(19) AUSTRALIAN PATENT OFFICE

(12) STANDARD PATENT (11) Application No. **AU 2014308813 B2**

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

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

26 February 2015 (26.02.2015) WIPO | PCT

WO 2015/026987 A1 **26 February 2015 (26.02.2015)**

(26) Publication Language: English

-
- (74) Agent: BERGGREN, William; **7090** 43rd St **N.,** Oaldale, Published:
- **(81)** Designated States *(unless otherwise indicated, for every kind of national protection available):* **AE, AG, AL,** AM,

<u> 1111 - 1111 - 1111 - 1111 - 1111 - 1111 - 1111 - 1111 - 1111 - 1111 - 1111 - 1111 - 1111 - 1111 - 1111 - 111</u>

(10) International Publication Number

(51) International Patent Classification: **AO, AT, AU,** AZ, BA, BB, BG, BH, **BN,** BR, BW, BY, **CloL** 5/44 *(2006.01)* BZ, **CA, CH, CL, CN,** *CO,* CR, **CU,** CZ, **DE,** DK, DM, (21) International Application Number:
PCT/US2014/051958 HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
EZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, (22) International Filing Date: 20 August 2014 (20.08.2014) MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, 20 August 2014 (20.08.2014) OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 20 August 2014 (20.08.2014) OM, PA, PE, **PG,** PH, PL, PT, **QA,** RO, RS, RU, RW, **SA, SC, SD, SE, SG,** SK, **SL, SM, ST, SV,** SY, TH, **TJ,** TM, **(25)** Filing Language: English **TN,** TR, TT, TZ, **UA, UG, US, UZ, VC, VN,** ZA, ZM,

 $kind$ of regional protection available): **ARIPO (BW, GH, 61/971,329 27** March 2014 (27.03.2014) **US GM,** KE, LR, **LS,** MW, MZ, **NA,** RW, **SD, SL, ST,** SZ, **61/974,876 3** April 2014 (03.04.2014) **US** TZ, **UG,** ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, **14/305,193 16** June 2014 (16.06.2014) **US TJ,** TM), European **(AL, AT,** BE, BG, **CH,** CY, CZ, **DE,** DK, **EE, ES,** Fl, FR, GB, GR, HR, **HU, IE, IS,** IT, LT, **LU, (72)** Inventor; and LV, **MC,** MK, MT, **NL, NO,** PL, PT, RO, RS, **SE, SI,** SK, **(71)** Applicant **:** TAIT, Carleton **[UY/US]; 265** Edgemont **SM,** TR), OAPI (BF, **BJ, CF, CG, CI, CM, GA, GN, GQ,** GW , KM, ML, MR, NE, SN, TD, TG).

with international search report (Art. 21(3))

(54) Title: BIOCHAR BY MICROWAVE WITH **BENEFICIATED FEEDSTOCK**

Fig. 4

(57) Abstract: **A** processed biochar composition made with an oxygen-starved microwave sub-system from a processed organic-car bon-containing feedstock made with a beneficiation sub-system is described. Renewable biomass feedstock passed through a beneficiation sub- system to reduce water content to below at least 20 wt% and water-soluble salt reduction of at least **60 %** from that of unprocessed organic-carbon-containing feedstock on a dry basis. The processed feedstock is introduced into a substantially mi ent wall of the reaction chamber to impinge on the feedstock within the reaction chamber. The microwave source may be rotated rel ative to the reaction chamber. The feedstock is subjected to microwaves until the desired reaction occurs to produce a solid pro cessed biochar fuel.

BIOCHAR BY MICROWAVE WITH **BENEFICIATED FEEDSTOCK**

FIELD OF THE **INVENTION**

5 The present invention relates generally to the production of solid char fuel from an organic-carbon-containing feedstock.

BACKGROUND OF **THE INVENTION**

The vast majority of fuels are distilled from crude oil pumped from limited **10** underground reserves or mined from coal. As the earth's crude oil supplies become more difficult and expensive to collect and there is growing concerns about the environmental effects of coal other than clean anthracite coal, the world-wide demand for energy is simultaneously growing. Over the next ten years, depletion of the remaining world's easily accessible crude oil reserves and clean anthracite coal reserves will lead to a

15 significant increase in cost for fuel obtained from crude oil and coal.

The search to find processes that can efficiently convert biomass to fuels and **by** products suitable for transportation and/or heating is an important factor in meeting the ever-increasing demand for energy. In addition, processes that have solid byproducts that have improved utility are also increasingly in demand.

20 Biomass is a renewable organic-carbon-containing feedstock that contains plant cells and has shown promise as an economical source of fuel. However, this feedstock typically contains too much water and contaminants such as water-soluble salts to make it an economical alternative to common sources of fuel such as coal, petroleum, or natural gas.

Historically, through traditional mechanical/chemical processes, plants would give *25* up a little less than *25* weight percent of their moisture. And, even if the plants were sun or kiln-dried, the natural and man-made chemicals and water-soluble salts that remain in the plant cells combine to create corrosion and disruptive glazes in furnaces. Also, the remaining moisture lowers the heat-producing MMBTU per ton energy density of the feedstock thus limiting a furnace's efficiency. Centuries of data obtained through

30 experimentation with a multitude of biomass materials all support the conclusion that increasingly larger increments of energy are required to achieve increasingly smaller increments of bulk density improvement. Thus, municipal waste facilities that process organic-carbon-containing feedstock, a broader class of feedstock that includes materials that contain plant cells, generally operate in an energy deficient manner that costs municipalities money. Similarly, the energy needed to process agricultural waste, also included under the general term of organic-carbon-containing feedstock, for the waste to be an effective substitute for coal or petroleum are not commercial without some sort of governmental subsidies and generally contain unsatisfactory levels of either or both water or water-soluble salts. The cost to suitably prepare such feedstock in a large enough volume to be commercially successful is expensive and currently uneconomical. Also, the suitable plant-cell-containing feedstock that is available in sufficient volume to be commercially useful generally has water-soluble salt contents that result in adverse fouling and contamination scenarios with conventional processes. Suitable land for growing a sufficient amount of energy crops to make economic sense typically are found in locations that result in high water-soluble salt content in the plant cells, i.e., often over 4000 mg/kg on a dry basis.

Organic-carbon-containing feedstock have been tried as a solid renewable fuel or coal substitute but have not been economically viable as they generally contain water-soluble salts that can contribute to corrosion, fouling, and slagging in combustion equipment, and have high water content that reduces the energy density to well below that of coal in large part because of the retained moisture. However, there remains a need for processed biochar as it is a clean renewable source of solid fuel if it could be made cost-effectively with a more substantial reduction in its content of water and water-soluble salt.

Solid byproducts **by** process that have more beneficial properties are an important factor in meeting the ever-increasing demand for energy and food. The present invention fulfills these needs and provides various advantages over the prior art.

The discussion of documents, acts, materials, devices, articles and the like is included in this specification solely for the purpose of providing a context for the present invention. It is not suggested or represented that any or all of these matters formed part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed before the priority date of each claim of this application.

SUMMARY OF THE **INVENTION**

After considering this specification it will be apparent to one skilled in the art how the invention is implemented in various alternative embodiments and alternative applications. However, although various embodiments of the present invention will be described herein, it is understood that these embodiments are presented **by** way of example only, and not limitation. As such, this description of various alternative embodiments should not be construed to limit the scope or breadth of the present invention. Furthermore, statements of advantages or other aspects apply to specific exemplary embodiments, and not necessarily to all embodiments covered **by** the claims.

Throughout the description and the claims of this specification the word "comprise" and variations of the word, such as "comprising" and "comprises" is not intended to exclude other additives, components, integers or steps.

Reference throughout this specification to "one embodiment" or "an embodiment" means that a particular feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment, but may.

It will be appreciated that not all embodiments of the invention described herein have all of the advantages disclosed herein. Some embodiments may have a single advantage, while others may have no advantage at all and are merely a useful alternative to the prior art.

In a first aspect, the present invention provides a composition comprising:

a processed biochar composition that comprises a solid renewable carbon fuel with characteristics that include an energy density of at least **17** MMBTU/ton (20 **GJ/MT),** a water content of less than **10** wt%, water-soluble salt that is decreased more than **60** wt% on a dry basis from that of renewable feedstock, and pores that have a variance in pore size of less than **10** percent, and

the processed biochar is made from renewable feedstock that is converted into the processed organic-carbon-containing feedstock with a beneficiation sub-system, and to the processed biochar with a microwave sub-system,

wherein the beneficiation sub-system, comprises:

a transmission device configured to convey into a reaction chamber renewable feedstock comprising free water, intercellular water, intracellular water, intracellular water soluble salts, and at least some plant cells comprising cell walls that include lignin, hemicellulose, and microfibrils within fibrils;

at least one reaction chamber comprising at least one entrance passageway, at least one exit passageway for fluid, at least one exit passageway for processed organic-carbon containing feedstock, and at least three sections, the sections comprising:

a wet fibril disruption section configured to interact with at least some of the lignin and hemicellulose between the fibrils to make at least some regions of the cell wall more susceptible to outflow **by** water-soluble salts;

a vapor explosion section in communication with the wet fibril disruption section and at least configured to volatilize plant fibril permeable fluid through rapid decompression to penetrate the more susceptible regions of the cell wall so as to create a porous organic carbon-containing feedstock with plant cell wall passageways for intracellular water and intracellular water-soluble salts to pass from the plant cell; and

a compaction section in communication with the vapor explosion section and configured to compress the porous organic-carbon-containing feedstock between pressure plates configured to minimize formation of water-impermeable felt so as to permit the escape of intracellular water and intracellular water-soluble salt from the reaction chamber fluid exit passageway and to create processed organic-carbon-containing feedstock that passes out through its reaction chamber exit passageway; and

a collection device in communication with the reaction chamber and configured to gather the processed organic-carbon-containing feedstock having a water content of less than 20% **by** weight and a water-soluble salt content that is decreased **by** at least **60 %** on a dry basis from that of the renewable feedstock.

In a second aspect, the present invention provides a process of making processed biochar comprising:

inputting into a system comprising a first and a second subsystem a renewable feedstock that includes free water, intercellular water, intracellular water, intracellular water soluble salts, and at least some plant cells comprising cell walls that include lignin, hemicellulose, and microfibrils within fibrils;

passing renewable feedstock through the first sub-system, a beneficiation sub-system process, to result in processed organic-carbon-containing feedstock having a water content of less than 20 wt% and a salt content that is reduced **by** at least **60** wt% on a dry basis from that of the renewable feedstock; and

passing the processed organic-carbon-containing feedstock through the second sub system, a microwave sub-system process, to result in a solid renewable fuel composition having an energy density of at least **17** MMBTU/ton (20 **GJ/MT)** a water content of less than **10** wt%, water-soluble salt that is decreased **by** at least **60** wt% on a dry basis from that of the renewable feedstock, wherein the beneficiation sub-system process comprises:

inputting into a beneficiation sub-system reaction chamber renewable feedstock comprising free water, intercellular water, intracellular water, intracellular water-soluble salts, and at least some plant cells comprising cell walls that include lignin, hemicellulose, and microfibrils within fibrils;

exposing the feedstock to hot solvent under pressure for a time at conditions specific to the feedstock to make some regions of the cell walls comprising crystallized cellulosic fibrils, lignin, and hemicellulose more able to be penetrable **by** water-soluble salts without dissolving more than **25** percent of the lignin and hemicellulose;

removing the pressure so as to penetrate the more penetrable regions to create porous feedstock with open pores in the plant cell walls; and

pressing the porous feedstock with conditions that include an adjustable compaction pressure versus time profile and compaction time duration to create processed organic carbon-containing feedstock that has a water content of less than 20 wt% and a water-soluble salt content that is decreased **by** at least **60** wt% on a dry basis from that of renewable feedstock,

and the microwave sub-system process further comprises:

inputting processed organic-carbon-containing feedstock into a substantially microwave-transparent reaction chamber containing no externally supplied oxygen and within a microwave reflective enclosure;

directing microwaves from a microwave source through walls of the reaction chamber to impinge on the feedstock;

providing relative motion between the microwave-transparent reaction chamber and the microwave source; and

microwaving the feedstock until the feedstock reacts to produce a solid fuel comprising less than **60** wt% on a dry basis of water-soluble salt from that of renewable feedstock, a water content of less than **10** wt%, and pores that have a variance in pore size of less than **10** percent.

Embodiments of the present are directed to a composition from renewable unprocessed organic-carbon-containing feedstock and a process. The composition is a processed biochar composition, a solid renewable carbon fuel whose characteristics include an energy density of at least **17** MMBTU/ton (20 **GJ/MT),** a water content of less than **10** wt%, water-soluble salt that is decreased more than **60** wt% on a dry basis from that of unprocessed organic-carbon-containing feedstock, and pores that have a variance in

pore size of less than **10** percent. The composition is made with a system configured to convert unprocessed organic-carbon-containing feedstock into processed from renewable feedstock with a beneficiation sub-system, and to the processed biochar with a microwave sub-system.

5 The process of making the solid renewable fuel composition comprises three steps. The first step is to input into a system, comprising a first and a second subsystem, an unprocessed organic-carbon-containing feedstock that includes free water, intercellular water, intracellular water, intracellular water-soluble salts, and at least some plant cells comprising cell walls that include lignin, hemicellulose, and microfibrils within fibrils.

- **10** The second step is to pass the unprocessed organic-carbon-containing feedstock through the first sub-system, a beneficiation sub-system process, to result in processed organic carbon-containing feedstock having a water content of less than 20 wt% and a salt content that is reduced **by** at least **60** wt% on a dry basis from that of the unprocessed organic carbon-containing feedstock, The third step is to pass the processed organic-carbon
- *15* containing feedstock through the second sub-system, a microwave sub-system process, to result in a solid renewable fuel composition having an energy density of at least **17** MMBTU/ton (20 **GJ/MT)** a water content of less than **10** wt%, water-soluble salt that is decreased **by** at least **60** wt% on a dry basis from that of the unprocessed organic-carbon containing feedstock.
- 20 The invention is a processed biochar that is a suitable clean coal substitute for devices that use coal as a feedstock to generate heat such as, for example, coal-fired boilers used to make electricity. The low salt content of the processed biochar substantially reduces adverse corrosive wear and maintenance cleaning of the devices that is typical today. The uniform low water content and uniform, high energy density of the
- **25** beneficiated organic-carbon-containing feedstock used to make the processed biochar allows for a wide variety of renewable organic-carbon-containing feedstock to be used in the microwave section of the process in a cost efficient manner. During the beneficiation section of the process, the substantial reduction of water-soluble salts reduces the adverse results that occur with the subsequent use of the processed organic-carbon-containing
- **30** feedstock. In addition, energy needed to remove water from unprocessed organic-carbon containing feedstock described above to a content of below 20 wt **%** and a substantial amount of the water-soluble salt with the invention is significantly less than for

conventional processes. In some embodiments, the total cost per weight of the beneficiated feedstock is reduced **by** at least **60%** of the cost to perform a similar task with known mechanical, physiochemical, or thermal processes to prepare renewable organic carbon-containing feedstock for use in subsequent fuel making operations.

5 The above summary is not intended to describe each embodiment or every implementation of the present invention. Advantages and attainments, together with a more complete understanding of the invention, will become apparent and appreciated **by** referring to the following detailed description and claims taken in conjunction with the accompanying drawings.

10

BRIEF **DESCRIPTION** OF THE DRAWINGS

Figure 1 is a diagram of a typical plant cell with an exploded view of a region of its cell wall showing the arrangement of fibrils, microfibrils, and cellulose in the cell wall.

15 Figure 2 is a diagram of a perspective side view of a part of two fibrils in a secondary plant cell wall showing fibrils containing microfibrils and connected **by** strands of hemicellulose, and lignin

Figure **3** is a diagram of a cross-sectional view of a section of bagasse fiber showing where water and water-soluble salts reside inside and outside plant cells.

20 Figure 4 is a diagram of a side view of an embodiment of a reaction chamber in a beneficiation sub-system.

Figure **5A** is a diagram of the front views of various embodiments of pressure plates in a beneficiation sub-system.

Figure 5B is a perspective view of a close-up of one embodiment of a pressure **25** plate shown in Figure **5A.**

Figure **5C** is a diagram showing the cross-sectional view down the center of a pressure plate with fluid vectors and a particle of pith exposed to the fluid vectors.

Figure **6A** is a graphical illustration of the typical stress-strain curve for lignocellulosic fibril.

30 Figure 6B is a graphical illustration of pressure and energy required to decrease the water content and increase the bulk density of typical organic-carbon-containing feedstock.

Figure **6C** is a graphical illustration of the energy demand multiplier needed to achieve a bulk density multiplier.

Figure **6D** is a graphical illustration of an example of a pressure cycle for decreasing water content in an organic-carbon-containing feedstock with an embodiment **5** of the invention tailored to a specific the organic-carbon-containing feedstock.

Figure **7** is a table illustrating the estimated energy consumption needed to remove at least **75** wt **%** water-soluble salt from organic-carbon-containing feedstock and reduce water content from **50** wt **%** to 12 wt **%** with embodiments of the beneficiation sub-system of the invention compared with known processes.

10 Figure **8** is a diagram of a side view of an embodiment of a beneficiation sub system having four reaction chambers in parallel, a pretreatment chamber, and a vapor condensation chamber.

Figures **9A** and 9B illustrate side and cross sectional views, respectively, of a reaction chamber of an embodiment of a microwave sub-system configured to convert *15* organic-carbon-containing materials to biochar.

Figure **9C** is a diagram of a tilted reaction chamber of an embodiment of the microwave sub-system.

Figure **9D** is a diagram of a side view of an embodiment of the microwave sub system.

20 Figure **1OA** is a block diagram of an embodiment of the microwave sub-system that uses the reaction chamber illustrated in Figures **9A** and 9B for water/air extraction and a reaction process.

Figure 10B illustrates an embodiment of the microwave sub-system that includes feedback control.

25 Figure 11 **A** shows a microwave sub-system which includes multiple stationary magnetrons arranged on a drum that is disposed outside a cylindrical reaction chamber having one or more microwave-transparent walls.

Figure 11 B illustrates an embodiment of a microwave sub-system having a drum supporting magnetrons which may be rotated around the longitudinal axis of the reaction **30** chamber while the reaction chamber is concurrently rotated around its longitudinal axis;

Figure 11C shows an embodiment of a microwave-sub system reaction chamber with a feedstock transport mechanism comprising baffles.

Figure 12 illustrates a system having a rotating magnetron in addition to a secondary heat source.

Figure **13** depicts a microwave sub-system wherein a magnetron is moved along the longitudinal axis of the reaction chamber and is rotated around the longitudinal axis of **5** the reaction chamber.

Figure 14 is a block diagram of an embodiment of a process for passing unprocessed organic-carbon-containing feedstock through a beneficiation sub-system to create a processed organic-carbon-containing feedstock with a water content of less than 20 wt% and a water-soluble salt content that is decreased **by** more than **60** wt% on a dry **10** basis from that of unprocessed organic-carbon-containing feedstock.

Figure **15** is a block diagram of an embodiment of a process for passing unprocessed organic-carbon-containing feedstock through a beneficiation sub-system to create a processed organic-carbon-containing feedstock with a water content of less than 20 wt%, a water-soluble salt content that is decreased **by** more than **60** wt% on a dry basis

15 from that of unprocessed organic-carbon-containing feedstock, and an energy cost of removing the water-soluble salt and water that is reduced to less than **60 %** of the cost per weight of similar removal from known mechanical, known physiochemical, or known thermal processes.

Figure **16** is a table showing relative process condition ranges and water and water 20 soluble salt content for three types of organic-carbon-containing feedstock used in the beneficiation sub-system.

Figure **17** is a block diagram of an embodiment of a process for passing processed organic-carbon-containing feedstock through a microwave sub-system to create a solid renewable fuel processed biochar having an energy density of at least **17** MMBTU/ton (20

25 GJ/MT), a water content of less than **10** wt%, water-soluble salt that is decreased more than **60** wt% on a dry basis from that of unprocessed organic-carbon-containing feedstock, and pores that have a variance in pore size of less than **10 %.**

While the invention is amenable to various modifications and alternative forms, specifics have been shown **by** way of example in the drawings and will be described in detail below. It is to be understood, however, that the intention is not to limit the invention to the particular embodiments described. On the contrary, the invention is

5 intended to cover all modifications, equivalents, and alternatives falling within the scope of the invention as defined **by** the appended claims.

DETAILED DESCRIPTION OF **VARIOUS EMBODIMENTS**

- **10** The processed biochar of the invention is a char made from passing beneficiated processed organic-carbon-containing feedstock through a microwave system. The processed biochar is at least equivalent to coal in energy density. The processed biochar of the invention has the advantages of coming from a renewable source, agricultural and plant materials, without the burdens of current biomass processes that are inefficient and
- *15* remove less if any of the salt found in unprocessed renewable biomass. There are several aspects of the invention that will be discussed: biochar, unprocessed renewable organic carbon-containing feedstock, beneficiation sub-system, microwave sub-system, beneficiation sub-system process, and microwave sub-system process.

Biochar

20 Char made from renewable organic-carbon-containing feedstock is referred to as processed biochar in this document. The processed biochar of the invention comprises a solid renewable carbon fuel comprising less than **10** wt% water, water-soluble salt that is less than **60** wt% on a dry basis that of unprocessed organic-carbon-containing feedstock, and pores that have a variance in pore size of less than **10** percent. The processed biochar **25** is made from unprocessed organic-carbon-containing feedstock that is converted into a processed organic-carbon-containing feedstock in a beneficiation sub-system, and that is then passed through a microwave sub-system. As used in this document, processed

biochar is the solid product of the devolatization of beneficiated organic-carbon containing feedstock. Organic-carbon-containing feedstock used to make the processed **30** biochar of the invention can contain mixtures of more than one renewable feedstock.

For coal, char is the solid material that remains after light gases and tar have been driven out or released from a carbonaceous material during the initial stage of an oxygen-

starved combustion, also known as carbonization, charring, devolatization, or pyrolysis. Light gases include, for example, coal gas, a flammable gaseous fuel that contains a variety of calorific gases including hydrogen, carbon monoxide, methane and volatile hydrocarbons together with small quantities of non-calorific gases such as carbon dioxide

- **5** and nitrogen. Coal tar is a brown or black liquid of extremely high viscosity that include complex and variable mixtures of phenols, polycyclic aromatic hydrocarbons (PAHs), and heterocyclic compounds. In contrast, combustion in the presence of a limited amount of oxygen (with or without char deposits) is known as gasification and is used to make such products as syngas and typically produces ash rather than char. This type of combustion
- **10** ends quickly upon the reaching of reversible gas phase, water gas shift reaction, a reversible chemical reaction in which carbon monoxide reacts with water vapor to form carbon dioxide and hydrogen (the mixture of carbon monoxide and hydrogen is known as syngas).
- Coal has inorganic impurities associated with its formation underground over *15* millions of years. The inorganic impurities are not combustible, appear in the ash after combustion of coal in such situations as, for example boilers, and contribute to air pollution as the **fly** ash particulate material is ejected into the atmosphere following combustion. The inorganic impurities result mainly from clay minerals washed into the rotting biomass prior to its eventual burial. A second important group of impurities are
- 20 carbonate minerals. During the early stages of coal formation, iron carbonate is precipitated either as concretions (hard oval nodules up to tens of centimeters in size) or as infillings of fissures in the coal, Other impurities are nitrogen and sulfur that are chemically reduced during coal formation to the gases ammonia **(NH4)** and hydrogen sulfide (H_2S) , which become trapped within the coal. However, most sulfur is present as
- **25** the mineral *pyrite* (FeS2), which may account for up to **a few** per cent of the coal volurne. Burning coal oxidizes these compounds, releasing oxides of nitrogen **(N20, NO, NO2 ,** etc.) and sulfur dioxide (SO₂), notorious contributors to acid rain. Also, trace elements (including mercury, germanium, arsenic, and uranium) are significantly enriched in coal and are released **by** burning it, contributing to atmospheric pollution.
- **30** In contrast, the processed biochar of the invention is cleaner than coal, The impurities discussed above are not present in any significant amount. In particular,

processed biochar contains substantially no sulfur, Some embodiments have a sulfur content of less than **1000** mg/kg **(0.1** wt%) or less than 1000 parts per million (ppm), some of less than **100** mg/kg **(100** ppm, some of less than **10** mg/kg **(10** ppm). **In** contrast coal **has** significantly more sulfur, The sulfur content in coal ranges of from 4000mg/kg (0.4

5 wt%) to 40,000 mg/kg (4 wt%) and varies with type of coal. The typical sulfur content in anthracite coal is from **6000** mg/kg (0.6 wt%) to **7700** mg/kg **(0.77** wt%). The typical sulfur content in bituminous coal is from **7000** ng/kg **(0.7** wt%) to 40,000 mg/kg (4 wt%). The typical sulfur content in lignite coal is about 4000 mg/kg **(0.4** wt%), Anthracite coal is too expensive for extensive use in burning. Lignite is poor quality coal, with a low **10** energy density or BTU/wt.

In addition, processed biochar has substantially no nitrate, arsenic, mercury *or* uranium. Some embodinients have a nitrate content of less than 500 mg/kg **(500** ppm), sonic **of** less than **150** mg/kg **(150** ppm), versus a nitrate content in coal of typically over 20,000 mg.kg (2 wt\%) . Some embodiments have a arsenic content of less than 2 mg/kg (2 wt\%) .

- *15* ppm), sone of **less** than 1 mg/kg **(1** ppm), some less than **0.1** mg/kg or **100** parts per billion **(ppb),** and **some** *less* than **0.01** mg/kg **(10 ppb)** versus a arsenic content in coal of from over 1 ng/kg to over **70** mg/kg (1 ppm to 70 ppm). Some embodiments have a mercury content that is negligible, i, e., less than 1 microgram/kg **(I ppb),** versus a mercury content in coal of from **0,02** img/kg **(20 ppb)** to **0.3** mg/kg **(300 ppb).** Similarly,
- 20 some embodiments have a uranium content that is also negligible, i. e., less than 1 microgram/kg **(1 ppb),** versus a uranium content in coal of from **20** mg/kg (20 ppn) to *315* mg/kg *(315* ppm) with an average of about **65** mg/kg (ppm) and the uranium content in the ash from the coal with an average of about **210** mg/kg **(210** ppm).

Other forms of char are also known. Some of these chars include, for example, **25** char made **by** the pyrolysis of biomass, also known as charcoal. Charcoal has various uses including, for example, a combustible fuel for generating heat for cooking and heating, as well as a soil amendment to supply minerals for fertilizing soils used for growing agricultural and horticultural products. Char has also been made with passing biomass through an open microwave oven similar to a bacon cooker that is exposed to the external

30 atmosphere containing oxygen and contains pores with a variance similar to that made **by** a thermal process that has a liquid phase.

In char made **by** thermal heat or infrared radiation (IR), the heat is absorbed on the surface of any organic-carbon-containing feedstock and then is re-radiated to the next level at a lower temperature. This process is repeated over and over again until the IR radiation penetrates to the inner most part of the feedstock. **All** the material in the

- *5* feedstock absorbs the IR radiation at its surfaces and different materials that make up the feedstock absorb the IR at different rates. **A** delta temperature of several hundreds of degrees **C** can exist between the surface and the inner most layers or regions of the feedstock. As a result, the solid organic-carbon-containing feedstock locally passes through a liquid phase before it is volatilized. This variation in temperature may appear in
- **10** a longitudinal direction as well as radial direction depending on the characteristics of the feedstock, the rate of heating, and the localization of the heat source. This variable heat transfer from the surface to the interior of the feedstock can cause cold and hot spots, thermal shocks, uneven surface and internal expansion cracks, fragmentation, eject surface material and create aerosols. **All** of this can result in microenvironments that cause side

15 reactions with the creation of many different end products. These side reactions are not only created in the feedstock but also in the volatiles that evaporate from the feedstock and occupy the vapor space in the internal reactor environment before being collected.

A common IR radiation process, pyrolysis, produces biochar, liquids, and gases from biomass **by** heating the biomass in a low/no oxygen environment. The absence of

- 20 oxygen prevents combustion. The relative yield of products from pyrolysis varies with temperature. Temperatures of 400–500 \degree C (752–932 \degree F) produce more char, while temperatures above 700 $\rm{^{\circ}C}$ (1,292 $\rm{^{\circ}F}$) favor the yield of liquid and gas fuel components. Pyrolysis occurs more quickly at the higher temperatures, typically requiring seconds instead of hours. Typical yields are **60%** bio-oil, 20% biochar, and 20% organic volatiles. **25** In the presence of stoichiometric oxygen concentration, high temperature pyrolysis is also
- known as gasification, and produces primarily syngas. **By** comparison, slow pyrolysis can produce substantially more char, on the order of about **50%.**

In all of the above processes, water-soluble salt that is in all renewable organic carbon-containing feedstock is not removed This has the adverse effect of increasing ash **30** content in combusted char and increasing wear and maintenance costs from corrosion and slagging, a deposition of a viscous residue of impurities during combustion. In contrast, the process to make the processed biochar of the invention used a beneficiation sub-system

to process the unprocessed organic-carbon -containing feedstock to remove most of the water and water-soluble salts, and a microwave subsystem to convert the processed organic-carbon-containing feedstock into a uniform porous char.

In contrast to thermal processes, the process to make the processed biochar of the **5** invention uses microwave radiation from the oxygen-starved microwave process system described herein. With microwave radiation, the solid part of the feedstock is nearly transparent to the microwave radiation and most of the microwave radiation just passes through. In contrast to the small absorption cross section of the solid feedstock, gaseous and liquid water strongly absorb the microwave radiation increasing the rotational and

10 torsional vibrational energy of the water molecules. Therefore, the gaseous and liquid water that is present is heated **by** the microwaves, and these water molecules subsequently indirectly heat the solid feedstock.

So any feedstock subjected to the microwave radiation field is exposed to the radiation evenly, inside to outside, no matter what the physical dimensions and content of

15 the feedstock. With microwaves, the radiation is preferentially absorbed **by** water molecules that heat up. This heat is then transferred to the surrounding environment resulting in the feedstock being evenly and thoroughly heated.

When the free water and intercellular water is all evaporated then some of the microwaves start to be absorbed **by** the remaining feedstock and further heat it up within a

- 20 reflecting enclosure that cause the microwave radiation to pass through the feedstock numerous times. Microwave radiation can complete the conversion of feedstock at lower temperatures than IR and thermal heating and occur during shorter timeframes. Operating temperature reductions may range from **10-30%** lower on a degrees **C** basis and heating times may be reduced **by** a quantity equal to one-half to one-tenth of that needed **by** IR
- **25** radiation to accomplish a similar degree of decomposition of a specified feedstock. **All** this can result in an evenly heated feedstock from the inside out so there are reduced microenvironments, fewer side reactions, and cleaner volatiles to collect.

The atmosphere in the reaction chamber is free of externally supplied oxygen. In some embodiments, the atmosphere is inert, such as, for example, nitrogen. In some **30** embodiments, the atmosphere may contain a small amount of water that previously had not been completely removed from the organic-carbon-containing feedstock being

processed before it entered the reaction chamber.

The resulting processed biochar from the microwave process system discussed herein is the devolatilized carbon residue of an irradiated processed organic-carbon containing hydrocarbon feedstock. The microwave system discussed herein can process organic-carbon-containing feedstock that does not contain much water when it enters the

- **5** reaction chamber. However, the conversion is more efficient, i.e., faster rates and at lower temperatures, when water or water-associated molecules are present. Some efficient conversions occur when the water content in the organic-containing feedstock as it enters the reaction chamber is at least **5** percent **by** weight and less than **15** percent **by** weight. Some occur when the water is at least **6** percent **by** weight and less than 12 percent **by**
- **10** weight. For purposes of this document, water includes free water, interstitial water, cellular water, and the water portion that may be combined with other molecules to form hydrated compounds. During the early exposure of the feedstock to the microwaves, the uniform heating of the water throughout the volume of the feedstock particles results in the creation of more numerous and more uniform pores. Because processed organic
- *15* carbon-containing feedstock contains water, the below discussion will focus on those feedstock. However, similar results may occur for those not containing water but less efficiently.

The processed biochar made with the microwave radiation of the process has several improved characteristics when compared to a similar feedstock that is processed

- 20 with IR radiation as discussed above. First, the processed biochar contains significantly less salt than that produced from current processes that use similar unprocessed organic carbon-containing feedstock. The salt in the processed organic-carbon-containing feedstock and thus in the resulting processed biochar is reduced **by** at least **60** wt% on a dry basis from that of the salt content of the unprocessed organic-carbon-containing
- **25** feedstock. As a result, the fixed carbon of the resulting processed biochar is higher and the ash content is lower because there is less salt that forms ash during combustion. Also, the adverse effect of salt in the boiler is reduced, wear is slower, and maintenance cleaning of the equipment is less often and less arduous.

Second, because substantially all of the free water is removed evenly from surface **30** to center and thoroughly during the microwave process, the pore number and pore size are greater and the variance throughout the processed biochar is less than for char made with similar feedstock in an IR process. Some embodiments have a pore number of greater

WO 2015/026987 PCT/US2014/051958

13

than **10%,** some have a pore number greater than 20%, some have a pore number greater than **30%,** and some have a pore number greater than 40%. Some embodiments have a pore size as measured in average diameter of a pore of greater than **10%,** some have a pore size greater than 20%, some have a pore size greater than **30%,** and some have a pore size

- **5** greater than 40%. Some embodiments have a pore number variance of less than **10%** and some have a pore number variance of less than **5%.** Some embodiments have a pore size variance of less than **10%,** and some have a pore size variance of less than **5%.** As a result of the increased pore density, size, and distribution, the surface to volume ratio for some embodiments is at least 4 times that for char made from a similar feedstock with an IR
- **10** process. In some embodiments the surface to volume ratio is increased **by** at least **6** times, in some at least **8** times, in some at least **10** times, and in some at least **15** times. The reactor conditions of the microwave process system may be controlled to produce a desired pore density, size, and distribution for a specific feedstock. One example of the superior porosity characteristics is that the processed biochar has better hydration

15 characteristics in soils than char of the same feedstock **by** IR.

Third, the processed biochar contains less volatiles than that made from a similar feedstock with an IR process. Volatiles present during depolymerization temperatures cause adverse reactions with carbons to form compounds other than the desired liquid fuels and processed biochar of the invention. In addition, volatiles in the processed

- 20 biochar reduce the heating content of the processed biochar **by** reducing the fixed carbon in the resulting biochar. In the invention, the processed biochar is thoroughly devolatilized of condensable and non-condensable gases and vapors. In some embodiments, the content of the gases and vapors is reduced **by** at least **95% by** weight, in some embodiments it is reduced **by** at least **97% by** weight, and in some it is reduced **by** at
- **25** least **99% by** weight versus char made with similar feedstock **by** IR processing with a volatile content of at least **10% by** weight. This is desirable in processed biochar applications such as a coke alternative for steel making, gasification, and combustion applications such as boilers because of the less content of adverse corrosive compounds in the processed biochar of the invention over that of char **by** IR process.

30 Fourth, the processed biochar has a higher heating value than that of char made with the same feedstock **by** an IR process. Because of better devolatization, there are less side reactions with the volatiles and carbon during later use involving combustion of the

processed biochar as fuel. Thus, a greater degree of fixed carbon can remain in the processed biochar of the invention than in the char from similar feedstock processed **by** an IR process. The fixed carbon content in some embodiments is increased **by** at least *5%* **by** weight, in some embodiments **by** at least **10% by** weight, in some embodiments **by** at least

- *5 15%* **by** weight, and in some embodiments **by** at least 20% **by** weight. This increase in fixed carbon can result in an increase in the heat content of some embodiments of the processed biochar of the invention over that of char from the same feedstock but processed **by** an IR process. Heat content is affected **by** the type of organic-carbon-containing feedstock used and generally ranges from at least **10,000** Btu/lb **(23 MJ/kg)** to over 14,000
- **10** Btu/lb **(33 MJ/kg)** compared with less than **6,000** Btu/lb (14 **MJ/kg)** to less than **10,000** Btu/lb **(23 MJ/kg)** for similar organic-carbon-containing feedstock processed with an IR method. In some embodiments, the heat content of the processed biochar is increased **by** at least 20% over char from the same feedstock with an IR process, in some **by** at least **30%,** in some **by** at least 40%, in some **by** at least *50%,* in some **by** at least **60%,** and **by**
- *15* some at least **70%.** In addition, because of the reduced amount of volatiles, the processed biochar of the invention can burn without visible smoke and with a smaller flame than seen with char made of a similar feedstock **by** an IR process. For some embodiments, the flame can be at least *5%* less, for some embodiments at least **10%** less, for some embodiments at least *15%* less, for some embodiments at least 20% less, for some
- 20 embodiments at least *25%* less, for some embodiments at least **30%** less, for some embodiments at least **35%** less, and for some embodiments at least 40% less.

Organic-carbon-containing feedstock used to make the char of the invention can contain mixtures of more than one renewable feedstock.

Unprocessed Organic-Carbon-Containing Feedstock

- **25** Cellulose bundles, interwoven **by** hemicellulose and lignin polymer strands, are the stuff that makes plants strong and proficient in retaining moisture. Cellulose has evolved over several billion years to resist being broken down **by** heat, chemicals, or microbes. In a plant cell wall, the bundles of cellulose molecules in the microfibrils provide the wall with tensile strength. The tensile strength of cellulose microfibrils is as high as **110**
- **30** kg/mm² , or approximately **2.5** times that of the strongest steel in laboratory conditions. When cellulose is wetted, as in the cell walls, its tensile strength declines rapidly, significantly reducing its ability to provide mechanical support. But in biological systems,

the cellulose skeleton is embedded in a matrix of pectin, hemicellulose, and lignin that act as waterproofing and strengthening material. That makes it difficult to produce fuels from renewable cellulose-containing biomass fast enough, cheap enough, or on a large enough scale to make economical sense. As used herein, organic-carbon-containing material

5 means renewable plant-containing material that can be renewed in less than **50** years and includes plant material such as, for example herbaceous materials such as grasses, energy crops, and agricultural plant waste; woody materials such as tree parts, other woody waste, and discarded items made from wood such as broken furniture and railroad ties; and animal material containing undigested plant cells such as animal manure. Organic-carbon **10** containing material that is used as a feedstock in a process is called an organic-carbon

containing feedstock

Unprocessed organic-carbon-containing material, also referred to as renewable biomass, encompasses a wide array of organic materials as stated above. It is estimated that the **U.S.** alone generates billions of tons of organic-carbon-containing material

- *15* annually. As used in this document, beneficiated organic-carbon-containing feedstock is processed organic-carbon-containing feedstock where the moisture content has been reduced, a significant amount of dissolved salts have been removed, and the energy density of the material has been increased. This processed feedstock can be used as input for processes that make several energy-producing products, including, for example, liquid
- 20 hydrocarbon fuels, solid renewable fuel to supplant coal, and synthetic renewable biogas to replace natural gas.

As everyone in the business of making organic-carbon-containing feedstock is reminded, the energy balance is the metric that matters most. The amount of energy used to beneficiate organic-carbon-containing feedstock and, thus, the cost of that energy must **25** be substantially offset **by** offset **by** the overall improvement realized **by** the beneficiation process in the first place. For example, committing **1000 BTU** to improve the heat content of the processed organic-carbon-containing feedstock **by 1000 BTU,** all other things being equal, does not make economic sense unless the concurrent removal of a significant amount of the water-soluble salt renders previously unusable organic-carbon-containing

30 feedstock usable as a fuel substitute for some processes such as boilers. As used herein, organic-carbon-containing feedstock comprises free water, intercellular water, intracellular water, intracellular water-salts, and at least some plant

cells comprising cell walls that include lignin, hemicellulose, and cellulosic microfibrils within fibrils. In some embodiments, the water-soluble salt content of the unprocessed organic-carbon-containing feedstock is at least 4000 mg/kg on a dry basis. In other embodiments the salt content may be more than **1000** mg/kg, 2000 mg/kg, or **3000** mg/kg.

5 The content is largely dependent on the soil where the organic-carbon-containing material is grown. Regions that are land rich and more able to allow land use for growing energy crops in commercial quantities often have alkaline soils that result in organic-carbon containing feedstock with water-soluble salt content of over 4000 mg/kg.

Water-soluble salts are undesirable in processes that use organic-carbon-containing **10** feedstock to create fuels. The salt tends to shorten the operating life of equipment through corrosion, fouling, or slagging when combusted. Some boilers have standards that limit the concentration of salt in fuels to less than **1500** mg/kg. This is to find a balance between availability of fuel for the boilers and expense of frequency of cleaning the equipment and replacing parts. **If** economical, less salt would be preferred. In fact, salt

15 reduction through beneficiation is an enabling technology for the use of salt-laden biomass (e.g. hogged fuels, mesquite, and pinyon-junipers) in boilers. Salt also frequently poisons catalysts and inhibits bacteria or enzyme use in processes used for creating beneficial fuels. While some salt concentration is tolerated, desirably the salt levels should be as low as economically feasible.

20 The water-soluble salt and various forms of water are located in various regions in plant cells. As used herein, plant cells are composed of cell walls that include microfibril bundles within fibrils and include intracellular water and intracellular water-soluble salt. Figure 1 is a diagram of a typical plant cell with an exploded view of a region of its cell wall showing the arrangement of fibrils, microfibrils, and cellulose in the cell wall. **A**

25 plant cell **(100)** is shown with a section of cell wall **(120)** magnified to show a fibril **(130).** Each fibril is composed of microfibrils (140) that include strands of cellulose **(150).** The strands of cellulose pose some degree of ordering and hence crystallinity.

Plant cells have a primary cell wall and a secondary cell wall. The secondary cell wall varies in thickness with type of plant and provides most of the strength of plant

30 material. Figure 2 is a diagram of a perspective side view of a part of two fibrils bundled together in a secondary plant cell wall showing the fibrils containing microfibrils and connected **by** strands of hemicellulose, and lignin. The section of plant cell wall (200) is

composed of many fibrils (210). Each fibril 210 includes a sheath (220) surrounding an aggregate of cellulosic microfibrils **(230).** Fibrils 210 are bound together **by** interwoven strands of hemicellulose (240) and lignin *(250).* In order to remove the intracellular water and intracellular water-soluble salt, sections of cell wall 200 must be punctured **by** at least *5* one of unbundling the fibrils from the network of strands of hemicellulose 240 and lignin

The plant cells are separated from each other **by** intercellular water. An aggregate of plant cells are grouped together in plant fibers, each with a wall of cellulose that is wet on its outside with free water also known as surface moisture. The amount of water

250, decrystallizing part of the strands, or depolymerizing part of the strands.

10 distributed within a specific organic-carbon-containing feedstock varies with the material. As an example, water is distributed in fresh bagasse from herbaceous plants as follows: about **50** wt **%** intracellular water, about **30** wt **%** intercellular water, and about 20 wt **%** free water. Bagasse is the fibrous matter that remains *after* sugarcane *or* sorghum stalks are crushed to extract their juice.

15 Figure **3** is diagram of a cross-sectional view of a fiber section of bagasse showing where water and water-soluble salts reside inside and outside plant cells. **A** fiber with an aggregate of plant cells **(300)** is shown with surface moisture **(310)** on the outer cellulosic wall **(320).** Within fiber **300** lays individual plant cells **(330)** separated **by** intercellular water (340). Within each individual plant cell **330** lays intracellular water **(350)** and 20 intracellular water-soluble salt **(360).**

Conventional methods to beneficiate organic-carbon-containing feedstock include thermal processes, mechanical processes, and physiochemical processes. Thermal methods include heat treatments that involve pyrolysis and torrefaction. The thermal methods do not effectively remove entrained salts and only serve to concentrate them.

25 Thus thermal processes are not acceptable for the creation of many energy creating products such as organic-carbon-containing feedstock used as a fuel substitute to the likes of coal and petroleum. Additionally, all conventional thermal methods are energy intensive, leading to an unfavorable overall energy balance, and thus economically limiting in the commercial use of organic-carbon-containing feedstock as a renewable

30 source of energy.

The mechanical method, also called pressure extrusion or densification, can be divided into two discrete processes where water and water-soluble salts are forcibly

extruded from the organic-carbon-containing material. These two processes are intercellular and intracellular extrusion. The extrusion of intercellular water and intercellular water-soluble salt occurs at a moderate pressure, depending upon the freshness of the organic-carbon-containing material, particle size, initial moisture content,

5 and the variety of organic-carbon-containing material. Appropriately sized particles of freshly cut herbaceous organic-carbon-containing feedstock with moisture content between **50** wt **%** and **60** wt **%** will begin extruding intercellular moisture at pressures as low as **1,000** psi and will continue until excessive pressure forces the moisture into the plant cells (essentially becoming intracellular moisture).

10 As the densification proceeds, higher pressures, and hence higher energy costs, are required to try to extrude intracellular water and intracellular water-soluble salt. However, stiff cell walls provide the biomass material with mechanical strength and are able to withstand high pressures without loss of structural integrity. In addition, the formation of impermeable felts more prevalent in weaker cell walled herbaceous material has been

- *15* observed during compaction of different herbaceous biomass materials above a threshold pressure. This method is energy intensive. In addition, it can only remove up to **50** percent of the water-soluble salts on a dry basis (the intracellular salt remains) and is unable to reduce more than the water content to below **30** wt percent.
- The felts are formed when long fibers form a weave and are bound together **by** 20 very small particles of pith. Pith is a tissue found in plants and is composed of soft, spongy parenchyma cells, which store and transport water-soluble nutrients throughout the plant. Pith particles can hold **50** times their own weight in water. As the compression forces exerted during the compaction force water into the forming felts, the entrained pith particles collect moisture up to their capacity. As a result, the moisture content of any felt
- **25** can approach **90%.** When felts form during compaction, regardless of the forces applied, the overall moisture content of the compacted biomass will be substantially higher than it would have been otherwise had the felt not formed. The felt blocks the exit ports of the compaction device as well as segments perpendicular to the applied force, and the water is blocked from expulsion from the compaction device. The felt also blocks water passing
- **30** through the plant fibers and plant cells resulting in some water passing back through cell wall pores into some plant cells. In addition, it can only remove up to **50** percent of the

water-soluble salts on a dry basis and is unable to reduce more than the water content to below **30** wt percent.

The physiochemical method involves a chemical pretreatment of organic-carbon containing feedstock and a pressure decompression prior to compaction to substantially

- **5** improve the quality of densified biomass while also reducing the amount of energy required during compaction to achieve the desired bulk density. Chemically, biomass comprises mostly cellulose, hemicellulose, and lignin located in the secondary cell wall of relevant plant materials. The strands of cellulose and hemicellulose are cross-linked **by** lignin, forming a lignin-carbohydrate complex **(LCC).** The **LCC** produces the
- **10** hydrophobic barrier to the elimination of intracellular water. In addition to the paper pulping process that solubilizes too much of the organic-carbon-containing material, conventional pre-treatments include acid hydrolysis, steam explosion, AFEX, alkaline wet oxidation, and ozone treatment. **All** of these processes, if not carefully engineered, can be can be expensive on a cost per product weight basis and are not designed to remove more

15 than **25%** water-soluble salt on a dry weight basis.

In addition, the energy density generally obtainable from an organic-carbon containing material is dependent on its type, i.e., herbaceous, soft woody, and hard woody. Also mixing types in subsequent uses such as fuel for power plants is generally undesirable because the energy density of current processed organic-carbon-containing 20 feedstock varies greatly with type of plant material.

As stated above, plant material can be further subdivided in to three sub classes, herbaceous, soft woody and hard woody, each with particular water retention mechanisms. **All** plant cells have a primary cell wall and a secondary cell wall. As stated earlier, the strength of the material comes mostly from the secondary cell wall, not the primary one. **25** The secondary cell wall for even soft woody materials is thicker than for herbaceous

material.

Herbaceous plants are relatively weak-walled plants, include corn, and have a maximum height of less than about **10** to **15** feet (about **3** to **5** meters (M)). While all plants contain pith particles, herbaceous plants retain most of their moisture through a high

30 concentration of pith particles within the plant cells that hold water like balloons because these plants have relatively weak cell walls. Pressure merely deforms the balloons and does not cause the plant to give up its water. Herbaceous plants have about **50 %** of their

water as intracellular water and have an energy density of unprocessed material at about *5.2* million BTUs per ton (MMBTU/ton) or **6** gigajoules per metric ton **(GJ/MT). By** comparison, pure carbon in the form of graphite has an energy density of **28** MMBTU/ton **(33 GJ/MT)** and, anthracite coal has an energy density of about 21 MMBTU/ton *(25 5* **GJ/MT)**

Soft woody materials are more sturdy plants than herbaceous plants. Soft woody materials include pines and typically have a maximum height of between *50* and **60** feet

(about **15** and **18** M). Their plant cells have stiffer walls and thus need less pith particles to retain moisture. Soft woody materials have about **50 %** of their water as intracellular **10** water and have an energy density of about 13-14 MMBTU/ton **(15-16 GJ/MT).**

Hard woody materials are the most sturdy of plants, include oak, and typically have a maximum height of between **60** and **90** feet **(18** and **27** M). They have cellulosic plant cells with the thickest secondary cell wall and thus need the least amount of pith particles to retain moisture. Hard woody materials have about **50 %** of their water as *15* intracellular water and have an energy density of about **15** MMBTU/ton **(18 GJ/MT).**

There is a need in the energy industry for a system and method to allow the energy industry to use organic-carbon-containing material as a commercial alternative or adjunct fuel source. Much of the land available to grow renewable organic-carbon-containing material on a commercial scale also results in organic-carbon-containing material that has

- 20 a higher than desired content of water-soluble salt that typically is at levels of at least 4000 mg/kg. Forest products in the Pacific Northwest are often transported via intracoastal waterways, exposing the biomass to salt from the ocean. Thus such a system and method must be able to remove sufficient levels of water-soluble salt to provide a suitable fuel substitute. As an example, boilers generally need salt contents of less than **1500** mg/kg to
- **25** avoid costly maintenance related to high salt in the fuel. In addition, the energy and resulting cost to remove sufficient water to achieve an acceptable energy density must be low enough to make the organic-carbon-containing material feedstock a suitable alternative in processes to make coal or hydrocarbon fuel substitutes.

There is also a need for a process that can handle the various types of plants and **30** arrive at processed organic-carbon-containing feedstock with similar energy densities.

The invention disclosed does allow the energy industry to use processed organic carbon-containing material as a commercial alternative fuel source. Some embodiments

of the invention remove almost all of the chemical contamination, man-made or natural, and lower the total water content to levels in the range of **5** wt **%** to **15** wt **%.** This allows the industries, such as the electric utility industry to blend the organic-carbon-containing feedstock on a ratio of up to **50** wt **%** processed organic-carbon-containing feedstock to **50**

- **5** wt **%** coal with a substantial reduction in the amount of water-soluble salt and enjoy the same MMBTU/ton **(GJ/MT)** efficiency as coal at coal competitive prices. Literature has described organic-carbon-containing feedstock to coal ratios of up to **30%. A** recent patent application publication, **EP2580307 A2,** has described a ratio of up to **50% by** mechanical compaction under heat, but there was no explicit reduction in water-soluble
- **10** salt content in the organic-carbon-containing feedstock. The invention disclosed herein explicitly comprises substantial water-soluble salt reduction through a reaction chamber with conditions tailored to each specific unprocessed organic-carbon-containing feedstock used. As discussed below, additional purposed rinse subsections and subsequent pressing algorithms in the compaction section of the Reaction Chamber may be beneficial to
- *15* process organic-carbon-containing feedstock that has a particularly high content of water soluble salt so that it may be used in a blend with coal that otherwise would be unavailable for burning in a coal boiler. This also includes, for example, hog fuel, mesquite, and Eastern red cedar.
- In addition, the invention disclosed does permit different types of organic-carbon 20 containing feedstock to be processed, each at tailored conditions, to result in processed outputs having preselected energy densities. In some embodiments of the invention, more than one type of feedstock with different energy densities that range from **5.2** to 14 MMBTU/ton **(6** to **16 GJ/MT)** may be fed into the reaction chamber in series or through different reaction chambers in parallel. Because each type of organic-carbon-containing
- **25** feedstock is processed under preselected tailored conditions, the resulting processed organic-carbon-containing feedstock for some embodiments of the system of the invention can have a substantially similar energy density. In some embodiments, the energy density is about 17 MMBTU/ton (20 **GJ/MT).** In others it is about **18, 19,** or 20 MMBTU/ton (21, 22, or **23 GJ/MT).** This offers a tremendous advantage for down-stream processes to be
- **30** able to work with processed organic-carbon-containing feedstock having similar energy density regardless of the type used as well as substantially reduced water-soluble content.

The process of the invention uses a beneficiation sub-system to create the processed organic-carbon-containing feedstock that is a clean economical material to be used for creating a satisfactory coal substitute solid fuel from renewable biomass and a microwave subsystem for converting the processed organic-carbon-containing feedstock

5 into the solid renewable fuel char of the invention. The first subsystem will now be discussed.

Beneficiation Sub-System

The Beneficiation sub-system is used to make processed organic-carbon containing feedstock comprises at least three elements, a transmission device, at least one **10** reaction chamber, and a collection device. As used in this document, the beneficiation

sub-system refers to the system that is used to convert unprocessed organic-carbon containing feedstock into processed organic-carbon-containing feedstock.

The first element, the transmission device, is configured to convey into a reaction chamber unprocessed organic-carbon-containing feedstock comprising free water,

15 intercellular water, intracellular water, intracellular water-soluble salt, and at least some plant cells comprising cell walls that include lignin, hemicellulose, and cellulosic microfibrils within fibrils. The transmission device may be any that is suitable to convey solid unprocessed organic-carbon-containing feedstock into the reaction chamber to obtain a consistent residence time of the feedstock in the reaction chamber. The transmission 20 devices include such devices at augers that are well known in the chemical industry.

Particle size of the unprocessed organic-carbon-containing feedstock should be sufficiently small to permit a satisfactorily energy balance as the unprocessed organic carbon-containing feedstock is passed through the system to create processed organic carbon-containing feedstock. In some embodiments, the unprocessed organic-carbon

- **25** containing feedstock arrives at some nominal size. Herbaceous material such as, for example, energy crops and agricultural waste, should have a particle size where the longest dimension is less than 1 inch **(2.5** cm). Preferably, most wood and wood waste that is freshly cut should have a longest length of less than **0.5** inches **(1.3** cm). Preferably, old wood waste, especially resinous types of wood such as, for example pine,
- **30** has a particle size with a longest dimension of less than **0.25** inches (about **0.6** cm) to obtain the optimum economic outcome, where throughput and energy/chemical consumption are weighed together.

Some embodiments of the system may also include a mastication chamber before the reaction chamber. This mastication chamber is configured to reduce particle size of the organic-carbon-containing feedstock to less than 1 inch **(2.5** cm) as the longest dimension. This allows the organic-carbon-containing feedstock to arrive with particle **5** sized having a longest dimension larger than 1 inch **(2.5** cm).

Some embodiments of the system may also include a pretreatment chamber to remove contaminants that hinder creation of the passageways for intracellular water and water-soluble salts to pass from the cellulosic-fibril bundles. The chamber is configured to use for each organic-carbon-containing feedstock a particular set of conditions

10 including time duration, temperature profile, and chemical content of pretreatment solution to at least initiate the dissolution of contaminates. The contaminants include resins, rosins, glue, and creosote. The solid slurry, including any incipient felts, may be collected for use as binders in the processed organic-carbon-containing feedstock that is the primary end product. Separate oils may be collected as a stand-alone product such as,

15 for example, cedar oil.

The second element, the reaction chamber, includes at least one entrance passageway, at least one exit passageway, and at least three sections, a wet fibril disruption section, a vapor explosion section, and a compaction section. The first section, the wet fibril disruption section, is configured to break loose at least some of the lignin and

- 20 hemicellulose between the cellulosic microfibrils in the fibril bundle to make at least some regions of cell wall more penetrable. This is accomplished **by** at least one of several means. The organic-carbon-containing feedstock is mixed with appropriate chemicals to permeate the plant fibrils and disrupt the lignin, hemicellulose, and **LCC** barriers. Additionally, the chemical treatment may also unbundle a portion of the cellulose fibrils
- **25** and/or microfibrils, de-crystallizing and/or de-polymerizing it. Preferably, the chemicals are tailored for the specific organic-carbon-containing feedstock. In some embodiments, the chemical treatment comprises an aqueous solution containing a miscible volatile gas. The miscible gas may include one or more of ammonia, bicarbonate/carbonate, or oxygen. Some embodiments may include aqueous solutions of methanol, ammonium carbonate, or
- **30** carbonic acid. The use of methanol, for example, may be desirable for organic-carbon containing feedstock having a higher woody content to dissolve resins contained in the woody organic-carbon-containing feedstock to allow beneficiation chemicals better

contact with the fibrils. After a predetermined residence time of mixing, the organic carbon-containing feedstock may be steam driven, or conveyer **by** another means such as a piston, into the next section of the reaction chamber. In some embodiments, process conditions should be chosen to not dissolve more than **25** wt **%** of the lignin or

5 hemicellulose as these are important contributors to the energy density of the processed organic-carbon-containing feedstock. Some embodiments of the system, depending on the specific organic-carbon-containing feedstock used, may have temperatures of at least **135'C,** at least **165'C,** or at least **180⁰ C;** pressures of at least **260** psig, at least **280** psig, at least **375** psig, or at least 640 psig; and residence times of at least **15** minutes (min), 20 **10** min, or **30** min.

The second section, the vapor explosion section, is in communication with the wet fibril disruption section. It at least is configured to volatilize plant fibril permeable fluid through rapid decompression to penetrate the more susceptible regions of the cell wall so as to create a porous organic-carbon-containing feedstock with cellulosic passageways for

- *15* intracellular water and water-soluble salts to pass from the cellulosic-fibril bundles. The organic-carbon-containing feedstock is isolated, heated, pressurized with a volatile fluid comprising steam. The applied volatile chemicals and steam penetrate into the plant fibrils within the vapor explosion section due to the high temperature and pressure. After a predetermined residence time dictated **by** the specific organic-carbon-containing
- 20 feedstock used, pressure is released rapidly from the reaction chamber **by** opening a fast opening valve into an expansion chamber that may be designed to retain the gases, separate them, and reuse at least some of them in the process for increased energy/chemical efficiency. Some embodiments may have no expansion chamber where retention of gasses is not desired. Some embodiments of the system, depending on the
- **25** specific organic-carbon-containing feedstock used, may have a specific pressure drop in psig of at least **230,** at least **250,** at least 345, or at least **600;** and explosive durations of less than **500** milliseconds (ms), less than **300** ms, less than 200 ms, less than **100** ms, or less than **50** ms.

Some embodiments may include gas inlets into the wet fibril disruption section of **30** the reaction chamber to deliver compressed air or other compressed gas such as, for example, oxygen. After delivery to the desired pressure, the inlet port would be closed and the heating for the reaction would proceed. Note that this could allow for at least one

of three things: First, an increase in total pressure would make subsequent explosion more powerful. Second, an increase in oxygen content would increase the oxidation potential of the processed organic-carbon-containing feedstock where desirable. Third, a provision would be provided for mixing of organic-carbon-containing feedstock, water, and **5** potentially other chemicals such as, for example, organic solvents, through bubbling

action of gas through a perforated pipe at bottom of reaction chamber.

The net effect on the organic-carbon-containing feedstock of passing through the wet fibril disruption section and the vapor explosion section is the disruption of fibril cell walls both physically through pressure bursts and chemically through selective and

10 minimal fibril cellulosic delinking, cellulose depolymerization and/or cellulose decrystallization. Chemical effects, such as hydrolysis of the cellulose, lignin, and hemicellulose also can occur. The resulting organic-carbon-containing feedstock particles exhibit an increase in the size and number of micropores in their fibrils and cell walls, and thus an increased surface area. The now porous organic-carbon-containing feedstock is

15 expelled from the vapor explosion section into the next section.

The third section, the compaction section is in communication with the vapor explosion section. The compression section at least is configured to compress the porous organic-carbon-containing feedstock between pressure plates configured to minimize formation of felt that would close the reaction chamber exit passageway made to permit

- 20 escape of intracellular and intercellular water, and intracellular and intercellular soluble salts. In this section **,** the principle process conditions for each organic-carbon-containing feedstock is the presence or absence of a raised pattern on the pressure plate, the starting water content, the processed water content, and final water content. The compaction section of the system of the invention requires a raised patterned surface on the pressure
- **25** plates for feedstock comprising herbaceous plant material feedstock. However, the section may or may not require the raised pattern surface for processing soft woody or hard woody plant material feedstock depending on the specific material used and its freshness from harvest. Some embodiments of the system, depending on the specific organic-carbon containing feedstock used, may have a starting water contents ranging from **70** to **80** wt **%,**
- **30** from 45 to **55** wt **%** or from 40 to **50** wt **%;** and processed water content of from 4 to **15** wt **%** depending on actual targets desired.

The third element, the collection device, is in communication with the reaction chamber. The collection chamber at least is configured to separate non-fuel components from fuel components and to create a processed organic-carbon-containing feedstock. This feedstock has a water content of less than 20 wt **%** and a water-soluble salt content

- **5** that is decreased **by** at least **60 %** on a dry basis. Some embodiments have the water content less than 20 wt **%** after allowing for surface moisture to air dry. Some embodiments have a processed organic-carbon-containing feedstock that has a water content of less than **15** wt **%.** Other embodiments have processed organic-carbon containing feedstock that has a water content of less than 12 wt **%,** less than **10** wt **%,** less
- **10** than **8** wt **%,** or less than **5** wt **%.** Some embodiments have a water-soluble salt content that is decreased **by** at least **65 %** on a dry basis. Other embodiments have a water-soluble salt content that is decreased **by** at least **70 %** on a dry basis, **75 %** on a dry basis, at least **80 %** on a dry basis, at least **85 %** on a dry basis, at least **90 %** on a dry basis, or at least **95 %** on a dry basis.

15 **15** Some embodiments of the system may further include at least one rinsing subsection. This subsection is configured to flush at least some of the water-soluble salt from the porous organic-carbon-containing feedstock before it is passed to the compaction section. In some embodiments where the salt content is particularly high, such as brine soaked hog fuel (wood chips, shavings, or residue from sawmills or grinding machine used

20 to create it and also known as "hammer hogs"), the system is configured to have more than one rinsing subsection followed **by** another compaction section. The separated water, complete with dissolved water soluble salts, may be collected and treated for release into the surrounding environment or even reused in the field that is used to grow the renewable organic-carbon-containing feedstock. The salts in this water are likely to include

25 constituents purposefully added to the crops such as fertilizer and pesticides.

The beneficiation sub-system of the invention can better be understood through depiction of several figures. Figure 4 is a diagram of a side view of an embodiment of a reaction chamber in communication with an expansion chamber to retain gasses emitted from the decompressed carbon-containing feedstock. **A** reaction chamber (400) is shown

30 with a wet fibril disruption section (410). Solvent (412) and unprocessed organic-carbon containing feedstock (414) are fed in to wet fibril disruption section 410 through valves (416) and (418), respectively to become prepared for the next section. The pretreated

organic-carbon-containing feedstock is then passed to a vapor explosion section (420) through a valve (422). Valves are used between chambers and to input materials to allow for attainment of specified targeted conditions in each chamber. Volatile expansion fluid, such as water, or water based volatile mixtures, are fed in to vapor expansion chamber 420

5 through a valve (424). The gas released from the porous organic-carbon-containing feedstock created during decompression is fed through a fast release valve (428) into an expansion chamber (not shown) to retain the gas for possible reuse. The compaction section (430) received the porous organic-carbon-containing feedstock through a valve (432) where the water and water-soluble salt are substantially removed from porous **10** organic-carbon-containing feedstock and it is now processed organic-carbon-containing feedstock.

As stated above, the pressure plates in the compaction section are configured to minimize felt formation. Felt is an agglomeration of interwoven fibers that interweave to form an impermeable barrier that stops water and water-soluble salts entrained in that

- *15* water from passing through the exit ports of the compaction section. Additionally, any pith particles that survived the beneficiation process in the first two sections of reaction chamber can be entrained in the felt to absorb water, thereby preventing expulsion of the water during pressing. Therefore, felt formation traps a significant fraction of the water and salts from being extruded from the interior of biomass being compressed. Figures *5A,*
- 20 **5B,** and **5C** show embodiments of pressure plates and how they work to minimize felt formation so that water and water-soluble salts are able to flow freely from the compaction section. Figure **5A** is a diagram of the front views of various embodiments of pressure plates. Shown is the surface of the pressure plate that is pressed against the downstream flow of porous organic-carbon-containing feedstock. Figure 5B is a perspective view of a
- *25* close-up of one embodiment of a pressure plate shown in Figure **5A.** Figure **5C** is a diagram showing the cross-sectional view down the center of a pressure plate with force vectors and felt exposed to the force vectors. The upstream beneficiation process in the first two sections of the reaction chamber has severely weakened the fibers in the biomass, thereby also contributing to the minimization of felt formation.

30 Some embodiments achieve the processed organic-carbon-containing feedstock water content and water-soluble salt reduction over unprocessed organic-carbon containing feedstock with a cost that is less than **60 %** that of the cost per weight of

processed organic-carbon-containing feedstock from known mechanical, known physiochemical, or known thermal processes. In these embodiments, the reaction chamber is configured to operate at conditions tailored for each unprocessed organic-carbon containing feedstock and the system is further engineered to re-capture and reuse heat to

- **5** minimize the energy consumed to lead to a particular set of processed organic-carbon containing feedstock properties. The reaction chamber sections are further configured as follows. The wet fibril disruption section is further configured to use fibril disruption conditions tailored for each organic-carbon-containing feedstock and that comprise at least a solvent medium, time duration, temperature profile, and pressure profile for each
- **10** organic-carbon-containing feedstock. The second section, the vapor explosion section, is configured to use explosion conditions tailored for each organic-carbon-containing feedstock and that comprise at least pressure drop, temperature profile, and explosion duration to form volatile plant fibril permeable fluid explosions within the plant cells. The third section, the compaction section, is configured to use compaction conditions tailored
- *15* for each organic-carbon-containing feedstock and pressure, pressure plate configuration, residence time, and pressure versus time profile.

The importance of tailoring process conditions to each organic-carbon-containing feedstock is illustrated **by** the following discussion on the viscoelastic/viscoplastic properties of plant fibrils. Besides the differences among plants in their cell wall

- 20 configuration, depending on whether they are herbaceous, soft woody or hard woody, plants demonstrate to a varying degree of some interesting physical properties. Organic carbon-containing material demonstrates both elastic and plastic properties, with a degree that depends on both the specific variety of plant and its condition such as, for example, whether it is fresh or old. The physics that governs the elastic/plastic relationship of
- **25** viscoelastic/viscoplastic materials is quite complex. Unlike purely elastic substances, a viscoelastic substance has an elastic component and a viscous component. Similarly, a viscoplastic material has a plastic component and a viscous component. The speed of pressing a viscoelastic substance gives the substance a strain rate dependence on the time until the material's elastic limit is reached. Once the elastic limit is exceeded, the fibrils in
- **30** the material begin to suffer plastic, i.e., Permanent, deformation. Figure **6A** is a graphical illustration of the typical stress-strain curve for lignocellulosic fibril. Since viscosity, a critical aspect of both viscoelasticity and viscoplasticity, is the resistance to thermally

activated deformation, a viscous material will lose energy throughout a compaction cycle. Plastic deformation also results in lost energy as observed **by** the fibril's failure to restore itself to its original shape. Importantly, viscoelasticity/viscoplasticity results in a molecular rearrangement. When a stress is applied to a viscoelastic material, such as a

- **5** particular organic-carbon-containing feedstock, some of its constituent fibrils and entrained water molecules change position and, while doing so, lose energy in the form of heat because of friction. It is important to stress that the energy that the material loses to its environment is energy that is received from the compactor and thus energy that is expended **by** the process. When additional stress is applied beyond the material's elastic **10** limit, the fibrils themselves change shape and not just position. **A** "visco"- substance will,
	- **by** definition, lose energy to its environment in the form of heat.

An example of how the compaction cycle is optimized for one organic-carbon containing feedstock to minimize energy consumption to achieve targeted product values follows. Through experimentation, a balance is made between energy consumed and

- *15* energy density achieved. Figure 6B is a graphical illustration of pressure and energy required to decrease the water content and increase the bulk density of typical organic carbon-containing feedstock. Bulk density is related to water content with higher bulk density equaling lower water content. The organic-carbon-containing feedstock compaction process will strike an optimum balance between cycle time affecting
- 20 productivity, net moisture extrusion together with associated water-soluble salts and minerals, permanent bulk density improvement net of the rebound effect due to viscoelastic/viscoplastic properties of the feedstock, and energy consumption.

Figure **6C** is an experimentally derived graphical illustration of the energy demand multiplier needed to achieve a bulk density multiplier. The compaction cycle can be **25** further optimized for each variety and condition of organic-carbon-containing feedstock to achieve the desired results at lesser pressures, i.e., energy consumption, **by** incorporating brief pauses into the cycle. Figure **6D** is a graphical illustration of an example of a pressure cycle for decreasing water content in an organic-carbon-containing feedstock with an embodiment of the invention tailored to a specific the organic-carbon-containing

30 feedstock.

In a similar manner, energy consumption can be optimized during the wet fibril disruption and the vapor explosion parts of the system. Chemical pretreatment prior to

compaction will further improve the quality of the product and also reduce the net energy consumption. For comparison purposes, the pressure applied to achieve a bulk density multiplier of **"10"** in Figure **6C** was on the order of **10,000** psi, requiring uneconomically high cost of capital equipment and unsatisfactorily high energy costs to decompress the

5 organic-carbon-containing feedstock.

Figure **7** is a table illustrating the estimated energy consumption needed to remove at least **75** wt **%** water-soluble salt from organic-carbon-containing feedstock and reduce water content from **50** wt **%** to 12 wt **%** with embodiments of the invention compared with known processes. Waste wood with a starting water content of **50** wt **%** was used in the

- **10** estimate to illustrate a side-by-side comparison of three embodiments of the invention with known mechanical, physiochemical, and thermal processes. The embodiments of the system selected use a fibril swelling fluid comprising water, water with methanol, water with carbon dioxide bubbled into it produces carbonic acid H_2CO_3 . As seen in the table, and discussed above, known mechanical processes are unable to reduce the water content
- *15* to 12 wt **%,** known physiochemical processes are unable to reduce water-soluble salt content **by** over **25** wt **%,** and known thermal processes are unable to remove any water soluble salt. The total energy requirement per ton for the three embodiments of the invention, that using methanol and water, carbon dioxide and water, and just water is **0.28** MMBTU/ton **(0.33 GJ/MT), 0.31** MMBTU/ton **(0.36 GJ/MT),** and 0.42 MMBTU/ton (.49
- 20 **GJ/MT),** respectively. This is compared to 0.41 MMBTU/ton (0.48 **GJ/MT), 0.90** MMBTU/ton **(1.05 GJ/MT),** and **0.78** MMBTU/ton **(0.91 GJ/MT)** for known mechanical, known physiochemical, and known thermal processes, respectively. Thus, the estimated energy requirements to remove water down to a content of less than 20 wt **%** and water soluble salt **by 75** wt **%** on a dry basis for embodiments of the system invention to less
- **25** than **60%** that of known physiochemical and known thermal processes that are able to remove that much water and water-soluble salt. In addition, the system invention is able to remove far more water-soluble salt than is possible with known physiochemical and known thermal processes that are able to remove that much water.

Multiple reaction chambers may be used in parallel to simulate a continuous **30** process. Figure **8** is a diagram of a side view of an embodiment of a beneficiation sub system having four reaction chambers in parallel, a pretreatment chamber, and a vapor condensation chamber. **A** system **(800)** includes an input section **(802)** that delivers

organic-carbon-containing feedstock to system **800.** Feedstock passes through a mastication chamber (804) prior to entry into an organic-carbon-containing feedstock hopper **((806)** from where is passes on to a pretreatment chamber **(810).** Contaminants are removed through a liquid effluent line **(812)** to a separation device (814) such as a

- *5* centrifuge and having an exit stream *(815)* for contaminants, a liquid discharge line **(816)** that moves liquid to a filter media tank **(818)** and beyond for reuse, and a solid discharge line **(820)** that places solids back into the porous organic-carbon-containing feedstock. Liquid from the filter medial tank **818** is passed to a remix tank **(822)** and then to a heat exchanger (824) or to a second remix tank **(830)** and to pretreatment chamber **810.** The
- **10** organic-carbon-containing feedstock passes onto one of four reaction chambers (840) comprising three sections. The first section of each reaction chamber, a wet fibril disruption section (842), is followed **by** the second section, a vapor explosion section (844), and a rinsing subsection (846). **A** high pressure steam boiler **(848)** is fed **by** a makeup water line *(850)* and the heat source (not shown) is additionally heated with fuel
- *15* from a combustion air line *(852).* The main steam line *(854)* supplies steam to pretreatment chamber **810** and through high pressure steam lines *(856)* to reaction chambers 840. **A** vapor expansion chamber **(860)** containing a vapor condensation loop is attached to each vapor explosion sections with vapor explosion manifolds **(862)** to condense the gas. **A** volatile organic components and solvent vapor line (864) passes the
- 20 vapor back to a combustion air line *(852)* and the vapors in vapor expansion chamber **860** are passes through a heat exchanger **(870)** to capture heat for reuse in reaction chamber 840. The now porous organic-carbon-containing feedstock now passes through the third section of reaction chamber 840, a compaction section **(880).** Liquid fluid passes through the liquid fluid exit passageway **(884)** back through fluid separation device (814) and solid
- **25** processed organic-carbon-containing feedstock exits at **(886).**

Microwave Sub-System

The microwave sub-system is used to convert the processed organic-carbon containing feedstock from the beneficiation sub-system into the clean porous processed biochar of the invention. The invention comprises a processed biochar composition made

30 from a processed organic-carbon-containing feedstock that passes through a microwave process sub-system. The sub-system includes at least one reaction chamber within a microwave reflective enclosure and comprising at least one microwave-transparent
chamber wall and a reaction cavity configured to hold the processed organic-carbon containing feedstock in an externally supplied oxygen-free atmosphere. **A** microwave sub-system includes at least one device configured to emit microwaves when energized. The microwave device is positioned relative to the reaction chamber so that the

- **5** microwaves are directed through the microwave-transparent chamber wall and into the reaction cavity. The sub-system also includes a mechanism that provides relative motion between the microwave device and the reaction chamber. The processed biochar composition includes substantially no free water. Also the processed biochar composition includes a number of pores per volume that is at least **10** percent more than would have
- **10** been in a char made with the same feedstock but using a thermal process that creates a liquid phase during the process. The characteristics of the feedstock and resulting processed biochar have already been discussed above. The microwave process used to make the processed biochar of the invention is now discussed.

In the following description of the illustrated embodiments, references are made to *15* the accompanying drawings that help to illustrate various embodiments of the microwave process used to make the processed biochar of the invention. It is to be understood that other embodiments of the process may be utilized and structural and functional changes may be made without departing from the scope of the present invention.

The following description relates to approaches for processing solid and/or liquid 20 organic-carbon-containing feedstock into fuels, e.g., diesel fuels, gasoline, kerosene, etc., **by** microwave enhanced reaction deconstruction processes.

Deconstruction, also referred to as "cracking", is a refining process that uses heat to break down (or "crack") hydrocarbon molecules into shorter hydrocarbon chains which are useful as fuels. Deconstruction may be enhanced **by** adding a catalyst to the feedstock

- **25** which increases the speed of the reaction and/or reduces the temperature and/or the radiation exposure required for the processes. Furthermore, the catalyst, such as zeolite, has a nanostructure which allows only molecules of a certain size to enter the crystalline grid or activate the surface areas of the catalyst and to interact with the catalyst. Thus, the catalyst advantageously is very effective at controlling the product produced **by** the
- **30** reaction processes because only substances having a specified chain length may be produced using the catalytic process. Catalytic deconstruction is particularly useful for

transforming biomass and other organic-carbon-containing feedstock into fuels useable as transportation or heating fuels.

One aspect of efficient deconstruction is the ability to heat and irradiate the feedstock substantially uniformly to the temperature that is sufficient to cause

- **5** deconstruction as well as activate the catalyst. Upon deconstruction, long hydrocarbon chains "crack" into shorter chains. Microwave heating has been shown to be particularly useful in heating systems for thermal deconstruction. Heating systems such as flame, steam, and/or electrical resistive heating, heat the feedstock **by** thermal conduction through the reaction chamber wall. These heating systems operate to heat the feedstock from the
- **10** outside of the reaction chamber walls to the inside of the feedstock, whereas microwaves heat uniformly throughout the width of the reaction chamber. Using non-microwave heating sources, the heat is transferred from the heat source outside wall to the inside of the vessel wall that is in direct contact with the feedstock mixture. The heat is then transferred to the surfaces of the feedstock and then transferred, again, through the
- *15* feedstock until the internal areas of the feedstock are at a temperature near the temperature of the reaction chamber wall.

One problem with this type of external heating is that there are time lags between vessel wall temperature transmission and raising the feedstock temperature that is contained in the center of the vessel as well as the internal area of the feedstock matrix.

- 20 Mixing the feedstock helps to mitigate these conditions. Still, millions of microenvironments exist within the reactor vessel environment and the feedstock particles themselves. This causes uneven heat distribution within the reaction chamber of varying degrees. These variant temperature gradients cause uncontrollable side reactions to occur as well as degradation of early conversion products that become over-reacted because of
- **25** the delay in conversion reaction timeliness. It is desirable to produce and retain consistent heating throughout the feedstock and the reaction products so that good conversion economics are achieved and controllable. Microwave heating is an efficient heating method and it also serves to activate catalytic sites.

Embodiments of the invention are directed to a reaction chamber system that can **30** be used to process any organic-carbon-containing feedstock, whether solid and/or liquid, to extract the volatile organic compounds in the feedstock at a temperature range that will produce liquid transportation fuels.

Microwaves are absorbed **by** the water molecules in the material that is irradiated in the microwave. When the water molecules absorb the microwaves, the molecules increase their vibrorotational motions, which create heat **by** friction, and the heat is convected to the surrounding material. The reason microwaves are absorbed **by** water

- **5** molecules is specific to the covalent bonds that attach the hydrogen to the oxygen in a water molecule. The oxygen atom in water has a large electronegativity associated with it. Electronegativity for an element is its propensity to collect extra electrons, either completely in an ionic bond or through skewing the electron cloud of a covalent bond toward that element. The driving force is from quantum chemistry, namely the filling of
- **10** the **2p** shell of oxygen from the addition of 2 electrons. The electronegativity scale, driven **by** the stability of filling the outer electron shell, starting at the most electronegative element, is F>O>N>Cl>Br>S>C>H. Therefore, the valence electrons in water are skewed toward the oxygen, creating a permanent electric dipole moment with the negative pole toward the oxygen and the positive pole between the two hydrogen atoms. The electrons
- *15* from the two hydrogen atoms are drawn closer to the oxygen atom. This gives this end of the molecule a slight negative charge and the two hydrogen atoms then have a slight positive charge. The consequence of this distortion is that the water molecule possesses a permanent electric dipole. The dipole feature of the water molecule allows the molecule to absorb the microwave radiation and increases the rotational speed of gaseous water
- 20 molecules and/or increases the low frequency vibrational movements associated with frustrated rotations of the extended structure of liquid water. The increased motion of the water molecules causes friction that turns to heat and then convects out into the irradiated material.

To take advantage of this feature of microwave radiation, a reaction chamber **25** system described herein takes advantage of microwave irradiation and heating in processing feedstock that contains carbon and can be converted to transportation fuels. The reactor may be made from a substantially microwave transparent substance such as quartz, a crystalline material that is substantially transparent to microwave radiation. Because quartz can be manipulated into many shapes, it provides design discretion for

30 shaping the reaction chamber, but in one example the reaction chamber is configured in the shape of a tube or cylinder. The cylindrical shape allows for the feedstock to feed in one end and exit at the opposite end. An example of a suitable reaction chamber would be

a quartz tube that is about four feet (1.2 meters) long with a wall thickness of about **3/16** inch (4.8 mm).

The microwave reaction chamber is surrounded **by** a microwave reflective enclosure. This causes the microwave radiation to pass repeatedly through the reaction **5** chamber and devolatize the organic-carbon-containing feedstock after the water, if present, is evaporated and driven off. The microwave reflective enclosure is any that reflects microwaves. Materials include, for example, sheet metal assembled as Faraday cages that are known to the art.

Microwave radiation is generated **by** a magnetron or other suitable device. One or **10** more microwave producing devices, e.g., magnetrons can be mounted external to the quartz tube wall. Magnetrons come in different power ranges and can be controlled **by** computers to irradiate the processing feedstock with the proper power to convert the feedstock to most desirable fuel products efficiently, given the residence time in the reactor. In one application, the magnetron can be mounted on a cage that would rotate

15 around the outside of the reactor tube as well as travel the length of the reactor tube. Feedstock traveling through the length of the inside of the tube will be traveling in a plug flow configuration and can be irradiated **by** fixed and/or rotating magnetrons. **A** computer may be used to control the power and/or other parameters of the microwave radiation so that different feedstock, with different sizes and densities can be irradiated at different

20 parameter settings specific to the feedstock and thus convert the feedstock more efficiently.

These configurations of a reactor will allow efficient processing of feedstock, from relatively pure feedstock streams to mixed feedstock streams that include feedstock of different densities, moisture contents, and chemical makeup. Efficiencies can occur

25 because the fuel products are extracted from the reactor chamber as they are vaporized from the feedstock, but further processing of the remaining feedstock occurs until different fuel products are vaporized and extracted. For example, dense feedstock, such as plastics, take longer to process into a useable fuel than less dense feedstock, such as foam or wood chips. The microwave sub-system described herein continues to process dense feedstock

30 without over-processing the earlier converted products from the less dense feedstock. This is accomplished **by** using both stationary and rotating microwave generators.

One example of a mixed feedstock would be unsorted municipal solid waste. In some implementations, catalyst may be added in the feedstock which helps in the conversion of the feedstock as well as the speed at which the conversion can progress. **A** catalyst can be designed to react at the preset processing temperature inside the reactor or **5** to react with the impinging microwave radiation. In some embodiments, no catalyst is

specific feedstock. The plug flow configuration with the reactors described herein will allow adjustments to the residence time that the feedstock resides within the reactor core for

required. In other embodiments, the catalyst may be a rationally designed catalyst for a

10 more efficient exposure to the heat and the radiation of the microwaves to produce the desired end products.

Inlets and/or outlets, e.g., quartz inlets and/or outlets can be placed along the walls of the reaction chamber to allow for pressure and/or vacuum control. The inlets and outlets may allow the introduction of inert gases, reactive gases and/or the extraction of *15* product gases.

Thus, the design of the microwave-transparent reaction chamber, the use of microwaves as a heating and radiation source with fixed and/or rotating magnetrons, plug flow processing control, with or without the use of catalysts, will allow the processing of any organic-carbon-containing feedstock. An advantage to beneficiating the organic

- 20 carbon-containing feedstock is that it has, to a large extent, already been brought to an acceptable moisture level and is already fairly homogeneous. For homogeneity on the macro-scale, the output from different organic-carbon-containing feedstock inputs have substantially similar characteristics (e.g. energy density, consistency, moisture content), and these characteristics extend throughout the material. On, the molecular scale, with
- **25** fewer salts present, there are fewer microenvironments where the microwaves would deposit energy differently than in the bulk of the organic-carbon-containing feedstock. Therefore, the heating would be more uniform from beneficiated organic-carbon containing feedstock than from raw unprocessed organic-carbon-containing feedstock inputs.

30 A microwave sub-system in accordance with embodiments of the invention includes a reaction chamber having one or more substantially microwave-transparent walls and a microwave heating/radiation system. The microwave heating/radiation system is

arranged so that microwaves generated **by** the heating/radiation system are directed through the substantially microwave-transparent walls of the reaction chamber and into the reaction cavity where the feedstock material is reacted without substantially heating the walls of the reaction chamber. To enhance the temperature uniformity of the feedstock,

- **5** the reaction chamber and the heating/radiation system may be in relative motion, e.g., relative rotational and/or translational motion. In some implementations, the heating system may rotate around a stationary reaction chamber. In some implementations, the feedstock within the reaction chamber may rotate **by** the use of flights with the heating/radiation system remaining stationary. In some implementations, the reaction
- **10** chamber may rotate with the heating system remaining stationary. In yet other implementations, both the reaction chamber and the heating/radiation system may rotate, e.g., in countercurrent, opposing directions. To further increase temperature uniformity, the system may include a mechanism for stirring and/or mixing the feedstock material within the reaction chamber. The reaction chamber may be tilted during reaction process,

15 for example, to force the feedstock to go through the catalytic bed.

Figures **9A** and 1OB illustrate side and cross sectional views, respectively, of a microwave sub-system **(900)** for converting organic-carbon-containing feedstock to liquid fuel and processed biochar fuel in accordance with embodiments of the invention. Although a reaction chamber **(910)** may be any suitable shape, reaction chamber **910** is

- 20 illustrated in Figures **9A** and 9B as a cylinder having a cylindrical wall **(911)** that is substantially transparent to microwaves in the frequency range and energy used for the reaction process. Reaction chamber **910** includes a reaction cavity **(912)** enclosed **by** cylindrical wall **911.** Microwave sub-system **900** includes a transport mechanism **(918)** configured to move the feedstock through the reaction chamber. The operation of
- **25** microwave sub-system **900** with regard to the reactions taking place within reaction chamber **910** may be modeled similarly to that of a plug flow reactor.

As illustrated in Figure **9A,** a microwave sub-system includes transport mechanism **918** for moving the feedstock material through reaction chamber **910.** Transport mechanism **918** is illustrated as a screw auger, although other suitable mechanisms, e.g.,

30 conveyer, may also be used. Transport mechanism **918** may further provide for mixing the feedstock within the reaction chamber. In some embodiments, reaction chamber wall **911** may have a thickness of about **3/16** inch (4.8 millimeters). The smoothness of

reaction chamber wall **911** facilitates the movement of the feedstock through reaction chamber **910.**

A heating/radiation subsystem *(915)* may include any type of heating and/or radiation sources, but preferably includes a microwave generator **(916)** such as a *5* magnetron which is configured to emit microwaves **(913)** having a frequency and energy sufficient to heat the organic-carbon-containing feedstock to a temperature sufficient to facilitate the desired reaction of the feedstock, for example, for deconstruction of the feedstock, microwaves in a frequency range of about **0.3** GHz to about **300** GHz may be used. For example, the operating power of the magnetrons may be in the range of about 1

- **10** Watt to **500** kilowatts. Magnetron **916** is positioned in relation to reaction chamber **910 so** that microwaves **913** are directed through wall **911** of reaction chamber **910** and into reaction cavity **912** to heat and irradiate the material therein. **A** mechanism **(917)** provides relative motion between magnetron **916** and reaction chamber **910** along and/or around longitudinal axis **920** of reaction chamber **910.** In some embodiments, mechanism **917**
- *15* may facilitate tilting reaction chamber **910** and/or magnetron **916** at an angle **0** (see Figure **9C)** to facilitate the reaction of the feedstock and/or the extraction of gases, for example. In the embodiment illustrated in Figures **9A-C,** magnetron **916** is positioned on rotational mechanism **917,** such as a rotatable cage or drum that rotates magnetron **916** around stationary reaction chamber **910.** In some implementations, the rotation around the
- 20 chamber may not be complete, but the rotation path may define an arc around the circumference of the reaction chamber. The rotation may occur back and forth along the path of the arc. As previously mentioned, in some embodiments, reaction chamber **910** may be the rotating component, or both magnetron **916** (also called the heating/radiation subsystem) and reaction chamber **910** may rotate, e.g., in opposing, countercurrent
- **25** directions. The rotation between the reaction chamber and the magnetron provides more even heating and more even microwave exposure of the feedstock within reaction cavity **912,** thus enhancing the efficient reaction chemistry of the feedstock and/or other processes that are temperature/radiation dependent, such as removal of water from the feedstock. The rotation lessens the temperature gradient and/or maintains a more constant
- **30** microwave flux across the plug inside the reaction chamber. Reaction chamber **910** may include one or more entry ports **(920),** e.g., quartz entry ports, configured to allow the injection or extraction of substances into or out of

reaction cavity **912.** Reaction chamber **910** is also surrounded **by** a microwave-reflective enclosure **(922).** In one implementation, the quartz ports may be used to extract air and/or oxygen from the reaction cavity. Extraction of air and/or oxygen may be used to suppress combustion which is desirable for some processes.

5 For example, in certain embodiments, microwave sub-system **900** may be used to preprocess the feedstock through compression and/or removal of air and/or water. In this application, gases such as hydrogen and/or nitrogen may be injected through one or more ports **920** to hydrogenate and/or suppress combustion of the feedstock. Reaction chamber **910** may also include one or more exit ports **(921), e.g.,** quartz exit ports, configured to

10 allow passage of water, water vapor, air, oxygen and/or other substances and/or **by** products from reaction chamber **910.** In other embodiments, the processed organic carbon-containing feedstock is already sufficiently compressed and reduced in both air and water to be introduced directly into the reaction chamber.

Figure **9D** is a diagram illustrating a microwave-sub-system *(950)* for producing *15* fuel from organic-carbon-containing feedstock in accordance with embodiments of the invention. Microwave sub-system **950** includes an input hopper (also referred to as a load hopper) *(951)* configured to allow introduction of the feedstock material into microwave sub-system **950. A** gearmotor auger drive **(952)** provides a drive system for the auger **(953)** that transports the feedstock through microwave sub-system **950.** As the feedstock

20 is compressed in load hopper **951,** air is extracted through an atmosphere outlet (954). **A** seal **(955)** isolates load hopper **951** from a reaction chamber **(956)** to maintain a level of vacuum. Reaction chamber **956** includes walls of a microwave-transparent material. One or more stationary microwave heads **957** are positioned at the walls of the reaction chamber **956.** In addition, microwave sub-system **950** includes one or more rotating

25 microwave heads **(958).** In one implementation, each rotating microwave head is located at a fixed position with respect the longitudinal axis **(960)** of reaction chamber **956.** The rotating microwave head is mounted on a slipring bearing **(959)** which allows microwave head **958** to rotate around reaction chamber **956. A** microwave reflective enclosure **(962)** encompasses reaction chamber **956.** In some implementations rotating microwave head(s)

30 958 may rotate around the longitudinal axis **960** of the reaction chamber **956** as well as moving back and forth along the longitudinal axis **960.** Microwave sub-system **950** includes a seal at the exit of reaction chamber **956** to maintain the reaction chamber

vacuum. In some embodiments, the organic-carbon-containing feedstock is compressed in the sub-beneficiation system discussed earlier before it enters the microwave sub-system and little if any air extraction is needed.

Figure **10A** is a block diagram of a microwave sub-system **1000** that uses one or **5** more of the reaction chamber illustrated in Figures **9A** and 9B. The reaction chamber 1020, **1030** may be arranged and/or operated in series or in a parallel configuration. An extraction process (1020) and a reaction process **(1030)** depicted in Figures **10A** and 1OB are illustrated as occurring in two separate reaction chambers, e.g., that operate at different temperatures. Alternatively, the extraction process and the reaction process may be **10** implemented in a single reaction chamber with two separate zones, e.g., two separate temperature zones.

In microwave sub-system **1000** of Figure **10,** one or both of water/air extraction section 1020 and reaction section **1030** may be similar to the reaction chamber in microwave sub-system **900** of Figures **9A** and 9B. Organic-carbon-containing feedstock,

- *15* such as, for example, one or more of manure containing plant cells, wood chips, and plant based cellulose, enters the microwave sub-system through a hopper **(1011),** and traverses an airlock (1012) to enter a feedstock preparation module **(1013). If** needed, a catalyst, such as zeolite, and/or other additives that enhance the reaction process, for example to adjust the **pH,** may be introduced into microwave sub-system **1000** through input hopper
- 20 **1011** and/or the entry ports (shown in Figure 9B). In the feedstock preparation module **1013,** the feedstock material may be shredded to a predetermined particle size that may be dependent on the properties of the feedstock, such as the purity, density, and/or chemical composition of the feedstock. **If** used, the catalyst may be added at the time that the feedstock is being prepared so that the catalyst is evenly dispersed within the feedstock
- **25** material before entering a reaction chamber **(1031).** In general, the less uniform the feedstock, the smaller the particle size needed to provide efficient reaction.

After the initial feedstock preparation stage, the shredded and mixed feedstock is transported **by** a transport mechanism **1015** into the extraction chamber 1021 of the next stage of the process. An air/water extraction subsystem (1020), which performs the

30 optional processes of water and/or air extraction prior to the reaction process, includes a heating/radiation module (1022) comprising at least a magnetron **(1023)** configured to generate microwaves **(1026)** that may be mounted on a rotational or stationary mechanism **WO 2015/026987 PCT/US2014/051958**

41

(1027). If mounted on a rotational mechanism, the mechanism rotates magnetron **1023** either partially or fully around extraction chamber 1021 as microwaves **1026** are directed through a wall (1024) of extraction chamber 1021 and into an extraction cavity **(1025)** impinging on and heating the feedstock therein. In some embodiments, heating module **5** 1022 may utilize only one magnetron **1023** or only two or more magnetrons without using

other heat/radiation sources.

In some embodiments, heating/radiation module 1022 may utilize magnetron **1023** in addition to other heat sources, such as heat sources that rely on thermal conduction through the wall of the extraction chamber, e.g., flame, steam, electrical resistive heating,

- **10** recycled heat from the process, and/or other heat sources. During the air and/or water extraction process, the feedstock may be heated to at least **100 C,** the boiling point of water, to remove excess water from the feedstock. The excess water (e.g., in the form of steam) and/or other substances may exit extraction chamber 1021 via one or more exit ports. Additives to the feedstock, such as inert and/or reactive gases including hydrogen
- *15* and/or nitrogen, may be introduced via one or more input ports into extraction chamber 1021 of the water/air extraction process. In addition to being heated and irradiated **by** microwaves, the feedstock may also be subjected to a pressurized atmosphere and/or a vacuum atmosphere and/or may be mechanically compressed to remove air from extraction chamber 1021.
- 20 After the optional air and/or water extraction process, transport mechanism **1015** moves the feedstock to the next processing stage, a reaction section **(1030)** which involves the reaction process, e.g., thermal deconstruction, of the feedstock. After the feedstock/catalyst mixture enters a reaction chamber **(1031)** surrounded **by** the microwave reflecting enclosure **(1038),** the mixture is heated to a temperature that is sufficient to
- **25** facilitate the desired reaction. For example a temperature of in a range of about 200 **C** to about **350 C** is used to crack the hydrocarbons in the feedstock into shorter chains to produce liquid fuel through deconstruction. In addition to being heated, the feedstock may also be subjected to a pressurized atmosphere or a vacuum atmosphere, and/or may be mechanically compressed in reaction chamber **1031.**

30 In some embodiments, heating/radiation in the reaction chamber **1031** is accomplished using a magnetron **(1033)** emitting microwaves **(1036).** Magnetron **1033** may rotate relative to reaction chamber **1031.** As previously described in connection with

the water extraction section 1020, a rotating magnetron **(1033)** may be supported **by** rotational mechanism **(91037),** such as a cage or drum. Rotational mechanism **1037** allows relative rotational motion between magnetron **1033** and reaction chamber **1031.** For example, magnetron **1033** may rotate completely around reaction chamber **1031** or the

5 rotation of magnetron **1033** may proceed back and forth along an arc that follows the circumference of reaction chamber **1031.** The rotating magnetron heating system **1033** may be supplemented using a stationary magnetron, and/or other conventional heat sources such as a flame or electrical resistive heating. Rotating magnetron **1033** provides more even heating/radiation of the feedstock material and catalyst within a reaction cavity **10 (1035)** and enhances the heating properties over that of stationary heat sources.

The cracked hydrocarbons vaporize and are collected in a condenser (1041) and liquefy and then are sent to a distiller (1040) to produce the diesel fuel, while heavier, longer chain hydrocarbon molecules may be recycled back to the reaction chamber. In some implementations, distillation may not be necessary, and the fuel product only needs

15 to be filtered.

In some configurations, it is desirable to control the processes of the reaction to allow a higher efficiency of fuel extraction from the feedstock. Figure 1OB is a block diagram of a microwave sub-system **(1005)** that includes the sub-system components described in connection with Figure **1OA** along with a feedback control system **(1050).**

- 20 The illustrated feedback control system **1050** includes a controller **(1051)** and one or more sensors **(1052), (1053),** (1054) which may be configured to sense parameters at various stages during the process. Feedback control system **1050** may include sensors **1052** at the feedstock preparation stage which are configured to sense parameters of the feedstock and/or feedstock preparation process. For example, sensors **1052,** may sense the chemical
- **25** composition of the feedstock, density, moisture content, particle size, energy content or other feedstock parameters. Sensors **1052** may additionally or alternatively sense the conditions within the feedstock preparation chamber, e.g., flow, pressure, temperature, humidity, composition of the gases present in the chamber, etc. Sensors **1052** develop signals (1055a) which are input to controller electronics **1051** where they are analyzed to
- **30** determine the condition of the feedstock and/or the feedstock preparation process. In response to sensed signals 1055a, controller **1051** develops feedback signals **(1055b)** which control the operation of the feedstock preparation module **(1013).** For example, in

some implementations, the controller **1051** may control feedstock preparation module **1013** to continue to shred and/or grind the feedstock material until a predetermined particle size and/or a predetermined particle size variation is detected. In another example, based on the sensed chemical composition of the feedstock, controller **1051** may cause a *5* greater or lesser amount of catalyst to be mixed with the feedstock or may cause different

types of catalyst to be mixed with the feedstock.

A control system **(1050)** may also develop feedback signals **(1056b), (1057b)** to control the operation of water extraction module 1020 and/or the reaction module **1030,** respectively, based on sensed signals 1056a, 1057a. For example, the sensors **(1053),**

10 (1054) may sense the temperature of the water extraction and/or reaction processes and controller **1051** may develop feedback signals **1056b, 1057b** to control the operation of heating/radiation systems 1022, **1032,** e.g., power, frequency, pulse width, rotational or translational velocity, etc. of one or both of magnetrons **1023, 1033.** Controller **1051** may develop feedback signals to the magnetrons to control the amount of radiation impinging

15 on the feedstock so that the feedstock will not be over-cooked or under-cooked and development of hot spots will be avoided. Controller system **1050** may control the injection of various substances into one or both of the extraction chamber and/or the reaction chamber 1021, **1031** through the entry ports to control the processes taking place within the chambers 1021, **1031.** Biochar, the residue of the depleted feedstock, is sent to

20 a storage unit. In some embodiments, controller system **0150** may be used to control conditions that beneficially affect the properties of the processed biochar where specific properties are desired beyond that resulting just from the feedstock choice. After the distillation stage, the heavy hydrocarbons may be recycled back into the reaction chamber and the lighter hydrocarbons may be sent on to a polymerization stage.

25 The reaction chambers may be made of quartz, glass, ceramic, plastic, and/or any other suitable material that is substantially transparent to microwaves in the frequency and energy range of the reaction processes. In some configurations, the heating/radiation systems described herein may include one or more magnetrons that rotate relative to the reaction chamber. In some embodiments, the magnetrons may be multiple and/or may be

30 stationary. Figure 11 **A** illustrates a reaction system **(1100)** which includes multiple stationary magnetrons **(1111)** arranged on a drum **(1112)** that acts as a Faraday cage and is disposed outside a cylindrical reaction chamber **(1113)** having one or more microwave-

transparent walls. In reaction system **1100,** the drums made of a material that is microwave opaque, such as, for example, metal, so as to cause the microwaves in reaction chamber **1113** to reflect back and forth through the feedstock, thus more efficiently being used to convert the feedstock into liquid renewable fuel and solid renewable fuel biochar.

5 The operation of the magnetrons may be continuous, or may be pulsed, e.g., in a multiplexed pattern. In some embodiments (Figurel 1lB), drum **1113** supporting magnetrons 1111 may be rotated **(1130)** around the longitudinal axis **(1150)** of reaction chamber **1112** and/or reaction chamber **1112** may be rotated (1120) around its longitudinal axis **1150.**

10 A feedstock transport mechanism may be disposed within a reaction chamber. For example, as illustrated in Figure 11C, the feedstock transport mechanism may comprise one or more baffles **(1161)** that are configured to move the feedstock through a reaction chamber **(1160)** as the reaction chamber rotates. The baffles **361** may be mounted to the walls of reaction chamber **1160** and/or may be otherwise installed within the reaction *15* chamber to provide movement of feedstock within and through reaction chamber **1160,** e.g., longitudinally through the reaction chamber.

In some embodiments, illustrated in Figure 12, one or more secondary heat sources **(1250),** such as a flame, steam, and/or electric resistive heating, or recycled heat, may be used in addition to magnetrons **(1216)** which are stationary, or are supported on a

- 20 mechanism **(1217)** that rotates around the circumference of the reaction chamber (1220) enclosed in a microwave-reflecting Faraday cage (1221). In some configurations, magnetrons **1216** may not make a complete revolution around reaction chamber 1220, but may rotate back and forth **(1219)** along an arc that follows the circumference of reaction chamber 1220. Various configurations are possible as long as the feedstock is exposed to **25** substantially uniform heat throughout the mass of the feedstock particles to form
- processed biochar having pore density, distribution, and variance in size and distribution as described above for processed biochar of the invention.

Movement of the one or more magnetrons relative to the reaction chamber may also include motion that moves the magnetron along the longitudinal axis of the reaction

30 chamber, as illustrated in Figure **13. A** reaction chamber **(1310)** and a cage **(1320)** are illustrated that support a magnetron **(1330).** Cage **1320** and magnetron **1330** may be moved **(1340)** back and forth along the longitudinal axis **(1350)** of reaction chamber **1310**

WO 2015/026987 PCT/US2014/051958

45

and over a metal microwave-reflecting Faraday cage *(1315)* enclosing reaction chamber **1310.** In some implementations, in addition to and/or concurrent with the motion (1340) of cage **1320** and magnetron **1330** along longitudinal axis **1350,** cage **1320,** and magnetron **1330** may be rotated **(1360)** around the longitudinal axis **1350.**

5 Process for making Biochar

The invention also comprises a process for making biochar. The process includes two aspects of the beneficiation process for making processed carbon-containing feedstock with the beneficiation sub-system discussed above and one aspect of the microwave process for converting the processed carbon-containing feedstock into biochar.

- **10** Specifically, the process is one of making a solid renewable fuel with three steps. The first is to input into a system, comprising a first sub-system and a second sub-system, an unprocessed organic-carbon-containing feedstock that includes free water, intercellular water, intracellular water, intracellular water-soluble salts, and at least some plant cells comprising cell walls that include lignin, hemicellulose, and microfibrils within fibrils.
- *15* The second step is to pass the unprocessed organic-carbon-containing feedstock through the first sub-system, a beneficiation sub-system, to make processed organic-carbon containing feedstock. The third step is to pass the processed organic-carbon-containing feedstock through a microwave sub-system to convert the processed organic-carbon containing feedstock into the solid processed biochar fuel.

20 Beneficiation Sub-System Process

The beneficiation process step comprises the step of passing unprocessed organic carbon-containing feedstock through a beneficiation sub-system process to result in processed organic-carbon-containing feedstock having a water content of less than 20 wt% and a salt content that is reduced **by** at least **60** wt% on a dry basis from that of the

- **25** unprocessed organic-carbon-containing feedstock. There are two aspects of the beneficiation sub-system process. The first focuses on the properties of the processed organic-carbon-containing feedstock and the second focuses on the energy efficiency of the process of the invention over that of currently known processes for converting unprocessed organic-carbon-containing feedstock into processed organic-carbon
- **30** containing feedstock suitable for use with downstream fuel producing systems. Both use the beneficiation sub-system disclosed above.

First Aspect

The first aspect of the beneficiation process step of the invention comprises four steps. The first step is inputting into a reaction chamber unprocessed organic-carbon containing feedstock comprising free water, intercellular water, intracellular water, intracellular water-soluble salts, and at least some plant cells comprising cell walls that **5** include lignin, hemicellulose, and microfibrils within fibrils. Some embodiments have

unprocessed organic-carbon-containing feedstock that comprises water-soluble salts having a content of at least 4000 mg/kg on a dry basis. The second step is exposing the feedstock to hot solvent under pressure for a time

at conditions specific to the feedstock to make at least some regions of the cell walls **10** comprising crystallized cellulosic fibrils, lignin, and hemicellulose more able to be penetrable **by** water-soluble salts without dissolving more than **25** percent of the lignin and hemicellulose. As mentioned above, this is accomplished **by** one or more of unbundling regions of at least some fibrils, depolymerizing at least some strands of lignin and/or hemicellulose, or detaching them from the cellulose fibrils, thereby disrupting their

15 interweaving of the fibrils. In addition, the cellulose fibrils and microfibrils can be partially depolymerized and/or decrystallized.

The third step is rapidly removing the elevated pressure so as to penetrate the more penetrable regions with intracellular escaping gases to create porous feedstock with open pores in at least some plant cell walls. In some embodiments the pressure is removed to 20 about atmospheric pressure in less than **500** milliseconds (ms), less than **300** ms, less than 200 ms, less than **100** ms, or less than **50** ms.

The fourth step is pressing the porous feedstock with conditions that include an adjustable compaction pressure versus time profile and compaction time duration, and between pressure plates configured to prevent felt from forming and blocking escape from

- **25** the reaction chamber of intracellular and intercellular water and intracellular water-soluble salts, and to create processed organic-carbon-containing feedstock that has a water content of less than 20 wt **%** and a water-soluble salt content that is decreased **by** at least **60 %** on a dry basis that of the unprocessed organic-carbon-containing feedstock. In some embodiments, the water content is measured after subsequent air-drying to remove
- **30** remaining surface water. In some embodiments, the pressure plate has a pattern that is adapted to particular organic-carbon-containing feedstock based on its predilection to form felts and pith content as discussed above. In some embodiments, the pressure amount and

pressure plate configuration is chosen to meet targeted processed organic-carbon containing feedstock goals for particular unprocessed organic-carbon-containing feedstock. In some embodiments, the pressure is applied in steps of increasing pressure, with time increments of various lengths depending on biomass input to allow the fibers to

5 relax and more water-soluble salt to be squeezed out in a more energy efficient manner. In some embodiments, clean water is reintroduced into the biomass as a rinse and the biomass is pressed again.

The process may further comprise a fifth step, prewashing the unprocessed organic-carbon-containing feedstock before it enters the reaction chamber with a particular **10** set of conditions for each organic-carbon-containing feedstock that includes time duration, temperature profile, and chemical content of pretreatment solution to at least initiate the dissolution of contaminates that hinder creation of the cell wall passageways for intracellular water and intracellular water-soluble salts to pass outward from the interior of the plant cells.

15 The process may further comprise a sixth step, masticating. The unprocessed organic-carbon-containing feedstock is masticated into particles having a longest dimension of less than 1 inch **(2.5** centimeters) before it enters the reaction chamber.

The process may further comprise a seventh step, separating out the contaminants. This step involves the separating out of at least oils, waxes, and volatile organic 20 compounds from the porous feedstock with solvents less polar than water.

As with the system aspect, the unprocessed organic-carbon-containing feedstock may comprise at least two from a group consisting of an herbaceous plant material, a soft woody plant material, and a hard woody plant material that are processed in series or in separate parallel reaction chambers. In addition, in some embodiments, the energy density

25 of each plant material in the processed organic-carbon-containing feedstock may be substantially the same. In some embodiments, the organic-carbon-containing feedstock comprises at least two from the group consisting of an herbaceous plant material, a soft woody plant material, and a hard woody plant material, and wherein the energy density of each plant material in the processed organic-carbon-containing feedstock is at least **17**

30 MMBTU/ton (20 **GJ/MT).**

WO *2015/026987* **PCT/US2014/051958**

48

Figure 14 is a block diagram of a process for making processed organic-carbon containing feedstock with less than **60** percent water-soluble salt on a dry basis over that of its unprocessed form and with less than 20 wt **%** water.

Second Aspect

5 The second aspect is similar to the first except steps have an efficiency feature and the resulting processed organic-carbon-containing feedstock has a cost feature. The second aspect also comprises four steps. The first step is inputting into a reaction chamber organic-carbon-containing feedstock comprising free water, intercellular water, intracellular water, intracellular water-salts, and at least some plant cells comprising

- **10** lignin, hemicellulose, and fibrils within fibril bundles. Each step emphasizes more specific conditions aimed at energy and material conservation. The second step is exposing the feedstock to hot solvent under pressure for a time at conditions specific to the feedstock to swell and unbundle the cellular chambers comprising partially crystallized cellulosic fibril bundles, lignin, hemicellulose, and water-soluble salts without dissolving
- *15* more than **25** percent of the lignin and to decrystallize at least some of the cellulosic bundles. The third step is removing the pressure to create porous feedstock with open pores in its cellulosic chambers. The fourth step is pressing the porous feedstock with an adjustable compaction pressure versus time profile and compaction duration between pressure plates configured to prevent felt from forming and blocking escape from the
- 20 reaction chamber of intracellular and intercellular water and intracellular water-soluble salts, and to create a processed organic-carbon-containing feedstock that has a water content of less than 20 wt **%,** a water-soluble salt content that is decreased **by** at least **60** wt **%** on a dry basis, and a cost per weight of removing the water and the water-soluble salt is reduced to less than **60 %** of the cost per weight of similar water removal from **25** known mechanical, known physiochemical, or known thermal processes.

Figure **15** is a block diagram of a process for making processed organic-carbon containing feedstock with less than **50** wt **%** water-soluble salt of a dry basis than that of unprocessed organic-carbon-containing feedstock and less than 20 wt **%** water, and at a cost per weight of less than **60 %** that of similar water removal from known mechanical,

30 known physiochemical, or known thermal processes that can remove similar amounts of water and water-soluble salt

Energy efficiencies are achieved in part **by** tailoring process conditions to specific organic-carbon-containing feedstock as discussed above. Some embodiments use systems engineered to re-capture and reuse heat to further reduce the cost per ton of the processed organic-carbon-containing feedstock. Some embodiments remove surface or free water

- **5** left from the processing of the organic-carbon-containing feedstock with air drying, a process that takes time but has no additional energy cost. Figure **16** is a table that shows some process variations used for three types of organic-carbon-containing feedstock together with the resulting water content and water-soluble salt content achieved. It is understood that variations in process conditions and processing steps may be used to raise
- **10** or lower the values achieved in water content and water-soluble salt content and energy cost to achieve targeted product values. Some embodiments have achieved water contents as low as less than **5** wt **%** and water-soluble salt contents reduced **by** as much as over **95** wt **%** on a dry basis from its unprocessed feedstock form.

Microwave Sub-system Process

15 The microwave sub-system process step comprises passing the processed organic carbon-containing feedstock through a microwave sub-system process to result in a solid renewable fuel composition having an energy density of at least **17** MMBTU/ton (20 **GJ/MT)** a water content of less than **10** wt%, water-soluble salt that is decreased **by** at least **60** wt% on a dry basis from that of the unprocessed organic-carbon-containing 20 feedstock, and pores that have a variance in pore size of less than **10 %.**

Figure **17** is a block diagram of an embodiment of a process for passing processed organic-carbon-containing feedstock through a microwave sub-system to create a solid renewable fuel processed biochar of the invention. The processed organic-carbon containing feedstock is input **(1710)** to a reaction chamber having walls that are

- **25** substantially transparent to microwaves used to heat and/or irradiate the feedstock. The heating and/or radiation occur **by** directing **(1720)** the microwave energy through the walls of the reaction chamber so that it impinges on the feedstock disposed within the reaction chamber. The feedstock is heated/irradiated **(1730) by** the microwaves, optionally in the presence of a catalyst, until reaction of the organic-carbon-containing molecules occurs to
- **30** produce the desirable end fuel product. The fuel product created **by** the reaction processes are collected (1740).

Various modifications and additions can be made to the preferred embodiments discussed hereinabove without departing from the scope of the present invention. Accordingly, the scope of the present invention should not be limited **by** the particular embodiments described above, but should be defined only **by** the claims set forth below

5 and equivalents thereof.

THE **CLAIMS DEFINING** THE **INVENTION** ARE **AS** FOLLOWS:

1. **A** composition comprising:

a processed biochar composition that comprises a solid renewable carbon fuel with characteristics that include an energy density of at least **17** MMBTU/ton (20 **GJ/MT),** a water content of less than **10** wt%, water-soluble salt that is decreased more than **60** wt% on a dry basis from that of renewable feedstock, and pores that have a variance in pore size of less than **10** percent, and

the processed biochar is made from renewable feedstock that is converted into the processed organic-carbon-containing feedstock with a beneficiation sub-system, and to the processed biochar with a microwave sub-system,

wherein the beneficiation sub-system, comprises:

a transmission device configured to convey into a reaction chamber renewable feedstock comprising free water, intercellular water, intracellular water, intracellular water-soluble salts, and at least some plant cells comprising cell walls that include lignin, hemicellulose, and microfibrils within fibrils;

at least one reaction chamber comprising at least one entrance passageway, at least one exit passageway for fluid, at least one exit passageway for processed organic-carbon-containing feedstock, and at least three sections, the sections comprising:

a wet fibril disruption section configured to interact with at least some of the lignin and hemicellulose between the fibrils to make at least some regions of the cell wall more susceptible to outflow **by** water-soluble salts;

a vapor explosion section in communication with the wet fibril disruption section and at least configured to volatilize plant fibril permeable fluid through rapid decompression to penetrate the more susceptible regions of the cell wall so as to create a porous organic-carbon-containing feedstock with plant cell wall passageways for intracellular water and intracellular water-soluble salts to pass from the plant cell; and

a compaction section in communication with the vapor explosion section and configured to compress the porous organic-carbon-containing feedstock between pressure plates configured to minimize formation of water-impermeable felt so as to permit the escape of intracellular water and intracellular water-soluble salt from the reaction

chamber fluid exit passageway and to create processed organic-carbon-containing feedstock that passes out through its reaction chamber exit passageway; and

a collection device in communication with the reaction chamber and configured to gather the processed organic-carbon-containing feedstock having a water content of less than 20% **by** weight and a water-soluble salt content that is decreased **by** at least **60 %** on a dry basis from that of the renewable feedstock.

2. The composition of claim **1,** wherein the microwave sub-system- comprises:

at least one reaction chamber within a microwave reflecting enclosure, the reaction chamber comprising at least one microwave-transparent chamber wall and at least one reaction cavity within the reaction chamber that is configured to hold the organic-carbon-containing feedstock in an externally supplied oxygen free atmosphere;

a microwave subsystem comprising at least one device configured to emit microwaves when energized, the microwave device positioned relative to the reaction chamber so that the microwaves are directed through the microwave-transparent chamber wall and into the reaction cavity; and

a mechanism configured to provide relative motion between the microwave device and the reaction chamber.

3. The composition of claim **1,** further comprising pores having a number of pores per volume that is at least **10** percent more than would have been in a char made with the same feedstock but using a thermal process that creates a liquid phase during the process.

4. The composition of claim **1,** further comprising pores that have a variance in pore distribution of less than **10** percent.

5. The composition of claim **1,** wherein a number of pores per volume that is at least 20 percent more than would have been in a char made with the same feedstock but using a thermal process that creates a liquid phase during the process.

6. The composition of claim **1,** wherein a number of pores per volume that is at least **30** percent more than would have been in a char made with the same feedstock but using a thermal process that creates a liquid phase during the process.

7. The composition of claim **1,** wherein a number of pores per volume that is at least 40 percent more than would have been in a char made with the same feedstock but using a thermal process that creates a liquid phase during the process.

8. The composition of claim **1,** wherein processed the biochar has a heat content of at least 20% more than the heat content in a char made with the same feedstock but using a thermal process that creates a liquid phase during the process.

9. The composition of claim **1,** wherein the processed organic-carbon-containing feedstock comprises at least **5** weight percent water.

10. The composition of claim **1,** wherein the processed organic-carbon-containing feedstock comprises at least **5** weight percent volatiles.

11. The composition of claim **1,** wherein the renewable feedstock comprises at least two from a group consisting of a herbaceous plant material, a soft woody plant material, and a hard woody plant material, wherein each type passes in series through the at least one reaction chamber, and wherein the energy density of each plant material in the processed organic-carbon-containing feedstock is at least **17** MMBTU/ton (20 **GJ/MT). .**

12. The composition of claim **1,** wherein the renewable feedstock has a water-soluble salt content of at least 4000 mg/kg on a dry basis.

13. The composition of claim **1,** wherein the renewable feedstock comprises at least two from a group consisting of a herbaceous plant material, a soft woody plant material, and a hard woody plant material, wherein each type passes in series through the at least one reaction chamber, and wherein the energy density of each plant material in the processed organic-carbon-containing feedstock is at least **17** MMBTU/ton (20 **GJ/MT).**

14. The composition of claim 2, wherein the beneficiation system, further comprises: a pretreatment chamber that is configured to use for each renewable feedstock a particular set of conditions including time duration, temperature profile, and the chemical content of pretreatment solution to at least initiate the dissolution of contaminates that would hinder creation of the plant cell wall passageways that allow intracellular water and intracellular water-soluble salts to pass outward from the plant cells.

15. The composition of claim 2, wherein the vapor explosion section, further comprises at least one rinsing subsection configured to flush at least some of the water-soluble salt from the porous organic-carbon-containing feedstock before it is passed to the compaction section.

16. A process of making processed biochar comprising:

inputting into a system comprising a first and a second subsystem a renewable feedstock that includes free water, intercellular water, intracellular water, intracellular water-soluble salts, and at least some plant cells comprising cell walls that include lignin, hemicellulose, and microfibrils within fibrils;

passing renewable feedstock through the first sub-system, a beneficiation sub-system process, to result in processed organic-carbon-containing feedstock having a water content of less than 20 wt% and a salt content that is reduced **by** at least **60** wt% on a dry basis from that of the renewable feedstock; and

passing the processed organic-carbon-containing feedstock through the second sub system, a microwave sub-system process, to result in a solid renewable fuel composition having an energy density of at least **17** MMBTU/ton (20 **GJ/MT)** a water content of less than **10** wt%, water-soluble salt that is decreased **by** at least **60** wt% on a dry basis from that of the renewable feedstock, wherein the beneficiation sub-system process comprises:

inputting into a beneficiation sub-system reaction chamber renewable feedstock comprising free water, intercellular water, intracellular water, intracellular water-soluble salts, and at least some plant cells comprising cell walls that include lignin, hemicellulose, and microfibrils within fibrils;

exposing the feedstock to hot solvent under pressure for a time at conditions specific to the feedstock to make some regions of the cell walls comprising crystallized cellulosic fibrils, lignin, and hemicellulose more able to be penetrable **by** water-soluble salts without dissolving more than 25 percent of the lignin and hemicellulose;

removing the pressure so as to penetrate the more penetrable regions to create porous feedstock with open pores in the plant cell walls; and

pressing the porous feedstock with conditions that include an adjustable compaction pressure versus time profile and compaction time duration to create processed organic-carbon containing feedstock that has a water content of less than 20 wt% and a water-soluble salt content that is decreased **by** at least **60** wt% on a dry basis from that of renewable feedstock,

and the microwave sub-system process further comprises:

inputting processed organic-carbon-containing feedstock into a substantially microwave transparent reaction chamber containing no externally supplied oxygen and within a microwave reflective enclosure;

directing microwaves from a microwave source through walls of the reaction chamber to impinge on the feedstock;

providing relative motion between the microwave-transparent reaction chamber and the microwave source; and

microwaving the feedstock until the feedstock reacts to produce a solid fuel comprising less than **60** wt% on a dry basis of water-soluble salt from that of renewable feedstock, a water content of less than **10** wt%, and pores that have a variance in pore size of less than **10** percent.

17. The process of claim **16,** wherein the pressure drop is at least **230** psig *(1.59* MPaG) and the duration of the pressure drop is **50** ms.

CONTA

T' B'

 \circ

 $\ddot{\circ}$

 \circ

 \circ

ັດ

 \bullet

 \circ

 \circ

 $\ddot{\circ}$

COLOR O \circ \circ \circ \circ \circ \circ ∞ \circledcirc ∞ \circ \circ \circ Ő $\mathbf O$ $\overline{\circ}$ \overline{O} \circ \circ \bigcirc \circ \circ $\ddot{\circ}$ \circ \circ \circ \circ \circ $^\prime \mathsf{O}$ \circ \circ $\ddot{\text{o}}$ \circ \circ \circ \circ $\ddot{\text{o}}$ \circ \circ ò \circ \circ \circ € \circ $\mathbf C$ \circ $\ddot{\text{o}}$ \circ \circ \circ \circ Ó \circ $\ddot{\circ}$ \circ \circ 00000 \circ $\overline{\circ}$ $\ddot{\circ}$ \circ $\ddot{\circ}$ \circ $^\prime\circ$ \circ $\ddot{\mathbf{O}}$ ی \circ

 $5/21$

Fig. 5A

 $\overline{\sigma}$ ^o

 \circ

Fig. 6B

PCT/US2014/051958

Fig. 11B

Fig. 11C

1221 250 \mathbb{S} ga je 1 , paad
Tarii
aadaad $1216 \frac{1}{2}$

WO 2015/026987

SS₀

1330

Fig. 14

rig: 15

Fig. 16

