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(71) Applicant: **CARBON TECHNOLOGY HOLDINGS, LLC** [US/US]; 1 Imation Way, Oakdale, MN 55128 (US).

(72) Inventors: **MENNELL, James, A.**; 12080 E. Big Cottonwood Canyon Road, Brighton, UT 84121 (US). **SLACK, Dustin**; 108 Provider Street, Gwinn, MI 49841 (US). **DAUGAARD, Daren**; 16191 County Road 7250, Newburg, MO 65550 (US).

(74) Agent: **FOURNIER, David, B.** et al.; Perkins Coie LLP, P.O. Box 1247, Seattle, WA 98111-1247 (US).

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(54) Title: BIOCARBON COMPOSITIONS WITH OPTIMIZED COMPOSITIONAL PARAMETERS, AND PROCESSES FOR PRODUCING THE SAME

(57) Abstract: In some variations, the disclosure provides a renewable biocarbon composition comprising from 50 wt% to 99 wt% total carbon, wherein the biocarbon composition is characterized by a base-acid ratio selected from 0.1 to 10, an iron-calcium ratio selected from 0.05 to 5, iron-plus-calcium parameter selected from 5 to 50 wt%, a slagging factor selected from 0.001 to 1, and/or a fouling factor or modified fouling factor selected from 0.1 to 10. Some variations provide a process comprising: providing a biomass feedstock; pyrolyzing the biomass feedstock to generate an intermediate biocarbon stream; washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, and/or introducing an additive in the process, to adjust a base-acid ratio or other compositional parameter; and recovering a biocarbon composition comprising from 50 wt% to 99 wt % total carbon and optimized for a compositional parameter.

# BIOCARBON COMPOSITIONS WITH OPTIMIZED COMPOSITIONAL PARAMETERS, AND PROCESSES FOR PRODUCING THE SAME

## CROSS-REFERENCE TO RELATED APPLICATION(S)

**[0001]** The application claims the priority benefit of U.S. Provisional Patent Application No. 63/278,573, filed on November 12, 2021, which is incorporated by reference herein in its entirety.

## TECHNICAL FIELD

**[0002]** The present invention generally relates to biocarbon compositions with optimized compositional parameters, and processes for producing such biocarbon compositions.

## BACKGROUND

**[0003]** Biomass is a term used to describe any biologically produced matter, or biogenic matter. 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. 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.

**[0004]** Carbonaceous materials commonly include fossil resources such as natural gas, petroleum, coal, and lignite, or renewable resources such as lignocellulosic biomass and various carbon-rich waste materials. There is increasing interest in using renewable biomass to produce carbon-based reagents due to the rising economic, environmental, and social costs associated with fossil resources.

**[0005]** There is a need for biocarbon compositions with optimized compositional parameters, and processes for producing optimized biocarbon compositions. The biocarbon compositional parameters should be optimized for various commercial applications.

SUMMARY

**[0006]** In some variations, the present invention provides a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by a base-acid ratio defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the base-acid ratio is selected from about 0.1 to about 10.

**[0007]** In some embodiments, the base-acid ratio is selected from about 0.1 to about 0.4, or from about 0.5 to about 10, or from about 0.8 to about 10, or from about 1.5 to about 5, or from about 0.4 to about 0.7. In certain embodiments, the base-acid ratio is at most 0.4 or at least 0.7.

**[0008]** In some embodiments, the biocarbon composition described above is further characterized by an iron-calcium ratio defined by the $Fe_2O_3$ divided by the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, wherein the iron-calcium ratio is selected from about 0.05 to about 5.

**[0009]** The present invention also provides a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by an iron-calcium ratio defined by the $Fe_2O_3$ divided by the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the iron-calcium ratio is selected from about 0.05 to about 5.

**[0010]** In some embodiments, the iron-calcium ratio is selected from about 0.1 to about 2, or from about 0.3 to about 1. In certain embodiments, the iron-calcium ratio is at most 0.3 or at least 3.

**[0011]** In some embodiments, the biocarbon composition described above is further characterized by an iron-plus-calcium parameter defined as the sum of the $Fe_2O_3$

and the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the iron-plus-calcium parameter is selected from about 5 wt% to about 50 wt%.

**[0012]** The present invention also provides a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by an iron-plus-calcium parameter defined as the sum of the $Fe_2O_3$ and the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the iron-plus-calcium parameter is selected from about 5 wt% to about 50 wt%.

**[0013]** In some embodiments, the iron-plus-calcium parameter is selected from about 10 wt% to about 40 wt%, or from about 20 wt% to about 50 wt%. In certain embodiments, the iron-plus-calcium parameter is at most 10 wt%. In other embodiments, the iron-plus-calcium parameter is at least 10 wt%.

**[0014]** In some embodiments, the biocarbon composition described above is further characterized by a slagging factor defined as a base-acid ratio multiplied by weight percentage of sulfur present in the biocarbon composition on a dry basis, wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the slagging factor is selected from about 0.001 to about 1.

**[0015]** The present invention also provides a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by a slagging factor defined as a base-acid ratio multiplied by weight percentage of sulfur present in the biocarbon composition on a dry basis, wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the slagging factor is selected from about 0.001 to about 1.

**[0016]** In some embodiments, the slagging factor is selected from about 0.01 to about 0.5, or from about 0.01 to about 0.1. In certain embodiments, the slagging factor is at most 0.6.

**[0017]** In some embodiments, the biocarbon composition described above is further characterized by a fouling factor defined as a base-acid ratio multiplied by the $Na_2O$ as weight percentage in the biocarbon composition pursuant to ASTM D4326, wherein the base-acid ratio defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the fouling factor is selected from about 0.1 to about 10.

**[0018]** The present invention also provides a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by a fouling factor defined as a base-acid ratio multiplied by the $Na_2O$ as weight percentage in the biocarbon composition pursuant to ASTM D4326, wherein the base-acid ratio defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the fouling factor is selected from about 0.1 to about 10.

**[0019]** In some embodiments, the fouling factor is at most 2. In certain embodiments, the fouling factor is at most 1. Typically, a low fouling factor is desirable. However, in certain embodiments, a moderate or even high fouling factor is beneficial to form alkali-bonded deposits, such as when fabricating alkali-comprising composites.

**[0020]** In some embodiments, the biocarbon composition described above is further characterized by a modified fouling factor defined as a base-acid ratio multiplied by water-soluble $Na_2O$, wherein the water-soluble $Na_2O$ is weight percentage of $Na_2O$ that leaches, in the presence of water, out of ash derived from the biocarbon composition pursuant to ASTM D4326, wherein the base-acid ratio defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the modified fouling factor is selected from about 0.1 to about 10.

**[0021]** The present invention also provides a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by a modified fouling factor defined as a base-acid ratio multiplied by water-soluble $Na_2O$, wherein the water-soluble $Na_2O$ is weight percentage of $Na_2O$ that leaches, in the presence of water, out of ash derived from the biocarbon composition pursuant to ASTM D4326, wherein the base-acid ratio defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the modified fouling factor is selected from about 0.1 to about 10.

**[0022]** In some embodiments, the modified fouling factor is at most 2. In certain embodiments, the modified fouling factor is at most 1.

**[0023]** In some embodiments, the biocarbon composition described above is further characterized by a silica percentage defined as weight percentage of the $SiO_2$ in the biocarbon composition pursuant to ASTM D4326, wherein the silica percentage is selected from about 5 wt% to about 50 wt%. In certain embodiments, the silica percentage is selected from about 10 wt% to about 30 wt%.

**[0024]** In some embodiments, the biocarbon composition described above is further characterized by a low mercury content. The biocarbon composition can comprise at most 100 ppm mercury (ppm = parts per million on weight basis), or can comprise at most 10 ppm mercury, or can be essentially free of mercury.

**[0025]** In some embodiments, the biocarbon composition is further characterized by an equilibrium moisture content according to ASTM D1412. The equilibrium moisture can be from about 0.1 wt% to about 10 wt%, such as about, at least about, or at most about 0.1, 0.2, 0.5, 0.8, 1, 1.2, 1.5, 2, 2.5, 2.6, 2.7, 2.8, 2.9, 3, 3.1, 3.2, 3.3, 3.4, 3.5, 4, 4.5, 5, 6, 7, 8, 9, or 10 wt%, including all intervening ranges.

**[0026]** The biocarbon composition can comprise from about 50 wt% to about 99 wt% fixed carbon on a dry basis. In some embodiments, the biocarbon composition comprises at least about 75 wt% fixed carbon or at least about 90 wt% fixed carbon on a dry basis.

**[0027]** In some embodiments, the 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. The total carbon within the biocarbon composition can be at least 99% 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.

**[0028]** In some embodiments, the fixed carbon within the biocarbon composition is at least 80% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the fixed carbon. The fixed 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 fixed carbon. The fixed carbon within the biocarbon composition can be at least 95% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the fixed carbon.

**[0029]** The biocarbon composition can be in the form of a pellet. The pellet can comprise 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, derivatives thereof, or a combination or a derivative thereof. In some embodiments, the biocarbon pellet does not comprise an externally added binder.

**[0030]** The biocarbon composition can be in the form of a powder, which can be a loose powder, a compacted powder, a granulated powder, or other form.

**[0031]** In some embodiments, the biocarbon composition described above is further characterized by an expanded base-acid ratio defined by the following formula:

$$\text{Expanded Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O + MnO + SrO + BaO}{SiO_2 + Al_2O_3 + TiO_2 + P_2O_5 + SO_3}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, MnO, SrO, BaO, $SiO_2$, $Al_2O_3$, $TiO_2$, $P_2O_5$, and $SO_3$ correspond to weight fractions in the biocarbon composition pursuant to ASTM D4326, and wherein the expanded base-acid ratio is selected from about 0.05 to about 8.

**[0032]** Some variations of the invention provide a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by an expanded base-acid ratio defined by the following formula:

$$\text{Expanded Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O + MnO + SrO + BaO}{SiO_2 + Al_2O_3 + TiO_2 + P_2O_5 + SO_3}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, MnO, SrO, BaO, $SiO_2$, $Al_2O_3$, $TiO_2$, $P_2O_5$, and $SO_3$ correspond to weight fractions in the biocarbon composition pursuant to

ASTM D4326, and wherein the expanded base-acid ratio is selected from about 0.05 to about 8.

**[0033]** In some embodiments, the expanded base-acid ratio is selected from about 0.1 to about 0.4, or from about 0.5 to about 10, or from about 0.8 to about 10, or from about 1.5 to about 5, or from about 0.4 to about 0.7. In certain embodiments, the expanded base-acid ratio is at most 0.4 or at least 0.7.

**[0034]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is characterized by an iron-calcium ratio defined by the $Fe_2O_3$ divided by the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the iron-calcium ratio is selected from about 0.05 to about 5. The iron-calcium ratio can be selected from about 0.1 to about 2, or from about 0.3 to about 1, for example. In certain embodiments, the iron-calcium ratio is at most 0.3 or at least 3.

**[0035]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is characterized by an iron-plus-calcium parameter defined as the sum of the $Fe_2O_3$ and the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the iron-plus-calcium parameter is selected from about 5 wt% to about 50 wt%. The iron-plus-calcium parameter can be selected from about 10 wt% to about 40 wt%, or from about 20 wt% to about 50 wt%, for example. In certain embodiments, the iron-plus-calcium parameter is at most 10 wt%. In other embodiments, the iron-plus-calcium parameter is at least 10 wt%.

**[0036]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is characterized by a slagging factor defined as the base-acid ratio multiplied by weight percentage of sulfur present in the biocarbon composition on a dry basis, and wherein the slagging factor is selected from about 0.001 to about 1. The slagging factor can be selected from about 0.01 to about 0.5, or from about 0.01 to about 0.1, for example. In certain embodiments, the slagging factor is at most 0.6.

**[0037]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is characterized by a fouling factor defined as the base-acid ratio multiplied by the $Na_2O$ as weight percentage in the

biocarbon composition pursuant to ASTM D4326, and wherein the fouling factor is selected from about 0.1 to about 10. The fouling factor can be at most 2 or at most 1, for example.

**[0038]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is characterized by a modified fouling factor defined as the base-acid ratio multiplied by water-soluble $Na_2O$, wherein the water-soluble $Na_2O$ is weight percentage of $Na_2O$ that leaches, in the presence of water, out of ash derived from the biocarbon composition pursuant to ASTM D4326, and wherein the modified fouling factor is selected from about 0.1 to about 10. The modified fouling factor can be at most 2 or at most 1, for example.

**[0039]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is characterized by a silica percentage defined as weight percentage of the $SiO_2$ in the biocarbon composition pursuant to ASTM D4326, wherein the silica percentage is selected from about 5 wt% to about 50 wt%. The silica percentage can be selected from about 10 wt% to about 30 wt%, for example.

**[0040]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition comprises at most 100 ppm mercury, or comprises at most 10 ppm mercury, or can be essentially free of mercury.

**[0041]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition comprises from about 50 wt% to about 99 wt% fixed carbon on a dry basis. In certain embodiments, the biocarbon composition comprises at least about 75 wt% fixed carbon or at least about 90 wt% fixed carbon on a dry basis.

**[0042]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the 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. The total carbon within the biocarbon composition can be at least 99% 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.

**[0043]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is in the form of a pellet. The pellet optionally comprises a binder.

**[0044]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is in the form of a powder. The powder can be a loose powder, a compacted powder, a granulated powder, or another form of powder.

**[0045]** Any of the disclosed biocarbon compositions can further comprise an additive, wherein the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0046]** Some variations of the invention provide a process for producing a biocarbon composition with an optimized base-acid ratio, the process comprising:

(a) providing a starting feedstock comprising biomass, wherein the starting feedstock is optionally dried;

(b) pyrolyzing the starting feedstock to generate an intermediate biocarbon stream and a pyrolysis vapor, wherein the intermediate biocarbon stream is characterized by a base-acid ratio defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages pursuant to ASTM D4326;

(c) washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, to adjust the base-acid

ratio; and/or introducing an additive during step (a) or step (b), to adjust the base-acid ratio; and

(d) recovering a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, and wherein the base-acid ratio of the biocarbon composition is selected from about 0.1 to about 10.

**[0047]** In some processes, the biomass 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.

**[0048]** In some embodiments, step (c) selectively removes basic components, thereby reducing the $Fe_2O_3$, the CaO, the MgO, the $K_2O$, or the $Na_2O$.

**[0049]** In some embodiments, step (c) utilizes acidic water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c). For example, acidic water can be obtained from condensation of the pyrolysis vapor to generate a condensed liquid having a pH from about 1 to about 7.

**[0050]** In some embodiments, step (c) selectively removes acidic components, thereby reducing the $SiO_2$, the $Al_2O_3$, or the $TiO_2$.

**[0051]** In some embodiments, step (c) utilizes alkaline water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c).

**[0052]** In some embodiments, step (c) utilizes steam cleaning of the intermediate biocarbon stream. Alternatively, or additionally, step (d) can utilize steam cleaning of the biocarbon composition.

**[0053]** In some processes, step (c) is conducted. In some processes, step (d) is conducted. In certain processes, steps (c) and (d) are both conducted.

**[0054]** When step (d) is employed, the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0055]** In some processes, the biocarbon composition has a higher heating value of at least about 25 MJ/kg on a dry basis.

**[0056]** The biocarbon composition can be pelletized to produce biocarbon pellets. A binder can be utilized to assist in pelletizing. A binder can be 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, derivatives thereof, or a combination or a derivative thereof.

**[0057]** In some processes, the base-acid ratio is optimized to be from about 0.1 to about 0.4, or from about 0.5 to about 10, or from about 0.8 to about 10, or from about 1.5 to about 5, or from about 0.4 to about 0.7. In certain embodiments, the base-acid ratio is optimized to be at most 0.4 or at least 0.7.

**[0058]** Some variations of the invention provide a process for producing a biocarbon composition with an optimized expanded base-acid ratio, the process comprising:

(a) providing a starting feedstock comprising biomass, wherein the starting feedstock is optionally dried;

(b) pyrolyzing the starting feedstock to generate an intermediate biocarbon stream and a pyrolysis vapor, wherein the intermediate biocarbon stream is characterized by an expanded base-acid ratio defined by the following formula:

$$\text{Expanded Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O + MnO + SrO + BaO}{SiO_2 + Al_2O_3 + TiO_2 + P_2O_5 + SO_3}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, MnO, SrO, BaO, $SiO_2$, $Al_2O_3$, $TiO_2$, $P_2O_5$, and $SO_3$ correspond to weight percentages pursuant to ASTM D4326;

(c) washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, to adjust the base-acid ratio; and/or introducing an additive during step (a) or step (b), to adjust the base-acid ratio; and

(d) recovering a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, and wherein the expanded base-acid ratio of the biocarbon composition is selected from about 0.05 to about 8.

**[0059]** In some processes in which the expanded base-acid ratio is optimized, step (c) selectively removes basic components, thereby reducing the $Fe_2O_3$, the CaO, the MgO, the $K_2O$, or the $Na_2O$.

**[0060]** In some processes in which the expanded base-acid ratio is optimized, step (c) utilizes acidic water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c). For example, acidic water can be obtained from condensation of the pyrolysis vapor to generate a condensed liquid having a pH from about 1 to about 7.

**[0061]** In some processes in which the expanded base-acid ratio is optimized, step (c) selectively removes acidic components, thereby reducing the $SiO_2$, the $Al_2O_3$, or the $TiO_2$.

**[0062]** In some processes in which the expanded base-acid ratio is optimized, step (c) utilizes alkaline water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c).

**[0063]** In some processes in which the expanded base-acid ratio is optimized, step (c) utilizes steam cleaning of the intermediate biocarbon stream. Alternatively, or additionally, step (d) can utilize steam cleaning of the biocarbon composition.

**[0064]** In some processes in which the expanded base-acid ratio is optimized, step (c) is conducted. In some processes in which the expanded base-acid ratio is optimized, step (d) is conducted. In certain processes, steps (c) and (d) are both conducted.

**[0065]** When step (d) is employed, the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0066]** In some processes in which the expanded base-acid ratio is optimized, the biocarbon composition has a higher heating value of at least about 25 MJ/kg on a dry basis.

**[0067]** The biocarbon composition can be pelletized to produce biocarbon pellets. A binder can be utilized to assist in pelletizing.

**[0068]** In some processes, the expanded base-acid ratio is optimized to be from about 0.1 to about 0.4, or from about 0.5 to about 10, or from about 0.8 to about 10, or from about 1.5 to about 5, or from about 0.4 to about 0.7. In certain embodiments, the expanded base-acid ratio is optimized to be at most 0.4 or at least 0.7.

**[0069]** In any of the processed disclosed, the biocarbon composition can be characterized by an iron-calcium ratio defined by the $Fe_2O_3$ divided by the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, wherein

the iron-calcium ratio of the biocarbon composition is selected from about 0.05 to about 5.

**[0070]** Some variations provide a process for producing a biocarbon composition with an optimized iron-calcium ratio, the process comprising:

(a) providing a starting feedstock comprising biomass, wherein the starting feedstock is optionally dried;

(b) pyrolyzing the starting feedstock to generate an intermediate biocarbon stream and a pyrolysis vapor, wherein the intermediate biocarbon stream is characterized by an iron-calcium ratio defined by the $Fe_2O_3$ divided by the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326;

(c) washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, to adjust the iron-calcium ratio; and/or introducing an additive during step (a) or step (b), to adjust the iron-calcium ratio; and

(d) recovering a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, and wherein the iron-calcium ratio of the biocarbon composition is selected from about 0.05 to about 5.

**[0071]** In some processes in which the iron-calcium ratio is optimized, step (c) selectively removes basic components, thereby reducing the $Fe_2O_3$, the CaO, the MgO, the $K_2O$, or the $Na_2O$.

**[0072]** In some processes in which the iron-calcium ratio is optimized, step (c) utilizes acidic water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c). For example, acidic water can be obtained from condensation of the pyrolysis vapor to generate a condensed liquid having a pH from about 1 to about 7.

**[0073]** In some processes in which the iron-calcium ratio is optimized, step (c) selectively removes acidic components, thereby reducing the $SiO_2$, the $Al_2O_3$, or the $TiO_2$.

**[0074]** In some processes in which the iron-calcium ratio is optimized, step (c) utilizes alkaline water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c).

**[0075]** In some processes in which the iron-calcium ratio is optimized, step (c) utilizes steam cleaning of the intermediate biocarbon stream. Alternatively, or additionally, step (d) can utilize steam cleaning of the biocarbon composition.

**[0076]** In some processes in which the iron-calcium ratio is optimized, step (c) is conducted. In some processes in which the iron-calcium ratio is optimized, step (d) is conducted. In certain processes, steps (c) and (d) are both conducted.

**[0077]** When step (d) is employed, the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0078]** In some processes in which the iron-calcium ratio is optimized, the biocarbon composition has a higher heating value of at least about 25 MJ/kg on a dry basis.

**[0079]** The biocarbon composition can be pelletized to produce biocarbon pellets. A binder can be utilized to assist in pelletizing.

**[0080]** In some processes, the iron-plus-calcium parameter is optimized to be from about 10 wt% to about 40 wt%, or from about 20 wt% to about 50 wt%. In certain embodiments, the iron-plus-calcium parameter is optimized to be at most 10 wt%. In other embodiments, the iron-plus-calcium parameter is optimized to be at least 10 wt%.

**[0081]** In any of the processed disclosed above, the biocarbon composition can be characterized by an iron-plus-calcium parameter defined as the sum of the $Fe_2O_3$ and the CaO, each as weight percentages in the biocarbon composition pursuant to

ASTM D4326, wherein the iron-plus-calcium parameter of the biocarbon composition is selected from 5 wt% to about 50 wt%.

**[0082]** Some variations provide a process for producing a biocarbon composition with an optimized iron-plus-calcium parameter, the process comprising:

(a) providing a starting feedstock comprising biomass, wherein the starting feedstock is optionally dried;

(b) pyrolyzing the starting feedstock to generate an intermediate biocarbon stream and a pyrolysis vapor, wherein the intermediate biocarbon stream is characterized by an iron-plus-calcium parameter defined as the sum of the $Fe_2O_3$ and the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326;

(c) washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, to adjust the iron-plus-calcium parameter; and/or introducing an additive during step (a) or step (b), to adjust the iron-plus-calcium parameter; and

(d) recovering a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, and wherein the iron-plus-calcium parameter of the biocarbon composition is selected from 5 wt% to about 50 wt%.

**[0083]** In some processes in which the iron-plus-calcium parameter is optimized, step (c) selectively removes basic components, thereby reducing the $Fe_2O_3$, the CaO, the MgO, the $K_2O$, or the $Na_2O$.

**[0084]** In some processes in which the iron-plus-calcium parameter is optimized, step (c) utilizes acidic water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c). For example, acidic water can be obtained from condensation of the pyrolysis vapor to generate a condensed liquid having a pH from about 1 to about 7.

**[0085]** In some processes in which the iron-plus-calcium parameter is optimized, step (c) selectively removes acidic components, thereby reducing the $SiO_2$, the $Al_2O_3$, or the $TiO_2$.

**[0086]** In some processes in which the iron-plus-calcium parameter is optimized, step (c) utilizes alkaline water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c).

**[0087]** In some processes in which the iron-plus-calcium parameter is optimized, step (c) utilizes steam cleaning of the intermediate biocarbon stream. Alternatively, or additionally, step (d) can utilize steam cleaning of the biocarbon composition.

**[0088]** In some processes in which the iron-plus-calcium parameter is optimized, step (c) is conducted. In some processes in which the iron-plus-calcium parameter is optimized, step (d) is conducted. In certain processes, steps (c) and (d) are both conducted.

**[0089]** When step (d) is employed, the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0090]** In some processes in which the iron-plus-calcium parameter is optimized, the biocarbon composition has a higher heating value of at least about 25 MJ/kg on a dry basis.

**[0091]** The biocarbon composition can be pelletized to produce biocarbon pellets. A binder can be utilized to assist in pelletizing.

**[0092]** In some processes, the iron-plus-calcium parameter is optimized to be from about 10 wt% to about 40 wt%, or from about 20 wt% to about 50 wt%. In certain embodiments, the iron-plus-calcium parameter is optimized to be at most 10 wt%. In other embodiments, the iron-plus-calcium parameter is optimized to be at least 10 wt%.

**[0093]** In any of the processed disclosed above, the biocarbon composition can be characterized by a slagging factor defined as a base-acid ratio multiplied by weight

percentage of sulfur present in the biocarbon composition on a dry basis, wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the slagging factor of the biocarbon composition is selected from about 0.001 to about 1.

**[0094]** Some variations provide a process for producing a biocarbon composition with an optimized slagging factor, the process comprising:

(a) providing a starting feedstock comprising biomass, wherein the starting feedstock is optionally dried;

(b) pyrolyzing the starting feedstock to generate an intermediate biocarbon stream and a pyrolysis vapor, wherein the intermediate biocarbon stream is characterized by a slagging factor defined as a base-acid ratio multiplied by weight percentage of sulfur present in the biocarbon composition on a dry basis;

wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326;

(c) washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, to adjust the slagging factor; and/or introducing an additive during step (a) or step (b), to adjust the slagging factor; and

(d) recovering a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, and wherein the slagging factor of the biocarbon composition is selected from about 0.001 to about 1.

**[0095]** In some processes in which the slagging factor is optimized, step (c) selectively removes basic components, thereby reducing the $Fe_2O_3$, the CaO, the MgO, the $K_2O$, or the $Na_2O$.

**[0096]** In some processes in which the slagging factor is optimized, step (c) utilizes acidic water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c). For example, acidic water can be obtained from condensation of the pyrolysis vapor to generate a condensed liquid having a pH from about 1 to about 7.

**[0097]** In some processes in which the slagging factor is optimized, step (c) selectively removes acidic components, thereby reducing the $SiO_2$, the $Al_2O_3$, or the $TiO_2$.

**[0098]** In some processes in which the slagging factor is optimized, step (c) utilizes alkaline water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c).

**[0099]** In some processes in which the slagging factor is optimized, step (c) utilizes steam cleaning of the intermediate biocarbon stream. Alternatively, or additionally, step (d) can utilize steam cleaning of the biocarbon composition.

**[0100]** In some processes in which the slagging factor is optimized, step (c) is conducted. In some processes in which the slagging factor is optimized, step (d) is conducted. In certain processes, steps (c) and (d) are both conducted.

**[0101]** When step (d) is employed, the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0102]** In some processes in which the slagging factor is optimized, the biocarbon composition has a higher heating value of at least about 25 MJ/kg on a dry basis.

**[0103]** The biocarbon composition can be pelletized to produce biocarbon pellets. A binder can be utilized to assist in pelletizing.

**[0104]** In some processes, the slagging factor is optimized to be from about 0.01 to about 0.5, or from about 0.01 to about 0.1. In certain embodiments, the slagging factor is optimized to be at most 0.6, such as about, or below about, 0.5, 0.4, 0.3, 0.2, 0.1, 0.05, 0.04, 0.03, 0.02, 0.01, 0.005, 0.002, or 0.001.

**[0105]** In any of the processed disclosed above, the biocarbon composition can be characterized by a fouling factor defined as a base-acid ratio multiplied by the $Na_2O$ as weight percentage in the biocarbon composition pursuant to ASTM D4326, wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the fouling factor of the biocarbon composition is selected from about 0.1 to about 10.

**[0106]** Some variations provide a process for producing a biocarbon composition with an optimized fouling factor, the process comprising:

(a) providing a starting feedstock comprising biomass, wherein the starting feedstock is optionally dried;

(b) pyrolyzing the starting feedstock to generate an intermediate biocarbon stream and a pyrolysis vapor, wherein the intermediate biocarbon stream is characterized by a fouling factor defined as a base-acid ratio multiplied by the $Na_2O$ as weight percentage in the biocarbon composition pursuant to ASTM D4326;

wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326;

(c) washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, to adjust the fouling factor; and/or introducing an additive during step (a) or step (b), to adjust the fouling factor; and

(d) recovering a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, and wherein the fouling factor of the biocarbon composition is selected from about 0.1 to about 10.

**[0107]** In some processes in which the fouling factor is optimized, step (c) selectively removes basic components, thereby reducing the $Fe_2O_3$, the CaO, the MgO, the $K_2O$, or the $Na_2O$.

**[0108]** In some processes in which the fouling factor is optimized, step (c) utilizes acidic water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c). For example, acidic water can be obtained from condensation of the pyrolysis vapor to generate a condensed liquid having a pH from about 1 to about 7.

**[0109]** In some processes in which the fouling factor is optimized, step (c) selectively removes acidic components, thereby reducing the $SiO_2$, the $Al_2O_3$, or the $TiO_2$.

**[0110]** In some processes in which the fouling factor is optimized, step (c) utilizes alkaline water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c).

**[0111]** In some processes in which the fouling factor is optimized, step (c) utilizes steam cleaning of the intermediate biocarbon stream. Alternatively, or additionally, step (d) can utilize steam cleaning of the biocarbon composition.

**[0112]** In some processes in which the fouling factor is optimized, step (c) is conducted. In some processes in which the fouling factor is optimized, step (d) is conducted. In certain processes, steps (c) and (d) are both conducted.

**[0113]** When step (d) is employed, the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum,

nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0114]** In some processes in which the fouling factor is optimized, the biocarbon composition has a higher heating value of at least about 25 MJ/kg on a dry basis.

**[0115]** The biocarbon composition can be pelletized to produce biocarbon pellets. A binder can be utilized to assist in pelletizing.

**[0116]** In some processes, the fouling factor is optimized to be at most 2. In certain embodiments, the fouling factor is optimized to be at most 1, such as about, or below about, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1.

**[0117]** In any of the processed disclosed above, the biocarbon composition can be characterized by a modified fouling factor defined as a base-acid ratio multiplied by water-soluble $Na_2O$, wherein the water-soluble $Na_2O$ is weight percentage of $Na_2O$ that leaches, in the presence of water, out of ash derived from the biocarbon composition pursuant to ASTM D4326, wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the fouling factor of the biocarbon composition is selected from about 0.1 to about 10.

**[0118]** Some variations provide a process for producing a biocarbon composition with an optimized modified fouling factor, the process comprising:

(a) providing a starting feedstock comprising biomass, wherein the starting feedstock is optionally dried;

(b) pyrolyzing the starting feedstock to generate an intermediate biocarbon stream and a pyrolysis vapor, wherein the intermediate biocarbon stream is characterized by a modified fouling factor a base-acid ratio multiplied by water-soluble $Na_2O$, wherein the water-soluble $Na_2O$ is weight percentage of $Na_2O$ that leaches, in the presence of water, out of ash derived from the biocarbon composition pursuant to ASTM D4326;

wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326;

(c) washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, to adjust the modified fouling factor; and/or introducing an additive during step (a) or step (b), to adjust the modified fouling factor; and

(d) recovering a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, and wherein the modified fouling factor of the biocarbon composition is selected from about 0.1 to about 10.

**[0119]** In some processes in which the modified fouling factor is optimized, step (c) selectively removes basic components, thereby reducing the $Fe_2O_3$, the CaO, the MgO, the $K_2O$, or the $Na_2O$.

**[0120]** In some processes in which the modified fouling factor is optimized, step (c) utilizes acidic water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c). For example, acidic water can be obtained from condensation of the pyrolysis vapor to generate a condensed liquid having a pH from about 1 to about 7.

**[0121]** In some processes in which the modified fouling factor is optimized, step (c) selectively removes acidic components, thereby reducing the $SiO_2$, the $Al_2O_3$, or the $TiO_2$.

**[0122]** In some processes in which the modified fouling factor is optimized, step (c) utilizes alkaline water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c).

**[0123]** In some processes in which the modified fouling factor is optimized, step (c) utilizes steam cleaning of the intermediate biocarbon stream. Alternatively, or additionally, step (d) can utilize steam cleaning of the biocarbon composition.

**[0124]** In some processes in which the modified fouling factor is optimized, step (c) is conducted. In some processes in which the modified fouling factor is optimized, step (d) is conducted. In certain processes, steps (c) and (d) are both conducted.

**[0125]** When step (d) is employed, the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0126]** In some processes in which the modified fouling factor is optimized, the biocarbon composition has a higher heating value of at least about 25 MJ/kg on a dry basis.

**[0127]** The biocarbon composition can be pelletized to produce biocarbon pellets. A binder can be utilized to assist in pelletizing.

**[0128]** In some processes, the modified fouling factor is optimized to be at most 2. In certain embodiments, the modified fouling factor is optimized to be at most 1, such as about, or below about, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0129]** FIG. 1 is a photograph of an exemplary biocarbon composition with an optimized base-acid ratio, in the form of biocarbon pellets.

**[0130]** FIG. 2 is a photograph of an exemplary biocarbon composition with an optimized base-acid ratio, in the form of biocarbon powder.

**[0131]** FIG. 3 is a simplified block-flow diagram of a process for converting a biomass feedstock into a biocarbon composition with an optimized base-acid ratio, in some embodiments. Dotted lines denote optional streams and units.

**[0132]** FIG. 4 is a simplified block-flow diagram of a process for converting a biomass feedstock into a biocarbon composition with an optimized enhanced base-acid ratio, in some embodiments. Dotted lines denote optional streams and units.

**[0133]** FIG. 5 is a data sheet showing composition, base-acid ratio, and other properties for the biocarbon composition of Example 1.

**[0134]** FIG. 6 is a data sheet showing composition, base-acid ratio, and other properties for the biocarbon composition of Example 2.

**[0135]** FIG. 7 is a data sheet showing composition, base-acid ratio, and other properties for the biocarbon composition of Example 3.

**[0136]** FIG. 8 is a data sheet showing composition, base-acid ratio, and other properties for the biocarbon composition of Example 4.

**[0137]** FIG. 9 is a data sheet showing composition (from which the base-acid ratio can be calculated) and other properties for the biocarbon composition of Example 5.

**[0138]** FIG. 10 is a data sheet showing composition, base-acid ratio, and other properties for the biocarbon composition of Example 6.

## DETAILED DESCRIPTION

**[0139]** 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.

**[0140]** 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.

**[0141]** 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.

**[0142]** The term "comprising," which is synonymous with "including," "comprising," 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.

**[0143]** 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.

**[0144]** 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.

**[0145]** For present purposes, "biogenic" is intended to mean a material (whether a feedstock, product, or intermediate) that comprises 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. Note that a biogenic material can include a mixture of biogenic and non-biogenic sources.

**[0146]** 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. In some embodiments, a reagent is a chemical reactant; in some embodiments, a reagent is 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.

**[0147]** In this disclosure, a "product" can be a composition, a material, an object, or a structure, for example. The term "product" shall not be limited by its commercial fate, such as whether it is sold, stored, traded, further processed, sold to another party as an intermediate for further processing, etc.

**[0148]** As used herein, "high-carbon," as describing biogenic reagents, means that the biogenic reagent has a high carbon content as compared to the initial feedstock utilized to produce the high-carbon biogenic reagent. A high-carbon biogenic reagent can comprise at least about half its weight as carbon. More typically, a high-carbon biogenic reagent will comprise at least 55 wt%, 60 wt%, 65 wt%, or 70 wt% carbon.

**[0149]** As used herein, the term "high-carbon biogenic reagent" describes materials that can be produced by processes and systems as disclosed herein, 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. For example it will be appreciated that a starting material having very low carbon content, subjected to the disclosed processes, can produce a high-carbon biogenic reagent that is highly enriched in carbon relative to the starting material (high yield of carbon), but nevertheless relatively low in carbon (low purity of carbon), including at most 50 wt% carbon.

**[0150]** There exist a variety of technologies to convert biomass feedstocks to high-carbon materials. Pyrolysis is a process for thermal conversion of solid materials in the complete absence of oxidizing agent (e.g., air or oxygen), or with such limited supply of

oxidant 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.

**[0151]** In many industrial applications, it is desirable to replace coal by providing biocarbon compositions derived from biomass pyrolysis. Like coal, a biocarbon product is rarely pure carbon. Many other components are typically present, including various metals. Reference to "ash" is really reference to the material remaining after combustion, which material itself comprises many individual components.

**[0152]** In this disclosure, a "compositional parameter" is any parameter that is a function of the biocarbon composition or correlates with the biocarbon composition. In some embodiments, a compositional parameter is determined according to ASTM D4326 and equations with inputs from the ASTM D4326 results.

**[0153]** The prior art does not teach biocarbon compositions with compositional parameters that are optimized for specific applications, and does not teach which compositional parameters might be important for various applications. An important compositional parameter is the base-acid ration which will now be described in detail.

**[0154]** In some variations, the present invention provides a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by a base-acid ratio defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the base-acid ratio is selected from about 0.1 to about 10.

**[0155]** In some embodiments, the base-acid ratio is selected from about 0.1 to about 0.4, or from about 0.5 to about 10, or from about 0.8 to about 10, or from about 1.5 to about 5, or from about 0.4 to about 0.7. In certain embodiments, the base-acid ratio is at most 0.4 or at least 0.7.

**[0156]** Note that the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ concentrations are those in the ash fraction following sample combustion, pursuant to ASTM D4326-13 "Standard Test Method for Major and Minor Elements by XRF", which is hereby incorporated by reference in its entirety and is referred to herein as "ASTM D4326".

**[0157]** It is not necessary that all of $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ be present in the ash of the biocarbon composition. However, in order to have a non-zero and finite base-acid ratio, there must be a detectible amount (according to ASTM D4326) of at least one of $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, as well as at least one of $SiO_2$, $Al_2O_3$, and $TiO_2$.

**[0158]** ASTM D4326 is a test method for the analysis of the commonly determined major and minor elements in ash from a carbon sample using X-ray fluorescence (XRF) techniques. The carbon to be analyzed is ashed under standard conditions and ignited to constant weight. Previously ashed materials are ignited to constant weight under standard conditions. The ash is fused with lithium tetraborate ($Li_2B_4O_7$) or other suitable flux and either ground and pressed into a pellet or cast into a glass disk. The pellet or disk is then irradiated by an X-ray beam of short wavelength. The characteristic X-rays that are emitted or fluoresced upon absorption of the primary or incident X-rays are dispersed, and intensities at selected wavelengths are measured by sensitive detectors. Detector output is related to concentration by calibration curves or computer algorithms. The K spectral lines are used for all of the elements determined by this procedure. All elements are determined as the element and reported as the oxide. The analyzed elements include Si, Al, Fe, Ca, Mg, Na, K, P, Ti, Mn, Sr, and Ba. A compositional analysis of ash is used in describing the quality of biocarbon for its complete characterization. Ash composition is useful in predicting slagging and fouling

characteristics as well as in assessing the potential utilization in various commercial applications.

**[0159]** Importantly, a determination of a component in the formula for base-acid ratio according to ASTM D4326 does not mean that such component is actually present as the specific oxide in the biocarbon composition, although the presence as that specific oxide is not precluded. For example, in the case of CaO which is returned from the ASTM D4326 analysis, the final calcium atoms may have been actually present in the starting biocarbon composition as pure calcium atoms (Ca), calcium oxide (CaO), calcium carbonate ($CaCO_3$), calcium hydroxide ($Ca(OH)_2$), calcium carbide ($CaC_2$), calcium hydride ($CaH_2$), free or loosely bonded calcium cations ($Ca^{2+}$), ionically bonded calcium cations ($Ca^{2+}$) such as in ionic crosslink bonds with other components, other forms of calcium, or a combination thereof. During the ASTM D4326 test protocol, Ca is oxidized to CaO, $CaCO_3$ is thermally decomposed to CaO, and so on.

**[0160]** Optionally, a separate analysis of the biocarbon composition may be performed to determine the exact atoms and molecules in the biocarbon composition. The separate analysis may employ atomic absorption spectroscopy, atomic emission spectroscopy, inductively coupled plasma mass spectrometry, inductively coupled plasma optical emission spectroscopy, or X-ray absorption fine structure spectroscopy, for example.

**[0161]** In some embodiments, the biocarbon composition described above is further characterized by an iron-calcium ratio defined by the $Fe_2O_3$ divided by the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, wherein the iron-calcium ratio is selected from about 0.05 to about 5.

**[0162]** The present invention also provides a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by an iron-calcium ratio defined by the $Fe_2O_3$ divided by the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the iron-calcium ratio is selected from about 0.05 to about 5.

**[0163]** In some embodiments, the iron-calcium ratio is selected from about 0.1 to about 2, or from about 0.3 to about 1. In certain embodiments, the iron-calcium ratio is

at most 0.3 or at least 3. In various embodiments, the iron-calcium ratio is about, at least about, or at most about 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.5, 2, 2.5, 3, 3.1, 3.2, 3.3, 3.4, 3.5, 4, 4.5, or 5, including all intervening ranges.

**[0164]** In some embodiments, the biocarbon composition described above is further characterized by an iron-plus-calcium parameter defined as the sum of the $Fe_2O_3$ and the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the iron-plus-calcium parameter is selected from about 5 wt% to about 50 wt%. In various embodiments, the iron-plus-calcium parameter is about, at least about, or at most about 5, 10, 15, 20, 25, 30, 35, 40, 45, or 50 wt%, including all intervening ranges.

**[0165]** The present invention also provides a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by an iron-plus-calcium parameter defined as the sum of the $Fe_2O_3$ and the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the iron-plus-calcium parameter is selected from about 5 wt% to about 50 wt%.

**[0166]** In some embodiments, the iron-plus-calcium parameter is selected from about 10 wt% to about 40 wt%, or from about 20 wt% to about 50 wt%. In certain embodiments, the iron-plus-calcium parameter is at most 10 wt%. In other embodiments, the iron-plus-calcium parameter is at least 10 wt%.

**[0167]** In some embodiments, the biocarbon composition described above is further characterized by a slagging factor defined as a base-acid ratio multiplied by weight percentage of sulfur present in the biocarbon composition on a dry basis, wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the slagging factor is selected from about 0.001 to about 1.

**[0168]** The present invention also provides a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by a slagging factor defined as a base-acid ratio multiplied by weight percentage of sulfur present in the biocarbon composition on a dry basis, wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the slagging factor is selected from about 0.001 to about 1.

**[0169]** In some embodiments, the slagging factor is selected from about 0.01 to about 0.5, or from about 0.01 to about 0.1. In certain embodiments, the slagging factor is at most 0.6. In various embodiments, the slagging factor is about, at least about, or at most about 0.001, 0.002, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.9, 0.95, or 1, including all intervening ranges.

**[0170]** In some embodiments, the biocarbon composition described above is further characterized by a fouling factor defined as a base-acid ratio multiplied by the $Na_2O$ as weight percentage in the biocarbon composition pursuant to ASTM D4326, wherein the base-acid ratio defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the fouling factor is selected from about 0.1 to about 10.

**[0171]** The present invention also provides a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by a fouling factor defined as a base-acid ratio multiplied by the $Na_2O$ as weight percentage in the

biocarbon composition pursuant to ASTM D4326, wherein the base-acid ratio defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the fouling factor is selected from about 0.1 to about 10.

**[0172]** In some embodiments, the fouling factor is at most 2. In certain embodiments, the fouling factor is at most 1. Typically, a low fouling factor is desirable. However, in certain embodiments, a moderate or even high fouling factor is beneficial to form alkali-bonded deposits, such as when fabricating alkali-comprising composites. In various embodiments, the fouling factor is about, at least about, or at most about 0.1, 0.2, 0.5, 0.6, 0.7, 0.75, 0.8, 0.85, 0.9, 1, 1.2, 1.5, 1.8, 2, 2.5, 3, 3.5, 4, 5, 6, 7, 8, 9, or 10, including all intervening ranges.

**[0173]** In some embodiments, the biocarbon composition described above is further characterized by a modified fouling factor defined as a base-acid ratio multiplied by water-soluble $Na_2O$, wherein the water-soluble $Na_2O$ is weight percentage of $Na_2O$ that leaches, in the presence of water, out of ash derived from the biocarbon composition pursuant to ASTM D4326, wherein the base-acid ratio defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the modified fouling factor is selected from about 0.1 to about 10.

**[0174]** The present invention also provides a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by a modified fouling factor defined as a base-acid ratio multiplied by water-soluble $Na_2O$, wherein the water-soluble $Na_2O$ is weight percentage of $Na_2O$ that leaches, in the presence of water, out

of ash derived from the biocarbon composition pursuant to ASTM D4326, wherein the base-acid ratio defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the modified fouling factor is selected from about 0.1 to about 10.

**[0175]** In some embodiments, the modified fouling factor is at most 2. In certain embodiments, the modified fouling factor is at most 1. In various embodiments, the modified fouling factor is about, at least about, or at most about 0.1, 0.2, 0.5, 0.6, 0.7, 0.75, 0.8, 0.85, 0.9, 1, 1.2, 1.5, 1.8, 2, 2.5, 3, 3.5, 4, 5, 6, 7, 8, 9, or 10, including all intervening ranges.

**[0176]** In some embodiments, the biocarbon composition described above is further characterized by an equilibrium moisture content according to ASTM D1412. The equilibrium moisture can be from about 0.1 wt% to about 10 wt%, such as about, at least about, or at most about 0.1, 0.2, 0.5, 0.8, 1, 1.2, 1.5, 2, 2.5, 2.6, 2.7, 2.8, 2.9, 3, 3.1, 3.2, 3.3, 3.4, 3.5, 4, 4.5, 5, 6, 7, 8, 9, or 10 wt%, including all intervening ranges.

**[0177]** In some embodiments, the biocarbon composition described above is further characterized by a silica percentage defined as weight percentage of the $SiO_2$ in the biocarbon composition pursuant to ASTM D4326, wherein the silica percentage is selected from about 5 wt% to about 50 wt%. Note that the silica percentage is $SiO_2$ concentration in the ash (ashing test under ASTM D4326), not in the original biocarbon composition. In certain embodiments, the silica percentage is selected from about 10 wt% to about 30 wt%. In various embodiments, the silica percentage is about, at least about, or at most about 5, 10, 15, 20, 25, 30, 35, 40, 45, or 50 wt%, including all intervening ranges.

**[0178]** In some embodiments, the biocarbon composition described above is further characterized by a low mercury content. The biocarbon composition can comprise at most 100 ppm mercury (ppm = parts per million on weight basis), at most 10 ppm mercury, or can be essentially free of mercury. By "essentially free of mercury" it is meant that Hg or Hg-comprising compounds are either absolutely zero (not present)

or are below the detection limit of mercury when a sample is analyzed according to ASTM D6414-14, which is hereby incorporated by reference. In various embodiments, the biocarbon composition comprises at most about 200, 150, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 5, 4, 3, 2, 1, 0.5, 0.2, or 0.1 ppm mercury.

**[0179]** The biocarbon composition can comprise from about 50 wt% to about 99 wt% fixed carbon on a dry basis. In some embodiments, the biocarbon composition comprises at least about 75 wt% fixed carbon or at least about 90 wt% fixed carbon on a dry basis.

**[0180]** In some embodiments, the 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. The total carbon within the biocarbon composition can be at least 99% 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. Note that total carbon within a biocarbon composition includes not only carbon derived from cellulose, hemicellulose, and lignin, but also carbon (if any) contained in other components present, such as metal carbonates (e.g., calcium carbonate).

**[0181]** In some embodiments, the *fixed* carbon within the biocarbon composition is at least 80% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the fixed carbon. The fixed 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 fixed carbon. The fixed carbon within the biocarbon composition can be at least 95% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the fixed carbon.

**[0182]** In certain embodiments, the biocarbon composition is in the form of a pellet with a binder, and the binder comprises non-renewable carbon and the rest of the pellet comprises at least 50%, at least 90%, at least 95%, or 100% renewable carbon.

**[0183]** The biocarbon composition may be in the form of a pellet. FIG. 1 is a photograph of an exemplary biocarbon composition with an optimized base-acid ratio, in the form of biocarbon pellets.

**[0184]** In certain embodiments, the biocarbon composition is in the form of a pellet with a binder, and the binder comprises carbon that is at least 50%, at least 90%, at least 95%, or 100% renewable carbon. The remainder of the pellet (i.e., not the binder) comprises at least 50%, at least 90%, at least 95%, or 100% renewable carbon. In some embodiments, all the carbon is fully renewable.

**[0185]** In certain embodiments, the biocarbon composition includes an additive, and the additive comprises non-renewable carbon but the rest of the pellet comprises at least 50%, at least 90%, at least 95%, or 100% renewable carbon.

**[0186]** In certain embodiments, the biocarbon composition includes an additive, and the additive comprises carbon that is at least 50%, at least 90%, at least 95%, or 100% renewable carbon. The remainder of the composition (i.e., not the additive) comprises at least 50%, at least 90%, at least 95%, or 100% renewable carbon. In some embodiments, all the carbon is fully renewable.

**[0187]** In this disclosure, 100% or "fully" renewable carbon allows for very minor adsorbed atmospheric $CO_2$ molecules that can have been derived from fossil fuels.

**[0188]** The biocarbon composition can be in the form of a pellet. The pellet can comprise a binder. The binder can be 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, or a combination or a derivative thereof. In some embodiments, the biocarbon pellet does not comprise an externally added binder.

**[0189]** When there is an organic or inorganic binder, the base-acid ratio and other compositional parameters are based on the total material including the binder. For example, when a composition parameter is derived from ASTM D4326, the entire pellet is ashed.

**[0190]** The biocarbon composition can be in the form of a powder, which can be a loose powder, a compacted powder, a granulated powder, or other form. FIG. 2 is a photograph of an exemplary biocarbon composition with an optimized base-acid ratio, in the form of biocarbon powder.

**[0191]** When there is an organic or inorganic additive in the biocarbon composition, the base-acid ratio and other compositional parameters are based on the total material including the additive. For example, when a composition parameter is derived from ASTM D4326, the entire sample is ashed.

**[0192]** In some embodiments, the biocarbon composition described above is further characterized by an expanded base-acid ratio defined by the following formula:

$$\text{Expanded Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O + MnO + SrO + BaO}{SiO_2 + Al_2O_3 + TiO_2 + P_2O_5 + SO_3}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, MnO, SrO, BaO, $SiO_2$, $Al_2O_3$, $TiO_2$, $P_2O_5$, and $SO_3$ correspond to weight fractions in the biocarbon composition pursuant to ASTM D4326, and wherein the expanded base-acid ratio is selected from about 0.05 to about 8.

**[0193]** Some variations of the invention provide a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by an expanded base-acid ratio defined by the following formula:

$$\text{Expanded Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O + MnO + SrO + BaO}{SiO_2 + Al_2O_3 + TiO_2 + P_2O_5 + SO_3}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, MnO, SrO, BaO, $SiO_2$, $Al_2O_3$, $TiO_2$, $P_2O_5$, and $SO_3$ correspond to weight fractions in the biocarbon composition pursuant to ASTM D4326, and wherein the expanded base-acid ratio is selected from about 0.05 to about 8.

**[0194]** It is not necessary that all of $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, MnO, SrO, BaO, $SiO_2$, $Al_2O_3$, $TiO_2$, $P_2O_5$, and $SO_3$ be present in the ash of the biocarbon composition. However, in order to have a non-zero and finite expanded base-acid ratio,

there must be a detectible amount (according to ASTM D4326) of at least one of $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, MnO, SrO, BaO, as well as at least one of $SiO_2$, $Al_2O_3$, $TiO_2$, $P_2O_5$, and $SO_3$.

**[0195]** In some embodiments, the expanded base-acid ratio is selected from about 0.1 to about 0.4, or from about 0.5 to about 10, or from about 0.8 to about 10, or from about 1.5 to about 5, or from about 0.4 to about 0.7. In certain embodiments, the expanded base-acid ratio is at most 0.4 or at least 0.7.

**[0196]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is characterized by an iron-calcium ratio defined by the $Fe_2O_3$ divided by the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the iron-calcium ratio is selected from about 0.05 to about 5. The iron-calcium ratio can be selected from about 0.1 to about 2, or from about 0.3 to about 1, for example. In certain embodiments, the iron-calcium ratio is at most 0.3 or at least 3.

**[0197]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is characterized by an iron-plus-calcium parameter defined as the sum of the $Fe_2O_3$ and the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the iron-plus-calcium parameter is selected from about 5 wt% to about 50 wt%. The iron-plus-calcium parameter can be selected from about 10 wt% to about 40 wt%, or from about 20 wt% to about 50 wt%, for example. In certain embodiments, the iron-plus-calcium parameter is at most 10 wt%. In other embodiments, the iron-plus-calcium parameter is at least 10 wt%.

**[0198]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is characterized by a slagging factor defined as the base-acid ratio multiplied by weight percentage of sulfur present in the biocarbon composition on a dry basis, and wherein the slagging factor is selected from about 0.001 to about 1. The slagging factor can be selected from about 0.01 to about 0.5, or from about 0.01 to about 0.1, for example. In certain embodiments, the slagging factor is at most 0.6.

**[0199]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is characterized by a fouling factor

defined as the base-acid ratio multiplied by the $Na_2O$ as weight percentage in the biocarbon composition pursuant to ASTM D4326, and wherein the fouling factor is selected from about 0.1 to about 10. The fouling factor can be at most 2 or at most 1, for example.

**[0200]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is characterized by a modified fouling factor defined as the base-acid ratio multiplied by water-soluble $Na_2O$, wherein the water-soluble $Na_2O$ is weight percentage of $Na_2O$ that leaches, in the presence of water, out of ash derived from the biocarbon composition pursuant to ASTM D4326, and wherein the modified fouling factor is selected from about 0.1 to about 10. The modified fouling factor can be at most 2 or at most 1, for example.

**[0201]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is characterized by a silica percentage defined as weight percentage of the $SiO_2$ in the biocarbon composition pursuant to ASTM D4326, wherein the silica percentage is selected from about 5 wt% to about 50 wt%. The silica percentage can be selected from about 10 wt% to about 30 wt%, for example.

**[0202]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is further characterized by an equilibrium moisture content according to ASTM D1412. The equilibrium moisture can be from about 0.1 wt% to about 10 wt%, such as about, at least about, or at most about 0.1, 0.2, 0.5, 0.8, 1, 1.2, 1.5, 2, 2.5, 2.6, 2.7, 2.8, 2.9, 3, 3.1, 3.2, 3.3, 3.4, 3.5, 4, 4.5, 5, 6, 7, 8, 9, or 10 wt%, including all intervening ranges.

**[0203]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition comprises at most about 100 ppm mercury, at most about 10 ppm mercury, or is essentially free of mercury.

**[0204]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition comprises from about 50 wt% to about 99 wt% fixed carbon on a dry basis. In certain embodiments, the biocarbon composition comprises at least about 75 wt% fixed carbon or at least about 90 wt% fixed carbon on a dry basis.

**[0205]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the 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. The total carbon within the biocarbon composition can be at least 99% 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.

**[0206]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is in the form of a pellet. The pellet optionally comprises a binder. The binder can be 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, or a combination or a derivative thereof.

**[0207]** In some embodiments of the biocarbon composition with optimized expanded base-acid ratio, the biocarbon composition is in the form of a powder. The powder can be a loose powder, a compacted powder, a granulated powder, or another form of powder.

**[0208]** Any of the disclosed biocarbon compositions can further comprise an additive, such as (but not limited to) an additive selected from calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina,

aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0209]** When an additive is present, the additive can be selected to adjust any of the compositional parameters disclosed herein (e.g., base-acid ratio, slagging factor, etc.). The additive can adjust the base-acid ratio directly, wherein the additive itself contains one or more of the metals that are used in the formula for base-acid ratio. For example, if the additive is pure alumina, then the base-acid ratio will be reduced, to an extent dictated by the concentration of additive in the biocarbon composition.

**[0210]** Some variations of the invention provide a process for producing a biocarbon composition with an optimized base-acid ratio, the process comprising:

(a) providing a starting feedstock comprising biomass, wherein the starting feedstock is optionally dried;

(b) pyrolyzing the starting feedstock to generate an intermediate biocarbon stream and a pyrolysis vapor, wherein the intermediate biocarbon stream is characterized by a base-acid ratio defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages pursuant to ASTM D4326;

(c) washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, to adjust the base-acid ratio; and/or introducing an additive during step (a) or step (b), to adjust the base-acid ratio; and

(d) recovering a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, and wherein the base-acid ratio of the biocarbon composition is selected from about 0.1 to about 10.

**[0211]** FIG. 3 is a simplified block-flow diagram of a process for converting a biomass feedstock into a biocarbon composition with an optimized base-acid ratio, in some embodiments. Dotted lines denote optional streams and units.

**[0212]** In some processes, the biomass is 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 or a derivative thereof.

**[0213]** In some embodiments, step (c) selectively removes basic components, thereby reducing the $Fe_2O_3$, the CaO, the MgO, the $K_2O$, or the $Na_2O$.

**[0214]** In some embodiments, step (c) utilizes acidic water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c). For example, acidic water can be obtained from condensation of the pyrolysis vapor to generate a condensed liquid having a pH from about 1 to about 7.

**[0215]** In some embodiments, step (c) selectively removes acidic components, thereby reducing the $SiO_2$, the $Al_2O_3$, or the $TiO_2$.

**[0216]** In some embodiments, step (c) utilizes alkaline water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c).

**[0217]** In some embodiments, step (c) utilizes steam cleaning of the intermediate biocarbon stream. Alternatively, or additionally, step (d) can utilize steam cleaning of the biocarbon composition.

**[0218]** In some processes, washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, is conducted. In some processes, an additive is introduced during step (a) or step (b). In certain processes, both of these options are used—that is, the intermediate biocarbon stream is washed or treated with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, and an additive (other than any component from the washing or treating) is introduced during step (a) or step (b).

**[0219]** In step (c), the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0220]** When the intermediate biocarbon stream is treated with $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, the chemistry to adjust the base-acid ratio may add hydrogen, oxygen, and/or carbon to one or more metals present in the intermediate biocarbon stream. Alternatively, or additionally, the treatment with $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof may remove hydrogen, oxygen, and/or carbon from one or more metals present in the intermediate biocarbon stream. It will be recognized that treatment with $H_2$, $H_2O$, CO, and/or $CO_2$ will not necessarily change the base-acid ratio even if the actual form of metals is altered, due to the ashing protocol of ASTM D4326. However, if the treatment with $H_2$, $H_2O$, CO, and/or $CO_2$ is followed by removal of a portion of the intermediate biocarbon stream, then the base-acid ratio can be adjusted. For example, liquid water or compressed $CO_2$ may be utilized to wash the intermediate biocarbon stream and change the base-acid ratio depending, for example, on the pH of the liquid. In certain embodiments, treatment with $H_2$, $H_2O$, CO, and/or $CO_2$ creates compounds that are more or less susceptible to forming ash under the ASTM D4326 test, in which case the base-acid ratio is adjusted.

**[0221]** In some processes, the biocarbon composition has a higher heating value of at least about 25 MJ/kg on a dry basis.

**[0222]** The biocarbon composition can be pelletized to produce biocarbon pellets. A binder can be utilized to assist in pelletizing. A binder can be 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, or a combination or a derivative thereof.

**[0223]** In some processes, the base-acid ratio is optimized to be from about 0.1 to about 0.4, or from about 0.5 to about 10, or from about 0.8 to about 10, or from about 1.5 to about 5, or from about 0.4 to about 0.7. In certain embodiments, the base-acid ratio is optimized to be at most 0.4 or at least 0.7.

**[0224]** Some variations of the invention provide a process for producing a biocarbon composition with an optimized expanded base-acid ratio, the process comprising:

(a) providing a starting feedstock comprising biomass, wherein the starting feedstock is optionally dried;

(b) pyrolyzing the starting feedstock to generate an intermediate biocarbon stream and a pyrolysis vapor, wherein the intermediate biocarbon stream is characterized by an expanded base-acid ratio defined by the following formula:

$$\text{Expanded Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O + MnO + SrO + BaO}{SiO_2 + Al_2O_3 + TiO_2 + P_2O_5 + SO_3}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, MnO, SrO, BaO, $SiO_2$, $Al_2O_3$, $TiO_2$, $P_2O_5$, and $SO_3$ correspond to weight percentages pursuant to ASTM D4326;

(c) washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, to adjust the expanded base-acid ratio; and/or introducing an additive during step (a) or step (b), to adjust the expanded base-acid ratio; and

(d) recovering a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, and wherein the expanded base-acid ratio of the biocarbon composition is selected from about 0.05 to about 8.

**[0225]** FIG. 4 is a simplified block-flow diagram of a process for converting a biomass feedstock into a biocarbon composition with an optimized enhanced base-acid ratio, in some embodiments. Dotted lines denote optional streams and units.

**[0226]** In some processes in which the expanded base-acid ratio is optimized, the biomass is 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 or a derivative thereof.

**[0227]** In some processes in which the expanded base-acid ratio is optimized, step (c) selectively removes basic components, thereby reducing the $Fe_2O_3$, the CaO, the MgO, the $K_2O$, or the $Na_2O$.

**[0228]** In some processes in which the expanded base-acid ratio is optimized, step (c) utilizes acidic water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c). For example, acidic water can be obtained from condensation of the pyrolysis vapor to generate a condensed liquid having a pH from about 1 to about 7.

**[0229]** In some processes in which the expanded base-acid ratio is optimized, step (c) selectively removes acidic components, thereby reducing the $SiO_2$, the $Al_2O_3$, or the $TiO_2$.

**[0230]** In some processes in which the expanded base-acid ratio is optimized, step (c) utilizes alkaline water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c).

**[0231]** In some processes in which the expanded base-acid ratio is optimized, step (c) utilizes steam cleaning of the intermediate biocarbon stream. Alternatively, or additionally, step (d) can utilize steam cleaning of the biocarbon composition.

**[0232]** In some processes in which the expanded base-acid ratio is optimized, step (c) is conducted. In some processes in which the expanded base-acid ratio is optimized, step (d) is conducted. In certain processes, steps (c) and (d) are both conducted.

**[0233]** When step (d) is employed, the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0234]** In some processes in which the expanded base-acid ratio is optimized, the biocarbon composition has a higher heating value of at least about 25 MJ/kg on a dry basis.

**[0235]** The biocarbon composition can be pelletized to produce biocarbon pellets. A binder can be utilized to assist in pelletizing. A binder can be 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, derivatives thereof, or a combination or a derivative thereof.

**[0236]** In some processes, the expanded base-acid ratio is optimized to be from about 0.1 to about 0.4, or from about 0.5 to about 10, or from about 0.8 to about 10, or

from about 1.5 to about 5, or from about 0.4 to about 0.7. In certain embodiments, the expanded base-acid ratio is optimized to be at most 0.4 or at least 0.7.

**[0237]** In any of the processed disclosed above, the biocarbon composition can be characterized by an iron-calcium ratio defined by the $Fe_2O_3$ divided by the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, wherein the iron-calcium ratio of the biocarbon composition is selected from about 0.05 to about 5.

**[0238]** Some variations provide a process for producing a biocarbon composition with an optimized iron-calcium ratio, the process comprising:

(a) providing a starting feedstock comprising biomass, wherein the starting feedstock is optionally dried;

(b) pyrolyzing the starting feedstock to generate an intermediate biocarbon stream and a pyrolysis vapor, wherein the intermediate biocarbon stream is characterized by an iron-calcium ratio defined by the $Fe_2O_3$ divided by the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326;

(c) washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, to adjust the iron-calcium ratio; and/or introducing an additive during step (a) or step (b), to adjust the iron-calcium ratio; and

(d) recovering a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, and wherein the iron-calcium ratio of the biocarbon composition is selected from about 0.05 to about 5.

**[0239]** In some processes in which the iron-calcium ratio is optimized, step (c) selectively removes basic components, thereby reducing the $Fe_2O_3$, the CaO, the MgO, the $K_2O$, or the $Na_2O$.

**[0240]** In some processes in which the iron-calcium ratio is optimized, step (c) utilizes acidic water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c). For example, acidic water can be obtained from condensation of the pyrolysis vapor to generate a condensed liquid having a pH from about 1 to about 7.

**[0241]** In some processes in which the iron-calcium ratio is optimized, step (c) selectively removes acidic components, thereby reducing the $SiO_2$, the $Al_2O_3$, or the $TiO_2$.

**[0242]** In some processes in which the iron-calcium ratio is optimized, step (c) utilizes alkaline water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c).

**[0243]** In some processes in which the iron-calcium ratio is optimized, step (c) utilizes steam cleaning of the intermediate biocarbon stream. Alternatively, or additionally, step (d) can utilize steam cleaning of the biocarbon composition.

**[0244]** In some processes in which the iron-calcium ratio is optimized, step (c) is conducted. In some processes in which the iron-calcium ratio is optimized, step (d) is conducted. In certain processes, steps (c) and (d) are both conducted.

**[0245]** When step (d) is employed, the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0246]** In some processes in which the iron-calcium ratio is optimized, the biocarbon composition has a higher heating value of at least about 25 MJ/kg on a dry basis.

**[0247]** The biocarbon composition can be pelletized to produce biocarbon pellets. A binder can be utilized to assist in pelletizing. A binder can be 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, derivatives thereof, or a combination or a derivative thereof.

**[0248]** In some processes, the iron-plus-calcium parameter is optimized to be from about 10 wt% to about 40 wt%, or from about 20 wt% to about 50 wt%. In certain embodiments, the iron-plus-calcium parameter is optimized to be at most 10 wt%. In other embodiments, the iron-plus-calcium parameter is optimized to be at least 10 wt%.

**[0249]** In any of the processed disclosed above, the biocarbon composition can be characterized by an iron-plus-calcium parameter defined as the sum of the $Fe_2O_3$ and the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, wherein the iron-plus-calcium parameter of the biocarbon composition is selected from 5 wt% to about 50 wt%.

**[0250]** Some variations provide a process for producing a biocarbon composition with an optimized iron-plus-calcium parameter, the process comprising:

(a) providing a starting feedstock comprising biomass, wherein the starting feedstock is optionally dried;

(b) pyrolyzing the starting feedstock to generate an intermediate biocarbon stream and a pyrolysis vapor, wherein the intermediate biocarbon stream is characterized by an iron-plus-calcium parameter defined as the sum of the $Fe_2O_3$ and the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326;

(c) washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, to adjust the iron-plus-calcium parameter; and/or introducing an additive during step (a) or step (b), to adjust the iron-plus-calcium parameter; and

(d) recovering a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, and wherein the iron-plus-calcium parameter of the biocarbon composition is selected from 5 wt% to about 50 wt%.

**[0251]** In some processes in which the iron-plus-calcium parameter is optimized, step (c) selectively removes basic components, thereby reducing the $Fe_2O_3$, the CaO, the MgO, the $K_2O$, or the $Na_2O$.

**[0252]** In some processes in which the iron-plus-calcium parameter is optimized, step (c) utilizes acidic water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c). For example, acidic water can be obtained from condensation of the pyrolysis vapor to generate a condensed liquid having a pH from about 1 to about 7.

**[0253]** In some processes in which the iron-plus-calcium parameter is optimized, step (c) selectively removes acidic components, thereby reducing the $SiO_2$, the $Al_2O_3$, or the $TiO_2$.

**[0254]** In some processes in which the iron-plus-calcium parameter is optimized, step (c) utilizes alkaline water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c).

**[0255]** In some processes in which the iron-plus-calcium parameter is optimized, step (c) utilizes steam cleaning of the intermediate biocarbon stream. Alternatively, or additionally, step (d) can utilize steam cleaning of the biocarbon composition.

**[0256]** In some processes in which the iron-plus-calcium parameter is optimized, step (c) is conducted. In some processes in which the iron-plus-calcium parameter is optimized, step (d) is conducted. In certain processes, steps (c) and (d) are both conducted.

**[0257]** When step (d) is employed, the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0258]** In some processes in which the iron-plus-calcium parameter is optimized, the biocarbon composition has a higher heating value of at least about 25 MJ/kg on a dry basis.

**[0259]** The biocarbon composition can be pelletized to produce biocarbon pellets. A binder can be utilized to assist in pelletizing. A binder can be 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, derivatives thereof, or a combination or a derivative thereof.

**[0260]** In some processes, the iron-plus-calcium parameter is optimized to be from about 10 wt% to about 40 wt%, or from about 20 wt% to about 50 wt%. In certain embodiments, the iron-plus-calcium parameter is optimized to be at most 10 wt%. In other embodiments, the iron-plus-calcium parameter is optimized to be at least 10 wt%.

**[0261]** In any of the processed disclosed above, the biocarbon composition can be characterized by a slagging factor defined as a base-acid ratio multiplied by weight percentage of sulfur present in the biocarbon composition on a dry basis, wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the slagging factor of the biocarbon composition is selected from about 0.001 to about 1.

**[0262]** Some variations provide a process for producing a biocarbon composition with an optimized slagging factor, the process comprising:

(a) providing a starting feedstock comprising biomass, wherein the starting feedstock is optionally dried;

(b) pyrolyzing the starting feedstock to generate an intermediate biocarbon stream and a pyrolysis vapor, wherein the intermediate biocarbon stream is characterized by a slagging factor defined as a base-acid ratio multiplied by weight percentage of sulfur present in the biocarbon composition on a dry basis;

wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326;

(c) washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, to adjust the slagging factor; and/or introducing an additive during step (a) or step (b), to adjust the slagging factor; and

(d) recovering a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, and wherein the slagging factor of the biocarbon composition is selected from about 0.001 to about 1.

**[0263]** In some processes in which the slagging factor is optimized, step (c) selectively removes basic components, thereby reducing the $Fe_2O_3$, the CaO, the MgO, the $K_2O$, or the $Na_2O$.

**[0264]** In some processes in which the slagging factor is optimized, step (c) utilizes acidic water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c). For example, acidic water can be obtained from condensation of the pyrolysis vapor to generate a condensed liquid having a pH from about 1 to about 7.

**[0265]** In some processes in which the slagging factor is optimized, step (c) selectively removes acidic components, thereby reducing the $SiO_2$, the $Al_2O_3$, or the $TiO_2$.

**[0266]** In some processes in which the slagging factor is optimized, step (c) utilizes alkaline water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c).

**[0267]** In some processes in which the slagging factor is optimized, step (c) utilizes steam cleaning of the intermediate biocarbon stream. Alternatively, or additionally, step (d) can utilize steam cleaning of the biocarbon composition.

**[0268]** In some processes in which the slagging factor is optimized, step (c) is conducted. In some processes in which the slagging factor is optimized, step (d) is conducted. In certain processes, steps (c) and (d) are both conducted.

**[0269]** When step (d) is employed, the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0270]** In some processes in which the slagging factor is optimized, the biocarbon composition has a higher heating value of at least about 25 MJ/kg on a dry basis.

**[0271]** The biocarbon composition can be pelletized to produce biocarbon pellets. A binder can be utilized to assist in pelletizing. A binder can be 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, derivatives thereof, or a combination or a derivative thereof.

**[0272]** In some processes, the slagging factor is optimized to be from about 0.01 to about 0.5, or from about 0.01 to about 0.1. In certain embodiments, the slagging factor is optimized to be at most 0.6.

**[0273]** In any of the processed disclosed above, the biocarbon composition can be characterized by a fouling factor defined as a base-acid ratio multiplied by the $Na_2O$ as weight percentage in the biocarbon composition pursuant to ASTM D4326, wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the fouling factor of the biocarbon composition is selected from about 0.1 to about 10.

**[0274]** Some variations provide a process for producing a biocarbon composition with an optimized fouling factor, the process comprising:

(a) providing a starting feedstock comprising biomass, wherein the starting feedstock is optionally dried;

(b) pyrolyzing the starting feedstock to generate an intermediate biocarbon stream and a pyrolysis vapor, wherein the intermediate biocarbon stream is characterized by a fouling factor defined as a base-acid ratio multiplied by the $Na_2O$ as weight percentage in the biocarbon composition pursuant to ASTM D4326;

wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326;

(c) washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, to adjust the fouling factor; and/or introducing an additive during step (a) or step (b), to adjust the fouling factor; and

(d) recovering a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, and wherein the fouling factor of the biocarbon composition is selected from about 0.1 to about 10.

**[0275]** In some processes in which the fouling factor is optimized, step (c) selectively removes basic components, thereby reducing the $Fe_2O_3$, the CaO, the MgO, the $K_2O$, or the $Na_2O$.

**[0276]** In some processes in which the fouling factor is optimized, step (c) utilizes acidic water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c). For example, acidic water can be obtained from condensation of the pyrolysis vapor to generate a condensed liquid having a pH from about 1 to about 7.

**[0277]** In some processes in which the fouling factor is optimized, step (c) selectively removes acidic components, thereby reducing the $SiO_2$, the $Al_2O_3$, or the $TiO_2$.

**[0278]** In some processes in which the fouling factor is optimized, step (c) utilizes alkaline water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c).

**[0279]** In some processes in which the fouling factor is optimized, step (c) utilizes steam cleaning of the intermediate biocarbon stream. Alternatively, or additionally, step (d) can utilize steam cleaning of the biocarbon composition.

**[0280]** In some processes in which the fouling factor is optimized, step (c) is conducted. In some processes in which the fouling factor is optimized, step (d) is conducted. In certain processes, steps (c) and (d) are both conducted.

**[0281]** When step (d) is employed, the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina,

aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0282]** In some processes in which the fouling factor is optimized, the biocarbon composition has a higher heating value of at least about 25, 26, 27, 28, 29, 30, 31, 32, or 33 MJ/kg on a dry basis.

**[0283]** The biocarbon composition can be pelletized to produce biocarbon pellets. A binder can be utilized to assist in pelletizing. A binder can be 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, derivatives thereof, or a combination or a derivative thereof.

**[0284]** In some processes, the fouling factor is optimized to be at most 2. In certain embodiments, the fouling factor is optimized to be at most 1.

**[0285]** In any of the processed disclosed above, the biocarbon composition can be characterized by a modified fouling factor defined as a base-acid ratio multiplied by water-soluble $Na_2O$, wherein the water-soluble $Na_2O$ is weight percentage of $Na_2O$ that leaches, in the presence of water, out of ash derived from the biocarbon composition pursuant to ASTM D4326, wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the fouling factor of the biocarbon composition is selected from about 0.1 to about 10.

**[0286]** Some variations provide a process for producing a biocarbon composition with an optimized modified fouling factor, the process comprising:

(a) providing a starting feedstock comprising biomass, wherein the starting feedstock is optionally dried;

(b) pyrolyzing the starting feedstock to generate an intermediate biocarbon stream and a pyrolysis vapor, wherein the intermediate biocarbon stream is characterized by a modified fouling factor a base-acid ratio multiplied by water-soluble $Na_2O$, wherein the water-soluble $Na_2O$ is weight percentage of $Na_2O$ that leaches, in the presence of water, out of ash derived from the biocarbon composition pursuant to ASTM D4326;

wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326;

(c) washing or treating the intermediate biocarbon stream with an acid, a base, a salt, a metal, $H_2$, $H_2O$, CO, $CO_2$, or a combination thereof, to adjust the modified fouling factor; and/or introducing an additive during step (a) or step (b), to adjust the modified fouling factor; and

(d) recovering a biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, and wherein the modified fouling factor of the biocarbon composition is selected from about 0.1 to about 10.

**[0287]** In some processes in which the modified fouling factor is optimized, step (c) selectively removes basic components, thereby reducing the $Fe_2O_3$, the CaO, the MgO, the $K_2O$, or the $Na_2O$.

**[0288]** In some processes in which the modified fouling factor is optimized, step (c) utilizes acidic water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c). For example, acidic water can be obtained from

condensation of the pyrolysis vapor to generate a condensed liquid having a pH from about 1 to about 7.

**[0289]** In some processes in which the modified fouling factor is optimized, step (c) selectively removes acidic components, thereby reducing the $SiO_2$, the $Al_2O_3$, or the $TiO_2$.

**[0290]** In some processes in which the modified fouling factor is optimized, step (c) utilizes alkaline water that is obtained from step (a), step (b), or another process step that is conducted prior to step (c).

**[0291]** In some processes in which the modified fouling factor is optimized, step (c) utilizes steam cleaning of the intermediate biocarbon stream. Alternatively, or additionally, step (d) can utilize steam cleaning of the biocarbon composition.

**[0292]** In some processes in which the modified fouling factor is optimized, step (c) is conducted. In some processes in which the modified fouling factor is optimized, step (d) is conducted. In certain processes, steps (c) and (d) are both conducted.

**[0293]** When step (d) is employed, the additive can be calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or a derivative thereof.

**[0294]** In some processes in which the modified fouling factor is optimized, the biocarbon composition has a higher heating value of at least about 25 MJ/kg on a dry basis.

**[0295]** The biocarbon composition can be pelletized to produce biocarbon pellets. A binder can be utilized to assist in pelletizing. A binder can be 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, derivatives thereof, or a combination or a derivative thereof.

**[0296]** In some processes, the modified fouling factor is optimized to be at most 2. In certain embodiments, the modified fouling factor is optimized to be at most 1.

**[0297]** Any of the processes disclosed herein can be optimized to achieve pre-selected values or ranges for a compositional parameter discussed earlier. Any discussion of properties for biocarbon compositions is hereby incorporated by reference into each instance of discussion of a process.

**[0298]** A process can be optimized to target a single compositional parameter (e.g., base-acid ratio), or more than one compositional parameter—e.g., 2, 3, 4, 5, 6, 7, 8, 9, 10 or more compositional parameters. It will be recognized that there is some covariance between certain compositional parameters, so that optimize of one will influence another. For example, optimization of the base-acid ratio to achieve a selected value will influence the expanded base-acid ratio since many of the factors are the same ($Fe_2O_3$, $SiO_2$, etc.). Another example is fouling factor, which is a linear function of base-acid ratio, which means that a change to base-acid ratio will cause a change to fouling factor unless the $Na_2O$ is adjusted in the other direction.

**[0299]** As will be appreciated by one skilled in the art, various process optimization methodologies can be undertaken. Examples include, but are not limited to, linear optimization, non-linear optimization, weighted optimization wherein certain compositional parameters are designated as more important, design and analysis of experiments, statistical process control, artificial intelligence, machine learning, and other techniques.

**[0300]** In some embodiments, a compositional parameter is pre-selected based on an intended use of the biocarbon composition. Then, a process to make the biocarbon composition is optimized using process control to realize the pre-selected compositional parameters, within a prescribed tolerance. The process optimization can utilize the results of previous experiments or production campaigns, simulations,

calculations, and analysis. For example, if a pre-selected base-acid ratio is 2.2, then the process can be designed using a wash treatment or an additive (or both) to target a continuous base-acid ratio set-point of 2.2 ± 0.2 (a tolerance of about 10%). The controlled base-acid ratio can be biased such that higher numbers are more acceptable than lower numbers; e.g., the process can be designed using a wash treatment or an additive (or both) to target a continuous base-acid ratio set-point of 2.2 +0.4/–0.1. In this disclosure, a compositional parameter can be a "pre-selected" compositional parameter when such parameter is selected in order to optimize a process to actually achieve the set-point via process control. Process control, in turn, can employ principles of process control such as feedback loops and proportional-integral-derivative logic programs.

**[0301]** The intended use of the biocarbon composition can vary widely, such as solid fuels, solid gasifier feedstocks, metallurgical-process inputs (for energy, for reduction chemistry, or for carbon content), agricultural carbon, activated carbon, electrodes, batteries (e.g., lithium-ion batteries), carbon composites, and carbon precursors for other materials, for example. When the biocarbon composition will ultimately be combusted or oxidized, either for energy production or as part of a metal-making process, the compositional parameters can be optimized to avoid complications such as slagging and fouling in the reactors, e.g., by using a relatively low base-acid ratio, slagging factor, and/or fouling factor. When the biocarbon composition will be used as filtration media to remove acidic components, the compositional parameters can be optimized to enhance neutralization of acids, e.g., by using a relatively high base-acid ratio, and consequently, a relatively high value for any parameter that is a linear function of the base-acid ratio (e.g., fouling factor). When the biocarbon composition will be used as a reducing agent in a metal-making process, the compositional parameters can be optimized to balance acid and base content to achieve a desirable pH for the reduction chemistry, such as generation of Fe from FeO, e.g., by using a moderate base-acid ratio. When the biocarbon composition will be used as agricultural carbon, the compositional parameters can be optimized to account for the soil into which the carbon will be placed, in order to select a base-acid ratio and other parameters.

**[0302]** Some embodiments pertain to combustion of a biocarbon composition. When a biocarbon composition is combusted to convert C and $O_2$ (usually from air) into

$CO_2$ and $H_2O$, metal oxides (and possibly pure metals) are left behind—unless the starting biocarbon composition contains essentially pure carbon. The residual metal oxides and any other non-combustible components form the component usually referred to as ash. The initial biomass feedstock may contain metals that oxidize to metal oxides during oxidation with air or oxygen, or the initial biomass feedstock may contain metal oxides that are not further oxidized during carbon oxidation. For example, in the case of silicon, Si may be present in a biomass feedstock as pure Si, as silica ($SiO_2$), and/or as various other compounds such as silicic acids (silicon attached to oxide and hydroxyl groups).

**[0303]** During combustion of a biocarbon composition in a reactor, the fine particle ash that rises up with the flue gases is known as a fly ash or flue ash, while the heavier ash that does not rise is called bottom ash. Ash that neither rises nor falls, but rather accumulates on the walls of the reactor, or on other heat-transfer surfaces, causes significant problems. Slagging is the accumulation of molten ash, possibly with partially fused deposits, on the walls of the furnace, gasifier, or boiler. Slagging is detrimental as it reduces the required heat transfer for steam generation. Fouling is the accumulation of solid ash on a heat-transfer surface, which may be a reactor wall, or a reheater/superheater area of a boiler, for example. A clean boiler tube surface results in maximum heat transfer for steam production and consequent electricity production in a power plant. Both slagging and fouling diminish the effectiveness of the combustion process in producing energy/electricity.

**[0304]** In some embodiments pertaining to use of the biocarbon composition as a coal-replacement product for steam or electricity production, the base-acid ratio is adjusted to be from about 0.1 to about 1.5, such as about, at least about, or at most about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, or 1.5, including any intervening ranges (e.g., 0.4–0.7).

**[0305]** In some embodiments pertaining to use of the biocarbon composition as a coal-replacement product for steam or electricity production, the expanded base-acid ratio is adjusted to be from about 0.05 to about 1.2, such as about, at least about, or at most about 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, or 1.2, including any intervening ranges.

**[0306]** In some embodiments pertaining to use of the biocarbon composition as a coal-replacement product for steam or electricity production, the fouling factor and/or the modified fouling factor is about, or below about, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1, including all intervening ranges. In some embodiments pertaining to use of the biocarbon composition as a coal-replacement product for steam or electricity production, the slagging factor is about, at least about, or at most about 0.001, 0.002, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.9, 0.95, or 1, including all intervening ranges.

**[0307]** Some embodiments pertain to gasification of a biocarbon composition, to produce syngas (CO and $H_2$) rather than solely combustion productions ($CO_2$ and $H_2O$). The slagging and fouling problems that can occur during combustion can also happen in gasification. In a gasifier, carbon in the biocarbon composition is converted to syngas, while the mineral matter in the biocarbon composition is transformed to ash. The majority of the ash is melted and deposited on the walls (i.e., refractory or membrane) of the gasifier, forming a liquid slag, which flows out of the bottom of the gasifier. For example, in entrained-flow gasifiers for integrated gasification combined cycle (IGCC) plants, the majority of mineral matter transforms to liquid slag on the wall of the gasifier and flows out the bottom where it is usually solidified in a water bath. Slag build-up in the gasifier will reduce the syngas production. Also, a small fraction of the mineral matter is entrained as fly ash with the raw syngas out of the gasifier to downstream processing. This molten/sticky fly ash can cause fouling of the syngas cooler, which in turn can cause problematic plugging of the slurry feed to an IGCC plant. Other concerns of ash slagging and fouling in gasification include large amounts of unconverted carbon from the gasifier and material failure of the refractory lining in the gasifier.

**[0308]** In some embodiments pertaining to use of the biocarbon composition for gasification, the base-acid ratio is adjusted to be from about 0.1 to about 2.0, such as about, at least about, or at most about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, or 2.0, including any intervening ranges (e.g., 0.5–1.5).

**[0309]** In some embodiments pertaining to use of the biocarbon composition for gasification, the expanded base-acid ratio is adjusted to be from about 0.05 to about

1.6, such as about, at least about, or at most about 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, or 1.6, including any intervening ranges.

**[0310]** In some embodiments pertaining to use of the biocarbon composition for gasification, the fouling factor and/or the modified fouling factor is about, or below about, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1, including all intervening ranges. In some embodiments pertaining to use of the biocarbon composition for gasification, the slagging factor is about, at least about, or at most about 0.001, 0.002, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.9, 0.95, or 1, including all intervening ranges.

**[0311]** Some embodiments pertain to use of biocarbon composition as metallurgical carbon to produce a metal or a reduced form of a metal oxide. The optimal base-acid ratio (and expanded base-acid ratio) for a metallurgical carbon may depend on the specific metal or metal alloy being produced, and the feedstock (metal ore) composition.

**[0312]** The optimal base-acid ratio (and expanded base-acid ratio) for a metallurgical carbon may also depend on the nature of the slag that is produced during metallurgical processing. In this context, note that there would be a slag derived from the starting metal ore, as well as a slag derived from the biocarbon composition. In the metallurgical process, the slag components typically become well-mixed and form a single slag. To distinguish between the sources of slag, reference can be made to the metal-ore slag and the biocarbon-composition slag. Many metal-ore slags can be described as either basic slags as is typical in ironmaking and steelmaking, or acid slags as is typical in non-ferrous smelting. If the metal-ore slag tends to be acidic, then a higher base-acid ratio for the metallurgical biocarbon is preferred, so that the biocarbon-composition slag counteracts the acidic metal-ore slag. If the metal-ore slag tends to be basic, then a lower base-acid ratio for the metallurgical biocarbon is preferred, so that the biocarbon-composition slag counteracts the basic metal-ore slag. For example, many iron ores contain a significant amount of $SiO_2$ and $Al_2O_3$ with the $FeO_x$ (iron oxides) that melt into the metal-ore slag. An optimized base-acid ratio can counteract those acidic components.

**[0313]** In some embodiments pertaining to use of the biocarbon composition as metallurgical carbon in making iron or iron alloys, the base-acid ratio is adjusted to be

from about 0.1 to about 10, such as about, at least about, or at most about 0.5, 1, 1.5, 2, 2.5, 3, 4, 5, 6, 7, 8, 9, or 10, including any intervening ranges (e.g., 0.5–3).

**[0314]** In some embodiments pertaining to use of the biocarbon composition as metallurgical carbon in making iron or iron alloys, the expanded base-acid ratio is adjusted to be from about 0.05 to about 8, such as about, at least about, or at most about 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 4, 5, 6, 7, 8, 9, or 8, including any intervening ranges.

**[0315]** In some embodiments pertaining to use of the biocarbon composition as metallurgical carbon in making non-ferrous alloys, the base-acid ratio is adjusted to be from about 0.1 to about 10, such as about, at least about, or at most about 0.2, 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7, 8, 9, or 10, including any intervening ranges (e.g., 1.5–6).

**[0316]** In some embodiments pertaining to use of the biocarbon composition as metallurgical carbon in making non-ferrous alloys, the expanded base-acid ratio is adjusted to be from about 0.05 to about 8, such as about, at least about, or at most about 0.1, 0.2, 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7, or 8, including any intervening ranges.

**[0317]** In some embodiments pertaining to use of the biocarbon composition as metallurgical carbon in making iron, iron alloys, or non-ferrous alloys, the fouling factor and/or the modified fouling factor is about, or below about, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1, including all intervening ranges. In some embodiments pertaining to use of the biocarbon composition as metallurgical carbon in making iron, iron alloys, or non-ferrous alloys, the slagging factor is about, at least about, or at most about 0.001, 0.002, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.9, 0.95, or 1, including all intervening ranges.

**[0318]** Some embodiments pertain to use of biocarbon composition as agricultural carbon. Agricultural carbon includes uses in various agricultural media, such as soil, soilless media, or hydroponic media, for example. See U.S. Patent No. 10,640,429, which is hereby incorporated by reference, for various uses of biocarbon compositions as agricultural carbon.

**[0319]** In applications of agricultural carbon, the base-acid ratio of the biocarbon composition may be adjusted to control the pH in the desired media. For example, a soil pH below about 5.6 is considered low for most crops. Generally, the ideal soil pH

range is between 6.0 and 7.0. Most plant nutrients reach their peak availability in near-neutral soil pH.

**[0320]** In some embodiments pertaining to use of the biocarbon composition as agricultural carbon, the base-acid ratio is adjusted to be from about 0.5 to about 2.0, such as about, at least about, or at most about 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, or 2.0, including any intervening ranges (e.g., 0.8–1.2).

**[0321]** In some embodiments pertaining to use of the biocarbon composition as agricultural carbon, the expanded base-acid ratio is adjusted to be from about 0.25 to about 1.6, such as about, at least about, or at most about 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, or 1.6, including any intervening ranges.

**[0322]** In certain embodiments, the base-acid ratio (or expanded base-acid ratio) is selected in conjunction with the selection of an additive that is intended to be added to the agricultural media at the time of incorporating the biocarbon composition into the agricultural media. In these embodiments, the additive (e.g., ammonia) is not necessarily present in the biocarbon composition itself, but would be present in the agricultural media along with the biocarbon composition.

**[0323]** Some embodiments pertain to use of biocarbon composition in battery electrodes. Carbon use in battery electrodes, such as lithium-ion batteries, is well-known. See Togonon et al., "Pure carbon-based electrodes for metal-ion batteries", *Carbon Trends* 3, 100035, 2021, which is hereby incorporated by reference. The biocarbon composition may be utilized as a conductive additive in an electrode, or as the primary electrode material, such as to an anode material to intercalate $Li^+$ ions in a lithium-ion battery. The base-acid ratio of the biocarbon composition for use as or in a battery electrode (anode or cathode) may be selected based on the active metal ion in the battery, as well as the other materials present in the electrode.

**[0324]** In some embodiments pertaining to use of the biocarbon composition in battery electrodes, the base-acid ratio is adjusted to be from about 0.2 to about 2.0, such as about, at least about, or at most about 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, or 2.0, including any intervening ranges (e.g., 0.4–1.5).

**[0325]** In some embodiments pertaining to use of the biocarbon composition in battery electrodes, the expanded base-acid ratio is adjusted to be from about 0.1 to about 1.6, such as about, at least about, or at most about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, or 1.6, including any intervening ranges.

**[0326]** Some embodiments pertain to use of biocarbon composition as activated carbon or as a precursor for making activated carbon. The base-acid ratio of the biocarbon composition for use as activated carbon may be selected based on the components to be removed via adsorption onto the activated carbon, such as whether the components are acidic, basic, or neutral in pH, for example.

**[0327]** In some embodiments pertaining to use of the biocarbon composition as activated carbon or as a precursor for making activated carbon, the base-acid ratio is adjusted to be from about 0.2 to about 2.0, such as about, at least about, or at most about 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, or 2.0, including any intervening ranges (e.g., 0.8–1.7).

**[0328]** In some embodiments pertaining to use of the biocarbon composition as activated carbon or as a precursor for making activated carbon, the expanded base-acid ratio is adjusted to be from about 0.1 to about 1.6, such as about, at least about, or at most about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, or 1.6, including any intervening ranges.

**[0329]** In some embodiments, acid water washing is utilized to optimize a compositional parameter. The biocarbon is produced by a non-combustion thermal process (typically, pyrolysis) that converts starting biomass to biochar, gas, vapors, or liquids. The process can be configured such that water coming in with the starting feedstock as well as water generated during pyrolysis reactions are both utilized in ways that displace some or all of the need for an external source of water.

**[0330]** In some variations, a process for producing a biocarbon composition comprises:

(a) providing a starting feedstock comprising biomass and from about 0 wt% to about 75 wt% water;

(b) drying the starting feedstock to generate a dried feedstock comprising from 0 wt% to about 50 wt% water, and a first vapor;

(c) pyrolyzing the dried feedstock to generate hot solids and a second vapor;

(d) condensing at least a portion of the first vapor to generate a first condensed liquid having a first pH from about 1 to about 7;

(e) condensing at least a portion of the second vapor to generate a second condensed liquid having a second pH from about 1 to about 7;

(f) forming acid water comprising at least some of the first condensed liquid, at least some of the second condensed liquid, or a mixture comprising at least some of the first condensed liquid as well as at least some of the second condensed liquid;

(g) washing and cooling the hot solids using at least a portion of the acid water, to generate washed, cooled solids, wherein at least one compositional parameter is adjusted; and

(h) recovering the washed, cooled solids as a biocarbon composition that comprises at least about 50 wt% carbon.

**[0331]** In some embodiments, the dried feedstock comprises from 0 wt% to about 25 wt% water. In various embodiments, the dried feedstock comprises at most about 10 wt% water.

**[0332]** Process step (b) can utilize a steam-driven dryer or an air-driven dryer, for example.

**[0333]** The generated vapors from the dryer, comprising primarily water and light acids, are condensed from the dryer flue gas stream, in step (d).

**[0334]** The acidity of the first condensed liquid can vary with the operating conditions of the dryer as well as the type of feedstock. More severe dryer environments will tend to cause non-water components to off-gas from the feed and allow for collection during condensation.

**[0335]** In some embodiments, the first pH is from about 2 to about 7, or from about 3 to about 6.5, or from about 4 to about 6.5, for example. In some embodiments, the second pH is from about 2 to about 7, or about 3 to about 6.5, or from about 4 to about 6.5, for example. In some embodiments, the first pH is at most 7, and the second pH is at most 7. In other embodiments, the first pH is at most 7, and the second pH is about 7. In other embodiments, the second pH is at most 7, and the first pH is about 7.

**[0336]** In some embodiments, in step (f), the acid water comprises only first condensed liquid. In other embodiments, in step (f), the acid water comprises only second condensed liquid. In still other embodiments, in step (f), the acid water comprises both first condensed liquid and second condensed liquid. The acid water can comprise some or all of the first condensed liquid, as well as some or all of the second condensed liquid. In certain embodiments, the acid water comprises all of the first condensed liquid as well as all of the second condensed liquid. When the acid water comprises a combination of first condensed liquid and second condensed liquid, the pH of the combined acid water will be the logarithmic average of the pH of each condensed liquid.

**[0337]** The acid water in step (f) can be formed in a quantity from about 1 to about 500 gallons per dry metric ton of the starting feedstock, such as from about 50 to about 100 gallons per dry metric ton of the starting feedstock, for example (dependent on the original moisture content of the feed).

**[0338]** In some embodiments, a portion of the acid water generated in step (f) is recovered as a water co-product that is not used in step (g) but rather is sold or transferred to another party.

**[0339]** In some embodiments, during step (g), no other water source (e.g., well water) is used to wash or cool the hot solids.

**[0340]** In some embodiments, in step (g), the hot solids are initially at a substrate temperature of about 300°C to about 800°C, and the acid water cools the hot solids to a cooled-substrate temperature that is less than the substrate temperature. The cooled-substrate temperature can be at most 300°C, at most 200°C, at most 100°C, at most 50°C, or about 20-30°C, for example.

**[0341]** In some embodiments, washing in step (g) removes ash from the hot solids, which generally can comprise high levels of ash (such as up to 50 wt% ash). The washed, cooled solids can comprise at most about 5 wt% total ash, at most about 1 wt% total ash, or at most about 0.2 wt% total ash, for example. The extent of ash reduction in step (g) can be at least about 25%, 50%, 60%, 70%, 80%, 90%, 95%, 99%, or 100%, for example.

**[0342]** In some embodiments, washing in step (g) removes, from the hot solids, an impurity comprising iron, aluminum, titanium, boron, silicon, calcium, potassium, zinc, lead, cadmium, manganese, chromium, arsenic, mercury, nickel, cobalt, copper, tin, antimony, vanadium, molybdenum, oxides of any of these elements, or a combination or a derivative thereof. A compositional parameter that is adjusted in the process can be an individual concentration, such as chromium content, or can be a function of multiple components either natively in the biocarbon composition or present in the ash according to ASTM D4326, for example.

**[0343]** Other elements or compounds can be present as impurities in the hot solids. The washed, cooled solids can comprise a total concentration of the impurity at most about 1000 ppm, at most about 100 ppm, or at most about 50 ppm. The extent of impurities reduction in step (g) can be at least about 25%, 50%, 60%, 70%, 80%, 90%, 95%, 99%, or 100%, for example. For instance, the hot solids can comprise impurity levels up to 20,000 ppm; a reduction down to 50 ppm translates to 99.7% extent of impurities reduction.

**[0344]** In some embodiments, washing in step (g) produces washed, cooled solids having a higher heating value (HHV) of at least about 22 MJ/kg on a dry basis, such as HHV of at least about 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, or 33 MJ/kg on a dry basis. The extent of HHV enhancement in step (g) can be at least about 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or 100%, for example. Note that the removal of ash, discussed above, leads to a higher HHV for the washed, cooled solids and thus the biocarbon composition.

**[0345]** The washed, cooled solids can be pelletized to generate biocarbon pellets, following step (g) or possibly integrated with step (g). As used in this specification, a "biocarbon pellet" means a pellet comprising biogenic carbon. The pellet geometry can vary widely, as taught later. In some embodiments, no external binder is introduced to the washed, cooled solids during the pelletizing. A binder can be introduced to the washed, cooled solids to assist in generating the biocarbon pellets. The binder can be 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, or a combination or a derivative thereof.

**[0346]** The water intensity of the process can be at most about –10 kg $H_2O$ per metric ton of the biocarbon composition, such as a water intensity at most about –100, –200, –500, or –1000 kg $H_2O$ per metric ton of the biocarbon composition. In some embodiments of the process, no external water is utilized.

**[0347]** When the starting feedstock is biomass, which comprises biogenic and renewable carbon, the resulting carbon from pyrolysis is also biogenic. This can be shown from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the carbon, using for example ASTM D6866. 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. In some embodiments, the total carbon within the biocarbon composition is fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

**[0348]** Any biogenic carbon that is oxidized to carbon dioxide creates biogenic $CO_2$. This also can be shown from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the carbon in a sample of the generated $CO_2$. This biogenic $CO_2$, which is derived from biomass, returns to the environment to be taken up again by growing biomass via photosynthesis. In this way, net $CO_2$ emissions are significantly reduced.

**[0349]** In the above or other embodiments, the biocarbon composition is characterized by a carbon intensity at most 0 kg $CO_2e$ per metric ton of the biocarbon composition, such as a carbon intensity at most about –100, –200, –300, –400, or –500 kg $CO_2e$ per metric ton of the biocarbon composition. The process can be simultaneously characterized by a negative carbon intensity and a negative water intensity.

**[0350]** The "carbon intensity" of a product (or a process) is the net quantity by weight of carbon dioxide generated per ton of product, or sometimes per ton of feedstock processed to make the product. A "$CO_2$-equivalent carbon intensity" can also be defined, as the net quantity of carbon dioxide equivalent generated per ton of

product. The "carbon dioxide equivalent" or "$CO_2e$" signifies the amount of $CO_2$ which would have the equivalent global-warming impact. The typical units of carbon intensity are kilograms carbon dioxide equivalent per metric ton (1000 kg) of product.

**[0351]** A greenhouse gas (or "GHG") is any gas in the atmosphere which absorbs and re-emits heat, and thereby keeps the planet's atmosphere warmer than it otherwise would be. The main GHGs in the Earth's atmosphere are water vapor, carbon dioxide, methane, nitrous oxide, and ozone. By convention, the global-warming potential of $CO_2$ is defined to be 1. The global-warming potential of $CH_4$ is about 30, i.e., methane is 30× more potent than $CO_2$ as a greenhouse gas. See "IPCC Fourth Assessment Report: Climate Change 2007", Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge (2007), which is hereby incorporated by reference herein.

**[0352]** In order to calculate the carbon intensity of a product and process in general, the carbon intensities of the starting materials need to be estimated, as do the carbon intensities associated with the conversion of starting materials to intermediates, and the carbon intensities associated with the conversion of intermediates to final products. One skilled in the art of chemical engineering is able to make these calculations, which can be aided by software, such as life-cycle analysis software (e.g., GREET® or SimaPro® software).

**[0353]** Known principles of life-cycle analysis can be employed in calculating carbon intensity as well as water intensity. Life-cycle assessment (LCA) is a known method used to evaluate the environmental impact of a product through its life cycle, encompassing processing of the raw materials, manufacturing, distribution, use, recycling, and final disposal. When conducting an LCA, the fate of the final product usually needs to be specified. For example, in the case of steel, the steel often is installed such that it is place for long periods of time. In some embodiments, end-of-life options for the steel are considered, including industrial recycling options (steel is the most recycled material on the planet).

**[0354]** LCA also can consider the status quo regarding environmental inputs and outputs associated with a particular material. For example, forest residues that are not harvested will undergo decomposition that emits large quantities of methane, which causes a severe GHG penalty. If those forest residues are instead directed to

production of biocarbon and then metal, the avoided methane emissions can be taken into account in the overall carbon intensity. Because there are so many possibilities and the status quo itself is evolving, a database within LCA software can be utilized such that appropriate industry averages are employed.

**[0355]** In some variations, a process for producing a biocarbon composition comprises:

(a) providing a starting feedstock comprising biomass and from about 0 wt% to about 75 wt% water;

(b) optionally drying the starting feedstock to generate a dried feedstock comprising from 0 wt% to about 50 wt% water, and a first vapor;

(c) pyrolyzing the dried feedstock (or, if step (b) is not conducted, the starting feedstock) to generate hot solids and a second vapor;

(d) if step (b) is conducted, condensing at least a portion of the first vapor to generate a first condensed liquid having a first pH from about 1 to about 7;

(e) condensing at least a portion of the second vapor to generate a second condensed liquid having a second pH from about 1 to about 7;

(f) forming acid water comprising at least some of the second condensed liquid, or, if step (b) is conducted, at least some of the first condensed liquid or a mixture comprising at least some of the first condensed liquid as well as at least some of the second condensed liquid;

(g) washing and cooling the hot solids using at least a portion of the acid water, to generate washed, cooled solids, wherein at least one compositional parameter is adjusted; and

(h) recovering the washed, cooled solids as a biocarbon composition that comprises at least about 50 wt% carbon.

**[0356]** The water intensity of the process can be at most about 1000 kg $H_2O$ per metric ton of the biocarbon composition, such as a water intensity at most about 900, 800, 700, 600, 500, 400, 300, 200, 100, 50, 25, 10, 0, –10, –25, –50, –100, –200, –500, or –1000 kg $H_2O$ per metric ton of the biocarbon composition.

**[0357]** The water intensity of the low-water-intensity process can be about 1%, 2%, 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 60%, 70%, 80%, 90%, 95%, 100%, or more, reduced compared to an otherwise-equivalent process that does not employ recovery and reuse of acid water in steps (f) and (g).

**[0358]** A biocarbon composition produced according to this disclosure can be metallurgical carbon. In this disclosure, "metallurgical carbon" means carbon that is intended to be used in a process involving a metal. The metallurgical carbon can be a feedstock in a process to convert a metal ore to a metal, a process to purify a metal, a process to add carbon as an alloy element to a metal, a process to make a carbon–metal composite, or a combination thereof, for example. It will be recognized that a metallurgical carbon has other uses that do not require addition to a metal-making process. Thus the adjective *metallurgical*, in some (but not all) embodiments, limits the carbon to the intended use of metallurgical processing. In cases for which the metallurgical carbon disclosed herein is not actually utilized in metallurgy, then the adjective *metallurgical* shall not be construed as otherwise limiting the carbon in terms of its physical structure, chemical composition, or material properties. Any embodiments that provide metallurgical carbon should be understand as references also to embodiments that provide non-metallurgical carbon that is used in non-metallurgical applications. Various embodiments thus provide a non-metallurgical carbon product.

**[0359]** In some embodiments, the biocarbon composition comprises at least about 60 wt% carbon, at least about 70 wt% carbon, at least about 80 wt% carbon, or at least about 90 wt% carbon on a dry basis. In some embodiments, the biocarbon composition comprises at least about 50 wt% fixed carbon, at least about 75 wt% fixed carbon, or at least about 90 wt% fixed carbon on a dry basis. Note that the removal of ash during the washing with acid water leads to a higher fixed-carbon content in the washed, cooled solids and thus in the biocarbon composition.

**[0360]** The biocarbon composition can comprise from about 1 wt% to about 30 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. Total moisture can be measured by ASTM D3302 or ASTM D3173, for example.

**[0361]** The biocarbon composition can comprise from 0 to about 30 wt% ash (or higher), such as from about 2 wt% to about 25 wt% ash, from about 5 wt% to about 20 wt% ash, or from about 8 wt% to about 15 wt% ash. "Ash" refers to non-carbon components that do not vaporize during pyrolysis. Ash content can be measured by ASTM D3175 or other techniques. Ash composition can be analyzed by ASTM D4326 or other techniques.

**[0362]** In some embodiments, the biocarbon composition further comprises an additive. The concentration of the additive can be from about 0.2 wt% to about 25 wt%, from about 2 wt% to about 25 wt%, from about 5 wt% to about 20 wt%, or from about 1 wt% to about 5 wt% based on the total weight of the biocarbon composition. In certain embodiments, the concentration of the additive is at most 1 wt%, such as about, or at most about, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.15, 0.10, 0.05, 0.02, 0.01 wt%. Since the additive is optional, in some embodiments the additive concentration is zero.

**[0363]** In some embodiments, an additive is capable of being partially oxidized or combusted. In certain embodiments, an additive is a renewable material. In certain embodiments, an additive is a carbon-neutral or carbon-negative additive. An example of a carbon-neutral or carbon-negative additive is starch, which is generated via photosynthesis. In particular, sunlight energy can be stored by biomass as starch.

**[0364]** In some embodiments, an additive is a binder for the biocarbon composition. The binder can be an organic binder, an inorganic binder, or a combination thereof. In some embodiments, the additive is a binder selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, carboxymethyl cellulose, cellulose esters, 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, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, or a combination or a derivative thereof.

**[0365]** In certain embodiments, the additive is a binder selected from starch, thermoplastic starch, crosslinked starch, starch polymers, or a combination or a derivative thereof. The binder can be a thermoplastic starch that can be crosslinked. The thermoplastic starch can be a reaction product of starch and a polyol, wherein the polyol can be ethylene glycol, propylene glycol, glycerol, butanediols, butanetriols, erythritol, xylitol, sorbitol, or a combination or a derivative thereof, and wherein the reaction product can be formed from a reaction that is catalyzed by an acid or by a base. When the reaction is catalyzed by an acid, the acid can be formic acid, acetic acid, lactic acid, citric acid, oxalic acid, uronic acids, glucuronic acids, or a combination or a derivative thereof.

**[0366]** In some embodiments, an additive reduces the reactivity of the biocarbon composition compared to an otherwise-equivalent biocarbon composition without the additive.

**[0367]** The reactivity can be thermal reactivity. For example, the biocarbon composition can have lower self-heating compared to the otherwise-equivalent biocarbon composition without the additive. The reactivity can be chemical reactivity with oxygen, water, hydrogen, carbon monoxide, metals (e.g., iron or iron oxides), or more than one of these species.

**[0368]** In some embodiments, an additive is pore-filling within the biocarbon composition. In these or other embodiments, an additive is disposed on the surface of the biocarbon composition.

**[0369]** The biocarbon composition can be in powder form. Alternatively, or additionally, the biocarbon composition can be in agglomerated form.

**[0370]** For example, the biocarbon composition can be in agglomerated form as a biocarbon pellet, optionally with a binder. The biocarbon pellet can be characterized by a Hardgrove Grindability Index of at least 30, for example. The biocarbon pellet can be characterized by a Pellet Durability Index of at least 80%.

**[0371]** The biocarbon composition can be used in metal processing to produce a base metal selected from iron, copper, nickel, magnesium, manganese, aluminum, tin, zinc, cobalt, chromium, tungsten, molybdenum, silicon, or a combination or a derivative thereof. A metal product can be produced with alloying elements, such as an element

selected from Al, Bi, B, C, Ce, Cr, Cu, Fe, H, Mg, Mn, Mo, N, Nb, Ni, P, Pb, Si, Sn, S, Ta, Ti, W, V, Zr, Zn, oxides, carbides, hydrides, nitrides, or sulfides of any of the foregoing elements, or a combination or a derivative thereof. Other elements can be included in the metal product, which other elements can or can not function as alloy elements.

**[0372]** In some embodiments, the alloying elements include carbon. When carbon is present in the metal product, the carbon can be present at an equilibrium concentration within the metal. Alternatively, the carbon can be present at a non-equilibrium concentration within the metal, which can be lower than the equilibrium concentration or higher than the equilibrium concentration for carbon.

**[0373]** In some embodiments, the alloying elements include carbon that is derived from the biocarbon composition as disclosed herein. Other elements can be derived from the biocarbon composition and utilized as alloying elements, including (but not limited to) hydrogen, nitrogen, oxygen, sulfur, or phosphorus.

**[0374]** When a low-water-intensity biocarbon composition is used in a metal-making process, the final metal product can be credited with reduced water intensity as well. Some embodiments provide a carbon-negative, reduced-water-intensity metal product ("carbon-negative" is synonymous with negative carbon intensity).

**[0375]** In certain embodiments, the alloying elements include hydrogen. When the hydrogen is derived from the biocarbon composition, which itself is derived from a biomass feedstock, the hydrogen can be carbon-neutral or carbon-negative hydrogen since it is added to growing biomass from atmospheric water via photosynthesis. Just like with carbon, the reduced water intensity associated with the hydrogen carries through to the final metal product, from a LCA perspective.

**[0376]** Measuring the $^{14}C/^{12}C$ isotopic ratio of carbon (in solid carbon, or in carbon in vapor form, such as CO, $CO_2$, or $CH_4$) is a proven technique. A similar concept can be applied to hydrogen, in which the $^{2}H/^{1}H$ isotopic ratio is measured ($^{2}H$ is also known as deuterium, D). Fossil sources tend to be depleted in deuterium compared to biomass. See Schiegl et al., "Deuterium content of organic matter", *Earth and Planetary Science Letters*, Volume 7, Issue 4, 1970, Pages 307-313; and Hayes, "Fractionation of the Isotopes of Carbon and Hydrogen in Biosynthetic Processes", Mineralogical

Society of America, National Meeting of the Geological Society of America, Boston, MA, 2001, which are hereby incorporated by reference herein.

**[0377]** Renewable hydrogen can be recognized in the market in various ways, such as through renewable-energy standards, renewable-energy credits, renewable identification numbers, and the like. As just one example, an oil refinery utilizing renewable hydrogen in producing gasoline can be able to receive renewable-energy credit for such $H_2$ content. In a metal product such as steel, renewable hydrogen can be utilized during production of the metal (e.g., metal ore reduction with $H_2$) or renewable hydrogen can be a measurable alloy element in the final product.

**[0378]** In certain embodiments, the alloying elements include nitrogen. High-strength austenitic stainless steels can benefit from nitrogen. Nitrogen has greater solid solubility than carbon, is a strong austenite stabilizer, is a good interstitial solid-solution strengthener, and improves pitting corrosion resistance. When the nitrogen is derived from the biocarbon composition, which itself is derived from a biomass feedstock, the nitrogen can be carbon-neutral or carbon-negative when the nitrogen is added to growing biomass from atmospheric $N_2$ via the nitrogen cycle. On the other hand, when alloying nitrogen is ultimately derived from $NH_3$-based fertilizer, and the $NH_3$ is derived from energy-intensive Haber synthesis, then such nitrogen would not generally be carbon-neutral or carbon-negative nitrogen. The contribution to the overall carbon intensity and water intensity of the metal product can be very low since the nitrogen content, when any is present, is usually at most 1 wt%. Even the Haber process can be made less energy-intensive by, for example, using renewable energy to split water for $H_2$ production, or by employing renewable hydrogen.

**[0379]** In certain embodiments, the alloying elements include oxygen. Oxygen is not a commonly utilized alloy element where metal oxides are to be avoided. However, certain alloys, especially non-iron alloys, can employ oxygen (as O atoms) as an interstitial alloy element that strengthens the metal through interstitial solid-solution strengthening. When the oxygen is derived from the biocarbon composition, which itself is derived from a biomass feedstock, it will be recognized that the oxygen is derived from atmospheric $CO_2$ via photosynthesis that has $O_2$ as an output.

**[0380]** In certain embodiments, the alloying elements include sulfur. When the sulfur is derived from the biocarbon composition, which itself is derived from a biomass

feedstock, the carbon intensity of the sulfur will depend on the source of sulfur (e.g., soil versus added fertilizer).

**[0381]** In certain embodiments, the alloying elements include phosphorus. When the phosphorus is derived from the biocarbon composition, which itself is derived from a biomass feedstock, the carbon intensity of the phosphorus will depend on the source of phosphorus (e.g., soil versus added fertilizer).

**[0382]** In various embodiments, a metal product is in a form selected from powder, pellets, sheets, rods, bars, wires, coils, pipes, plates, walls, tanks, cast structures, engineered structures, electromagnets, permanent magnets, or a combination thereof. The metal product can be a final structure or can be a feedstock for making a metal-comprising structure, via conventional subtractive manufacturing, additive manufacturing, or other techniques.

**[0383]** In some embodiments, a carbon-negative, reduced-water-intensity steel product can comprise at least about 80 wt% iron, at least about 90 wt% iron, or at least about 95 wt% iron. The carbon-negative, reduced-water-intensity steel product can comprise from about 0.01 wt% to about 10 wt% of the alloying element. The alloying element can be Al, Bi, B, C, Ce, Cr, Cu, H, Mg, Mn, Mo, N, Nb, Ni, P, Pb, Si, Sn, S, Ta, Ti, W, V, Zr, Zn, oxides, carbides, hydrides, nitrides, or sulfides of any of the foregoing elements, or a combination or a derivative thereof.

**[0384]** Variations of the invention employ optimized pyrolysis of biomass 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, optionally with adjustable Hardgrove Grindability Index (HGI). Moisture levels of the biocarbon pellets can be optimized to vary the densification within the pellets. The ability to adjust the HGI of the biocarbon pellets is very beneficial because downstream applications (e.g., use in blast furnaces) have varying HGI requirements. HGI is at least somewhat dependent on composition, and for that reason, HGI can be regarded as a compositional parameter.

**[0385]** In the context of a wide variety of biorefinery processes to convert biomass (e.g., wood chips) to products, particle-size reduction is necessary. The size reduction step is essential, but highly energy-intensive owing to the strong bonds in the naturally occurring cellulose, hemicellulose, and lignin polymers present. The problem is

especially severe when small particles are desired. For example, the energy consumption of hammer-mill grinding of biomass increases exponentially as a function of decreasing screen mesh size.

**[0386]** Raw biomass is inferior to pyrolyzed forms of biomass for a wide variety of commercial applications, many of which are described in this patent application. When biomass is pyrolyzed into a biogenic reagent, it often has mechanical properties that are not conducive to downstream uses, such as blast furnaces or pulverized coal boilers. For that reason, pelletizing the biogenic reagent to biocarbon pellets is preferred in many cases. However, once pelletized, the problematic grinding energy that was mentioned above for raw biomass again becomes challenging—and often even worse—to convert pellets to powders for industrial use. This can be potentially overcome by making loose agglomerates that are essentially weak pellets, but that then defeats the purposes of pelletizing in many cases when pellet durability is required during transport and plant handling, and sometimes within a reactor itself (e.g., to support a metal bed). The problem is difficult to solve because on the one hand, pellet durability is desired, but on the other hand, pellet grindability is desired. Yet, the present disclosure provides biocarbon pellets, and a process to make them, with good grindability and adequate durability.

**[0387]** 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. The present inventors have designed processes and compositions that are well-suited for adjustably grindable biocarbon pellets.

**[0388]** In some variations, the technology provides a biocarbon pellet comprising:

(a) about 35 wt% to about 99 wt% of a biogenic reagent, wherein the biogenic reagent comprises, on a dry basis, at least about 60 wt% carbon;

(b) about 0 wt% to about 35 wt% water moisture; and

(c) about 1 wt% to about 30 wt% of a binder,

wherein the biocarbon pellet is characterized by a Hardgrove Grindability Index of at least 30.

**[0389]** In some embodiments, the biogenic reagent comprises, on a dry basis, at least about 70 wt% carbon, at least about 80 wt% carbon, or at least about 90 wt%

carbon. In various embodiments, the biogenic reagent comprises, on a dry basis, about or at least about 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 wt% carbon. These percentages refer to the concentration of total carbon (fixed carbon and volatile carbon) relative to the entire biogenic reagent.

**[0390]** In some embodiments, the biogenic reagent comprises at least about 50 wt% fixed carbon, at least about 75 wt% fixed carbon, or at least about 90 wt% fixed carbon on a dry basis. In various embodiments, the biogenic reagent comprises about or at least about 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 wt% fixed carbon on a dry basis. These percentages refer to the concentration of fixed carbon relative to the entire biogenic reagent (excluding water), not relative to total carbon. Fixed carbon equals total carbon minus volatile carbon.

**[0391]** In some biocarbon pellets, the carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the carbon. For example, the carbon can at least 60%, at least 70%, at least 80%, at least 90%, at least 95%, at least 99%, or at least 99.9% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the carbon. In certain embodiments, the carbon is fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the carbon. The measurement of the $^{14}C/^{12}C$ isotopic ratio of the carbon can utilize ASTM D6866.

**[0392]** In certain embodiments, the biogenic reagent comprises, on a dry basis, from about 75 wt% to about 94 wt% carbon, from about 3 wt% to about 15 wt% oxygen, and from about 1 wt% to about 10 wt% hydrogen.

**[0393]** 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.

**[0394]** Various moisture levels can be present in the pellet product. 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.

**[0395]** 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. For some market applications, such as in agriculture, higher moisture levels are desirable for dust control or other reasons. For other market applications, lower moisture levels can be desirable (e.g., 1 wt% moisture or even less). In some metallurgical applications, low moisture is desirable, while in other metallurgical applications, some moisture is tolerable or even desirable to aid the overall chemistry.

**[0396]** 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.

**[0397]** 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.

**[0398]** The binder can be an organic binder or an inorganic binder. In some embodiments, the binder is or includes a renewable material. In some embodiments, the binder is or includes a biodegradable material. In some embodiments, the binder is capable of being partially oxidized or combusted.

**[0399]** In various embodiments, the binder is selected from starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, carboxymethyl cellulose, cellulose esters, 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, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, derivatives thereof, or a combination or a derivative thereof. The binder can be, or comprise, a grindable plasticizer.

**[0400]** In some embodiments, the binder is selected from starch, thermoplastic starch, crosslinked starch, starch-based polymers (e.g., polymers based on amylose and amylopectin), or a combination or a derivative thereof. Starch can be non-ionic starch, anionic starch, cationic starch, or zwitterionic starch.

**[0401]** 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 higher than 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 by relatively low levels of molecules that are capable of hydrogen bonding with the starch hydroxyl groups, such as water, glycerol, or sorbitol.

**[0402]** 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.

**[0403]** In some embodiments, a starch-comprising binder is or includes 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.

**[0404]** 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.

**[0405]** 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.

**[0406]** 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.

**[0407]** 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).

**[0408]** 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. 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".

**[0409]** 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.

**[0410]** Optionally, the carbon-comprising pellets comprise an additive (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.

**[0411]** 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 or a derivative thereof. For example, an 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, titanium compounds, or a combination or a derivative thereof.

**[0412]** Additives can be introduced 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. However, when during the process the additive is introduced is significant and can be critical, depending on the desired product. For example, where an additive is added before pyrolysis, the final product will comprise the derivative of the additive or the additive itself, depending on how the additive behaves under pyrolysis conditions.

**[0413]** 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.

**[0414]** 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.).

**[0415]** The biocarbon pellet (e.g., a carbon-negative and negative-water-intensity 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 at most 99%, at most 95%, at most 90%, at most 85%, or at most 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.

**[0416]** 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", "granule", and "prill". The pellet geometry can be spherical (round or ball shape), cube (square), octagon, hexagon, honeycomb/beehive shape, oval shape, egg shape, column shape, bar shape, disk shape, pillow shape, random shape, or a combination thereof. For convenience of disclosure, the term "pellet" will generally be used for any object comprising a powder agglomerated, optionally with a binder.

**[0417]** The biocarbon pellets can be characterized by an average pellet diameter, which is the true diameter in the case of a sphere, 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.

**[0418]** In some embodiments, there is a plurality of biocarbon pellets that is relatively uniform in size, such as a standard deviation of at most ±100%, at most ±50%, at most ±25%, at most ±10%, or at most ±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.

**[0419]** Some variations of the technology provide a biocarbon pellet comprising:

(a) about 35 wt% to about 99 wt% of a biogenic reagent, wherein the biogenic reagent comprises, on a dry basis, at least about 60 wt% carbon;

(b) about 0 wt% to about 35 wt% water moisture; and

(c) about 1 wt% to about 30 wt% of a reactivity-moderating agent,

wherein the reactivity-moderating agent reduces the reactivity of the biocarbon pellet compared to an otherwise-equivalent biocarbon pellet without the reactivity-moderating agent.

**[0420]** In some embodiments, the biogenic reagent comprises, on a dry basis, at least about 70 wt% carbon. The biogenic reagent can comprise at least about 50 wt% fixed carbon.

**[0421]** The biogenic reagent can comprise, on a dry basis, from about 75 wt% to about 94 wt% carbon, from about 3 wt% to about 15 wt% oxygen, and from about 1 wt% to about 10 wt% hydrogen.

**[0422]** In some embodiments, the biocarbon pellet comprises from about 1 wt% to about 30 wt% moisture

**[0423]** In some embodiments, the carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the carbon. In certain embodiments, the carbon is fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the carbon.

**[0424]** In some biocarbon pellets, the biocarbon pellet comprises from about 2 wt% to about 25 wt% of the reactivity-moderating agent. The biocarbon pellet can

comprise from about 5 wt% to about 20 wt%, or from about 1 wt% to about 5 wt% of the reactivity-moderating agent, for example.

**[0425]** The reactivity-moderating agent can be organic or inorganic. The reactivity-moderating agent can be a renewable material. In some embodiments, the reactivity-moderating agent is capable of being partially oxidized or combusted. The reactivity-moderating agent is preferably capable of adjusting a compositional parameter.

**[0426]** The reactivity-moderating agent can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, carboxymethyl cellulose, cellulose esters, 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, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, or a combination or a derivative thereof.

**[0427]** In some embodiments, the reactivity-moderating agent is selected from starch, thermoplastic starch, crosslinked starch, starch polymers, or a combination or a derivative thereof.

**[0428]** In certain embodiments, the reactivity-moderating agent is a thermoplastic starch that is optionally crosslinked. For example, the thermoplastic starch can be a reaction product of starch and a polyol. The polyol can be selected from ethylene glycol, propylene glycol, glycerol, butanediols, butanetriols, erythritol, xylitol, sorbitol, or a combination or a derivative thereof. The reaction product can be formed from a 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 a combination thereof, or by a base.

**[0429]** In some biocarbon pellets wherein the reactivity-moderating agent reduces the reactivity of the biocarbon pellet, the reactivity is thermal reactivity. For example, the biocarbon pellet can be characterized by lower self-heating compared to the otherwise-equivalent biocarbon pellet without the reactivity-moderating agent.

**[0430]** In some biocarbon pellets in which the reactivity-moderating agent reduces the reactivity of the biocarbon pellet, the reactivity is chemical reactivity with oxygen, water, hydrogen, carbon monoxide, metals (such as iron), or a combination thereof.

**[0431]** In some biocarbon pellets, the reactivity-moderating agent is pore-filling within the biogenic reagent of the biocarbon pellets. In other biocarbon pellets, the reactivity-moderating agent is disposed on the surface of the biocarbon pellets. In still other biocarbon pellets, the reactivity-moderating agent is both pore-filling within the biogenic reagent, and disposed on the surfaces, of the biocarbon pellets.

**[0432]** The reactivity-moderating agent can function as a binder to adjustably control the Hardgrove Grindability Index of the biocarbon pellet. In some embodiments, the biocarbon pellet is characterized by a Hardgrove Grindability Index of at least 30, such as from about 30 to about 50 or from about 50 to about 70. Other HGI ranges have been disclosed elsewhere in this specification and are equally applicable to embodiments in which a reactivity-moderating agent is employed and functions as a binder.

**[0433]** For example, a binder can be selected that functions both to controllably adjust the HGI as well as to serve as a reactivity-moderating agent. In these cases, it can be desirable to ensure the binder is dispersed throughout the biogenic carbon (filling the pores of the biocarbon pellet) as well as disposed on the surfaces of biocarbon pellets. The concentration of binder can differ on the surface compared to the bulk (internally) of the pellet. In some cases, a higher concentration of binder is present in the pellet bulk versus the surface, while in other cases (e.g., certain embodiments for reduced self-heating pellets), a higher binder concentration is desired at the surface. It is also possible to have two different binders (chemical species)—one within the bulk of the pellets and one at the surface. In such cases, the bulk binding agent can be referred to as the binder and the pellet surface agent can be referred to as the pellet reactivity-moderating agent. It will be appreciated that even in such embodiments, if the binder is added during the pellet production process, some amount of binder will be present at the pellet surface. Likewise, if the reactivity-moderating agent is coated onto the pellets after they are formed, some amount of diffusion of reactivity-moderating agent into the pellet pores can be expected.

**[0434]** Other variations of the technology provide a process of producing biocarbon pellets, the process comprising:

(a) drying a biomass feedstock;

(b) pyrolyzing the biomass feedstock to generate a biogenic reagent, wherein the biogenic reagent comprises at least about 50 wt% carbon and at least about 5 wt% moisture;

(c) mechanically treating the biogenic reagent to generate a plurality of carbon-comprising particles;

(d) combining the carbon-comprising particles with a binder to form a carbon-binder mixture;

(e) pelletizing the carbon-binder mixture, following step (d) or simultaneously with step (d), to generate biocarbon pellets; and

(f) optionally, at least partially drying the biocarbon pellets;

(g) condensing at least a portion of a first vapor collected in step (a) to generate a first condensed liquid having a first pH from about 1 to about 7;

(h) condensing at least a portion of a second vapor collected in step (b) or step (f) to generate a second condensed liquid having a second pH from about 1 to about 7;

(i) forming acid water comprising at least some of the first condensed liquid, at least some of the second condensed liquid, or a mixture comprising at least some of the first condensed liquid as well as at least some of the second condensed liquid;

(j) washing and cooling the hot solids using at least a portion of the acid water, to generate washed, cooled solids, wherein at least one compositional parameter is adjusted; and

(k) recovering the biocarbon pellets that comprises at least about 50 wt% carbon.

**[0435]** In some process embodiments, the biogenic reagent comprises, on a dry basis, at least about 70 wt% carbon, at least about 80 wt% carbon, or at least about 90 wt% carbon.

**[0436]** In some process embodiments, the biogenic reagent comprises at least about 50 wt% fixed carbon, at least about 75 wt% fixed carbon, or at least about 90 wt% fixed carbon.

**[0437]** The carbon can be at least 50%, at least 90%, at least 95%, or fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the carbon. In some embodiments, the measurement of the $^{14}C/^{12}C$ isotopic ratio of the carbon utilizes ASTM D6866.

**[0438]** In certain processes, the biogenic reagent comprises, on a dry basis, from about 75 wt% to about 94 wt% carbon, from about 3 wt% to about 15 wt% oxygen, and from about 1 wt% to about 10 wt% hydrogen.

**[0439]** In some processes, the biogenic reagent comprises at least about 10 wt%, 15 wt%, 20 wt%, 25 wt%, 30 wt%, 35 wt%, or 40 wt% moisture in step (b). At moisture contents at least 40 wt%, while a biocarbon pellet can still be made, the pellet density is expected to be inferior (too low for many applications). In some embodiments, step (c), step (d), or step (e) is conducted at a lower moisture than the moisture of step (b). For example, when step (f) is conducted, drying can result in a lower moisture than the moisture in step (b) and optionally lower moisture than the moisture in step (c), step (d), or step (e).

**[0440]** In some embodiments, step (f) is conducted after step (e). In these or other embodiments, step (f) is integrated with step (e). For example, a pelletizing unit can allow water release from the pellets as they are being formed, i.e., the pelletizing unit can act as a dryer as well. In certain embodiments, some amount of drying takes place during pelletizing, and additional drying takes places following pelletizing, such as in a drying unit or under ambient conditions.

**[0441]** In some embodiments, the biogenic reagent is not dried during step (c). In these or other embodiments, the biogenic reagent is not dried during step (d). In these or other embodiments, the biogenic reagent is not dried during step (e).

**[0442]** The biocarbon pellet can comprise from about 1 wt% to about 30 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.

**[0443]** In some processes, step (b) is conducted at a 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 (b) is conducted for a pyrolysis time selected from about 10 second to about 24 hours. Other possible pyrolysis conditions are described later in this specification.

**[0444]** Step (c) can utilize 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.

**[0445]** In some processes, step (c) and step (d) are integrated. For example, a binder can be fed directly to a hammer mill or extruder, or other mechanical-treatment apparatus.

**[0446]** The biocarbon pellet can comprise from about 2 wt% to about 25 wt% of the binder, such as about 5 wt% to about 20 wt% of the binder, or from about 1 wt% to about 5 wt% of the binder. The binder can be organic or inorganic.

**[0447]** The binder can be selected from starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, carboxymethyl cellulose, cellulose esters, 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, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, or a combination or a derivative thereof. In certain processes, the binder is selected from starch, crosslinked starch, starch polymers, or a combination or a derivative thereof.

**[0448]** Step (e) 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.

**[0449]** In some processes, step (d) and step (e) are integrated. For example, the binder can be introduced directly into the pelletizing unit. When step (d) and step (e)

are performed separately, the binder is combined with the carbon-comprising particles to form a carbon-binder mixture prior to introducing such mixture into the unit configured for pelletizing the carbon-binder mixture.

**[0450]** In some embodiments of the invention, 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. The average pellet diameter of the smaller biocarbon pellets can be larger than the average particle diameter of the initial carbon-comprising particles that were used to make the pellets with the binder.

**[0451]** When the biocarbon pellets are crushed to generate smaller biocarbon pellets, a step of crushing (and optionally screening) can be integrated with step (e), can follow step (e), can be integrated with step (f), or can follow step (f), 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.

**[0452]** 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.

**[0453]** 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.).

**[0454]** In some processes, the biocarbon pellet is characterized by a Pellet Durability Index of at least 80%, at least 90%, or at least 95%.

**[0455]** 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.

**[0456]** The 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, 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 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 gasifier for purposes of making syngas from the biocarbon pellets.

**[0457]** In some embodiments, the biocarbon pellets are negative-water-intensity and carbon-negative metallurgical carbon pellets 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.

**[0458]** 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 comprising biocarbon pellets, the pellets can then be ground, combusted, gasified, or otherwise reused or recycled.

Pyrolysis Processes and Systems

**[0459]** Processes and systems suitable for pyrolyzing a biomass feedstock to generate a biogenic reagent comprising carbon will now be further described in detail.

**[0460]** "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 at most 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.

**[0461]** Exemplary changes that can occur during pyrolysis include 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.

**[0462]** Pyrolysis can at least partially dehydrate a starting feedstock (e.g., lignocellulosic biomass). In various embodiments, pyrolysis removes at least about 50%, 75%, 90%, 95%, 99%, or more of the water from the starting feedstock.

**[0463]** In various 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 or a derivative thereof. A biomass feedstock comprises at least carbon, hydrogen, and oxygen.

**[0464]** The biogenic reagent can comprise at least about 50 wt%, at least about 75 wt%, or at least about 90 wt% carbon (total carbon). In various embodiments, the biogenic reagent comprises about, at least about, or at most about 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.

**[0465]** The biogenic reagent can comprise at least about 50 wt%, at least about 75 wt%, or at least about 90 wt% fixed carbon. In various embodiments, the biogenic reagent comprises about, at least about, or at most about 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, or 99 wt% fixed carbon.

**[0466]** The carbon (within the biogenic reagent) can be at least about 50 wt%, at least about 75 wt%, or at least about 90 wt% fixed carbon, for example, with the remainder of the carbon being volatile carbon. In various embodiments, the carbon comprises about, at least about, or at most about 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 99, or 100 wt% fixed carbon.

**[0467]** 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.

**[0468]** 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.

**[0469]** In some embodiments, the temperatures and residence times are selected to achieve relatively slow pyrolysis chemistry. The benefit is potentially the substantial preservation of cell walls contained 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 utilized. Various reactor configurations are discussed following the process description below.

**[0470]** 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.

**[0471]** In some embodiments, a first zone of a pyrolysis reactor is configured for feeding biomass (or another carbon-comprising 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.

**[0472]** 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.

**[0473]** 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-comprising components that are in the gas phase can decompose to form additional fixed carbon or become adsorbed onto the carbon. Thus, in some embodiments, the final carbonaceous material is not simply the solid, devolatilized residue of the processing steps, but rather includes additional carbon that has been deposited from the gas phase, such as by decomposition of organic vapors (e.g., tars) that can form carbon.

**[0474]** 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-comprising 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.

**[0475]** There are many 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.

**[0476]** 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.

**[0477]** In some embodiments, a pyrolysis process for producing a high-carbon biogenic reagent comprises the following steps:

(a) providing a carbon-comprising 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 high-carbon biogenic reagent comprising at least a portion of the cooled pyrolyzed solids.

**[0478]** "Biomass," for purposes of this disclosure, shall be construed as any biogenic feedstock or mixture of a biogenic and non-biogenic feedstocks. Elementally, biomass includes at least carbon, hydrogen, and oxygen. The methods and apparatus of the invention can accommodate a wide range of feedstocks of various types, sizes, and moisture contents.

**[0479]** Biomass includes, 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 of the invention utilizing biomass, the biomass feedstock can include a material 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, or cloth. A person of ordinary skill in the art will readily appreciate that the feedstock options are virtually unlimited.

**[0480]** The present invention can also be used for mixtures of biomass and fossil fuels (such as biomass/coal blends), recognizing that the carbon intensity of the final product will not be as low as with pure biomass feedstocks, but lower than if pure fossil-fuel feedstocks are used. In some embodiments, a feedstock includes, coal, oil shale, crude oil, asphalt, or solids from crude-oil processing (such as petcoke). Feedstocks

can include waste tires, recycled plastics, recycled paper, construction waste, deconstruction waste, and other waste or recycled materials.

**[0481]** 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. Carbon-comprising 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.

**[0482]** 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.

**[0483]** It is noted that size reduction is a costly and energy-intensive process. Pyrolyzed material can be sized with significantly less energy input. Accordingly, it can be desirable to reduce the particle size of the product, not the feedstock. This is an option in the present invention 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 of this invention. 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.

**[0484]** 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 invention. 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.

**[0485]** 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.

**[0486]** 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.

**[0487]** It is 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.

**[0488]** 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.

**[0489]** 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.

**[0490]** 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.

**[0491]** Various types of deaeration units can be employed. Where drying is to be performed, drying can be performed before deaeration due to the inefficiencies of scrubbing 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.

**[0492]** 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.

**[0493]** 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.

**[0494]** References to "zones" shall be broadly construed to include 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.

**[0495]** 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.

**[0496]** 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 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.

**[0497]** All references to zone temperatures in this specification should be construed in a non-limiting way to include 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.

**[0498]** 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 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.

**[0499]** 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.

**[0500]** 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-comprising 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.

**[0501]** 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.

**[0502]** 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.

**[0503]** 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 is usually not desirable as it would contribute to higher capital cost, unless some amount of mild pyrolysis is intended in the preheating zone.

**[0504]** 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.

**[0505]** 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.

**[0506]** 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 is not desirable, unless some amount of secondary pyrolysis is preferred.

**[0507]** 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.

**[0508]** 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.

**[0509]** 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.

**[0510]** 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.

**[0511]** 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).

**[0512]** 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.

**[0513]** 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.

**[0514]** 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.

**[0515]** 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.

**[0516]** 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.

**[0517]** 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.

**[0518]** 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.

**[0519]** 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.

**[0520]** 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.

**[0521]** 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.

**[0522]** The volatiles-comprising sweep gas can exit from the one or more reactor zones, and can be combined if obtained from multiple zones. The resulting gas stream, comprising 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 contained therein.

**[0523]** 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. The energy content of the thermal oxidizer effluent can be 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.

**[0524]** 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.

**[0525]** 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 contained 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.

**[0526]** 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, comprising 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.

**[0527]** 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 at most 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 include containers, tanks, pipes, or portions thereof.

**[0528]** 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.

**[0529]** 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.

**[0530]** Screening or some other means for separation based on particle size can be included. 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.

**[0531]** 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 properties of the high-carbon biogenic reagent, or a downstream product incorporating the reagent. Certain additives can provide enhanced process *and* product (biogenic reagents or products comprising biogenic reagents) characteristics.

**[0532]** 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.

**[0533]** 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, and combinations thereof.

**[0534]** 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.

**[0535]** 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.

**[0536]** 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.

**[0537]** 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.

**[0538]** 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 includes the additive, thereby improving the final strength.

**[0539]** 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 containers.

**[0540]** 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.

**[0541]** 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.

**[0542]** 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.

**[0543]** 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.

**[0544]** 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. In some embodiments, the secondary process can be conducted in a simple container, such as a steel drum, in which heated inert gas (such as heated $N_2$) is passed through. Other containers useful for this purpose include 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.

**[0545]** Some variations of the technology utilize a high-carbon biogenic reagent production system comprising:

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

(b) an optional dryer, disposed in operable communication with the feeder, configured to remove moisture comprised within a carbon-comprising 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 high-carbon biogenic reagent recovery unit, disposed in operable communication with the solids cooler.

**[0546]** Some variations utilize a high-carbon biogenic reagent production system comprising:

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

(b) an optional dryer, disposed in operable communication with the feeder, configured to remove moisture comprised within a carbon-comprising 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 high-carbon 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.

**[0547]** 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.

**[0548]** 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.

**[0549]** 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).

**[0550]** The system can include 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.

**[0551]** The multiple-zone reactor can be 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.

**[0552]** 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.

**[0553]** 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.

**[0554]** In some 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.

**[0555]** As intended herein, "monitor and control" via reaction gas probes should be construed to include 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.).

**[0556]** 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).

**[0557]** 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.

**[0558]** 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. Terpene concentration in the gas phase could be measured and used as an indication of the pyrolysis selectivity toward liquids, for example.

**[0559]** 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).

**[0560]** 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.

**[0561]** 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.

**[0562]** 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.

**[0563]** 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 include, 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.

**[0564]** 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.

**[0565]** 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.

**[0566]** 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 include 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.

**[0567]** Circulating fluidized-bed reactors can be employed, wherein gas, sand, and feedstock move together. Exemplary transport gases include 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.

**[0568]** 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.

**[0569]** In various embodiments the reactor includes 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.

**[0570]** 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.

**[0571]** 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.

**[0572]** 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.

**[0573]** 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.

**[0574]** Other means of agitating solids can be employed, such as augers, screws, or paddle conveyors. In some embodiments, the reactor includes a single, continuous

auger disposed throughout each of the reaction zones. In other embodiments, the reactor includes twin screws disposed throughout each of the reaction zones.

**[0575]** 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.

**[0576]** In some embodiments of the invention, the system further includes a thermal oxidizer disposed in operable communication with the outlet at which condensable vapors and non-condensable gases are removed. The thermal oxidizer can be 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 $CO_2$.

**[0577]** When a thermal oxidizer is employed, the system can include 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.

**[0578]** 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 high-carbon biogenic reagent obtained from the recovery unit.

**[0579]** The system can further include a separate pyrolysis unit adapted to further pyrolyze the high-carbon biogenic reagent to further increase its carbon content. The separate pyrolysis unit can be a relatively simply container, unit, or device, such as a tank, barrel, bin, drum, tote, sack, or roll-off.

**[0580]** 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.

**[0581]** Some variations relating to carbon enhancement of solids will now be further described. In some embodiments, a process for producing a high-carbon biogenic reagent comprises:

(a) providing a carbon-comprising 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 high-carbon biogenic reagent comprising at least a portion of the enhanced pyrolyzed solids.

**[0582]** In some embodiments, step (h) includes 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) includes 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.

**[0583]** Alternatively, or additionally, vapors or gases can be contacted with the cool pyrolyzed solids. In some embodiments, step (h) includes 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) includes 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.

**[0584]** In certain embodiments, step (h) includes 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) includes 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.

**[0585]** The process can include various methods of treating or separating the vapors or gases prior to using them for carbon enhancement. For example, an intermediate feed stream consisting essentially 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.

**[0586]** Separation techniques can include 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.

**[0587]** 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.

**[0588]** 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 include at least one carbon-comprising compound selected from terpenes, alcohols, acids, aldehydes, or ketones. The vapors from pyrolysis can include 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 include at least one carbon-comprising molecule selected from carbon monoxide, carbon dioxide, or methane.

**[0589]** 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.

**[0590]** 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-comprising molecule selected from methanol, furfural, or acetic acid. The non-polar compounds can comprise at least one carbon-comprising molecule selected from carbon monoxide, carbon dioxide, methane, a terpene, or a terpene derivative.

**[0591]** Step (h) can increase the total carbon content of the high-carbon 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.

**[0592]** In some embodiments, step (h) increases the fixed carbon content of the high-carbon biogenic reagent. In these or other embodiments, step (h) increases the volatile carbon content of the high-carbon 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.

**[0593]** 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.

**[0594]** Step (h) can increase the energy content (i.e., energy density) of the high-carbon 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.

**[0595]** Further separations can be employed to recover a non-condensable gas or condensable vapor, for use within the process or further processing. For example, further processing can be included to produce refined carbon monoxide or hydrogen.

**[0596]** 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.

**[0597]** 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 high-carbon 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.

**[0598]** 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.

**[0599]** 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.

**[0600]** In some embodiments, a batch or continuous process for producing a high-carbon biogenic reagent comprises:

(a) providing a solid stream comprising a carbon-comprising material;

(b) providing a gas stream comprising condensable carbon-comprising vapors, non-condensable carbon-comprising gases, or a mixture of condensable carbon-comprising vapors and non-condensable carbon-comprising gases; and

(c) passing the gas stream across the solid stream under suitable conditions to form a carbon-comprising product with increased carbon content relative to the carbon-comprising material.

**[0601]** In some embodiments, the starting carbon-comprising material is pyrolyzed biomass or torrefied biomass. The gas stream can be obtained during an integrated process that provides the carbon-comprising material. Or, the gas stream can be obtained from separate processing of the carbon-comprising 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-comprising materials, from a variety of sources, are possible.

**[0602]** 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-comprising 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-comprising material.

**[0603]** In some embodiments, the process further includes 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-comprising vapors and non-condensable carbon-comprising 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-comprising material.

**[0604]** 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-comprising 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.

**[0605]** The carbon-comprising 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-comprising material.

**[0606]** In related variations, a high-carbon biogenic reagent production system comprises:

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

(b) an optional dryer, disposed in operable communication with the feeder, configured to remove moisture comprised within a carbon-comprising 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 high-carbon biogenic reagent recovery unit, disposed in operable communication with the material-enrichment unit.

**[0607]** 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.

**[0608]** 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.

**[0609]** 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.

**[0610]** The present invention is capable of producing a variety of compositions useful as high-carbon biogenic reagents, and products incorporating such reagents. In some variations, a high-carbon biogenic reagent is produced by any process disclosed herein, such as a process comprising the steps of:

(a) providing a carbon-comprising 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 within 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 high-carbon biogenic reagent comprising at least a portion of the cool pyrolyzed solids.

**[0611]** 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 includes at least fixed carbon, and can further include 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 high-carbon biogenic reagent. Fixed carbon can be measured using ASTM D3172, while volatile carbon can be measured using ASTM D3175, for example.

**[0612]** The high-carbon 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.

**[0613]** 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.

**[0614]** 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.

**[0615]** 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.

**[0616]** Various amounts of non-combustible matter, such as ash, can be present. The high-carbon 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.

**[0617]** Various amounts of moisture can be present. On a total mass basis, the high-carbon 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.

**[0618]** The high-carbon 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 high-carbon 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.

**[0619]** The high-carbon 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.

**[0620]** In some embodiments, the high-carbon 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.

**[0621]** In some embodiments, the high-carbon 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 high-carbon biogenic reagent. Or, feedstock cylinders can produce high-carbon biogenic reagent cylinders, which can be somewhat smaller but otherwise maintain the basic structure and geometry of the starting material.

**[0622]** A high-carbon biogenic reagent according to the present invention 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.

**[0623]** Other variations of the invention relate to the incorporation of additives into the process, into the product, or both. In some embodiments, the high-carbon biogenic reagent includes at least one process additive incorporated during the process. In these or other embodiments, the reagent includes at least one product additive introduced to the reagent following the process.

**[0624]** In some embodiments, a high-carbon 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.

**[0625]** 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, and combinations thereof.

**[0626]** In some embodiments, a high-carbon 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.

**[0627]** 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.

**[0628]** In certain embodiments, a high-carbon 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.

**[0629]** 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, and combinations 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.

**[0630]** A certain high-carbon 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 combinations thereof.

**[0631]** A certain high-carbon 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 combinations thereof.

**[0632]** 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 higher than 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 high-carbon 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.

**[0633]** 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.

**[0634]** In some embodiments, the majority of carbon contained in the high-carbon 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 high-carbon biogenic reagent.

**[0635]** 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.

**[0636]** The high-carbon biogenic reagents produced as described herein is useful for a wide variety of carbonaceous products. The high-carbon biogenic reagent can be a desirable market product itself. High-carbon 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.

**[0637]** In variations, a product includes any of the high-carbon biogenic reagents that can be obtained by the disclosed processes, or that are described in the compositions set forth herein, or any portions, combinations, or derivatives thereof.

**[0638]** Generally speaking, the high-carbon 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 high-carbon biogenic reagents can be utilized for any market application of carbon-based commodities or advanced materials, including specialty uses to be developed.

**[0639]** Prior to suitability or actual use in any product applications, the disclosed high-carbon 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, include density, particle size, surface area, microporosity, absorptivity, adsorptivity, binding capacity, reactivity, desulfurization activity, and basicity, to name a few properties.

**[0640]** Products or materials that can incorporate these high-carbon biogenic reagents include, 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, 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.

**[0641]** Use of the disclosed high-carbon biogenic reagents in metals production can reduce slag, increase overall efficiency, and reduce lifecycle environmental impacts. Therefore, embodiments of this invention are particularly well-suited for metal processing and manufacturing.

**[0642]** Some variations of the invention utilize the high-carbon 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.

**[0643]** The reducing agent can consist essentially of or comprise a high-carbon biogenic reagent. In a blast furnace, high-carbon 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.

**[0644]** 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.

**[0645]** 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.

**[0646]** In some embodiments, the high-carbon biogenic reagent provides a carbon product having suitable properties for introduction directly into a blast furnace.

**[0647]** The strength of the high-carbon 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 high-carbon 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 high-carbon biogenic reagent is suitable for use as an additive or replacement for met coal, met coke, coke breeze, foundry coke, or injectable coal.

**[0648]** Some embodiments employ an additive in an amount sufficient to provide a high-carbon 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, an additive is present in an amount sufficient to provide a high-carbon biogenic reagent having a CRI of not more than about 40%, 30%, or 20%.

**[0649]** In some embodiments, an additive selected from the alkaline earth metals, or oxides or carbonates thereof, are introduced during or after the process of producing a high-carbon 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 high-carbon 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., $SO_2$).

**[0650]** In some embodiments, a blast furnace replacement product is a high-carbon biogenic reagent according to the present invention 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 an additive. 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.

**[0651]** In some embodiments, a high-carbon biogenic reagent according to the present invention 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.

**[0652]** Some variations of the invention utilize the high-carbon biogenic reagents as carbon-based taconite pellet addition products. The ores used in making iron and steel are iron oxides. Major iron oxide ores include 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.

**[0653]** 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, comprising 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.

**[0654]** 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 high-carbon biogenic reagent is introduced to the blast furnace. In these or other embodiments, a high-carbon biogenic reagent is incorporated into the

taconite pellet itself. For example, taconite ore powder, after beneficiation, can be mixed with a high-carbon 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.

**[0655]** Some variations of the invention utilize the high-carbon 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.

**[0656]** High-carbon 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 high-carbon biogenic reagent according to the present invention, 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.

**[0657]** In some embodiments, a high carbon biogenic reagent according to the present invention 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).

**[0658]** 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.

**[0659]** 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 high-carbon 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.

**[0660]** 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 contained in iron nuggets, or any portion thereof, can be the high-carbon biogenic reagent provided herein. Iron nuggets can be produced through the reduction of iron ore in a rotary hearth furnace, using a high-carbon biogenic reagent as the reductant and energy source.

**[0661]** Some variations of the invention utilize the high-carbon 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.

**[0662]** Metallurgical coke is used where a high-quality, tough, resilient, wearing carbon is required. Applications include, 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.

**[0663]** 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 high-carbon biogenic reagent according to the present invention (e.g., a carbon-negative pellet) 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 high-carbon biogenic reagent according to the present invention, when used as a met coke replacement product, can have a size range from about 2 cm to about 15 cm, for example.

**[0664]** 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 and combinations thereof.

**[0665]** Some variations of the invention utilize the high-carbon biogenic reagents as coal replacement products. Any process or system using coal can in principle be adapted to use a high-carbon biogenic reagent.

**[0666]** In some embodiments, a high-carbon biogenic reagent is combined with a coal-based product to form a composite product having a higher rank than the coal-based product or having fewer emissions, when burned, than the coal-based product.

**[0667]** 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 high-carbon biogenic reagent according to the present invention 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 high-carbon biogenic reagent. The amount of a high-carbon 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 high-carbon biogenic reagent (e.g., carbon content, heat value, etc.) and the desired rank of the final combined product.

**[0668]** 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 high-carbon 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.

**[0669]** In some embodiments, a high-carbon 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 high-carbon 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.

**[0670]** Some variations of the invention utilize the high-carbon biogenic reagents as carbon-based coking products. Any coking process or system can be adapted to use high-carbon biogenic reagents to produce coke, or use it as a coke feedstock.

**[0671]** In some embodiments, a high-carbon biogenic reagent is useful as a thermal coal or coke replacement product. For example, a thermal coal or coke replacement product can consist of or consist essentially of a high-carbon 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 include about 0.4 wt% to about 15 wt% moisture.

**[0672]** In some embodiments, a high-carbon 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 high-carbon 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.

**[0673]** In some embodiments, a high-carbon 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 high-carbon 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 an additive.

**[0674]** Some variations of the invention utilize the high-carbon 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 high-carbon biogenic reagent according to the present invention 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 high-carbon biogenic reagent according to the present invention 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.

**[0675]** In some embodiments, a high-carbon biogenic reagent is useful as a carbon breeze replacement product during, for example, taconite pellet production or in an iron-making process.

**[0676]** Some variations utilize the high-carbon 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).

**[0677]** In some embodiments, a high-carbon biogenic reagent according to the present invention 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).

**[0678]** Some variations utilize the high-carbon 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 high-carbon 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.

**[0679]** In some embodiments, a high-carbon 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.

**[0680]** In some embodiments, a furnace addition carbon additive is a high-carbon 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.

**[0681]** Some variations utilize the high-carbon biogenic reagents as stoker furnace carbon-based products. In some embodiments, a high-carbon biogenic reagent according to the present invention 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).

**[0682]** Some variations utilize the high-carbon biogenic reagents as injectable (e.g., pulverized) carbon-based materials. In some embodiments, a high-carbon 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 high-carbon 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.

**[0683]** In some embodiments, a high-carbon 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).

**[0684]** In some embodiments, a high-carbon 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.

**[0685]** Some variations utilize the high-carbon biogenic reagents as carbon addition product for metals production. In some embodiments, a high-carbon biogenic reagent according to the present invention 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 of this invention, 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.

**[0686]** Some variations utilize the high-carbon biogenic reagents within carbon electrodes. In some embodiments, a high-carbon biogenic reagent is useful as an electrode (e.g., anode) material suitable for use, for example, in aluminum production.

**[0687]** Other uses of the high-carbon biogenic reagent in carbon electrodes include applications in batteries, fuel cells, capacitors, and other energy-storage or energy-delivery devices. For example, in a lithium-ion battery, the high-carbon biogenic reagent can be used on the anode side to intercalate lithium. In these applications, carbon purity and low ash can be very important.

**[0688]** Some variations of the invention utilize the high-carbon 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.

**[0689]** Some variations utilize the high-carbon 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 high-carbon 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.

**[0690]** It should be recognized that in the above description of market applications of high-carbon biogenic reagents, the described applications are not exclusive, nor are they exhaustive. Thus a high-carbon 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 high-carbon biogenic reagents.

**[0691]** 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 high-carbon 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.

**[0692]** Some embodiments can employ a biogenic reagent both for its reactive or 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.

**[0693]** Significant environmental and product use advantages can be associated with high-carbon biogenic reagents, compared to conventional fossil-fuel-based products. The high-carbon biogenic reagents can be not only environmentally superior, but also functionally superior from a processing standpoint because of greater purity, for example.

**[0694]** 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.

**[0695]** Use of high-carbon biogenic reagents in place of coal or coke also significantly reduces environmental emissions of $SO_2$, hazardous air pollutants, and mercury.

**[0696]** Also, because of the purity of these high-carbon 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.

**[0697]** In some embodiments, the biogenic reagent functions as an activated carbon. 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 include pulverizing back to a powder, and can also include chemical treatment with, e.g., steam, acids, or bases. In these embodiments, the biocarbon pellets can be regarded as activated-carbon precursor pellets.

**[0698]** 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).

**[0699]** 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 can be 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.

**[0700]** 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.

**[0701]** 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 can be 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.

**[0702]** Activated carbon produced by the processes disclosed herein can be used in a number of ways.

**[0703]** In some embodiments, the activated carbon is utilized internally at the process site to purify the primary product. 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.

**[0704]** 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 at least 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, at least, or at most 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.

**[0705]** 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 include density, particle size, surface area, microporosity, absorptivity, adsorptivity, binding capacity, reactivity, desulfurization activity, basicity, hardness, and Iodine Number.

**[0706]** 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 include 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.

**[0707]** The bulk density for the biogenic activated carbon can be from about 50 g/liter to about 650 g/liter, for example.

**[0708]** 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.

**[0709]** The pore-size distribution can be important to determine ultimate performance of the activated carbon. Pore-size measurements can include micropore content, mesopore content, and macropore content.

**[0710]** 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 include 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.

**[0711]** 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 include 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.

**[0712]** 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 include about 100, 150, 200, 250,

300, 350, and 400, including all intervening ranges. The units of Molasses Number are milligram molasses per gram carbon.

**[0713]** 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.

**[0714]** 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%.

**[0715]** 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 at least about 99%.

**[0716]** 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 at least about 99%.

**[0717]** 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.

**[0718]** 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.

**[0719]** 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.

**[0720]** A selected contaminant (in the gas-phase emissions stream) can be a metal, such as a metal is selected from mercury, boron, selenium, arsenic, or any compound, salt, or combination 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 a VOC. In some embodiments, the biogenic activated carbon comprises at least about 1 wt% hydrogen or at least about 10 wt% oxygen.

**[0721]** 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 included in possible selected contaminants in the present context.

**[0722]** 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 include 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 §51.100, which is incorporated by reference herein in its entirety.

**[0723]** Non-condensable gases are gases that do not condense under ordinary, room-temperature conditions. Non-condensable gas can include, 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.

**[0724]** Multiple contaminants can be removed by the disclosed activated carbon particles. In some embodiments, the contaminant-adsorbed carbon particles include 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).

**[0725]** In some embodiments, contaminant-adsorbed carbon particles are treated to regenerate activated carbon particles. In some embodiments, the method includes thermally oxidizing the contaminant-adsorbed carbon particles. The contaminant-

adsorbed carbon particles, or a regenerated form thereof, can be combusted to provide energy.

**[0726]** 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 some 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 or a derivative thereof.

**[0727]** In some embodiments, the gas-phase emissions stream is derived from metals processing, such as the processing of high-sulfur-content metal ores.

**[0728]** 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.

**[0729]** 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-comprising compounds can drastically improve the performance of electrostatic precipitators for mercury control. Furthermore, inclusion of iron or iron-comprising compounds can drastically change end-of-life options, since the spent activated carbon solids can be separated from other ash.

**[0730]** 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.

**[0731]** 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.

**[0732]** 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" includes 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.

**[0733]** In one embodiment, the present disclosure provides a method of using activated carbon to purify a liquid, in some variations, includes 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.

**[0734]** 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.

**[0735]** 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 or a derivative thereof.

**[0736]** 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, or any compound, salt, or combination 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 include 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 a VOC. In some embodiments, the biogenic activated carbon comprises at least about 1 wt% hydrogen or at least about 10 wt% oxygen.

**[0737]** 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.

**[0738]** 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-comprising contaminant from a liquid, the method comprising:

(a) providing activated-carbon particles recovered from the second reactor disclosed herein;

(b) providing a liquid comprising a sulfur-comprising contaminant;

(c) providing an additive selected to assist in removal of the sulfur-comprising 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-comprising contaminant onto or into the activated-carbon particles.

**[0739]** In some embodiments, the sulfur-comprising 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-comprising contaminant can be a sulfate, in anionic or salt form.

**[0740]** 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, or any other industrial process that is capable of discharging sulfur-comprising contaminants in wastewater. The water can also be (or be part of) a natural body of water, such as a lake, river, or stream.

**[0741]** 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 comprising 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.

**[0742]** 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.

**[0743]** 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-comprising 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.

**[0744]** 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.

**[0745]** The present disclosure also provides a method of using a biogenic activated carbon composition to remove a sulfur-comprising contaminant from a gas phase, the method comprising:

(a) providing activated-carbon particles recovered from the second reactor disclosed herein;

(b) providing a gas-phase emissions stream comprising at least one sulfur-comprising contaminant;

(c) providing an additive selected to assist in removal of the sulfur-comprising contaminant from the gas-phase emissions stream;

(d) introducing the activated-carbon particles and the additive into the gas-phase emissions stream, to adsorb or absorb at least a portion of the sulfur-comprising contaminant onto the activated-carbon particles; and

(e) separating at least a portion of the activated-carbon particles from the gas-phase emissions stream.

**[0746]** In some embodiments, the sulfur-comprising 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.

**[0747]** The disclosed activated carbon can be used in applications 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.

**[0748]** 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 in Metal Oxide Reduction

**[0749]** There are various embodiments in which biocarbon, such as in the form of pellets or a pulverized form thereof, is fed to a metal ore furnace or a chemical-reduction furnace.

**[0750]** 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.

**[0751]** 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.

**[0752]** Some variations of the technology 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.

**[0753]** "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.

**[0754]** 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.

**[0755]** 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.

**[0756]** 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.

**[0757]** 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.

**[0758]** 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.

**[0759]** 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.

**[0760]** 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.).

**[0761]** 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:

$$2\ C + O_2 \rightarrow 2\ CO$$

**[0762]** 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, $Fe_3O_4$:

$$3\ Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2$$

**[0763]** At temperatures around 850°C, further down in the furnace, the iron(II,III) is reduced further to iron(II) oxide, FeO:

$$Fe_3O_4 + CO \rightarrow 3\ FeO + CO_2$$

**[0764]** 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:

$$CaCO_3 \rightarrow CaO + CO_2$$

**[0765]** 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, $CaSiO_3$:

$$SiO_2 + CaO \rightarrow CaSiO_3$$

**[0766]** 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:

$$FeO + CO \rightarrow Fe + CO_2$$

**[0767]** The carbon dioxide formed in this process can be converted back to carbon monoxide by reacting with carbon via the reverse Boudouard reaction:

$$C + CO_2 \rightarrow 2\ CO$$

**[0768]** 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 includes 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.

**[0769]** 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). Alternatively, or additionally, hydrogen can be available as a result of water-gas shift that reacts $H_2O$ and CO to generate $H_2$ and $CO_2$, or from steam-reforming reactions of carbon. Either of these reactions (water-gas shift or steam reforming) can be assisted by incoming moisture with the biocarbon (e.g., carbon-negative biocarbon pellets). 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.

**[0770]** 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.

**[0771]** Desulfurization conventionally is performed during the transport of the liquid iron to the steelworks, by adding calcium oxide, which reacts with iron sulfide contained 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, $H_2S$.

**[0772]** 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 essentially renewable carbon. This disclosure provides renewable carbon in biogenic reagents produced via pyrolysis of biomass. However, 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%.

**[0773]** In some variations of the invention, 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.

**[0774]** 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.

**[0775]** 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. 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 as well.

**[0776]** 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 contained, 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.

**[0777]** 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 (e.g., a 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.

**[0778]** 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 can comprise or consist 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.

**[0779]** 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 include pulverized biocarbon pellets. The self-reducing agglomerates can be the biocarbon pellets disclosed herein. The quantity of carbon fines required is established by a C/F (carbon to ore fines) ratio, which can be selected to achieve full reduction of the metal oxides.

**[0780]** 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 ($2\ CO + O_2 \rightarrow 2\ CO_2$).

**[0781]** In certain exemplary embodiments, a modified-Tecnored process comprises pelletizing iron ore fines with a size at most 140 mesh, biogenic-reagent fines with a size at most 200 mesh, and a flux such as hydrated lime of size at most 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.

**[0782]** Conventionally, external CO or $H_2$ does not play a significant role in the self-reduction process using a Tecnored furnace. However, in the context of the present disclosure, 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 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.

**[0783]** 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 invention can be applied to essentially any furnace or process that uses carbon somewhere in the process of making a metal from a metal ore.

**[0784]** 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 can be 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 to Reducing Gas

**[0785]** Some variations employ biocarbon to generate carbon-negative reducing gas (e.g., carbon-negative syngas or carbon-negative hydrogen). The reducing gas can be utilized *in situ* in a process (e.g., a metal-making process) or can be recovered and sold.

**[0786]** The optional production of reducing gas (also referred to herein as "bio-reductant gas") will now be further described with reference to the carbon-negative biocarbon being in the form of biocarbon pellets. These are non-limiting embodiments, it being understood that the carbon-negative biocarbon can be in powder form, slurry form, or another form.

**[0787]** The conversion of the biocarbon pellets to reducing gas takes place in a reactor, which can be referred to as a bio-reductant formation unit. A reactant is employed to react with the biocarbon and produce the 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.

**[0788]** In some embodiments, steam is a preferred reactant. Steam (i.e., $H_2O$ in a vapor phase) can be introduced into the reactor in an input stream. Steam can include steam generated by moisture contained in the biocarbon pellets, as well as steam generated by any chemical reactions that produce water.

**[0789]** 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.

**[0790]** 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-comprising 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* | $C_6H_{10}O_5 + 6\ O_2 \rightarrow 6\ CO_2 + 5\ H_2O$ |

**[0791]** 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 include 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.

**[0792]** 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.

**[0793]** 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 contained in the biocarbon pellets can be accounted for in determining how much additional water (steam) to add in the process.

**[0794]** Exemplary ratios of oxygen to steam ($O_2/H_2O$) are equal to or at most 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 at least 1, the combustion reaction starts to dominate over partial oxidation, which can produce undesirably low $CO/CO_2$ ratios.

**[0795]** 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, or 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., at most 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.

**[0796]** 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.

**[0797]** Catalysts can be utilized in the reactor for generating the reducing gas. Catalysts can include, 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 include, 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.

**[0798]** Other exemplary catalysts include, but are not limited to, nickel, nickel oxide, rhodium, ruthenium, iridium, palladium, and platinum. Such catalysts can be coated or deposited onto a support material, such as, for example, gamma-alumina, where the support materials can be doped with a stabilizing element such as magnesium, lanthanum, or barium.

**[0799]** 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 include, but are not limited to, calcining, washcoat addition, particle-size reduction, and surface activation by thermal or chemical means.

**[0800]** 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.

**[0801]** 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. A fixed bed of biocarbon pellets can be utilized 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.

**[0802]** In some embodiments, the reactor employs gasification of the biocarbon pellets, or a powder formed therefrom, 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.

**[0803]** 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.

**[0804]** 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.

**[0805]** 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.

**[0806]** 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.

**[0807]** The biocarbon pellets can be introduced to a gasifier as a "dry feed," where moisture can be present, but there is 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.

**[0808]** 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.

**[0809]** 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.

**[0810]** 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 can be 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.

**[0811]** 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.

**[0812]** 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.

**[0813]** Circulating fluidized-bed gasifiers can be employed, wherein gas, sand, and feedstock (e.g., crushed or pulverized biocarbon pellets) move together. Exemplary transport gases include 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.

**[0814]** In some embodiments in which a countercurrent fixed-bed gasifier is used, the reactor consists essentially 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.

**[0815]** 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.

**[0816]** 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.

**[0817]** 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.

**[0818]** 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.

**[0819]** 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.

**[0820]** A gasifier can include a catalyst, such as a catalyst effective for partial oxidation, reverse water-gas shift, or dry ($CO_2$) reforming of carbon-comprising species.

**[0821]** 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.

**[0822]** 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 include 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.

**[0823]** Circulating fluidized-bed reactors can be employed, wherein gas, sand, and feedstock move together. Exemplary transport gases include 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.

**[0824]** In some embodiments in which a countercurrent fixed-bed reactor is used, the reactor consists essentially 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.

**[0825]** 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.

**[0826]** 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.

**[0827]** 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.

**[0828]** Water sources can include direct piping from process condensate, other recycle water, wastewater, make-up water, boiler feed water, city water, and so on. Water can be first 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.

**[0829]** 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 removed from the reducing gas.

**[0830]** Some embodiments include a reducing-gas cleanup unit. The reducing-gas cleanup unit is not particularly limited in its design. Exemplary reducing-gas cleanup units include 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 included and can be any means known in the art for removing $H_2S$, $CO_2$, or other acid gases from the reducing gas.

**[0831]** Examples of acid-gas removal steps include removal of $CO_2$ with a solvent for $CO_2$, or removal of $CO_2$ by a pressure-swing adsorption unit. Suitable solvents for reactive solvent-based acid gas removal include monoethanolamine, diethanolamine, methyldiethanolamine, diisopropylamine, and aminoethoxyethanol. Suitable solvents for physical solvent-based acid gas removal include dimethyl ethers of polyethylene glycol (such as in the Selexol® process) and refrigerated methanol (such as in the Rectisol® process).

**[0832]** The reducing gas produced as described according to the present invention 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.

**[0833]** In this detailed description, reference has been made to multiple embodiments of the invention and non-limiting examples relating to how the invention 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 present invention. This invention 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 invention defined by the claims.

**[0834]** 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.

**[0835]** 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 invention. Additionally, certain of the steps can be performed concurrently in a parallel process when possible, as well as performed sequentially.

**[0836]** Therefore, to the extent there are variations of the invention, which are within the spirit of the disclosure or equivalent to the inventions found in the appended claims, it is the intent that this patent will cover those variations as well. The present invention shall only be limited by what is claimed.

EXAMPLES

**[0837]** Examples 1 to 6 demonstrate that biocarbon compositions can be made with adjustable base-acid ratios, according to the disclosure set forth herein.

Example 1: Biocarbon Composition with a Base-Acid Ratio of 0.74.

**[0838]** Douglas fir wood is pyrolyzed, thereby generating a biocarbon reagent, at a pyrolysis temperature of 650°C and a pyrolysis time of 15-30 minutes. The biogenic reagent is combined with a binder of starch and bentonite clay, forming a mixture. The mixture is mechanically treated using an extruder to form a powder. The powder is

pelletized using a pelletizing apparatus consisting essentially of a vertical ring die pelletizer, thereby generating pellets with a diameter of about 8 mm. The pellets are further carbonized at 650°C for 15-30 minutes and then dried to about 4 wt% moisture. The composition and other properties are shown in the data sheet of FIG. 5. The base-acid ratio is measured to be 0.74, determined according to ASTM-Standard D4326. Note that the X labels in FIG. 5 indicate that the particular measurement was not made.

Example 2: Biocarbon Composition with a Base-Acid Ratio of 0.85.

**[0839]** Douglas fir wood is pyrolyzed, thereby generating a biocarbon reagent, at a pyrolysis temperature of 650°C and a pyrolysis time of 15-30 minutes. The biogenic reagent, 320 lb, dry basis, is combined with starch binder, 50 lb, thereby forming a mixture. The mixture is mechanically treated using an extruder to form a powder. The powder is pelletized using a pelletizing apparatus, comprising a vertical ring die pelletizer, to generate pellets with a diameter of about 8 mm. The pellets are dried to about 11 wt% moisture. The composition and other properties are shown in the data sheet of FIG. 6. The base-acid ratio is measured to be 0.85, determined according to ASTM-Standard D4326. Note that the X labels in FIG. 6 indicate that the particular measurement was not made.

Example 3: Biocarbon Composition with a Base-Acid Ratio of 1.39.

**[0840]** Douglas fir wood is pyrolyzed to thereby generate a biocarbon reagent, at a pyrolysis temperature of 650°C and a pyrolysis time of 15-30 minutes. The biogenic reagent, 320 lb (dry basis), is combined with a starch binder, 40 lb, forming a mixture. The mixture is mechanically treated using an extruder to form a powder. The powder is pelletized using a pelletizing apparatus consisting essentially of a vertical ring die pelletizer, thereby generating pellets with a diameter of about 8 mm. The pellets are dried to about 10 wt% moisture. The composition and other properties are shown in the data sheet of FIG. 7. The base-acid ratio is measured to be 1.39, determined according to ASTM-Standard D4326. Note that the X labels in FIG. 7 indicate that the particular measurement was not made.

Example 4: Biocarbon Composition with a Base-Acid Ratio of 1.57.

**[0841]** Douglas fir wood is pyrolyzed, thereby generating a biocarbon reagent, at a pyrolysis temperature of 650°C and a pyrolysis time of 15-30 minutes. The biogenic

reagent, 320 lb (dry basis), is combined with a starch binder, 30 lb, forming a mixture. The mixture is mechanically treated using an extruder to form a powder. The powder is pelletized using a pelletizing apparatus consisting essentially of a vertical ring die pelletizer, thereby generating pellets with a diameter of about 8 mm. The pellets are dried to about 9 wt% moisture. The composition and other properties are shown in the data sheet of FIG. 8. The base-acid ratio is measured to be 1.57, determined according to ASTM-Standard D4326. Note that the X labels in FIG. 8 indicate that the particular measurement was not made.

Example 5: Biocarbon Composition with a Base-Acid Ratio of 5.13.

**[0842]** Douglas fir wood is pyrolyzed, thereby generating a biocarbon reagent, at a pyrolysis temperature of 650°C and a pyrolysis time of 15-30 minutes. The biogenic reagent, 320 lb (dry basis), is combined with a starch binder, 30 lb, forming a mixture. The mixture is mechanically treated using an extruder to form a powder. The powder is pelletized using a pelletizing apparatus consisting essentially of a vertical ring die pelletizer, thereby generating pellets with a diameter of about 8 mm. The pellets are acidic water-washed and then dried to about 4 wt% moisture. The composition and other properties are shown in the data sheet of FIG. 9. The base-acid ratio is calculated to be 5.13, determined according to ASTM-Standard D4326. Note that the X labels in FIG. 9 indicate that the particular measurement was not made.

Example 6: Biocarbon Composition with a Base-Acid Ratio of 7.62.

**[0843]** Red pine wood is pyrolyzed, thereby generating a biocarbon reagent, at a pyrolysis temperature of 650°C and a pyrolysis time of 15-30 minutes. The biogenic reagent, 320 lb (dry basis), is combined with a starch binder, 24 lb, forming a mixture. The mixture is mechanically treated using an extruder to form a powder. The powder is pelletized using a pelletizing apparatus consisting essentially of a vertical ring die pelletizer, thereby generating pellets with a diameter of about 8 mm. The pellets are then dried to about 7 wt% moisture. The composition and other properties are shown in the data sheet of FIG. 10. The base-acid ratio is measured to be 7.62, determined according to ASTM-Standard D4326. Note that the X labels in FIG. 10 indicate that the particular measurement was not made.

# CLAIMS

What is claimed is:

1. A biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by a base-acid ratio defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the base-acid ratio is at least about 0.1 to at most about 10.

2. The biocarbon composition of claim 1, wherein the base-acid ratio is at least about 0.1 to at most about 0.4.

3. The biocarbon composition of claim 1, wherein the base-acid ratio is at least about 0.5 to at most about 10.

4. The biocarbon composition of claim 1, wherein the base-acid ratio is at least about 0.8 to at most about 10.

5. The biocarbon composition of claim 1, wherein the base-acid ratio is at least about 1.5 to at most about 5.

6. The biocarbon composition of claim 1, wherein the base-acid ratio is at least about 0.4 to at most about 0.7.

7. The biocarbon composition of claim 1, wherein the base-acid ratio is at most about 0.4 or at least about 0.7.

8. The biocarbon composition of any one of claims 1 to 7, wherein the biocarbon composition is characterized by an iron-calcium ratio defined by the $Fe_2O_3$ divided by the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the iron-calcium ratio is at least about 0.05 to at most about 5.

9. The biocarbon composition of claim 8, wherein the iron-calcium ratio is selected from about 0.1 to about 2.

10. The biocarbon composition claim 8, wherein the iron-calcium ratio is selected from about 0.3 to about 1.

11. The biocarbon composition of claim 8, wherein the iron-calcium ratio is at most about 0.3 or at least about 3.

12. The biocarbon composition of any one of claims 1 to 11, wherein the biocarbon composition is characterized by an iron-plus-calcium parameter defined as the sum of the $Fe_2O_3$ and the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the iron-plus-calcium parameter is selected from about 5 wt% to about 50 wt%.

13. The biocarbon composition of claim 12, wherein the iron-plus-calcium parameter is selected from about 10 wt% to about 40 wt%.

14. The biocarbon composition of claim 12, wherein the iron-plus-calcium parameter is selected from about 20 wt% to about 50 wt%.

15. The biocarbon composition of claim 12, wherein the iron-plus-calcium parameter is at most 10 wt%.

16. The biocarbon composition of claim 12, wherein the iron-plus-calcium parameter is at least 10 wt%.

17. The biocarbon composition of any one of claims 1 to 16, wherein the biocarbon composition is characterized by a slagging factor defined as the base-acid ratio multiplied by weight percentage of sulfur present in the biocarbon composition on a dry basis, and wherein the slagging factor is selected from about 0.001 to about 1.

18. The biocarbon composition of claim 17, wherein the slagging factor is selected from about 0.01 to about 0.5.

19. The biocarbon composition of claim 17, wherein the slagging factor is selected from about 0.01 to about 0.1.

20. The biocarbon composition of claim 17, wherein the slagging factor is at most about 0.6.

21. The biocarbon composition of any one of claims 1 to 20, wherein the biocarbon composition is characterized by a fouling factor defined as the base-acid ratio multiplied by the $Na_2O$ as weight percentage in the biocarbon composition pursuant to ASTM D4326, and wherein the fouling factor is selected from about 0.1 to about 10.

22. The biocarbon composition of claim 21, wherein the fouling factor is at most about 2.

23. The biocarbon composition of claim 22, wherein the fouling factor is at most about 1.

24. The biocarbon composition of any one of claims 1 to 23, wherein the biocarbon composition is characterized by a modified fouling factor defined as the base-acid ratio multiplied by water-soluble $Na_2O$, wherein the water-soluble $Na_2O$ is weight percentage of $Na_2O$ that leaches, in the presence of water, out of ash derived from the biocarbon composition pursuant to ASTM D4326, and wherein the modified fouling factor is selected from about 0.1 to about 10.

25. The biocarbon composition of claim 24, wherein the modified fouling factor is at most about 2.

26. The biocarbon composition of claim 24, wherein the modified fouling factor is at most about 1.

27. The biocarbon composition of any one of claims 1 to 26, wherein the biocarbon composition is characterized by an equilibrium moisture content defined according to ASTM D1412, wherein the equilibrium moisture content is selected from about 0.1 wt% to about 10 wt%.

28. The biocarbon composition of claim 27, wherein the equilibrium moisture content is selected from about 1 wt% to about 5 wt%.

29. The biocarbon composition of any one of claims 1 to 28, wherein the biocarbon composition is characterized by a silica percentage defined as weight percentage of the $SiO_2$ in the biocarbon composition pursuant to ASTM D4326, wherein the silica percentage is selected from about 5 wt% to about 50 wt%.

30. The biocarbon composition of claim 29, wherein the silica percentage is selected from about 10 wt% to about 30 wt%.

31. The biocarbon composition of any one of claims 1 to 30, wherein the biocarbon composition comprises at most 10 ppm mercury.

32. The biocarbon composition of any one of claims 1 to 30, wherein the biocarbon composition is essentially free of mercury.

33. The biocarbon composition of any one of claims 1 to 32, wherein the biocarbon composition comprises from about 50 wt% to about 99 wt% fixed carbon on a dry basis.

34. The biocarbon composition of claim 33, wherein the biocarbon composition comprises at least about 75 wt% fixed carbon on a dry basis.

35. The biocarbon composition of claim 33, wherein the biocarbon composition comprises at least about 90 wt% fixed carbon on a dry basis.

36. The biocarbon composition of any one of claims 1 to 35, wherein the 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.

37. The biocarbon composition of any one of claims 1 to 35, wherein the total carbon within the biocarbon composition is fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

38. The biocarbon composition of any one of claims 1 to 37, wherein the biocarbon composition is in the form of a pellet.

39. The biocarbon composition of claim 38, wherein the pellet further comprises a binder.

40. The biocarbon composition of claim 39, wherein the binder comprises 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, or a combination or a derivative thereof.

41. The biocarbon composition of any one of claims 1 to 37, wherein the biocarbon composition is in the form of a powder.

42. The biocarbon composition of any one of claims 1 to 41, wherein the biocarbon composition further comprises an additive, wherein the additive comprises calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or derivative thereof.

43. A biocarbon composition comprising from about 50 wt% to about 99 wt% total carbon, wherein the total carbon is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon, wherein the biocarbon composition is characterized by an expanded base-acid ratio defined by the following formula:

$$\text{Expanded Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O + MnO + SrO + BaO}{SiO_2 + Al_2O_3 + TiO_2 + P_2O_5 + SO_3}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, MnO, SrO, BaO, $SiO_2$, $Al_2O_3$, $TiO_2$, $P_2O_5$, and $SO_3$ correspond to weight fractions in the biocarbon composition pursuant to ASTM D4326, and wherein the expanded base-acid ratio is selected from about 0.05 to about 8.

44. The biocarbon composition of claim 43, wherein the expanded base-acid ratio is selected from about 0.1 to about 0.4.

45. The biocarbon composition of claim 43, wherein the expanded base-acid ratio is selected from about 0.5 to about 10.

46. The biocarbon composition of claim 43, wherein the expanded base-acid ratio is selected from about 0.8 to about 10.

47. The biocarbon composition of claim 43, wherein the expanded base-acid ratio is selected from about 0.5 to about 5.

48. The biocarbon composition of claim 43, wherein the expanded base-acid ratio is selected from about 0.4 to about 0.7.

49. The biocarbon composition of claim 43, wherein the expanded base-acid ratio is at most about 0.4 or at least about 0.7.

50. The biocarbon composition of any one of claims 43 to 49, wherein the biocarbon composition is characterized by an iron-calcium ratio defined by the $Fe_2O_3$ divided by the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the iron-calcium ratio is selected from about 0.05 to about 5.

51. The biocarbon composition of claim 50, wherein the iron-calcium ratio is selected from about 0.1 to about 2.

52. The biocarbon composition of claim 50, wherein the iron-calcium ratio is selected from about 0.3 to about 1.

53. The biocarbon composition of claim 56, wherein the iron-calcium ratio is at most about 0.3 or at least about 3.

54. The biocarbon composition of any one of claims 43 to 53, wherein the biocarbon composition is characterized by an iron-plus-calcium parameter defined as the sum of the $Fe_2O_3$ and the CaO, each as weight percentages in the biocarbon composition pursuant to ASTM D4326, and wherein the iron-plus-calcium parameter is selected from about 5 wt% to about 50 wt%.

55. The biocarbon composition of claim 54, wherein the iron-plus-calcium parameter is selected from about 10 wt% to about 40 wt%.

56. The biocarbon composition of claim 54, wherein the iron-plus-calcium parameter is selected from about 20 wt% to about 50 wt%.

57. The biocarbon composition of claim 54, wherein the iron-plus-calcium parameter is at most 10 wt%.

58. The biocarbon composition of claim 54, wherein the iron-plus-calcium parameter is at least 10 wt%.

59. The biocarbon composition of any one of claims 43 to 58, wherein the biocarbon composition is characterized by a slagging factor defined as the base-acid ratio multiplied by weight percentage of sulfur present in the biocarbon composition on a dry basis, wherein the slagging factor is selected from about 0.001 to about 1, and wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326.

60. The biocarbon composition of claim 59, wherein the slagging factor is selected from about 0.01 to about 0.5.

61. The biocarbon composition of claim 59, wherein the slagging factor is selected from about 0.01 to about 0.1.

62. The biocarbon composition of claim 59, wherein the slagging factor is at most about 0.6.

63. The biocarbon composition of any one of claims 43 to 62, wherein the biocarbon composition is characterized by a fouling factor defined as the base-acid ratio multiplied by the $Na_2O$ as weight percentage in the biocarbon composition pursuant to

ASTM D4326, wherein the fouling factor is selected from about 0.1 to about 10, and wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326.

64. The biocarbon composition of claim 63, wherein the fouling factor is at most about 2.

65. The biocarbon composition of claim 63, wherein the fouling factor is at most about 1.

66. The biocarbon composition of any one of claims 43 to 65, wherein the biocarbon composition is characterized by a modified fouling factor defined as the base-acid ratio multiplied by water-soluble $Na_2O$, wherein the water-soluble $Na_2O$ is weight percentage of $Na_2O$ that leaches, in the presence of water, out of ash derived from the biocarbon composition pursuant to ASTM D4326, wherein the modified fouling factor is selected from about 0.1 to about 10, and wherein the base-acid ratio is defined by the following formula:

$$\text{Base-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

wherein each of the $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, $SiO_2$, $Al_2O_3$, and $TiO_2$ correspond to weight percentages in the biocarbon composition pursuant to ASTM D4326.

67. The biocarbon composition of claim 66, wherein the modified fouling factor is at most about 2.

68. The biocarbon composition of claim 66, wherein the modified fouling factor is at most about 1.

69. The biocarbon composition of any one of claims 43 to 68, wherein the biocarbon composition is characterized by an equilibrium moisture content defined according to ASTM D1412, wherein the equilibrium moisture content is selected from about 0.1 wt% to about 10 wt%.

70. The biocarbon composition of claim 69, wherein the equilibrium moisture content is selected from about 1 wt% to about 5 wt%.

71. The biocarbon composition of any one of claims 43 to 70, wherein the biocarbon composition is characterized by a silica percentage defined as weight percentage of the $SiO_2$ in the biocarbon composition pursuant to ASTM D4326, wherein the silica percentage is selected from about 5 wt% to about 50 wt%.

72. The biocarbon composition of claim 71, wherein the silica percentage is selected from about 10 wt% to about 30 wt%.

73. The biocarbon composition of any one of claims 43 to 72, wherein the biocarbon composition comprises at most 10 ppm mercury.

74. The biocarbon composition of any one of claims 43 to 72, wherein the biocarbon composition is essentially free of mercury.

75. The biocarbon composition of any one of claims 43 to 74, wherein the biocarbon composition comprises from about 50 wt% to about 99 wt% fixed carbon on a dry basis.

76. The biocarbon composition of claim 75, wherein the biocarbon composition comprises at least about 75 wt% fixed carbon on a dry basis.

77. The biocarbon composition of claim 75, wherein the biocarbon composition comprises at least about 90 wt% fixed carbon on a dry basis.

78. The biocarbon composition of any one of claims 43 to 77, wherein the 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.

79. The biocarbon composition of any one of claims 43 to 77, wherein the total carbon within the biocarbon composition is fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

80. The biocarbon composition of any one of claims 43 to 79, wherein the biocarbon composition is in the form of a pellet.

81. The biocarbon composition of claim 80, wherein the pellet further comprises a binder.

82. The biocarbon composition of claim 81, wherein the binder comprises 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, or a combination or a derivative thereof.

83. The biocarbon composition of any one of claims 43 to 79, wherein the biocarbon composition is in the form of a powder.

84. The biocarbon composition of any one of claims 43 to 83, wherein the biocarbon composition further comprises an additive, wherein the additive comprises calcium, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, limestone, lime, dolomite, dolomitic lime, bentonite, gypsum, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus,

tungsten, vanadium, iron chloride, iron bromide, iron ore concentrate, fluorite, fluorospar, sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, borax, silica, alumina, aluminosilicates, titanium, titanium dioxide, titanium carbide, titanium hydride, titanium nitride, or a combination or derivative thereof.



FIG. 1



FIG. 2

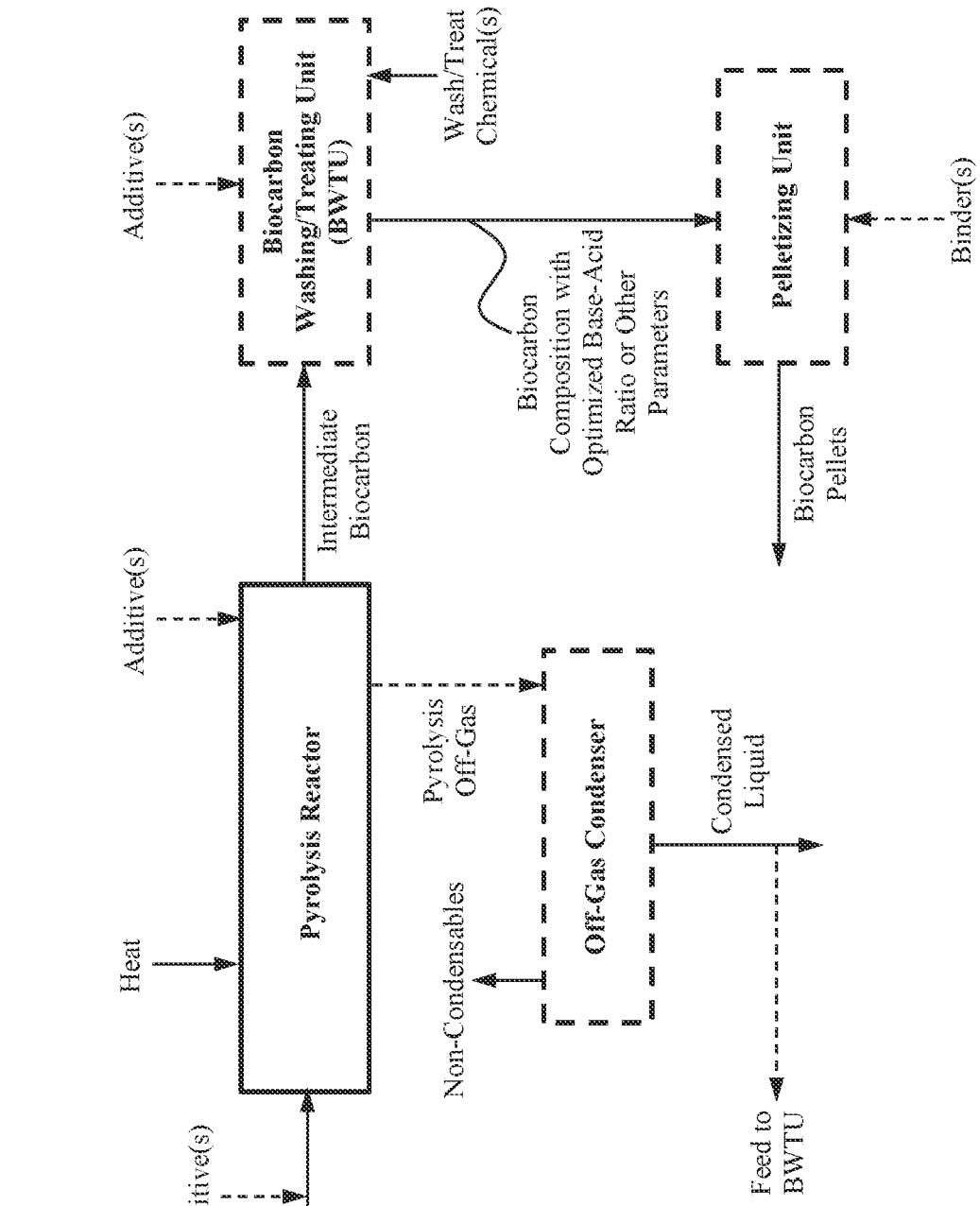

Biomass
Additive(s)
Heat
Additive(s)
Pyrolysis Reactor
Intermediate Biocarbon
Additive(s)
Biocarbon Washing/Treating Unit (BWTU)
Wash/Treat Chemical(s)
Biocarbon Composition with Optimized Base-Acid Ratio or Other Parameters
Pyrolysis Off-Gas
Non-Condensables
Off-Gas Condenser
Condensed Liquid
Feed to BWTU
Pelletizing Unit
Biocarbon Pellets
Binder(s)

FIG. 3

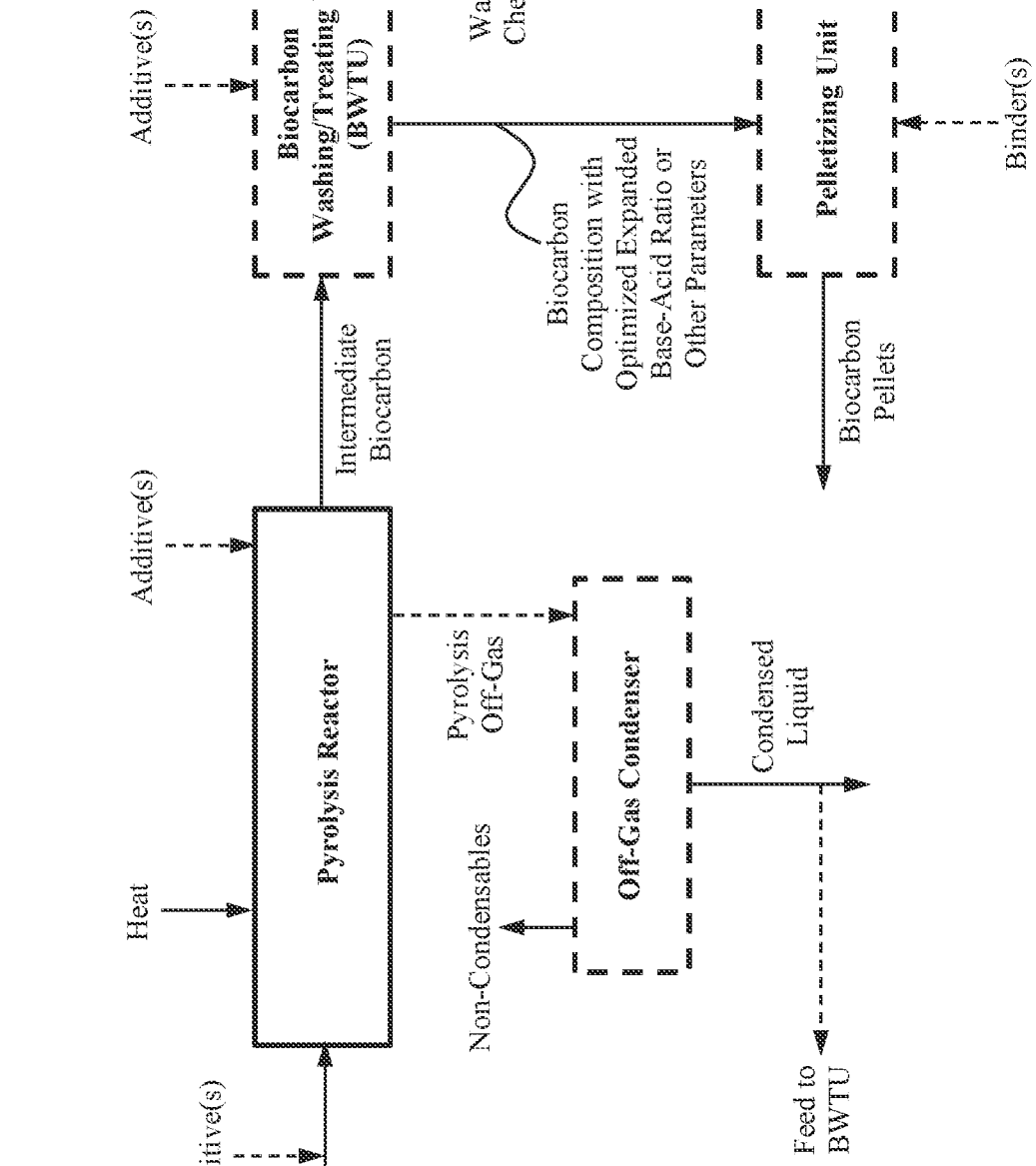

Biomass
Additive(s)
Heat
Additive(s)
Pyrolysis Reactor
Intermediate Biocarbon
Additive(s)
Biocarbon Washing/Treating Unit (BWTU)
Wash/Treat Chemical(s)
Biocarbon Composition with Optimized Expanded Base-Acid Ratio or Other Parameters
Pyrolysis Off-Gas
Non-Condensables
Off-Gas Condenser
Condensed Liquid
Feed to BWTU
Biocarbon Pellets
Pelletizing Unit
Binder(s)

FIG. 4

MINERAL LABS INC.
Box 549
Salyersville, Kentucky 41465
Phone (606) 349-6145

*Certificate of Analysis*

PJLA Testing
ISO/IEC 17025:2005 Accredited

| COMPANY REQUESTING ANALYSIS: | | Date Analyzed: | 10/22/2021 |
|---|---|---|---|
| NATIONAL CARBON TECHNOLOGIES<br>513 4TH STREET<br>GWINN, MI 49841 | | Lab No. 11370 | 11025636 |
| | | Sampled By/Type: | CUSTOMER |

Sample ID: MAIL-IN
ISC100821-01 RC CARBON
10/22/21 3PF.DG

| PROXIMATE ANALYSIS | As Received | Dry Basis |
|---|---|---|
| % Moisture (D3302/D3173) | 6.97 | |
| % Ash (D3174) | 8.44 | 9.07 |
| % Volatile (D3175) | 3.38 | 3.63 |
| % Fixed Carbon (Calculated) | 81.22 | 87.30 |
| B.T.U. (D5865/D5864) | 13,935 | 13,904 |
| M.A.F.B.T.U. (Calculated) | 15,291 | |
| % Sulfur (D4239) | 0.02 | 0.03 |
| $SO_2$ lbs. /mm Btu | 0.04 | |
| Ash lbs./mm Btu | 6.52 | |

| ULTIMATE ANALYSIS (ASTM D5373) | As Received | Dry Basis |
|---|---|---|
| Moisture | 6.97 | |
| Carbon | 81.92 | 88.05 |
| Hydrogen | <0.47 | <0.50 |
| Nitrogen | 0.55 | 0.59 |
| Sulfur | 0.02 | 0.03 |
| Ash | 8.44 | 9.07 |
| Oxygen (diff.) | 1.63 | 1.75 |

| SULFUR FORMS (ASTM D2492) | As Received | Dry Basis |
|---|---|---|
| % Pyritic Sulfur | xxxxx | xxxxx |
| % Sulfate Sulfur | xxxxx | xxxxx |
| % Organic Sulfur | xxxxx | xxxxx |
| % Total Sulfur | xxxxx | xxxxx |

| MINERAL ANALYSIS (ASTM D4326) | | % Wt. Ignited Basis |
|---|---|---|
| Silicon dioxide | $SiO_2$ | 39.27 |
| Aluminum oxide | $Al_2O_3$ | 10.40 |
| Titanium dioxide | $TiO_2$ | 0.12 |
| Iron oxide | $Fe_2O_3$ | 2.92 |
| Calcium oxide | CaO | 22.32 |
| Magnesium oxide | MgO | 3.18 |
| Potassium oxide | $K_2O$ | 7.51 |
| Sodium oxide | $Na_2O$ | 0.79 |
| Sulfur trioxide | $SO_3$ | 5.24 |
| Phosphorus pentoxide | $P_2O_5$ | 1.33 |
| Strontium oxide | SrO | 0.12 |
| Barium oxide | BaO | 0.28 |
| Manganese oxide | MnO | 0.77 |
| Undetermined | | 4.65 |

| FUSION TEMPERATURE OF ASH (D1857) | Reducing (°F) | Oxidizing (°F) |
|---|---|---|
| Initial Temp. | xxxxx | xxxxx |
| Softening Temp. H=W | xxxxx | xxxxx |
| Hemispherical Temp. H=1/2 W | xxxxx | xxxxx |
| Fluid Temp | xxxxx | xxxxx |

| T-250 Temp. of Ash | 2190 |
|---|---|

| Base/Acid Ratio | 0.7375 |
|---|---|
| Fouling Factor | 0.5830 |
| Slagging Factor | 0.0220 |

| Bulk Density(g/cm3) | 1.068 |
|---|---|
| %Equilibrium Moisture(ASTM D1412 | 2.8 |

| WATER SOLUBLE ALKALIES (Reported as %) | |
|---|---|
| $K_2O$ | xxxxx |
| $Na_2O$ | xxxxx |

Submitted By: Sherlinda Matthews

Sample Preperation by ASTM D2013 and ASTM D6188

FIG. 5

MINERAL LABS INC.
Box 549
Salyersville, Kentucky 41465
Phone (606) 349-6145

*Certificate of Analysis*

ISO/IEC 17025:2005 Accredited

| COMPANY REQUESTING ANALYSIS: | Date Analyzed: | 10/21/2020 |
|---|---|---|
| National Carbon Technologies<br>513 4th Street<br>Gwinn MI 49841<br>906-281-4679 | Lab No. | 10023650 |
| | Sampled By/Type: | Customer |

Sample ID: Mail In: Carbon Pellets: 10-16-20: Douglas 50

| PROXIMATE ANALYSIS | As Received | Dry Basis |
|---|---|---|
| % Moisture (D3302/D3173) | 10.67 | |
| % Ash (D3174) | 3.89 | 3.24 |
| % Volatile (D3175) | 25.22 | 28.23 |
| % Fixed Carbon (Calculated) | 61.22 | 68.53 |
| B.T.U. (D5865/D5864) | 10940 | 12247 |
| M.A.F.B.T.U. (Calculated) | 12857 | |
| % Sulfur (D4239) | 6.62 | 6.62 |
| $SO_2$ lbs. /mm Btu | 6.03 | |
| Ash lbs./mm Btu | 2.65 | |

| ULTIMATE ANALYSIS (ASTM D5373) | As Received | Dry Basis |
|---|---|---|
| Moisture | 10.67 | |
| Carbon | 71.86 | 80.54 |
| Hydrogen | 5.00 | 5.60 |
| Nitrogen | 1.56 | 1.75 |
| Sulfur | 6.62 | 6.62 |
| Ash | 2.89 | 3.24 |
| Oxygen (diff.) | 7.91 | 8.85 |

| SULFUR FORMS (ASTM D3177) | As Received | Dry Basis |
|---|---|---|
| % Pyritic Sulfur | xxxxx | xxxxx |
| % Sulfate Sulfur | xxxxx | xxxxx |
| % Organic Sulfur | xxxxx | xxxxx |
| % Total Sulfur | xxxxx | xxxxx |

| MINERAL ANALYSIS (ASTM D4326) | | % Wt. Ignited Basis |
|---|---|---|
| Silicon dioxide | $SiO_2$ | 39.73 |
| Aluminum oxide | $Al_2O_3$ | 8.64 |
| Titanium dioxide | $TiO_2$ | 0.88 |
| Iron oxide | $Fe_2O_3$ | 7.81 |
| Calcium oxide | $CaO$ | 20.47 |
| Magnesium oxide | $MgO$ | 5.36 |
| Potassium oxide | $K_2O$ | 7.48 |
| Sodium oxide | $Na_2O$ | 0.74 |
| Sulfur trioxide | $SO_3$ | 0.84 |
| Phosphorus pentoxide | $P_2O_5$ | 2.54 |
| Strontium oxide | $SrO$ | 0.15 |
| Barium oxide | $BaO$ | 0.21 |
| Manganese oxide | $MnO$ | 0.81 |
| Undetermined | | 4.46 |

| FUSION TEMPERATURE OF ASH (D1857) | Reducing (°F) | Oxidizing (°F) |
|---|---|---|
| Initial Temp. | xxxxx | xxxxx |
| Softening Temp. H=W | xxxxx | xxxxx |
| Hemispherical Temp. H=1/2 W | xxxxx | xxxxx |
| Fluid Temp | xxxxx | xxxxx |

| T-250 Temp. of Ash | xxxxx |
|---|---|

| Base/Acid Ratio | 0.8533 |
|---|---|
| Fouling Factor | 0.6341 |
| Slagging Factor | xxxxx |

| WATER SOLUBLE ALKALIES (Reported in %) | |
|---|---|
| $K_2O$ | xxxxx |
| $Na_2O$ | xxxxx |

| Boron ppm (ASTM D6357) | xxxxx |
|---|---|
| Chlorine ppm (ASTM 6721) | xxxxx |
| Chromium ppm (ASTM D6357) | xxxxx |
| Oxidation (ASTM D5263) | xxxxx |
| Selenium ppm (ASTM D6357 MOD) | xxxxx |
| Free Swelling Index (D720) | xxxxx |
| Equilibrium Moisture (ASTM D1412) | xxxxx |
| Grindability Index (D409) | 40 |

Submitted By: Sharlinda Hoffman

Sample Preparation by ASTM D2013 and ASTM D5198

FIG. 6

MINERAL LABS INC.
Box 549
Salyersville, Kentucky 41465
Phone (606) 349-6145

*Certificate of Analysis*

P3LA Testing
(ISO/IEC 17025:2005 Accredited

| COMPANY REQUESTING ANALYSIS: | Date Analyzed: | 10/21/2020 |
|---|---|---|
| National Carbon Technologies<br>513 4th Street<br>Gwinn MI 49841<br>906-281-4679 | Lab No. | 10023649 |
| | Sampled By/Type: | Customer |

Sample ID: Mail In: Carbon Pellets: 10-16-20: Douglas 40

| PROXIMATE ANALYSIS | As Received | Dry Basis |
|---|---|---|
| % Moisture (D2302/D2179) | 9.71 | |
| % Ash (D3174) | 1.66 | 1.84 |
| % Volatile (D3175) | 20.16 | 22.33 |
| % Fixed Carbon (Calculated) | 68.47 | 75.83 |
| B.T.U. (D5865/D5864) | 11827 | 13099 |
| M.A.F B.T.U. (Calculated) | 13345 | |
| % Sulfur (D4239) | 0.02 | 0.02 |
| $SO_2$ lbs. /mm Btu | 0.03 | |
| Ash lbs /mm Btu | 1.40 | |

| ULTIMATE ANALYSIS (ASTM D5373) | As Received | Dry Basis |
|---|---|---|
| Moisture | 9.71 | |
| Carbon | 76.05 | 84.23 |
| Hydrogen | 2.59 | 2.87 |
| Nitrogen | 0.37 | 0.41 |
| Sulfur | 0.02 | 0.02 |
| Ash | 1.66 | 1.84 |
| Oxygen (diff.) | 9.60 | 10.63 |

| SULFUR FORMS (ASTM D3177) | As Received | Dry Basis |
|---|---|---|
| % Pyritic Sulfur | xxxxx | xxxxx |
| % Sulfate Sulfur | xxxxx | xxxxx |
| % Organic Sulfur | xxxxx | xxxxx |
| % Total Sulfur | xxxxx | xxxxx |

| MINERAL ANALYSIS (ASTM D4326) | | % Wt. Ignited Basis |
|---|---|---|
| Silicon dioxide | $SiO_2$ | 29.79 |
| Aluminum oxide | $Al_2O_3$ | 7.06 |
| Titanium dioxide | $TiO_2$ | 0.98 |
| Iron oxide | $Fe_2O_3$ | 16.44 |
| Calcium oxide | CaO | 26.31 |
| Magnesium oxide | MgO | 4.52 |
| Potassium oxide | $K_2O$ | 10.69 |
| Sodium oxide | $Na_2O$ | 0.60 |
| Sulfur trioxide | $SO_3$ | 2.33 |
| Phosphorus pentoxide | $P_2O_5$ | 3.99 |
| Strontium oxide | SrO | 0.15 |
| Barium oxide | BaO | 0.37 |
| Manganese oxide | MnO | 1.18 |
| Undetermined | | 1.72 |

| FUSION TEMPERATURE OF ASH (D1857) | Reducing (°F) | Oxidizing (°F) |
|---|---|---|
| Initial Temp. | xxxxx | xxxxx |
| Softening Temp. (H=W | xxxxx | xxxxx |
| Hemispherical Temp. (H=1/2 W | xxxxx | xxxxx |
| Fluid Temp | xxxxx | xxxxx |

| T-250 Temp. of Ash | xxxxx |
|---|---|

| Base/Acid Ratio | 1.3801 |
|---|---|
| Fouling Factor | 0.8368 |
| Slagging Factor | xxxxx |

| WATER SOLUBLE ALKALIES (Reported in %) | |
|---|---|
| $K_2O$ | xxxxx |
| $Na_2O$ | xxxxx |

| | |
|---|---|
| Boron ppm (ASTM D6357) | xxxxx |
| Chlorine ppm (ASTM 6721) | xxxxx |
| Chromium ppm (ASTM D6357) | xxxxx |
| Oxidation (ASTM D5263) | xxxxx |
| Selenium ppm (ASTM D6357 MOD) | xxxxx |
| Free Swelling Index (D720) | xxxxx |
| Equilibrium Moisture (ASTM D1412) | xxxxx |
| Grindability Index (D409) | 45 |

Submitted By: Sarah Jeffers

Sample Preperation by ASTM D2013 and ASTM D8198

FIG. 7

**MINERAL LABS INC.**
Box 549
Salyersville, Kentucky 41465
Phone (606) 349-6145

*Certificate of Analysis*

ISO/IEC 17025:2005 Accredited

| COMPANY REQUESTING ANALYSIS: | | |
|---|---|---|
| National Carbon Technologies<br>513 4th Street<br>Gwinn MI 49841<br>906-221-4679 | Date Analyzed: | 10/21/2020 |
| | Lab No. | 10023847 |
| | Sampled By/Type. | Customer |

Sample ID: Mail In: Carbon Pellets: 10-16-20: Douglas 30

| PROXIMATE ANALYSIS | As Received | Dry Basis |
|---|---|---|
| % Moisture (D3302/D3173) | 9.08 | |
| % Ash (D3174) | 1.12 | 1.23 |
| % Volatile (D3175) | 16.82 | 18.61 |
| % Fixed Carbon (Calculated) | 72.98 | 80.16 |
| B.T.U. (D5865/D5864) | 12232 | 13454 |
| M.A.F.B.T.U. (Calculated) | 13622 | |
| % Sulfur (D4239) | 0.02 | 0.02 |
| $SO_2$ lbs. /mm Btu | 0.03 | |
| Ash lbs. /mm Btu | 0.91 | |

| ULTIMATE ANALYSIS (ASTM D5373) | As Received | Dry Basis |
|---|---|---|
| Moisture | 9.08 | |
| Carbon | 78.56 | 86.41 |
| Hydrogen | 2.37 | 2.61 |
| Nitrogen | 0.38 | 0.42 |
| Sulfur | 0.02 | 0.02 |
| Ash | 1.12 | 1.23 |
| Oxygen (diff.) | 8.46 | 9.31 |

| SULFUR FORMS (ASTM D2492) | As Received | Dry Basis |
|---|---|---|
| % Pyritic Sulfur | xxxxx | xxxxx |
| % Sulfate Sulfur | xxxxx | xxxxx |
| % Organic Sulfur | xxxxx | xxxxx |
| % Total Sulfur | xxxxx | xxxxx |

| MINERAL ANALYSIS (ASTM D4326) | | % Wt. Ignited Basis |
|---|---|---|
| Silicon dioxide | $SiO_2$ | 25.84 |
| Aluminum oxide | $Al_2O_3$ | 6.75 |
| Titanium dioxide | $TiO_2$ | 1.04 |
| Iron oxide | $Fe_2O_3$ | 10.11 |
| Calcium oxide | CaO | 27.03 |
| Magnesium oxide | MgO | 4.30 |
| Potassium oxide | $K_2O$ | 10.83 |
| Sodium oxide | $Na_2O$ | 0.53 |
| Sulfur trioxide | $SO_3$ | 3.15 |
| Phosphorus pentoxide | $P_2O_5$ | 4.13 |
| Strontium oxide | SrO | 0.15 |
| Barium oxide | BaO | 0.40 |
| Manganese oxide | MnO | 1.19 |
| Undetermined | | 4.56 |

| FUSION TEMPERATURE OF ASH (D1857) | Reducing (°F) | Oxidizing (°F) |
|---|---|---|
| Initial Temp. | xxxxx | xxxxx |
| Softening Temp. (t=w | xxxxx | xxxxx |
| Hemispherical Temp. (t=1/2 w | xxxxx | xxxxx |
| Fluid Temp. | xxxxx | xxxxx |

| T-250 Temp. of Ash | xxxxx |
|---|---|

| Base/Acid Ratio | 1.5702 |
|---|---|
| Fouling Factor | 0.9275 |
| Slagging Factor | xxxxx |

| WATER SOLUBLE ALKALIES (Reported in %) | |
|---|---|
| $K_2O$ | xxxxx |
| $Na_2O$ | xxxxx |

| | |
|---|---|
| Boron ppm (ASTM D6357) | xxxxx |
| Chlorine ppm (ASTM D721) | xxxxx |
| Chromium ppm (ASTM D6357) | xxxxx |
| Oxidation (ASTM D5287) | xxxxx |
| Selenium ppm (ASTM D6357 Mod) | xxxxx |
| Free Swelling Index (D720) | xxxxx |
| Equilibrium Moisture (ASTM D1412) | xxxxx |
| Grindability Index (D409) | 49 |

Submitted By: Sabrina Jeffers

Sample Preperation by ASTM D2013 and ASTM D5198

FIG. 8

MINERAL LABS INC.
Box 549
Salyersville, Kentucky 41465
Phone (606) 349-6145

*Certificate of Analysis*

FJLA Testing
ISO/IEC 17025:2005 Accredited

| COMPANY REQUESTING ANALYSIS: | Date Analyzed: | 6/17/2021 |
|---|---|---|
| National Carbon Technologies | Lab No. | 11014001 |
| | Sampled By/Type: | Customer |

Sample ID: Mail In: Carbon: 74.2g: Sample 61421-01

| PROXIMATE ANALYSIS | As Received | Dry Basis |
|---|---|---|
| % Moisture (D3302/D3173) | 4.16 | |
| % Ash (D3174) | 1.32 | 1.38 |
| % Volatile (D3175) | 5.29 | 5.52 |
| % Fixed Carbon (Calculated) | 89.23 | 93.10 |
| B.T.U. (D5865/D5864) | 13605 | 14195 |
| M.A.F.B.T.U. (Calculated) | 14395 | |
| % Sulfur (D4239) | 0.01 | 0.01 |
| $SO_2$ lbs. /mm Btu | 0.01 | |
| Ash lbs /mm Btu | 0.97 | |

| ULTIMATE ANALYSIS (ASTM D5373) | As Received | Dry Basis |
|---|---|---|
| Moisture | 4.16 | |
| Carbon | 90.42 | 94.34 |
| Hydrogen | 0.64 | 0.67 |
| Nitrogen | 0.71 | 0.74 |
| Sulfur | 0.01 | 0.01 |
| Ash | 1.32 | 1.38 |
| Oxygen (diff.) | 2.74 | 2.86 |

| SULFUR FORMS (ASTM D2492) | As Received | Dry Basis |
|---|---|---|
| % Pyritic Sulfur | xxxxx | xxxxx |
| % Sulfate Sulfur | xxxxx | xxxxx |
| % Organic Sulfur | xxxxx | xxxxx |
| % Total Sulfur | xxxxx | xxxxx |

| MINERAL ANALYSIS (ASTM D4326) | | % Wt. Ignited Basis |
|---|---|---|
| Silicon dioxide | $SiO_2$ | 12.05 |
| Aluminum oxide | $Al_2O_3$ | 1.11 |
| Titanium dioxide | $TiO_2$ | 0.14 |
| Iron oxide | $Fe_2O_3$ | 8.85 |
| Calcium oxide | CaO | 14.80 |
| Magnesium oxide | MgO | 22.69 |
| Potassium oxide | $K_2O$ | 19.64 |
| Sodium oxide | $Na_2O$ | 1.58 |
| Sulfur trioxide | $SO_3$ | 5.24 |
| Phosphorus pentoxide | $P_2O_5$ | 4.56 |
| Strontium oxide | SrO | 0.23 |
| Barium oxide | BaO | 0.13 |
| Manganese oxide | MnO | 6.85 |
| Undetermined | | 2.03 |

| FUSION TEMPERATURE OF ASH (D1857) | Reducing (°F) | Oxidizing (°F) |
|---|---|---|
| Initial Temp. | xxxxx | xxxxx |
| Softening Temp. H=W | xxxxx | xxxxx |
| Hemispherical Temp. H=1/2 W | xxxxx | xxxxx |
| Fluid Temp. | xxxxx | xxxxx |

| T-250 Temp. of Ash | xxxxx |
|---|---|

| Base/Acid Ratio | xxxxx |
|---|---|
| Fouling Factor | xxxxx |
| Slagging Factor | xxxxx |

| WATER SOLUBLE ALKALIES (Reported in %) | |
|---|---|
| $K_2O$ | xxxxx |
| $Na_2O$ | xxxxx |

| Arsenic ppm (ASTM D6357) | xxxxx |
|---|---|
| Calcium Carbonate Equivalency | xxxxx |
| Mercury ppm (ASTM D6722) | xxxxx |
| Chlorine (ASTM 6721) | xxxxx |
| Thallium ppm (ASTM D6357) | xxxxx |
| Free Swelling Index (D720) | xxxxx |
| Equilibrium Moisture (ASTM D1412) | xxxxx |
| Grindability Index (D409) | xxxxx |

Submitted By:

FIG. 9

MINERAL LABS INC.
Box 549
Salyersville, Kentucky 41465
Phone (606) 349-6145

*Certificate of Analysis*

| COMPANY REQUESTING ANALYSIS: | | |
|---|---|---|
| National Carbon Technologies<br>513 4th Street<br>Gwinn, MI 49841 | Date Analyzed: | 9/24/2020 |
| | Lab Number | 1602/1531 |
| | Sampled By/Type: | Customer |

Sample ID: Mail In: Carbon Pellets: 91820-02: 780.4g

| PROXIMATE ANALYSIS | As Received | Dry Basis |
|---|---|---|
| % Moisture (D2961) | 7.31 | |
| % Ash (D3174) | 1.18 | 1.27 |
| % Volatile (D3175) | 9.60 | 10.36 |
| % Fixed Carbon (Calculated) | 81.91 | 88.37 |
| Gross Calorific Value Kcal/kg (D | 7151 | 7715 |
| Net Calorific Value Kcal/kg | 7016 | 7569 |
| M.A.F B.T.U. (Calculated) | 14054 | |
| % Sulfur (D4239) | 0.07 | 0.08 |
| lbs. $SO_2$/mmBtu | 0.21 | |

| ULTIMATE ANALYSIS (ASTM D5373) | As Received | Dry Basis |
|---|---|---|
| Moisture | 7.31 | |
| Carbon | 84.80 | 91.48 |
| Hydrogen | 2.01 | 2.17 |
| Nitrogen | 0.44 | 0.47 |
| Sulfur | 0.07 | 0.08 |
| Ash | 1.18 | 1.27 |
| Oxygen (diff.) | 4.19 | 4.52 |

| Particle Size Distribution | |
|---|---|
| 0.15 mm (EN15149-2) | 99.80 |
| 0.15mm x 0mm (EN15149) | 0.60 |

| MINERAL ANALYSIS (ASTM 6349) | | % Wt. Ignited Basis |
|---|---|---|
| Silicon dioxide | $SiO_2$ | 7.57 |
| Aluminum oxide | $Al_2O_3$ | 2.19 |
| Titanium dioxide | $TiO_2$ | 0.11 |
| Iron oxide | $Fe_2O_3$ | 7.66 |
| Calcium oxide | $CaO$ | 45.52 |
| Magnesium oxide | $MgO$ | 11.09 |
| Potassium oxide | $K_2O$ | 8.41 |
| Sodium oxide | $Na_2O$ | 1.19 |
| Sulfur trioxide | $SO_3$ | 2.08 |
| Phosphorus pentoxide | $P_2O_5$ | 4.90 |
| Strontium oxide | $SrO$ | 0.10 |
| Barium oxide | $BaO$ | 0.17 |
| Manganese oxide | $MgO$ | 4.74 |
| Undetermined | | 3.92 |

| FUSION TEMPERATURE OF ASH (D1857) | Reducing (°F) | Oxidizing (°F) |
|---|---|---|
| Initial Temp. | xxxxx | xxxxx |
| Softening Temp. H=W | xxxxx | xxxxx |
| Hemispherical Temp. H=1/2 W | xxxxx | xxxxx |
| Fluid Temp | xxxxx | xxxxx |

| T-250 Temp. of Ash | N/A |
|---|---|

| Base/Acid Ratio | 7.6158 |
|---|---|
| Fouling Factor | 8.7584 |
| Slagging Factor | 9.6093 |

| Chlorine ppm (ASTM 6721) | xxxxx |
|---|---|
| Selenium ppm (ASTM D6357M) | xxxxx |
| FSI (D720) | xxxxx |
| Mercury ppm (ASTM D6722) | xxxxx |
| Fluorine (ASTM D6721M) | xxxxx |
| Grindability Index (D409) | 71 |

Comments: *Bulk Density (EN15103): 0.849 g/cc *PDI: 95.21. *Average Pellet Length (EN16127): 16.28 mm *Average Pellet Diameter (EN16127): 8.24 mm

Submitted By: Belinda Mullins

FIG. 10