(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
09 February 2023 (09.02.2023)

WIPO | PCT

(10) International Publication Number
WO 2023/014682 A1

(51) International Patent Classification:
C09C 1/44 (2006.01) *C10B 53/02* (2006.01)
C09C 1/48 (2006.01) *C09C 1/00* (2006.01)
C01B 32/312 (2017.01)

(21) International Application Number:
PCT/US2022/039119

(22) International Filing Date:
02 August 2022 (02.08.2022)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/228,536 02 August 2021 (02.08.2021) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

WO 2023/014682 A1

(54) Title: PROCESSES AND SYSTEMS FOR RECAPTURING CARBON FROM BIOMASS PYROLYSIS LIQUIDS

(57) Abstract: This disclosure provides a method of making a high-fixed-carbon material comprising pyrolyzing biomass to generate intermediate solids and a pyrolysis vapor; condensing the pyrolysis vapor to generate pyrolysis liquid; blending the pyrolysis liquid with the intermediate solids, to generate a mixture; and further pyrolyzing the mixture to generate a high-fixed-carbon material. A process can comprise: pyrolyzing a biomass-comprising feedstock in a first pyrolysis reactor to generate a first biogenic reagent and a first pyrolysis vapor; introducing the first pyrolysis vapor to a condensing system to generate a condenser liquid; contacting the first biogenic reagent with the condenser liquid, thereby generating an intermediate material; further pyrolyzing the intermediate material in a second pyrolysis reactor to generate a second biogenic reagent and a second pyrolysis vapor; and recovering the second biogenic reagent as a high-yield biocarbon composition. The process can further comprise pelletizing the intermediate material. Many process and system configurations are disclosed.

PROCESSES AND SYSTEMS FOR RECAPTURING CARBON FROM BIOMASS PYROLYSIS LIQUIDS

CROSS-REFERENCE TO RELATED APPLICATION(S)

[0001] The application claims the priority benefit of U.S. Provisional Patent Application No. 63/228,536, filed on August 2, 2021, which is incorporated by reference herein in its entirety.

TECHNICAL FIELD

[0002] The present technology generally relates to pyrolysis processes utilizing recapture of carbon from pyrolysis oil, for making high-yield biocarbon compositions.

BACKGROUND

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

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

[0005] 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. Photosynthesis is the process by which plants take in

carbon dioxide and water from their surroundings and, using energy from sunlight, convert them into sugars, starches, cellulose, hemicellulose, and lignin. Of all the renewable energy sources, biomass is unique in that it is, effectively, stored solar energy. Furthermore, biomass is the only renewable source of carbon.

[0006] There exist a variety of conversion technologies to turn biomass feedstocks into high-carbon materials. Pyrolysis is a process for thermal conversion of solid materials in the complete absence of oxidizing agent (air or oxygen), or with such limited supply that oxidation does not occur to any appreciable extent. Depending on process conditions and additives, biomass pyrolysis can be adjusted to produce widely varying amounts of gas, liquid, and solid. Lower process temperatures and longer vapor residence times favor the production of solids. High temperatures and longer residence times increase the biomass conversion to syngas, while moderate temperatures and short vapor residence times are generally optimum for producing liquids. Historically, slow pyrolysis of wood has been performed in large piles, in a simple batch process, with no emissions control. Traditional charcoal-making technologies are energy-inefficient as well as highly polluting.

[0007] There is a desire for improved or optimized processes for producing biocarbon compositions, especially with respect to carbon yield and biocarbon properties.

SUMMARY

[0008] Some variations provide a process for producing a biocarbon composition, the process comprising:

pyrolyzing a feedstock in a first pyrolysis reactor, wherein the feedstock comprises biomass, thereby generating a first biogenic reagent and a first pyrolysis vapor;

introducing the first pyrolysis vapor to a condensing system, thereby generating a condenser liquid and a condenser vapor;

contacting the first biogenic reagent with the condenser liquid, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the condenser liquid;

thermally treating the intermediate material in a thermal-treatment unit, thereby generating a second biogenic reagent and an off-gas;

recovering the second biogenic reagent as a biocarbon composition.

[0009] In some embodiments, the 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 and/or demolition waste, railroad ties, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof.

[0010] In some embodiments, the process further comprises pelletizing the first biogenic reagent. In these or other embodiments, the process can further comprise pelletizing the intermediate material. In certain embodiments, pelletizing the intermediate material is integrated with the step of contacting the first biogenic reagent with the condenser liquid. In other embodiments, pelletizing the intermediate material occurs after contacting the first biogenic reagent with the condenser liquid.

[0011] Pelletizing the intermediate material, when performed, can include introducing a binder to the intermediate material. The binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-

formaldehyde resins, vegetable resins, recycled shingles, recycled tires, derivatives thereof, or a combination of the foregoing.

[0012] In some embodiments, pelletizing the intermediate material does not comprise introducing an external binder to the intermediate material.

[0013] In some processes, a carbon recapture unit is disposed upstream of the thermal-treatment unit. In certain processes, a carbon recapture unit is a first stage of the thermal-treatment unit. The carbon recapture unit can be a mixing unit contacting the first biogenic reagent with the condenser liquid. Alternatively, or additionally, a carbon recapture unit can be distinct from a mixing unit. A carbon recapture unit can be fed a carbon source different than the condenser liquid, such as an external carbon source or a waste carbon-containing stream from the process.

[0014] In some embodiments, the condensing system comprises multiple condenser stages. The condenser liquid can be a condensed product of a first stage of the multiple condenser stages, for example. In some embodiments, the condenser liquid is a condensed product of a plurality of stages of the multiple condenser stages. In certain embodiments, the plurality of stages does not include the final stage of the multiple condenser stages, especially when the final stage is configured or operated such that the final condenser product contains a high concentration of water.

[0015] In some embodiments, the intermediate material comprises the condenser liquid adsorbed onto a surface of the first biogenic reagent. Alternatively, or additionally, the intermediate material can comprise the condenser liquid absorbed into a bulk phase of the first biogenic reagent.

[0016] In some embodiments, the thermal-treatment unit is a second pyrolysis reactor operated at a temperature of at least about 250°C, wherein the second pyrolysis reactor is configured for pyrolyzing the intermediate material. In other embodiments, the thermal-treatment unit is operated at a relatively low temperature selected from about 80°C to about 250°C, for example.

[0017] The thermal-treatment unit can contain an internal oxygen-free environment, or at least a low-oxygen environment. In some embodiments, an inert gas is introduced to the

thermal-treatment unit. In certain embodiments, the thermal-treatment unit is operated under vacuum.

[0018] In some embodiments, the process further comprises introducing the off-gas from the thermal-treatment unit to the condensing system. These embodiments can be desirable when the off-gas contains a high concentration of carbon.

[0019] In some embodiments, the thermal-treatment unit is configured for drying the second biogenic reagent. In these embodiments, the off-gas from the thermal-treatment unit comprises or consists essentially of water vapor.

[0020] The process can further comprise drying of the biocarbon composition after the thermally treating in the thermal-treatment unit.

[0021] In typical embodiments, the first pyrolysis reactor is distinct from the second pyrolysis reactor. In other embodiments, the first pyrolysis reactor and the second pyrolysis reactor are physically the same unit, while the pyrolyzing and the thermally treating are conducted at different times.

[0022] In some embodiments, the process comprises performing fixed-carbon formation reactions of the condenser liquid. The fixed-carbon formation reactions can utilize the first biogenic reagent as a catalyst. Alternatively, or additionally, the fixed-carbon formation reactions can utilize the first biogenic reagent as a reaction matrix.

[0023] In some processes, the process comprises converting at least 25 wt%, at least 50 wt%, or at least 75 wt% of the total carbon comprised within the condenser liquid to fixed carbon comprised within the second biogenic reagent.

[0024] In some embodiments, at least about 10 wt% to at most about 80 wt% of fixed carbon in the second biogenic reagent is derived from the condenser liquid. In certain embodiments, at least about 20 wt% to at most about 60 wt% of fixed carbon in the second biogenic reagent is derived from the condenser liquid.

[0025] In some processes, all of the condenser liquid is contacted with the first biogenic reagent. In other processes, less than all of the condenser liquid is contacted with the first biogenic reagent. In this disclosure, reference to "the condenser liquid" can be in reference

to either some of the condenser liquid formed in the process or all of the condenser liquid formed in the process, unless otherwise stated.

[0026] In some processes, the condenser liquid is contacted with the first biogenic reagent without any intermediate chemical processing. In other processes, the condenser liquid is chemically processed prior to contacting with the first biogenic reagent. There are various types of chemical processing that can be performed on the condenser liquid; generally speaking, chemical processing refers to the introduction or removal of mass or energy from the condenser liquid. Exemplary types of chemical processing include separating a specific component (e.g., water or acetic acid) from the condenser liquid or chemically reacting the condenser liquid with a reactant (e.g., CO and/or H_2).

[0027] In some embodiments, the condenser liquid is subjected to a purification step prior to contacting with the first biogenic reagent. In these or other embodiments, the condenser liquid is subjected to a reaction step prior to contacting with the first biogenic reagent. In certain embodiments, there is a reaction step as well as a purification step to remove not only undesired impurities initially in the condenser liquid, but also chemical-reaction byproducts that are not desired in the intermediate material.

[0028] In some embodiments, pyrolyzing the feedstock (in the first pyrolysis reactor) is conducted at a first pyrolysis temperature of at least about 250°C to at most about 1250°C. In certain embodiments, the first pyrolysis temperature is at least about 300°C to at most about 700°C. In some embodiments, pyrolyzing the feedstock (in the first pyrolysis reactor) is conducted for a first pyrolysis time of at least about 10 seconds to at most about 24 hours.

[0029] In some embodiments in which thermally treating is at a pyrolysis temperature, pyrolyzing the intermediate material is conducted at a second pyrolysis temperature of at least about 250°C to at most about 1250°C. In certain embodiments, the second pyrolysis temperature is at least about 300°C to at most about 700°C. In some embodiments, pyrolyzing the intermediate material is conducted for a second pyrolysis time of at least about 10 seconds to at most about 24 hours.

[0030] The process can further comprise oxidizing the condenser vapor, thereby generating heat. Additionally, or alternatively, the process can further comprise oxidizing

the off-gas (from the thermal-treatment unit), thereby generating heat. Heat generated from oxidation of condenser vapor and/or off-gas can be reused in the process, such as to provide heat for the first pyrolysis reactor.

[0031] In some embodiments, the process further comprises milling the first biogenic reagent using a mechanical-treatment apparatus, wherein the mechanical-treatment apparatus is 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.

[0032] In some embodiments, the process further comprises milling the intermediate material using a mechanical-treatment apparatus, wherein the mechanical-treatment apparatus is 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.

[0033] In some embodiments that employ pelletizing the intermediate material, the pelletizing 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.

[0034] In some embodiments, the process further comprises generating fines, in the thermal-treatment unit, wherein the fines comprise carbon; and further comprising recycling the fines to the step of contacting the first biogenic reagent with the condenser liquid.

[0035] In some embodiments, the process further comprises generating fines, in the thermal-treatment unit, wherein the fines comprise carbon; and further comprising recycling the fines to the step of recovering the second biogenic reagent.

[0036] In various processes, the biocarbon composition is in the form of a powder.

[0037] In various processes, the biocarbon composition is in the form of pellets. After pellets are formed, the process can further comprise powderizing the pellets to form a powder again.

[0038] In some embodiments, the process comprises comprising drying the second biogenic reagent, and further comprises pelletizing the second biogenic reagent to generate

pellets, wherein the pelletizing the second biogenic reagent occurs during the drying, after the drying, or after the recovering.

[0039] In some embodiments, the biocarbon composition comprises at least 50 wt% fixed carbon, at least 60 wt% fixed carbon, at least 70 wt% fixed carbon, at least 80 wt% fixed carbon, or at least 90 wt% fixed carbon.

[0040] In some embodiments, the biocarbon composition comprises less than 10 wt% ash, less than 5 wt% ash, or less than 1 wt% ash.

[0041] In some embodiments, the condenser liquid comprises less than 1 wt% ash, less than 0.1 wt% ash, or essentially no ash.

[0042] The total carbon within the biocarbon composition can be at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. The total carbon within the biocarbon composition can be at least 90% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. The total carbon within the biocarbon composition can be fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

[0043] In some embodiments, the biocarbon composition is characterized by a bulk density of at least about 5 lb/ft^3, at least about 10 lb/ft^3, or at least about 20 lb/ft^3 on a dry basis.

[0044] In some embodiments, the biocarbon composition is hydrophobic, such as being characterized by at most 20 wt% water uptake at 25°C after 24 hours of soaking in water.

[0045] In some embodiments, the biocarbon composition is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances".

[0046] When the biocarbon composition is in the form of a pellet, the pellet can be characterized by a bulk density of at least about 10 lb/ft^3, at least about 25 lb/ft^3, or at least about 35 lb/ft^3 on a dry basis, for example.

[0047] When the biocarbon composition is in the form of a pellet, the pellet can be characterized by a Hardgrove Grindability Index of at least 30, at least 50, or at least 70, for example.

[0048] When the biocarbon composition is in the form of a pellet, the pellet can be characterized by a pellet compressive strength at 25°C of at least about 100 lb_f/in^2 or at least about 150 lb_f/in^2.

[0049] Other variations provide a system for producing a biocarbon composition, the system comprising:

a first pyrolysis reactor configured for pyrolyzing a feedstock comprising biomass to generate a first biogenic reagent and a first pyrolysis vapor;

a condensing system in flow communication with the first pyrolysis reactor, wherein the condensing system is configured for condensing the first pyrolysis vapor to generate a condenser liquid and a condenser vapor;

a mixing unit in flow communication with the first biogenic reagent and the condensing system, wherein the mixing unit is configured for contacting the first biogenic reagent with the condenser liquid to generate an intermediate material;

a thermal-treatment unit in flow communication with the mixing unit, wherein the thermal-treatment unit is configured for thermally treating the intermediate material to generate a second biogenic reagent and an off-gas; and

a system output disposed in the thermal-treatment unit or in flow communication with the thermal-treatment unit, wherein the system output is configured for recovering the second biogenic reagent as a biocarbon composition.

[0050] In some systems, the mixing unit is a pelletizing unit. In other systems, the system comprises a pelletizing unit that is distinct from the mixing unit, wherein the pelletizing unit is disposed between the mixing unit and the thermal-treatment unit.

[0051] In some systems, the condensing system comprises multiple condenser stages, such as 2, 3, 4, or more condenser stages.

[0052] In some systems, a recycle line is configured to recycle off-gas from the thermal-treatment unit to the condensing system, when there is an off-gas from the thermal-treatment unit.

[0053] In some systems, the thermal-treatment unit is a second pyrolysis reactor. In other systems, the thermal-treatment unit is a dryer. In still other systems, there is first thermal-treatment unit that is a dryer, and a second thermal-treatment unit that is a second pyrolysis reactor, arranged in either order.

[0054] Some systems further comprise a mechanical-treatment apparatus configured to mill the first biogenic reagent, wherein the mechanical-treatment apparatus is 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.

[0055] Some systems further comprise a mechanical-treatment apparatus configured to mill the intermediate material, wherein the mechanical-treatment apparatus is 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.

[0056] Some systems further comprise a pelletizing apparatus configured to pelletize the intermediate material, wherein the pelletizing apparatus is 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.

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

pyrolyzing a feedstock in a first pyrolysis reactor, wherein the feedstock comprises biomass, thereby generating a first pyrolysis solid and a first pyrolysis vapor;

introducing the first pyrolysis vapor to a condensing system, thereby generating a condenser liquid and a condenser vapor;

thermally treating the condenser liquid in a second reactor, thereby generating a solid or semi-solid material;

blending the first pyrolysis solid with the solid or semi-solid material, thereby generating a biogenic reagent; and

recovering the biogenic reagent as a biocarbon composition.

[0058] The feedstock can be selected from softwood chips, hardwood chips, timber harvesting residues, tree branches, tree stumps, leaves, bark, sawdust, corn, corn stover, wheat, wheat straw, rice, rice straw, sugarcane, sugarcane bagasse, sugarcane straw, energy cane, sugar beets, sugar beet pulp, sunflowers, sorghum, canola, algae, miscanthus, alfalfa, switchgrass, fruits, fruit shells, fruit stalks, fruit peels, fruit pits, vegetables, vegetable shells, vegetable stalks, vegetable peels, vegetable pits, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, food waste, commercial waste, grass pellets, hay pellets, wood pellets, cardboard, paper, paper pulp, paper packaging, paper trimmings, food packaging, construction and/or demolition waste, railroad ties, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof.

[0059] In some embodiments, the process further comprises drying or thermally treating the biogenic reagent.

[0060] In some embodiments, the process further comprises pelletizing the biogenic reagent.

[0061] In certain embodiments, the process further comprises drying or thermally treating the biogenic reagent, and further comprises pelletizing the biogenic reagent, wherein the pelletizing and the drying or thermally treating are integrated.

[0062] In embodiments in which pellets are formed, the pelletizing can be integrated with the step of blending the first pyrolysis solid with the solid or semi-solid material.

[0063] In embodiments in which pellets are formed, the process can comprise introducing a binder to the biogenic reagent. The binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium

hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, derivatives thereof, or a combination of the foregoing.

[0064] In certain embodiments in which pellets are formed, no external binder is introduced to the biogenic reagent during the pelletizing.

[0065] In some processes, the condensing system comprises multiple condenser stages. The condenser liquid can be a condensed product of a first stage of the multiple condenser stages. The condenser liquid can be a condensed product of a plurality of stages of the multiple condenser stages. In certain embodiments, the plurality of stages does not include the final stage of the multiple condenser stages.

[0066] In some embodiments, the second reactor is a non-pyrolytic thermal reactor or a non-pyrolytic catalytic reactor.

[0067] In some embodiments, the second reactor is a second pyrolysis reactor that generates the solid or semi-solid material as well as a pyrolysis off-gas. In certain embodiments, the process can further comprise conveying, to the condensing system, the pyrolysis off-gas. The second pyrolysis reactor can be distinct from the first pyrolysis reactor. Alternatively, the first pyrolysis reactor and the second pyrolysis reactor are the same unit, wherein the pyrolyzing the feedstock and the thermally treating the condenser liquid occur at different times.

[0068] In some processes, at least 25 wt%, at least 50 wt%, or at least 75 wt% of total carbon comprised in the condenser liquid is converted to fixed carbon in the solid or semi-solid material.

[0069] In some processes, the solid or semi-solid material forms at least 5 wt%, at least 10 wt%, or at least 20 wt% of the biogenic reagent on an absolute basis.

[0070] In some embodiments, at least about 10 wt% to at most about 80 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid. In certain embodiments, at least about 20 wt% to at most about 60 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid.

[0071] In some processes, all of the condenser liquid is thermally treated in the second reactor. In other processes, less than all of the condenser liquid is thermally treated in the second reactor.

[0072] In some processes, the condenser liquid is thermally treated in the second reactor without any intermediate chemical processing between the condensing system and the second reactor.

[0073] In some processes, the condenser liquid is chemically processed prior to thermally treating in the second reactor. In certain processes, the condenser liquid is subjected to a purification step prior to thermally treating in the second reactor. In certain processes, the condenser liquid is subjected to a reaction step prior to thermally treating in the second reactor. In some specific processes, the condenser liquid is subjected to a reaction step as well as a purification step (in either order) prior to thermally treating in the second reactor.

[0074] In some embodiments, the pyrolyzing the feedstock (in the first pyrolysis reactor) is conducted at a first pyrolysis temperature of at least about 250°C to at most about 1250°C, such as at least about 300°C to at most about 700°C.

[0075] In some embodiments, the second reactor is a second pyrolysis reactor operated at a second pyrolysis temperature, wherein the second pyrolysis temperature is at least about 250°C to at most about 1250°C, such as at least about 300°C to at most about 700°C.

[0076] In other embodiments, the second reactor is operated at a temperature selected from about 80°C to about 250°C.

[0077] The process can further comprise oxidizing the condenser vapor, thereby generating heat. Additionally, or alternatively, the process can further comprise oxidizing the reactor off-gas, thereby generating heat.

[0078] Some processes further comprise milling the biogenic reagent using a mechanical-treatment apparatus, wherein the mechanical-treatment apparatus is 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.

[0079] In some processes employing pelletizing the biogenic reagent, the pelletizing utilizes a pelletizing apparatus selected from an extruder, a ring die pellet mill, a flat die pellet mill, a roll compactor, a roll briquetter, a wet agglomeration mill, a dry agglomeration mill, or a combination thereof.

[0080] In various embodiments, the biocarbon composition comprises at least 50 wt%, at least 60 wt%, at least 70 wt%, at least 80 wt%, or at least 90 wt% fixed carbon.

[0081] In some embodiments, the biocarbon composition comprises less than 10 wt% ash, less than 5 wt% ash, or less than 1 wt% ash.

[0082] In some embodiments, the condenser liquid comprises less than 1 wt% ash, less than 0.1 wt% ash, or essentially no ash.

[0083] The total carbon within the biocarbon composition can be at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. The total carbon within the biocarbon composition can be at least 90% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. The total carbon within the biocarbon composition can be fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

[0084] In some embodiments, the biocarbon composition is characterized by a bulk density of at least about 5 lb/ft^3, at least about 10 lb/ft^3, or at least about 20 lb/ft^3 on a dry basis.

[0085] In some embodiments, the biocarbon composition is characterized by at most 20 wt% water uptake at 25°C after 24 hours of soaking in water.

[0086] In some embodiments, the biocarbon composition is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances".

[0087] In some embodiments, the biocarbon composition is in the form of a pellet. The pellet can be characterized by a bulk density of at least about 10 lb/ft^3, at least about 25 lb/ft^3, or at least about 35 lb/ft^3 on a dry basis. The pellet can be characterized by a

Hardgrove Grindability Index of at least 30, at least 50, or at least 70. The pellet can be characterized by a pellet compressive strength at 25°C of at least about 100 lb_f/in^2 or at least about 150 lb_f/in^2.

[0088] Other variations provide a system for producing a biocarbon composition, the system comprising:

a first pyrolysis reactor configured for pyrolyzing a feedstock comprising biomass to generate a first pyrolysis solid and a first pyrolysis vapor;

a condensing system in flow communication with the first pyrolysis reactor, wherein the condensing system is configured for condensing the first pyrolysis vapor to generate a condenser liquid and a condenser vapor;

a second reactor in flow communication with the condensing system, wherein the second reactor is configured for thermally treating the condenser liquid to generate a solid or semi-solid material;

a mixing unit in flow communication with the first pyrolysis reactor and the second reactor, wherein the mixing unit is configured for blending the first pyrolysis solid with the solid or semi-solid material to generate a biogenic reagent; and

a system output in flow communication with the mixing unit, wherein the system output is configured for recovering the biogenic reagent as a biocarbon composition.

[0089] In some systems, the mixing unit is a pelletizing unit. In some systems, the system comprises a pelletizing unit that is distinct from the mixing unit, wherein the pelletizing unit is disposed between the mixing unit and the system output.

[0090] In some systems, the condensing system comprises multiple condenser stages.

[0091] In some systems, the second reactor is a second pyrolysis reactor. The system can further comprise a recycle line configured to recycle pyrolysis off-gas to the condensing system.

[0092] In some systems, the second reactor is a non-pyrolytic thermal reactor or a non-pyrolytic catalytic reactor.

[0093] The system can further comprise a mechanical-treatment apparatus configured to mill the biogenic reagent, wherein the mechanical-treatment apparatus is 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.

[0094] The system can further comprise a pelletizing apparatus configured to pelletize the biogenic reagent, wherein the pelletizing apparatus is 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.

[0095] Still other variations provide a process for producing a biocarbon composition, the process comprising:

pyrolyzing a first feedstock in a first pyrolysis reactor, thereby generating a biogenic reagent and a pyrolysis vapor;

introducing the pyrolysis vapor to a condensing system, thereby generating a condenser liquid and a condenser vapor;

contacting a second feedstock with the condenser liquid, wherein the second feedstock comprises biomass, thereby generating the first feedstock, wherein the first feedstock comprises the second feedstock and the condenser liquid; and

recovering the biogenic reagent as a biocarbon composition.

[0096] The biomass can be selected from softwood chips, hardwood chips, timber harvesting residues, tree branches, tree stumps, leaves, bark, sawdust, corn, corn stover, wheat, wheat straw, rice, rice straw, sugarcane, sugarcane bagasse, sugarcane straw, energy cane, sugar beets, sugar beet pulp, sunflowers, sorghum, canola, algae, miscanthus, alfalfa, switchgrass, fruits, fruit shells, fruit stalks, fruit peels, fruit pits, vegetables, vegetable shells, vegetable stalks, vegetable peels, vegetable pits, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, food waste, commercial waste, grass pellets, hay pellets, wood pellets, cardboard, paper, paper pulp, paper packaging, paper trimmings, food packaging, construction and/or demolition waste, railroad ties, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof.

[0097] Some processes further comprise pelletizing the biogenic reagent. Pelletizing the biogenic reagent can comprise introducing a binder to the biogenic reagent. The binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, derivatives thereof, or a combination of the foregoing. Optionally, pelletizing the biogenic reagent can be done without introducing an external binder to the biogenic reagent.

[0098] In some embodiments, the condensing system comprises multiple condenser stages. The condenser liquid can be a condensed product of a first stage of the multiple condenser stages. In certain embodiments, the condenser liquid is a condensed product of a plurality of stages of the multiple condenser stages, wherein optionally the plurality of stages does not include the final stage of the multiple condenser stages.

[0099] In some processes, the step of contacting the second feedstock with the condenser liquid comprises spraying the condenser liquid onto the biomass. Other means of contacting the second feedstock with the condenser liquid can be employed, including (but not limited to) submerging the biomass in the condenser liquid, coating particles of biomass with a film of condenser liquid, or other techniques.

[0100] In some processes, the first feedstock comprises the condenser liquid adsorbed onto a surface of the biomass. Alternatively, or additionally, the first feedstock can comprise the condenser liquid absorbed into a bulk phase of the biomass.

[0101] In some processes pertaining to contacting biomass with condenser liquid, the process further comprises thermally treating the biogenic reagent in a thermal-treatment unit. If the biogenic reagent is subjected to pelletizing, the thermally treating can be before, during, or after the pelletizing.

[0102] In some processes employing a thermal-treatment unit, the thermal-treatment unit is a second pyrolysis reactor operated at a second pyrolysis temperature of at least about 250°C. The second pyrolysis reactor is configured for pyrolyzing the biogenic reagent. The second pyrolysis reactor is typically distinct from (i.e., physically different than) the first pyrolysis reactor. Alternatively, the first pyrolysis reactor and the second pyrolysis reactor can be the same unit, wherein the pyrolyzing and the thermally treating are conducted at different times.

[0103] In some embodiments, pyrolyzing the biogenic reagent in a thermal-treatment unit generates an off-gas, which can be recycled to the condensing system.

[0104] In other processes employing a thermal-treatment unit, the thermal-treatment unit is operated at a temperature selected from about 80°C to about 250°C.

[0105] In some embodiments employing a thermal-treatment unit, the thermal-treatment unit contains an internal oxygen-free environment. An inert gas can be introduced to the thermal-treatment unit. The thermal-treatment unit can be operated under vacuum.

[0106] A thermal-treatment unit can be configured for drying the biogenic reagent. Alternatively, or additionally, the process can further comprise drying of the biocarbon composition after thermally treating in the optional thermal-treatment unit.

[0107] Some processes comprise converting at least 25 wt%, at least 50 wt%, or at least 75 wt% of the total carbon comprised within the condenser liquid to fixed carbon comprised within the biogenic reagent.

[0108] In some processes, at least about 10 wt% to at most about 80 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid. In certain processes, at least about 20 wt% to at most about 60 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid.

[0109] All of the condenser liquid can be contacted with the second feedstock. Alternatively, less than all of the condenser liquid is contacted with the second feedstock.

[0110] In some processes, the condenser liquid is contacted with the second feedstock without any intermediate chemical processing. In other processes, the condenser liquid is

chemically processed prior to contacting with the second feedstock. For example, the condenser liquid can be subjected to a purification step and/or a reaction step prior to contacting with the second feedstock.

[0111] In some embodiments pertaining to contacting biomass with condenser liquid, a portion of the condenser liquid is added to the biogenic reagent, rather than being contacted with the biomass.

[0112] Pyrolyzing the first feedstock in the first pyrolysis reactor can be conducted at a first pyrolysis temperature of at least about 250°C to at most about 1250°C, such as at least about 300°C to at most about 700°C. The first pyrolysis time in the first pyrolysis reactor can be at least about 10 seconds to at most about 24 hours.

[0113] When there is a thermal-treatment unit configured as a second pyrolysis reactor, the second pyrolysis temperature can at least about 250°C to at most about 1250°C, such as at least about 300°C to at most about 700°C. The second pyrolysis time can be at least about 10 seconds to at most about 24 hours.

[0114] In some embodiments, the process further comprises oxidizing the condenser vapor, thereby generating heat. In these or other embodiments, the process further comprises oxidizing an off-gas derived from the thermal-treatment unit, thereby generating heat. Heat can be used within the process for various purposes.

[0115] Some processes further comprise milling the biogenic reagent using a mechanical-treatment apparatus, wherein the mechanical-treatment apparatus is 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.

[0116] When the process employs pelletizing the biogenic reagent, a pelletizing apparatus can be 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.

[0117] Some processes further comprise drying the biogenic reagent, and further comprise pelletizing the biogenic reagent to generate pellets. Pelletizing the biogenic reagent can be prior to the drying, during the drying, or after the drying.

[0118] In some processes, the biocarbon composition comprises at least 50 wt%, at least 60 wt%, at least 70 wt%, at least 80 wt%, or at least 90 wt% fixed carbon.

[0119] In some processes, the biocarbon composition comprises less than 10 wt% ash, less than 5 wt% ash, or less than 1 wt% ash.

[0120] In some processes, the condenser liquid comprises less than 1 wt% ash, less than 0.1 wt% ash, or essentially no ash.

[0121] The total carbon within the biocarbon composition can be at least 50%, at least 90%, or 100% (fully) renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

[0122] In some processes, the biocarbon composition is characterized by a bulk density of at least about 5 lb/ft^3, at least about 10 lb/ft^3, or at least about 20 lb/ft^3 on a dry basis.

[0123] In some processes, the biocarbon composition is characterized by at most 20 wt% water uptake at 25°C after 24 hours of soaking in water.

[0124] In some processes, the biocarbon composition is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances".

[0125] In some processes, the biocarbon composition is in the form of a pellet. The pellet can be characterized by a bulk density of at least about 10 lb/ft^3, at least about 25 lb/ft^3, or at least about 35 lb/ft^3 on a dry basis. The pellet can be characterized by a Hardgrove Grindability Index of at least 30, at least 50, or at least 70. The pellet can be characterized by a pellet compressive strength at 25°C of at least about 100 lb_f/in^2 or at least about 150 lb_f/in^2.

[0126] Certain variations provide a system for producing a biocarbon composition, the system comprising:

a first pyrolysis reactor configured for pyrolyzing a first feedstock to generate a biogenic reagent and a pyrolysis vapor;

a condensing system in flow communication with the first pyrolysis reactor, wherein the condensing system is configured for condensing the pyrolysis vapor to generate a condenser liquid and a condenser vapor;

a mixing unit in flow communication with the condensing system, wherein the mixing unit is configured for contacting a second feedstock comprising biomass with the condenser liquid to generate a first feedstock; and

a system output in flow communication with the first pyrolysis reactor, wherein the system output is configured for recovering the biogenic reagent as a biocarbon composition.

[0127] Some systems further comprise a pelletizing unit in flow communication with the first pyrolysis reactor, wherein the pelletizing unit is configured for pelletizing the biogenic reagent to generate pellets.

[0128] Some systems further comprise a thermal-treatment unit in flow communication with the pelletizing unit, if present, or in flow communication with the first pyrolysis reactor. In certain systems, a thermal-treatment unit is disposed downstream of the pelletizing unit, wherein the thermal-treatment unit is configured to receive the pellets. In certain systems, the thermal-treatment unit is disposed between the first pyrolysis reactor and the pelletizing unit, wherein the pelletizing unit is configured to receive a thermally treated biogenic reagent.

[0129] In some systems, the thermal-treatment unit is a second pyrolysis reactor operated at a second pyrolysis temperature of at least about 250°C, wherein the second pyrolysis reactor is configured for pyrolyzing the biogenic reagent. The system can include a recycle line configured to recycle pyrolysis off-gas, from the second pyrolysis reactor, to the condensing system.

[0130] In certain systems, the thermal-treatment unit is operated at a temperature selected from about 80°C to about 250°C.

[0131] In some systems, the condensing system comprises multiple condenser stages, such as 2, 3, 4, 5, or more stages.

[0132] In some systems, the mixing unit is configured to spray the condenser liquid onto the biomass.

[0133] The system can further comprise a mechanical-treatment apparatus configured to mill the biogenic reagent, wherein the mechanical-treatment apparatus is 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.

[0134] The system can further comprise a pelletizing unit 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.

BRIEF DESCRIPTION OF THE DRAWINGS

[0135] In FIGS. 1 to 8, dotted boxes and lines denote optional units and streams, respectively.

[0136] FIG. 1 depicts an exemplary block-flow diagram of a process and system in which biomass is pyrolyzed in a pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser having at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. A condenser liquid is fed to a mixing unit, into which is also fed the biogenic reagent. The combined material is optionally sent to a pelletizing unit to generate pellets. Pellets are then fed to a thermal-treatment unit which generates a biocarbon product.

[0137] FIG. 2 depicts an exemplary block-flow diagram of a process and system in which biomass is pyrolyzed in a pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser having at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. A condenser liquid is optionally fed to a pelletizing unit, into which is also fed the biogenic reagent, to generate pellets. Pellets (or the condenser liquid plus biogenic reagent) are fed to a thermal-treatment unit which generates a biocarbon product.

[0138] FIG. 3 depicts an exemplary block-flow diagram of a process and system in which biomass is pyrolyzed in a pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser having at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. The biogenic reagent is fed to a pelletizing unit, to generate pellets. The pellets and the condenser liquid

(or one of the condenser liquids if there are multiple fractions) are fed to a carbon recapture unit, to generate an intermediate material. The intermediate material is then fed to a thermal-treatment unit which generates a biocarbon product.

[0139] FIG. 4 depicts an exemplary block-flow diagram of a process and system in which biomass is pyrolyzed in a first pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser having at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. The biogenic reagent and the condenser liquid (or one of the condenser liquids if there are multiple fractions) are fed to a carbon recapture unit, to generate an intermediate material. The intermediate material is then fed to a thermal-treatment unit which generates a biocarbon product.

[0140] FIG. 5 depicts an exemplary block-flow diagram of a process and system in which biomass is pyrolyzed in a first pyrolysis reactor to generate a first pyrolysis solids and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser comprising at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. The condenser liquid (or one of the condenser liquids if there are multiple fractions) are fed to a second pyrolysis reactor to generate second pyrolysis solids and a pyrolysis off-gas. The first and second pyrolysis solids can be combined. A blended material can be pelletized. Whether or not the blended material is pelletized, the blended material can be dried or thermally treated, to generate a final biocarbon product.

[0141] FIG. 6 depicts an exemplary block-flow diagram of a process and system in which biomass is pyrolyzed in a first pyrolysis reactor to generate a first pyrolysis solids and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser comprising at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. The condenser liquid (or one of the condenser liquids if there are multiple fractions) are fed to a second reactor to generate a solid or semi-solid material and a reactor off-gas. The first and second pyrolysis solids can be combined. A blended material can be pelletized. Whether or not the blended material is pelletized, the blended material can be dried or thermally treated, to generate a final biocarbon product.

[0142] FIG. 7 depicts an exemplary block-flow diagram of a process and system in which biomass, impregnated with condenser liquid, is pyrolyzed in a pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser comprising at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. The condenser liquid (or one of the condenser liquids if there are multiple fractions) is fed to a mixing unit, along with incoming biomass, to generate a feed material (biomass plus condenser liquid). In some embodiments, the biogenic reagent from the pyrolysis reactor is pelletized. Whether or not the biogenic reagent is pelletized, the biogenic reagent can be dried or thermally treated, to generate a final biocarbon product.

[0143] FIG. 8 depicts an exemplary block-flow diagram of a process and system in which biomass, impregnated with condenser liquid, is pyrolyzed in a first pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser comprising at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. The condenser liquid (or one of the condenser liquids if there are multiple fractions) is fed to a mixing unit, along with incoming biomass, to generate a feed material (biomass plus condenser liquid). In some embodiments, the biogenic reagent from the first pyrolysis reactor is pelletized. Whether or not the biogenic reagent is pelletized, the biogenic reagent can be sent to a second pyrolysis reactor, to generate a final biocarbon product.

DETAILED DESCRIPTION

[0144] This description will enable one skilled in the art to make and use the disclosed technology, and it describes several embodiments, adaptations, variations, alternatives, and uses of the technology. These and other embodiments, features, and advantages of the present disclosure will become more apparent to those skilled in the art when taken with reference to the following detailed description in conjunction with the accompanying drawings.

[0145] As used herein, where the indefinite article "a" or "an" is used with respect to a statement or description of the presence of a step in a process disclosed herein, unless the

statement or description explicitly provides to the contrary, the use of such indefinite article does not limit the presence of the step in the process to one in number. As used herein, when an amount, concentration, or other value or parameter is given as a range or a list of upper values and lower values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or value and any lower range limit or value, regardless of whether ranges are separately disclosed.

[0146] Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the disclosure be limited to the specific values recited when defining a range.

[0147] As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having," "contains," or "containing," or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a composition, a mixture, process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but can include other elements not expressly listed or inherent to such composition, mixture, process, method, article, or apparatus.

[0148] Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. Unless the word "or" is expressly limited to mean only a single item exclusive from the other items in reference to a list of two or more items, then the use of "or" in such a list is to be interpreted as including (a) any single item in the list, (b) all of the items in the list, or (c) any combination of the items in the list. As used herein, the phrase "and/or" as in "A and/or B" refers to A alone, B alone, and both A and B. Where the context permits, singular or plural terms can also include the plural or singular term, respectively.

[0149] As used herein, the term "about" refers to variation in the reported numerical quantity that can occur. The term "about" means within 10, 9, 8, 7, 6, 5, 4, 3, 2, or 1% of the reported numerical value.

[0150] Reference in this specification to "any intervening ranges" of a list of values means that the parameter, in some embodiments, is selected from a sub-range that starts with one of the values and ends with another, higher value in this list. For example, when a

temperature can be 150°C, 200°C, 250°C, or 300°C, including any intervening ranges, then the temperature can be selected from the sub-ranges 150–200°C, 150–250°C, 150–300°C, 200–250°C, 200–300°C, or 250–300°C.

[0151] As used herein, the term "substantially" refers to the complete or nearly complete extent or degree of an action, characteristic, property, state, structure, item, or result. For example, an object that is "substantially" enclosed would mean that the object is either completely enclosed or nearly completely enclosed. The exact allowable degree of deviation from absolute completeness can in some cases depend on the specific context. However, generally speaking the nearness of completion will be so as to have the same overall result as if absolute and total completion were obtained. The use of "substantially" is equally applicable when used in a negative connotation to refer to the complete or near complete lack of an action, characteristic, property, state, structure, item, or result.

[0152] To the extent any materials incorporated herein by reference conflict with the present disclosure, the present disclosure controls.

[0153] For present purposes, "biogenic" is intended to mean a material (whether a feedstock, product, or intermediate) that contains an element, such as carbon, that is renewable on time scales of months, years, or decades. Non-biogenic materials can be non-renewable, or can be renewable on time scales of centuries, thousands of years, millions of years, or even longer geologic time scales. A biogenic material can comprise a mixture of biogenic and non-biogenic sources.

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

[0155] Plants take up ^{14}C by fixing atmospheric carbon through photosynthesis. Animals then take ^{14}C into their bodies when they consume plants or consume other animals

that consume plants. Accordingly, living plants and animals have the same ratio of ^{14}C to ^{12}C as the atmospheric CO_2. Once an organism dies, it stops exchanging carbon with the atmosphere, and thus no longer takes up new ^{14}C. Radioactive decay then gradually depletes the ^{14}C in the organism. This effect is the basis of radiocarbon dating.

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

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

[0158] The measurement of the $^{14}C/^{12}C$ isotopic ratio of the carbon can utilize ASTM D6866.

[0159] 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.

[0160] For present purposes, "reagent" is intended to mean a material in its broadest sense; a reagent can be a fuel, a chemical, a material, a compound, an additive, a blend

component, a solvent, and so on. A reagent is not necessarily a chemical reagent that causes or participates in a chemical reaction. A reagent can be a chemical reactant that is consumed in a reaction, but that is not necessarily the case. 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.

[0161] The terms "low fixed carbon" and "high fixed carbon" are used herein for practical purposes to describe materials that can be produced by processes and systems as disclosed, in various embodiments. Limitations as to carbon content, or any other concentrations, shall not be imputed from the term itself but rather only by reference to particular embodiments and equivalents thereof.

[0162] In this disclosure, reference to "the condenser liquid" can be in reference to either some of the condenser liquid formed in the process or all of the condenser liquid formed in the process, unless otherwise stated.

[0163] Some variations provide a process for producing a biocarbon composition, the process comprising:

pyrolyzing a feedstock in a first pyrolysis reactor, wherein the feedstock comprises biomass, thereby generating a first biogenic reagent and a first pyrolysis vapor;

introducing the first pyrolysis vapor to a condensing system, thereby generating a condenser liquid and a condenser vapor;

contacting the first biogenic reagent with the condenser liquid, thereby generating an intermediate material, wherein the intermediate material comprises the first biogenic reagent and the condenser liquid;

thermally treating the intermediate material in a thermal-treatment unit, thereby generating a second biogenic reagent and an off-gas;

recovering the second biogenic reagent as a biocarbon composition.

[0164] In some embodiments, the 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 and/or demolition waste, railroad ties, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof.

[0165] In some embodiments, the process further comprises pelletizing the first biogenic reagent. In these or other embodiments, the process can further comprise pelletizing the intermediate material. In certain embodiments, pelletizing the intermediate material is integrated with the step of contacting the first biogenic reagent with the condenser liquid. In other embodiments, pelletizing the intermediate material occurs after contacting the first biogenic reagent with the condenser liquid.

[0166] Pelletizing the intermediate material, when performed, can include introducing a binder to the intermediate material. The binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, derivatives thereof, or a combination of the foregoing.

[0167] In some embodiments, pelletizing the intermediate material does not comprise introducing an external binder to the intermediate material. In these cases, the condenser liquid can act as a binder for the pellets.

[0168] In some processes (see, for example, FIGS. 3 or 4), a carbon recapture unit is disposed upstream of the thermal-treatment unit. In certain processes, a carbon recapture unit is a first stage of the thermal-treatment unit. The carbon recapture unit can be a mixing unit contacting the first biogenic reagent with the condenser liquid. Alternatively, or additionally, a carbon recapture unit can be distinct from a mixing unit. In some embodiments, a carbon recapture unit is disposed upstream of the second pyrolysis reactor. In other embodiments, a carbon recapture unit is a first stage of the second pyrolysis reactor. The carbon recapture unit can be configured to form a coating of condenser liquid onto pellets, for example. A carbon recapture unit can be fed a carbon source different than the condenser liquid, such as an external carbon source or a waste carbon-containing stream from the process.

[0169] In some embodiments, the condensing system comprises multiple condenser stages. The condenser liquid can be a condensed product of a first stage of the multiple condenser stages, for example. In some embodiments, the condenser liquid is a condensed product of a plurality of stages of the multiple condenser stages. In certain embodiments, the plurality of stages does not include the final stage of the multiple condenser stages, especially when the final stage is configured or operated such that the final condenser product contains a high concentration of water.

[0170] In some embodiments, the intermediate material comprises the condenser liquid adsorbed onto a surface of the first biogenic reagent. Alternatively, or additionally, the intermediate material can comprise the condenser liquid absorbed into a bulk phase of the first biogenic reagent.

[0171] In some embodiments, the thermal-treatment unit is a second pyrolysis reactor operated at a temperature of at least about 250°C, wherein the second pyrolysis reactor is configured for pyrolyzing the intermediate material. Pyrolysis conditions are described in detail later in this specification.

[0172] In other embodiments, the thermal-treatment unit is operated at a relatively low temperature selected from about 80°C to about 250°C, for example. In various embodiments, the thermal-treatment unit is operated at a temperature of about, at least about, or at most about 80°C, 90°C, 100°C, 110°C, 120°C, 130°C, 140°C, 150°C, 160°C, 170°C, 180°C, 190°C, 200°C, 210°C, 220°C, 230°C, 240°C, or 250°C, including any intervening ranges.

[0173] The thermal-treatment unit preferably contains an internal oxygen-free environment, or at least a low-oxygen environment. In various embodiments, the internal environment of the thermal-treatment unit is at most about 5 vol% O_2, 4 vol% O_2, 3 vol% O_2, 2 vol% O_2, 1 vol% O_2, 0.5 vol% O_2, 0.2 vol% O_2, 0.1 vol% O_2, 0.05 vol% O_2, 0.02 vol% O_2, or 0.01 vol% O_2, including any intervening ranges. The internal environment of the thermal-treatment unit can be measured using a gas-phase sample probe and an oxygen sensor, such as an ultrasonic oxygen sensor or a tunable diode laser.

[0174] In some embodiments, an inert gas is introduced to the thermal-treatment unit. The inert gas can be nitrogen, argon, carbon dioxide, or a mixture thereof.

[0175] In certain embodiments, the thermal-treatment unit is operated under a pressure greater than atmospheric pressure. The absolute pressure within the thermal-treatment unit can be from about 1 bar to about 10 bar, such as from about 1 bar to about 5 bar, or from about 1 bar to about 2 bar.

[0176] In certain embodiments, the thermal-treatment unit is operated under vacuum. The absolute pressure within a thermal-treatment vacuum unit can be about, or at most about 0.99 bar, 0.9 bar, 0.8 bar, 0.7 bar, 0.6 bar, 0.5 bar, 0.4 bar, 0.3 bar, 0.2 bar, or 0.1 bar, including any intervening ranges, for example.

[0177] In some embodiments, the process further comprises introducing the off-gas from the thermal-treatment unit to the condensing system. These embodiments can be desirable when the off-gas contains a high concentration of carbon.

[0178] In some embodiments, the thermal-treatment unit is configured for drying the second biogenic reagent. In these embodiments, the off-gas from the thermal-treatment unit comprises or consists essentially of water vapor.

[0179] The process can further comprise drying of the biocarbon composition after the thermally treating in the thermal-treatment unit. Drying toward the end of the process can be desirable because thermal treatment can cause water-forming chemical reactions, i.e., reaction water that was not present with the feedstock or present prior to the chemical formation of water.

[0180] In typical embodiments, the first pyrolysis reactor is distinct from the second pyrolysis reactor. In other embodiments, the first pyrolysis reactor and the second pyrolysis reactor are physically the same unit, while the pyrolyzing and the thermally treating are conducted at different times.

[0181] In some embodiments, the process comprises performing fixed-carbon formation reactions of the condenser liquid. The fixed-carbon formation reactions can utilize the first biogenic reagent as a catalyst. Alternatively, or additionally, the fixed-carbon formation reactions can utilize the first biogenic reagent as a reaction matrix.

[0182] In some processes, the process comprises converting at least 25 wt%, at least 50 wt%, or at least 75 wt% of the total carbon comprised within the condenser liquid to fixed carbon comprised within the second biogenic reagent. In various embodiments, the process comprises converting about, or at least about, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 wt%, including any intervening ranges, of the total carbon comprised within the condenser liquid to fixed carbon comprised within the second biogenic reagent.

[0183] In some embodiments, at least about 10 wt% to at most about 80 wt% of fixed carbon in the second biogenic reagent is derived from the condenser liquid. In certain embodiments, at least about 20 wt% to at most about 60 wt% of fixed carbon in the second biogenic reagent is derived from the condenser liquid. In various embodiments, the percentage of fixed carbon in the second biogenic reagent that is derived from the condenser liquid is about, at least about, or at most about 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, or 95%, including any intervening ranges.

[0184] In some processes, all of the condenser liquid is contacted with the first biogenic reagent. In other processes, less than all of the condenser liquid is contacted with the first

biogenic reagent. In various embodiments, the percentage of the condenser liquid that is contacted with the first biogenic reagent is about, at least about, or at most about 1%, 5%, 10%, 15%, 20%, 25%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, 99%, or 100%, including any intervening ranges.

[0185] In some processes, the condenser liquid is contacted with the first biogenic reagent without any intermediate chemical processing. In other processes, the condenser liquid is chemically processed prior to contacting with the first biogenic reagent. There are various types of chemical processing that can be performed on the condenser liquid; generally speaking, chemical processing refers to the introduction or removal of mass or energy from the condenser liquid. Exemplary types of chemical processing include separating a specific component (e.g., water or acetic acid) from the condenser liquid or chemically reacting the condenser liquid with a reactant (e.g., CO and/or H_2).

[0186] In some embodiments, the condenser liquid is subjected to a purification step prior to contacting with the first biogenic reagent. In these or other embodiments, the condenser liquid is subjected to a reaction step prior to contacting with the first biogenic reagent. In certain embodiments, there is a reaction step as well as a purification step to remove not only undesired impurities initially in the condenser liquid, but also chemical-reaction byproducts that are not desired in the intermediate material.

[0187] In some embodiments, pyrolyzing the feedstock (in the first pyrolysis reactor) is conducted at a first pyrolysis temperature of at least about 250°C to at most about 1250°C. In certain embodiments, the first pyrolysis temperature is at least about 300°C to at most about 700°C. In some embodiments, pyrolyzing the feedstock (in the first pyrolysis reactor) is conducted for a first pyrolysis time of at least about 10 seconds to at most about 24 hours. Pyrolysis conditions that can be employed in the first pyrolysis reactor, in various embodiments, are described in detail later in this specification. The conditions of the first pyrolysis reactor can be any pyrolysis conditions described later in this specification (see section entitled "Pyrolysis Processes and Systems").

[0188] In some embodiments in which thermally treating is at a pyrolysis temperature, pyrolyzing the intermediate material is conducted at a second pyrolysis temperature of at least about 250°C to at most about 1250°C. In certain embodiments, the second pyrolysis

temperature is at least about 300°C to at most about 700°C. In some embodiments, pyrolyzing the intermediate material is conducted for a second pyrolysis time of at least about 10 seconds to at most about 24 hours. The second pyrolysis temperature can be lower or higher than the first pyrolysis temperature, or they could potentially be the same. The second pyrolysis time can be shorter or longer than the first pyrolysis time, or they could potentially be the same. Pyrolysis conditions that can be employed in the second pyrolysis reactor, in various embodiments, are described in detail later in this specification. The conditions of the second pyrolysis reactor can be any pyrolysis conditions described later in this specification (see section entitled "Pyrolysis Processes and Systems").

[0189] The process can further comprise oxidizing the condenser vapor, thereby generating heat. Additionally, or alternatively, the process can further comprise oxidizing the off-gas (from the thermal-treatment unit), thereby generating heat. Heat generated from oxidation of condenser vapor and/or off-gas can be reused in the process, such as to provide heat for the first pyrolysis reactor.

[0190] In some embodiments, the process further comprises milling the first biogenic reagent using a mechanical-treatment apparatus, wherein the mechanical-treatment apparatus is 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.

[0191] In some embodiments, the process further comprises milling the intermediate material using a mechanical-treatment apparatus, wherein the mechanical-treatment apparatus is 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.

[0192] In some embodiments that employ pelletizing the intermediate material, the pelletizing 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.

[0193] In some embodiments, the process further comprises generating fines, in the thermal-treatment unit, wherein the fines comprise carbon; and further comprises recycling the fines to the step of contacting the first biogenic reagent with the condenser liquid.

[0194] In some embodiments, the process further comprises generating fines, in the thermal-treatment unit, wherein the fines comprise carbon; and further comprises recycling some or all of the fines to the step of recovering the second biogenic reagent.

[0195] In various processes, the biocarbon composition is in the form of a powder. The powder particle size can vary widely, as described elsewhere in this specification.

[0196] In various processes, the biocarbon composition is in the form of pellets. The pellet size and shape can vary widely, as described elsewhere in this specification.

[0197] After pellets are formed, the process can further comprise powderizing the pellets to form a powder again. The reformed powder can be similar to the initial powder (prior to pellet formation) or can have a different particle size, for example.

[0198] In some embodiments, the process comprises comprising drying the second biogenic reagent, and further comprises pelletizing the second biogenic reagent to generate pellets, wherein the pelletizing the second biogenic reagent occurs during the drying, after the drying, or after the recovering.

[0199] In some embodiments, the biocarbon composition comprises at least 50 wt% fixed carbon, at least 60 wt% fixed carbon, at least 70 wt% fixed carbon, at least 80 wt% fixed carbon, or at least 90 wt% fixed carbon.

[0200] In some embodiments, the biocarbon composition comprises less than 10 wt% ash, less than 5 wt% ash, or less than 1 wt% ash.

[0201] In some embodiments, the condenser liquid comprises less than 1 wt% ash, less than 0.1 wt% ash, or essentially no ash.

[0202] The total carbon within the biocarbon composition can be at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. The total carbon within the biocarbon composition can be at least 90% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. The total carbon within the biocarbon composition can be fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

[0203] In some embodiments, the biocarbon composition is characterized by a bulk density of at least about 5 lb/ft^3, at least about 10 lb/ft^3, or at least about 20 lb/ft^3 on a dry basis. In various embodiments, the biocarbon composition is characterized by a bulk density of about, at least about, or at most about 5, 10, 15, 20, 25, or 30 lb/ft^3, including any intervening ranges. The bulk density is the apparent density according to ASTM D 1895 B, which is hereby incorporated by reference. The bulk density does not correct for porosity and is an extrinsic material property.

[0204] Another measure of density is intrinsic material density, which is the material density in the absence of any porosity (porous voids). The intrinsic material density is also referred to as the packed density or the solid density. In some embodiments, the biocarbon composition is characterized by an intrinsic material density of at least about 50 lb/ft^3, at least about 75 lb/ft^3, at least about 100 lb/ft^3, or at least about 125 lb/ft^3 on a dry basis. In various embodiments, the biocarbon composition is characterized by an intrinsic material density of about, at least about, or at most about 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, or 140 lb/ft^3, including any intervening ranges. When the biocarbon composition is in the form of a powder, i.e. a plurality of particles, there is void space between particles, and there can be micropores within the volume of each particle. The intrinsic material density is the density solely of the continuous solid material in a particle and between any pores in that particle.

[0205] In some embodiments, the biocarbon composition is hydrophobic, such as being characterized by at most 20 wt% water uptake at 25°C after 24 hours of soaking in water. In various embodiments, the biocarbon composition is characterized by at most 20, 15, 10, 5, or 2 wt% water uptake at 25°C after 24 hours of soaking in water.

[0206] In some embodiments, the biocarbon composition is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances".

[0207] When the biocarbon composition is in the form of a pellet, the pellet can be characterized by a bulk density of at least about 10 lb/ft^3, at least about 25 lb/ft^3, or at least about 35 lb/ft^3 on a dry basis, for example. In various embodiments, the biocarbon pellet is

characterized by a bulk density of about, at least about, or at most about 10, 15, 20, 25, 30, 35, or 40 lb/ft^3, including any intervening ranges.

[0208] When the biocarbon composition is in the form of a pellet, the pellet can be characterized by a Hardgrove Grindability Index of at least 30, at least 50, or at least 70, for example. In various embodiments, the pellet is characterized by a Hardgrove Grindability Index of about, at least about, or at most about 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, or 125, including any intervening ranges.

[0209] When the biocarbon composition is in the form of a pellet, the pellet can by characterized by a pellet compressive strength at 25°C of at least about 100 lb_f/in^2 or at least about 150 lb_f/in^2. In various embodiments, the pellet is characterized by a pellet compressive strength at 25°C of about, or at least about 50, 75, 100, 125, 150, 175, or 200 lb_f/in^2, including any intervening ranges.

[0210] Other variations provide a system for producing a biocarbon composition, the system comprising:

a first pyrolysis reactor configured for pyrolyzing a feedstock comprising biomass to generate a first biogenic reagent and a first pyrolysis vapor;

a condensing system in flow communication with the first pyrolysis reactor, wherein the condensing system is configured for condensing the first pyrolysis vapor to generate a condenser liquid and a condenser vapor;

a mixing unit in flow communication with the first biogenic reagent and the condensing system, wherein the mixing unit is configured for contacting the first biogenic reagent with the condenser liquid to generate an intermediate material;

a thermal-treatment unit in flow communication with the mixing unit, wherein the thermal-treatment unit is configured for thermally treating the intermediate material to generate a second biogenic reagent and an off-gas; and

a system output disposed in the thermal-treatment unit or in flow communication with the thermal-treatment unit, wherein the system output is configured for recovering the second biogenic reagent as a biocarbon composition.

[0211] In some systems, the mixing unit is a pelletizing unit. In other systems, the system comprises a pelletizing unit that is distinct from the mixing unit, wherein the pelletizing unit is disposed between the mixing unit and the thermal-treatment unit.

[0212] The condensing system can be designed according to known principles of condensers, configured to condense at least a portion of the pyrolysis vapor according to vapor–liquid thermodynamics.

[0213] When the pyrolysis vapor enters the condensing system that is operated at a selected temperature and pressure, some of the pyrolysis vapor typically condenses to form a condenser liquid. The remaining portion of the pyrolysis vapor that does not condense at the selected temperature and pressure is referred to as the condenser vapor. In order to utilize only the condenser liquid for downstream processing, there is a vapor–liquid separation, which is a complete disengagement of vapor and liquid created in the condensing system. Complete disengagement of vapor and liquid at a selected temperature and pressure is equivalent to one equilibrium stage of separation.

[0214] The condensing system can be configured to accomplish one equilibrium stage of separation, less than one equilibrium stage of separation, or more than one equilibrium stage of separation. The condensing system can be configured to accomplish at least one equilibrium stage of separation. When the condensing system is a multiple-stage condensing system, generally speaking there number of equilibrium stages of separation will be greater than one.

[0215] In certain embodiments for certain feedstocks and process conditions (e.g., a low pyrolysis temperature applies to a dry feedstock with high volatile carbon content), in the condensing system, only pyrolysis liquid and no pyrolysis vapor is formed. In these embodiments, there is no vapor–liquid separation *per se* since there is no condenser vapor—i.e., all pyrolysis vapor is condensed to pyrolysis liquid.

[0216] Exemplary condensing system configurations include double tube, shell and tube, shell and coil, or a combination thereof. Exemplary condensing system equipment includes horizontal in-shell condensers, vertical in-shell condensers, horizontal in-tube

condensers, vertical in-tube condensers, tanks, distillation columns, or a combination thereof.

[0217] Condensing systems in the form of a column can be operated in horizontal, vertical, or angled and can be operated in upflow (against the force of gravity), downflow (with the force of gravity), parallel to the force of gravity, or at an angle with gravity.

[0218] Condensing systems can be operated continuously or semi-continuously, such as with a continuous input of pyrolysis vapor and a continuous output of both condenser vapor and condenser liquid. A semi-continuous condensing system means that there is intermittent input of pyrolysis vapor and/or intermittent output of at least one of condenser vapor and condenser liquid.

[0219] In other embodiments, a batch condensing system is utilized, in which a quantity of pyrolysis vapor is introduced to a batch vessel (e.g., a tank) for condensing. After a batch condensation time, a condenser vapor is drawn off, leaving a condenser liquid in the batch vessel. Or, after a batch condensation time, a condenser liquid is drawn out, leaving a condenser vapor in the batch vessel.

[0220] Condensing systems can be air-cooled, gas-cooled (other than by air), water-cooled, liquid-cooled (other than by water, such as using a liquid coolant), or a combination thereof. Heat transfer for condensation can be accomplished by natural convection, forced convection, thermal conduction, or a combination thereof.

[0221] In some embodiments, the primary heat transfer in the condensing system occurs by direct liquid contact, such as via liquid spraying. The liquid being sprayed through the vapor can be water or another liquid, such as an external liquid (e.g., biodiesel), an internal liquid (e.g., the condenser liquid), or a combination thereof. Typically, in embodiments employing direct liquid contact, the liquid sprayed through the vapor becomes part of the condenser liquid. In certain embodiments, the liquid sprayed through the vapor is itself a carbon-containing liquid, and some or all carbon contained in the liquid ultimately becomes carbon in the final biocarbon composition.

[0222] In some embodiments, a condensing system includes a unit operation for separation of liquid (e.g., aerosol droplets) from vapors. For example, following

condensation of vapor to liquid, or integrated with the vapor condensation, there can be an electrostatic precipitator, a filter, an inertial-impaction collection surface, or a combination thereof.

[0223] In some embodiments, a condensing system includes not only one or more condensers but also a separation stage that is not based on vapor–liquid equilibrium separation by differences in boiling points. Rather, the additional separation stage can be based on polarity, molecular size, affinity with another phase, or ionic bonding potential, for example. In various embodiments, the condensing system further includes means for filtration, scrubbing, membrane separation, activated carbon adsorption, chromatography, ion exchange, liquid–liquid extraction, chemical precipitation, and/or electrostatic precipitation.

[0224] In various embodiments, the condensing system includes a condensing sub-system as well as another sub-system selected from a liquid-vapor cyclone separator, a demister, a distillation unit, a filtration unit, a membrane unit, a scrubbing unit (also referred to as a scrubber), a chemical precipitation unit, a liquid-liquid extraction unit, an electrostatic precipitation unit, or a combination thereof.

[0225] This specification hereby incorporates by reference pages 11-1 to 11-12 of *Perry's Chemical Engineers' Handbook,* 9th Ed., McGraw-Hill, 2019, for its teaching of condenser equipment design.

[0226] In some systems, the condensing system comprises multiple condenser stages, such as 2, 3, 4, 5, 6, 7, 8, 9, 10 or more condenser stages. When there are multiple condenser stages operating at different temperatures and/or pressures, the liquid and vapor compositions generally vary by stage. This configuration allows for tailored composition profiles across stages and the ability to recover and utilize fractions with desirably high carbon content, or other properties (e.g., low water content). The condenser liquid that is contacted with a biogenic reagent can be optimized and can include some, but not all, of the individual condenser stage condensates, for example. As one example, in some embodiments, the last stage of a multiple-stage condenser system generates a water-rich condensate. It can be undesirable to add the water-rich condensate to the biogenic reagent

when a high-fixed-carbon product is desired. In this scenario, the water-rich condensate can instead be recycled for other plant purposes.

[0227] In certain embodiments, the composition of a liquid from a specific stage, or from a plurality of stages, is compositionally analyzed to determine suitability for use in combining with the biogenic reagent to increase carbon content. For example, it a liquid contains too much water or organic acids, the liquid could be used for other purposes, while if the liquid contains high organics, phenolics, aromatics, and the like, then the liquid could be added to the biogenic reagent for thermal treatment (e.g., secondary pyrolysis).

[0228] In some systems, a recycle line is configured to recycle off-gas from the thermal-treatment unit back to the condensing system, in cases for which there is an off-gas from the thermal-treatment unit.

[0229] In some systems, the thermal-treatment unit is a second pyrolysis reactor. In other systems, the thermal-treatment unit is a dryer. In still other systems, there is first thermal-treatment unit that is a dryer, and a second thermal-treatment unit that is a second pyrolysis reactor, arranged in either order.

[0230] Some systems further comprise a mechanical-treatment apparatus configured to mill the first biogenic reagent, wherein the mechanical-treatment apparatus is 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.

[0231] Some systems further comprise a mechanical-treatment apparatus configured to mill the intermediate material, wherein the mechanical-treatment apparatus is 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.

[0232] Some systems further comprise a pelletizing apparatus configured to pelletize the intermediate material, wherein the pelletizing apparatus is 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.

[0233] Other variations of the technology are premised on thermal treatment of the condenser liquid to make a solid or semi-solid material, which can be blended with the solid

biogenic reagent. These variations provide a process for producing a biocarbon composition, the process comprising:

pyrolyzing a feedstock in a first pyrolysis reactor, wherein the feedstock comprises biomass, thereby generating a first pyrolysis solid and a first pyrolysis vapor;

introducing the first pyrolysis vapor to a condensing system, thereby generating a condenser liquid and a condenser vapor;

thermally treating the condenser liquid in a second reactor, thereby generating a solid or semi-solid material;

blending the first pyrolysis solid with the solid or semi-solid material, thereby generating a biogenic reagent; and

recovering the biogenic reagent as a biocarbon composition.

[0234] The feedstock can be selected from softwood chips, hardwood chips, timber harvesting residues, tree branches, tree stumps, leaves, bark, sawdust, corn, corn stover, wheat, wheat straw, rice, rice straw, sugarcane, sugarcane bagasse, sugarcane straw, energy cane, sugar beets, sugar beet pulp, sunflowers, sorghum, canola, algae, miscanthus, alfalfa, switchgrass, fruits, fruit shells, fruit stalks, fruit peels, fruit pits, vegetables, vegetable shells, vegetable stalks, vegetable peels, vegetable pits, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, food waste, commercial waste, grass pellets, hay pellets, wood pellets, cardboard, paper, paper pulp, paper packaging, paper trimmings, food packaging, construction and/or demolition waste, railroad ties, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof.

[0235] In some embodiments, the process further comprises drying or thermally treating the biogenic reagent.

[0236] In some embodiments, the process further comprises pelletizing the biogenic reagent.

[0237] In certain embodiments, the process further comprises drying or thermally treating the biogenic reagent, and further comprises pelletizing the biogenic reagent, wherein the pelletizing and the drying or thermally treating are integrated.

[0238] In embodiments in which pellets are formed, the pelletizing can be integrated with the step of blending the first pyrolysis solid with the solid or semi-solid material.

[0239] In embodiments in which pellets are formed, the process can comprise introducing a binder to the biogenic reagent. The binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, derivatives thereof, or a combination of the foregoing.

[0240] In certain embodiments in which pellets are formed, no external binder is introduced to the biogenic reagent during the pelletizing. In these cases, the condenser liquid can act as a binder for the pellets.

[0241] In some processes, the condensing system comprises multiple condenser stages. The condenser liquid can be a condensed product of a first stage of the multiple condenser stages. The condenser liquid can be a condensed product of a plurality of stages of the multiple condenser stages. In certain embodiments, the plurality of stages does not include the final stage of the multiple condenser stages.

[0242] In some embodiments, the second reactor is a non-pyrolytic thermal reactor or a non-pyrolytic catalytic reactor.

[0243] In some embodiments, the second reactor is a second pyrolysis reactor that generates the solid or semi-solid material as well as a pyrolysis off-gas. In certain embodiments, the process can further comprise conveying, to the condensing system, the pyrolysis off-gas. The second pyrolysis reactor can be distinct from the first pyrolysis reactor. Alternatively, the first pyrolysis reactor and the second pyrolysis reactor are the

same unit, wherein the pyrolyzing the feedstock and the thermally treating the condenser liquid occur at different times.

[0244] In some processes, at least 25 wt%, at least 50 wt%, or at least 75 wt% of total carbon comprised in the condenser liquid is converted to fixed carbon in the solid or semi-solid material. In various embodiments, the percentage of total carbon comprised in the condenser liquid that is converted to fixed carbon in the solid or semi-solid material is about, at least about, or at most about 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 wt%, including any intervening ranges.

[0245] In some processes, the solid or semi-solid material forms at least 5 wt%, at least 10 wt%, or at least 20 wt% of the biogenic reagent on an absolute basis. In various embodiments, the percentage of the biogenic reagent that is the solid or semi-solid material is about, at least about, or at most about 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 wt%, including any intervening ranges.

[0246] The solid or semi-solid material is optionally further processed, such as chemically processed, prior to blending with the first pyrolysis solids. For example, the solid or semi-solid material can be separated according to particle size. The solid or semi-solid material can be reacted with one or more reactants.

[0247] In some embodiments, at least about 10 wt% to at most about 80 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid. In certain embodiments, at least about 20 wt% to at most about 60 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid. In various embodiments, the percentage of fixed carbon in the biogenic reagent that is derived from the condenser liquid is about, at least about, or at most about 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 wt%, including any intervening ranges.

[0248] In some processes, all of the condenser liquid is thermally treated in the second reactor. In other processes, less than all of the condenser liquid is thermally treated in the second reactor. In various embodiments, the percentage of the condenser liquid that is thermally treated in the second reactor is about, at least about, or at most about 1%, 5%,

10%, 15%, 20%, 25%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, 99%, or 100%, including any intervening ranges.

[0249] In some processes, the condenser liquid is thermally treated in the second reactor without any intermediate chemical processing between the condensing system and the second reactor.

[0250] In some processes, the condenser liquid is chemically processed prior to thermally treating in the second reactor. In certain processes, the condenser liquid is subjected to a purification step prior to thermally treating in the second reactor. In certain processes, the condenser liquid is subjected to a reaction step prior to thermally treating in the second reactor. In some specific processes, the condenser liquid is subjected to a reaction step as well as a purification step (in either order) prior to thermally treating in the second reactor.

[0251] In some embodiments, the pyrolyzing the feedstock (in the first pyrolysis reactor) is conducted at a first pyrolysis temperature of at least about 250°C to at most about 1250°C, such as at least about 300°C to at most about 700°C. The conditions of the first pyrolysis reactor can be any pyrolysis conditions described later in this specification (see section entitled "Pyrolysis Processes and Systems").

[0252] In some embodiments, the second reactor is a second pyrolysis reactor operated at a second pyrolysis temperature, wherein the second pyrolysis temperature is at least about 250°C to at most about 1250°C, such as at least about 300°C to at most about 700°C. The conditions of the second pyrolysis reactor can be any pyrolysis conditions described later in this specification (see section entitled "Pyrolysis Processes and Systems").

[0253] In other embodiments, the second reactor is operated at a temperature selected from about 80°C to about 250°C. In various embodiments, the second reactor is operated at a temperature of about, at least about, or at most about 80°C, 90°C, 100°C, 110°C, 120°C, 130°C, 140°C, 150°C, 160°C, 170°C, 180°C, 190°C, 200°C, 210°C, 220°C, 230°C, 240°C, or 250°C, including any intervening ranges. At these temperatures (about 250°C or less),

pyrolysis is not expected, although at long residence times a very small amount of pyrolysis can occur.

[0254] The process can further comprise oxidizing the condenser vapor, thereby generating heat. Additionally, or alternatively, the process can further comprise oxidizing the reactor off-gas, thereby generating heat.

[0255] Some processes further comprise milling the biogenic reagent using a mechanical-treatment apparatus, wherein the mechanical-treatment apparatus is 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.

[0256] In some processes employing pelletizing the biogenic reagent, the pelletizing utilizes a pelletizing apparatus selected from an extruder, a ring die pellet mill, a flat die pellet mill, a roll compactor, a roll briquetter, a wet agglomeration mill, a dry agglomeration mill, or a combination thereof.

[0257] In various embodiments, the biocarbon composition comprises at least 50 wt%, at least 60 wt%, at least 70 wt%, at least 80 wt%, or at least 90 wt% fixed carbon.

[0258] In some embodiments, the biocarbon composition comprises less than 10 wt% ash, less than 5 wt% ash, or less than 1 wt% ash.

[0259] In some embodiments, the condenser liquid comprises less than 1 wt% ash, less than 0.1 wt% ash, or essentially no ash.

[0260] The total carbon within the biocarbon composition can be at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. The total carbon within the biocarbon composition can be at least 90% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. The total carbon within the biocarbon composition can be fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. In various embodiments, the percentage of renewable carbon according to the $^{14}C/^{12}C$ isotopic ratio within the total carbon of the biocarbon composition is about, or at least about 50%, 60%, 70%, 80%, 90%, 95%, 99%, 99.5%, 99.9%, or 100%, including any intervening ranges.

[0261] In some embodiments, the biocarbon composition is characterized by a bulk density of at least about 5 lb/ft^3, at least about 10 lb/ft^3, or at least about 20 lb/ft^3 on a dry basis. In various embodiments, the biocarbon composition is characterized by a bulk density of about, at least about, or at most about 5, 10, 15, 20, 25, or 30 lb/ft^3, including any intervening ranges.

[0262] In some embodiments, the biocarbon composition is characterized by an intrinsic material density of at least about 50 lb/ft^3, at least about 75 lb/ft^3, at least about 100 lb/ft^3, or at least about 125 lb/ft^3 on a dry basis. In various embodiments, the biocarbon composition is characterized by an intrinsic material density of about, at least about, or at most about 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, or 140 lb/ft^3, including any intervening ranges.

[0263] In some embodiments, the biocarbon composition is hydrophobic, such as being characterized by at most 20 wt% water uptake at 25°C after 24 hours of soaking in water. In various embodiments, the biocarbon composition is characterized by at most 20, 15, 10, 5, or 2 wt% water uptake at 25°C after 24 hours of soaking in water.

[0264] In some embodiments, the biocarbon composition is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances".

[0265] When the biocarbon composition is in the form of a pellet, the pellet can be characterized by a bulk density of at least about 10 lb/ft^3, at least about 25 lb/ft^3, or at least about 35 lb/ft^3 on a dry basis, for example. In various embodiments, the biocarbon pellet is characterized by a bulk density of about, at least about, or at most about 10, 15, 20, 25, 30, 35, or 40 lb/ft^3, including any intervening ranges.

[0266] When the biocarbon composition is in the form of a pellet, the pellet can be characterized by a Hardgrove Grindability Index of at least 30, at least 50, or at least 70, for example. In various embodiments, the pellet is characterized by a Hardgrove Grindability Index of about, at least about, or at most about 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, or 125, including any intervening ranges.

[0267] When the biocarbon composition is in the form of a pellet, the pellet can by characterized by a pellet compressive strength at 25°C of at least about 100 lb_f/in^2 or at least about 150 lb_f/in^2. In various embodiments, the pellet is characterized by a pellet compressive strength at 25°C of about, or at least about 50, 75, 100, 125, 150, 175, or 200 lb_f/in^2, including any intervening ranges.

[0268] Other variations provide a system for producing a biocarbon composition, the system comprising:

a first pyrolysis reactor configured for pyrolyzing a feedstock comprising biomass to generate a first pyrolysis solid and a first pyrolysis vapor;

a condensing system in flow communication with the first pyrolysis reactor, wherein the condensing system is configured for condensing the first pyrolysis vapor to generate a condenser liquid and a condenser vapor;

a second reactor in flow communication with the condensing system, wherein the second reactor is configured for thermally treating the condenser liquid to generate a solid or semi-solid material;

a mixing unit in flow communication with the first pyrolysis reactor and the second reactor, wherein the mixing unit is configured for blending the first pyrolysis solid with the solid or semi-solid material to generate a biogenic reagent; and

a system output in flow communication with the mixing unit, wherein the system output is configured for recovering the biogenic reagent as a biocarbon composition.

[0269] In some systems, the mixing unit is a pelletizing unit. In some systems, the system comprises a pelletizing unit that is distinct from the mixing unit, wherein the pelletizing unit is disposed between the mixing unit and the system output.

[0270] The condensing system can be designed according to known principles of condensers, configured to condense at least a portion of the pyrolysis vapor according to vapor–liquid thermodynamics.

[0271] The condensing system can be configured to accomplish one equilibrium stage of separation, less than one equilibrium stage of separation, or more than one equilibrium

stage of separation. The condensing system can be configured to accomplish at least one equilibrium stage of separation. When the condensing system is a multiple-stage condensing system, generally speaking there number of equilibrium stages of separation will be greater than one.

[0272] Exemplary condensing system configurations include double tube, shell and tube, shell and coil, or a combination thereof. Exemplary condensing system equipment includes horizontal in-shell condensers, vertical in-shell condensers, horizontal in-tube condensers, vertical in-tube condensers, tanks, distillation columns, or a combination thereof.

[0273] Condensing systems in the form of a column can be operated in horizontal, vertical, or angled and can be operated in upflow (against the force of gravity), downflow (with the force of gravity), parallel to the force of gravity, or at an angle with gravity.

[0274] Condensing systems can be operated continuously or semi-continuously, such as with a continuous input of pyrolysis vapor and a continuous output of both condenser vapor and condenser liquid. A semi-continuous condensing system means that there is intermittent input of pyrolysis vapor and/or intermittent output of at least one of condenser vapor and condenser liquid.

[0275] In other embodiments, a batch condensing system is utilized, in which a quantity of pyrolysis vapor is introduced to a batch vessel (e.g., a tank) for condensing. After a batch condensation time, a condenser vapor is drawn off, leaving a condenser liquid in the batch vessel. Or, after a batch condensation time, a condenser liquid is drawn out, leaving a condenser vapor in the batch vessel.

[0276] Condensing systems can be air-cooled, gas-cooled (other than by air), water-cooled, liquid-cooled (other than by water, such as using a liquid coolant), or a combination thereof. Heat transfer for condensation can be accomplished by natural convection, forced convection, thermal conduction, or a combination thereof.

[0277] In some embodiments, the primary heat transfer in the condensing system occurs by direct liquid contact, such as via liquid spraying. The liquid being sprayed through the vapor can be water or another liquid, such as an external liquid (e.g., biodiesel), an

internal liquid (e.g., the condenser liquid), or a combination thereof. Typically, in embodiments employing direct liquid contact, the liquid sprayed through the vapor becomes part of the condenser liquid. In certain embodiments, the liquid sprayed through the vapor is itself a carbon-containing liquid, and some or all carbon contained in the liquid ultimately becomes carbon in the final biocarbon composition.

[0278] In some embodiments, a condensing system includes a unit operation for separation of liquid (e.g., aerosol droplets) from vapors. For example, following condensation of vapor to liquid, or integrated with the vapor condensation, there can be an electrostatic precipitator, a filter, an inertial-impaction collection surface, or a combination thereof.In some embodiments, a condensing system includes not only one or more condensers but also a separation stage that is not based on vapor–liquid equilibrium separation by differences in boiling points. Rather, the additional separation stage can be based on polarity, molecular size, affinity with another phase, or ionic bonding potential, for example. In various embodiments, the condensing system further includes means for filtration, scrubbing, membrane separation, activated carbon adsorption, chromatography, ion exchange, liquid–liquid extraction, chemical precipitation, and/or electrostatic precipitation.

[0279] In various embodiments, the condensing system includes a condensing sub-system as well as another sub-system selected from a liquid-vapor cyclone separator, a demister, a distillation unit, a filtration unit, a membrane unit, a scrubbing unit, a chemical precipitation unit, a liquid-liquid extraction unit, an electrostatic precipitation unit, or a combination thereof.

[0280] In some systems, the condensing system comprises multiple condenser stages, such as 2, 3, 4, 5, 6, 7, 8, 9, 10 or more condenser stages.

[0281] In some systems, the second reactor is a second pyrolysis reactor. The system can further comprise a recycle line configured to recycle pyrolysis off-gas to the condensing system.

[0282] In some systems, the second reactor is a non-pyrolytic thermal reactor or a non-pyrolytic catalytic reactor.

[0283] The system can further comprise a mechanical-treatment apparatus configured to mill the biogenic reagent, wherein the mechanical-treatment apparatus is 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.

[0284] The system can further comprise a pelletizing apparatus configured to pelletize the biogenic reagent, wherein the pelletizing apparatus is 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.

[0285] Still other variations are premised on the addition of the condenser liquid to the starting biomass (feeding to the pyrolysis reactor), rather than to the solids made during pyrolysis. These variations provide a process for producing a biocarbon composition, the process comprising:

pyrolyzing a first feedstock in a first pyrolysis reactor, thereby generating a biogenic reagent and a pyrolysis vapor;

introducing the pyrolysis vapor to a condensing system, thereby generating a condenser liquid and a condenser vapor;

contacting a second feedstock with the condenser liquid, wherein the second feedstock comprises biomass, thereby generating the first feedstock, wherein the first feedstock comprises the second feedstock and the condenser liquid; and

recovering the biogenic reagent as a biocarbon composition.

[0286] The biomass can be selected from softwood chips, hardwood chips, timber harvesting residues, tree branches, tree stumps, leaves, bark, sawdust, corn, corn stover, wheat, wheat straw, rice, rice straw, sugarcane, sugarcane bagasse, sugarcane straw, energy cane, sugar beets, sugar beet pulp, sunflowers, sorghum, canola, algae, miscanthus, alfalfa, switchgrass, fruits, fruit shells, fruit stalks, fruit peels, fruit pits, vegetables, vegetable shells, vegetable stalks, vegetable peels, vegetable pits, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, food waste, commercial waste, grass pellets, hay pellets, wood pellets, cardboard, paper, paper pulp, paper packaging, paper trimmings,

food packaging, construction and/or demolition waste, railroad ties, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof.

[0287] Some processes further comprise pelletizing the biogenic reagent. Pelletizing the biogenic reagent can comprise introducing a binder to the biogenic reagent. The binder can be selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, derivatives thereof, or a combination of the foregoing. Optionally, pelletizing the biogenic reagent can be done without introducing an external binder to the biogenic reagent. In these cases, the condenser liquid can act as a binder for the pellets.

[0288] In some embodiments, the condensing system comprises multiple condenser stages. The condenser liquid can be a condensed product of a first stage of the multiple condenser stages. In certain embodiments, the condenser liquid is a condensed product of a plurality of stages of the multiple condenser stages, wherein optionally the plurality of stages does not include the final stage of the multiple condenser stages.

[0289] In some processes, the step of contacting the second feedstock with the condenser liquid comprises spraying the condenser liquid onto the biomass. Other means of contacting the second feedstock with the condenser liquid can be employed, including (but not limited to) submerging the biomass in the condenser liquid, coating particles of biomass with a film of condenser liquid, or other techniques.

[0290] In some processes, the first feedstock comprises the condenser liquid adsorbed onto a surface of the biomass. Alternatively, or additionally, the first feedstock can comprise the condenser liquid absorbed into a bulk phase of the biomass.

[0291] In some processes pertaining to contacting biomass with condenser liquid, the process further comprises thermally treating the biogenic reagent in a thermal-treatment unit. If the biogenic reagent is subjected to pelletizing, the thermally treating can be before, during, or after the pelletizing.

[0292] In some processes employing a thermal-treatment unit, the thermal-treatment unit is a second pyrolysis reactor operated at a second pyrolysis temperature of at least about 250°C. The second pyrolysis reactor is configured for (further) pyrolyzing the biogenic reagent. The second pyrolysis reactor is typically distinct from (i.e., physically different than) the first pyrolysis reactor. Alternatively, the first pyrolysis reactor and the second pyrolysis reactor can be the same unit, wherein the pyrolyzing and the thermally treating are conducted at different times.

[0293] In some embodiments, pyrolyzing the biogenic reagent in a thermal-treatment unit generates an off-gas, which can be recycled to the condensing system.

[0294] In other processes employing a thermal-treatment unit, the thermal-treatment unit is operated at a temperature selected from about 80°C to about 250°C, such as from about 90°C to about 200°C, from about 100°C to about 250°C, or from about 125°C to about 225°C.

[0295] In some embodiments employing a thermal-treatment unit, the thermal-treatment unit contains an internal oxygen-free environment. An inert gas can be introduced to the thermal-treatment unit. The thermal-treatment unit can be operated under vacuum.

[0296] A thermal-treatment unit can be configured for drying the biogenic reagent. Alternatively, or additionally, the process can further comprise drying of the biocarbon composition after thermally treating in the optional thermal-treatment unit.

[0297] Some processes comprise converting at least 25 wt%, at least 50 wt%, or at least 75 wt% of the total carbon comprised within the condenser liquid to fixed carbon comprised within the biogenic reagent. In various embodiments, the process comprises converting about, or at least about, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 wt%, including any intervening ranges, of the total carbon comprised within the condenser liquid to fixed carbon comprised within the biogenic reagent.

[0298] In some embodiments, at least about 10 wt% to at most about 80 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid. In certain embodiments, at least about 20 wt% to at most about 60 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid. In various embodiments, the percentage of fixed carbon in the biogenic reagent that is derived from the condenser liquid is about, at least about, or at most about 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, or 95%, including any intervening ranges.

[0299] In some processes, all of the condenser liquid is contacted with the second feedstock. In other processes, less than all of the condenser liquid is contacted with the second feedstock. In various embodiments, the percentage of the condenser liquid that is contacted with the second feedstock is about, at least about, or at most about 1%, 5%, 10%, 15%, 20%, 25%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, 99%, or 100%, including any intervening ranges.

[0300] In some processes, the condenser liquid is contacted with the second feedstock without any intermediate chemical processing. In other processes, the condenser liquid is chemically processed prior to contacting with the second feedstock. For example, the condenser liquid can be subjected to a purification step and/or a reaction step prior to contacting with the second feedstock.

[0301] In some embodiments pertaining to contacting biomass with condenser liquid, a portion of the condenser liquid is added to the biogenic reagent, rather than being contacted with the biomass.

[0302] Pyrolyzing the first feedstock in the first pyrolysis reactor can be conducted at a first pyrolysis temperature of at least about 250°C to at most about 1250°C, such as at least about 300°C to at most about 700°C. The first pyrolysis time in the first pyrolysis reactor can be at least about 10 seconds to at most about 24 hours. The conditions of the first pyrolysis reactor can be any pyrolysis conditions described later in this specification (see section entitled "Pyrolysis Processes and Systems").

[0303] When there is a thermal-treatment unit configured as a second pyrolysis reactor, the second pyrolysis temperature can at least about 250°C to at most about 1250°C, such

as at least about 300°C to at most about 700°C. The second pyrolysis time can be at least about 10 seconds to at most about 24 hours. The conditions of the second pyrolysis reactor can be any pyrolysis conditions described later in this specification (see section entitled "Pyrolysis Processes and Systems").

[0304] In some embodiments, the process further comprises oxidizing the condenser vapor, thereby generating heat. In these or other embodiments, the process further comprises oxidizing an off-gas derived from the thermal-treatment unit, thereby generating heat. Heat can be used within the process for various purposes.

[0305] Some processes further comprise milling the biogenic reagent using a mechanical-treatment apparatus, wherein the mechanical-treatment apparatus is 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.

[0306] When the process employs pelletizing the biogenic reagent, a pelletizing apparatus can be 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.

[0307] Some processes further comprise drying the biogenic reagent, and further comprise pelletizing the biogenic reagent to generate pellets. Pelletizing the biogenic reagent can be prior to the drying, during the drying, or after the drying.

[0308] In some processes, the biocarbon composition comprises at least 50 wt%, at least 60 wt%, at least 70 wt%, at least 80 wt%, or at least 90 wt% fixed carbon.

[0309] In some processes, the biocarbon composition comprises less than 10 wt% ash, less than 5 wt% ash, or less than 1 wt% ash.

[0310] In some processes, the condenser liquid comprises less than 1 wt% ash, less than 0.1 wt% ash, or essentially no ash.

[0311] The total carbon within the biocarbon composition can be at least 50%, at least 90%, or 100% (fully) renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. In various embodiments, the percentage of renewable carbon

according to the $^{14}C/^{12}C$ isotopic ratio within the total carbon of the biocarbon composition is about, or at least about 50%, 60%, 70%, 80%, 90%, 95%, 99%, 99.5%, 99.9%, or 100%, including any intervening ranges.

[0312] In some embodiments, the biocarbon composition is characterized by a bulk density of at least about 5 lb/ft^3, at least about 10 lb/ft^3, or at least about 20 lb/ft^3 on a dry basis. In various embodiments, the biocarbon composition is characterized by a bulk density of about, at least about, or at most about 5, 10, 15, 20, 25, or 30 lb/ft^3, including any intervening ranges.

[0313] In some embodiments, the biocarbon composition is characterized by an intrinsic material density of at least about 50 lb/ft^3, at least about 75 lb/ft^3, at least about 100 lb/ft^3, or at least about 125 lb/ft^3 on a dry basis. In various embodiments, the biocarbon composition is characterized by an intrinsic material density of about, at least about, or at most about 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, or 140 lb/ft^3, including any intervening ranges.

[0314] In some embodiments, the biocarbon composition is hydrophobic, such as being characterized by at most 20 wt% water uptake at 25°C after 24 hours of soaking in water. In various embodiments, the biocarbon composition is characterized by at most 20, 15, 10, 5, or 2 wt% water uptake at 25°C after 24 hours of soaking in water.

[0315] In some embodiments, the biocarbon composition is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances".

[0316] When the biocarbon composition is in the form of a pellet, the pellet can be characterized by a bulk density of at least about 10 lb/ft^3, at least about 25 lb/ft^3, or at least about 35 lb/ft^3 on a dry basis, for example. In various embodiments, the biocarbon pellet is characterized by a bulk density of about, at least about, or at most about 10, 15, 20, 25, 30, 35, or 40 lb/ft^3, including any intervening ranges.

[0317] When the biocarbon composition is in the form of a pellet, the pellet can be characterized by a Hardgrove Grindability Index of at least 30, at least 50, or at least 70, for

example. In various embodiments, the pellet is characterized by a Hardgrove Grindability Index of about, at least about, or at most about 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, or 125, including any intervening ranges.

[0318] When the biocarbon composition is in the form of a pellet, the pellet can by characterized by a pellet compressive strength at 25°C of at least about 100 lb_f/in^2 or at least about 150 lb_f/in^2. In various embodiments, the pellet is characterized by a pellet compressive strength at 25°C of about, or at least about 50, 75, 100, 125, 150, 175, or 200 lb_f/in^2, including any intervening ranges.

[0319] Certain variations provide a system for producing a biocarbon composition, the system comprising:

a first pyrolysis reactor configured for pyrolyzing a first feedstock to generate a biogenic reagent and a pyrolysis vapor;

a condensing system in flow communication with the first pyrolysis reactor, wherein the condensing system is configured for condensing the pyrolysis vapor to generate a condenser liquid and a condenser vapor;

a mixing unit in flow communication with the condensing system, wherein the mixing unit is configured for contacting a second feedstock comprising biomass with the condenser liquid to generate a first feedstock; and

a system output in flow communication with the first pyrolysis reactor, wherein the system output is configured for recovering the biogenic reagent as a biocarbon composition.

[0320] Some systems further comprise a pelletizing unit in flow communication with the first pyrolysis reactor, wherein the pelletizing unit is configured for pelletizing the biogenic reagent to generate pellets.

[0321] Some systems further comprise a thermal-treatment unit in flow communication with the pelletizing unit, if present, or in flow communication with the first pyrolysis reactor. In certain systems, a thermal-treatment unit is disposed downstream of the pelletizing unit, wherein the thermal-treatment unit is configured to receive the pellets. In certain systems,

the thermal-treatment unit is disposed between the first pyrolysis reactor and the pelletizing unit, wherein the pelletizing unit is configured to receive a thermally treated biogenic reagent.

[0322] In some systems, the thermal-treatment unit is a second pyrolysis reactor operated at a second pyrolysis temperature of at least about 250°C, wherein the second pyrolysis reactor is configured for pyrolyzing the biogenic reagent. The conditions of the second pyrolysis reactor can be any pyrolysis conditions described later in this specification (see section entitled "Pyrolysis Processes and Systems"). The system can include a recycle line configured to recycle pyrolysis off-gas, from the second pyrolysis reactor, to the condensing system.

[0323] In certain systems, the thermal-treatment unit is operated at a temperature selected from about 80°C to about 250°C. In various embodiments, the thermal-treatment unit is operated at a temperature of about, at least about, or at most about 80°C, 90°C, 100°C, 110°C, 120°C, 130°C, 140°C, 150°C, 160°C, 170°C, 180°C, 190°C, 200°C, 210°C, 220°C, 230°C, 240°C, or 250°C, including any intervening ranges.

[0324] The condensing system can be designed according to known principles of condensers, configured to condense at least a portion of the pyrolysis vapor according to vapor–liquid thermodynamics.

[0325] The condensing system can be configured to accomplish one equilibrium stage of separation, less than one equilibrium stage of separation, or more than one equilibrium stage of separation. The condensing system can be configured to accomplish at least one equilibrium stage of separation. When the condensing system is a multiple-stage condensing system, generally speaking there number of equilibrium stages of separation will be greater than one.

[0326] Exemplary condensing system configurations include double tube, shell and tube, shell and coil, or a combination thereof. Exemplary condensing system equipment includes horizontal in-shell condensers, vertical in-shell condensers, horizontal in-tube condensers, vertical in-tube condensers, tanks, distillation columns, or a combination thereof.

[0327] Condensing systems in the form of a column can be operated in horizontal, vertical, or angled and can be operated in upflow (against the force of gravity), downflow (with the force of gravity), parallel to the force of gravity, or at an angle with gravity.

[0328] Condensing systems can be operated continuously or semi-continuously, such as with a continuous input of pyrolysis vapor and a continuous output of both condenser vapor and condenser liquid. A semi-continuous condensing system means that there is intermittent input of pyrolysis vapor and/or intermittent output of at least one of condenser vapor and condenser liquid.

[0329] In other embodiments, a batch condensing system is utilized, in which a quantity of pyrolysis vapor is introduced to a batch vessel (e.g., a tank) for condensing. After a batch condensation time, a condenser vapor is drawn off, leaving a condenser liquid in the batch vessel. Or, after a batch condensation time, a condenser liquid is drawn out, leaving a condenser vapor in the batch vessel.

[0330] Condensing systems can be air-cooled, gas-cooled (other than by air), water-cooled, liquid-cooled (other than by water, such as using a liquid coolant), or a combination thereof. Heat transfer for condensation can be accomplished by natural convection, forced convection, thermal conduction, or a combination thereof.

[0331] In some embodiments, the primary heat transfer in the condensing system occurs by direct liquid contact, such as via liquid spraying. The liquid being sprayed through the vapor can be water or another liquid, such as an external liquid (e.g., biodiesel), an internal liquid (e.g., the condenser liquid), or a combination thereof. Typically, in embodiments employing direct liquid contact, the liquid sprayed through the vapor becomes part of the condenser liquid. In certain embodiments, the liquid sprayed through the vapor is itself a carbon-containing liquid, and some or all carbon contained in the liquid ultimately becomes carbon in the final biocarbon composition.

[0332] In some embodiments, a condensing system includes a unit operation for separation of liquid (e.g., aerosol droplets) from vapors. For example, following condensation of vapor to liquid, or integrated with the vapor condensation, there can be an

electrostatic precipitator, a filter, an inertial-impaction collection surface, or a combination thereof.

[0333] In some embodiments, a condensing system includes not only one or more condensers but also a separation stage that is not based on vapor–liquid equilibrium separation by differences in boiling points. Rather, the additional separation stage can be based on polarity, molecular size, affinity with another phase, or ionic bonding potential, for example. In various embodiments, the condensing system further includes means for filtration, scrubbing, membrane separation, activated carbon adsorption, chromatography, ion exchange, liquid–liquid extraction, chemical precipitation, and/or electrostatic precipitation.

[0334] In various embodiments, the condensing system includes a condensing sub-system as well as another sub-system selected from a liquid-vapor cyclone separator, a demister, a distillation unit, a filtration unit, a membrane unit, a scrubbing unit, a chemical precipitation unit, a liquid-liquid extraction unit, an electrostatic precipitation unit, or a combination thereof.

[0335] In some systems, the condensing system comprises multiple condenser stages, such as 2, 3, 4, 5, 6, 7, 8, 9, 10 or more condenser stages. Multiple condenser stages can be stages of a single unit—for example, stages delineated by trays in a distillation column—or physically distinct units arranged in series, for example.

[0336] In some systems, the mixing unit is configured to spray the condenser liquid onto the biomass. In other systems, the mixing unit is configured to submerge the biomass into the condenser liquid.

[0337] The system can further comprise a mechanical-treatment apparatus configured to mill the biogenic reagent, wherein the mechanical-treatment apparatus is 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.

[0338] The system can further comprise a pelletizing unit 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.

[0339] In various embodiments in which the condenser liquid is chemically processed prior to contacting with another material (e.g., the biomass reagent or the second feedstock), the chemical processing can be purification which can involve another separation step beyond condensation. For example, chromatography or another type of separation based on polarity can be conducted to remove, oxygen-containing molecules, such as water, organic acids, and/or alcohols. The chemical processing can be purification that involves adding a purification agent, such as a flocculant or filter aid, followed by filtration or membrane separation, for example. The chemical processing can be purification based on liquid–liquid extraction, such as with an organic, aromatic solvent to target extraction of aromatic molecules that can be beneficial for fixed-carbon formation later.

[0340] In various embodiments in which the condenser liquid is chemically processed prior to contacting with another material, the chemical processing can be reaction. The reaction can be catalyzed or uncatalyzed. If a catalyst is employed, the catalyst can be a homogeneous catalyst (e.g., an inorganic acid such as sulfuric acid) or a heterogeneous catalyst (e.g., aluminosilicates). A chemical reaction of the condenser liquid can or can not involve another reactant. That is, the chemical reaction can involve solely reactants that are already present in the condenser liquid—e.g., acids, esters, alcohols, aldehydes, ketones, furans, and phenolic compounds.

[0341] Alternatively, or additionally, an external reactant can be added to the condenser liquid. The external reactant can be a gas, such as H_2 or CO; a liquid, such as methanol or ethanol; or solids, such as sugars or cellulose. Reaction with H_2 or CO can be useful to form new bonds, or rearrange bonds, in the condenser liquid, for example. Reaction with methanol or ethanol (or larger alcohols) can be useful to stabilize the condenser liquid by converting carboxylic acids and reactive carbonyl compounds into esters, ethers, and acetals, for example. Reaction with sugars or cellulose can be useful to form longer polymers in the condenser liquid, which can assist later carbonization, for example.

[0342] Just as the initial condensation to make a condenser liquid can be done in a multiple-stage condensing system, the chemical processing can be carried out in multiple stages. The multiple stages can be stages of purification or reaction, in various sequences.

It can be desirable to use a temperature profile of increasing temperature with interstage removal of one phase (e.g., a vapor phase or an aqueous phase), to assist in the chemistry in later stages. For example, when the formation of carbon–carbon bonds (single, double, triple, and/or aromatic bonds) is desired, it can be useful to separate out small molecules such as water to promote the reaction equilibrium toward the desired product.

[0343] Note that in variations in which the condenser liquid is thermally treated to form a solid or semi-solid material, the condenser liquid is chemically processed all the way to a solid or semi-solid state. There are many embodiments in which the condenser liquid is chemically processed but not all the way to a solid or semi-solid state; rather the condenser liquid remains in the liquid state when added to the biogenic reagent or the second feedstock. Of course, many combinations are possible. For example, a portion of the condenser liquid could be converted to a solid or semi-solid material while another portion is chemically processed and then combined with the biogenic reagent, further pyrolyzed, and the resulting solids added to the solid or semi-solid material.

[0344] In some embodiments, at least 25 wt% of total carbon contained in the condenser liquid is converted to fixed carbon in the second biogenic reagent. In various embodiments, about, at least about, or at most about 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%, 80 wt%, or 90 wt% (including all intervening ranges) of total carbon contained in the condenser liquid is converted to fixed carbon in the second biogenic reagent.

[0345] In some embodiments, at least about 10 wt% to at most about 80 wt% of fixed carbon in the second biogenic reagent is derived from the first condenser liquid. In certain embodiments, at least about 20 wt% to at most about 60 wt% of fixed carbon in the second biogenic reagent is derived from the first condenser liquid. In various embodiments, about, at least about, or at most about 1 wt%, 2 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%, 75 wt%, or 80 wt% (including any intervening ranges) of fixed carbon in the second biogenic reagent is derived from the first condenser liquid.

[0346] In some processes, step (a) is conducted at a first pyrolysis temperature selected at least about 250°C to at most about 1250°C, such as at least about 300°C to at most about 700°C. In these or other processes, step (e) is conducted at a second pyrolysis

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

[0347] In some processes, step (a) is conducted for a first pyrolysis time selected at least about 10 seconds to at most about 24 hours, such as at least about 10 minutes to at most about 4 hours. In these or other processes, step (e) is conducted at a second pyrolysis time selected at least about 10 seconds to at most about 24 hours, such as at least about 15 minutes to at most about 5 hours. The first pyrolysis time can be less than, equal, or greater than the second pyrolysis time. In some embodiments, the second pyrolysis time is longer than the first pyrolysis time to enable effective pyrolysis of compounds that did not form fixed carbon in the first pyrolysis reactor. In such embodiments, the second pyrolysis time can be about 5, 10, 15, 20, 30, 40, 50, 60, 90, or 120 minutes longer than the first pyrolysis time, for example.

[0348] In some embodiments, some or all of the condenser vapor is at least partially oxidized to generate heat, wherein the heat can be used within the process. In these or other embodiments, some or all of the second pyrolysis vapor is at least partially oxidized (together with the condenser vapor, or separately) to generate heat, wherein the heat can be used within the process.

[0349] In certain embodiments, a pyrolysis off-gas or a condenser vapor is at least partially oxidized to generate a reducing gas comprising hydrogen and/or carbon monoxide. Such partial oxidation still generates useful heat but also produces a reducing gas that can be converted into other chemicals (e.g., methanol or Fischer-Tropsch hydrocarbons) if desired.

[0350] In some embodiments, the first biogenic reagent is milled utilizing a mechanical-treatment apparatus selected from the group comprising 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, for example. In these or other embodiments, the intermediate material can be milled utilizing a mechanical-treatment apparatus selected from the group comprising 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, for example.

[0351] In embodiments employing step (d), step (d) can utilize a pelletizing apparatus selected from the group comprising an extruder, a ring die pellet mill, a flat die pellet mill, a roll compactor, a roll briquetter, a wet agglomeration mill, a dry agglomeration mill, or a combination thereof, for example.

[0352] In some processes, carbon-comprising fines are generated in the second pyrolysis reactor. In some embodiments, the carbon-comprising fines are recycled to step (c). When step (d) is conducted, carbon-comprising fines generated in the second pyrolysis reactor can be recycled to step (d) instead of, or in addition to, recycling to step (c). Alternatively, or additionally, carbon-comprising fines can be combusted to generate energy or used for other purposes.

[0353] In some embodiments, the biocarbon composition is in the form of powder. In some embodiments, the biocarbon composition is in the form of pellets.

[0354] The biocarbon composition can comprise at least 50 wt% fixed carbon, at least 60 wt% fixed carbon, at least 70 wt% fixed carbon, at least 75 wt% fixed carbon, at least 80 wt% fixed carbon, at least 85 wt% fixed carbon, or at least 90 wt% fixed carbon. In various embodiments, the biocarbon composition comprises about, at least about, or at most about 55, 60, 65, 70, 75, 80, 85, or 90 wt% fixed carbon.

[0355] The biocarbon composition can comprise at least 55 wt% total carbon, at least 60 wt% total carbon, at least 70 wt% total carbon, at least 75 wt% total carbon, at least 80 wt% total carbon, at least 85 wt% total carbon, at least 90 wt% total carbon, or at least 95 wt% total carbon. In various embodiments, the biocarbon composition comprises about, at least about, or at most about 60, 65, 70, 75, 80, 85, 90, or 95 wt% total carbon, including all intervening ranges.

[0356] In some embodiments, the biocarbon composition comprises less than 10 wt% ash, less than 5 wt% ash, less than 2 wt% ash, or less than 1 wt% ash. In various

embodiments, the biocarbon composition comprises about, or at most about, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, 0.5, 0.2, or 0.1 wt% ash, including all intervening ranges.

[0357] The ash content of the biocarbon composition benefits (i.e., is lower) when condenser liquid with low ash is incorporated into the material in the second pyrolysis reactor. In some embodiments, the first condenser liquid comprises less than 1 wt% ash, less than 0.1 wt% ash, or essentially no ash. In various embodiments, the first condenser liquid comprises about, or at most about, 5, 4, 3, 2, 1, 0.5, 0.2, 0.1, 0.05, 0.02, or 0.01 wt% ash, including all intervening ranges.

[0358] In some embodiments, the total carbon within the biocarbon composition is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. In some embodiments, total carbon within the biocarbon composition is at least 90% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. In some embodiments, 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.

[0359] In some processes, the second biogenic reagent is pelletized in step (f), in step (g), or after step (g). The final biocarbon composition can therefore be in the form of pellets.

[0360] In some processes, the biocarbon composition is characterized by a Hardgrove Grindability Index of at least 30 or at least 50. In various embodiments, the biocarbon composition is characterized by a Hardgrove Grindability Index of about, at least about, or at most about 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, or 100, including all intervening ranges.

[0361] In some processes, the biocarbon composition is characterized by a bulk density of at least about 35 lb/ft^3 on a dry basis, or at least about 45 lb/ft^3 on a dry basis. In various embodiments, the bulk density of the biocarbon composition is about, or at least about, 25, 30, 35, 40, 45, or 50 lb/ft^3 on a dry basis, including all intervening ranges.

[0362] In some processes, the biocarbon composition is characterized as hydrophobic biocarbon or partially hydrophobic biocarbon.

[0363] In some processes, the biocarbon composition is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances".

[0364] In some processes, the biocarbon composition is characterized by a lack of odor generation at 25°C for 24 hours. In some embodiments, the biocarbon composition is characterized by a lack of odor generation at 50°C for 24 hours. In some embodiments, the biocarbon composition is characterized by a lack of odor generation at 25°C for 48 hours. Odor generation in this context refers to organic molecules being vaporized from the biocarbon composition, wherein such organic molecules are ordinarily detectible by humans. Examples include formaldehyde, acetic acid, ethanol, methanol, or mercaptan.

[0365] Some variations provide a method of making a high-fixed-carbon material comprising: pyrolyzing biomass to generate intermediate solids and a pyrolysis vapor; condensing the pyrolysis vapor to generate pyrolysis liquid; and introducing the pyrolysis liquid to the intermediate solids, to generate a solid-liquid mixture. In some embodiments, the method also comprises pelletizing to produce pellets comprising the solid-liquid mixture. In some embodiments, the method further comprises further pyrolyzing the solid-liquid mixture to generate a high-yield, high-fixed-carbon material.

[0366] In some methods, the method comprises pelletizing to produce pellets comprising the solid-liquid mixture. In some embodiments, pelletizing does not utilize a binder other than the pyrolysis liquid. In other embodiments, pelletizing utilizes a binder other than the pyrolysis liquid. The step of further pyrolyzing the solid-liquid mixture can be enhanced by the pelletizing, such as when carbon comprised in the solid-liquid mixture acts as a catalyst or reaction matrix for forming additional fixed carbon.

[0367] In some methods, at least 60 wt% of total carbon comprised in the biomass forms fixed carbon in the high-fixed-carbon material. In certain methods, at least 70 wt%, at least 80 wt%, at least 90 wt%, or at least 95 wt% of total carbon comprised in the biomass forms fixed carbon in the high-fixed-carbon material.

[0368] Some variations provide a high-fixed-carbon material produced by a process comprising a method of making a high-fixed-carbon material comprising: pyrolyzing biomass to generate intermediate solids and a pyrolysis vapor; condensing the pyrolysis vapor to generate pyrolysis liquid; and introducing the pyrolysis liquid to the intermediate solids, to generate a solid-liquid mixture. In some embodiments, the method also comprises pelletizing to produce pellets containing the solid-liquid mixture. In some embodiments, the method further comprises further pyrolyzing the solid-liquid mixture to generate a high-yield, high-fixed-carbon material.

[0369] In some processes incorporating blending of first and second pyrolysis solids (e.g., FIG. 5), the second pyrolysis solids form at least 5 wt% of the biogenic reagent on an absolute basis. In certain processes, the second pyrolysis solids form at least 10 wt% or at least 20 wt% of the biogenic reagent on an absolute basis.

[0370] In some processes, at least about 10 wt% to at most about 80 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid. In certain processes, at least about 20 wt% to at most about 60 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid. In various embodiments, about, at least about, or at most about 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, or 90 wt% (including all intervening ranges) of fixed carbon in the biogenic reagent is derived from the condenser liquid.

[0371] The biocarbon composition can comprise at least 50 wt% fixed carbon, at least 60 wt% fixed carbon, at least 70 wt% fixed carbon, at least 80 wt% fixed carbon, or at least 90 wt% fixed carbon. Other fixed carbon contents have been described previously and apply to these process embodiments (and other processes disclosed herein) as well.

[0372] The biocarbon composition can comprise less than 10 wt% ash, less than 5 wt% ash, less than 2 wt% ash, or less than 1 wt% ash. Other ash contents have been described previously and apply to these process embodiments (and other processes disclosed herein) as well.

[0373] In some embodiments, the condenser liquid comprises less than 1 wt% ash, less than 0.1 wt% ash, or essentially no ash. Low ash content of the condenser liquid

reduces the final ash content of the biocarbon composition. Other condenser-liquid ash contents have been described previously and apply to these process embodiments (and other processes disclosed herein) as well.

[0374] In some processes, total carbon within the biocarbon composition is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. In some embodiments, total carbon within the biocarbon composition is at least 90% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. In some embodiments, 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.

[0375] Some variations provide a process for producing a biocarbon composition, the process comprising:

(a) pyrolyzing a first feedstock (also described as a "biomass-comprising feedstock") in a pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor;

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

(c) contacting a second feedstock (also described as a "starting biomass feedstock") with the condenser liquid, thereby generating the first feedstock containing the second feedstock and the condenser liquid; and

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

[0376] In some embodiments, the process further comprises pelletizing the biogenic reagent and/or drying the biogenic reagent.

[0377] The starting biomass feedstock can be selected from the group comprising 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 and/or demolition waste, railroad ties, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof.

[0378] In some embodiments, step (c) utilizes spraying at least the condenser liquid onto the starting biomass feedstock. The biomass-comprising feedstock can comprise condenser liquid adsorbed onto a surface of the starting biomass feedstock. Alternatively, or additionally, the biomass-comprising feedstock comprises condenser liquid absorbed into a bulk phase of the starting biomass feedstock.

[0379] When step (d) is conducted, a binder can be introduced to the biogenic reagent. The binder can be selected from the group comprising 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 thereof. In certain embodiments, the binder is selected from the group comprising starch, thermoplastic starch, crosslinked starch, starch polymers, derivatives thereof, or a combination thereof.

[0380] When step (d) is conducted, in some embodiments, no external binder is introduced to the biogenic reagent during the pelletizing.

[0381] In some processes, steps (c) and (d) integrated and both performed in a pelletizing unit. In some processes, steps (d) and (e) are both conducted and are integrated.

[0382] The condensing system can include multiple condenser stages. The condenser liquid can be a condensed product of an individual stage (e.g., a first stage) of the multiple condenser stages.

[0383] In some processes, at least 25 wt% of total carbon contained in the condenser liquid is converted to fixed carbon in the biogenic reagent. In certain processes, at least 50 wt% of total carbon contained in the condenser liquid is converted to fixed carbon in the biogenic reagent.

[0384] In some processes, at least about 10 wt% to at most about 80 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid. In certain processes, at least about 20 wt% to at most about 60 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid.

[0385] Step (a) can be conducted at a pyrolysis temperature selected at least about 250°C to at most about 1250°C, such as at least about 300°C to at most about 700°C. Step (a) can be conducted for a first pyrolysis time selected at least about 10 seconds to at most about 24 hours.

[0386] In some processes, some or all of the condenser vapor is at least partially oxidized to generate heat, wherein the heat can be used within the process.

[0387] The biogenic reagent can be milled utilizing a mechanical-treatment apparatus selected from the group comprising 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.

[0388] In processes employing step (d), that step can utilize a pelletizing apparatus selected from the group comprising 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.

[0389] The final biocarbon composition can be in the form of powder or pellets, for example.

[0390] In some embodiments, the biocarbon composition comprises at least 50 wt% fixed carbon, at least 60 wt% fixed carbon, at least 70 wt% fixed carbon, at least 80 wt% fixed carbon, or at least 90 wt% fixed carbon.

[0391] In some embodiments, the biocarbon composition comprises less than 10 wt% ash, less than 5 wt% ash, less than 2 wt% ash, or less than 1 wt% ash.

[0392] In some embodiments, the condenser liquid comprises less than 1 wt% ash, less than 0.1 wt% ash, or essentially no ash.

[0393] In some embodiments, the total carbon within the biocarbon composition is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. 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. 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.

[0394] The present disclosure provides biocarbon compositions produced by any of the disclosed processes. The present disclosure provides systems configured for carrying out any of the processes disclosed.

[0395] Some embodiments will be described with reference to the accompanying drawings, FIGS. 1 to 8, which illustration various processes and systems. In the block-flow diagrams, dotted boxes and lines denote optional units and streams, respectively.

[0396] FIG. 1 depicts an exemplary block-flow diagram of a process and system in which biomass is pyrolyzed in a pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser having at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. If there are multiple condenser stages, then there are multiple condenser vapors and multiple condenser liquids. A condenser liquid is fed to a mixing unit, into which is also fed the biogenic reagent, to generate an intermediate material. The intermediate material is optionally sent to a pelletizing unit to generate pellets, optionally with the addition of an external binder. Pellets, or the intermediate material, are then fed to a thermal-treatment

unit which generates a biocarbon product. The thermal-treatment unit also generates an off-gas, which could be fed to the condenser shown in FIG. 1, or fed to a different condenser, or otherwise processed (e.g., combusted).

[0397] FIG. 2 depicts an exemplary block-flow diagram of a process and system in which biomass is pyrolyzed in a pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser having at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. If there are multiple condenser stages, then there are multiple condenser vapors and multiple condenser liquids. A condenser liquid is optionally fed to a pelletizing unit, into which is also fed the biogenic reagent, to generate pellets, optionally with the addition of an external binder. Pellets (or the intermediate material comprising the biogenic reagent and the condenser liquid) are then fed to a thermal-treatment unit which generates a biocarbon product. The thermal-treatment unit also generates an off-gas, which could be fed to the condenser shown in FIG. 2, or fed to a different condenser, or otherwise processed (e.g., combusted).

[0398] FIG. 3 depicts an exemplary block-flow diagram of a process and system in which biomass is pyrolyzed in a pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser comprising at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. If there are multiple condenser stages, then there are multiple condenser vapors and multiple condenser liquids. The biogenic reagent is fed to a pelletizing unit, to generate pellets. In some embodiments, a binder is added to the pelletizing unit. The pellets and the condenser liquid (or one of the condenser liquids if there are multiple fractions) are fed to a carbon recapture unit, to generate an intermediate material. The intermediate material is then optionally fed to a thermal-treatment unit which generates a biocarbon product. The thermal-treatment unit also generates an off-gas, which could be fed to the condenser shown in FIG. 3, or fed to a different condenser, or otherwise processed (e.g., combusted).

[0399] FIG. 4 depicts an exemplary block-flow diagram of a process and system in which biomass is pyrolyzed in a pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser comprising at least one

condensing stage. The condenser generates a condenser vapor and a condenser liquid. If there are multiple condenser stages, then there are multiple condenser vapors and multiple condenser liquids. The biogenic reagent and the condenser liquid (or one of the condenser liquids if there are multiple fractions) are fed to a carbon recapture unit, to generate an intermediate material. The intermediate material is then fed to a thermal-treatment unit which generates a biocarbon product. The thermal-treatment unit also generates an off-gas, which could be fed to the condenser shown in FIG. 4, or fed to a different condenser, or otherwise processed (e.g., combusted).

[0400] FIG. 5 depicts an exemplary block-flow diagram of a process and system in which biomass is pyrolyzed in a first pyrolysis reactor to generate a first pyrolysis solids and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser comprising at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. If there are multiple condenser stages, then there are multiple condenser vapors and multiple condenser liquids. The condenser liquid (or one of the condenser liquids if there are multiple fractions) are fed to a second pyrolysis reactor to generate second pyrolysis solids and a pyrolysis off-gas. The second pyrolysis reactor can be a coking reactor for coking or carbonizing condenser liquid. The pyrolysis off-gas can be recycled back to the condenser or otherwise processed (e.g., combusted). The first and second pyrolysis solids can be combined to generate a biocarbon product. In some embodiments, the first pyrolysis solids and/or the second pyrolysis solids are recovered as a product without combining with the other of the second pyrolysis solids or first pyrolysis solids. A blended material can be pelletized. Whether or not the blended material is pelletized, the blended material can be dried or thermally treated, to generate a final biocarbon product.

[0401] FIG. 6 depicts an exemplary block-flow diagram of a process and system in which biomass is pyrolyzed in a first pyrolysis reactor to generate a first pyrolysis solids and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser comprising at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. If there are multiple condenser stages, then there are multiple condenser vapors and multiple condenser liquids. The condenser liquid (or one of the condenser liquids if there are multiple fractions) are fed to a second reactor to generate a solid or semi-solid material and a reactor

off-gas. The second reactor can be a coking reactor for coking or carbonizing condenser liquid, or the second reactor can be a reactor operated at a temperature that is lower than a pyrolysis temperature. The reactor off-gas can be recycled back to the condenser or otherwise processed (e.g., combusted). The first and second pyrolysis solids can be combined to generate a biocarbon product. In some embodiments, the first pyrolysis solids and/or the second pyrolysis solids are recovered as a product without combining with the other of the second pyrolysis solids or first pyrolysis solids. A blended material can be pelletized. Whether or not the blended material is pelletized, the blended material can be dried or thermally treated, to generate a final biocarbon product.

[0402] FIG. 7 depicts an exemplary block-flow diagram of a process and system in which biomass, impregnated with condenser liquid, is pyrolyzed in a pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser comprising at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. If there are multiple condenser stages, then there are multiple condenser vapors and multiple condenser liquids. The condenser liquid (or one of the condenser liquids if there are multiple fractions) is fed to a mixing unit, along with incoming biomass, to generate a feed material (biomass plus condenser liquid). The feed material is what is fed to the pyrolysis reactor. In some embodiments, the biogenic reagent from the pyrolysis reactor is pelletized. Whether or not the biogenic reagent is pelletized, the biogenic reagent can be dried or thermally treated, to generate a final biocarbon product.

[0403] FIG. 8 depicts an exemplary block-flow diagram of a process and system in which biomass, impregnated with condenser liquid, is pyrolyzed in a first pyrolysis reactor to generate a biogenic reagent and a pyrolysis vapor. The pyrolysis vapor is sent to a condenser comprising at least one condensing stage. The condenser generates a condenser vapor and a condenser liquid. If there are multiple condenser stages, then there are multiple condenser vapors and multiple condenser liquids. The condenser liquid (or one of the condenser liquids if there are multiple fractions) is fed to a mixing unit, along with incoming biomass, to generate a feed material (biomass plus condenser liquid). The feed material is what is fed to the first pyrolysis reactor. In some embodiments, the biogenic reagent from the first pyrolysis reactor is pelletized. Whether or not the biogenic reagent is

pelletized, the biogenic reagent can be sent to a second pyrolysis reactor, to generate a final biocarbon product. The pyrolysis off-gas from the optional second pyrolysis reactor can be recycled back to the condenser, or fed to a different condenser, or otherwise processed (e.g., combusted).

[0404] A variation of FIGS. 5 and 6 is that the pyrolysis vapor can be coked directly, rather than a condensed fraction of the pyrolysis vapor being coked. However, this decreases the coking efficiency due to the presence of non-condensable gases (e.g., CO_2) that can be difficult to convert to solid carbon.

[0405] In another variation, the condenser in FIG. 5 or FIG. 6 is replaced by a different separation unit, such as a liquid-vapor cyclone separator.

[0406] In another variation, the principles of FIGS. 5 and 7 are both employed. For example, the condenser liquid can be mixed with incoming biomass (such as shown in FIG. 7) while the condenser liquid can be coked in a second pyrolysis reactor (such as shown in FIG. 5). This optionality applies to all process configurations. For instance, in FIG. 1, rather than all the condenser liquid feeding to the mixing unit, some of the condenser liquid can instead be mixed with incoming biomass, or be separately coked, or both of these options.

[0407] In some embodiments relating to the configuration of FIG. 5 or FIG. 6, the first pyrolysis solids form a high-fixed-carbon material while the second pyrolysis solids (FIG. 5) or the solid or semi-solid material (FIG. 6) form(s) a low-fixed-carbon material. In these embodiments, generally speaking, a relatively high temperature in the first pyrolysis reactor is useful.

[0408] In other embodiments relating to the configuration of FIG. 5 or FIG. 6, the first pyrolysis solids form a low-fixed-carbon material while the second pyrolysis solids (FIG. 5) or the solid or semi-solid material (FIG. 6) form(s) a high-fixed-carbon material. In these embodiments, generally speaking, a relatively high temperature in the second reactor (e.g., second pyrolysis reactor) is useful.

[0409] In some embodiments, the biocarbon product (composition) comprises:

(a) at least about 1 wt% to at most about 99 wt% of a low-fixed-carbon material with a first fixed-carbon concentration at least about 20 wt% to at most about 55 wt% fixed carbon on an absolute basis;

(b) at least about 1 wt% to at most about 99 wt% of a high-fixed-carbon material with a second fixed-carbon concentration at least about 50 wt% to at most about 100 wt% fixed carbon on an absolute basis, wherein the second fixed-carbon concentration is higher than the first fixed-carbon concentration;

(c) from 0 to at most about 30 wt% moisture;

(d) from 0 to at most about 15 wt% ash; and

(e) from 0 to at most about 20 wt% of one or more additives.

[0410] In some embodiments, the low-fixed-carbon material and the high-fixed-carbon material are present in the biocarbon composition as a homogenous physical blend. The first fixed-carbon concentration can be uniform throughout the biocarbon composition. The second fixed-carbon concentration can be uniform throughout the biocarbon composition. In certain embodiments, the first fixed-carbon concentration and the second fixed-carbon concentration are both uniform throughout the biocarbon composition.

[0411] In other embodiments, the low-fixed-carbon material and the high-fixed-carbon material are present in the biocarbon composition as a heterogeneous physical blend. For example, the low-fixed-carbon material and the high-fixed-carbon material can be present in the biocarbon composition as distinct layers. The low-fixed-carbon material can be comprised in a shell or coating around a core comprising the high-fixed-carbon material. Or, the high-fixed-carbon material can be comprised in a shell or coating around a core comprising the low-fixed-carbon material. In some embodiments, the high-fixed-carbon material is in the form of particulates in a continuous phase of the low-fixed-carbon material. In other embodiments, the low-fixed-carbon material is in the form of particulates in a continuous phase of the high-fixed-carbon material.

[0412] The low-fixed-carbon material and the high-fixed-carbon material can form distinct phases that do not dissolve into each other at equilibrium and at low temperatures. In some embodiments, the low-fixed-carbon material and the high-fixed-carbon material can

comprise high equilibrium (thermodynamic) solubilities in each other, but nevertheless remain kinetically frozen in the composition such that distinct materials are observable. The distinct materials can be observable by measuring compositions, densities, particle sizes, reactivities, or other physical or chemical properties. During final use of the biocarbon composition, it is possible (e.g., at elevated temperatures or during carbon oxidation) for the material distinction to be lost.

[0413] In one technique to demonstrate that a given biocarbon composition comprises both a low-fixed-carbon material and a distinct high-fixed-carbon material, thermogravimetric analysis (TGA) of combustion of a biocarbon composition test sample is performed. In some embodiments, the resulting TGA thermal curve comprises two peaks characteristic of distinct mass-loss events that correlate with the low-fixed-carbon material and the high-fixed-carbon material. This can be compared against a control sample of a biocarbon composition that comprises a single material comprising a uniform fixed-carbon concentration, to show a TGA thermal curve with a single peak characteristic of one mass-loss event for the material. In similar embodiments, the TGA thermal curve for the test sample comprises three or more peaks, while the TGA thermal curve for the control sample comprises at least one less peak than for the test sample.

[0414] Another technique to demonstrate that a given biocarbon composition comprises both a low-fixed-carbon material and a distinct high-fixed-carbon material is a particle-size analysis. This is a viable approach when the particle sizes associated with the low-fixed-carbon material and the high-fixed-carbon material are different, or when the particle-size distributions associated with the low-fixed-carbon material and the high-fixed-carbon material are different. In some embodiments, the high-fixed-carbon material tends to comprise smaller particles compared to the low-fixed-carbon material. In some embodiments, a bimodal particle-size distribution arising from the presence of both a low-fixed-carbon material and a high-fixed-carbon material, in contrast to a control sample that comprises a unimodal particle-size distribution characteristic of a uniform material. In similar embodiments, the test sample can comprise a particle-size distribution with at least one more mode than the control-sample particle-size distribution. It is possible, for example, for each of the low-fixed-carbon material and the high-fixed-carbon material to comprise

bimodal particle-size distributions (with peaks centered at different sizes) and the control sample to also comprise a bimodal particle-size distribution, depending on how the control sample was produced.

[0415] Particle sizes can be measured by a variety of techniques, including dynamic light scattering, laser diffraction, image analysis, or sieve separation, for example. Dynamic light scattering is a non-invasive, well-established technique for measuring the size and size distribution of particles typically in the submicron region, and with the latest technology down to 1 nanometer. Laser diffraction is a widely used particle-sizing technique for materials ranging from hundreds of nanometers up to several millimeters in size. Exemplary dynamic light scattering instruments and laser diffraction instruments for measuring particle sizes are available from Malvern Instruments Ltd., Worcestershire, UK. Image analysis to estimate particle sizes and distributions can be done directly on photomicrographs, scanning electron micrographs, or other images. Finally, sieving is a conventional technique of separating particles by size.

[0416] Imaging techniques can alternatively, or additionally, be utilized to demonstrate that a given biocarbon composition comprises both a low-fixed-carbon material and a distinct high-fixed-carbon material. Imaging techniques include, but are not limited to, optical microscopy; dark-field microscopy; scanning electron microscopy (SEM); transmission electron microscopy (TEM); and X-ray tomography (XRT), for example. An imaging technique can be used to demonstrate distinct materials in a blend, rather than a homogeneous material, for example. Or, an imaging technique can be used to select subsamples for further analysis. Further analysis can be compositional analysis to show three-dimensional variations in fixed carbon content. Further analysis can be property analysis to show three-dimensional variations in chemical or physical properties, such as density, particle size, or reactivity, for example.

[0417] Spectroscopy techniques can alternatively, or additionally, be utilized to demonstrate that a given biocarbon composition comprises both a low-fixed-carbon material and a distinct high-fixed-carbon material. Spectroscopy techniques comprise, but are not limited to, energy dispersive X-ray spectroscopy (EDS), X-ray fluorescence (XRF), infrared (IR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy, for example.

[0418] In some embodiments, such as (but not limited to) those relating to FIG. 6, the biocarbon composition comprises at least about 10 wt% to at most about 90 wt% of a low-fixed-carbon material. In some embodiments, the biocarbon composition comprises at least about 10 wt% to at most about 90 wt% of a high-fixed-carbon material. The weight ratio of the low-fixed-carbon material to the high-fixed-carbon material can be selected at least about 0.1 to at most about 10, such as at least about 0.2 to at most about 5, at least about 0.5 to at most about 2, or at least about 0.8 to at most about 1.2.

[0419] In some embodiments, the first fixed-carbon concentration is at least about 20 wt% to at most about 40 wt%, or at least about 25 wt% to at most about 50 wt%, or at least about 30 wt% to at most about 55 wt%, for example.

[0420] In some embodiments, the second fixed-carbon concentration is at least about 80 wt% to at most about 100 wt%, or at least about 70 wt% to at most about 95 wt%, or at least about 60 wt% to at most about 90 wt%, for example.

[0421] In some embodiments, the unweighted average of the first fixed-carbon concentration and the second fixed-carbon concentration is at least about 30 wt% to at most about 90 wt%, such as at least about 40 wt% to at most about 80 wt%.

[0422] The biocarbon composition can comprise an overall fixed-carbon concentration at least about 25 wt% to at most about 95 wt% on an absolute basis. In some embodiments, the biocarbon composition comprises an overall fixed-carbon concentration at least about 35 wt% to at most about 85 wt% on an absolute basis.

[0423] The low-fixed-carbon material can comprise at least about 45 wt% to at most about 80 wt% volatile carbon on an absolute basis (i.e., comprising ash and moisture). In various embodiments, the low-fixed-carbon material can comprise about, at least about, or at most about 45, 50, 55, 60, 65, 70, 75, or 80 wt% volatile carbon on an absolute basis. The low-fixed-carbon material can comprise at least about 1 wt% to at most about 20 wt% oxygen on an absolute basis, for example. The low-fixed-carbon material can comprise at least about 0.1 wt% to at most about 10 wt% hydrogen on an absolute basis, for example.

[0424] The high-fixed-carbon material can comprise at least about 0 to at most about 50 wt% volatile carbon on an absolute basis. In various embodiments, the high-fixed-carbon

material can comprise about, at least about, or at most about 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, or 50 wt% volatile carbon on an absolute basis. The high-fixed-carbon material can comprise at least about 1 wt% to at most about 20 wt% oxygen on an absolute basis, for example. The high-fixed-carbon material can comprise at least about 0.1 wt% to at most about 10 wt% hydrogen on an absolute basis, for example.

[0425] The "biocarbon composition" is generally synonymous with "biocarbon product" when reference is to the final composition of a process. In some embodiments, the biocarbon composition comprises at least about 0.1 wt% to at most about 20 wt% moisture. In various embodiments, the biocarbon composition comprises about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 wt% moisture, comprising all intervening ranges. The low-fixed-carbon material can comprise from 0 to at most about 50 wt% moisture, such as about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 wt% moisture, comprising all intervening ranges. Independently, the high-fixed-carbon material can comprise from 0 to at most about 50 wt% moisture, such as about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 wt% moisture, comprising all intervening ranges. Drying can be employed at one or more points in the process.

[0426] In some embodiments, the biocarbon composition comprises at least about 0.1 wt% to at most about 10 wt% ash. In various embodiments, the biocarbon composition comprises about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 wt% ash, comprising all intervening ranges. The low-fixed-carbon material can comprise from 0 to at most about 25 wt% ash, such as about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25 wt% ash, comprising all intervening ranges. Independently, the high-fixed-carbon material can comprise from 0 to at most about 50 wt% ash, such as about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25 wt% ash, comprising all intervening ranges.

[0427] In some embodiments, the biocarbon composition comprises at least about 0.1 wt% to at most about 10 wt% of one or more additives. In some embodiments, the biocarbon

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

[0428] The low-fixed-carbon material can comprise from 0 to at most about 20 wt% additives, such as about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 wt% additive(s), comprising all intervening ranges. Independently, the high-fixed-carbon material can comprise from 0 to at most about 50 wt% additives, such as about, at least about, or at most about 0, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 wt% additive(s), comprising all intervening ranges.

[0429] The additives can comprise an organic additive and/or an inorganic additive. In some embodiments, one or more additives comprise a renewable material. In some embodiments, one or more additives comprise a material that is capable of being partially oxidized and/or combusted.

[0430] In some embodiments, one or more additives comprise (or are) a binder. A binder can be selected from the group comprising 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 thereof.

[0431] In certain embodiments, a binder is selected from the group comprising starch, thermoplastic starch, crosslinked starch, starch polymers, derivatives thereof, or a combination thereof. A binder can be a thermoplastic starch. In some embodiments, the thermoplastic starch is crosslinked. The thermoplastic starch can be a reaction product of

starch and a polyol, which can be selected from the group comprising ethylene glycol, propylene glycol, glycerol, butanediols, butanetriols, erythritol, xylitol, sorbitol, or a combination thereof. The reaction product can be formed from a reaction that is catalyzed by an acid, which can be selected from the group comprising formic acid, acetic acid, lactic acid, citric acid, oxalic acid, uronic acids, glucuronic acids, or a combination thereof. Alternatively, the reaction product can be formed from a reaction that is catalyzed by a base.

[0432] One or more additives can reduce the reactivity of the biocarbon composition compared to an otherwise-equivalent biocarbon composition without the one or more additives. The reactivity can be thermal reactivity. For example, the biocarbon composition with one or more additives can comprise a lower self-heating compared to the otherwise-equivalent biocarbon composition without the one or more additives. Alternatively, or additionally, the reactivity is chemical reactivity with oxygen, water, hydrogen, carbon monoxide, and/or metals (e.g., iron).

[0433] When additives are employed, the additives do not need to be uniformly distributed throughout the biomass composition. The additives can be present within one of the low-fixed-carbon material or high-fixed-carbon material, or even solely present within one of those materials. For example, a binder can be present in the overall biomass composition at 5 wt%, but of that amount, 4 percentage points are disposed within the low-fixed-carbon material and 1 percentage point is disposed within the high-fixed-carbon material (i.e., 80% of the binder is placed within the low-fixed-carbon material). In various embodiments, the percentage of total additives disposed within the low-fixed-carbon material can be about, at least about, or at most about 0, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or 100%; the percentage of total additives disposed within the high-fixed-carbon material can be about, at least about, or at most about 0, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or 100%; and the percentage of total additives disposed within neither the low-fixed-carbon material nor the high-fixed-carbon material, but elsewhere within the biocarbon composition (e.g., as a separate additive phase) can be about, at least about, or at most about 0, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or 100%.

[0434] When the one or more additives are present, some or all of the additives can be pore-filling within the low-fixed-carbon material. When the one or more additives are present, some or all of the additives can be pore-filling within the high-fixed-carbon material. In some embodiments, one or more additives are present and are pore-filling within both of the low-fixed-carbon material and the high-fixed-carbon material.

[0435] Alternatively, or additionally, one or more additives can be disposed on an outer surface of the biocarbon composition (e.g., an outer surface of pellets or powder particles).

[0436] In some embodiments, the biocarbon composition is in the form of powder.

[0437] In some embodiments, the biocarbon composition is in the form of pellets. When the form is pellets, one or more additives can comprise a binder for the pellets. Alternatively, or additionally, pellets can utilize the low-fixed-carbon material itself as a binder within the pellets.

[0438] When one or more additives are present, the additive(s) can be located within one of the low-fixed-carbon material or the high-fixed-carbon material. Alternatively, the additive(s) can be uniformly distributed such that the additive(s) comprise the same average concentration within the low-fixed-carbon material and the high-fixed-carbon material.

[0439] In some embodiments, the biocarbon composition is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances", which is hereby incorporated by reference herein.

[0440] The fixed-carbon concentration is an important parameter for the biocarbon composition. The present disclosure allows fixed-carbon concentration to be maximized, or optimized but not necessarily maximized, in various embodiments.

[0441] In some embodiments, the fixed-carbon concentration is selected to optimize energy content associated with the biocarbon composition. In some embodiments, the fixed-carbon concentration, and the additive type and/or concentration, are selected to optimize energy content associated with the biocarbon composition

[0442] In some embodiments, the fixed-carbon concentration is selected to optimize bulk density associated with the biocarbon composition. In some embodiments, the fixed-carbon concentration, and the additive type and/or concentration, are selected to optimize bulk density associated with the biocarbon composition.

[0443] In some embodiments, the fixed-carbon concentration is selected to optimize hydrophobicity associated with the biocarbon composition. In some embodiments, the fixed-carbon concentration, and the additive type and/or concentration, are selected to optimize hydrophobicity associated with the biocarbon composition.

[0444] In some embodiments, the fixed-carbon concentration is selected to optimize pore sizes associated with the biocarbon composition. In some embodiments, the fixed-carbon concentration, and the additive type and/or concentration, are selected to optimize pore sizes associated with the biocarbon composition.

[0445] In some embodiments, the fixed-carbon concentration is selected to optimize ratios of pore sizes associated with the biocarbon composition. In some embodiments, the fixed-carbon concentration, and the additive type and/or concentration, are selected to optimize ratios of pore sizes associated with the biocarbon composition.

[0446] In some embodiments, the fixed-carbon concentration is to optimize surface area associated with the biocarbon composition. In some embodiments, the fixed-carbon concentration, and the additive type and/or concentration, are selected to optimize surface area associated with the biocarbon composition.

[0447] In some embodiments, the fixed-carbon concentration is selected to optimize reactivity associated with the biocarbon composition. In some embodiments, the fixed-carbon concentration, and the additive type and/or concentration, are selected to optimize reactivity associated with the biocarbon composition.

[0448] In some embodiments, the fixed-carbon concentration is selected to optimize ion-exchange capacity associated with the biocarbon composition. In some embodiments, the fixed-carbon concentration, and the additive type and/or concentration, are selected to optimize ion-exchange capacity associated with the biocarbon composition.

[0449] In some embodiments, the biocarbon composition is in the form of pellets, and the fixed-carbon concentration is selected to optimize Hardgrove Grindability Index associated with the pellets. In some embodiments, the biocarbon composition is in the form of pellets, and the fixed-carbon concentration, and the additive type and/or concentration, are selected to optimize Hardgrove Grindability Index associated with the pellets.

[0450] In some embodiments, the biocarbon composition is in the form of pellets, and the fixed-carbon concentration is selected to optimize Pellet Durability Index associated with the pellets. In some embodiments, the biocarbon composition is in the form of pellets, and the fixed-carbon concentration, and the additive type and/or concentration, are selected to optimize Pellet Durability Index associated with the pellets.

[0451] In some embodiments, the total carbon within the biocarbon composition is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. In some embodiments, the total carbon is at least 90% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon. In certain embodiments, the total carbon is fully renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

[0452] It is important to note that while renewable biocarbon compositions are preferred, the disclosed principles can be applied to non-renewable materials. In certain embodiments, a biomass-comprising feedstock comprises biomass (such as a biomass source recited herein) as well as a non-renewable feedstock, such as coal. Thus, a biomass-coal mixture can be utilized as biomass-comprising feedstock—which can replace "biomass" in any of FIGS. 1 to 6, for example. Other non-biomass feedstocks that can be used in feedstock mixtures comprise pyrolyzed coal, coke, petroleum coke, metallurgical coke, activated carbon, carbon black, graphite, graphene, pyrolyzed polymers, or combinations thereof, for example.

[0453] In some processes, two or more distinct pyrolysis reactors are employed. The pyrolysis reactors are typically all conducted continuously or all conducted in batch, but in principle, a mixture of reaction modes can be used. Also, when distinct pyrolysis reactors are employed, they can be at a common site or at different sites.

[0454] In other embodiments, a process is conducted in a common pyrolysis reactor at different times, such as in distinct production campaigns. When a single pyrolysis reactor is used, it can be operated in batch mode with distinct batches of low-fixed-carbon material and high-fixed-carbon material, for example, or using different pyrolysis conditions. Alternatively, a single pyrolysis reactor can be operated continuously or semi-continuously, such that a first material is produced for a first period of time and then a second material is produced for a second period of time, after which the reactor can be switched back to producing the first material or something else.

[0455] In some process embodiments, a first pyrolysis reactor is operated at a first pyrolysis temperature selected at least about 250°C to at most about 1250°C, such as at least about 300°C to at most about 700°C. A second pyrolysis reactor can be operated at a second pyrolysis temperature selected at least about 250°C to at most about 1250°C, such as at least about 300°C to at most about 700°C. The second pyrolysis temperature can be the same as, or different than, the first pyrolysis temperature.

[0456] In some embodiments, a first pyrolysis reactor is operated for a first pyrolysis time selected at least about 10 seconds to at most about 24 hours. In these or other embodiments, a second pyrolysis reactor is operated for a second pyrolysis time selected at least about 10 seconds to at most about 24 hours. The second pyrolysis time can be the same as, or different than, the first pyrolysis time.

[0457] Some embodiments are predicated on optimized pyrolysis of biomass along with carbon recapture—using principles taught herein—to generate a carbon substrate, mechanical size reduction of the carbon substrate, and use of a binder to agglomerate the carbon substrate to form biocarbon pellets. The carbon substrate can be or comprise a blend of low-fixed-carbon material and high-fixed-carbon material.

[0458] Hardgrove Grindability Index ("HGI") is a measure of the grindability of a material, such as biomass or coal. The HGI parameter for coal is important in power applications, such as pulverized coal boilers where coal is pulverized and burned in suspension, and in iron making, such as in pulverized coal injection where pulverized coal is injected through a lance into a blast furnace where pulverized coal can displace coke to reduce iron ores to metallic iron.

[0459] In some embodiments, varying the fixed-carbon content enables optimization of HGI. The incorporation of binders or other additives also can enable HGI adjustability.

[0460] The ability to adjust the HGI of biocarbon pellets is beneficial because downstream applications (e.g., replacement of coal in boilers) that utilize biocarbon pellets comprise varying HGI requirements. HGI adjustability addresses to well-known problems industrially: the difficulty to grind raw biomass, and the difficulty to grind pellets. Furthermore, because there are so many downstream uses of biocarbon pellets, each comprising its own requirements, it is highly advantageous to be able to adjust the grindability of the pellets. It is desirable to be able to adjust HGI to suit a particular application, such as combustion in boilers, metal-making, or gasification to make syngas.

[0461] For many applications, pellets are preferred over powders (isolated biomass particles) due to advantages in shipping, storage, safety. Ultimately, the pellets can need to be converted back to powders, or at least smaller objects, at some point. Grindability of the pellets is thus often an important parameter that impacts operating costs and capital costs.

[0462] In some cases, pellets need to be ground or pulverized to a powder, such as when the boiler or gasifier utilizes a fluidized bed or a suspension of carbon particles. Another example is pulverized carbon injection into a blast furnace, for reducing metal ores to metals. In these cases, high grindability of the pellets is desired, but not too high such that the pellets fall apart during shipping and handling. In other cases, it is desired to feed pellets themselves to a process, such as a metal-making process. In these cases, lower grindability can be desirable since some pellet strength can be necessary to support a material bed in the reactor. Different technologies comprise different pellet grindability requirements.

[0463] 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 at least about 30 to at most about 50 or at least about 50 to at most 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.

[0464] 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, comprising all intervening ranges (e.g., 25–40, 30–60, etc.).

[0465] The biocarbon pellet can be characterized by a Pellet Durability Index of at least 80%, at least 85%, at least 90%, at least 95%, or at least 99%. The biocarbon pellet can be characterized by a Pellet Durability Index less than 99%, less than 95%, less than 90%, less than 85%, or less than 80%. Unless otherwise indicated, all references in this disclosure to Pellet Durability Index are in reference to ISO 17831-1:2015 "Solid biofuels — Determination of mechanical durability of pellets and briquettes — Part 1: Pellets", which is hereby incorporated by reference herein in its entirety.

[0466] In some embodiments, the biocarbon pellets are utilized as a starting material to make smaller objects, which can also be referred to as biocarbon pellets since "pellet" does not limit the geometry. For example, initial biocarbon pellets that are 10 mm in average pellet diameter can be fabricated. Then, these initial biocarbon pellets can be crushed using various mechanical means (e.g., using a hammer mill). The crushed pellets can be separated according to size, such as by screening. In this manner, smaller biocarbon pellets can be produced, with an average pellet diameter of about, at least about, or at most about 50, 100, 150, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1500, 2000, 3000, 4000, or 5000 microns, for example. In some embodiments, the average pellet diameter of the smaller biocarbon pellets is larger than the average particle diameter of the initial carbon-comprising particles that were used to make the pellets with the binder.

[0467] When the biocarbon pellets are crushed to generate smaller biocarbon pellets, a step of crushing, and in some embodiments screening, can be integrated with another process step, including potentially at a site of industrial use. The optional step to generate smaller biocarbon pellets can utilize a crushing apparatus selected from the group

comprising 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.

[0468] 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 at least about 30 to at most about 50 or at least about 50 to at most about 70.

[0469] 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, comprising all intervening ranges (e.g., 30–60, 33–47, etc.).

[0470] In some processes, the biocarbon pellet is characterized by a Pellet Durability Index of at least 80%, at least 90%, or at least 95%.

[0471] 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.

[0472] The size and geometry of the biocarbon pellet can vary. By "pellet" as used herein, it is meant an agglomerated object rather than a loose powder. The pellet geometry is not limited to spherical or approximately spherical. Also, in this disclosure, "pellet" is synonymous with "briquette". The pellet geometry can be spherical (round or ball shape), cylindrical, cube (square), octagon, hexagon, honeycomb/beehive shape, oval shape, egg shape, column shape, bar shape, pillow shape, random shape, or a combination thereof.

For convenience of disclosure, the term "pellet" will generally be used for any object containing a powder agglomerated with a binder. It is also reiterated that this technology is by no means limited to biocarbon compositions in the form of pellets.

[0473] The biocarbon pellets can be characterized by an average pellet diameter, which is the true diameter in the case of a sphere or cylinder, or an equivalent diameter in the case of any other 3D geometry. The equivalent diameter of a non-spherical pellet is the diameter of a sphere of equivalent volume to the actual pellet. In some embodiments, the average pellet diameter is about, or at least about, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 20, or 25 millimeters, comprising 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, comprising all intervening ranges.

[0474] In some embodiments, there is a plurality of biocarbon pellets that is uniform in size, such as a standard deviation of less than ±100%, less than ±50%, less than ±25%, less than ±10%, or less than ±5% of the average pellet diameter. In other embodiments, there is a wide range of sizes of biocarbon pellets, as this can be advantageous in some applications.

[0475] Biocarbon pellets can comprise moisture. The moisture present in a biocarbon pellet can be water that is chemically bound to carbon or binder, water that is physically bound (absorbed or adsorbed) to carbon or binder, free water present in an aqueous phase that is not chemically or physically bound to carbon or binder, or a combination thereof. When moisture is desired during the binding process, it is preferred that such moisture is chemically or physically bound to carbon and/or binder, rather than being free water.

[0476] Various moisture levels can be present. For example, the biocarbon pellet can comprise at least about 1 wt% to at most about 30 wt% (e.g., 32 wt%) moisture, such as at least about 5 wt% to at most about 15 wt% moisture, at least about 2 wt% to at most about 10 wt% moisture, or at least about 0.1 wt% to at most 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, comprising all intervening ranges. Moisture levels of the biocarbon pellets can be optimized to vary the densification within the pellets.

[0477] For some market applications, such as in agriculture, higher moisture levels are desirable for dust control or other reasons. For other market applications, such as metallurgy, lower moisture levels can be desirable (e.g., 1 wt% moisture or even less). Note that although water is present during the process of making biocarbon pellets, those pellets can then be dried which means the final biocarbon pellets do not necessarily comprise moisture.

[0478] In some biocarbon pellets, the biocarbon pellet comprises at least about 2 wt% to at most about 25 wt% of the binder, at least about 5 wt% to at most about 20 wt% of the binder, or at least about 1 wt% to at most 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, comprising all intervening ranges. In some embodiments, there is an inverse relationship between moisture content and binder concentration.

[0479] 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.

[0480] The binder can be an organic binder or an inorganic binder. In some embodiments, the binder is or comprises a renewable material. In some embodiments, the binder is or comprises a biodegradable material. In some embodiments, the binder is capable of being partially oxidized and/or combusted.

[0481] In various embodiments, the binder is selected from the group comprising 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 thereof. The binder can be, or comprise, a grindable plasticizer.

[0482] In certain embodiments, the binder is selected from the group comprising starch, thermoplastic starch, crosslinked starch, starch-based polymers (e.g., polymers based on amylose and amylopectin), derivatives thereof, or a combination thereof. Starch can be non-ionic starch, anionic starch, cationic starch, or zwitterionic starch.

[0483] 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 and/or glycols can be added. The natural crystallinity can then be disrupted by vigorous mixing (shearing) at elevated temperatures which yields thermoplastic starch. Starch can be plasticized (destructurized) by low levels of molecules that are capable of hydrogen bonding with the starch hydroxyl groups, such as water, glycerol, or sorbitol.

[0484] Thermoplastic starch can be chemically modified and/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) and/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.

[0485] In some embodiments, a starch-containing binder is or comprises a crosslinked starch. Various methods for crosslinking starch are known in the art. A starch material can be crosslinked under acidic or alkaline conditions after dissolving or dispersing it in an

aqueous medium, for example. Aldehydes (e.g., glutaraldehyde or formaldehyde) can be used to crosslink starch.

[0486] 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 and/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.

[0487] 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.

[0488] 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.

[0489] 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).

[0490] In the case of thermal reactivity, the biocarbon pellet can comprise 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 low temperatures and in an oxidative atmosphere, to cause the internal temperature of a biocarbon pellet to rise.

[0491] 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.

[0492] In some embodiments, biocarbon pellets comprise one or more additives (that are not necessarily binders), such as inorganic bentonite clay, limestone, starch, cellulose, lignin, or acrylamides. When lignin is used as a binder or other additive, the lignin can be obtained from the same biomass feedstock as used in the pyrolysis process. For example, a starting biomass feedstock can be subjected to a lignin-extraction step, removing a quantity of lignin for use as a binder or additive.

[0493] Other possible additives comprising 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 the group comprising a metal, a metal oxide, a metal hydroxide, a metal halide, or a combination thereof. For example, an additive can be selected from (but not limited to) the group comprising sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron halide, iron chloride, iron bromide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, or a combination thereof. Additives can be added before, during, or after any one or more steps of the process, including into the feedstock itself at any time, before or after it is harvested.

[0494] Biocarbon pellets disclosed herein comprise a wide variety of downstream uses. The biocarbon pellets can be stored, sold, shipped, and converted to other products. The biocarbon pellets can be pulverized for use in a boiler, to combust the carbon and generate electrical energy and/or heat. The biocarbon pellets can be pulverized, crushed, or milled for feeding into a furnace, such as a blast furnace in metal making. The biocarbon pellets can be fed directly into a furnace, such as a Tecnored furnace in metal making. The biocarbon pellets can be pulverized, crushed, or milled for feeding into a gasifier for purposes of making syngas from the biocarbon pellets.

[0495] In many embodiments, the biocarbon pellets are fed to a furnace, either directly or following a step to pulverize, crush, mill, or otherwise reduce particle size. A furnace can be a blast furnace, a top-gas recycling blast furnace, a shaft furnace, a reverberatory furnace (also known as an air furnace), a crucible furnace, a muffling furnace, a retort furnace, a

flash furnace, a Tecnored furnace, an Ausmelt furnace, an ISASMELT furnace, a puddling furnace, a Bogie hearth furnace, a continuous chain furnace, a pusher furnace, a rotary hearth furnace, a walking beam furnace, an electric arc furnace, an induction furnace, a basic oxygen furnace, a puddling furnace, a Bessemer furnace, a direct-reduced-metal furnace, or a combination or derivative thereof.

[0496] 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 containing biocarbon pellets, the pellets can then be ground, combusted, gasified, or otherwise reused or recycled.

Pyrolysis Processes and Systems

[0497] Processes and systems suitable for pyrolyzing a biomass feedstock, or a biogenic reagent together with condenser liquid, will now be further described in detail. Descriptions of a pyrolysis reactor (or reaction) will be understood as references to a reactor (or reaction) specifically for producing a high-fixed-carbon material in some instances.

[0498] "Pyrolysis" and "pyrolyze" generally refer to thermal decomposition of a carbonaceous material. In pyrolysis, less oxygen is present than is required for complete combustion of the material, such as less than 10%, 5%, 1%, 0.5%, 0.1%, or 0.01% of the oxygen (O_2 molar basis) that is required for complete combustion. In some embodiments, pyrolysis is performed in the absence of oxygen.

[0499] Exemplary changes that can occur during pyrolysis comprise any of the following: (i) heat transfer from a heat source increases the temperature inside the feedstock; (ii) the initiation of primary pyrolysis reactions at this higher temperature releases volatiles and forms a char; (iii) the flow of hot volatiles toward cooler solids results in heat transfer between hot volatiles and cooler unpyrolyzed feedstock; (iv) condensation of some of the volatiles in the cooler parts of the feedstock, followed by secondary reactions, can produce tar; (v) autocatalytic secondary pyrolysis reactions proceed while primary pyrolytic reactions simultaneously occur in competition; and (vi) further thermal decomposition,

reforming, water-gas shift reactions, free-radical recombination, and/or dehydrations can also occur, which are a function of the residence time, temperature, and pressure profile.

[0500] Pyrolysis can at least partially dehydrate a starting feedstock (e.g., lignocellulosic biomass). In various embodiments, pyrolysis removes greater than about 50%, 75%, 90%, 95%, 99%, or more of the water from the starting feedstock.

[0501] In some embodiments, a starting biomass feedstock is selected from the group comprising 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 and/or demolition waste, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof. Note that typically a biomass feedstock comprises at least carbon, hydrogen, and oxygen.

[0502] The biogenic reagent can comprise at least about 50 wt%, at least about 75 wt%, or at least about 90 wt% total carbon. In various embodiments, the biogenic reagent comprises about, at least about, or at most about 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, or 99 wt% carbon. The total carbon is fixed carbon plus non-fixed carbon that is present in volatile matter. In some embodiments, component weight percentages are on an absolute basis, which is assumed unless stated otherwise. In other embodiments, component weight percentages are on a moisture-free and ash-free basis. Compositions of low-fixed-carbon materials and high-fixed-carbon materials have been discussed in detail above.

[0503] 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.

[0504] 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.

[0505] In some non-limiting embodiments, the temperatures and residence times are selected to achieve slow pyrolysis chemistry. The benefit is potentially the substantial preservation of cell walls comprised in the biomass structure, which means the final product can retain some, most, or all of the shape and strength of the starting biomass. In order to maximize this potential benefit, it is preferred to utilize apparatus that does not mechanically destroy the cell walls or otherwise convert the biomass particles into small fines. Certain reactor configurations are discussed following the process description below.

[0506] 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.

[0507] 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.

[0508] 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.

[0509] 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 and/or become adsorbed onto the carbon. Thus, in some embodiments, the final carbonaceous material is not simply be the solid, devolatilized residue of the processing steps, but rather can comprise additional carbon that has been deposited from the gas phase, such as by decomposition of organic vapors (e.g., tars) that can form carbon.

[0510] Certain embodiments extend the concept of additional carbon formation by comprising a separate unit in which cooled carbon is subjected to an environment comprising 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.

[0511] There are a large number of options as to intermediate input and output (purge or probe) streams of one or more phases present in any particular zone, various mass and energy recycle schemes, various additives that can be introduced anywhere in the process, adjustability of process conditions comprising 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.

[0512] Some embodiments do not employ fast pyrolysis, and some embodiments do not employ slow pyrolysis. Surprisingly high-quality carbon materials, comprising compositions with very high fractions of fixed carbon, can be obtained from the disclosed processes and systems.

[0513] In some embodiments, a pyrolysis process for producing a biogenic reagent comprises the following steps:

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

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

(c) separating at least the condensable vapors and at least the non-condensable gases from the hot pyrolyzed solids;

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

(e) recovering a biogenic reagent comprising at least the cooled pyrolyzed solids.

The pyrolysis process can further comprise:

(f) drying the feedstock to remove at least moisture comprised within the feedstock; and/or

(g) deaerating the feedstock to remove at least interstitial oxygen, if any, comprised with the feedstock.

[0514] "Biomass," for purposes of this disclosure, shall be construed as any biogenic feedstock or mixture of a biogenic and non-biogenic feedstocks. Elementally, biomass comprises at least carbon, hydrogen, and oxygen. The methods and apparatus can accommodate a wide range of feedstocks of various types, sizes, and moisture contents.

[0515] Biomass comprises, for example, plant and plant-derived material, vegetation, agricultural waste, forestry waste, wood waste, paper waste, animal-derived waste, poultry-derived waste, and municipal solid waste. In various embodiments utilizing biomass, the biomass feedstock can comprise one or more materials selected from: timber harvesting residues, softwood chips, hardwood chips, tree branches, tree stumps, knots, leaves, bark, sawdust, off-spec paper pulp, cellulose, corn, corn stover, wheat straw, rice straw, sugarcane bagasse, switchgrass, miscanthus, animal manure, municipal garbage, municipal sewage, commercial waste, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, grass pellets, hay pellets, wood pellets, cardboard, paper, carbohydrates, plastic, and cloth. A person of ordinary skill in the art will readily appreciate that the feedstock options are virtually unlimited.

[0516] The present technology can also be used for carbon-comprising feedstocks other than biomass, such as a fossil fuel (e.g., coal or petroleum coke), or any mixtures of biomass and fossil fuels (such as biomass/coal blends). In some embodiments, a biogenic feedstock is, or comprises, coal, oil shale, crude oil, asphalt, or solids from crude-oil processing (such as petcoke). Feedstocks can comprise waste tires, recycled plastics, recycled paper, construction waste, deconstruction waste, and other waste or recycled materials. For the avoidance of doubt, any method, apparatus, or system described herein can be used with any carbonaceous feedstock. Carbon-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.

[0517] 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. In some embodiments, the feedstock can be dried prior to processing.

[0518] 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.

[0519] It is noted that size reduction is a costly and energy-intensive process. Pyrolyzed material can be sized with significantly less energy input—that is, it can be preferred to reduce the particle size of the product, not the feedstock. This is an option because the process does not require a fine starting material, and there is not necessarily any significant particle-size reduction during processing. The ability to process very large pieces of feedstock is a significant economic advantage. Notably, some market applications of the high-carbon product actually require large sizes (e.g., on the order of centimeters), so that in some embodiments, large pieces are fed, produced, and sold.

[0520] When it is desired to produce a final carbonaceous biogenic reagent that comprises structural integrity, such as in the form of cylinders, there are at least two options. 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 and/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 comprise similar geometrical shapes, such as spheres, cylinders, or cubes.

[0521] 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.

[0522] 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.

[0523] It is usually desirable to provide a 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, comprising partial oxidation to syngas, will reduce the carbon yield to solids.

[0524] 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.

[0525] 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 comprises lower than 21 vol% O_2 can be employed, at varying effectiveness. In some embodiments, nitrogen is employed. In some embodiments, CO and/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.

[0526] In principle, the effluent 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.

[0527] Various types of deaeration units can be employed. If drying it to be performed, it can be preferable to dry and then deaerate since it can be inefficient to scrub soluble oxygen out of the moisture present. In certain embodiments, the drying and deaerating steps are combined into a single unit, or some amount of deaeration is achieved during drying, and so on.

[0528] In some embodiments, the dried and/or 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, comprising screw feeders or lock hoppers, for example. In some embodiments, a material feed system incorporates an air knife.

[0529] In some embodiments, when a single reactor is employed, multiple zones are 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, and/or pressure in order to adjust the overall process performance.

[0530] References to "zones" shall be broadly construed to comprise regions of space within a single physical unit, physically separate units, or a 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.

[0531] 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 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.

[0532] Some embodiments employ a first zone that is operated under conditions of preheating and/or mild pyrolysis. The temperature of the first zone can be selected at least about 150°C to at most about 500°C, such as about 300°C to at most about 400°C. In some embodiments, 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.

[0533] All references to zone temperatures in this specification should be construed in a non-limiting way to comprise temperatures that can apply to the bulk solids present, or the gas phase, or the reactor walls (on the process side). It will be understood that there will be a temperature gradient in each zone, both axially and radially, as well as temporally (i.e., following start-up or due to transients). Thus, references to zone temperatures can be references to average temperatures or other effective temperatures that can influence the actual kinetics. Temperatures can be directly measured by thermocouples or other temperature probes, or indirectly measured or estimated by other means.

[0534] 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 at least about 250°C to at most about 700°C, such as about, or at least about, or at most about 300°C, 350°C, 400°C, 450°C, 500°C, 550°C, 600°C, or 650°C. Within this zone, preheated biomass undergoes pyrolysis chemistry to release gases and condensable vapors, leaving a significant amount of solid material as a high-carbon reaction intermediate. Biomass components (primarily cellulose, hemicellulose, and lignin) decompose and create vapors, which escape by penetrating through pores or creating new pores. The preferred temperature will at least depend on the residence time of the second zone, as well as the nature of the feedstock and desired product properties.

[0535] 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 at least about 100°C to at most about 550°C, such as about 150°C to at most about 350°C.

[0536] 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.

[0537] 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.

[0538] 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.

[0539] The solids residence time of the preheating zone can be selected at least about 5 min to at most 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 might not be desirable as it would contribute to higher capital cost, unless some amount of mild pyrolysis is intended in the preheating zone.

[0540] The solids residence time of the pyrolysis zone can be selected at least about 10 min to at most 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.

[0541] 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.

[0542] The solids residence time of the cooling zone can be selected at least about 5 min to at most 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 might not be desirable, unless some amount of secondary pyrolysis is desired.

[0543] 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 at least about 0.1 min to at most 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 at least about 0.1 min to at most 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 at least about 0.1 min to at most 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.

[0544] 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.

[0545] 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.

[0546] The pressure in each zone can be separately selected and controlled. The pressure of each zone can be independently selected at least about 1 kPa to at most 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.

[0547] 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).

[0548] 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.

[0549] The step of separating at least the condensable vapors and at least 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.

[0550] 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.

[0551] 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.

[0552] 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.

[0553] In certain embodiments, the sweep gas in conjunction with a low process pressure, such as atmospheric pressure, provides for fast vapor removal without large amounts of inert gas necessary.

[0554] 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.

[0555] 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 and/or pyrolysis zones. In some embodiments, the sweep gas is introduced into the pyrolysis zone and extracted from the pyrolysis and/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.

[0556] 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.

[0557] 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.

[0558] The volatiles-containing sweep gas can exit from the one or more reactor zones, and can be combined if obtained from multiple zones. The resulting gas stream, containing 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.

[0559] 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. In some embodiments, the energy content of the thermal oxidizer effluent is recovered, such as in a waste-heat recovery unit. The energy content can also be recovered by heat exchange with another stream (such as the sweep gas). The energy content can be utilized by directly or indirectly heating, or assisting with heating, a unit elsewhere in the process, such as the dryer or the reactor. In some embodiments, essentially all of the thermal oxidizer effluent is employed for indirect heating (utility side) of the dryer. The thermal oxidizer can employ other fuels than natural gas.

[0560] 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.

[0561] 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.

[0562] In alternative embodiments, these compounds are 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, containing various vapors, can be condensed, at least in part, and then passed over cooled pyrolyzed solids derived from the cooling zone and/or from the separate cooling unit. These embodiments are described in more detail below.

[0563] 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 and/or rapidly cool the solids to, for example, a temperature less than 40°C, such as ambient temperature. In some embodiments, a water quench is employed for rapid cooling. In some embodiments, a fluidized-bed cooler is employed. A "cooling unit" should be broadly construed to also include containers, tanks, pipes, or portions thereof.

[0564] 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. In some embodiments, 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.

[0565] 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.

[0566] 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. 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.

[0567] Various additives can be introduced throughout the process, before, during, or after any step disclosed herein. The additives can be broadly classified as process additives, selected to improve process performance such as carbon yield or pyrolysis time/temperature to achieve a desired carbon purity; and product additives, selected to improve one or more properties of the biogenic reagent, or a downstream product incorporating the reagent. Certain additives can provide enhanced process *and* product (biogenic reagents or products containing biogenic reagents) characteristics.

[0568] 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.

[0569] In some embodiments, an additive is selected from a metal, a metal oxide, a metal hydroxide, or a combination thereof. For example an additive can be selected from, but is by no means limited to, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, magnesium oxide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, or a combination thereof.

[0570] 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.

[0571] 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 ($FeCl_2$ and/or $FeCl_3$), iron bromide ($FeBr_2$ and/or $FeBr_3$), or hydrates thereof, and any combinations thereof.

[0572] 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.

[0573] 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.

[0574] 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 the biogenic reagent that comprises the additive, thereby improving the final strength.

[0575] 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.

[0576] 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.

[0577] In some embodiments, additives applied to the feedstock can reduce energy requirements for the pyrolysis, and/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.

[0578] The throughput, or process capacity, can vary widely from small laboratory-scale units to full operations, comprising 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.

[0579] In some embodiments, 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.

[0580] In some embodiments, pyrolyzed material is recovered and then fed to a separate unit for further pyrolysis, to create a product with higher carbon purity (e.g., conversion of low-fixed-carbon material to high-fixed-carbon material). In some embodiments, the secondary process can be conducted in a simple 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 comprise process tanks, barrels, bins, totes, sacks, and roll-offs. This secondary sweep gas with volatiles can be sent to the thermal oxidizer, or back to the main process reactor, for example. To cool the final product, another stream of inert gas, which is initially at ambient temperature for example, can be passed through the solids to cool the solids, and then returned to an inert gas preheat system.

[0581] Some variations utilize a 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 biogenic reagent recovery unit, disposed in operable communication with the solids cooler.

[0582] Some variations utilize a 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 and/or mildly pyrolyze the feedstock;

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

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

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

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

[0583] 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.

[0584] 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.

[0585] In some embodiments, the dryer can be configured as a drying zone within the multiple-zone reactor. In some embodiments, 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).

[0586] The system can comprise a purging means for removing oxygen from the system. For example, the purging means can comprise one or more inlets to introduce a substantially inert gas, and one or more outlets to remove the substantially inert gas and displaced oxygen from the system. In some embodiments, the purging means is a deaerater disposed in operable communication between the dryer and the multiple-zone reactor.

[0587] In some embodiments, the multiple-zone reactor is 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.

[0588] In some embodiments, the multiple-zone reactor is configured with a second gas inlet and/or a second gas outlet. In some embodiments, the multiple-zone reactor is configured with a third gas inlet and/or a third gas outlet. In some embodiments, the multiple-zone reactor is configured with a fourth gas inlet and/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.

[0589] 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 comprising 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.

[0590] In certain 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.

[0591] As intended herein, "monitor and control" via reaction gas probes should be construed to comprise any one or more sample extractions via reaction gas probes, and in some embodiments 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.).

[0592] A reaction gas probe can be configured to withdraw gas samples in a number of ways. For example, a sampling line can comprise 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).

[0593] 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 comprise 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.

[0594] 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 and/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.

[0595] 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).

[0596] 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.

[0597] 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.

[0598] 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.

[0599] The pyrolysis reactor or reactors can be selected from any suitable reactor configuration that is capable of carrying out the pyrolysis process. Exemplary reactor

configurations comprise, but are not limited to, fixed-bed reactors, fluidized-bed reactors, entrained-flow reactors, augers, ablative reactors, rotating cones, rotary drum kilns, calciners, roasters, moving-bed reactors, transport-bed reactors, ablative reactors, rotating cones, or microwave-assisted pyrolysis reactors.

[0600] In some embodiments in which an auger is used, sand or another heat carrier can 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.

[0601] 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.

[0602] In some embodiments in which a fluidized-bed reactor is used, the feedstock can be introduced into a bed of hot sand fluidized by a gas, which is typically a recirculated product gas. Reference herein to "sand" shall also comprise similar, substantially inert materials, such as glass particles, recovered ash particles, and the like. High heat-transfer rates from fluidized sand can result in rapid heating of the feedstock. There can be some ablation by attrition with the sand particles. Heat is usually provided by heat-exchanger tubes through which hot combustion gas flows.

[0603] Circulating fluidized-bed reactors can be employed, wherein gas, sand, and feedstock move together. Exemplary transport gases comprise recirculated product gases and combustion gases. High heat-transfer rates from the sand ensure rapid heating of the feedstock, and ablation is expected to be stronger than with regular fluidized beds. A separator can be employed to separate the product gases from the sand and char particles. The sand particles can be reheated in a fluidized burner vessel and recycled to the reactor.

[0604] 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.

[0605] In various embodiments the reactor comprises at least two, three, four, or more reaction zones. Each of the reaction zones is disposed in communication with separately adjustable heating means independently selected from the group comprising 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.

[0606] 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 comprising all reaction zones present in the reactor.

[0607] The reactor can be equipped with a second gas inlet and/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.

[0608] 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.

[0609] 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.

[0610] Other means of agitating solids can be employed, such as augers, screws, or paddle conveyors. In some embodiments, the reactor comprises a single, continuous auger disposed throughout each of the reaction zones. In other embodiments, the reactor comprises twin screws disposed throughout each of the reaction zones.

[0611] 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.

[0612] In some embodiments, the system further comprises a thermal oxidizer disposed in operable communication with the outlet at which condensable vapors and non-condensable gases are removed. In some embodiments, the thermal oxidizer is 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 the condensable vapors. Certain non-condensable gases can also be oxidized, such as CO or CH_4, to CO_2.

[0613] When a thermal oxidizer is employed, the system can comprise a heat exchanger disposed between the thermal oxidizer and the dryer, configured to utilize the heat of the combustion for the dryer. This embodiment can contribute significantly to the overall energy efficiency of the process.

[0614] In some embodiments, the system further comprises a carbon-enhancement unit, disposed in operable communication with the solids cooler, configured for combining condensable vapors, in at least partially condensed form, with the solids. The carbon-enhancement unit can increase the carbon content of the biogenic reagent obtained from the recovery unit.

[0615] The system can further comprise a separate pyrolysis unit adapted to further pyrolyze the biogenic reagent to further increase its carbon content. The separate pyrolysis unit can be a simply container, unit, or device, such as a tank, barrel, bin, drum, tote, sack, or roll-off.

[0616] 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.

[0617] Some variations relating to carbon enhancement of solids will now be further described. In some embodiments, a process for producing a biogenic reagent comprises:

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

(b) 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 at least about 250°C to at most about 700°C, to generate hot pyrolyzed solids, condensable vapors, and non-condensable gases;

(c) separating at least the condensable vapors and at least the non-condensable gases from the hot pyrolyzed solids;

(d) 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;

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

(f) recovering a biogenic reagent comprising at least the enhanced pyrolyzed solids.

The process can further comprise:

(g) drying the feedstock to remove at least moisture comprised within the feedstock;

(h) deaerating the feedstock to remove at least interstitial oxygen, if any, comprised with the feedstock; and/or

(i) cooling the warm pyrolyzed solids to generate cool pyrolyzed solids;

[0618] In some embodiments, step (h) comprises passing at least the condensable vapors from step (e), in vapor and/or condensed form, across the warm pyrolyzed solids, to produce enhanced pyrolyzed solids with increased carbon content. In some embodiments, step (h) comprises passing at least the non-condensable gases from step (e) across the warm pyrolyzed solids, to produce enhanced pyrolyzed solids with increased carbon content.

[0619] Alternatively, or additionally, vapors or gases can be contacted with the cool pyrolyzed solids. In some embodiments, step (h) comprises passing at least the condensable vapors from step (e), in vapor and/or condensed form, across the cool pyrolyzed solids, to produce enhanced pyrolyzed solids with increased carbon content. In some embodiments, step (h) comprises passing at least the non-condensable gases from step (e) across the cool pyrolyzed solids, to produce enhanced pyrolyzed solids with increased carbon content.

[0620] In certain embodiments, step (h) comprises passing substantially all of the condensable vapors from step (e), in vapor and/or condensed form, across the cool pyrolyzed solids, to produce enhanced pyrolyzed solids with increased carbon content. In certain embodiments, step (h) comprises passing substantially all of the non-condensable gases from step (e) across the cool pyrolyzed solids, to produce enhanced pyrolyzed solids with increased carbon content.

[0621] The process can comprise various methods of treating or separating the vapors or gases prior to using them for carbon enhancement. For example, an intermediate feed stream comprising at least the condensable vapors and at least 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.

[0622] Separation techniques can comprise or use distillation columns, flash vessels, centrifuges, cyclones, membranes, filters, packed beds, capillary columns, and so on. Separation can be principally based, for example, on distillation, absorption, adsorption, or diffusion, and can utilize differences in vapor pressure, activity, molecular weight, density, viscosity, polarity, chemical functionality, affinity to a stationary phase, and any combinations thereof.

[0623] 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.

[0624] Thus in some embodiments, the first output stream comprises the condensable vapors, and the second output stream comprises the non-condensable gases. The condensable vapors can comprise at least one carbon-comprising compound selected from terpenes, alcohols, acids, aldehydes, or ketones. The vapors from pyrolysis can comprise aromatic compounds such as benzene, toluene, ethylbenzene, and xylenes. Heavier aromatic compounds, such as refractory tars, can be present in the vapor. The non-condensable gases can comprise at least one carbon-comprising molecule selected from the group comprising carbon monoxide, carbon dioxide, and methane.

[0625] 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.

[0626] 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 the group comprising methanol, furfural, and acetic acid. The non-polar compounds can comprise at least one carbon-comprising molecule selected from the group comprising carbon monoxide, carbon dioxide, methane, a terpene, and a terpene derivative.

[0627] Step (h) can increase the total carbon content of the biogenic reagent, relative to an otherwise-identical process without step (h). The extent of increase in carbon content can be, for example, about 1%, 2%, 5%, 10%, 15%, 25%, or even higher, in various embodiments.

[0628] In some embodiments, step (h) increases the fixed carbon content of the biogenic reagent. In these or other embodiments, step (h) increases the volatile carbon content of the biogenic reagent. Volatile carbon content is the carbon attributed to volatile matter in the reagent. The volatile matter can be, but is not limited to, hydrocarbons comprising aliphatic or aromatic compounds (e.g., terpenes); oxygenates comprising 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.

[0629] 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 volatile. This residual volatility can be more advantageous for fuel applications, compared to product applications requiring high surface area and porosity.

[0630] Step (h) can increase the energy content (i.e., energy density) of the biogenic reagent. The increase in energy content can result from an increase in total carbon, fixed carbon, volatile carbon, or even hydrogen. The extent of increase in energy content can be, for example, about 1%, 2%, 5%, 10%, 15%, 25%, or even higher, in various embodiments.

[0631] Further separations can be employed to recover one or more non-condensable gases or condensable vapors, for use within the process or further processing. For example, further processing can be comprised to produce refined carbon monoxide and/or hydrogen.

[0632] 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.

[0633] Condensable vapors can be used for either energy in the process (such as by thermal oxidation) or in carbon enrichment, to increase the carbon content of the biogenic reagent. Certain non-condensable gases, such as CO or CH_4, can be utilized either for energy in the process, or as part of the substantially inert gas for the pyrolysis step. Combinations of any of the foregoing are also possible.

[0634] A potential benefit of comprising 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, and/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.

[0635] 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.

[0636] In some embodiments, a batch or continuous process for producing a 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.

[0637] 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 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.

[0638] In some embodiments, the process further comprises recycling or reusing the gas stream for repeating the process to further increase carbon and/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 and/or energy content of another feedstock different from the carbon-comprising material.

[0639] In some embodiments, the process further comprises introducing the gas stream to a separation unit configured to generate at least first and second output streams, wherein the gas stream comprises a mixture of condensable carbon-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.

[0640] 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.

[0641] The carbon-comprising product can comprise an increased total carbon content, a higher fixed carbon content, a higher volatile carbon content, a higher energy content, or a combination thereof, relative to the starting carbon-comprising material.

[0642] In related variations, a 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 and/or the non-condensable gases across the solids, to form enhanced solids with increased carbon content; and

(f) a biogenic reagent recovery unit, disposed in operable communication with the material-enrichment unit.

[0643] 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.

[0644] 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 and/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.

[0645] 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 the condensable vapors and/or the non-condensable gases.

[0646] The present technology is capable of producing a variety of compositions useful as biogenic reagents, and products incorporating such reagents. In some variations, a biogenic reagent is produced by any process disclosed herein, such as a process comprising the steps of:

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

(b) 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 at least about 250°C to at most about 700°C, to generate hot pyrolyzed solids, condensable vapors, and non-condensable gases;

(c) separating at least the condensable vapors and at least the non-condensable gases from the hot pyrolyzed solids;

(d) 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;

(e) cooling the warm pyrolyzed solids to generate cool pyrolyzed solids; and

(f) recovering a biogenic reagent comprising at least the cool pyrolyzed solids.

In some embodiments, the process further comprises the steps of:

(g) drying the feedstock to remove at least moisture comprised within the feedstock; and/or

(h) deaerating the feedstock to remove at least interstitial oxygen, if any, comprised with the feedstock.

[0647] In some embodiments, the reagent comprises about at least 70 wt%, at least 80 wt%, at least 90 wt%, or at least 95 wt% total carbon on a dry basis. The total carbon comprises at least fixed carbon, and can further comprise carbon from volatile matter. In some embodiments, carbon from volatile matter is about at least 5%, at least 10%, at least 25%, or at least 50% of the total carbon present in the biogenic reagent. Fixed carbon can be measured using ASTM D3172, while volatile carbon can be measured using ASTM D3175, for example.

[0648] The biogenic reagent can comprise about 10 wt% or less, such as about 5 wt% or less, hydrogen on a dry basis. The biogenic reagent can comprise about 1 wt% or less, such as about 0.5 wt% or less, nitrogen on a dry basis. The biogenic reagent can comprise about 0.5 wt% or less, such as about 0.2 wt% or less, phosphorus on a dry basis. The biogenic reagent can comprise about 0.2 wt% or less, such as about 0.1 wt% or less, sulfur on a dry basis.

[0649] 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.

[0650] 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 comprising 100% carbon, on a dry/ash-free (DAF) basis.

[0651] Generally speaking, feedstocks such as biomass comprise non-volatile species, comprising 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.

[0652] Various amounts of non-combustible matter, such as ash, can be present. The biogenic reagent can comprise about 10 wt% or less, such as about 5 wt%, about 2 wt%, about 1 wt% or less non-combustible matter on a dry basis. In certain embodiments, the reagent comprises little ash, or even essentially no ash or other non-combustible matter. Therefore, some embodiments provide essentially pure carbon, comprising 100% carbon, on a dry basis.

[0653] Various amounts of moisture can be present. On a total mass basis, the biogenic reagent can comprise at least 1 wt%, 2 wt%, 5 wt%, 10 wt%, 15 wt%, 25 wt%, 35 wt%, 50 wt%, or more moisture. As intended herein, "moisture" is to be construed as comprising any form of water present in the biogenic reagent, comprising 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.

[0654] The biogenic reagent can comprise various energy contents which for present purposes means the energy density based on the higher heating value associated with total combustion of the bone-dry reagent. For example, the biogenic reagent can possess an energy content of about at least 11,000 Btu/lb, at least 12,000 Btu/lb, at least 13,000 Btu/lb, at least 14,000 Btu/lb, or at least 15,000 Btu/lb. In certain embodiments, the energy content

is between about 14,000-15,000 Btu/lb. The energy content can be measured using ASTM D5865, for example.

[0655] The biogenic reagent can be formed into a powder, such as a coarse powder or a fine powder. For example, the reagent can be formed into a powder with an average mesh size of about 200 mesh, about 100 mesh, about 50 mesh, about 10 mesh, about 6 mesh, about 4 mesh, or about 2 mesh, in embodiments.

[0656] In some embodiments, the biogenic reagent is formed into structural objects comprising pressed, binded, or agglomerated particles. The starting material to form these objects can be a powder form of the reagent, such as an intermediate obtained by particle-size reduction. The objects can be formed by mechanical pressing or other forces. In some embodiments, the objects can be formed by mechanical pressing or other forces with a binder or other means of agglomerating particles together.

[0657] In some embodiments, the biogenic reagent is produced in the form of structural objects whose structure substantially derives from the feedstock. For example, feedstock chips can produce product chips of biogenic reagent. Or, feedstock cylinders can produce biogenic reagent cylinders, which can be somewhat smaller but otherwise maintain the basic structure and geometry of the starting material.

[0658] A biogenic reagent can be produced as, or formed into, an object that comprises 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.

[0659] Other variations relate to the incorporation of additives into the process, into the product, or both. In some embodiments, the biogenic reagent comprises at least one process additive incorporated during the process. In these or other embodiments, the reagent comprises at least one product additive introduced to the reagent following the process.

[0660] In some embodiments, a biogenic reagent comprises, on a dry basis:

70 wt% or more total carbon;

5 wt% or less hydrogen;

1 wt% or less nitrogen;

0.5 wt% or less phosphorus;

0.2 wt% or less sulfur; and

an additive selected from a metal, a metal oxide, a metal hydroxide, a metal halide, or a combination thereof.

[0661] The additive can be selected from, but is by no means limited to, magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, magnesium oxide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, or a combination thereof.

[0662] In some embodiments, a biogenic reagent comprises, on a dry basis:

70 wt% or more total carbon;

5 wt% or less hydrogen;

1 wt% or less nitrogen;

0.5 wt% or less phosphorus;

0.2 wt% or less sulfur; and

an additive selected from an acid, a base, or a salt thereof.

[0663] 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.

[0664] In certain embodiments, a biogenic reagent comprises, on a dry basis:

70 wt% or more total carbon;

5 wt% or less hydrogen;

1 wt% or less nitrogen;

0.5 wt% or less phosphorus;

0.2 wt% or less sulfur;

a first additive selected from a metal, metal oxide, metal hydroxide, a metal halide, or a combination thereof; and

a second additive selected from an acid, a base, or a salt thereof,

wherein the first additive is different from the second additive.

[0665] The first additive can be selected from magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, magnesium oxide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, or a combination thereof, while the second additive can be independently selected from sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, or combinations thereof.

[0666] A certain biogenic reagent consists essentially of, on a dry basis, carbon, hydrogen, nitrogen, phosphorus, sulfur, non-combustible matter, and an additive selected from the group comprising magnesium, manganese, aluminum, nickel, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, magnesium oxide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, or a combination thereof.

[0667] A certain biogenic reagent consists essentially of, on a dry basis, carbon, hydrogen, nitrogen, phosphorus, sulfur, non-combustible matter, and an additive selected from the group comprising sodium hydroxide, potassium hydroxide, magnesium oxide, hydrogen bromide, hydrogen chloride, sodium silicate, or a combination thereof.

[0668] The amount of additive (or total additives) can vary widely, such as at least about 0.01 wt% to at most about 25 wt%, comprising about 0.1 wt%, about 1 wt%, about 5 wt%, about 10 wt%, or about 20 wt%. It will be appreciated then when 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 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.

[0669] 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.

[0670] In certain embodiments, the majority of carbon contained in the biogenic reagent is classified as renewable carbon. In some embodiments, substantially all of the carbon is classified as renewable carbon. There can be certain market mechanisms (e.g., Renewable Identification Numbers, tax credits, etc.) wherein value is attributed to the renewable carbon content within the biogenic reagent.

[0671] 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.

[0672] The biogenic reagents produced as described herein is useful for a wide variety of carbonaceous products. The biogenic reagent can be a desirable market product itself. Biogenic reagents as provided herein are associated with lower levels of impurities, reduced process emissions, and improved sustainability (including higher renewable carbon content) compared to the state of the art.

[0673] In variations, a product comprises any of the biogenic reagents that can be obtained by the disclosed processes, or that are described in the compositions set forth herein, or any portions, combinations, or derivatives thereof.

[0674] Generally speaking, the biogenic reagents can be combusted to produce energy (including electricity and heat); partially oxidized, gasified, or steam-reformed to produce syngas; utilized for their adsorptive or absorptive properties; utilized for their reactive properties during metal refining (such as reduction of metal oxides) or other industrial processing; or utilized for their material properties in carbon steel and various other metal alloys. Essentially, the biogenic reagents can be utilized for any market application of carbon-based commodities or advanced materials, including specialty uses to be developed.

[0675] Prior to suitability or actual use in any product applications, the disclosed biogenic reagents can be analyzed and measured in various ways. In some embodiments, the disclosed biogenic reagents can be further 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.

[0676] Products or materials that can incorporate these 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.

[0677] Use of the disclosed biogenic reagents in metals production can reduce slag, increase overall efficiency, and reduce lifecycle environmental impacts. Therefore, some embodiments are particularly well-suited for metal processing and manufacturing.

[0678] Some variations utilize the biogenic reagents as carbon-based blast furnace addition products. A blast furnace is a type of metallurgical furnace used for smelting to produce industrial metals, such as (but not limited to) iron. Smelting is a form of extractive metallurgy; its main use is to produce a metal from its ore. Smelting uses heat and a chemical reducing agent to decompose the ore. The carbon and/or the carbon monoxide derived from the carbon removes oxygen from the ore, leaving behind elemental metal.

[0679] The reducing agent can consist of, or comprise, a biogenic reagent. In a blast furnace, biogenic reagent, ore, and typically limestone can be continuously supplied through the top of the furnace, while air is blown into the bottom of the chamber, so that the chemical reactions take place throughout the furnace as the material moves downward. In some embodiments, the air is enriched with oxygen. 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.

[0680] 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.

[0681] The Coke Reactivity test is a highly regarded measure of the performance of carbon in a blast furnace. This test comprises 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.

[0682] In some embodiments, the biogenic reagent provides a carbon product comprising suitable properties for introduction directly into a blast furnace.

[0683] The strength of the biogenic reagent can be determined by any suitable method known in the art, for example by a drop-shatter test, or a CSR test. In some embodiments, the biogenic reagent, which can be blended with another source of carbon, provides a final carbon product comprising CSR of at least about 50%, 60%, or 70%. A combination product can also provide a final coke product comprising a suitable reactivity for combustion in a blast furnace. In some embodiments, the product comprises a CRI such that the biogenic reagent is suitable for use as an additive or replacement for met coal, met coke, coke breeze, foundry coke, or injectable coal.

[0684] Some embodiments employ one or more additives in an amount sufficient to provide a biogenic reagent that, when added to another carbon source (e.g., coke) comprising a CRI or CSR insufficient for use as a blast furnace product, provides a composite product with a CRI and/or CSR sufficient for use in a blast furnace. In some

embodiments, one or more additives are present in an amount sufficient to provide a biogenic reagent comprising a CRI of at most about 40%, 30%, or 20%.

[0685] In some embodiments, one or more additives selected from the alkaline earth metals, or oxides or carbonates thereof, are introduced during or after the process of producing a biogenic reagent. For example, calcium, calcium oxide, calcium carbonate, magnesium oxide, or magnesium carbonate can be introduced as additives. The addition of these compounds before, during, or after pyrolysis can increase the reactivity of the biogenic reagent in a blast furnace. These compounds can lead to stronger materials, i.e. higher CSR, thereby improving blast-furnace efficiency. In addition, additives such as those selected from the alkaline earth metals, or oxides or carbonates thereof, can lead to lower emissions (e.g., SO_2).

[0686] In some embodiments, a blast furnace replacement product is a biogenic reagent comprising at least about 55 wt% carbon, at most about 0.5 wt% sulfur, at most 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 at most about 0.035 wt% phosphorous, and about 0.5 wt% to at most about 50 wt% volatile matter. In some embodiments, the blast furnace replacement product further comprises one or more additives. In some embodiments, the blast furnace replacement product comprises about 2 wt% to at most about 15 wt% dolomite, about 2 wt% to at most about 15 wt% dolomitic lime, about 2 wt% to at most about 15 wt% bentonite, and/or about 2 wt% to at most about 15 wt% calcium oxide. In some embodiments, the blast furnace replacement product has dimensions substantially in the range of about 1 cm to at most about 10 cm.

[0687] In some embodiments, a biogenic reagent is useful as a foundry coke replacement product. Foundry coke is generally characterized as having a carbon content of at least about 85 wt%, a sulfur content of about 0.6 wt%, at most about 1.5 wt% volatile matter, at most about 13 wt% ash, at most about 8 wt% moisture, about 0.035 wt% phosphorus, a CRI value of about 30, and dimensions ranging at least about 5 cm to at most about 25 cm.

[0688] Some variations utilize the biogenic reagents as carbon-based taconite pellet addition products. The ores used in making iron and steel are iron oxides. Major iron oxide

ores include hematite, limonite (also called brown ore), taconite, and magnetite, a black ore. Taconite is a low-grade but important ore, which contains 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.

[0689] 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, containing 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.

[0690] The taconite pellets can be fed to a blast furnace to produce iron, as described above with reference to blast furnace addition products. In some embodiments, a biogenic reagent is introduced to the blast furnace. In these or other embodiments, a biogenic reagent is incorporated into the taconite pellet itself. For example, taconite ore powder, after beneficiation, can be mixed with a biogenic reagent and a binder and rolled into small objects, then baked to hardness. In such embodiments, taconite-carbon pellets with the appropriate composition can conveniently be introduced into a blast furnace without the need for a separate source of carbon.

[0691] Some variations utilize the biogenic reagents as ladle addition carbon-based products. A ladle is a vessel used to transport and pour out molten metals. Casting ladles are used to pour molten metal into molds to produce the casting. Transfers ladle are used to transfer a large amount of molten metal from one process to another. Treatment ladles are used for a process to take place within the ladle to change some aspect of the molten metal, such as the conversion of cast iron to ductile iron by the addition of various elements into the ladle.

[0692] Biogenic reagents can be introduced to any type of ladle, but typically carbon will be added to treatment ladles in suitable amounts based on the target carbon content. Carbon injected into ladles can be in the form of fine powder, for good mass transport of the

carbon into the final composition. In some embodiments, a biogenic reagent, when used as a ladle addition product, has a minimum dimension of about 0.5 cm, such as about 0.75 cm, about 1 cm, about 1.5 cm, or higher.

[0693] In some embodiments, a high-carbon biogenic reagent is useful as a ladle addition carbon additive at, for example, basic oxygen furnace or electric arc furnace facilities wherever ladle addition of carbon would be used (e.g., added to ladle carbon during steel manufacturing).

[0694] In some embodiments, the ladle addition carbon additive additionally comprises at most about 5 wt% manganese, at most about 5 wt% calcium oxide, and/or at most about 5 wt% dolomitic lime.

[0695] Direct-reduced iron (DRI), also called sponge iron, is produced from direct reduction of iron ore (in the form of lumps, pellets, or fines) by a reducing gas conventionally produced from natural gas or coal. The reducing gas is typically syngas, a mixture of hydrogen and carbon monoxide which acts as reducing agent. The biogenic reagent as provided herein can be converted into a gas stream comprising CO, to act as a reducing agent to produce direct-reduced iron.

[0696] Iron nuggets are a high-quality steelmaking and iron-casting feed material. Iron nuggets are essentially all iron and carbon, with almost no gangue (slag) and low levels of metal residuals. They are a premium grade pig iron product with superior shipping and handling characteristics. The carbon comprised in iron nuggets can be the biogenic reagent provided herein. Iron nuggets can be produced through the reduction of iron ore in a rotary hearth furnace, using a biogenic reagent as the reductant and energy source.

[0697] Some variations utilize the biogenic reagents as metallurgical coke carbon-based products. Metallurgical coke, also known as "met" coke, is a carbon material normally manufactured by the destructive distillation of various blends of bituminous coal. The final solid is a non-melting carbon called metallurgical coke. As a result of the loss of volatile gases and of partial melting, met coke comprises an open, porous morphology. Met coke comprises 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.

[0698] 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.

[0699] Met coke can be characterized as comprising a heat value of about 10,000 to 14,000 Btu per pound and an ash content of about 10 wt% or greater. Thus, in some embodiments, a met coke replacement product comprises a biogenic reagent comprising at least about 80 wt%, 85 wt%, or 90 wt% carbon, at most about 0.8 wt% sulfur, at most about 3 wt% volatile matter, at most about 15 wt% ash, at most about 13 wt% moisture, and at most about 0.035 wt% phosphorus. A biogenic reagent, when used as a met coke replacement product, can have a size range at least about 2 cm to at most about 15 cm, for example.

[0700] In some embodiments, the met coke replacement product further comprises an additive such as chromium, nickel, manganese, magnesium oxide, silicon, aluminum, dolomite, fluorospar, calcium oxide, lime, dolomitic lime, bentonite or a combination thereof.

[0701] Some variations utilize the biogenic reagents as coal replacement products. Any process or system using coal can in principle be adapted to use a biogenic reagent.

[0702] In some embodiments, a biogenic reagent is combined with one or more coal-based products to form a composite product comprising a higher rank than the coal-based product(s) and/or comprising fewer emissions, when burned, than the pure coal-based product.

[0703] For example, a low-rank coal such as sub-bituminous coal can be used in applications normally calling for a higher-rank coal product, such as bituminous coal, by combining a selected amount of a biogenic reagent with the low-rank coal product. In other embodiments, the rank of a mixed coal product (e.g., a combination of a plurality of coals of different rank) can be improved by combining the mixed coal with some amount of biogenic

reagent. The amount of a biogenic reagent to be mixed with the coal product(s) can vary depending on the rank of the coal product(s), the characteristics of the biogenic reagent (e.g., carbon content, heat value, etc.) and the desired rank of the final combined product.

[0704] For example, anthracite coal is generally characterized as comprising at least about 80 wt% carbon, about 0.6 wt% sulfur, about 5 wt% volatile matter, at most about 15 wt% ash, at most about 10 wt% moisture, and a heat value of about 12,494 Btu/lb. In some embodiments, an anthracite coal replacement product is a biogenic reagent comprising at least about 80 wt% carbon, at most about 0.6 wt% sulfur, at most about 15 wt% ash, and a heat value of at least about 12,000 Btu/lb.

[0705] In some embodiments, a biogenic reagent is useful as a thermal coal replacement product. Thermal coal products are generally characterized as comprising high sulfur levels, high phosphorus levels, high ash content, and heat values of up to at most about 15,000 Btu/lb. In some embodiments, a thermal coal replacement product is a biogenic reagent comprising at most about 0.5 wt% sulfur, at most about 4 wt% ash, and a heat value of at least about 12,000 Btu/lb.

[0706] Some variations utilize the biogenic reagents as carbon-based coking products. Any coking process or system can be adapted to use biogenic reagents to produce coke, or use it as a coke feedstock.

[0707] In some embodiments, a biogenic reagent is useful as a thermal coal or coke replacement product. For example, a thermal coal or coke replacement product can consist of a biogenic reagent comprising at least about 50 wt% carbon, at most about 8 wt% ash, at most 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 at most about 50 wt % volatile matter. The thermal coal or coke replacement product can comprise about 0.4 wt% to at most about 15 wt% moisture.

[0708] In some embodiments, a biogenic reagent is useful as a petroleum (pet) coke or calcine pet coke replacement product. Calcine pet coke is generally characterized as comprising at least about 66 wt% carbon, up to 4.6 wt% sulfur, at most about 5.5 wt% volatile matter, at most about 19.5 wt% ash, and at most about 2 wt% moisture, and is typically sized

at about 3 mesh or less. In some embodiments, the calcine pet coke replacement product is a biogenic reagent comprising at least about 66 wt% carbon, at most about 4.6 wt% sulfur, at most about 19.5 wt% ash, at most about 2 wt% moisture, and is sized at about 3 mesh or less.

[0709] In some embodiments, a biogenic reagent is useful as a coking carbon replacement carbon (e.g., co-fired with metallurgical coal in a coking furnace). In one embodiment, a coking carbon replacement product is a biogenic reagent comprising at least about 55 wt% carbon, at most about 0.5 wt% sulfur, at most 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 at most about 50 wt% volatile matter, and/or one or more additives.

[0710] Some variations utilize the biogenic reagents as carbon breeze products, which typically comprise very fine particle sizes such as 6 mm, 3 mm, 2 mm, 1 mm, or smaller. In some embodiments, a biogenic reagent is useful as a coke breeze replacement product. Coke breeze is generally characterized as comprising a maximum dimension of at most 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, at most about 13 wt% ash, and at most about 13 wt% moisture. In some embodiments, a coke breeze replacement product is a biogenic reagent comprising at least about 80 wt% carbon, at most about 0.8 wt% sulfur, at most about 20 wt% volatile matter, at most about 13 wt% ash, at most about 13 wt% moisture, and a maximum dimension of about 6 mm.

[0711] In some embodiments, a biogenic reagent is useful as a carbon breeze replacement product during, for example, taconite pellet production or in an iron-making process.

[0712] Some variations utilize the biogenic reagents as feedstocks for various fluidized beds, or as fluidized-bed carbon-based feedstock replacement products. The carbon can be employed in fluidized beds for total combustion, partial oxidation, gasification, steam reforming, or the like. The carbon can be primarily converted into syngas for various downstream uses, comprising production of energy (e.g., combined heat and power), or liquid fuels (e.g., methanol or Fischer-Tropsch diesel fuels).

[0713] In some embodiments, a biogenic reagent is useful as a fluidized-bed coal replacement product in, for example, fluidized bed furnaces wherever coal would be used (e.g., for process heat or energy production).

[0714] Some variations utilize the biogenic reagents as carbon-based furnace addition products. Coal-based carbon furnace addition products are generally characterized as comprising high sulfur levels, high phosphorus levels, and high ash content, which contribute to degradation of the metal product and create air pollution. In some embodiments, a carbon furnace addition replacement product comprising a biogenic reagent comprises at most about 0.5 wt% sulfur, at most about 4 wt% ash, at most 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 at most about 50 wt% volatile matter and about 0.4 wt% to at most about15 wt% moisture.

[0715] In some embodiments, a biogenic reagent is useful as a furnace addition carbon additive at, for example, basic oxygen furnace or electric arc furnace facilities wherever furnace addition carbon would be used. For example, furnace addition carbon can be added to scrap steel during steel manufacturing at electric-arc furnace facilities). For electric-arc furnace applications, high-purity carbon is desired so that impurities are not introduced back into the process following earlier removal of impurities.

[0716] In some embodiments, a furnace addition carbon additive is a biogenic reagent comprising at least about 80 wt% carbon, at most about 0.5 wt% sulfur, at most 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 at most about 5 wt% manganese, at most about 5 wt% fluorospar, about 5 wt% to at most about 10 wt% dolomite, about 5 wt% to at most about 10 wt% dolomitic lime, and/or about 5 wt% to at most about 10 wt% calcium oxide.

[0717] Some variations utilize the biogenic reagents as stoker furnace carbon-based products. In some embodiments, a biogenic reagent is useful as a stoker coal replacement product at, for example, stoker furnace facilities wherever coal would be used (e.g., for process heat or energy production).

[0718] Some variations utilize the biogenic reagents as injectable (e.g., pulverized) carbon-based materials. In some embodiments, a biogenic reagent is useful as an injection-grade calcine pet coke replacement product. Injection-grade calcine pet coke is generally characterized as comprising at least about 66 wt% carbon, about 0.55 to at most about 3 wt% sulfur, up to at most about 5.5 wt% volatile matter, up to at most about 10 wt% ash, up to at most about 2 wt% moisture, and is sized at about 6 mesh or less. In some embodiments, a calcine pet coke replacement product is a biogenic reagent comprising at least about 66 wt% carbon, at most about 3 wt% sulfur, at most about 10 wt% ash, at most about 2 wt% moisture, and is sized at about 6 mesh or less.

[0719] In some embodiments, a biogenic reagent is useful as an injectable carbon replacement product at, for example, basic oxygen furnace or electric arc furnace facilities in any application where injectable carbon would be used (e.g., injected into slag or ladle during steel manufacturing).

[0720] In some embodiments, a biogenic reagent is useful as a pulverized carbon replacement product, for example, wherever pulverized coal would be used (e.g., for process heat or energy production). In some embodiments, the pulverized coal replacement product comprises at most about 10 percent calcium oxide.

[0721] Some variations utilize the biogenic reagents as carbon addition product for metals production. In some embodiments, a biogenic reagent is useful as a carbon addition product for production of carbon steel or another metal alloy comprising carbon. Coal-based late-stage carbon addition products are generally characterized as comprising high sulfur levels, high phosphorous levels, and high ash content, and high mercury levels which degrade metal quality and contribute to air pollution. In some embodiments, the carbon addition product comprises at most about 0.5 wt% sulfur, at most about 4 wt% ash, at most about 0.03 wt% phosphorus, a minimum dimension of about 1 to 5 mm, and a maximum dimension of about 8 to 12 mm.

[0722] Some variations utilize the biogenic reagents within carbon electrodes. In some embodiments, a biogenic reagent is useful as an electrode (e.g. anode) material suitable for use, for example, in aluminum production.

[0723] Other uses of the biogenic reagent in carbon electrodes comprise applications in batteries, fuel cells, capacitors, and other energy-storage or energy-delivery devices. For example, in a lithium-ion battery, the biogenic reagent can be used on the anode side to intercalate lithium. In these applications, carbon purity and low ash can be very important.

[0724] Some variations utilize the biogenic reagents as catalyst supports. Carbon is a known catalyst support in a wide range of catalyzed chemical reactions, such as mixed-alcohol synthesis from syngas using sulfided cobalt-molybdenum metal catalysts supported on a carbon phase, or iron-based catalysts supported on carbon for Fischer-Tropsch synthesis of higher hydrocarbons from syngas.

[0725] Some variations utilize the biogenic reagents as activated carbon products. Activated carbon is used in a wide variety of liquid and gas-phase applications, comprising water treatment, air purification, solvent vapor recovery, food and beverage processing, and pharmaceuticals. For activated carbon, the porosity and surface area of the material are generally important. The biogenic reagent provided herein can provide a superior activated carbon product, in various embodiments, due to (i) greater surface area than fossil-fuel based activated carbon; (ii) carbon renewability; (iii) vascular nature of biomass feedstock in conjunction with additives better allows penetration/distribution of additives that enhance pollutant control; and (iv) less inert material (ash) leads to greater reactivity.

[0726] It should be recognized that in the above description of market applications of biogenic reagents, the described applications are not exclusive, nor are they exhaustive. Thus a biogenic reagent that is described as being suitable for one type of carbon product can be suitable for any other application described, in various embodiments. These applications are exemplary only, and there are other applications of biogenic reagents.

[0727] In addition, in some embodiments, the same physical material can be used in multiple market processes, either in an integrated way or in sequence. Thus, for example, a biogenic reagent that is used as a carbon electrode or an activated carbon can, 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.

[0728] Some embodiments can employ a biogenic reagent both for its reactive/adsorptive properties and also as a fuel. For example, a biogenic reagent injected into an emissions stream can be suitable to remove contaminants, followed by combustion of the biogenic reagent particles and possibly the contaminants, to produce energy and thermally destroy or chemically oxidize the contaminants.

[0729] Significant environmental and product use advantages can be associated with biogenic reagents, compared to conventional fossil-fuel-based products. The biogenic reagents can be not only environmentally superior, but also functionally superior from a processing standpoint because of greater purity, for example.

[0730] 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.

[0731] Use of biogenic reagents in place of coal or coke also significantly reduces environmental emissions of SO_2, hazardous air pollutants, and mercury.

[0732] Also, because of the purity of these biogenic reagents (including low ash content), the disclosed biogenic reagents have the potential to reduce slag and increase production capacity in batch metal-making processes.

[0733] In some embodiments, a biogenic reagent functions as an activated carbon. For example, the low-fixed-carbon material can be activated, the high-fixed-carbon material can be activated, or both materials can be activated such that the biocarbon composition (blend) functions as an activated carbon.

[0734] In certain embodiments, the biogenic reagent is recovered as an activated carbon product, while 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.

[0735] 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).

[0736] 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. In some embodiments, the activated carbon is 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.

[0737] 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.

[0738] The activated carbon can be characterized by an Iodine Number of at least about 500, 750, 1000, 1500, or 2000, for example. In some embodiments, the activated carbon is 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.

[0739] Activated carbon produced by the processes disclosed herein can be used in a number of ways.

[0740] In some embodiments, the activated carbon is utilized internally at the process site to purify the one or more primary products. In some embodiments, the activated carbon is utilized at the site to purify water. In these or other embodiments, the activated carbon is utilized at the site to treat a liquid waste stream to reduce liquid-phase emissions and/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.

[0741] Activated carbon prepared according to the processes disclosed herein can comprise the same or better characteristics as traditional fossil fuel-based activated carbon. In some embodiments, the activated carbon comprises a surface area that is comparable to, equal to, or greater than surface area associated with fossil fuel-based activated carbon. In some embodiments, the activated carbon can control pollutants as well as or better than traditional activated carbon products. In some embodiments, the activated carbon comprises 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 comprises a particle size and/or a particle size distribution that is comparable to, equal to, greater than, or less than a particle size and/or a particle size distribution associated with a traditional activated carbon product. In some embodiments, the activated carbon comprises 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 comprises a particle shape that is substantially different than a particle shape associated with a traditional activated carbon product. In some embodiments, the activated carbon comprises 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 comprises 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 comprises 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 comprises 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 comprises 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 comprises an adsorptive capacity that is comparable to, substantially similar to, or the same as an adsorptive capacity associated with a traditional activated carbon product.

[0742] Prior to suitability or actual use in any product applications, the disclosed activated carbons can be analyzed and measured in various ways. In some embodiments, the disclosed activated carbons can be further modified (such as through additives) in various ways. Some properties of potential interest comprise density, particle size, surface area, microporosity, absorptivity, adsorptivity, binding capacity, reactivity, desulfurization activity, basicity, hardness, and Iodine Number.

[0743] Activated carbon is used commercially in a wide variety of liquid and gas-phase applications, comprising water treatment, air purification, solvent vapor recovery, food and beverage processing, sugar and sweetener refining, automotive uses, and pharmaceuticals. For activated carbon, key product attributes can comprise particle size, shape, composition, surface area, pore volume, pore dimensions, particle-size distribution, the chemical nature of the carbon surface and interior, attrition resistance of particles, hardness, bulk density, and adsorptive capacity.

[0744] The bulk density for the biogenic activated carbon can be at least about 50 g/liter to at most about 650 g/liter, for example.

[0745] The surface area of the biogenic activated carbon can vary widely. Exemplary surface areas (e.g., BET surface areas) range at least about 400 m^2/g to at most 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.

[0746] The pore-size distribution can be important to determine ultimate performance of the activated carbon. Pore-size measurements can comprise micropore content, mesopore content, and macropore content.

[0747] The Iodine Number is a parameter used to characterize activated carbon performance. The Iodine Number measures the degree of activation of the carbon, and is a measure of micropore (e.g., 0–20 Å) content. It is an important measurement for liquid-phase applications. Exemplary Iodine Numbers for activated carbon products produced by embodiments of the disclosure comprise about 500, 600, 750, 900, 1000, 1100, 1200, 1300, 1500, 1600, 1750, 1900, 2000, 2100, and 2200, comprising all intervening ranges. The units of Iodine Number are milligram iodine per gram carbon.

[0748] Another pore-related measurement is Methylene Blue Number, which measures mesopore content (e.g., 20–500 Å). Exemplary Methylene Blue Numbers for activated carbon products produced by embodiments of the disclosure comprise about 100, 150, 200, 250, 300, 350, 400, 450, and 500, comprising all intervening ranges. The units of Methylene Blue Number are milligram methylene blue (methylthioninium chloride) per gram carbon.

[0749] Another pore-related measurement is Molasses Number, which measures macropore content (e.g., >500 Å). Exemplary Molasses Numbers for activated carbon products produced by embodiments of the disclosure comprise about 100, 150, 200, 250, 300, 350, and 400, comprising all intervening ranges. The units of Molasses Number are milligram molasses per gram carbon.

[0750] 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.

[0751] The activated carbon can be characterized by its water-holding capacity. In various embodiments, activated carbon products produced by embodiments of the disclosure comprise a water-holding capacity at 25°C of about 10% to at most about 300% (water weight divided by weight of dry activated carbon), such as at least about 50% to at most about 100%, e.g. about 60-80%.

[0752] 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 at least about 1% to great than about 99%, such as about 1%, about 5%, about 10%, about 15%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, about 50%, about 55%, 60%, about 65%, about 70%, about 75%, about 80%, about 85%, about 90%, about 95%, about 96%, about 97%, about 98%, about 99%, or greater than about 99%.

[0753] 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 comprising an Abrasion Number of about 75%, about 80%, about 85%, about 90%, about 95%, about 96%, about 97%, about 98%, about 99%, or greater than about 99%.

[0754] The biogenic activated carbon provided by the present disclosure comprises 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.

[0755] 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 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 the contaminant-adsorbed carbon particles from the gas-phase emissions stream, to produce a contaminant-reduced gas-phase emissions stream.

[0756] 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.

[0757] A selected contaminant (in the gas-phase emissions stream) can be a metal, such as a metal is selected from the group comprising mercury, boron, selenium, arsenic, and any compound, salt, and mixture thereof. A selected contaminant can be a hazardous air pollutant, an organic compound (such as a VOC), or a non-condensable gas, for example. In some embodiments, a biogenic activated carbon product adsorbs, absorbs and/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 a combination thereof. In some embodiments, the selected contaminant comprises mercury. In some embodiments, the selected contaminant comprises one or more VOCs. In some embodiments, the biogenic activated carbon comprises at least about 1 wt% hydrogen and/or at least about 10 wt% oxygen.

[0758] 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.

[0759] 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 Section 51.100, which is incorporated by reference herein in its entirety.

[0760] 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.

[0761] 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).

[0762] In some embodiments, contaminant-adsorbed carbon particles are treated to regenerate activated carbon particles. In some embodiments, the method comprises thermally oxidizing the contaminant-adsorbed carbon particles. The contaminant-adsorbed carbon particles, or a regenerated form thereof, can be combusted to provide energy.

[0763] In some embodiments, an additive for activated carbon is selected from an acid, a base, a salt, a metal, a metal oxide, a metal hydroxide, a metal halide, or a combination thereof. In certain embodiments, the additive is selected from the group comprising magnesium, manganese, aluminum, nickel, iron, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, magnesium

oxide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide, lime, sodium hydroxide, potassium hydroxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, organic acids (e.g., citric acid), or a combination thereof.

[0764] In some embodiments, the gas-phase emissions stream is derived from metals processing, such as the processing of high-sulfur-content metal ores.

[0765] 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.

[0766] For boilers currently equipped with particulate matter control devices, implementing biogenic activated carbon injection for mercury control could entail: (i) injection of powdered activated carbon upstream of the existing particulate matter control device (electrostatic precipitator or fabric filter); (ii) injection of powdered activated carbon downstream of an existing electrostatic precipitator and upstream of a retrofit fabric filter; or (iii) injection of powdered activated carbon between electrostatic precipitator electric fields. Inclusion of iron or iron-containing compounds can drastically improve the performance of electrostatic precipitators for mercury control. Furthermore, inclusion of iron or iron-containing compounds can drastically change end-of-life options, since the spent activated carbon solids can be separated from other ash.

[0767] 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.

[0768] 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

can, 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.

[0769] The biogenic activated carbon and the principles of the disclosure can be applied to liquid-phase applications, comprising processing of water, aqueous streams of varying purities, solvents, liquid fuels, polymers, molten salts, and molten metals, for example. As intended herein, "liquid phase" comprises slurries, suspensions, emulsions, multiphase systems, or any other material that comprises (or can be adjusted to comprise) an amount of a liquid state present.

[0770] In one embodiment, the present disclosure provides a method of using activated carbon to purify a liquid, in some variations, comprises the following steps:

(a) providing activated carbon particles recovered from the second reactor;

(b) providing a liquid comprising at least one selected contaminant;

(c) providing an additive selected to assist in removal of the selected contaminant from the liquid; and

(d) contacting the liquid with the activated carbon particles and the additive, to adsorb at least the at least one selected contaminant onto the activated carbon particles, thereby generating contaminant-adsorbed carbon particles and a contaminant-reduced liquid.

[0771] 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.

[0772] 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 the group comprising magnesium, manganese, aluminum, nickel, iron, chromium, silicon, boron, cerium, molybdenum, phosphorus, tungsten, vanadium, iron chloride, iron bromide, magnesium oxide, dolomite, dolomitic lime, fluorite, fluorospar, bentonite, calcium oxide,

lime, sodium hydroxide, potassium hydroxide, hydrogen bromide, hydrogen chloride, sodium silicate, potassium permanganate, organic acids (e.g., citric acid), or a combination thereof.

[0773] In some embodiments, the selected contaminant (in the liquid to be treated) is a metal, such as a metal selected from the group comprising arsenic, boron, selenium, mercury, and any compound, salt, and mixture thereof. In some embodiments, the selected contaminant is an organic compound (such as a VOC), a halogen, a biological compound, a pesticide, or a herbicide. The contaminant-adsorbed carbon particles can comprise two, three, or more contaminants. In some embodiments, an activated carbon product adsorbs, absorbs and/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 a combination thereof. In some embodiments, the selected contaminant comprises mercury. In some embodiments, the selected contaminant comprises one or more VOCs. In some embodiments, the biogenic activated carbon comprises at least about 1 wt% hydrogen and/or at least about 10 wt% oxygen.

[0774] 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.

[0775] In one embodiment, the present disclosure provides a method of using a biogenic activated carbon composition to remove at least a sulfur-containing contaminant from a liquid, the method comprising:

(a) providing activated-carbon particles recovered from the second reactor disclosed herein;

(b) providing a liquid containing a sulfur-containing contaminant;

(c) providing an additive selected to assist in removal of the sulfur-containing contaminant from the liquid; and

(d) contacting the liquid with the activated-carbon particles and the additive, to adsorb or absorb at least the sulfur-containing contaminant onto or into the activated-carbon particles.

[0776] In some embodiments, the sulfur-containing contaminant is selected from the group comprising 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, and combinations, salts, or derivatives thereof. For example, the sulfur-containing contaminant can be a sulfate, in anionic and/or salt form.

[0777] The liquid can be an aqueous liquid, such as water. In some embodiments, the water is wastewater associated with a process selected from the group comprising metal mining, acid mine drainage, mineral processing, municipal sewer treatment, pulp and paper, ethanol, and any other industrial process that is capable of discharging sulfur-containing contaminants in wastewater. The water can also be (or be part of) a natural body of water, such as a lake, river, or stream.

[0778] 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 containing 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 the sulfates onto or into the activated-carbon particles.

[0779] 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 and/or bisulfate anions. Depending on pH, the sulfate can also be present in the form of sulfate salts.

[0780] The water can be derived from, part of, or the entirety of a wastewater stream. Exemplary wastewater streams are those that can be associated with a metal mining, acid mine drainage, mineral processing, municipal sewer treatment, pulp and paper, ethanol, or any other industrial process that could discharge sulfur-containing contaminants to wastewater. The water can be a natural body of water, such as a lake, river, or stream. In some embodiments, the process is conducted continuously. In other embodiments, the process is conducted in batch.

[0781] When water is treated with activated carbon, there can be filtration of the water, osmosis of the water, and/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. In some embodiments, the activated-carbon particles and the additive are 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.

[0782] In some embodiments, an activated carbon is effective for removing a sulfur-containing contaminant selected from the group comprising 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, and combinations, salts, or derivatives thereof.

[0783] Generally speaking, the disclosed activated carbon can be used in any application in which traditional activated carbon might be used. In some embodiments, the

activated carbon is used as a total (i.e., 100%) replacement for traditional activated carbon. In some embodiments, the activated carbon comprises essentially all or substantially all of the activated carbon used for a particular application. In some embodiments, the activated carbon comprises about 1% to at most about 100% of biogenic activated carbon.

[0784] 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 comprises a size characteristic suitable for the particular packed bed or packed column. Injection of biogenic activated carbon into gas streams can be useful for control of contaminant emissions in gas streams or liquid streams derived from coal-fired power plants, biomass-fired power plants, metal processing plants, crude-oil refineries, chemical plants, polymer plants, pulp and paper plants, cement plants, waste incinerators, food processing plants, gasification plants, and syngas plants.

Use of Biocarbon Compositions in Metal Oxide Reduction

[0785] There are various embodiments in which the biocarbon pellets, or a pulverized form thereof, or other biocarbon compositions disclosed herein, are fed to a metal ore furnace and/or a chemical-reduction furnace.

[0786] 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.

[0787] A metal ore furnace or a chemical-reduction furnace can be arranged horizontally, vertically, or inclined. The flow of solids and fluids (liquids and/or gases) can be cocurrent or countercurrent. The solids within a furnace can be in a fixed bed and/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.

[0788] Some variations relate specifically to a blast furnace. A blast furnace is a type of metallurgical furnace used for smelting to produce industrial metals, such as iron or copper. Blast furnaces are utilized in smelting iron ore to produce pig iron, an intermediate material used in the production of commercial iron and steel. Blast furnaces are also used in combination with sinter plants in base metals smelting, for example.

[0789] "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 is blown into the lower section of the furnace through a series of pipes called tuyeres. In some embodiments, the hot blast of air is enriched with oxygen. 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.

[0790] 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.

[0791] The blast furnace remains an important part of modern iron production. Modern furnaces are highly efficient, comprising 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.

[0792] 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

and/or limestone flux can be integrated within the biocarbon pellets. In some embodiments, 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.

[0793] 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 and/or electrostatic precipitator and/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 and/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.

[0794] Blast furnaces operate on the principle of chemical reduction whereby carbon monoxide, comprising 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.

[0795] 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 can also be low in sulfur, phosphorus, and ash.

[0796] 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 comprise various concentrations of different iron oxides (Fe_3O_4, Fe_2O_3, FeO, etc.).

[0797] 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:

$$2\ C + O_2 \rightarrow 2\ CO$$

[0798] 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:

$$3\ Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2$$

[0799] At temperatures around 850°C, further down in the furnace, the iron(II,III) is reduced further to iron(II) oxide, FeO:

$$Fe_3O_4 + CO \rightarrow 3\ FeO + CO_2$$

[0800] 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:

$$CaCO_3 \rightarrow CaO + CO_2$$

[0801] 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, $CaSiO_3$:

$$SiO_2 + CaO \rightarrow CaSiO_3$$

[0802] 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:

$$FeO + CO \rightarrow Fe + CO_2$$

[0803] The carbon dioxide formed in this process can be converted back to carbon monoxide by reacting with carbon via the reverse Boudouard reaction:

$$C + CO_2 \rightarrow 2\ CO$$

[0804] In the chemical reactions shown above, it is important to note that a reducing gas can alternatively or additionally be directly introduced into the blast furnace, rather than being an *in-situ* product within the furnace. Typically, in these embodiments, the reducing gas comprises both hydrogen and carbon monoxide, which both function to chemically reduce metal oxide. In some embodiments, the reducing gas can be separately produced from biocarbon pellets by reforming, gasification, or partial oxidation.

[0805] In conventional blast furnaces, there is no hydrogen available for causing metal oxide reduction. Hydrogen can be injected directly into the blast furnace. Alternatively, or additionally, hydrogen can be available within the biocarbon pellets that are fed to the blast furnace, when the biocarbon pellets comprise volatile carbon that is associated with hydrogen (e.g., heavy tar components). Regardless of the source, hydrogen can cause additional reduction reactions that are similar to those above, but replacing CO with H_2:

$$3\ Fe_2O_3 + H_2 \rightarrow 2\ Fe_3O_4 + H_2O$$

$$Fe_3O_4 + 4\ H_2 \rightarrow 3\ Fe + 4\ H_2O$$

which occur in parallel to the reduction reactions with CO. The hydrogen can also react with carbon dioxide to generate more CO, in the reverse water-gas shift reaction. In certain embodiments, a reducing gas consisting essentially of hydrogen is fed to a blast furnace.

[0806] The "pig iron" produced by the blast furnace typically comprises a 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.

[0807] Desulfurization conventionally is performed during the transport of the liquid iron to the steelworks, by adding calcium oxide, which reacts with iron sulfide comprised in the pig iron to form calcium sulfide. In some embodiments, desulfurization can also take place within a furnace or downstream of a furnace, by reacting a metal sulfide with CO (in the reducing gas) to form a metal and carbonyl sulfide, CSO. In these or other embodiments, desulfurization can also take place within a furnace or downstream of a furnace, by reacting a metal sulfide with H_2 (in the reducing gas) to form a metal and hydrogen sulfide, H_2S.

[0808] 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 and/or a reducing gas in the conversion, that carbon can be renewable carbon. This disclosure provides renewable carbon in biogenic reagents produced via pyrolysis of biomass. In certain embodiments, some carbon utilized in the furnace is not renewable carbon. In various embodiments, of the total carbon that is consumed in the metal ore furnace, that percentage of that carbon that is renewable can be at least about 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, 99%, or 100%.

[0809] In some variations, a Tecnored furnace, or modification thereof, is utilized. The Tecnored process was originally developed by Tecnored Desenvolvimento Tecnológico S.A. of Brazil and is based on a low-pressure moving-bed reduction furnace which reduces cold-bonded, carbon-bearing, self-fluxing, and self-reducing pellets. Reduction is carried out in a short-height shaft furnace at typical reduction temperatures. The process produces hot metal (typically liquid iron) at high efficiency.

[0810] 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.

[0811] In the present disclosure, the Tecnored process can be adapted for use in various ways. Some embodiments provide self-reducing agglomerates (such as biocarbon pellets), produced from iron ore fines or iron-bearing residues, plus a biogenic reagent disclosed herein. These materials, mixed with fluxing and binding agents, are agglomerated and thermally cured, producing biocarbon pellets which have sufficient strength for the physical and metallurgical demands of the Tecnored process. The agglomerates produced are then smelted in a Tecnored furnace. The fuel for the Tecnored furnace can itself be biocarbon pellets, or a non-pellet biocarbon composition (e.g., a powder).

[0812] 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 contain sufficient reductant to allow full reduction of the iron-bearing feed contained. In some embodiments, the iron-bearing feed is contained 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.

[0813] A Tecnored furnace comprises three zones: (i) upper shaft zone; (ii) melting zone; and (iii) lower shaft zone. In the upper shaft zone, solid fuel (e.g., 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.

[0814] 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 biocarbon pellets. In some embodiments, the solid fuel comprises 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.

[0815] This modified Tecnored process employs two different inputs of carbon units—namely the reductant and the solid fuel. The reducing agent is conventionally coal fines, but in this disclosure, the reducing agent can comprise pulverized biocarbon pellets. The self-reducing agglomerates can be the biocarbon pellets disclosed herein. The quantity of carbon fines required is established by a ratio of carbon to ore fines, which can be selected to achieve full reduction of the metal oxides.

[0816] 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 ($2\ CO + O_2 \rightarrow 2\ CO_2$).

[0817] In certain exemplary embodiments, a modified-Tecnored process comprises pelletizing iron ore fines with a size less than 140 mesh, biogenic-reagent fines with a size less than 200 mesh, and a flux such as hydrated lime of size less than 140 mesh using cement as the binder. The pellets are cured and dried at 200°C before they are fed to the top of the Tecnored furnace. The total residence time of the charge in the furnace is around 30-40 minutes. Biogenic reagent in the form of solid fuel of size ranging from 40 mm to 80

mm is fed in the furnace below the hot pellet area using side feeders. Hot blast air at around 1150°C is blown in through tuyeres located in the side of the furnace to provide combustion air for the biogenic carbon. A small amount of furnace gas is allowed to flow through the side feeders to use for the solid fuel drying and preheating. Cold blast air is blown in at a higher point to promote post-combustion of CO in the upper shaft. The hot metal produced is tapped into a ladle on a ladle car, which can tilt the ladle for de-slagging. In some embodiments, the liquid iron is desulfurized in the ladle, and the slag is raked into a slag pot. The hot metal typically comprises about 3-5 wt% carbon.

[0818] Conventionally, external CO or H_2 does not play a significant role in the self-reduction process using a Tecnored furnace. However, external H_2 and/or CO (from reducing gas) can assist the overall chemistry by increasing the rate and/or conversion of iron oxides in the above reaction ($Fe_xO_y + y\ CO \rightarrow x\ Fe + y\ CO_2$) or in a reaction with hydrogen as reactant ($Fe_xO_y + y\ H_2 \rightarrow x\ Fe + y\ H_2O$). The reduction chemistry can be assisted at least at the surface of the pellets or briquettes, and possibly within the bulk phase of the pellets or briquettes since mass transfer of hot reducing gas is fast. Some embodiments of this disclosure combine aspects of a blast furnace with aspects of a Tecnored furnace, so that a self-reducing pellet or briquette is utilized, in addition to the use of reducing gas within the furnace.

[0819] 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 disclosed herein can be applied to essentially any furnace or process that uses carbon somewhere in the process of making a metal from a metal ore.

[0820] 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%. In some embodiments, the other carbon usage is from the biocarbon pellets. Alternatively, some or all of the other carbon usage can be from conventional carbon inputs, such as coal fines.

Conversion of Biocarbon Compositions to Reducing Gas

[0821] Some variations employ a biocarbon composition (as pellets, powder, or another form) to generate reducing gas, wherein the reducing gas can be utilized *in situ* in a process or can be recovered and sold. In related embodiments, low-fixed-carbon material and/or high-fixed-carbon material (e.g., an off-spec portion of one of these materials, or an extra quantity of material not needed for final product demand) can be diverted from the blending operation and instead utilized to generate a reducing gas.

[0822] The optional production of reducing gas (also referred to herein as "bio-reductant gas") will now be further described. The conversion of a biocarbon composition to reducing gas takes place in a reactor, which can be referred to as a bio-reductant formation unit.

[0823] A reactant can be employed to react with the biocarbon composition and produce a reducing gas. The reactant can be selected from oxygen, steam, or a combination thereof. In some embodiments, oxygen is mixed with steam, and the resulting mixture is added to the second reactor. Oxygen or oxygen-enriched air can be added to cause an exothermic reaction such as the partial or total oxidation of carbon with oxygen; to achieve a more favorable H_2/CO ratio in the reducing gas; (iii) to increase the yield of reducing gas; and/or (iv) to increase the purity of reducing gas, e.g. by reducing the amount of CO_2, pyrolysis products, tar, aromatic compounds, and/or other undesirable products.

[0824] Steam is a reactant, in some embodiments. Steam (i.e. H_2O in a vapor phase) can be introduced into the reactor in one or more input streams. Steam can include steam

generated by moisture contained in the biocarbon pellets, as well as steam generated by any chemical reactions that produce water.

[0825] 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.

[0826] Steam reforming, partial oxidation, water-gas shift (WGS), and/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, comprising 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	$C_6H_{10}O_5 + 6\ O_2 \rightarrow 6\ CO_2 + 5\ H_2O$

[0827] 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.

[0828] 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.

[0829] 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 (and/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.

[0830] Exemplary ratios of oxygen to steam (O_2/H_2O) are equal to or less than about any of 2, 1.5, 1, 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, or less, in the second reactor. When the ratio of O_2/H_2O is greater than 1, the combustion reaction starts to dominate over partial oxidation, which can produce undesirably low CO/CO_2 ratios.

[0831] 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. In some embodiments, the air is enriched with oxygen. In some embodiments, air that is not enriched with oxygen is added. In other embodiments, enriched air from an off-spec or recycle stream, which can be a stream from a nearby air-separation plant, for example, can be used. In some embodiments, the use of enriched air with a reduced amount of N_2 (i.e., less than 79 vol%) results in less N_2 in the resulting reducing gas. Because removal of N_2 can be expensive, methods of producing reducing gas with less or no N_2 are typically desirable.

[0832] 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 at most 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.

[0833] In some embodiments, 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.

[0834] 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 one or more support materials, such as, for example, gamma-alumina. In some embodiments, the gamma-alumina is doped with a stabilizing element such as magnesium, lanthanum, or barium.

[0835] 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, and/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.

[0836] 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 and/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.

[0837] Material can generally be conveyed into and out of the reactor by single screws, twin screws, rams, and the like. Material can be conveyed mechanically by physical force (metal contact), pressure-driven flow, pneumatically driven flow, centrifugal flow, gravitational flow, fluidized flow, or some other known means of moving solid and gas phases. It can be suitable to utilize a fixed bed of biocarbon pellets in the reactor, especially in embodiments that employ a bed of metal oxide disposed above the biocarbon pellet bed which need to be mechanically robust.

[0838] In some embodiments, the reactor employs gasification of a biocarbon composition to generate a reducing gas. Gasification is carried out at elevated

temperatures, typically about 600°C to at most 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 at most 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.

[0839] 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.

[0840] 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.

[0841] 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.

[0842] 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.

[0843] The biocarbon composition can be introduced to a gasifier as a "dry feed", or as a slurry or suspension in water. In some embodiments, the dry feed is introduced with moisture but no free liquid phase. 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.

[0844] In some embodiments, the feed to the gasifier is biocarbon pellets with high hydrogen content. The resulting reducing gas is rich in hydrogen, with high H_2/CO ratios, such as $H_2/CO > 1.5$ or more.

[0845] In some embodiments, the feed to the gasifier is biocarbon pellets with low hydrogen content. The resulting reducing gas is expected to have 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 and/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.

[0846] 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. In some embodiments, the gasifier temperature is 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.

[0847] 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.

[0848] 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.

[0849] Circulating fluidized-bed gasifiers can be employed, wherein gas, sand, and feedstock (e.g., crushed or pulverized biocarbon pellets) move together. Exemplary transport gases comprise recirculated product gas, combustion gas, or recycle gas. High heat-transfer rates from the sand ensure rapid heating of the feedstock, and ablation is expected to be stronger than with regular fluidized beds. A separator can be employed to separate the reducing gas from the sand and char particles. The sand particles can be reheated in a fluidized burner vessel and recycled to the reactor.

[0850] In some embodiments in which a countercurrent fixed-bed gasifier is used, the reactor consists of a fixed bed of a feedstock through which a gasification agent (such as steam, oxygen, and/or recycle gas) flows in countercurrent configuration. The ash is either removed dry or as a slag.

[0851] 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.

[0852] In some embodiments in which a fluidized-bed reactor is used, the feedstock is fluidized in recycle gas, oxygen, air, and/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.

[0853] 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.

[0854] 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 comprise an inner water- or steam-cooled wall covered with partially solidified slag.

[0855] 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.

[0856] A gasifier can comprise one or more catalysts, such as catalysts effective for partial oxidation, reverse water-gas shift, or dry (CO_2) reforming of carbon-comprising species.

[0857] 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.

[0858] When a fluidized-bed gasifier is employed, the feedstock can be introduced into a bed of hot sand fluidized by a gas, such as recycle gas. Reference herein to "sand" shall also comprise similar, substantially inert materials, such as glass particles, recovered ash particles, and the like. High heat-transfer rates from fluidized sand can result in rapid heating of the feedstock. There can be some ablation by attrition with the sand particles. Heat can be provided by heat-exchanger tubes through which hot combustion gas flows.

[0859] Circulating fluidized-bed reactors can be employed, wherein gas, sand, and feedstock move together. Exemplary transport gases comprise recirculated product gas, combustion gas, or recycle gas. High heat-transfer rates from the sand ensure rapid heating of the feedstock, and ablation is expected to be stronger than with regular fluidized beds. A separator can be employed to separate the reducing gas from the sand and char particles. The sand particles can be reheated in a fluidized burner vessel and recycled to the reactor.

[0860] In some embodiments in which a countercurrent fixed-bed reactor is used, the reactor consists of a fixed bed of a feedstock through which a gasification agent (such as steam, oxygen, and/or recycle gas) flows in countercurrent configuration. The ash is either removed dry or as a slag.

[0861] 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.

[0862] In some embodiments in which a fluidized-bed reactor is used, the feedstock is fluidized in recycle gas, oxygen, air, and/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.

[0863] 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.

[0864] Water sources can comprise direct piping from process condensate, other recycle water, wastewater, make-up water, boiler feed water, city water, and so on. In some embodiments, water can first be cleaned, purified, treated, ionized, distilled, and the like. When several water sources are used, various volume ratios of water sources are possible. In some embodiments, the water for the second reactor is wastewater.

[0865] 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, and/or other impurities can be removed from the reducing gas.

[0866] Some embodiments comprise a reducing-gas cleanup unit. The reducing-gas cleanup unit is not particularly limited in its design. Exemplary reducing-gas cleanup units comprise cyclones, centrifuges, filters, membranes, solvent-based systems, and other means of removing particulates and/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, and/or other acid gases from the reducing gas.

[0867] Examples of acid-gas removal steps comprise removal of CO_2 with one or more solvents for CO_2, or removal of CO_2 by a pressure-swing adsorption unit. Suitable solvents for reactive solvent-based acid gas removal comprise monoethanolamine, diethanolamine, methyldiethanolamine, diisopropylamine, and aminoethoxyethanol. Suitable solvents for physical solvent-based acid gas removal comprise dimethyl ethers of polyethylene glycol (such as in the Selexol® process) and refrigerated methanol (such as in the Rectisol® process).

[0868] The reducing gas produced as described can be utilized in a number of ways. Reducing gas can generally be chemically converted and/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 comprising 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.

[0869] In this detailed description, reference has been made to multiple embodiments of the technology and non-limiting examples relating to how the technology can be understood and practiced. Other embodiments that do not provide all of the features and advantages set forth herein can be utilized, without departing from the spirit and scope of the disclosure. This technology incorporates routine experimentation and optimization of the methods and systems described herein. Such modifications and variations are considered to be within the scope defined by the claims.

[0870] 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.

[0871] 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 technology. Additionally, certain of the steps can be performed concurrently in a parallel process when possible, as well as performed sequentially.

[0872] Therefore, to the extent there are variations, which are within the spirit of the disclosure or equivalent to the appended claims, it is the intent that this patent will cover those variations as well. The present technology shall only be limited by what is claimed.

EXAMPLES

Example 1: Production of Biocarbon with Pyrolysis Oil Recarbonization.

[0873] Douglas fir (*Pseudotsuga menziesii*) in the form of wood chips is provided as a biomass feedstock. The average size of the wood chips is about 25 millimeters long, about 25 millimeters wide, and about 5 millimeters thick.

[0874] The biomass feedstock is pyrolyzed in a continuous pyrolysis reactor at a pyrolysis temperature of about 600°C at a pyrolysis residence time of about 30 minutes. The pyrolysis pressure is about 1 bar (atmospheric pressure) under an inert gas consisting essentially of N_2. There is a solid output and a vapor output from the pyrolysis reactor. The solid output is a first biogenic reagent comprising carbon and is collected in a hopper. The vapor output is a pyrolysis vapor.

[0875] The pyrolysis vapor is directed to a cooled vessel at a temperature of about 110°C and a pressure of about 1 bar, functioning as a continuous single-stage condenser. A condenser liquid is collected from a bottom port of the cooled vessel, and a condenser vapor is purged from a top port of the cooled vessel. The condenser liquid can be referred to as pyrolysis oil.

[0876] In a mixing unit, the condenser liquid is combined and stirred with the first biogenic reagent, in a batch mixing procedure, forming an intermediate material.

[0877] The intermediate material is thermally treated in the continuous pyrolysis reactor at a second pyrolysis temperature of about 500°C at a second pyrolysis residence time of about 60 minutes. The second pyrolysis pressure is about 1 bar under an inert gas consisting essentially of N_2. There is a solid output and a vapor output from the pyrolysis reactor. The solid output is a second biogenic reagent comprising carbon and is collected in another hopper. The vapor output is an off-gas that is purged.

[0878] The second biogenic reagent is collected as a biocarbon composition.

Example 2: Production of Biocarbon with Pyrolysis Oil Secondary Pyrolysis.

[0879] Douglas fir (*Pseudotsuga menziesii*) in the form of wood chips is provided as a biomass feedstock. The average size of the wood chips is about 25 millimeters long, about 25 millimeters wide, and about 5 millimeters thick.

[0880] The biomass feedstock is pyrolyzed in a continuous pyrolysis reactor at a pyrolysis temperature of about 550°C at a pyrolysis residence time of about 45 minutes. The pyrolysis pressure is about 1 bar (atmospheric pressure) under an inert gas consisting essentially of N_2. There is a solid output and a vapor output from the pyrolysis reactor. The

solid output is a first pyrolysis solid comprising carbon and is collected in a hopper. The vapor output is a first pyrolysis vapor.

[0881] The first pyrolysis vapor is directed to a cooled vessel at a temperature of about 120°C and a pressure of about 1 bar, functioning as a continuous single-stage condenser. A condenser liquid is collected from a bottom port of the cooled vessel, and a condenser vapor is purged from a top port of the cooled vessel. The condenser liquid can be referred to as pyrolysis oil.

[0882] The condenser liquid is continuously thermally treated in a second reactor at a second temperature of about 300°C at a second residence time of about 120 minutes. The pressure of the second reactor is about 2 bar under an inert gas consisting essentially of N_2. There is a solid output from the second reactor. The solid output is a solid or semi-solid material comprising carbon and is collected in another hopper. There is no vapor output; generated vapor is allowed to remain in the second reactor (in other examples, the vapor can be withdrawn).

[0883] In a mixing unit, the first pyrolysis solid is combined and blended with the solid or semi-solid material, in a batch mixing procedure, forming a biogenic reagent.

[0884] The biogenic reagent is collected as a biocarbon composition.

Example 3: Production of Biocarbon with Pyrolysis Oil Added to Biomass.

[0885] Douglas fir (*Pseudotsuga menziesii*) in the form of wood chips is provided as a biomass feedstock. The average size of the wood chips is about 25 millimeters long, about 25 millimeters wide, and about 5 millimeters thick.

[0886] A feedstock material is pyrolyzed in a continuous pyrolysis reactor at a pyrolysis temperature of about 770°C at a pyrolysis residence time of about 20 minutes. The pyrolysis pressure is about 1 bar (atmospheric pressure) under an inert gas consisting essentially of N_2. There is a solid output and a vapor output from the pyrolysis reactor. The solid output is a biogenic reagent comprising carbon and is collected in a hopper. The vapor output is a pyrolysis vapor.

[0887] The pyrolysis vapor is directed to a cooled, two-stage vessel functioning as a continuous two-stage condenser. The two-stage vessel is operated at a first-stage temperature of about 115°C and a first-stage pressure of about 1.2 bar, and a second-stage temperature of about 85°C and a second-stage pressure of about 1 bar. A first condenser liquid is collected from a bottom port of the first stage of the cooled vessel, and a first condenser vapor is purged from a top port of the first stage of the cooled vessel. A second condenser liquid is collected from a bottom port of the second stage of the cooled vessel, and a second condenser vapor is purged from a top port of the second stage of the cooled vessel. The first condenser liquid can be referred to as pyrolysis oil. The second condenser liquid is a water-rich liquid that is not used in this example.

[0888] In a mixing unit, the first condenser liquid is combined and stirred with the starting biomass, in a batch mixing procedure, forming the feedstock material that is pyrolyzed in the continuous pyrolysis reactor (see above).

[0889] The biogenic reagent is collected as a biocarbon composition.

CLAIMS

I/We claim:

1. A process for producing a biocarbon composition, the process comprising:

pyrolyzing a first feedstock in a first pyrolysis reactor, thereby generating a biogenic reagent and a pyrolysis vapor;

introducing the pyrolysis vapor to a condensing system, thereby generating a condenser liquid and a condenser vapor;

contacting a second feedstock with the condenser liquid, wherein the second feedstock comprises biomass, thereby generating the first feedstock, wherein the first feedstock comprises the second feedstock and the condenser liquid; and

recovering the biogenic reagent as a biocarbon composition.

2. The process of claim 1, wherein 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 and/or demolition waste, railroad ties, lignin, animal manure, municipal solid waste, municipal sewage, or a combination thereof.

3. The process of either one of claims 1 or 2, further comprising pelletizing the biogenic reagent.

4. The process of claim 3, wherein the pelletizing the biogenic reagent comprises introducing a binder to the biogenic reagent.

5. The process of claim 4, wherein the binder is selected from starch, thermoplastic starch, crosslinked starch, starch polymers, cellulose, cellulose ethers, hemicellulose, methylcellulose, chitosan, lignin, lactose, sucrose, dextrose, maltodextrin, banana flour, wheat flour, wheat starch, soy flour, corn flour, wood flour, coal tars, coal fines, met coke, asphalt, coal-tar pitch, petroleum pitch, bitumen, pyrolysis tars, gilsonite, bentonite clay, borax, limestone, lime, waxes, vegetable waxes, baking soda, baking powder, sodium hydroxide, potassium hydroxide, iron ore concentrate, silica fume, gypsum, Portland cement, guar gum, xanthan gum, polyvidones, polyacrylamides, polylactides, phenol-formaldehyde resins, vegetable resins, recycled shingles, recycled tires, derivatives thereof, or a combination of the foregoing.

6. The process of claim 3, wherein the pelletizing the biogenic reagent does not comprise introducing an external binder to the biogenic reagent.

7. The process of any one of the above claims, wherein the condensing system comprises multiple condenser stages.

8. The process of claim 7, wherein the condenser liquid is a condensed product of a first stage of the multiple condenser stages.

9. The process of claim 8, wherein the condenser liquid is a condensed product of a plurality of stages of the multiple condenser stages, and wherein optionally the plurality of stages does not include the final stage of the multiple condenser stages.

10. The process of any one of the above claims, wherein the contacting comprises spraying the condenser liquid onto the biomass.

11. The process of any one of the above claims, wherein the first feedstock comprises the condenser liquid adsorbed onto a surface of the biomass.

12. The process of any one of the above claims, wherein the first feedstock comprises the condenser liquid absorbed into a bulk phase of the biomass.

13. The process of any one of the above claims, further comprising thermally treating the biogenic reagent in a thermal-treatment unit, wherein if the biogenic reagent is subjected to pelletizing, the thermally treating is before, during, or after the pelletizing.

14. The process of claim 13, wherein the thermal-treatment unit is a second pyrolysis reactor operated at a second pyrolysis temperature of at least about 250°C, and wherein the second pyrolysis reactor is configured for pyrolyzing the biogenic reagent.

15. The process of claim 13, wherein the thermal-treatment unit is operated at a temperature selected from about 80°C to about 250°C.

16. The process of claim 13, wherein the thermal-treatment unit contains an internal oxygen-free environment.

17. The process claim 13, wherein an inert gas is introduced to the thermal-treatment unit.

18. The process claim 13, wherein the thermal-treatment unit is operated under vacuum.

19. The process of claim 13, wherein the thermal-treatment unit is configured for drying the biogenic reagent.

20. The process of claim 13, further comprising drying of the biocarbon composition after the thermally treating.

21. The process of claim 14, wherein the first pyrolysis reactor is distinct from the second pyrolysis reactor.

22. The process of claim 14, wherein the first pyrolysis reactor and the second pyrolysis reactor are the same unit, and wherein the pyrolyzing and the thermally treating are conducted at different times.

23. The process of any one of the above claims, wherein the condenser liquid comprises total carbon, and wherein the process further comprises converting at least 25 wt% of the total carbon comprised within the condenser liquid to fixed carbon comprised within the biogenic reagent.

24. The process of any one of the above claims, wherein the condenser liquid comprises total carbon, and wherein the process further comprises converting at least 50 wt% of the total carbon comprised within the condenser liquid to fixed carbon comprised within the biogenic reagent.

25. The process of any one of the above claims, wherein the condenser liquid comprises total carbon, and wherein the process further comprises converting at least 75 wt% of the total carbon comprised within the condenser liquid to fixed carbon comprised within the biogenic reagent.

26. The process of any one of the above claims, wherein at least about 10 wt% to at most about 80 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid.

27. The process of any one of the above claims, wherein at least about 20 wt% to at most about 60 wt% of fixed carbon in the biogenic reagent is derived from the condenser liquid.

28. The process of any one of the above claims, wherein all of the condenser liquid is contacted with the second feedstock.

29. The process of any one claims 1-27, wherein less than all of the condenser liquid is contacted with the second feedstock.

30. The process of any one of claims 1-29, wherein the condenser liquid is contacted with the second feedstock without any intermediate chemical processing.

31. The process of any one of claims 1-29, wherein the condenser liquid is chemically processed prior to contacting with the second feedstock.

32. The process of claim 31, wherein the condenser liquid is subjected to a purification step prior to contacting with the second feedstock.

33. The process of either one of claims 31 or 32, wherein the condenser liquid is subjected to a reaction step prior to contacting with the second feedstock.

34. The process of claim 29, further comprising introducing a portion of the condenser liquid to the biogenic reagent.

35. The process of claim 14, wherein the pyrolyzing the biogenic reagent generates an off-gas, and wherein the off-gas is recycled to the condensing system.

36. The process of any one of the above claims, wherein the pyrolyzing in the first pyrolysis reactor is conducted at a first pyrolysis temperature of at least about 250°C to at most about 1250°C.

37. The process of claim 36, wherein the first pyrolysis temperature is at least about 300°C to at most about 700°C.

38. The process of claim 14, wherein the second pyrolysis temperature is at least about 250°C to at most about 1250°C.

39. The process of claim 38, wherein the second pyrolysis temperature is at least about 300°C to at most about 700°C.

40. The process of any one of the above claims, wherein the pyrolyzing in the first pyrolysis reactor is conducted for a first pyrolysis time of at least about 10 seconds to at most about 24 hours.

41. The process of claim 14, wherein the pyrolyzing the biogenic reagent is conducted for a second pyrolysis time of at least about 10 seconds to at most about 24 hours.

42. The process of any one of the above claims, further comprising oxidizing the condenser vapor, thereby generating heat.

43. The process of claim 42, further comprising oxidizing an off-gas derived from the thermal-treatment unit, thereby generating heat.

44. The process of any one of the above claims, further comprising milling the biogenic reagent using a mechanical-treatment apparatus, wherein the mechanical-

treatment apparatus is 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.

45. The process of claim 3, wherein the pelletizing the biogenic reagent utilizes a pelletizing apparatus selected from an extruder, a ring die pellet mill, a flat die pellet mill, a roll compactor, a roll briquetter, a wet agglomeration mill, a dry agglomeration mill, or a combination thereof.

46. The process of any one of the above claims, further comprising drying the biogenic reagent, and further comprising pelletizing the biogenic reagent to generate pellets, wherein the pelletizing the biogenic reagent occurs prior to the drying, during the drying, or after the drying.

47. The process of any one of claims 1-46, wherein the biocarbon composition comprises at least 50 wt% fixed carbon.

48. The process of any one of claims 1-46, wherein the biocarbon composition comprises at least 60 wt% fixed carbon.

49. The process of any one of claims 1-46, wherein the biocarbon composition comprises at least 70 wt% fixed carbon.

50. The process of any one of claims 1-46, wherein the biocarbon composition comprises at least 80 wt% fixed carbon.

51. The process of any one of claims 1-46, wherein the biocarbon composition comprises at least 90 wt% fixed carbon.

52. The process of any one of claims 1-51, wherein the biocarbon composition comprises less than 10 wt% ash.

53. The process of any one of claims 1-51, wherein the biocarbon composition comprises less than 5 wt% ash.

54. The process of any one of claims 1-51, wherein the biocarbon composition comprises less than 1 wt% ash.

55. The process of any one of claims 1-54, wherein the condenser liquid comprises less than 1 wt% ash.

56. The process of any one of claims 1-54, wherein the condenser liquid comprises less than 0.1 wt% ash.

57. The process of any one of claims 1-54, wherein the condenser liquid comprises essentially no ash.

58. The process of any one of the above claims, wherein total carbon within the biocarbon composition is at least 50% renewable as determined from a measurement of the $^{14}C/^{12}C$ isotopic ratio of the total carbon.

59. The process of any one of the above claims, wherein 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.

60. The process of any one of the above claims, wherein 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.

61. The process of any one of claims 1-60, wherein the biocarbon composition is characterized by a bulk density of at least about 5 lb/ft^3 on a dry basis.

62. The process of any one of claims 1-60, wherein the biocarbon composition is characterized by a bulk density of at least about 10 lb/ft^3 on a dry basis.

63. The process of any one of claims 1-60, wherein the biocarbon composition is characterized by a bulk density of at least about 20 lb/ft^3 on a dry basis.

64. The process of any one of the above claims, wherein the biocarbon composition is characterized by at most 20 wt% water uptake at 25°C after 24 hours of soaking in water.

65. The process of any one of the above claims, wherein the biocarbon composition is characterized as non-self-heating when subjected to a self-heating test according to *Manual of Tests and Criteria*, Seventh revised edition 2019, United Nations, Page 375, 33.4.6 Test N.4: "Test method for self-heating substances".

66. The process of any one of the above claims, wherein the biocarbon composition is in the form of a pellet.

67. The process of claim 66, wherein the pellet is characterized by a bulk density of at least about 10 lb/ft^3 on a dry basis.

68. The process of claim 66, wherein the pellet is characterized by a bulk density of at least about 25 lb/ft^3 on a dry basis.

69. The process of claim 66, wherein the pellet is characterized by a bulk density of at least about 35 lb/ft^3 on a dry basis.

70. The process of claim 66, wherein the pellet is characterized by a Hardgrove Grindability Index of at least 30.

71. The process of claim 66, wherein the pellet is characterized by a Hardgrove Grindability Index of at least 50.

72. The process of claim 66, wherein the pellet is characterized by a Hardgrove Grindability Index of at least 70.

73. The process of claim 66, wherein the pellet is characterized by a pellet compressive strength at 25°C of at least about 100 lb_f/in^2.

74. The process of claim 66, wherein the pellet is characterized by a pellet compressive strength at 25°C of at least about 150 lb_f/in^2.

75. A system for producing a biocarbon composition, the system comprising:

a first pyrolysis reactor configured for pyrolyzing a first feedstock to generate a biogenic reagent and a pyrolysis vapor;

a condensing system in flow communication with the first pyrolysis reactor, wherein the condensing system is configured for condensing the pyrolysis vapor to generate a condenser liquid and a condenser vapor;

a mixing unit in flow communication with the condensing system, wherein the mixing unit is configured for contacting a second feedstock comprising biomass with the condenser liquid to generate a first feedstock; and

a system output in flow communication with the first pyrolysis reactor, wherein the system output is configured for recovering the biogenic reagent as a biocarbon composition.

76. The system of claim 75, further comprising a pelletizing unit in flow communication with the first pyrolysis reactor, wherein the pelletizing unit is configured for pelletizing the biogenic reagent to generate pellets.

77. The system of either one of claims 75 or 76, further comprising a thermal-treatment unit in flow communication with the pelletizing unit, if present, or in flow communication with the first pyrolysis reactor.

78. The system of claim 77, wherein a thermal-treatment unit is disposed downstream of the pelletizing unit, and wherein the thermal-treatment unit is configured to receive the pellets.

79. The system of claim 77, wherein the thermal-treatment unit is disposed between the first pyrolysis reactor and the pelletizing unit, wherein the pelletizing unit is configured to receive a thermally treated biogenic reagent.

80. The system of any one of claims 75-79, wherein the condensing system comprises multiple condenser stages.

81. The system of any one of claims 75-80, wherein the mixing unit is configured to spray the condenser liquid onto the biomass.

82. The system of any one of claims 77-79, wherein the thermal-treatment unit is a second pyrolysis reactor operated at a second pyrolysis temperature of at least about 250°C, and wherein the second pyrolysis reactor is configured for pyrolyzing the biogenic reagent.

83. The system of claim 82, further comprising a recycle line configured to recycle pyrolysis off-gas, from the second pyrolysis reactor, to the condensing system.

84. The system of any one of claims 77-79, wherein the thermal-treatment unit is operated at a temperature selected from about 80°C to about 250°C.

85. The system of any one of claims 75-84, further comprising a mechanical-treatment apparatus configured to mill the biogenic reagent, wherein the mechanical-treatment apparatus is 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.

86. The system of claim 76, wherein the pelletizing unit is 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.

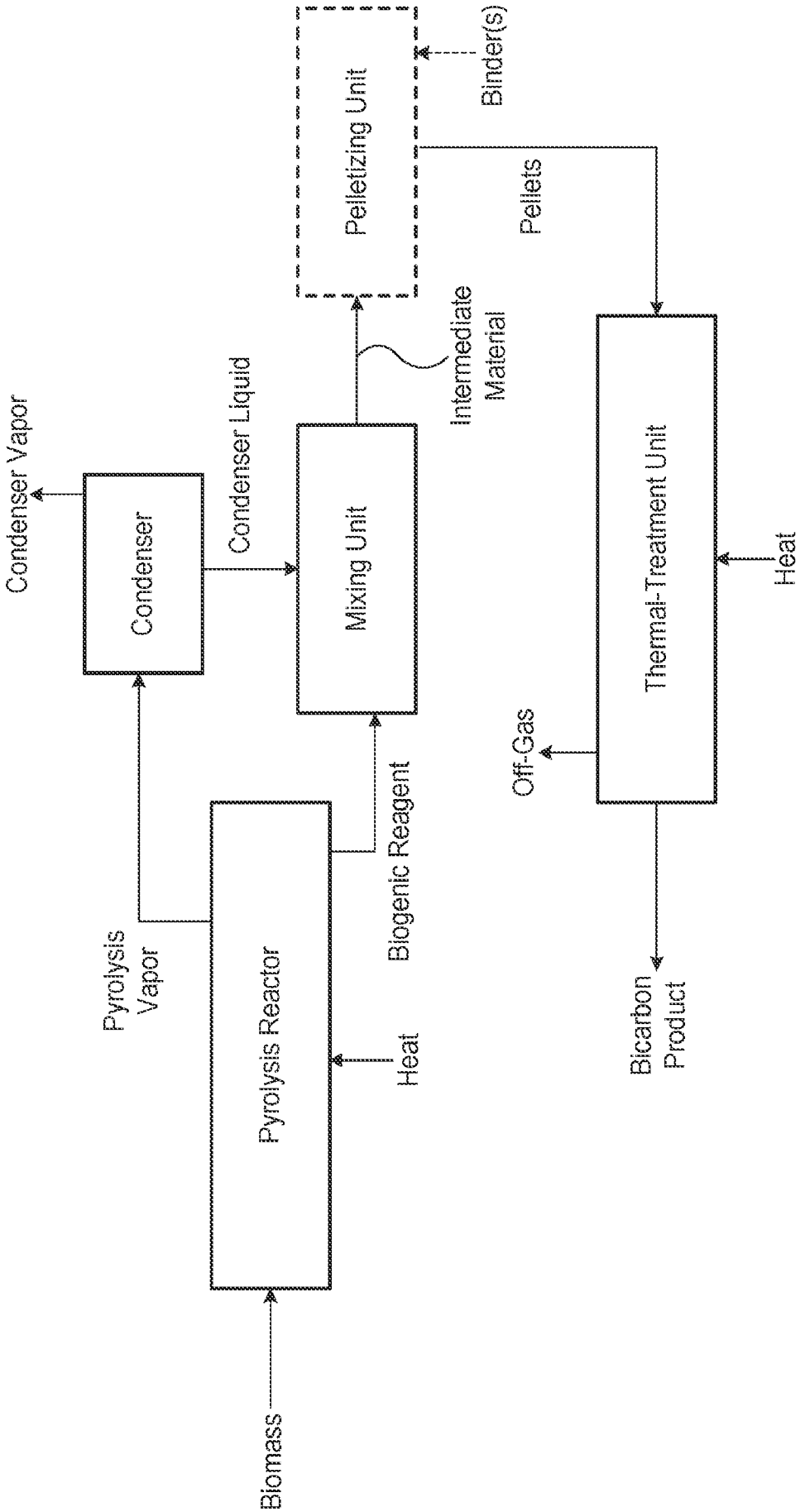

Biomass
Pyrolysis Reactor
Heat
Pyrolysis Vapor
Biogenic Reagent
Condenser
Condenser Vapor
Condenser Liquid
Mixing Unit
Intermediate Material
Pelletizing Unit
Binder(s)
Pellets
Thermal-Treatment Unit
Heat
Off-Gas
Bicarbon Product

FIG. 1

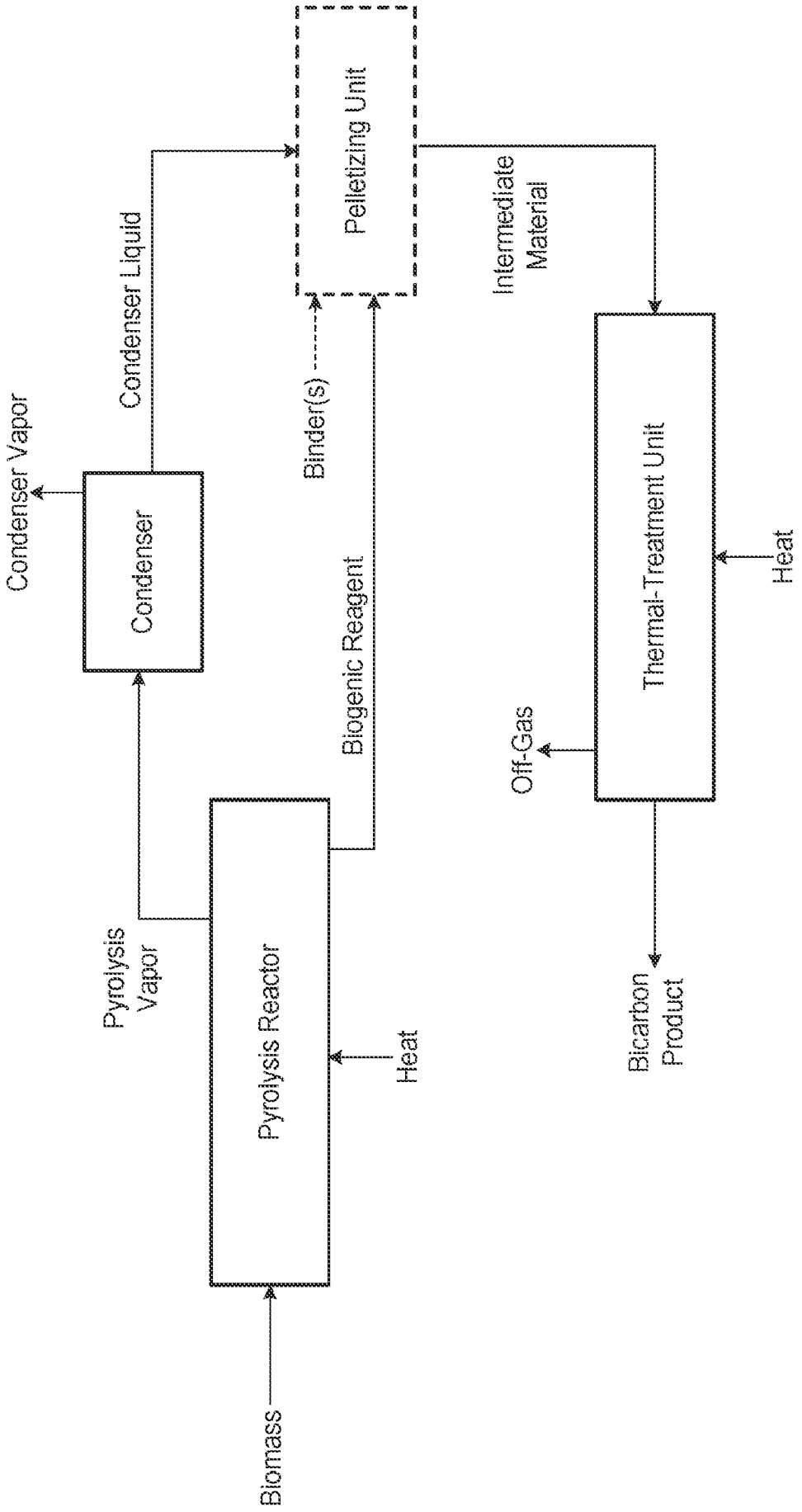

Biomass
Pyrolysis Reactor
Heat
Pyrolysis Vapor
Biogenic Reagent
Condenser
Condenser Vapor
Condenser Liquid
Pelletizing Unit
Binder(s)
Intermediate Material
Thermal-Treatment Unit
Heat
Off-Gas
Bicarbon Product

FIG. 2

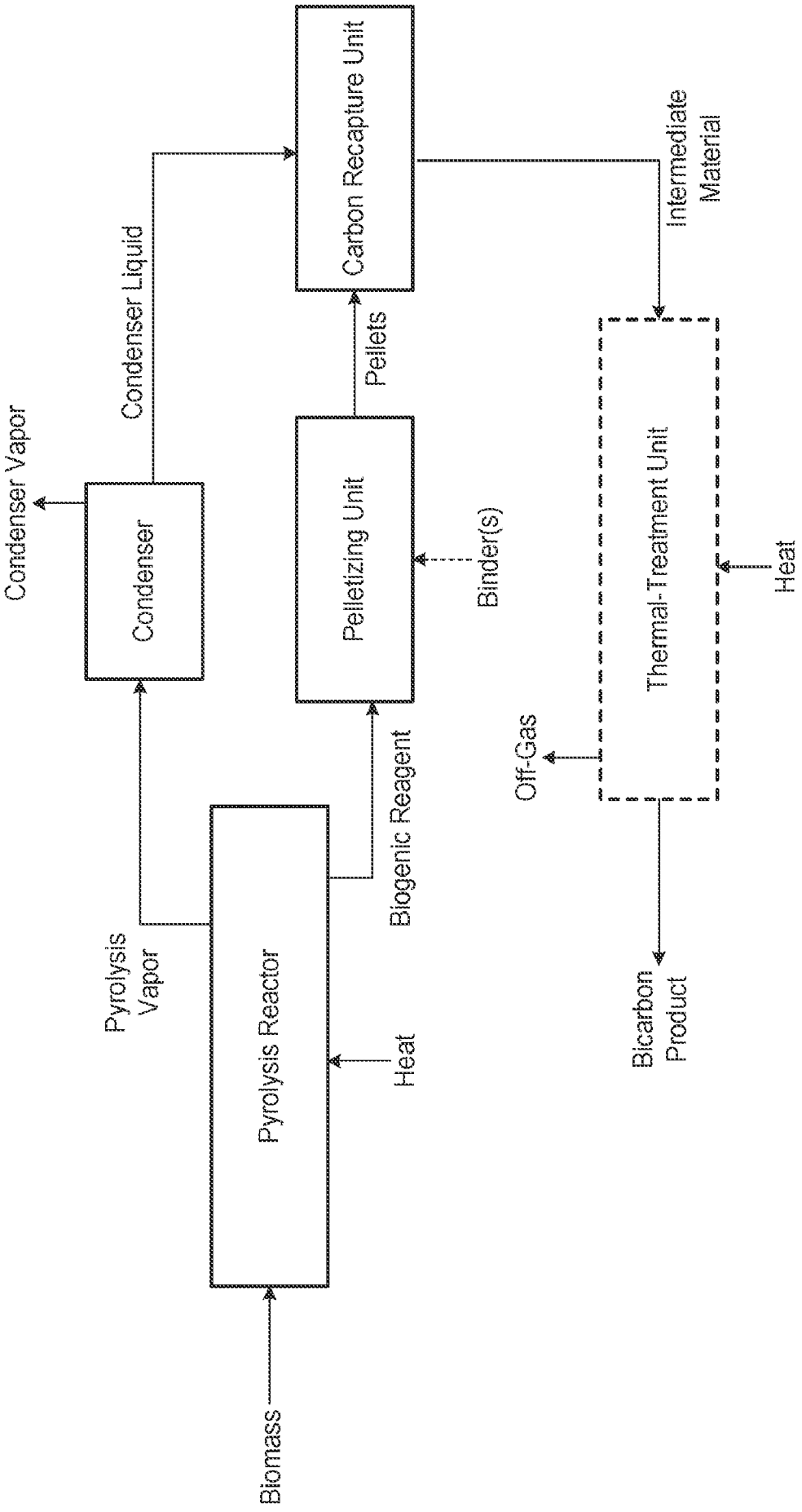

Carbon Recapture Unit
Intermediate Material
Condenser Liquid
Pellets
Condenser Vapor
Condenser
Pelletizing Unit
Binder(s)
Thermal-Treatment Unit
Heat
Off-Gas
Biogenic Reagent
Pyrolysis Vapor
Pyrolysis Reactor
Heat
Bicarbon Product
Biomass

FIG. 3

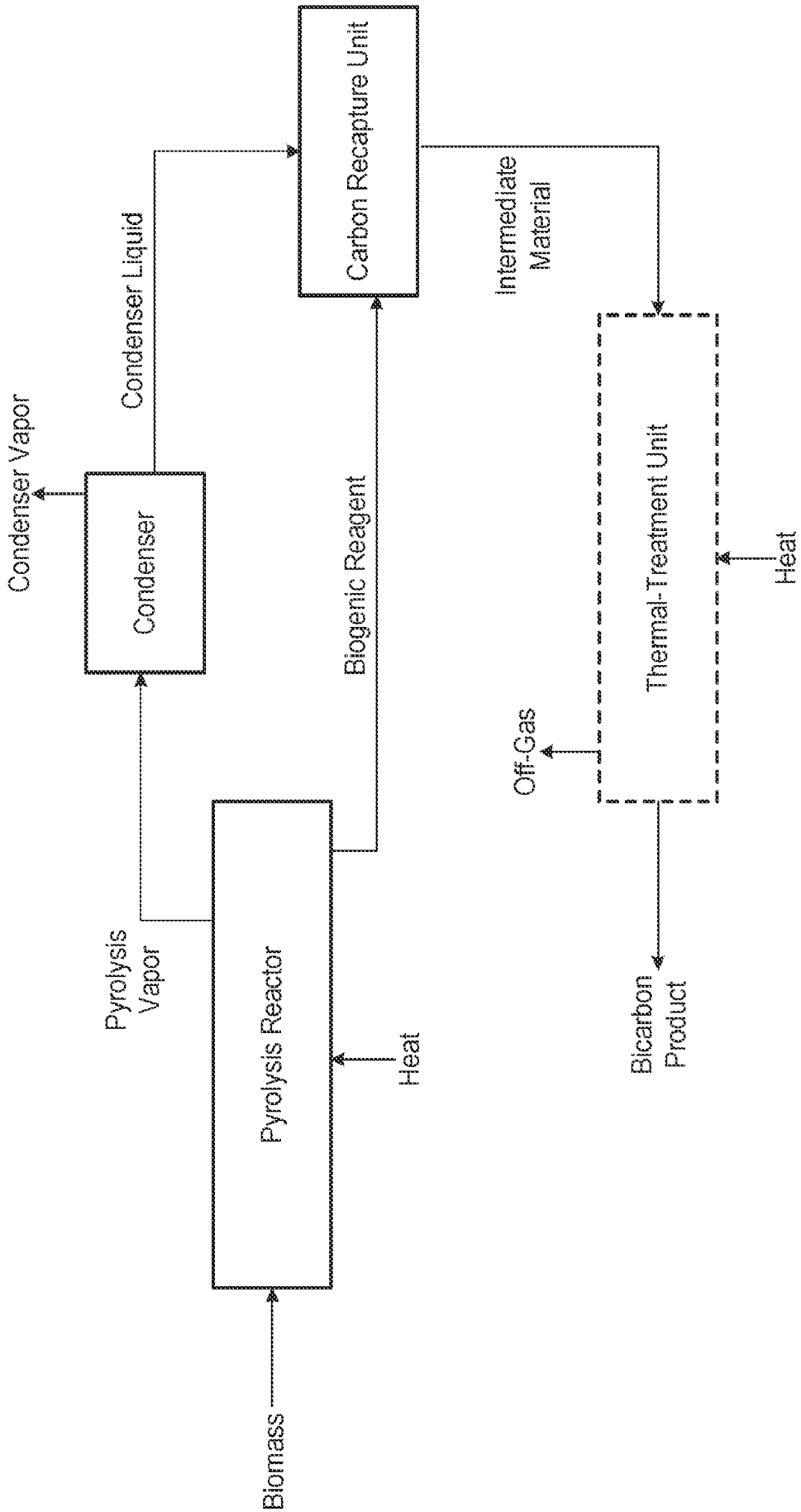

Carbon Recapture Unit
Intermediate Material
Condenser Liquid
Condenser Vapor
Condenser
Biogenic Reagent
Thermal-Treatment Unit
Heat
Off-Gas
Pyrolysis Vapor
Pyrolysis Reactor
Heat
Bicarbon Product
Biomass

FIG. 4

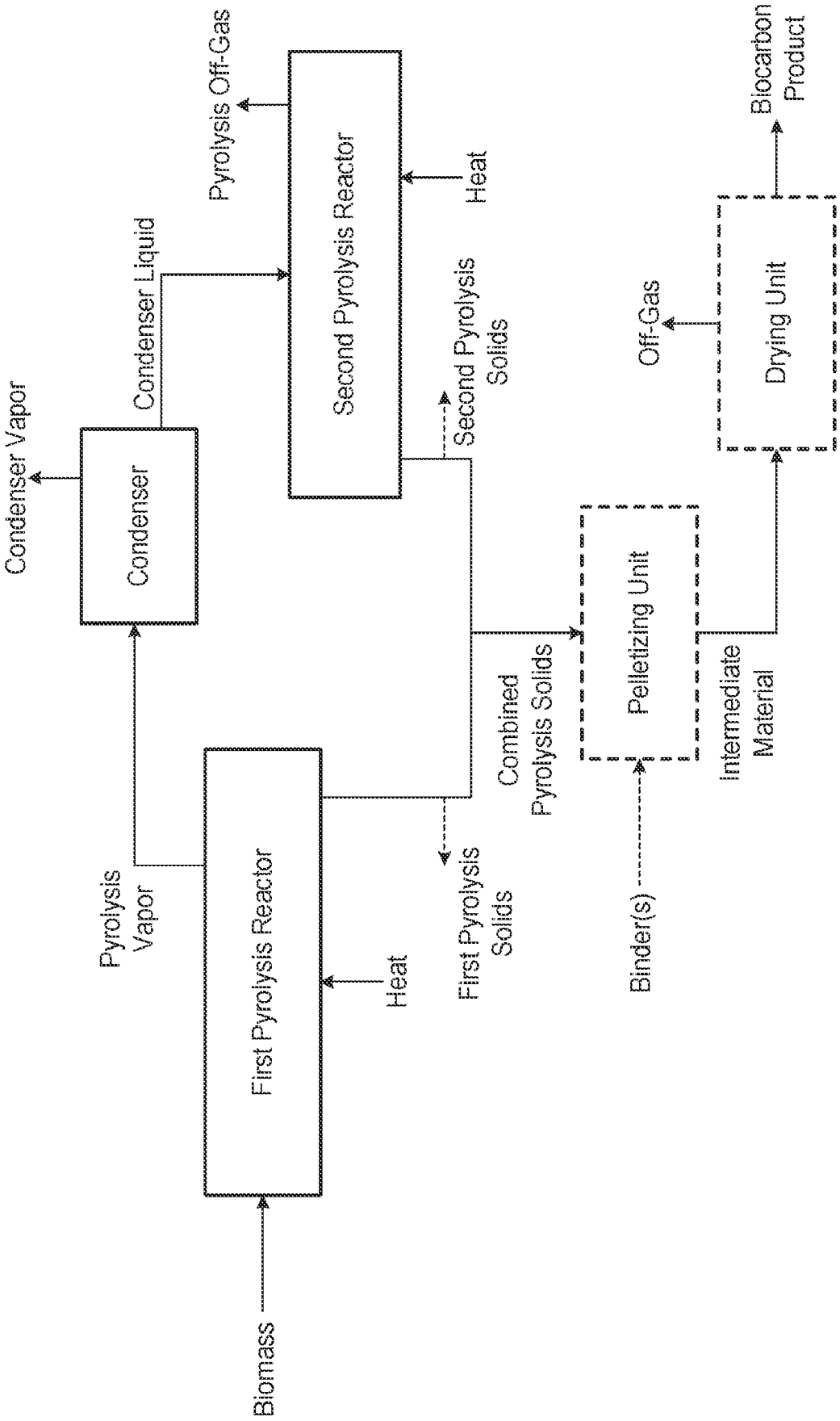

Biomass
First Pyrolysis Reactor
Pyrolysis Vapor
Heat
First Pyrolysis Solids
Combined Pyrolysis Solids
Binder(s)
Pelletizing Unit
Intermediate Material
Off-Gas
Drying Unit
Biocarbon Product
Second Pyrolysis Solids
Heat
Second Pyrolysis Reactor
Pyrolysis Off-Gas
Condenser Liquid
Condenser
Condenser Vapor

FIG. 5

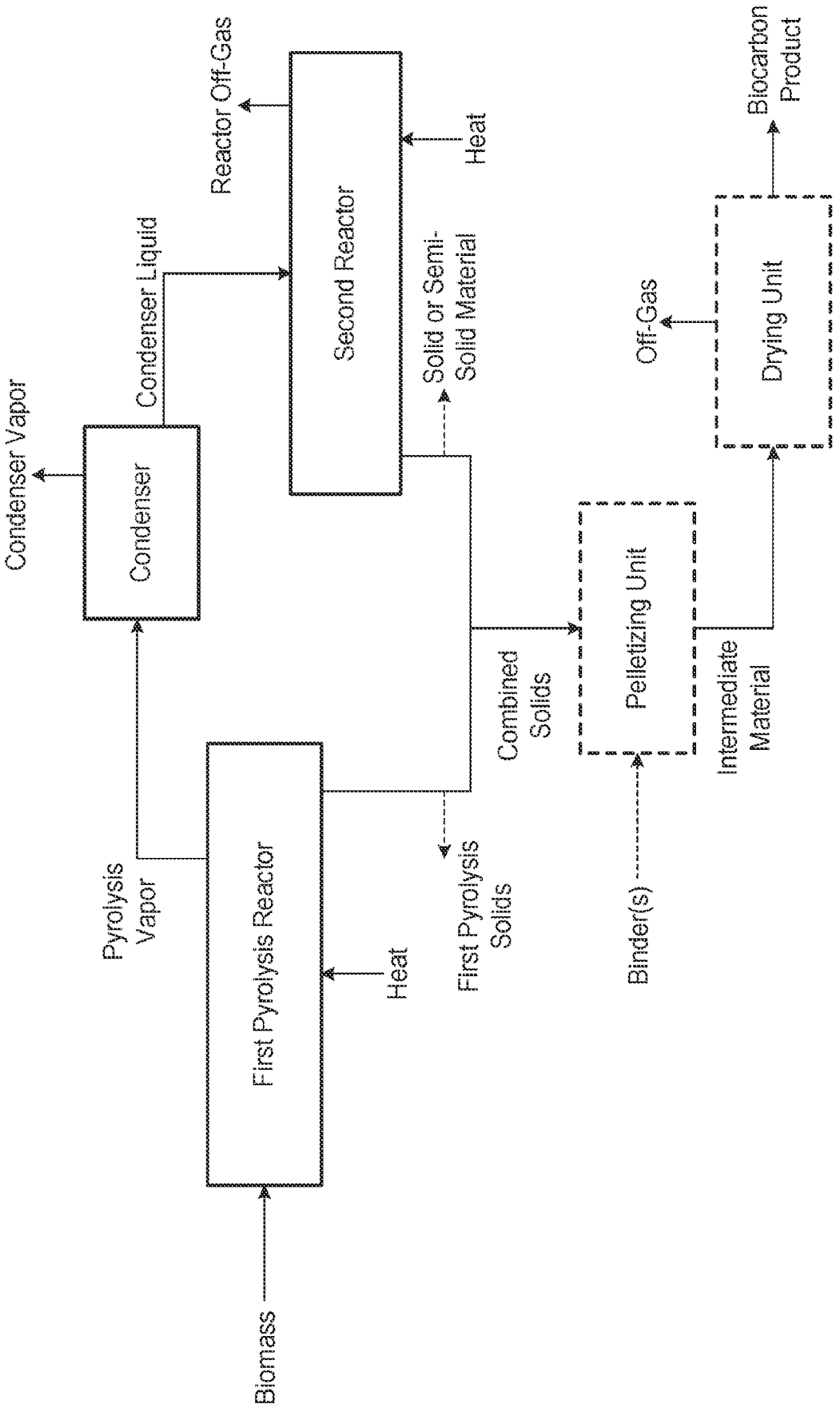

Biomass
First Pyrolysis Reactor
Heat
Pyrolysis Vapor
Condenser
Condenser Vapor
Condenser Liquid
Second Reactor
Reactor Off-Gas
Heat
Solid or Semi-Solid Material
First Pyrolysis Solids
Combined Solids
Pelletizing Unit
Binder(s)
Intermediate Material
Drying Unit
Off-Gas
Biocarbon Product

FIG. 6

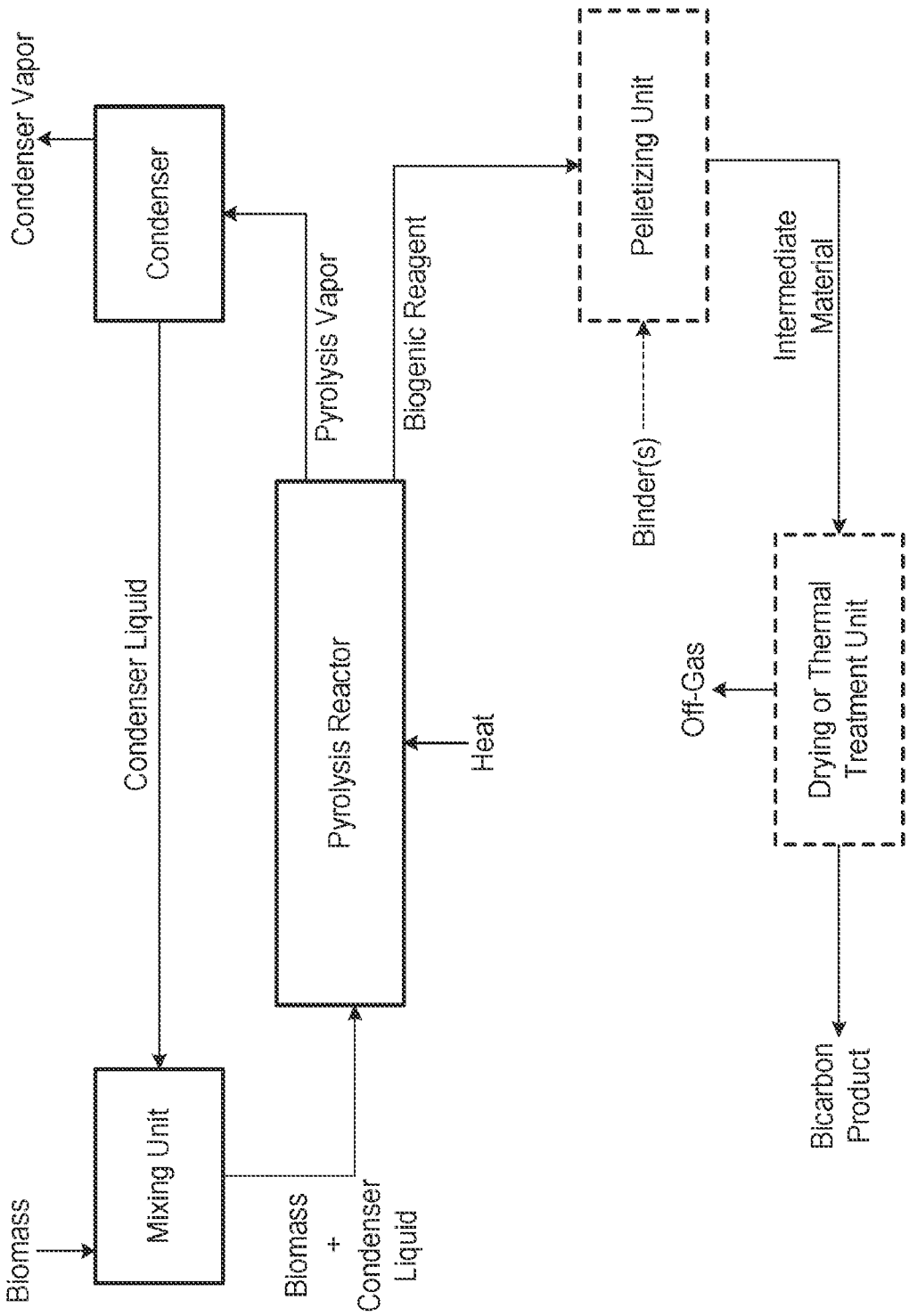

Condenser Vapor
Condenser
Pyrolysis Vapor
Biogenic Reagent
Pelletizing Unit
Intermediate Material
Condenser Liquid
Pyrolysis Reactor
Heat
Binder(s)
Off-Gas
Drying or Thermal Treatment Unit
Biomass
Mixing Unit
Biomass + Condenser Liquid
Bicarbon Product

FIG. 7

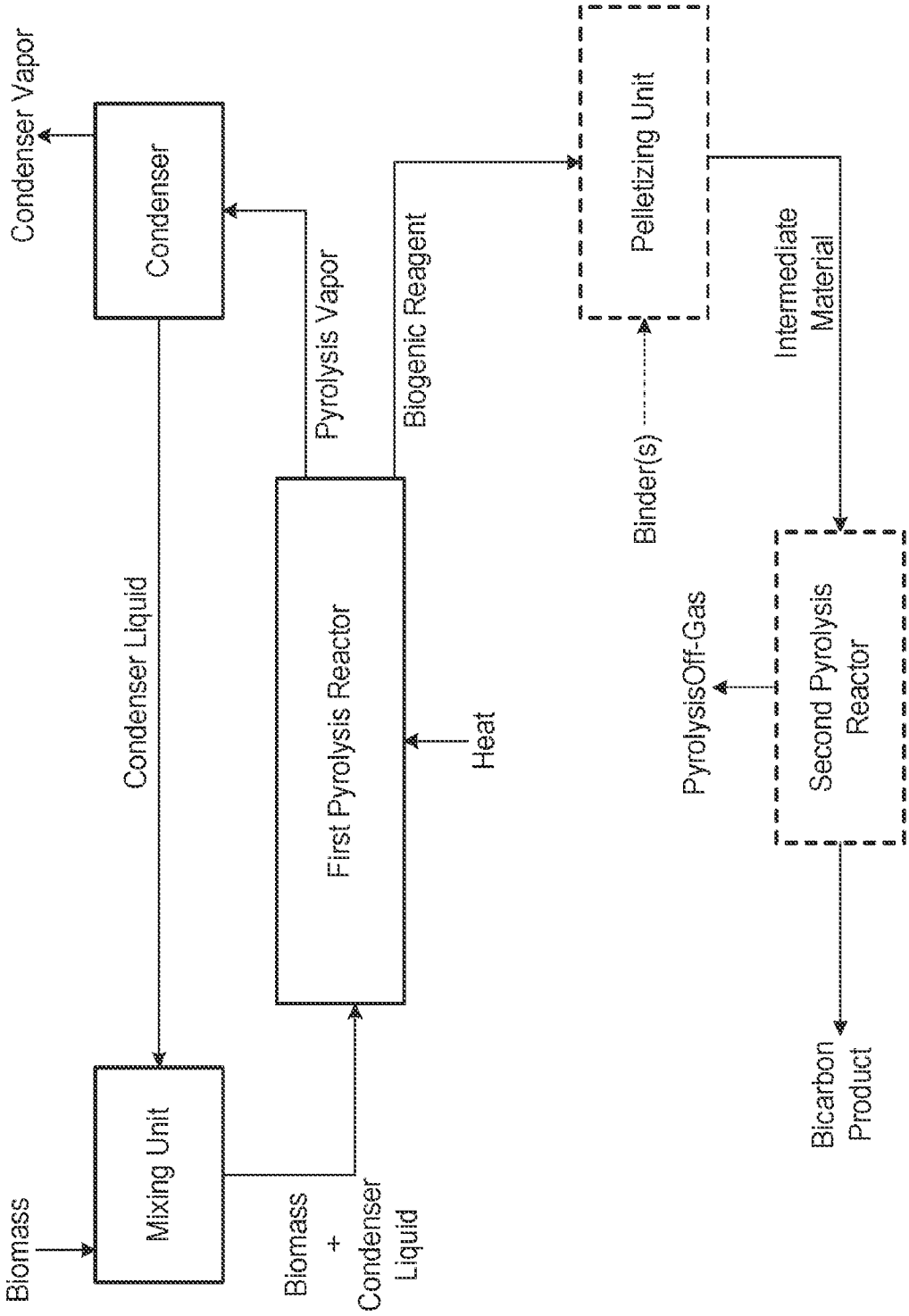

Condenser Vapor
Condenser
Pyrolysis Vapor
Biogenic Reagent
Pelletizing Unit
Intermediate Material
Condenser Liquid
First Pyrolysis Reactor
Heat
Binder(s)
PyrolysisOff-Gas
Second Pyrolysis Reactor
Biomass
Mixing Unit
Biomass + Condenser Liquid
Bicarbon Product

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 22/39119

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. C09C 1/44, C09C 1/48, C01B 32/312, C10B 53/02 (2022.01)
ADD. C09C 1/00 (2022.01)

CPC - INV. C09C 1/44, C09C 1/48, C01B 32/312, C10B 53/02
ADD. C09C 1/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	US 2017/0152440 A1 (Cool Planet energy Systems Inc) 1 June 2017 (01.06.2017) Abstract; Figure 5, claims, especially 7-9, para [0027],para [0028],para [0019],para [0009],para [0010], and entire document	1,2,75,77/75 ---------- 3-6,45,76,77/76,78,79,86
Y	US 2015/0144831 A1 (Biogenic Reagent Ventures LLC) 28 May 2015 (28.05.2015) Abstract; Figures 1,6,para [0011],para [0002],para [0079],para [00170],para [00242],para [00607],para [00606],	3-6,45,76,77/76,78,79,86
A	US 2020/0055736 A1 (Carbon Technology Holdings LLC) 20 February 2020 (20.02.2020) Abstract; para [0003]-[0024]	1-6,45,75-79,86
A	US 2,448,223 A (Lantz) 31 August 1948 (31.08.1948) Abstract; Figure 1; col 1 ln 1 - col 2 ln 35	1-6,45,75-79,86
A	WO 2011/045473 A1 (Teknologian Tutkimuskeskus VTT) Abstract; Fig 1	1-6,45,75-79,86

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 September 2022	NOV 17 2022
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Kari Rodriquez Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 22/39119

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 7-44, 46-74, 80-85
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.