** The biogenic reagent can be formed into a powder, such as a coarse powder or a fine powder. For example, the reagent can be formed into a powder with an average mesh size of about 200 mesh, about 100 mesh, about 50 mesh, about 10 mesh, about 6 mesh, about 4 mesh, or about 2 mesh, in embodiments.

**[0629]** In some embodiments, the biogenic reagent is formed into structural objects comprising pressed, binded, or agglomerated particles. The starting material to form these objects can be a powder form of the reagent, such as an intermediate obtained by particle-size reduction. The objects can be formed by mechanical pressing or other forces, optionally with a binder or other means of agglomerating particles together.

**[0630]** In some embodiments, the biogenic reagent is produced in the form of structural objects whose structure substantially derives from the feedstock. For example, feedstock chips can produce product chips of biogenic reagent. Or, feedstock cylinders can produce biogenic reagent cylinders, which can be somewhat smaller but otherwise maintain the basic structure and geometry of the starting material.

**[0631]** A biogenic reagent can be produced as, or formed into, an object that has a minimum dimension of at least about 1 cm, 2 cm, 3 cm, 4 cm, 5 cm, 6 cm, 7 cm, 8 cm, 9 cm, 10 cm, or higher. In various embodiments, the minimum dimension or maximum dimension can be a length, width, or diameter.

**[0632]** Other variations relate to the incorporation of additives into the process, into the product, or both. In some embodiments, the biogenic reagent comprises at least one process additive incorporated during the process. In these or other embodiments, the reagent comprises at least one product additive introduced to the reagent following the process.

**[0633]** In some embodiments, a biogenic reagent comprises, on a dry basis:

70 wt% or more total carbon;

5 wt% or less hydrogen;

1 wt% or less nitrogen;

0.5 wt% or less phosphorus;

0.2 wt% or less sulfur; and

an additive selected from a metal, a metal oxide, a metal hydroxide, a metal halide, or a combination thereof.

**[0634]** The additive can be selected from, but is by no means limited to, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, magnesium oxide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, or a combination thereof.

**[0635]** In some embodiments, a biogenic reagent comprises, on a dry basis:

70 wt% or more total carbon;

5 wt% or less hydrogen;

1 wt% or less nitrogen;

0.5 wt% or less phosphorus;

0.2 wt% or less sulfur; and

an additive selected from an acid, a base, or a salt thereof.

**[0636]** The additive can be selected from, but is by no means limited to, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, or combinations thereof.

**[0637]** In certain embodiments, a biogenic reagent comprises, on a dry basis:

70 wt% or more total carbon;

5 wt% or less hydrogen;

1 wt% or less nitrogen;

0.5 wt% or less phosphorus;

0.2 wt% or less sulfur;

a first additive selected from a metal, metal oxide, metal hydroxide, a metal halide, or a combination thereof; and

a second additive selected from an acid, a base, or a salt thereof,

wherein the first additive is different from the second additive.

**[0638]** The first additive can be selected from magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, magnesium oxide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, or a combination thereof, while the second additive can be independently selected from sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, or combinations thereof.

**[0639]** A certain biogenic reagent consists essentially of, on a dry basis, carbon, hydrogen, nitrogen, phosphorus, sulfur, non-combustible matter, and an additive selected from magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, magnesium oxide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, or a combination thereof.

**[0640]** A certain biogenic reagent consists essentially of, on a dry basis, carbon, hydrogen, nitrogen, phosphorus, sulfur, non-combustible matter, and an additive selected from sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, or a combination thereof.

**[0641]** The amount of additive (or total additives) can vary widely, such as from about 0.01 wt% to about 25 wt%, including about 0.1 wt%, about 1 wt%, about 5 wt%, about 10 wt%, or about 20 wt%. It will be appreciated then when relatively large

amounts of additives are incorporated, such as of at least about about 1 wt%, there will be a reduction in energy content calculated on the basis of the total reagent weight (inclusive of additives). Still, in various embodiments, the biogenic reagent with additive(s) can possess an energy content of about at least 11,000 Btu/lb, at least 12,000 Btu/lb, at least 13,000 Btu/lb, at least 14,000 Btu/lb, or at least 15,000 Btu/lb.

**[0642]** The above discussion regarding product form applies also to embodiments that incorporate additives. In fact, certain embodiments incorporate additives as binding agents, fluxing agents, or other modifiers to enhance final properties for a particular application.

**[0643]** In preferred embodiments, the majority of carbon comprised in the biogenic reagent is classified as renewable carbon. In some embodiments, substantially all of the carbon is classified as renewable carbon. There can be certain market mechanisms (e.g., Renewable Identification Numbers, tax credits, etc.) wherein value is attributed to the renewable carbon content within the biogenic reagent.

**[0644]** In certain embodiments, the fixed carbon can be classified as non-renewable carbon (e.g., from coal) while the volatile carbon, which can be added separately, can be renewable carbon to increase not only energy content but also renewable carbon value.

**[0645]** The biogenic reagents produced as described herein is useful for a wide variety of carbonaceous products. The biogenic reagent can be a desirable market product itself. Biogenic reagents as provided herein are associated with lower levels of impurities, reduced process emissions, and improved sustainability (including higher renewable carbon content) compared to the state of the art.

**[0646]** In variations, a product comprises any of the biogenic reagents that can be obtained by the disclosed processes, or that are described in the compositions set forth herein, or any portion, combination, or derivative thereof.

**[0647]** Generally speaking, the biogenic reagents can be combusted to produce energy (including electricity and heat); partially oxidized, gasified, or steam-reformed to produce syngas; utilized for their adsorptive or absorptive properties; utilized for their reactive properties during metal refining (such as reduction of metal oxides) or other industrial processing; or utilized for their material properties in carbon steel and various

other metal alloys. Essentially, the biogenic reagents can be utilized for any market application of carbon-based commodities or advanced materials, including specialty uses to be developed.

**[0648]** Prior to suitability or actual use in any product applications, the disclosed biogenic reagents can be analyzed, measured, and optionally modified (such as through additives) in various ways. Some properties of potential interest, other than chemical composition and energy content, comprise density, particle size, surface area, microporosity, absorptivity, adsorptivity, binding capacity, reactivity, desulfurization activity, and basicity, to name a few properties.

**[0649]** Products or materials that can incorporate these biogenic reagents comprise, but are by no means limited to, carbon-based blast furnace addition products, carbon-based taconite pellet addition products, ladle addition carbon-based products, met coke carbon-based products, coal replacement products, carbon-based coking products, carbon breeze products, foundry carbon, sintering carbon, fluidized-bed carbon-based feedstocks, carbon-based furnace addition products, injectable carbon-based products, pulverized carbon-based products, stoker carbon-based products, carbon electrodes, or activated carbon products.

**[0650]** Use of the disclosed biogenic reagents in metals production can reduce slag, increase overall efficiency, and reduce lifecycle environmental impacts. Therefore, some embodiments are particularly well-suited for metal processing and manufacturing.

**[0651]** Some variations utilize the biogenic reagents as carbon-based blast furnace addition products. A blast furnace is a type of metallurgical furnace used for smelting to produce industrial metals, such as (but not limited to) iron. Smelting is a form of extractive metallurgy; its main use is to produce a metal from its ore. Smelting uses heat and a chemical reducing agent to decompose the ore. The carbon or the carbon monoxide derived from the carbon removes oxygen from the ore, leaving behind elemental metal.

**[0652]** The reducing agent can consist of, or comprise, a biogenic reagent. In a blast furnace, biogenic reagent, ore, and typically limestone can be continuously supplied through the top of the furnace, while air (optionally with oxygen enrichment) is blown into the bottom of the chamber, so that the chemical reactions take place

throughout the furnace as the material moves downward. The end products are usually molten metal and slag phases tapped from the bottom, and flue gases exiting from the top of the furnace. The downward flow of the ore in contact with an upflow of hot, carbon monoxide-rich gases is a countercurrent process.

**[0653]** Carbon quality in the blast furnace is measured by its resistance to degradation. The role of the carbon as a permeable medium is crucial in economic blast furnace operation. The degradation of the carbon varies with the position in the blast furnace and involves the combination of reaction with $CO_2$, $H_2O$, or $O_2$ and the abrasion of carbon particles against each other and other components of the burden. Degraded carbon particles can cause plugging and poor performance.

**[0654]** The Coke Reactivity test is a highly regarded measure of the performance of carbon in a blast furnace. This test has two components: the Coke Reactivity Index (CRI) and the Coke Strength after Reaction (CSR). A carbon-based material with a low CRI value (high reactivity) and a high CSR value is preferable for better blast furnace performance. CRI can be determined according to any suitable method known in the art, for example by ASTM Method DS341 on an as-received basis.

**[0655]** In some embodiments, the biogenic reagent provides a carbon product having suitable properties for introduction directly into a blast furnace.

**[0656]** The strength of the biogenic reagent can be determined by any suitable method known in the art, for example by a drop-shatter test, or a CSR test. In some embodiments, the biogenic reagent, optionally when blended with another source of carbon, provides a final carbon product having CSR of at least about 50%, 60%, or 70%. A combination product can also provide a final coke product having a suitable reactivity for combustion in a blast furnace. In some embodiments, the product has a CRI such that the biogenic reagent is suitable for use as an additive or replacement for met coal, met coke, coke breeze, foundry coke, sintering carbon, or injectable coal.

**[0657]** Some embodiments employ one or more additives in an amount sufficient to provide a biogenic reagent that, when added to another carbon source (e.g., coke) having a CRI or CSR insufficient for use as a blast furnace product, provides a composite product with a CRI or CSR sufficient for use in a blast furnace. In some embodiments, one or more additives are present in an amount sufficient to provide a biogenic reagent having a CRI of not more than about 40%, 30%, or 20%.

**[0658]** In some embodiments, one or more additives selected from the alkaline earth metals, or oxides or carbonates thereof, are introduced during or after the process of producing a biogenic reagent. For example, calcium, calcium oxide, calcium carbonate, magnesium oxide, or magnesium carbonate can be introduced as additives. The addition of these compounds before, during, or after pyrolysis can increase the reactivity of the biogenic reagent in a blast furnace. These compounds can lead to stronger materials, i.e. higher CSR, thereby improving blast-furnace efficiency. In addition, additives such as those selected from the alkaline earth metals, or oxides or carbonates thereof, can lead to lower emissions (e.g., $SO_2$).

**[0659]** In some embodiments, a blast furnace replacement product is a biogenic reagent comprising at least about 55 wt% carbon, not more than about 0.5 wt% sulfur, not more than about 8 wt% non-combustible material, and a heat value of at least about 11,000 Btu per pound. In some embodiments, the blast furnace replacement product further comprises not more than about 0.035 wt% phosphorous, about 0.5 wt% to about 50 wt% volatile matter, and optionally one or more additives. In some embodiments, the blast furnace replacement product comprises about 2 wt% to about 15 wt% dolomite, about 2 wt% to about 15 wt% dolomitic lime, about 2 wt% to about 15 wt% bentonite, or about 2 wt% to about 15 wt% calcium oxide. In some embodiments, the blast furnace replacement product has dimensions substantially in the range of about 1 cm to about 10 cm.

**[0660]** In some embodiments, a biogenic reagent is useful as a foundry coke replacement product. Foundry coke is generally characterized as having a carbon content of at least about 85 wt%, a sulfur content of about 0.6 wt%, not more than about 1.5 wt% volatile matter, not more than about 13 wt% ash, not more than about 8 wt% moisture, about 0.035 wt% phosphorus, a CRI value of about 30, and dimensions ranging from about 5 cm to about 25 cm.

**[0661]** Some variations utilize the biogenic reagents as carbon-based taconite pellet addition products. The ores used in making iron and steel are iron oxides. Major iron oxide ores comprise hematite, limonite (also called brown ore), taconite, and magnetite, a black ore. Taconite is a low-grade but important ore, which comprises both magnetite and hematite. The iron content of taconite is generally 25 wt% to 30 wt%. Blast furnaces typically require at least a 50 wt% iron content ore for efficient

operation. Iron ores can undergo beneficiation including crushing, screening, tumbling, flotation, and magnetic separation. The refined ore is enriched to over 60% iron and is often formed into pellets before shipping.

**[0662]** For example, taconite can be ground into a fine powder and combined with a binder such as bentonite clay and limestone. Pellets about one centimeter in diameter can be formed, compriseing approximately 65 wt% iron, for example. The pellets are fired, oxidizing magnetite to hematite. The pellets are durable which ensures that the blast furnace charge remains porous enough to allow heated gas to pass through and react with the pelletized ore.

**[0663]** The taconite pellets can be fed to a blast furnace to produce iron, as described above with reference to blast furnace addition products. In some embodiments, a biogenic reagent is introduced to the blast furnace. In these or other embodiments, a biogenic reagent is incorporated into the taconite pellet itself. For example, taconite ore powder, after beneficiation, can be mixed with a biogenic reagent and a binder and rolled into small objects, then baked to hardness. In such embodiments, taconite-carbon pellets with the appropriate composition can conveniently be introduced into a blast furnace without the need for a separate source of carbon.

**[0664]** Some variations utilize the biogenic reagents as ladle addition carbon-based products. A ladle is a vessel used to transport and pour out molten metals. Casting ladles are used to pour molten metal into molds to produce the casting. Transfers ladle are used to transfer a large amount of molten metal from one process to another. Treatment ladles are used for a process to take place within the ladle to change some aspect of the molten metal, such as the conversion of cast iron to ductile iron by the addition of various elements into the ladle.

**[0665]** Biogenic reagents can be introduced to any type of ladle, but typically carbon will be added to treatment ladles in suitable amounts based on the target carbon content. Carbon injected into ladles can be in the form of fine powder, for good mass transport of the carbon into the final composition. In some embodiments, a biogenic reagent, when used as a ladle addition product, has a minimum dimension of about 0.5 cm, such as about 0.75 cm, about 1 cm, about 1.5 cm, or higher.

**[0666]** In some embodiments, a high-carbon biogenic reagent is useful as a ladle addition carbon additive at, for example, basic oxygen furnace or electric arc furnace facilities wherever ladle addition of carbon would be used (e.g., added to ladle carbon during steel manufacturing).

**[0667]** In some embodiments, the ladle addition carbon additive additionally comprises up to about 5 wt% manganese, up to about 5 wt% calcium oxide, or up to about 5 wt% dolomitic lime.

**[0668]** Direct-reduced iron (DRI), also called sponge iron, is produced from direct reduction of iron ore (in the form of lumps, pellets, or fines) by a reducing gas conventionally produced from natural gas or coal. The reducing gas is typically syngas, a mixture of hydrogen and carbon monoxide which acts as reducing agent. The biogenic reagent as provided herein can be converted into a gas stream comprising CO, to act as a reducing agent to produce direct-reduced iron.

**[0669]** Iron nuggets are a high-quality steelmaking and iron-casting feed material. Iron nuggets are essentially all iron and carbon, with almost no gangue (slag) and low levels of metal residuals. They are a premium grade pig iron product with superior shipping and handling characteristics. The carbon comprised in iron nuggets, or any portion thereof, can be the biogenic reagent provided herein. Iron nuggets can be produced through the reduction of iron ore in a rotary hearth furnace, using a biogenic reagent as the reductant and energy source.

**[0670]** Some variations utilize the biogenic reagents as metallurgical coke carbon-based products. Metallurgical coke, also known as "met" coke, is a carbon material normally manufactured by the destructive distillation of various blends of bituminous coal. The final solid is a non-melting carbon called metallurgical coke. As a result of the loss of volatile gases and of partial melting, met coke has an open, porous morphology. Met coke has a very low volatile content. However, the ash constituents, that were part of the original bituminous coal feedstock, remain encapsulated in the resultant coke. Met coke feedstocks are available in a wide range of sizes from fine powder to basketball-sized lumps. Typical purities range from 86-92 wt% fixed carbon.

**[0671]** Metallurgical coke is used where a high-quality, tough, resilient, wearing carbon is required. Applications comprise, but are not limited to, conductive flooring, friction materials (e.g., carbon linings), foundry coatings, foundry carbon raiser,

corrosion materials, drilling applications, reducing agents, heat-treatment agents, ceramic packing media, electrolytic processes, and oxygen exclusion.

**[0672]** Met coke can be characterized as having a heat value of about 10,000 to 14,000 Btu per pound and an ash content of about 10 wt% or greater. Thus, in some embodiments, a met coke replacement product comprises a biogenic reagent comprising at least about 80 wt%, 85 wt%, or 90 wt% carbon, not more than about 0.8 wt% sulfur, not more than about 3 wt% volatile matter, not more than about 15 wt% ash, not more than about 13 wt% moisture, and not more than about 0.035 wt% phosphorus. A biogenic reagent, when used as a met coke replacement product, can have a size range from about 2 cm to about 15 cm, for example.

**[0673]** In some embodiments, the met coke replacement product further comprises an additive such as chromium, nickel, manganese, magnesium oxide, silicon, aluminum, dolomite, fluorospar, calcium oxide, lime, dolomitic lime, bentonite or a combination thereof.

**[0674]** Some variations utilize the biogenic reagents as coal replacement products. Any process or system using coal can in principle be adapted to use a biogenic reagent.

**[0675]** In some embodiments, a biogenic reagent is combined with one or more coal-based products to form a composite product having a higher rank than the coal-based product(s) or having fewer emissions, when burned, than the pure coal-based product.

**[0676]** For example, a low-rank coal such as sub-bituminous coal can be used in applications normally calling for a higher-rank coal product, such as bituminous coal, by combining a selected amount of a biogenic reagent with the low-rank coal product. In other embodiments, the rank of a mixed coal product (e.g., a combination of a plurality of coals of different rank) can be improved by combining the mixed coal with some amount of biogenic reagent. The amount of a biogenic reagent to be mixed with the coal product(s) can vary depending on the rank of the coal product(s), the characteristics of the biogenic reagent (e.g., carbon content, heat value, etc.) and the desired rank of the final combined product.

**[0677]** For example, anthracite coal is generally characterized as having at least about 80 wt% carbon, about 0.6 wt% sulfur, about 5 wt% volatile matter, up to about 15 wt% ash, up to about 10 wt% moisture, and a heat value of about 12,494 Btu/lb. In some embodiments, an anthracite coal replacement product is a biogenic reagent comprising at least about 80 wt% carbon, not more than about 0.6 wt% sulfur, not more than about 15 wt% ash, and a heat value of at least about 12,000 Btu/lb.

**[0678]** In some embodiments, a biogenic reagent is useful as a thermal coal replacement product. Thermal coal products are generally characterized as having high sulfur levels, high phosphorus levels, high ash content, and heat values of up to about 15,000 Btu/lb. In some embodiments, a thermal coal replacement product is a biogenic reagent comprising not more than about 0.5 wt% sulfur, not more than about 4 wt% ash, and a heat value of at least about 12,000 Btu/lb.

**[0679]** Some variations utilize the biogenic reagents as carbon-based coking products. Any coking process or system can be adapted to use biogenic reagents to produce coke, or use it as a coke feedstock.

**[0680]** In some embodiments, a biogenic reagent is useful as a thermal coal or coke replacement product. For example, a thermal coal or coke replacement product can consist of a biogenic reagent comprising at least about 50 wt% carbon, not more than about 8 wt% ash, not more than about 0.5 wt% sulfur, and a heat value of at least about 11,000 Btu/lb. In other embodiments, the thermal coke replacement product further comprises about 0.5 wt% to about 50 wt % volatile matter. The thermal coal or coke replacement product can comprise about 0.4 wt% to about 15 wt% moisture.

**[0681]** In some embodiments, a biogenic reagent is useful as a petroleum (pet) coke or calcine pet coke replacement product. Calcine pet coke is generally characterized as having at least about 66 wt% carbon, up to 4.6 wt% sulfur, up to about 5.5 wt% volatile matter, up to about 19.5 wt% ash, and up to about 2 wt% moisture, and is typically sized at about 3 mesh or less. In some embodiments, the calcine pet coke replacement product is a biogenic reagent comprising at least about 66 wt% carbon, not more than about 4.6 wt% sulfur, not more than about 19.5 wt% ash, not more than about 2 wt% moisture, and is sized at about 3 mesh or less.

**[0682]** In some embodiments, a biogenic reagent is useful as a coking carbon replacement carbon (e.g., co-fired with metallurgical coal in a coking furnace). In one

embodiment, a coking carbon replacement product is a biogenic reagent comprising at least about 55 wt% carbon, not more than about 0.5 wt% sulfur, not more than about 8 wt% non-combustible material, and a heat value of at least about 11,000 Btu per pound. In some embodiments, the coking carbon replacement product comprises about 0.5 wt% to about 50 wt% volatile matter, or one or more additives.

**[0683]** Some variations utilize the biogenic reagents as carbon breeze products, which typically have very fine particle sizes such as 6 mm, 3 mm, 2 mm, 1 mm, or smaller. In some embodiments, a biogenic reagent is useful as a coke breeze replacement product. Coke breeze is generally characterized as having a maximum dimension of not more than about 6 mm, a carbon content of at least about 80 wt%, 0.6 to 0.8 wt% sulfur, 1% to 20 wt% volatile matter, up to about 13 wt% ash, and up to about 13 wt% moisture. In some embodiments, a coke breeze replacement product is a biogenic reagent comprising at least about 80 wt% carbon, not more than about 0.8 wt% sulfur, not more than about 20 wt% volatile matter, not more than about 13 wt% ash, not more than about 13 wt% moisture, and a maximum dimension of about 6 mm.

**[0684]** In some embodiments, a biogenic reagent is useful as a carbon breeze replacement product during, for example, taconite pellet production or in an iron-making process.

**[0685]** Some variations utilize the biogenic reagents as feedstocks for various fluidized beds, or as fluidized-bed carbon-based feedstock replacement products. The carbon can be employed in fluidized beds for total combustion, partial oxidation, gasification, steam reforming, or the like. The carbon can be primarily converted into syngas for various downstream uses, including production of energy (e.g., combined heat and power), or liquid fuels (e.g., methanol or Fischer-Tropsch diesel fuels).

**[0686]** In some embodiments, a biogenic reagent is useful as a fluidized-bed coal replacement product in, for example, fluidized bed furnaces wherever coal would be used (e.g., for process heat or energy production).

**[0687]** Some variations utilize the biogenic reagents as carbon-based furnace addition products. Coal-based carbon furnace addition products are generally characterized as having high sulfur levels, high phosphorus levels, and high ash content, which contribute to degradation of the metal product and create air pollution. In some embodiments, a carbon furnace addition replacement product comprising a

biogenic reagent comprises not more than about 0.5 wt% sulfur, not more than about 4 wt% ash, not more than about 0.03 wt% phosphorous, and a maximum dimension of about 7.5 cm. In some embodiments, the carbon furnace addition replacement product replacement product comprises about 0.5 wt% to about 50 wt% volatile matter and about 0.4 wt% to about 15 wt% moisture.

**[0688]** In some embodiments, a biogenic reagent is useful as a furnace addition carbon additive at, for example, basic oxygen furnace or electric arc furnace facilities wherever furnace addition carbon would be used. For example, furnace addition carbon can be added to scrap steel during steel manufacturing at electric-arc furnace facilities). For electric-arc furnace applications, high-purity carbon is desired so that impurities are not introduced back into the process following earlier removal of impurities.

**[0689]** In some embodiments, a furnace addition carbon additive is a biogenic reagent comprising at least about 80 wt% carbon, not more than about 0.5 wt% sulfur, not more than about 8 wt% non-combustible material, and a heat value of at least about 11,000 Btu per pound. In some embodiments, the furnace addition carbon additive further comprises up to about 5 wt% manganese, up to about 5 wt% fluorospar, about 5 wt% to about 10 wt% dolomite, about 5 wt% to about 10 wt% dolomitic lime, or about 5 wt% to about 10 wt% calcium oxide.

**[0690]** Some variations utilize the biogenic reagents as stoker furnace carbon-based products. In some embodiments, a biogenic reagent is useful as a stoker coal replacement product at, for example, stoker furnace facilities wherever coal would be used (e.g., for process heat or energy production).

**[0691]** Some variations utilize the biogenic reagents as injectable (e.g., pulverized) carbon-based materials. In some embodiments, a biogenic reagent is useful as an injection-grade calcine pet coke replacement product. Injection-grade calcine pet coke is generally characterized as having at least about 66 wt% carbon, about 0.55 to about 3 wt% sulfur, up to about 5.5 wt% volatile matter, up to about 10 wt% ash, up to about 2 wt% moisture, and is sized at about 6 mesh or less. In some embodiments, a calcine pet coke replacement product is a biogenic reagent comprising at least about 66 wt% carbon, not more than about 3 wt% sulfur, not more than about 10 wt% ash, not more than about 2 wt% moisture, and is sized at about 6 mesh or less.

**[0692]** In some embodiments, a biogenic reagent is useful as an injectable carbon replacement product at, for example, basic oxygen furnace or electric arc furnace facilities in any application where injectable carbon would be used (e.g., injected into slag or ladle during steel manufacturing).

**[0693]** In some embodiments, a biogenic reagent is useful as a pulverized carbon replacement product, for example, wherever pulverized coal would be used (e.g., for process heat or energy production). In some embodiments, the pulverized coal replacement product comprises up to about 10 percent calcium oxide.

**[0694]** Some variations utilize the biogenic reagents as carbon addition product for metals production. In some embodiments, a biogenic reagent is useful as a carbon addition product for production of carbon steel or another metal alloy comprising carbon. Coal-based late-stage carbon addition products are generally characterized as having high sulfur levels, high phosphorous levels, and high ash content, and high mercury levels which degrade metal quality and contribute to air pollution. In some embodiments, the carbon addition product comprises not more than about 0.5 wt% sulfur, not more than about 4 wt% ash, not more than about 0.03 wt% phosphorus, a minimum dimension of about 1 to 5 mm, and a maximum dimension of about 8 to 12 mm.

**[0695]** Some variations utilize the biogenic reagents within carbon electrodes. In some embodiments, a biogenic reagent is useful as an electrode (e.g. anode) material suitable for use, for example, in aluminum production.

**[0696]** Other uses of the biogenic reagent in carbon electrodes comprise applications in batteries, fuel cells, capacitors, and other energy-storage or energy-delivery devices. For example, in a lithium-ion battery, the biogenic reagent can be used on the anode side to intercalate lithium. In these applications, carbon purity and low ash can be very important.

**[0697]** Some variations utilize the biogenic reagents as catalyst supports. Carbon is a known catalyst support in a wide range of catalyzed chemical reactions, such as mixed-alcohol synthesis from syngas using sulfided cobalt-molybdenum metal catalysts supported on a carbon phase, or iron-based catalysts supported on carbon for Fischer-Tropsch synthesis of higher hydrocarbons from syngas.

**[0698]** Some variations utilize the biogenic reagents as activated carbon products. Activated carbon is used in a wide variety of liquid and gas-phase applications, including water treatment, air purification, solvent vapor recovery, food and beverage processing, and pharmaceuticals. For activated carbon, the porosity and surface area of the material are generally important. The biogenic reagent provided herein can provide a superior activated carbon product, in various embodiments, due to (i) greater surface area than fossil-fuel based activated carbon; (ii) carbon renewability; (iii) vascular nature of biomass feedstock in conjunction with additives better allows penetration/distribution of additives that enhance pollutant control; and (iv) less inert material (ash) leads to greater reactivity.

**[0699]** It should be recognized that in the above description of market applications of biogenic reagents, the described applications are not exclusive, nor are they exhaustive. Thus a biogenic reagent that is described as being suitable for one type of carbon product can be suitable for any other application described, in various embodiments. These applications are exemplary only, and there are other applications of biogenic reagents.

**[0700]** In addition, in some embodiments, the same physical material can be used in multiple market processes, either in an integrated way or in sequence. Thus, for example, a biogenic reagent that is used as a carbon electrode or an activated carbon may, at the end of its useful life as a performance material, then be introduced to a combustion process for energy value or to a metal-making (e.g., metal ore reduction) process, etc.

**[0701]** Some embodiments can employ a biogenic reagent both for its reactive/adsorptive properties and also as a fuel. For example, a biogenic reagent injected into an emissions stream can be suitable to remove contaminants, followed by combustion of the biogenic reagent particles and possibly the contaminants, to produce energy and thermally destroy or chemically oxidize the contaminants.

**[0702]** Significant environmental and product use advantages can be associated with biogenic reagents, compared to conventional fossil-fuel-based products. The biogenic reagents can be not only environmentally superior, but also functionally superior from a processing standpoint because of greater purity, for example.

**[0703]** With regard to some embodiments of metals production, production of biogenic reagents with disclosed processes can result in significantly lower emissions of CO, $CO_2$, $NO_x$, $SO_2$, and hazardous air pollutants compared to the coking of coal-based products necessary to prepare them for use in metals production.

**[0704]** Use of biogenic reagents in place of coal or coke also significantly reduces environmental emissions of $SO_2$, hazardous air pollutants, and mercury.

**[0705]** Also, because of the purity of these biogenic reagents (including low ash content), the disclosed biogenic reagents have the potential to reduce slag and increase production capacity in batch metal-making processes.

**[0706]** In some embodiments, a biogenic reagent functions as an activated carbon. For example, the low-fixed-carbon material can be activated, the high-fixed-carbon material can be activated, or both materials can be activated such that the biocarbon composition (blend) functions as an activated carbon.

**[0707]** In certain embodiments, a portion of the biogenic reagent is recovered as an activated carbon product, while another portion (e.g., the remainder) of the biogenic reagent is pelletized with a binder to produce biocarbon pellets. In other embodiments, the biogenic reagent is pelletized with a binder to produce biocarbon pellets that are shipped for later conversion to an activated carbon product. The later conversion can comprise pulverizing back to a powder, and can also comprise chemical treatment with e.g. steam, acids, or bases. In these embodiments, the biocarbon pellets can be regarded as activated-carbon precursor pellets.

**[0708]** In certain embodiments, the fixed carbon within the biogenic reagent can be primarily used to make activated carbon while the volatile carbon within the biogenic reagent can be primarily used to make reducing gas. For example, at least 50 wt%, at least 90 wt%, or essentially all of the fixed carbon within the biogenic reagent generated in step (b) can be recovered as activated carbon in step (f), while, for example, at least 50 wt%, at least 90 wt%, or essentially all of the volatile carbon within the biogenic reagent generated in step (b) can be directed to the reducing gas (e.g., via steam-reforming reactions of volatile carbon to CO).

**[0709]** The activated carbon, when produced, can be characterized by an Iodine Number of at least about 500, 750, 800, 1000, 1500, or 2000, for example. The

activated carbon is preferably characterized by a renewable carbon content of at least 50%, 60%, 70%, 80%, 90%, or 95% as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the activated carbon. In some embodiments, the activated carbon is characterized as (fully) renewable activated carbon as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the activated carbon.

**[0710]** In some embodiments, the pyrolysis reactor is configured for optimizing the production of different types of activated carbon. For example, reaction conditions (e.g., time, temperature, and steam concentration) can be selected for an activated carbon product with certain attributes such as Iodine Number. Different reaction conditions can be selected for a different activated carbon product, such as one with a higher Iodine Number. The pyrolysis reactor can be operated in a campaign mode to produce one product and then switched to another mode for another product. The first product can have been continuously or periodically removed during the first campaign, or can be removed prior to switching the reaction conditions of the pyrolysis reactor.

**[0711]** The activated carbon can be characterized by an Iodine Number of at least about 500, 750, 1000, 1500, or 2000, for example. The activated carbon is preferably characterized by a renewable carbon content of at least 90% as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the activated carbon. In some embodiments, the activated carbon is characterized as (fully) renewable activated carbon as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the activated carbon.

**[0712]** Activated carbon produced by the processes disclosed herein can be used in a number of ways.

**[0713]** In some embodiments, the activated carbon is utilized internally at the process site to purify the one or more primary products. In some embodiments, the activated carbon is utilized at the site to purify water. In these or other embodiments, the activated carbon is utilized at the site to treat a liquid waste stream to reduce liquid-phase emissions or to treat a vapor waste stream to reduce air emissions. In some embodiments, the activated carbon is utilized as a soil amendment to assist generation of new biomass, which can be the same type of biomass utilized as local feedstock at the site.

**[0714]** Activated carbon prepared according to the processes disclosed herein can have the same or better characteristics as traditional fossil fuel-based activated carbon. In some embodiments, the activated carbon has a surface area that is comparable to, equal to, or greater than surface area associated with fossil fuel-based activated carbon. In some embodiments, the activated carbon can control pollutants as well as or better than traditional activated carbon products. In some embodiments, the activated carbon has an inert material (e.g., ash) level that is comparable to, equal to, or less than an inert material (e.g., ash) level associated with a traditional activated carbon product. In some embodiments, the activated carbon has a particle size or a particle size distribution that is comparable to, equal to, greater than, or less than a particle size or a particle size distribution associated with a traditional activated carbon product. In some embodiments, the activated carbon has a particle shape that is comparable to, substantially similar to, or the same as a particle shape associated with a traditional activated carbon product. In some embodiments, the activated carbon has a particle shape that is substantially different than a particle shape associated with a traditional activated carbon product. In some embodiments, the activated carbon has a pore volume that is comparable to, equal to, or greater than a pore volume associated with a traditional activated carbon product. In some embodiments, the activated carbon has pore dimensions that are comparable to, substantially similar to, or the same as pore dimensions associated with a traditional activated carbon product. In some embodiments, the activated carbon has an attrition resistance of particles value that is comparable to, substantially similar to, or the same as an attrition resistance of particles value associated with a traditional activated carbon product. In some embodiments, the activated carbon has a hardness value that is comparable to, substantially similar to, or the same as a hardness value associated with a traditional activated carbon product. In some embodiments, the activated carbon has a bulk density value that is comparable to, substantially similar to, or the same as a bulk density value associated with a traditional activated carbon product. In some embodiments, the activated carbon product has an adsorptive capacity that is comparable to, substantially similar to, or the same as an adsorptive capacity associated with a traditional activated carbon product.

**[0715]** Prior to suitability or actual use in any product applications, the disclosed activated carbons can be analyzed, measured, and optionally modified (such as through additives) in various ways. Some properties of potential interest comprise density,

particle size, surface area, microporosity, absorptivity, adsorptivity, binding capacity, reactivity, desulfurization activity, basicity, hardness, and Iodine Number.

**[0716]** Activated carbon is used commercially in a wide variety of liquid and gas-phase applications, including water treatment, air purification, solvent vapor recovery, food and beverage processing, sugar and sweetener refining, automotive uses, and pharmaceuticals. For activated carbon, key product attributes can comprise particle size, shape, composition, surface area, pore volume, pore dimensions, particle-size distribution, the chemical nature of the carbon surface and interior, attrition resistance of particles, hardness, bulk density, and adsorptive capacity.

**[0717]** The bulk density for the biogenic activated carbon can be from about 50 g/liter to about 650 g/liter, for example.

**[0718]** The surface area of the biogenic activated carbon can vary widely. Exemplary surface areas (e.g., BET surface areas) range from about 400 $m^2/g$ to about 2000 $m^2/g$ or higher, such as about 500 $m^2/g$, 600 $m^2/g$, 800 $m^2/g$, 1000 $m^2/g$, 1200 $m^2/g$, 1400 $m^2/g$, 1600 $m^2/g$, or 1800 $m^2/g$. Surface area generally correlates to adsorption capacity.

**[0719]** The pore-size distribution can be important to determine ultimate performance of the activated carbon. Pore-size measurements can comprise micropore content, mesopore content, and macropore content.

**[0720]** The Iodine Number is a parameter used to characterize activated carbon performance. The Iodine Number measures the degree of activation of the carbon, and is a measure of micropore (e.g., 0–20 Å) content. It is an important measurement for liquid-phase applications. Exemplary Iodine Numbers for activated carbon products produced by embodiments of the disclosure comprise about 500, 600, 750, 900, 1000, 1100, 1200, 1300, 1500, 1600, 1750, 1900, 2000, 2100, and 2200, including all intervening ranges. The units of Iodine Number are milligram iodine per gram carbon.

**[0721]** Another pore-related measurement is Methylene Blue Number, which measures mesopore content (e.g., 20–500 Å). Exemplary Methylene Blue Numbers for activated carbon products produced by embodiments of the disclosure comprise about 100, 150, 200, 250, 300, 350, 400, 450, and 500, including all intervening ranges. The

units of Methylene Blue Number are milligram methylene blue (methylthioninium chloride) per gram carbon.

**[0722]** Another pore-related measurement is Molasses Number, which measures macropore content (e.g., >500 Å). Exemplary Molasses Numbers for activated carbon products produced by embodiments of the disclosure comprise about 100, 150, 200, 250, 300, 350, and 400, including all intervening ranges. The units of Molasses Number are milligram molasses per gram carbon.

**[0723]** In some embodiments, the activated carbon is characterized by a mesopore volume of at least about 0.5 $cm^3/g$, such as at least about 1 $cm^3/g$, for example.

**[0724]** The activated carbon can be characterized by its water-holding capacity. In various embodiments, activated carbon products produced by embodiments of the disclosure have a water-holding capacity at 25°C of about 10% to about 300% (water weight divided by weight of dry activated carbon), such as from about 50% to about 100%, e.g. about 60-80%.

**[0725]** Hardness or Abrasion Number is measure of activated carbon's resistance to attrition. It is an indicator of activated carbon's physical integrity to withstand frictional forces and mechanical stresses during handling or use. Some amount of hardness is desirable, but if the hardness is too high, excessive equipment wear can result. Exemplary Abrasion Numbers, measured according to ASTM D3802, range from about 1% to great than about 99%, such as about 1%, about 5%, about 10%, about 15%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, about 50%, about 55%, 60%, about 65%, about 70%, about 75%, about 80%, about 85%, about 90%, about 95%, about 96%, about 97%, about 98%, about 99%, or greater than about 99%.

**[0726]** In some embodiments, an optimal range of hardness can be achieved in which the activated carbon is reasonably resistant to attrition but does not cause abrasion and wear in capital facilities that process the activated carbon. This optimum is made possible in some embodiments of this disclosure due to the selection of feedstock as well as processing conditions. In some embodiments in which the downstream use can handle high hardness, the process of this disclosure can be operated to increase or maximize hardness to produce biogenic activated carbon

products having an Abrasion Number of about 75%, about 80%, about 85%, about 90%, about 95%, about 96%, about 97%, about 98%, about 99%, or greater than about 99%.

**[0727]** The biogenic activated carbon provided by the present disclosure has a wide range of commercial uses. For example, without limitation, the biogenic activated carbon can be utilized in emissions control, water purification, groundwater treatment, wastewater treatment, air stripper applications, PCB removal applications, odor removal applications, soil vapor extractions, manufactured gas plants, industrial water filtration, industrial fumigation, tank and process vents, pumps, blowers, filters, pre-filters, mist filters, ductwork, piping modules, adsorbers, absorbers, and columns.

**[0728]** In one embodiment, a method of using activated carbon to reduce emissions comprises:

(a) providing activated carbon particles comprising a biogenic activated carbon composition recovered from the second reactor disclosed herein;

(b) providing a gas-phase emissions stream comprising at least one selected contaminant;

(c) providing an additive selected to assist in removal of the selected contaminant from the gas-phase emissions stream;

(d) introducing the activated carbon particles and the additive into the gas-phase emissions stream, to adsorb at least a portion of the selected contaminant onto the activated carbon particles, thereby generating contaminant-adsorbed carbon particles within the gas-phase emissions stream; and

(e) separating at least a portion of the contaminant-adsorbed carbon particles from the gas-phase emissions stream, to produce a contaminant-reduced gas-phase emissions stream.

**[0729]** An additive for the biogenic activated carbon composition can be provided as part of the activated carbon particles. Alternatively, or additionally, an additive can be introduced directly into the gas-phase emissions stream, into a fuel bed, or into a combustion zone. Other ways of directly or indirectly introducing the additive into the gas-phase emissions stream for removal of the selected contaminant are possible, as will be appreciated by one of skill in the art.

**[0730]** A selected contaminant (in the gas-phase emissions stream) can be a metal, such as a metal is selected from mercury, boron, selenium, arsenic, and any compound, salt, and mixture thereof. A selected contaminant can be a hazardous air pollutant, an organic compound (such as a VOC), or a non-condensable gas, for example. In some embodiments, a biogenic activated carbon product adsorbs, absorbs or chemisorbs a selected contaminant in greater amounts than a comparable amount of a non-biogenic activated carbon product. In some such embodiments, the selected contaminant is a metal, a hazardous air pollutant, an organic compound (such as a VOC), a non-condensable gas, or any combination thereof. In some embodiments, the selected contaminant comprises mercury. In some embodiments, the selected contaminant comprises one or more VOCs. In some embodiments, the biogenic activated carbon comprises at least about 1 wt% hydrogen or at least about 10 wt% oxygen.

**[0731]** Hazardous air pollutants are those pollutants that cause or can cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental and ecological effects. Section 112 of the Clean Air Act, as amended, is incorporated by reference herein in its entirety. Pursuant to the Section 112 of the Clean Air Act, the United States Environmental Protection Agency (EPA) is mandated to control 189 hazardous air pollutants. Any current or future compounds classified as hazardous air pollutants by the EPA are comprised in possible selected contaminants in the present context.

**[0732]** Volatile organic compounds, some of which are also hazardous air pollutants, are organic chemicals that have a high vapor pressure at ordinary, room-temperature conditions. Examples comprise short-chain alkanes, olefins, alcohols, ketones, and aldehydes. Many volatile organic compounds are dangerous to human health or cause harm to the environment. EPA regulates volatile organic compounds in air, water, and land. EPA's definition of volatile organic compounds is described in 40 CFR Section 51.100, which is incorporated by reference herein in its entirety.

**[0733]** Non-condensable gases are gases that do not condense under ordinary, room-temperature conditions. Non-condensable gas can comprise, but are not limited to, nitrogen oxides, carbon monoxide, carbon dioxide, hydrogen sulfide, sulfur dioxide, sulfur trioxide, methane, ethane, ethylene, ozone, ammonia, or combinations thereof.

**[0734]** Multiple contaminants can be removed by the disclosed activated carbon particles. In some embodiments, the contaminant-adsorbed carbon particles comprise at least two contaminants, at least three contaminants, or more. The activated carbon as disclosed herein can allow multi-pollutant control as well as control of certain targeted pollutants (e.g. selenium).

**[0735]** In some embodiments, contaminant-adsorbed carbon particles are treated to regenerate activated carbon particles. In some embodiments, the method comprises thermally oxidizing the contaminant-adsorbed carbon particles. The contaminant-adsorbed carbon particles, or a regenerated form thereof, can be combusted to provide energy.

**[0736]** In some embodiments, an additive for activated carbon is selected from an acid, a base, a salt, a metal, a metal oxide, a metal hydroxide, a metal halide, or a combination thereof. In certain embodiments, the additive is selected from magnesium, manganese, aluminum, nickel, iron, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, magnesium oxide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, sodium hydroxide, potassium hydroxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, organic acids (e.g., citric acid), or a combination thereof.

**[0737]** In some embodiments, the gas-phase emissions stream is derived from metals processing, such as the processing of high-sulfur-content metal ores.

**[0738]** As an exemplary embodiment relating to mercury control, activated carbon can be injected (such as into the ductwork) upstream of a particulate matter control device, such as an electrostatic precipitator or fabric filter. In some cases, a flue gas desulfurization (dry or wet) system can be downstream of the activated carbon injection point. The activated carbon can be pneumatically injected as a powder. The injection location will typically be determined by the existing plant configuration (unless it is a new site) and whether additional downstream particulate matter control equipment is modified.

**[0739]** For boilers currently equipped with particulate matter control devices, implementing biogenic activated carbon injection for mercury control could entail: (i) injection of powdered activated carbon upstream of the existing particulate matter control device (electrostatic precipitator or fabric filter); (ii) injection of powdered

activated carbon downstream of an existing electrostatic precipitator and upstream of a retrofit fabric filter; or (iii) injection of powdered activated carbon between electrostatic precipitator electric fields. Inclusion of iron or iron-containing compounds can drastically improve the performance of electrostatic precipitators for mercury control. Furthermore, inclusion of iron or iron-containing compounds can drastically change end-of-life options, since the spent activated carbon solids can be separated from other ash.

**[0740]** In some embodiments, powdered activated carbon injection approaches can be employed in combination with existing $SO_2$ control devices. Activated carbon could be injected prior to the $SO_2$ control device or after the $SO_2$ control device, subject to the availability of a means to collect the activated carbon sorbent downstream of the injection point.

**[0741]** In some embodiments, the same physical material can be used in multiple processes, either in an integrated way or in sequence. Thus, for example, activated carbon may, at the end of its useful life as a performance material, then be introduced to a combustion process for energy value or to a metal-making process that requires carbon but does not require the properties of activated carbon, etc.

**[0742]** The biogenic activated carbon and the principles of the disclosure can be applied to liquid-phase applications, including processing of water, aqueous streams of varying purities, solvents, liquid fuels, polymers, molten salts, and molten metals, for example. As intended herein, "liquid phase" comprises slurries, suspensions, emulsions, multiphase systems, or any other material that has (or can be adjusted to have) at least some amount of a liquid state present.

**[0743]** In one embodiment, the present disclosure provides a method of using activated carbon to purify a liquid, in some variations, comprises the following steps:

(a) providing activated carbon particles recovered from the second reactor;

(b) providing a liquid comprising at least one selected contaminant;

(c) providing an additive selected to assist in removal of the selected contaminant from the liquid; and

(d) contacting the liquid with the activated carbon particles and the additive, to adsorb at least a portion of the at least one selected contaminant onto the activated

carbon particles, thereby generating contaminant-adsorbed carbon particles and a contaminant-reduced liquid.

**[0744]** The additive can be provided as part of the activated carbon particles. Or, the additive can be introduced directly into the liquid. In some embodiments, additives—which can be the same, or different—are introduced both as part of the activated carbon particles as well as directly into the liquid.

**[0745]** In some embodiments relating to liquid-phase applications, an additive is selected from an acid, a base, a salt, a metal, a metal oxide, a metal hydroxide, a metal halide, or a combination thereof. For example an additive can be selected from magnesium, manganese, aluminum, nickel, iron, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, magnesium oxide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, sodium hydroxide, potassium hydroxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, organic acids (e.g., citric acid), or a combination thereof.

**[0746]** In some embodiments, the selected contaminant (in the liquid to be treated) is a metal, such as a metal selected from arsenic, boron, selenium, mercury, and any compound, salt, and mixture thereof. In some embodiments, the selected contaminant is an organic compound (such as a VOC), a halogen, a biological compound, a pesticide, or a herbicide. The contaminant-adsorbed carbon particles can comprise two, three, or more contaminants. In some embodiments, an activated carbon product adsorbs, absorbs or chemisorbs a selected contaminant in greater amounts than a comparable amount of a non-biogenic activated carbon product. In some such embodiments, the selected contaminant is a metal, a hazardous air pollutant, an organic compound (such as a VOC), a non-condensable gas, or any combination thereof. In some embodiments, the selected contaminant comprises mercury. In some embodiments, the selected contaminant comprises one or more VOCs. In some embodiments, the biogenic activated carbon comprises at least about 1 wt% hydrogen or at least about 10 wt% oxygen.

**[0747]** The liquid to be treated will typically be aqueous, although that is not necessary for the principles of this disclosure. In some embodiments, a liquid is treated

with activated carbon particles in a fixed bed. In other embodiments, a liquid is treated with activated carbon particles in solution or in a moving bed.

**[0748]** In one embodiment, the present disclosure provides a method of using a biogenic activated carbon composition to remove at least a portion of a sulfur-containing contaminant from a liquid, the method comprising:

(a) providing activated-carbon particles recovered from the second reactor disclosed herein;

(b) providing a liquid compriseing a sulfur-containing contaminant;

(c) providing an additive selected to assist in removal of the sulfur-containing contaminant from the liquid; and

(d) contacting the liquid with the activated-carbon particles and the additive, to adsorb or absorb at least a portion of the sulfur-containing contaminant onto or into the activated-carbon particles.

**[0749]** In some embodiments, the sulfur-containing contaminant is selected from elemental sulfur, sulfuric acid, sulfurous acid, sulfur dioxide, sulfur trioxide, sulfate anions, bisulfate anions, sulfite anions, bisulfite anions, thiols, sulfides, disulfides, polysulfides, thioethers, thioesters, thioacetals, sulfoxides, sulfones, thiosulfinates, sulfimides, sulfoximides, sulfonediimines, sulfur halides, thioketones, thioaldehydes, sulfur oxides, thiocarboxylic acids, thioamides, sulfonic acids, sulfinic acids, sulfenic acids, sulfonium, oxosulfonium, sulfuranes, persulfuranes, or a combination, salt, or derivative thereof. For example, the sulfur-containing contaminant can be a sulfate, in anionic or salt form.

**[0750]** The liquid can be an aqueous liquid, such as water. In some embodiments, the water is wastewater associated with a process selected from metal mining, acid mine drainage, mineral processing, municipal sewer treatment, pulp and paper, ethanol, and any other industrial process that is capable of discharging sulfur-containing contaminants in wastewater. The water can also be (or be part of) a natural body of water, such as a lake, river, or stream.

**[0751]** In one embodiment, the present disclosure provides a process to reduce the concentration of sulfates in water, the process comprising:

(a) providing activated-carbon particles recovered from the second reactor disclosed herein;

(b) providing a volume or stream of water compriseing sulfates;

(c) providing an additive selected to assist in removal of the sulfates from the water; and

(d) contacting the water with the activated-carbon particles and the additive, to adsorb or absorb at least a portion of the sulfates onto or into the activated-carbon particles.

**[0752]** In some embodiments, the sulfates are reduced to a concentration of about 50 mg/L or less in the water, such as a concentration of about 10 mg/L or less in the water. In some embodiments, the sulfate is present primarily in the form of sulfate anions or bisulfate anions. Depending on pH, the sulfate can also be present in the form of sulfate salts.

**[0753]** The water can be derived from, part of, or the entirety of a wastewater stream. Exemplary wastewater streams are those that can be associated with a metal mining, acid mine drainage, mineral processing, municipal sewer treatment, pulp and paper, ethanol, or any other industrial process that could discharge sulfur-containing contaminants to wastewater. The water can be a natural body of water, such as a lake, river, or stream. In some embodiments, the process is conducted continuously. In other embodiments, the process is conducted in batch.

**[0754]** When water is treated with activated carbon, there can be filtration of the water, osmosis of the water, or direct addition (with sedimentation, clarification, etc.) of the activated-carbon particles to the water. When osmosis is employed, the activated carbon can be used in several ways within, or to assist, an osmosis device. In some embodiments, the activated-carbon particles and the additive are directly introduced to the water prior to osmosis. The activated-carbon particles and the additive are optionally employed in pre-filtration prior to the osmosis. In certain embodiments, the activated-carbon particles and the additive are incorporated into a membrane for osmosis.

**[0755]** In some embodiments, an activated carbon is effective for removing a sulfur-containing contaminant selected from elemental sulfur, sulfuric acid, sulfurous

acid, sulfur dioxide, sulfur trioxide, sulfate anions, bisulfate anions, sulfite anions, bisulfite anions, thiols, sulfides, disulfides, polysulfides, thioethers, thioesters, thioacetals, sulfoxides, sulfones, thiosulfinates, sulfimides, sulfoximides, sulfonediimines, sulfur halides, thioketones, thioaldehydes, sulfur oxides, thiocarboxylic acids, thioamides, sulfonic acids, sulfinic acids, sulfenic acids, sulfonium, oxosulfonium, sulfuranes, persulfuranes, or a combination, salt, or derivative thereof.

**[0756]** Generally speaking, the disclosed activated carbon can be used in any application in which traditional activated carbon might be used. In some embodiments, the activated carbon is used as a total (i.e., 100%) replacement for traditional activated carbon. In some embodiments, the activated carbon comprises essentially all or substantially all of the activated carbon used for a particular application. In some embodiments, the activated carbon comprises about 1% to about 100% of biogenic activated carbon.

**[0757]** For example and without limitation, the activated carbon can be used—alone or in combination with a traditional activated carbon product—in filters. In some embodiments, a packed bed or packed column comprises the disclosed activated carbon. In such embodiments, the biogenic activated carbon has a size characteristic suitable for the particular packed bed or packed column. Injection of biogenic activated carbon into gas streams can be useful for control of contaminant emissions in gas streams or liquid streams derived from coal-fired power plants, biomass-fired power plants, metal processing plants, crude-oil refineries, chemical plants, polymer plants, pulp and paper plants, cement plants, waste incinerators, food processing plants, gasification plants, and syngas plants.

*Use of Biocarbon Compositions in Metal Oxide Reduction*

**[0758]** There are various embodiments in which the biocarbon pellets, or a pulverized form thereof, or other biocarbon compositions disclosed herein, are fed to a metal ore furnace or a chemical-reduction furnace.

**[0759]** A metal ore furnace or a chemical-reduction furnace can be a blast furnace, a top-gas recycling blast furnace, a shaft furnace, a reverberatory furnace (also known as an air furnace), a crucible furnace, a muffling furnace, a retort furnace, a flash furnace, a Tecnored furnace, an Ausmelt furnace, an ISASMELT furnace, a puddling furnace, a Bogie hearth furnace, a continuous chain furnace, a pusher furnace, a rotary

hearth furnace, a walking beam furnace, an electric arc furnace, an induction furnace, a basic oxygen furnace, a puddling furnace, a Bessemer furnace, a direct-reduced-metal furnace, or a combination or derivative thereof.

**[0760]** A metal ore furnace or a chemical-reduction furnace can be arranged horizontally, vertically, or inclined. The flow of solids and fluids (liquids or gases) can be cocurrent or countercurrent. The solids within a furnace can be in a fixed bed or a fluidized bed. A metal ore furnace or a chemical-reduction furnace can be operated at a variety of process conditions of temperature, pressure, and residence time.

**[0761]** Some variations relate specifically to a blast furnace. A blast furnace is a type of metallurgical furnace used for smelting to produce industrial metals, such as iron or copper. Blast furnaces are utilized in smelting iron ore to produce pig iron, an intermediate material used in the production of commercial iron and steel. Blast furnaces are also used in combination with sinter plants in base metals smelting, for example.

**[0762]** "Blast" refers to the combustion air being forced or supplied above atmospheric pressure. In a blast furnace, metal ores, carbon (in the present disclosure, biogenic reagent or a derivative thereof), and usually flux (e.g., limestone) are continuously supplied through the top of the furnace, while a hot blast of air (optionally with oxygen enrichment) is blown into the lower section of the furnace through a series of pipes called tuyeres. The chemical reduction reactions take place throughout the furnace as the material falls downward. The end products are usually molten metal and slag phases tapped from the bottom, and waste gases (reduction off-gas) exiting from the top of the furnace. The downward flow of the metal ore along with the flux in countercurrent contact with an upflow of hot, CO-rich gases allows for an efficient chemical reaction to reduce the metal ore to metal.

**[0763]** Air furnaces (such as reverberatory furnaces) are naturally aspirated, usually by the convection of hot gases in a chimney flue. According to this broad definition, bloomeries for iron, blowing houses for tin, and smelt mills for lead would be classified as blast furnaces.

**[0764]** The blast furnace remains an important part of modern iron production. Modern furnaces are highly efficient, including Cowper stoves which preheat incoming blast air with waste heat from flue gas, and recovery systems to extract the heat from

the hot gases exiting the furnace. A blast furnace is typically built in the form of a tall structure, lined with refractory brick, and profiled to allow for expansion of the feed materials as they heat during their descent, and subsequent reduction in size as melting starts to occur.

**[0765]** In some embodiments pertaining to iron production, biocarbon pellets, iron ore (iron oxide), and limestone flux are charged into the top of the blast furnace. The iron ore or limestone flux can be integrated within the biocarbon pellets. Optionally, the biocarbon pellets are size-reduced before feeding to the blast furnace. For example, the biocarbon pellets can be pulverized to a powder which is fed to the blast furnace.

**[0766]** The blast furnace can be configured to allow the hot, dirty gas high in carbon monoxide content to exit the furnace throat, while bleeder valves can protect the top of the furnace from sudden gas pressure surges. The coarse particles in the exhaust gas settle and can be disposed, while the gas can flow through a venturi scrubber or electrostatic precipitator or a gas cooler to reduce the temperature of the cleaned gas. A casthouse at the bottom of the furnace comprises equipment for casting the liquid iron and slag. A taphole can be drilled through a refractory plug, so that liquid iron and slag flow down a trough through an opening, separating the iron and slag. Once the pig iron and slag has been tapped, the taphole can be plugged with refractory clay. Nozzles, called tuyeres, are used to implement a hot blast to increase the efficiency of the blast furnace. The hot blast is directed into the furnace through cooled tuyeres near the base. The hot blast temperature can be from 900°C to 1300°C (air temperature), for example. The temperature within the blast furnace can be 2000°C or higher. Other carbonaceous materials or oxygen can also be injected into the furnace at the tuyere level to combine with the carbon (from biocarbon pellets) to release additional energy and increase the percentage of reducing gases present which increases productivity.

**[0767]** Blast furnaces operate on the principle of chemical reduction whereby carbon monoxide, having a stronger affinity for the oxygen in metal ore (e.g., iron ore) than the corresponding metal does, reduces the metal to its elemental form. Blast furnaces differ from bloomeries and reverberatory furnaces in that in a blast furnace, flue gas is in direct contact with the ore and metal, allowing carbon monoxide to diffuse

into the ore and reduce the metal oxide to elemental metal mixed with carbon. The blast furnace usually operates as a continuous, countercurrent exchange process.

**[0768]** Silica usually is removed from the pig iron. Silica reacts with calcium oxide and forms a silicate which floats to the surface of the molten pig iron as slag. The downward-moving column of metal ore, flux, carbon, and reaction products must be porous enough for the flue gas to pass through. This requires the biogenic-reagent carbon to be in large enough particles (e.g., biocarbon pellets or smaller objects derived from the pellets) to be permeable. Therefore, pellets, or crushed pellets, must be strong enough so it will not be crushed by the weight of the material above it. Besides physical strength of the carbon, it is preferably also low in sulfur, phosphorus, and ash.

**[0769]** Many chemical reactions take place in a blast furnace. The chemistry can be understood with reference to hematite ($Fe_2O_3$) as the starting metal oxide. This form of iron oxide is common in iron ore processing, either in the initial feedstock or as produced within the blast furnace. Other forms of iron ore (e.g., taconite) will have various concentrations of different iron oxides ($Fe_3O_4$, $Fe_2O_3$, FeO, etc.).

**[0770]** The main overall chemical reaction producing molten iron in a blast furnace is

$$Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$$

which is an endothermic reaction. This overall reaction occurs over many steps, with the first being that preheated blast air blown into the furnace reacts with carbon (e.g., from the biocarbon pellets) to produce carbon monoxide and heat:

$$2\ C + O_2 \rightarrow 2\ CO$$

The hot carbon monoxide is the reducing agent for the iron ore and reacts with the iron oxide to produce molten iron and carbon dioxide. Depending on the temperature in the different parts of the furnace (typically highest at the bottom), the iron is reduced in several steps. At the top, where the temperature usually is in the range of 200-700°C, the iron oxide is partially reduced to iron(II,III) oxide, $Fe_3O_4$:

$$3\ Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2$$

At temperatures around 850°C, further down in the furnace, the iron(II,III) is reduced further to iron(II) oxide, FeO:

$$Fe_3O_4 + CO \rightarrow 3\ FeO + CO_2$$

Hot carbon dioxide, unreacted carbon monoxide, and nitrogen from the air pass up through the furnace as fresh feed material travels down into the reaction zone. As the material travels downward, countercurrent gases both preheat the feed charge and decompose the limestone (when employed) to calcium oxide and carbon dioxide:

$$CaCO_3 \rightarrow CaO + CO_2$$

The calcium oxide formed by decomposition reacts with various acidic impurities in the iron (notably silica) to form a slag which is primarily calcium silicate, $CaSiO_3$:

$$SiO_2 + CaO \rightarrow CaSiO_3$$

As the FeO moves down to the region with higher temperatures, ranging up to 1200°C, FeO is reduced further to iron metal, again with carbon monoxide as reactant:

$$FeO + CO \rightarrow Fe + CO_2$$

The carbon dioxide formed in this process can be converted back to carbon monoxide by reacting with carbon via the reverse Boudouard reaction:

$$C + CO_2 \rightarrow 2\ CO$$

**[0771]** In the chemical reactions shown above, it is important to note that a reducing gas can alternatively or additionally be directly introduced into the blast furnace, rather than being an *in-situ* product within the furnace. Typically, in these embodiments, the reducing gas comprises both hydrogen and carbon monoxide, which both function to chemically reduce metal oxide. Optionally, the reducing gas can be separately produced from biocarbon pellets by reforming, gasification, or partial oxidation.

**[0772]** In conventional blast furnaces, there is no hydrogen available for causing metal oxide reduction. Hydrogen can be injected directly into the blast furnace. Alternatively, or additionally, hydrogen can be available within the biocarbon pellets that are fed to the blast furnace, when the biocarbon pellets comprise volatile carbon that is associated with hydrogen (e.g., heavy tar components). Regardless of the source, hydrogen can cause additional reduction reactions that are similar to those above, but replacing CO with $H_2$:

$$3\ Fe_2O_3 + H_2 \rightarrow 2\ Fe_3O_4 + H_2O$$

$$Fe_3O_4 + 4\ H_2 \rightarrow 3\ Fe + 4\ H_2O$$

which occur in parallel to the reduction reactions with CO. The hydrogen can also react with carbon dioxide to generate more CO, in the reverse water-gas shift reaction. In certain embodiments, a reducing gas consisting essentially of hydrogen is fed to a blast furnace.

**[0773]** The "pig iron" produced by the blast furnace typically has a relatively high carbon content of around 3-6 wt%. Pig iron can be used to make cast iron. Pig iron produced by blast furnaces normally undergoes further processing to reduce the carbon and sulfur content and produce various grades of steel used commercially. In a further process step referred to as basic oxygen steelmaking, the carbon is oxidized by blowing oxygen onto the liquid pig iron to form crude steel.

**[0774]** Desulfurization conventionally is performed during the transport of the liquid iron to the steelworks, by adding calcium oxide, which reacts with iron sulfide comprised in the pig iron to form calcium sulfide. In some embodiments, desulfurization can also take place within a furnace or downstream of a furnace, by reacting a metal sulfide with CO (in the reducing gas) to form a metal and carbonyl sulfide, CSO. In these or other embodiments, desulfurization can also take place within a furnace or downstream of a furnace, by reacting a metal sulfide with $H_2$ (in the reducing gas) to form a metal and hydrogen sulfide, $H_2S$.

**[0775]** Other types of furnaces can employ other chemical reactions. It will be understood that in the chemical conversion of a metal oxide into a metal, which employs carbon or a reducing gas in the conversion, that carbon is preferably renewable carbon. This disclosure provides renewable carbon in biogenic reagents produced via pyrolysis of biomass. In certain embodiments, some carbon utilized in the furnace is not renewable carbon. In various embodiments, of the total carbon that is consumed in the metal ore furnace, that percentage of that carbon that is renewable can be at least about 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, 99%, or 100%.

**[0776]** In some variations, a Tecnored furnace, or modification thereof, is utilized. The Tecnored process was originally developed by Tecnored Desenvolvimento Tecnológico S.A. of Brazil and is based on a low-pressure moving-bed reduction furnace which reduces cold-bonded, carbon-bearing, self-fluxing, and self-reducing

pellets. Reduction is carried out in a short-height shaft furnace at typical reduction temperatures. The process produces hot metal (typically liquid iron) at high efficiency.

**[0777]** Tecnored technology was developed to be a coke-less ironmaking process, thus avoiding the investment and operation of environmentally harmful coke ovens besides significantly reducing greenhouse gas emissions in the production of hot metal. The Tecnored process uses a combination of hot and cold blasts and requires no additional oxygen. It eliminates the need for coke plants, sinter plants, and tonnage oxygen plants. Hence, the process has much lower operating and investment costs than those of traditional ironmaking routes.

**[0778]** In the present disclosure, the Tecnored process can be adapted for use in various ways. Some embodiments provide self-reducing agglomerates (such as biocarbon pellets), produced from iron ore fines or iron-bearing residues, plus a biogenic reagent disclosed herein. These materials, mixed with fluxing and binding agents, are agglomerated and thermally cured, producing biocarbon pellets which have sufficient strength for the physical and metallurgical demands of the Tecnored process. The agglomerates produced are then smelted in a Tecnored furnace. The fuel for the Tecnored furnace can itself be biocarbon pellets, or a non-pellet biocarbon composition (e.g., a powder).

**[0779]** By combining fine particles of iron oxide and the reductant within the briquette, both the surface area of the oxide in contact with reductant and, consequently, the reaction kinetics are increased dramatically. The self-reducing briquettes can be designed to comprise sufficient reductant to allow full reduction of the iron-bearing feed comprised, optionally with fluxes to provide the desired slag chemistry. The self-reducing briquettes are cured at low temperatures prior to feeding to the furnace. The heat required to drive the reaction within the self-reducing briquettes is provided by a bed of solid fuel, which can also be in the form of briquettes, onto which the self-reducing briquettes are fed within the furnace.

**[0780]** A Tecnored furnace has three zones: (i) upper shaft zone; (ii) melting zone; and (iii) lower shaft zone. In the upper shaft zone, solid fuel (preferably biogenic reagent) is charged. In this zone, the Boudouard reaction ($C + CO_2 \rightarrow 2\ CO$) is prevented which saves energy. Post-combustion in this zone of the furnace burns CO

which provides energy for preheating and reduction of the charge. Inside the pellets, the following reactions take place at a very fast rate:

$$Fe_xO_y + y\,CO \rightarrow x\,Fe + y\,CO_2$$

$$y\,CO_2 + y\,C = 2y\,CO$$

where $x$ is from 1 to typically 5 and $y$ is from 1 to typically 7.

**[0781]** In the melting zone, reoxidation is prevented because of the reducing atmosphere in the charge. The melting of the charge takes place under reducing atmosphere. In the lower shaft zone, solid fuel is charged. The solid fuel preferably comprises, and more preferably consists essentially of, biocarbon pellets. In this zone, further reduction of residual iron oxides and slagging reactions of gangue materials and fuel ash takes place in the liquid state. Also, superheating of metal and slag droplets take place. These superheated metal and slag droplets sink due to gravity to the furnace hearth and accumulate there.

**[0782]** This modified Tecnored process employs two different inputs of carbon units— namely the reductant and the solid fuel. The reducing agent is conventionally coal fines, but in this disclosure, the reducing agent can comprise pulverized biocarbon pellets. The self-reducing agglomerates can be the biocarbon pellets disclosed herein. The quantity of carbon fines required is established by a ratio of carbon to ore fines, which is preferably selected to achieve full reduction of the metal oxides.

**[0783]** The solid fuel need not be in the form of fines. For example, the solid fuel can be in the form of lumps, such as about 40-80 mm in size to handle the physical and thermal needs required from the solid fuels in the Tecnored process. These lumps can be made by breaking apart (e.g., crushing) biocarbon pellets, but not all the way down to powder. The solid fuel is charged through side feeders (to avoid the endothermic Boudouard reaction in the upper shaft) and provides most of the energy demanded by the process. This energy is formed by the primary blast ($C + O_2 \rightarrow CO_2$) and by the secondary blast, where the upstream CO, generated by the gasification of the solid fuel at the hearth, is burned ($2\,CO + O_2 \rightarrow 2\,CO_2$).

**[0784]** In certain exemplary embodiments, a modified-Tecnored process comprises pelletizing iron ore fines with a size less than 140 mesh, biogenic-reagent fines with a size less than 200 mesh, and a flux such as hydrated lime of size less than

140 mesh using cement as the binder. The pellets are cured and dried at 200°C before they are fed to the top of the Tecnored furnace. The total residence time of the charge in the furnace is around 30-40 minutes. Biogenic reagent in the form of solid fuel of size ranging from 40 mm to 80 mm is fed in the furnace below the hot pellet area using side feeders. Hot blast air at around 1150°C is blown in through tuyeres located in the side of the furnace to provide combustion air for the biogenic carbon. A small amount of furnace gas is allowed to flow through the side feeders to use for the solid fuel drying and preheating. Cold blast air is blown in at a higher point to promote post-combustion of CO in the upper shaft. The hot metal produced is tapped into a ladle on a ladle car, which can tilt the ladle for de-slagging. The liquid iron is optionally desulfurized in the ladle, and the slag is raked into a slag pot. The hot metal typically comprises about 3-5 wt% carbon.

**[0785]** Conventionally, external CO or $H_2$ does not play a significant role in the self-reduction process using a Tecnored furnace. However, external $H_2$ or CO (from reducing gas) can assist the overall chemistry by increasing the rate or conversion of iron oxides in the above reaction ($Fe_xO_y + y\ CO \rightarrow x\ Fe + y\ CO_2$) or in a reaction with hydrogen as reactant ($Fe_xO_y + y\ H_2 \rightarrow x\ Fe + y\ H_2O$). The reduction chemistry can be assisted at least at the surface of the pellets or briquettes, and possibly within the bulk phase of the pellets or briquettes since mass transfer of hot reducing gas is fast. Some embodiments of this disclosure combine aspects of a blast furnace with aspects of a Tecnored furnace, so that a self-reducing pellet or briquette is utilized, in addition to the use of reducing gas within the furnace.

**[0786]** As stated previously, there are a large number of possible furnace configurations for metal ore processing. This specification will not describe in details the various conditions and chemistry that can take place in all possible furnaces, but it will be understood by one skilled in the art that the principles of this disclosure can be applied to essentially any furnace or process that uses carbon somewhere in the process of making a metal from a metal ore.

**[0787]** It will also be observed that some processes utilize biocarbon pellets, some processes utilize reducing gas, and some processes utilize both biocarbon pellets and reducing gas. The processes provided herein can produce both solid biocarbon pellets as well as a reducing gas. In some embodiments, only the solid biocarbon pellets are

employed in a metal ore conversion process. In other embodiments, only the reducing gas is employed in a metal ore conversion process. In still other embodiments, both the biocarbon pellets and the reducing gas are employed in a metal ore conversion process. In these embodiments employing both sources of renewable carbon, the percentage of overall carbon usage in the metal ore conversion from the reducing gas can be about, at least about, or at most about 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, or 100%. The other carbon usage is preferably from the biocarbon pellets. Alternatively, some or all of the other carbon usage can be from conventional carbon inputs, such as coal fines.

*Conversion of Biocarbon Compositions to Reducing Gas*

**[0788]** Some variations employ a biocarbon composition (as pellets, powder, or another form) to generate reducing gas, wherein the reducing gas can be utilized *in situ* in a process or can be recovered and sold. In related embodiments, a portion of low-fixed-carbon material or a portion of high-fixed-carbon material (e.g., an off-spec portion of one of these materials, or an extra quantity of material not needed for final product demand) can be diverted from the blending operation and instead utilized to generate a reducing gas.

**[0789]** The optional production of reducing gas (also referred to herein as "bio-reductant gas") will now be further described. The conversion of a biocarbon composition to reducing gas takes place in a reactor, which can be referred to as a bio-reductant formation unit.

**[0790]** A reactant can be employed to react with the biocarbon composition and produce a reducing gas. The reactant can be selected from oxygen, steam, or a combination thereof. In some embodiments, oxygen is mixed with steam, and the resulting mixture is added to the second reactor. Oxygen or oxygen-enriched air can be added to cause an exothermic reaction such as the partial or total oxidation of carbon with oxygen; to achieve a more favorable $H_2$/CO ratio in the reducing gas; (iii) to increase the yield of reducing gas; or (iv) to increase the purity of reducing gas, e.g. by reducing the amount of $CO_2$, pyrolysis products, tar, aromatic compounds, or other undesirable products.

**[0791]** Steam is a preferred reactant, in some embodiments. Steam (i.e. $H_2O$ in a vapor phase) can be introduced into the reactor in one or more input streams. Steam

can comprise steam generated by moisture comprised in the biocarbon pellets, as well as steam generated by any chemical reactions that produce water.

**[0792]** All references herein to a "ratio" of chemical species are references to molar ratios unless otherwise indicated. For example, a $H_2$/CO ratio of 1 means one mole of hydrogen per mole of carbon dioxide.

**[0793]** Steam reforming, partial oxidation, water-gas shift (WGS), or combustion reactions can occur when oxygen or steam are added. Exemplary reactions are shown below with respect to a cellulose repeat unit ($C_6H_{10}O_5$) found, for example, in cellulosic feedstocks. Similar reactions can occur with any carbon-containing feedstock, including biocarbon pellets.

| | |
|---|---|
| *Steam Reforming* | $C_6H_{10}O_5 + H_2O \rightarrow 6\ CO + 6\ H_2$ |
| *Partial Oxidation* | $C_6H_{10}O_5 + ½\ O_2 \rightarrow 6\ CO + 5\ H_2$ |
| *Water-Gas Shift* | $CO + H_2O \leftrightarrow H_2 + CO_2$ |
| *Complete Combustion* | $C_6H_{10}O_5 + 6\ O_2 \rightarrow 6\ CO_2 + 5\ H_2O$ |

**[0794]** The bio-reductant formation unit is any reactor capable of causing at least one chemical reaction that produces reducing gas. Conventional steam reformers, well-known in the art, can be used either with or without a catalyst. Other possibilities comprise autothermal reformers, partial-oxidation reactors, and multistaged reactors that combine several reaction mechanisms (e.g., partial oxidation followed by water-gas shift). The reactor configuration can be a fixed bed, a fluidized bed, a plurality of microchannels, or some other configuration.

**[0795]** In some embodiments, the total amount of steam as reactant is at least about 0.1 mole of steam per mole of carbon in the feed material. In various embodiments, at least about any of 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, or more moles of steam are added or are present per mole of carbon. In some embodiments, between about 1.5-3.0 moles of steam are added or are present per mole carbon.

**[0796]** The amount to steam that is added to the second reactor can vary depending on factors such as the conditions of the pyrolysis reactor. When pyrolysis produces a carbon-rich solid material, generally more steam (or more oxygen) is used to add the necessary H and O atoms to the C available to generate CO and $H_2$. From the perspective of the overall system, the moisture comprised in the biocarbon pellets

can be accounted for in determining how much additional water (steam) to add in the process.

**[0797]** Exemplary ratios of oxygen to steam ($O_2/H_2O$) are equal to or less than about any of 2, 1.5, 1, 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, or less, in the second reactor. When the ratio of $O_2/H_2O$ is greater than 1, the combustion reaction starts to dominate over partial oxidation, which can produce undesirably low $CO/CO_2$ ratios.

**[0798]** In some embodiments, oxygen without steam is used as the reactant. Oxygen can be added in substantially pure form, or it can be fed to the process via the addition of air, optionally enriched with oxygen. In some embodiments, air that is not enriched with oxygen is added. In other embodiments, enriched air from an off-spec or recycle stream, which can be a stream from a nearby air-separation plant, for example, can be used. In some embodiments, the use of enriched air with a reduced amount of $N_2$ (i.e., less than 79 vol%) results in less $N_2$ in the resulting reducing gas. Because removal of $N_2$ can be expensive, methods of producing reducing gas with less or no $N_2$ are typically desirable.

**[0799]** In some embodiments, the presence of oxygen alters the ratio of $H_2/CO$ in the reducing gas, compared to the ratio produced by the same method in the absence of oxygen. The $H_2/CO$ ratio of the reducing gas can be between about 0.5 to about 2.0, such as between about 0.75-1.25, about 1-1.5, or about 1.5-2.0. As will be recognized, increased water-gas shift (by higher rates of steam addition) will tend to produce higher $H_2/CO$ ratios, such as at least 2.0, 3.0. 4.0. 5.0, or even higher, which can be desired for certain applications, including hydrogen production.

**[0800]** Catalysts can optionally be utilized in the reactor for generating the reducing gas. Catalysts can comprise, but are not limited to, alkali metal salts, alkaline earth metal oxides and salts, mineral substances or ash in coal, transition metals and their oxides and salts, and eutectic salt mixtures. Specific examples of catalysts comprise, but are not limited to, potassium hydroxide, potassium carbonate, lithium hydroxide, lithium carbonate, cesium hydroxide, nickel oxide, nickel-substituted synthetic mica montmorillonite (NiSMM), NiSMM-supported molybdenum, iron hydroxyoxide, iron nitrate, iron-calcium-impregnated salts, nickel uranyl oxide, sodium fluoride, and cryolite.

**[0801]** Other exemplary catalysts comprise, but are not limited to, nickel, nickel oxide, rhodium, ruthenium, iridium, palladium, and platinum. Such catalysts can be coated or deposited onto one or more support materials, such as, for example, gamma-alumina (optionally doped with a stabilizing element such as magnesium, lanthanum, or barium).

**[0802]** Before being added to the system, any catalyst can be pretreated or activated using known techniques that impact total surface area, active surface area, site density, catalyst stability, catalyst lifetime, catalyst composition, surface roughness, surface dispersion, porosity, density, or thermal diffusivity. Pretreatments of catalysts comprise, but are not limited to, calcining, washcoat addition, particle-size reduction, and surface activation by thermal or chemical means.

**[0803]** Catalyst addition can be performed by first dissolving or slurrying the catalyst(s) into a solvent such as water or any hydrocarbon that can be gasified or reformed. In some embodiments, the catalyst is added by direct injection of such a slurry into a vessel. In some embodiments, the catalyst is added to steam and the steam/catalyst mixture is added to the system. In these embodiments, the added catalyst can be at or near its equilibrium solubility in the steam or can be introduced as particles entrained in the steam and thereby introduced into the system.

**[0804]** Material can generally be conveyed into and out of the reactor by single screws, twin screws, rams, and the like. Material can be conveyed mechanically by physical force (metal contact), pressure-driven flow, pneumatically driven flow, centrifugal flow, gravitational flow, fluidized flow, or some other known means of moving solid and gas phases. It can be preferable to utilize a fixed bed of biocarbon pellets in the reactor, especially in embodiments that employ a bed of metal oxide disposed above the biocarbon pellet bed which need to be mechanically robust.

**[0805]** In some embodiments, the reactor employs gasification of a biocarbon composition to generate a reducing gas. Gasification is carried out at elevated temperatures, typically about 600°C to about 1100°C. Less-reactive biogenic reagents require higher operating temperatures. The amount of reactant introduced (e.g., air, oxygen, enriched air, or oxygen-steam mixtures) will typically be the primary factor controlling the gasification temperature. Operating pressures from atmospheric to

about 50 bar have been employed in biomass gasification. Gasification also requires a reactant, commonly air, high-purity oxygen, steam, or some mixture of these gases.

**[0806]** Gasifiers can be differentiated based on the means of supporting solids within the vessel, the directions of flow of both solids and gas, and the method of supplying heat to the reactor. Whether the gasifier is operated at near atmospheric or at elevated pressures, and the gasifier is air-blown or oxygen-blown, are also distinguishing characteristics. Common classifications are fixed-bed updraft, fixed-bed downdraft, bubbling fluidized bed, and circulating fluidized bed.

**[0807]** Fixed-bed gasifiers, in general, cannot handle fibrous herbaceous feedstocks, such as wheat straw, corn stover, or yard wastes. However, in the disclosed processes, biomass is first pyrolyzed to a biogenic reagent, which is pelletized, and the biocarbon pellets can be gasified. The biocarbon pellets can be directly gasified using a fixed-bed gasifier, without necessarily reducing the size of the pellets.

**[0808]** Circulating fluidized-bed gasification technology is available from Lurgi and Foster Wheeler, and represents the majority of existing gasification technology utilized for biomass and other wastes. Bubbling fluidized-bed gasification (e.g., U-GAS® technology) has been commercially used.

**[0809]** Directly heated gasifiers conduct endothermic and exothermic gasification reactions in a single reaction vessel; no additional heating is needed. In contrast, indirectly heated gasifiers require an external source of heat. Indirectly heated gasifiers commonly employ two vessels. The first vessel gasifies the feed with steam (an endothermic process). Heat is supplied by circulating a heat-transfer medium, commonly sand. Reducing gas and solid char produced in the first vessel, along with the sand, are separated. The mixed char and sand are fed to the second vessel, where the char is combusted with air, heating the sand. The hot sand is circulated back to the first vessel.

**[0810]** The biocarbon composition can be introduced to a gasifier as a "dry feed" (optionally with moisture, but no free liquid phase), or as a slurry or suspension in water. Dry-feed gasifiers typically allow for high per-pass carbon conversion to reducing gas and good energy efficiency. In a dry-feed gasifier, the energy released by the

gasification reactions can cause the gasifier to reach extremely high temperatures. This problem can be resolved by using a wet-wall design.

**[0811]** In some embodiments, the feed to the gasifier is biocarbon pellets with high hydrogen content. The resulting reducing gas is relatively rich in hydrogen, with high $H_2/CO$ ratios, such as $H_2/CO > 1.5$ or more.

**[0812]** In some embodiments, the feed to the gasifier is biocarbon pellets with low hydrogen content. The resulting reducing gas is expected to have relatively low $H_2/CO$ ratios. For downstream processes that require $H_2/CO > 1$, it can be desirable to inject water or steam into the gasifier to both moderate the gasifier temperature (via sensible-heat effects or endothermic chemistry), and to shift the $H_2/CO$ ratio to a higher, more-desirable ratio. Water addition can also contribute to temperature moderation by endothermic consumption, via steam-reforming chemistry. In steam reforming, $H_2O$ reacts with carbon or with a hydrocarbon, such as tar or benzene/toluene/xylenes, to produce reducing gas and lower the adiabatic gasification temperature.

**[0813]** In certain variations, the gasifier is a fluidized-bed gasifier, such as a bubbling fluidized gasification reactor. Fluidization results in a substantially uniform temperature within the gasifier bed. A fluidizing bed material, such as alumina sand or silica sand, can reduce potential attrition issues. The gasifier temperature is preferably moderated to a sufficiently low temperature so that ash particles do not begin to transform from solid to molten form, which can cause agglomeration and loss of fluidization within the gasifier.

**[0814]** When a fluidized-bed gasifier is used, the total flow rate of all components should ensure that the gasifier bed is fluidized. The total gas flow rate and bed diameter establish the gas velocity through the gasifier. The correct velocity must be maintained to ensure proper fluidization.

**[0815]** In variations, the gasifier type can be entrained-flow slagging, entrained flow non-slagging, transport, bubbling fluidized bed, circulating fluidized bed, or fixed bed. Some embodiments employ gasification catalysts.

**[0816]** Circulating fluidized-bed gasifiers can be employed, wherein gas, sand, and feedstock (e.g., crushed or pulverized biocarbon pellets) move together. Exemplary transport gases comprise recirculated product gas, combustion gas, or

recycle gas. High heat-transfer rates from the sand ensure rapid heating of the feedstock, and ablation is expected to be stronger than with regular fluidized beds. A separator can be employed to separate the reducing gas from the sand and char particles. The sand particles can be reheated in a fluidized burner vessel and recycled to the reactor.

**[0817]** In some embodiments in which a countercurrent fixed-bed gasifier is used, the reactor consists of a fixed bed of a feedstock through which a gasification agent (such as steam, oxygen, or recycle gas) flows in countercurrent configuration. The ash is either removed dry or as a slag.

**[0818]** In some embodiments in which a cocurrent fixed-bed gasifier is used, the reactor is similar to the countercurrent type, but the gasification agent gas flows in cocurrent configuration with the feedstock. Heat is added to the upper part of the bed, either by combusting small amounts of the feedstock or from external heat sources. The produced gas leaves the reactor at a high temperature, and much of this heat is transferred to the gasification agent added in the top of the bed, resulting in good energy efficiency.

**[0819]** In some embodiments in which a fluidized-bed reactor is used, the feedstock is fluidized in recycle gas, oxygen, air, or steam. The ash can be removed dry or as heavy agglomerates that defluidize. Recycle or subsequent combustion of solids can be used to increase conversion. Fluidized-bed reactors are useful for feedstocks that form highly corrosive ash that would damage the walls of slagging reactors.

**[0820]** In some embodiments in which an entrained-flow gasifier is used, biocarbon pellets are pulverized and gasified with oxygen, air, or recycle gas in cocurrent flow. The gasification reactions take place in a dense cloud of very fine particles. High temperatures can be employed, thereby providing for low quantities of tar and methane in the reducing gas.

**[0821]** Entrained-flow reactors remove the major part of the ash as a slag, as the operating temperature is typically well above the ash fusion temperature. A smaller fraction of the ash is produced either as a very fine dry fly ash or as a fly-ash slurry. Certain entrained-bed reactors have an inner water- or steam-cooled wall covered with partially solidified slag.

**[0822]** The gasifier chamber can be designed, by proper configuration of the freeboard or use of internal cyclones, to keep the carryover of solids downstream operations at a level suitable for recovery of heat. Unreacted carbon can be drawn from the bottom of the gasifier chamber, cooled, and recovered.

**[0823]** A gasifier can comprise one or more catalysts, such as catalysts effective for partial oxidation, reverse water-gas shift, or dry ($CO_2$) reforming of carbon-containing species.

**[0824]** In some embodiments, a bubbling fluid-bed devolatilization reactor is utilized. The reactor is heated, at least in part, by the hot recycle gas stream to approximately 600°C—below the expected slagging temperature. Steam, oxygen, or air can also be introduced to the second reactor. The second can be designed, by proper configuration of a freeboard or use of internal cyclones, to keep the carryover of solids at a level suitable for recovery of heat downstream. Unreacted char can be drawn from the bottom of the devolatilization chamber, cooled, and then fed to a utility boiler to recover the remaining heating value of this stream.

**[0825]** When a fluidized-bed gasifier is employed, the feedstock can be introduced into a bed of hot sand fluidized by a gas, such as recycle gas. Reference herein to "sand" shall also comprise similar, substantially inert materials, such as glass particles, recovered ash particles, and the like. High heat-transfer rates from fluidized sand can result in rapid heating of the feedstock. There can be some ablation by attrition with the sand particles. Heat can be provided by heat-exchanger tubes through which hot combustion gas flows.

**[0826]** Circulating fluidized-bed reactors can be employed, wherein gas, sand, and feedstock move together. Exemplary transport gases comprise recirculated product gas, combustion gas, or recycle gas. High heat-transfer rates from the sand ensure rapid heating of the feedstock, and ablation is expected to be stronger than with regular fluidized beds. A separator can be employed to separate the reducing gas from the sand and char particles. The sand particles can be reheated in a fluidized burner vessel and recycled to the reactor.

**[0827]** In some embodiments in which a countercurrent fixed-bed reactor is used, the reactor consists of a fixed bed of a feedstock through which a gasification agent

(such as steam, oxygen, or recycle gas) flows in countercurrent configuration. The ash is either removed dry or as a slag.

**[0828]** In some embodiments in which a cocurrent fixed-bed reactor is used, the reactor is similar to the countercurrent type, but the gasification agent gas flows in cocurrent configuration with the feedstock. Heat is added to the upper part of the bed, either by combusting small amounts of the feedstock or from external heat sources. The reducing gas leaves the reactor at a high temperature, and much of this heat is transferred to the reactants added in the top of the bed, resulting in good energy efficiency. Since tars pass through a hot bed of carbon in this configuration, tar levels are expected to be lower than when using the countercurrent type.

**[0829]** In some embodiments in which a fluidized-bed reactor is used, the feedstock is fluidized in recycle gas, oxygen, air, or steam. The ash is removed dry or as heavy agglomerates that defluidize. Recycle or subsequent combustion of solids can be used to increase conversion.

**[0830]** To enhance heat and mass transfer, water can be introduced into the reactor using a nozzle, which is generally a mechanical device designed to control the direction or characteristics of a fluid flow as it enters an enclosed chamber or pipe via an orifice. Nozzles are capable of reducing the water droplet size to generate a fine spray of water. Nozzles can be selected from atomizer nozzles (similar to fuel injectors), swirl nozzles which inject the liquid tangentially, and so on.

**[0831]** Water sources can comprise direct piping from process condensate, other recycle water, wastewater, make-up water, boiler feed water, city water, and so on. Water can optionally first be cleaned, purified, treated, ionized, distilled, and the like. When several water sources are used, various volume ratios of water sources are possible. In some embodiments, a portion or all of the water for the second reactor is wastewater.

**[0832]** In some variations, the reducing gas is filtered, purified, or otherwise conditioned prior to being converted to another product. For example, cooled reducing gas can be introduced to a conditioning unit, where benzene, toluene, ethyl benzene, xylene, sulfur compounds, nitrogen, metals, or other impurities are optionally removed from the reducing gas.

**[0833]** Some embodiments comprise a reducing-gas cleanup unit. The reducing-gas cleanup unit is not particularly limited in its design. Exemplary reducing-gas cleanup units comprise cyclones, centrifuges, filters, membranes, solvent-based systems, and other means of removing particulates or other specific contaminants. In some embodiments, an acid-gas removal unit is comprised and can be any means known in the art for removing $H_2S$, $CO_2$, or other acid gases from the reducing gas.

**[0834]** Examples of acid-gas removal steps comprise removal of $CO_2$ with one or more solvents for $CO_2$, or removal of $CO_2$ by a pressure-swing adsorption unit. Suitable solvents for reactive solvent-based acid gas removal comprise monoethanolamine, diethanolamine, methyldiethanolamine, diisopropylamine, and aminoethoxyethanol. Suitable solvents for physical solvent-based acid gas removal comprise dimethyl ethers of polyethylene glycol (such as in the Selexol® process) and refrigerated methanol (such as in the Rectisol® process).

**[0835]** The reducing gas produced as described can be utilized in a number of ways. Reducing gas can generally be chemically converted or purified into hydrogen, carbon monoxide, methane, olefins (such as ethylene), oxygenates (such as dimethyl ether), alcohols (such as methanol and ethanol), paraffins, and other hydrocarbons. Reducing gas can be converted into linear or branched $C_5$-$C_{15}$ hydrocarbons, diesel fuel, gasoline, waxes, or olefins by Fischer-Tropsch chemistry; mixed alcohols by a variety of catalysts; isobutane by isosynthesis; ammonia by hydrogen production followed by the Haber process; aldehydes and alcohols by oxosynthesis; and many derivatives of methanol including dimethyl ether, acetic acid, ethylene, propylene, and formaldehyde by various processes. The reducing gas can also be converted to energy using energy-conversion devices such as solid-oxide fuel cells, Stirling engines, micro-turbines, internal combustion engines, thermo-electric generators, scroll expanders, gas burners, or thermo-photovoltaic devices.

**[0836]** In this detailed description, reference has been made to multiple embodiments and non-limiting examples relating to how the technology can be understood and practiced. Other embodiments that do not provide all of the features and advantages set forth herein can be utilized, without departing from the spirit and scope of the disclosure. This disclosure incorporates routine experimentation and

optimization of the methods and systems described herein. Such modifications and variations are considered to be within the scope of the technology defined by the claims.

**[0837]** All publications, patents, and patent applications cited in this specification are herein incorporated by reference in their entirety as if each publication, patent, or patent application were specifically and individually put forth herein.

**[0838]** Where methods and steps described above indicate certain events occurring in certain order, those of ordinary skill in the art will recognize that the ordering of certain steps can be modified and that such modifications are in accordance with the variations of the disclosure. Additionally, certain of the steps can be performed concurrently in a parallel process when possible, as well as performed sequentially.

**[0839]** Therefore, to the extent there are variations which are within the spirit of the disclosure or equivalent to the appended claims, it is the intent that this patent will cover those variations as well.

EXAMPLES

Example 1

**[0840]** A biomass feedstock consisting essentially of Douglas fir is pyrolyzed in a continuous pyrolysis reactor at a temperature of about 650°C for about 25 minutes.

**[0841]** The products collected from the pyrolysis reactor comprise char (solid biogenic reagent) and pyrolysis vapor. The pyrolysis vapor is separated into heavy pyrolysis tar (also called the pyrolysis precipitate) and an off-gas, using a condenser. On a dry basis, the char yield is 21.6 wt% and the yield of heavy tar is 9.1 wt%, for a combined total yield of 30.7 wt%.

**[0842]** The char is characterized as 2.0 wt% moisture, 7.6 wt% volatile matter, and 3.0 wt% ash; the remainder is fixed carbon. The heavy tar is characterized as 46.6 wt% moisture, 85.6 wt% volatile matter, 0.04 wt% ash, and 14.3 wt% fixed carbon (calculated).

**[0843]** Next the heavy tar and the char are blended together at the same mass ratio as they were initially produced, to generate an intermediate material. The intermediate material comprises no additives except for some water to aid in pelletizing.

The intermediate material comprises 70.3 wt% char and 29.7% wt% heavy tar, on a dry basis.

**[0844]** The intermediate material is pelletized using a flat-die pellet mill and the pellets are dried in an oven at 105°C for about 18 hours.

**[0845]** The dried pellets are then carbonized (further pyrolyzed) at 650°C for 15 minutes in a continuous pyrolysis reactor, to generate biocarbon pellets. The yield of biocarbon pellets is 88.3 wt% based on the mass of the intermediate material. This further pyrolysis brings the overall yield down from 30.7 wt% to 28.8 wt%, based on the starting wood feedstock. The biocarbon pellets comprise only 7.4 wt% volatile matter, whereas typically there would be about 20 wt% volatile matter remaining in a normal char at this cook profile. The ash content of the biocarbon pellets is 2.7 wt%. The finished product (biocarbon pellets) is about 90.0 wt% fixed carbon. As much as 60.4 wt% of the added heavy tar is converted to fixed carbon. This is surprising, considering that none of that heavy tar had converted to fixed carbon in the first pyrolysis.

**[0846]** The dramatically improved yield is even more surprising when compared to a separate side experiment that attempts to pyrolyze the same heavy tar at identical time and temperature. In the side experiment, the heavy tar only achieves a char yield of 10-16 wt%. In another side experiment, a char yield of about 16.5 wt% is achieved when a feedstock is prepared with 40 wt% heavy tar and 60 wt% biomass feedstock. These yields are significantly lower than the ~60 wt% yield of fixed carbon from heavy tar in the biocarbon pellets described in this Example above. Without being limited by speculation, it is believed that the pelletization prior to, or in combination with, re-carbonization of the heavy tar leads to a superior yield. In particular, it is believed that the biogenic reagent acts as a catalyst or reaction matrix for fixed-carbon formation reactions of the pyrolysis precipitate.

**[0847]** The biocarbon pellets are characterized by an oxygen reactivity as shown in the thermogravimetric analysis (TGA) of FIG. 3. The TGA test assesses oxidation in oxygen using a temperature ramp from room temperature to over 900°C, as shown on the right-hand y-axis, with mass loss shown on the left-hand y-axis. The oxidation reactions are complete within about 6 hours (time is x-axis on FIG. 3).

**[0848]** FIG. 3 shows the TGA results of the Example 1 biocarbon pellet with pyrolysis tar carbonization, compared to the profile of a biocarbon pellet without

pyrolysis tar carbonization. It is observed that by incorporating the pyrolysis precipitate as a binder in the biocarbon pellets, the oxygen reactivity of the pellets is reduced significantly, which is beneficial for many commercial applications. The moderated oxygen reactivity is an advantage in addition to a yield benefit.

Example 2

**[0849]** In this Example 2, several samples of biocarbon pellets according to some embodiments of the disclosure (referred to as RC1, RC2, RC3, RC4, and RC5) are compared using thermogravimetric analysis to a comparative biocarbon sample and an anthracite control sample.

**[0850]** Sample RC1 is produced by first generating a low-fixed-carbon biocarbon composition compriseing 50 wt% volatile matter. Biomass is pyrolyzed in a reactor to generate a low-fixed-carbon solid. This solid material is pelletized without any binders. Water is added in the mixing stage to aid in pelletizing. The pellets are dried and then further carbonized via a secondary pyrolysis to generate the sample.

**[0851]** Sample RC2 is produced by first pyrolyzing biomass to generate a high-fixed-carbon biocarbon material and mixing the pyrolyzed material with 29.4 wt% pyrolysis precipitate, to generate a mixture. The pyrolysis precipitate is a condensed form of pyrolysis vapor generated from pyrolysis of the biomass to generate the high-fixed-carbon biocarbon material. The mixture is then pelletized without an external binder. Water is added in the mixing stage to aid in pelletizing. The pellets are dried and then further carbonized via a secondary pyrolysis to generate the sample.

**[0852]** Sample RC3 is produced by first pyrolyzing biomass to generate a high-fixed-carbon biocarbon material and mixing that pyrolyzed material with 10 wt% powdered phenolic resin, to generate a mixture. The mixture is then pelletized. Water is added in the mixing stage to aid in pelletizing. The pellets are dried and then further carbonized via a secondary pyrolysis to generate the sample.

**[0853]** Sample RC4 is produced by first pyrolyzing biomass to generate a high-fixed-carbon biocarbon material and mixing that material with 20 wt% powdered phenolic resin, to generate a mixture. The mixture is then pelletized. Water is added in the mixing stage to aid in pelletizing. The pellets are dried and then further carbonized via a secondary pyrolysis to generate the sample.

**[0854]** Solid carbon comes out the carbon recovery unit formed from secondary reactions and pyrolysis vapor condensing inside the unit, the material was recovered and sent through a secondary pyrolysis unit to generate a high(er) fixed carbon solid.

**[0855]** Sample RC5 is produced by first recovering solid carbon from a carbon recovery unit, wherein the solid carbon is formed by secondary reactions and condensation of pyrolysis vapors inside the carbon recovery unit. The condensed pyrolysis vapor is generated from pyrolysis of the biomass to generate the solid carbon. The solid carbon is then sent through a secondary pyrolysis unit to generate a higher-fixed-carbon solid sample.

**[0856]** Samples RC1, RC2, RC3, RC4, and RC5, and the granules comparative sample are initially in approximately cylindrical pellet form with about 8 millimeter length. All samples are ground to a powder for the thermogravimetric analysis, in order to avoid mass-transfer limitations for the oxidation reactions (standardized granulometry). The anthracite control sample is also in powder form. All powders have a D99 particle size of about 75 microns; 99% of powder particles have diameter of about 75 microns or less.

**[0857]** The comparative sample, labeled "100 mt Granules" in FIG. 4, is generated from biomass pyrolysis with no additional carbonization or pyrolysis after the initial pyrolysis. Water is added in the mixing stage to aid in pelletizing.

**[0858]** The anthracite control sample is a typical powdered anthracite coal material. Anthracite is a high-rank coal, representing a coal that has been subjected to the highest grade of metamorphism. Anthracite is shiny black, hard, and brittle and has a high fixed-carbon content of about 90–95 wt%.

**[0859]** All seven samples are characterized by their oxygen reactivity as shown in the thermogravimetric analysis (TGA) of FIG. 4. The TGA test assesses oxidation in pure oxygen (ASTM D7582) using a temperature ramp at 40°C/min from room temperature to about 950°C, as shown on the right-hand y-axis, with mass loss shown on the left-hand y-axis. The oxidation reactions are complete within about 5 hours (time is x-axis on FIG. 4).

**[0860]** Samples RC2 and RC3, and the anthracite control sample, all reach substantial completion of oxidation at about 4 hours, 51 minutes, according to FIG. 4.

Sample RC4 reaches substantial completion of oxidation at about 4 hours, 25 minutes. Sample RC5 reaches substantial completion of oxidation at about 4 hours, 35 minutes. Sample RC1 appears to reach substantial completion of oxidation at about 4 hours, 20 minutes, although the mass-loss curve does not become completely flat as it does for the other samples. The comparative sample reaches substantial completion of oxidation at about 4 hours, 25 minutes.

**[0861]** Each sample in FIG. 4 displays three distinct mass-loss events. At a temperature of about 100°C and at about 30 minutes, a first mass loss associated with water vaporization is observed. At a time from about 90 minutes to about 150 minutes, a second mass loss associated with oxidation of volatile carbon is observed. This can also be referred to as a first carbon-oxidation regime. Finally, at a time of about 165 minutes, a third mass loss associated with oxidation of fixed carbon is observed. This can also be referred to as a second carbon-oxidation regime, which follows in time the first carbon-oxidation regime. Inspection of the individual curves of FIG. 4 shows that the time for the first and third mass loss is approximately the same for all samples, but the time for the second mass loss varies. In addition to that, the dynamics of the second mass loss including the exact time (and temperature) of initiation, the derivative of the mass loss with time or temperature, and the extent of mass reduction all vary significantly across samples.

**[0862]** According to the TGA graph of FIG. 4, the oxygen reactivity of samples RC1, RC2, RC3, RC4, and RC5 are qualitatively similar to that of anthracite, to varying degrees. The comparative control sample performs worse than all samples RC1, RC2, RC3, RC4, and RC5, and anthracite, with respect to oxygen reactivity. Another way to view these results is that the additional pyrolysis and carbonization that resulted in samples RC1, RC2, RC3, RC4, and RC5 cause these exemplary biocarbon materials to behave similar to anthracite, with respect to oxygen reactivity. This moderated oxygen reactivity is beneficial for many commercial applications of biocarbon products.

# CLAIMS

We claim:

1. A biocarbon pellet composition, wherein the biocarbon pellet comprises a fixed carbon content of at least 60 wt% and wherein the biocarbon pellet requires at least 240 minutes to reach 99% carbon oxidation, as determined by thermogravimetric analysis and recorded to a thermogravimetric analysis graph of weight loss versus time from a thermogravimetric analysis that measures the oxygen reactivity of the biocarbon pellet, wherein the thermogravimetric analysis is performed using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

2. The biocarbon pellet of claim 1, wherein, according to the TGA graph of weight loss versus time from the thermogravimetric analysis, the biocarbon pellet requires at least 270 minutes to reach 99% carbon oxidation.

3. The biocarbon pellet of claim 1, wherein, according to the TGA graph of weight loss versus time from the thermogravimetric analysis, the biocarbon pellet requires at least 300 minutes to reach 99% carbon oxidation.

4. The biocarbon pellet of any one of claims 1-3, wherein thermogravimetric analysis is performed on an anthracite control sample, wherein the anthracite control sample requires a control time to reach 99% carbon oxidation, and wherein the time required for the biocarbon pellet to reach 99% carbon oxidation is from about 85% to about 100% of the control time.

5. The biocarbon pellet of any one of claims 1-4, wherein the biocarbon pellet comprises volatile carbon, and wherein the TGA graph shows a first carbon-oxidation regime associated with oxidation of volatile carbon, which is succeeded by a second carbon-oxidation regime associated with oxidation of fixed carbon.

6. The biocarbon pellet of claim 5, wherein the thermogravimetric analysis shows a first-derivative curve peak within the first carbon-oxidation regime for the biocarbon pellet at a temperature of at least about 500°C.

7. The biocarbon pellet of any one of claims 1-6, wherein the biocarbon pellet comprises at least 60 wt% fixed carbon.

8. The biocarbon pellet of any one of claims 1-6, wherein the biocarbon pellet comprises at least 70 wt% fixed carbon.

9. The biocarbon pellet of any one of claims 1-6, wherein the biocarbon pellet comprises at least 80 wt% fixed carbon.

10. The biocarbon pellet of any one of claims 1-6, wherein the biocarbon pellet comprises at least 85 wt% fixed carbon.

11. The biocarbon pellet of any one of claims 1-6, wherein the biocarbon pellet comprises at least 90 wt% fixed carbon.

12. The biocarbon pellet of any one of claims 1-11, wherein the biocarbon pellet comprises at most 10 wt% ash.

13. The biocarbon pellet of any one of claims 1-11, wherein the biocarbon pellet comprises at most 5 wt% ash.

14. The biocarbon pellet of any one of claims 1-11, wherein the biocarbon pellet comprises at most 1 wt% ash.

15. The biocarbon pellet of any one of claims 1-14, wherein the biocarbon pellet comprises at most 20 wt% total volatile matter.

16. The biocarbon pellet of any one of claims 1-14, wherein the biocarbon pellet comprises at most 10 wt% total volatile matter.

17. The biocarbon pellet of any one of claims 1-16, wherein the biocarbon pellet comprises a binder.

18. The biocarbon pellet of claim 17, wherein the binder is selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, a derivative thereof, or a combination of any of the foregoing.

19. The biocarbon pellet of claim 17, wherein the binder is selected from starch, thermoplastic starch, crosslinked starch, starch polymers, a derivative thereof, or a combination of any of the foregoing.

20. The biocarbon pellet of any one of claims 1-16, wherein the biocarbon pellet does not comprise a binder.

21. The biocarbon pellet of any one of claims 1-20, wherein the biocarbon pellet comprises an additive.

22. The biocarbon pellet of claim 21, wherein the additive is selected from acids, bases, or salts thereof.

23. The biocarbon pellet of claim 21, wherein the additive is selected from metals, metal oxides, metal hydroxides, metal halides, or a combination thereof.

24. The biocarbon pellet of claim 21, wherein the additive is selected from sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide,

hydrogen chloride, sodium silicate, potassium permanganate, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron halide, iron chloride, iron bromide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, titanium dioxide, or a combination thereof.

25. The biocarbon pellet of any one of claims 1-24, wherein total carbon within the biocarbon pellet is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

26. The biocarbon pellet of any one of claims 1-24, wherein total carbon within the biocarbon pellet is at least 90% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

27. The biocarbon pellet of any one of claims 1-24, wherein total carbon within the biocarbon pellet is fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

28. The biocarbon pellet of any one of claims 1-27, wherein the biocarbon pellet is characterized by a Hardgrove Grindability Index of at least 30.

29. The biocarbon pellet of any one of claims 1-28, wherein the biocarbon pellet is characterized by a bulk density of at least about 20 $lb/ft^3$ on a dry basis.

30. The biocarbon pellet of any one of claims 1-29, wherein the biocarbon pellet has an average pellet size selected from about 1 mm to about 10 cm, calculated as effective diameter of the biocarbon pellet.

31. The biocarbon pellet of any one of claims 1-30, wherein the biocarbon pellet has a pellet shape selected from sphere, cylinder, cube, octagon, hexagon, honeycomb, oval, column, bar, pillow, lentil, random granular, or a combination thereof.

32. The biocarbon pellet of any one of claims 1-31, wherein the biocarbon pellet is characterized by a pellet compressive strength at 25°C of at least about 100 $lb_f/in^2$.

33. The biocarbon pellet of any one of claims 1-31, wherein the biocarbon pellet is characterized by a pellet compressive strength at 25°C of at least about 150 $lb_f/in^2$.

34. The biocarbon pellet of any one of claims 1-33, wherein the biocarbon pellet is characterized by at most 20 wt% water uptake at 25°C after 24 hours of soaking in water.

35. The biocarbon pellet of any one of claims 1-34, wherein the biocarbon pellet is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances."

36. The biocarbon pellet of any one of claims 1-35, wherein the biocarbon pellet is produced by a process comprising:

(a) pyrolyzing, in a first pyrolysis reactor, a biomass-containing feedstock, thereby generating a first biogenic reagent and a pyrolysis vapor;

(b) introducing, to a separation unit, the pyrolysis vapor, thereby generating a pyrolysis precipitate, wherein the pyrolysis precipitate is in liquid, solid, or slurry form;

(c) contacting the first biogenic reagent with the pyrolysis precipitate, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the pyrolysis precipitate;

(d) pelletizing the intermediate material, thereby generating an intermediate pellet;

(e) optionally, drying the intermediate pellet;

(f) separately from step (a), pyrolyzing, in a second pyrolysis reactor, the intermediate pellet, thereby generating a second biogenic reagent and a

pyrolysis off-gas, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same reactor or distinct reactors; and

(g) recovering the second biogenic reagent as the biocarbon pellet,

wherein a fixed carbon content of the second biogenic reagent is greater than a fixed carbon content of the first biogenic reagent; and

wherein, according to a thermogravimetric analysis, an oxygen reactivity of the second biogenic reagent is less than an oxygen reactivity of the first biogenic reagent, wherein the thermogravimetric analysis is performed using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

36. The biocarbon pellet of any one of claims 1-35, wherein the biocarbon pellet is produced by a process comprising:

(a) pyrolyzing, in a first pyrolysis reactor, a biomass-containing feedstock, thereby generating a first biogenic reagent and a pyrolysis vapor;

(b) providing a carbon-containing condensed-matter material, wherein the carbon-containing condensed-matter material is a liquid, a solid, or a slurry;

(c) contacting the first biogenic reagent with the carbon-containing condensed-matter material, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the carbon-containing condensed-matter material;

(d) pelletizing the intermediate material, thereby generating an intermediate pellet;

(e) optionally, drying the intermediate pellet;

(f) separately from step (a), pyrolyzing, in a second pyrolysis reactor, the intermediate pellet, thereby generating a second biogenic reagent and a pyrolysis off-gas, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same reactor or distinct reactors; and

(g) recovering the second biogenic reagent as the biocarbon pellet,

wherein a fixed carbon content of the second biogenic reagent is greater than a fixed carbon content of the first biogenic reagent; and

wherein the second biogenic reagent has lower oxygen reactivity than the first biogenic reagent according to a thermogravimetric analysis using a 40°C/min temperature ramp from 25°C to 950°C in the presence of pure oxygen.

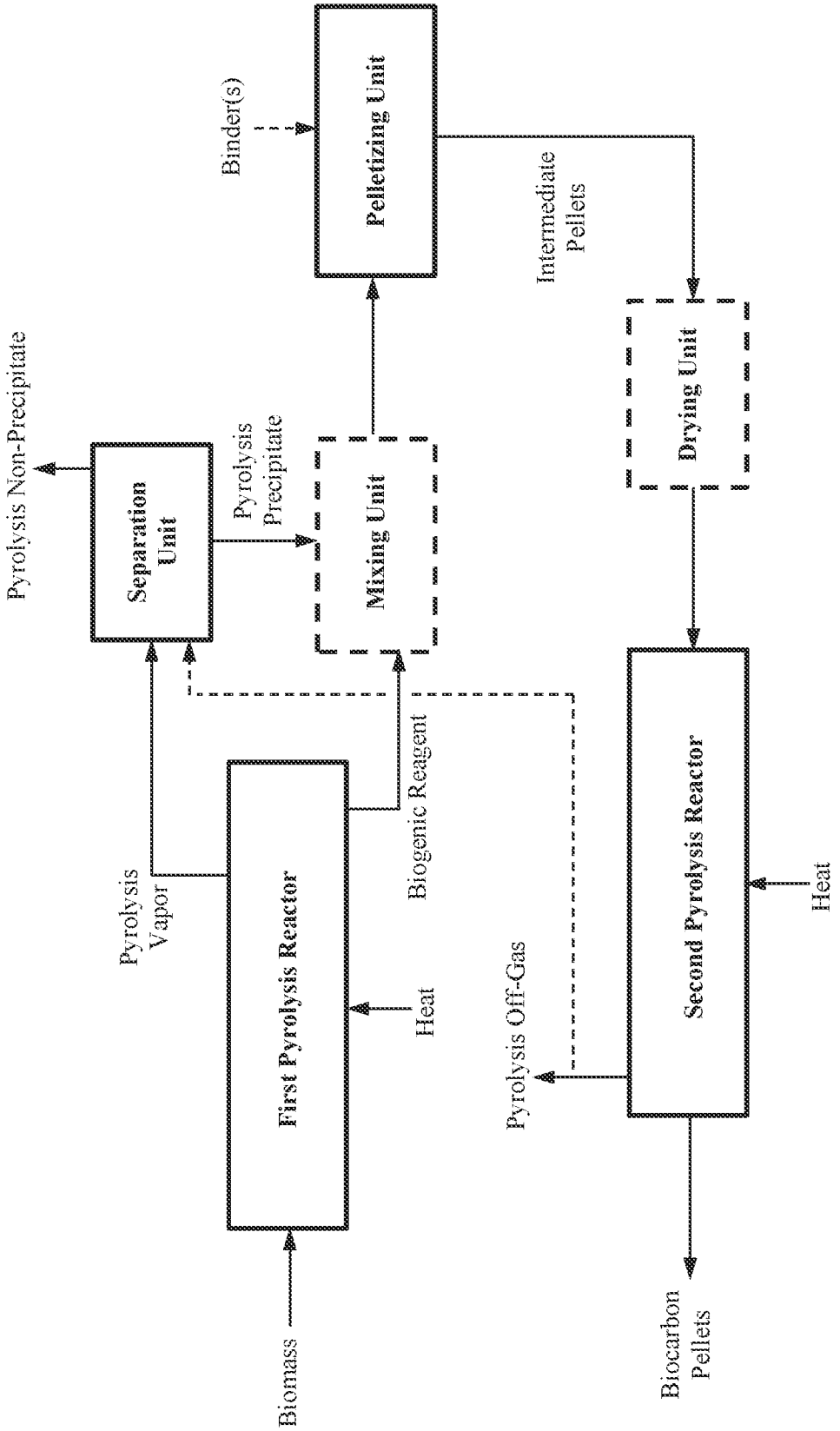

Biomass
First Pyrolysis Reactor
Pyrolysis Vapor
Heat
Biogenic Reagent
Separation Unit
Pyrolysis Non-Precipitate
Pyrolysis Precipitate
Mixing Unit
Binder(s)
Pelletizing Unit
Intermediate Pellets
Drying Unit
Second Pyrolysis Reactor
Pyrolysis Off-Gas
Heat
Biocarbon Pellets

FIG. 1

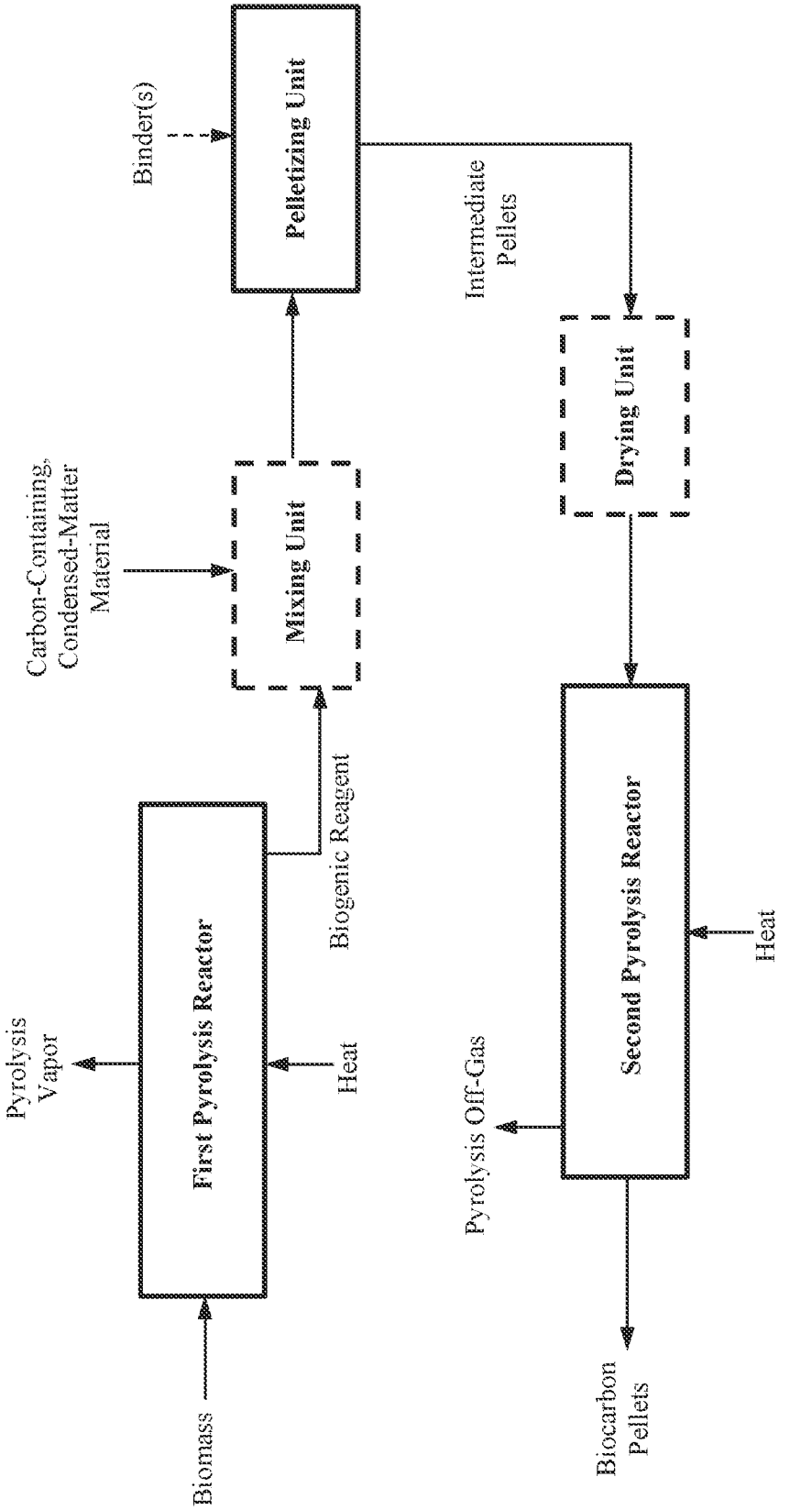

Biomass
First Pyrolysis Reactor
Pyrolysis Vapor
Heat
Biogenic Reagent
Carbon-Containing, Condensed-Matter Material
Mixing Unit
Binder(s)
Pelletizing Unit
Intermediate Pellets
Drying Unit
Second Pyrolysis Reactor
Pyrolysis Off-Gas
Heat
Biocarbon Pellets

FIG. 2

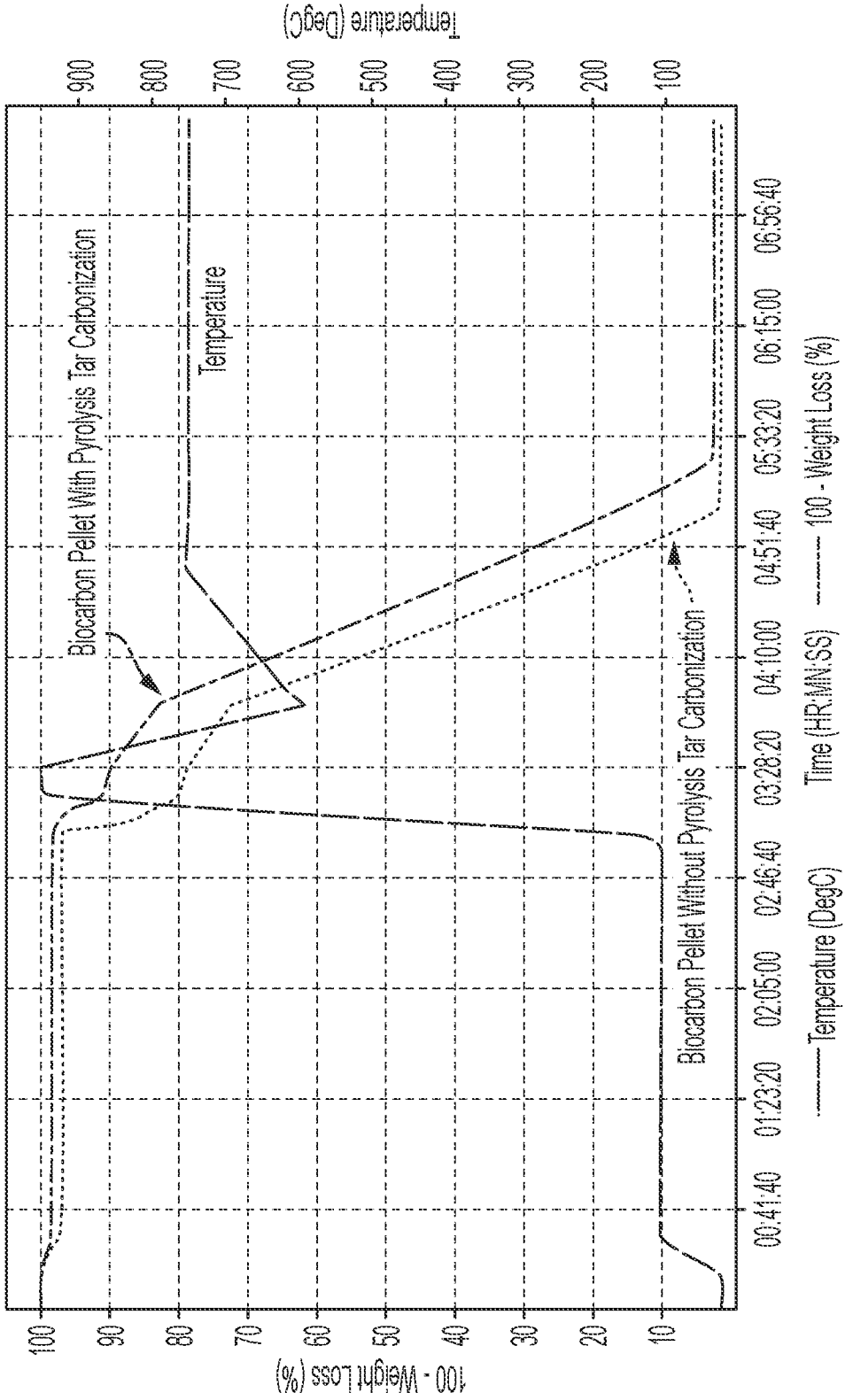

Temperature (DegC)
900
800
700
600
500
400
300
200
100
100 - Weight Loss (%)
100
90
80
70
60
50
40
30
20
10
Biocarbon Pellet With Pyrolysis Tar Carbonization
Temperature
Biocarbon Pellet Without Pyrolysis Tar Carbonization
00:41:40
01:23:20
02:05:00
02:46:40
03:28:20
04:10:00
04:51:40
05:33:20
06:15:00
06:56:40
Temperature (DegC)
Time (HR:MN:SS)
100 - Weight Loss (%)

FIG. 3

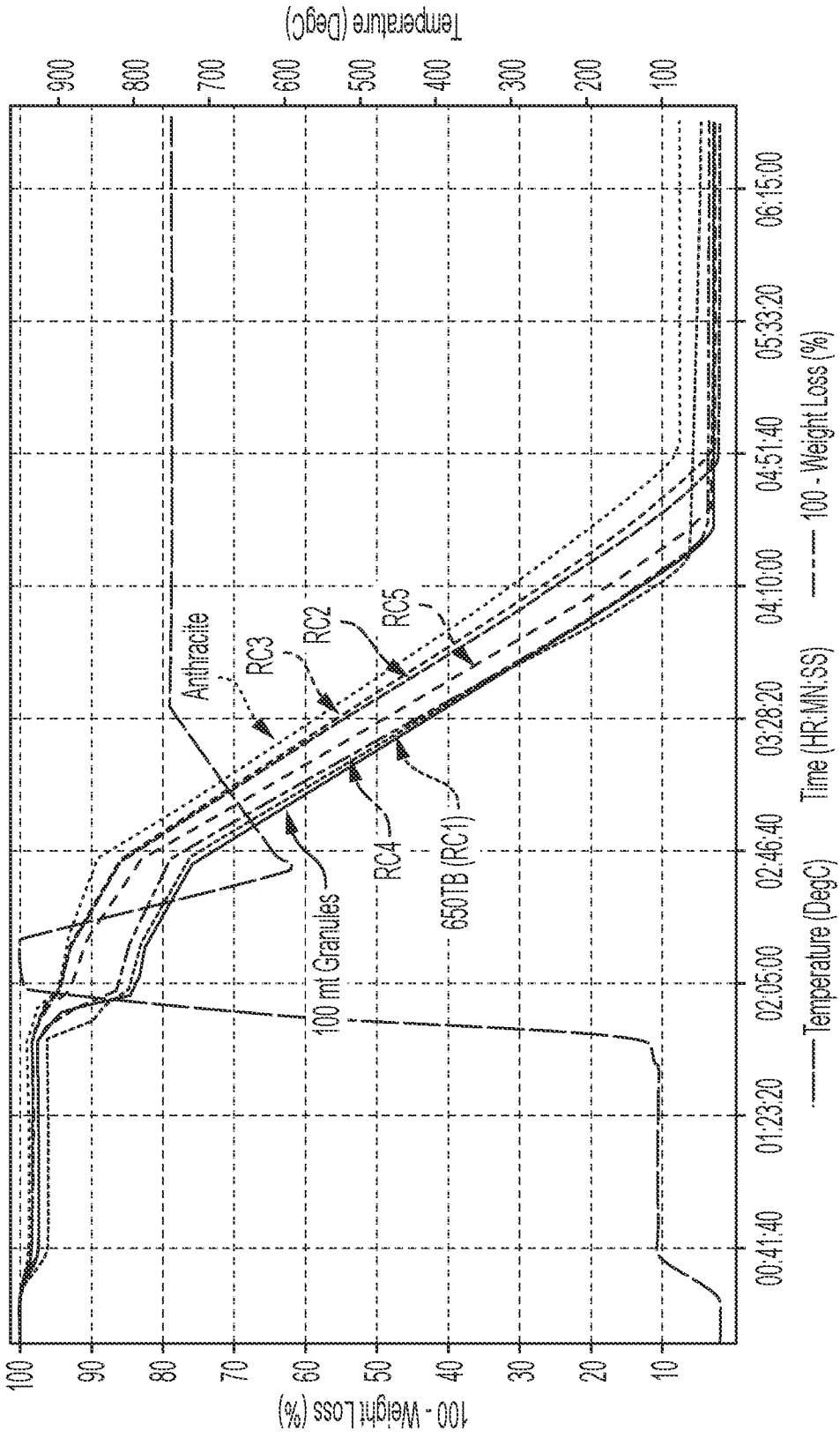

Temperature (DegC)
100 - Weight Loss (%)
Time (HR:MN:SS)
Temperature (DegC)
100 - Weight Loss (%)
Anthracite
RC3
RC2
RC5
RC4
650TB (RC1)
100 mt Granules
00:41:40
01:23:20
02:05:00
02:46:40
03:28:20
04:10:00
04:51:40
05:33:20
06:15:00

FIG. 4

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 22/36294

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. C10B 49/00, C10B 49/04, C10B 53/02; ADD. C10K 3/00 (2022.01)

CPC - INV. C10B 49/00, C10B 49/04, C10B 53/02; ADD. C10K 3/00

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)
See Search History document

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X<br>---<br>Y | US 2018/0119040 A1 (NORTH-WEST UNIVERSITY) 3 May 2018 (03.05.2018)- entire document especially Table 1, Table 3, Fig 6(a), Fig 6(c), and para [0129], [0140], [0133], [0110], [0101], [0060], [0099], [0013], [0007], [0100] | 1-3<br>-----<br>4 |
| Y | US 2018/0208852 A1 (BRITISH COLUMBIA BIOCARBON LTD.) 26 July 2018 (26.07.2018)- entire document especially Table 8 and para [0077], [0104], [0166], [0116], [0078]-[0079] | 4 |
| A | US 2017/0197192 A1 (COOL PLANET ENERGY SYSTEMS, INC.) 13 July 2017 (13.07.2017)- entire document | 1-4 |
| A | US 2020/0381732 A1 (THE GEORGE WASHINGTON UNIVERSITY) 3 December 2020 (03.12.2020)- entire document | 1-4 |
| A | US 2018/0327329 A1 (COOL PLANET ENERGY SYSTEMS, INC.) 15 November 2018 (15.11.2018)- entire document | 1-4 |
| A | US 2011/0219679 A1 (BUDARIN ET AL.) 15 September 2011 (15.09.2011)- entire document | 1-4 |

☐ 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
"D" document cited by the applicant in the international application
"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 |
|---|---|
| 12 September 2022 | OCT 06 2022 |
| Name and mailing address of the ISA/US<br>Mail Stop PCT, Attn: ISA/US, Commissioner for Patents<br>P.O. Box 1450, Alexandria, Virginia 22313-1450<br>Facsimile No. 571-273-8300 | Authorized officer<br>Kari Rodriquez<br>Telephone No. PCT Helpdesk: 571-272-4300 |

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 22/36294

**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-35, 36a, 36b
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.