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(54) **SYNTHETIC COAL AND METHODS OF
PRODUCING SYNTHETIC COAL FROM
FERMENTATION RESIDUE**

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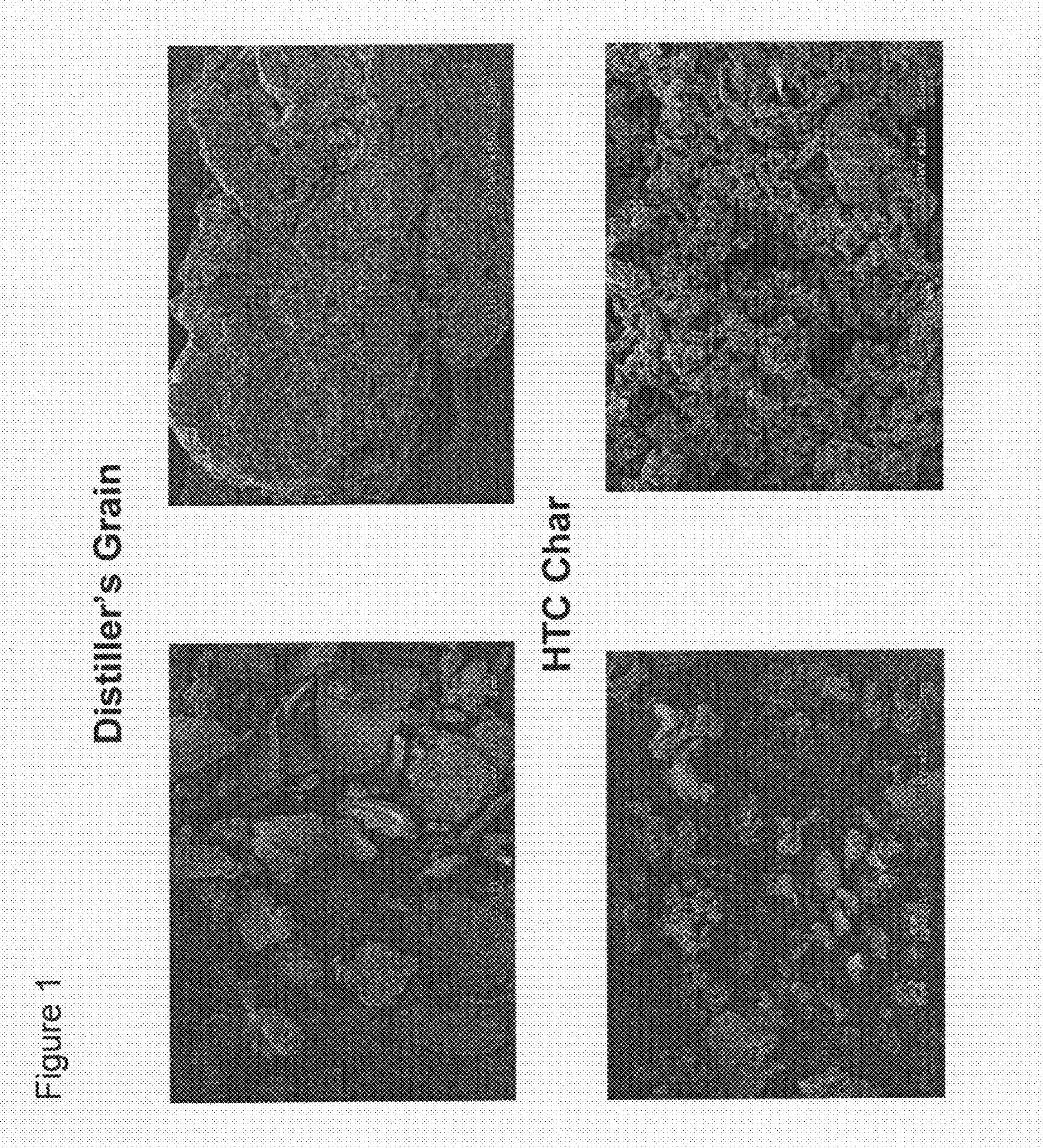
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(57) **ABSTRACT**

The invention herein describe a novel process for producing a novel synthetic coal product from fermentation residues, such as, the waste materials from fermentation based ethanol production. The fermentation residue is subject to a hydrothermal carbonization process in an aqueous solution at a temperature and at a pressure sufficient to form a synthetic coal solid and a liquid component. This process does not require drying of the fermentation residue which provides for a more energy efficient method of processing thereof. The synthetic coal solid has a high heat content combustive material. The liquid component has nutrient value so that it can be recycled thereby permitting the sustainable recycling of such nutrients and the water in which those nutrients are dissolved.



SYNTHETIC COAL AND METHODS OF PRODUCING SYNTHETIC COAL FROM FERMENTATION RESIDUE

BACKGROUND OF THE INVENTION

[0001] A major pollution problem concerns the effect of carbon dioxide, a greenhouse gas, being released into the atmosphere as the result of burning fossil fuels. Currently, approximately 70 million tons of carbon dioxide gas enters the earth's atmosphere every day due to the worldwide burning of coal, oil, diesel fuel, kerosene, gasoline, natural gas and the like. This fossil fuel use causes a concentrating of an unnatural amount of carbon dioxide in the atmosphere. Carbon dioxide is able to absorb heat energy that radiates from the earth and thereby captures and retains heat energy within the earth's atmosphere. Thus, the overwhelming majority of climatologists agree that the burning of fossil fuels is the major contributor to the current warming of the earth's atmosphere. For this reason, there will be increased regulation of fossil fuel-based carbon dioxide gas emissions and a proportional increased interest in finding alternative renewable, non-polluting heating fuel sources.

[0002] In response to the concern of global warming and to significantly increased crude oil prices and politically and economically uncomfortable dependence on imports thereof, there exists substantial pressure to find alternatives to oil, diesel fuel and gasoline. One possible alternative liquid fuel is ethanol. Ethanol was first used in 1980 as an additive to gasoline and has now commonly reached concentrations of 10% by volume with 20% by volume being legislated to occur in Minnesota in 2013. Several states, including Minnesota, also currently offer a fuel referred to as "E85" which is a blend of 85% ethanol and 15% gasoline. While the combustion of ethanol, as with any organic compound containing carbon, will release carbon dioxide, carbon dioxide released from ethanol is not derived from a fossil fuel but from plants and photosynthesis. As a result, ethanol-derived carbon dioxide does not originate from sequestered subterranean carbon sources and is not "new" to earth's atmosphere.

[0003] Ethanol is obtained in the United States primarily by the fermentation of the starch in corn kernels using enzymes to breakdown the starch into fermentable dextrins after which yeast is used to then convert the latter into ethanol. After the formation of the ethanol, it is distilled off leaving behind a liquid suspension of fermented grains or "mash" referred to as whole stillage. Whole stillage can be separated by filtration or centrifugation into its two basic components, the liquid or supernatant referred to as thin stillage and the solid fermented grain residues referred to as wet distiller's grain (WDG). The thin stillage is typically condensed by evaporation to a condensed distiller's solubles (CDS). The CDS can then be recombined with the WDG to form wet distiller's grain with solubles (WDGS). The WDGS can then be further processed by drying to form a dried distiller's grain with solubles (DDGS). It is also possible to dry the WDG to form a dry distiller's grain (DDG) without the soluble portion. A bushel of corn can provide 2.8 gallons of ethanol, 18 pounds of dried distiller's grains (DDGS), and 16 pounds of carbon dioxide. The fermentation residue or whole stillage is comprised of small amounts of residual fermentable dextrins and yeast, unfermentable dextrins, protein, less than 20% by dry weight of cellulose, fat, low concentrations of metal salts and water. Often the protein content can be quite high, ca. 30%, and the material is utilized as a high-grade feed for ruminants such as

cattle, with small amounts able to be employed in feeds for mono-gastric animals such as swine and poultry. However, WDG has a very short "shelf life" and can only be used as animal feed within days of its production, as bacterial and mold growth will otherwise render it unsuitable for animal consumption. This constraint limits its shipment to farm sites to within essentially a 30 mile radius of the ethanol production facility. In order to store and effectively transport outside that radius, microbial growth must be prevented. Doing so requires that the WDG be dried and converted into the aforementioned DDG or DDGS.

[0004] Unfortunately, the drying process requires substantial amounts of heat energy adding considerable cost to the feed and negatively impacting the overall energy balance for the production of fuel ethanol. As a consequence, ethanol manufacturers are often in a situation of having a large surplus of WDG that must be dried at the manufacturing site to prevent it from spoilage by microbial attack. In 2008, 23 million metric tons of corn ethanol based DDGS were produced annually in the United States. Other fermentation residues that have similar negative economic and/or waste disposal issues include; brewer's grains from production of beer and whiskey manufacture, *E. Coli* residues from production of antibiotics, and residues from other bacterial, fungal and yeast fermentation processes.

[0005] A further concern relative to fermentation processes generally, and especially in the production of corn based ethanol, are the large volumes of water that are used. Thin stillage alone, for example, having a moisture content of 90-95% is obtained at ca. 7 times the volume of ethanol produced. The result is that for every 100 million gallons/year dry-grind ethanol plant, which ethanol output size is common in the US, 700 million gallons of thin stillage are produced. This means that more than 4 billion pounds of water/year/facility are required to be removed by energy-intensive drying operations. Thus, there has been a long felt need in the ethanol distilling industry to find a better solution for not only dealing with the millions of tons of fermentation residue that are produced each year but to create processes that are sustainable in terms of raw material, energy and water use.

[0006] There has been one report (Elliot, et. al., Ind. Eng. Chem. Res. 2004, 43:1999-2004) of hydrothermal gasification (with catalyst) conducted using DDGS. The report subjected DDGS to 320-360° C. over a Ru on carbon catalyst in a continuous fixed-bed reactor; the pressure obtained was 21 MPa. The purpose of this operation was to create gaseous products such as methane, hydrogen, ammonia and carbon dioxide. This report discloses a reaction condition employing an expensive catalyst and at high reaction temperatures that were designed to create gaseous products that contribute to high reaction pressures that lead to increased cost and complexity of reaction systems.

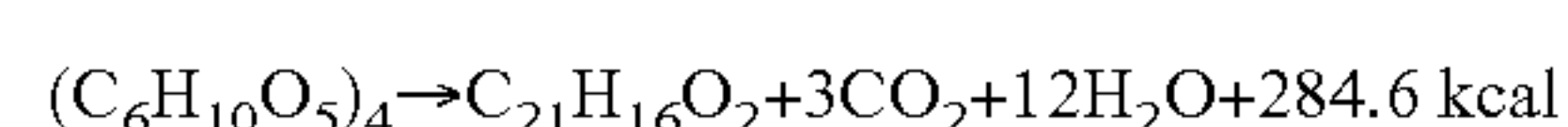
[0007] Accordingly, there remains a need to lower the costs of ethanol production and make it truly sustainable from energy and water use perspectives.

SUMMARY OF THE INVENTION

[0008] The present invention uses the process of hydrothermal carbonization (HTC) to treat fermentation residues to produce a char product therefrom. The HTC process presents the large energy advantage of not first requiring drying of the fermentation residue. HTC is a process whereby a substrate is held in a suspension of water and is then heated under pres-

sure, either in a batch or continuous process manner, for a period of time to produce a char/charcoal end product.

[0009] The basic HTC process was developed in 1913 by Bergius and Specht, see, *Die anwendung hoher Drucke bei chemischen Vorgangen*. They conducted experiments to examine coalification of lignocellulosic materials (wood products) into artificial coal. As is understood in the art, wood and wood-like materials found in straw, corn, switch grass and the like are made up of various proportions of cellulose, hemicelluloses and lignins, often chemically cross-linked in a complex manner. This chemical structure provides trees and plants with the structural strength and rigidity needed to grow and endure against the elements and microbial attack. Of course, it is this very chemical nature that makes it difficult for these plant structural materials to be chemically or enzymatically attacked and broken down. Nevertheless, Bergius and Sprecht found that the cellulosic component of peat when heated in liquid water at 300° C. was principal in this conversion according to the following equation in which carbonization was accomplished by both dehydration and decarboxylation, i.e., loss of carbon dioxide:



[0010] Thus HTC was developed to treat wood and wood-like substances having a 90+ percentage by weight of cellulose, hemi-cellulose and lignins in an aqueous suspension at high temperatures and pressures to carbonize such materials. Two product streams are created: a coal-like char, also referred to as a “hydrochar”. The solid char is typically separated from the aqueous solution by centrifugation or filtration.

[0011] In 1960, the hydrothermal “carbonification” of cellulose, lignin and wood was examined separately. See, Schumacher J. P., Huntjens F. J., van Krevelen D. W. *Fuel* 1960; 39(3):223. With each substrate, significant carbonization, i.e., >75% carbon in the hydrochar residue, was not achieved until temperatures >275° C. were employed with a 3 hour reaction time. Use of alkaline catalysts resulted in increased carbonization rates by facilitating loss of carbon dioxide. This confirmed the earlier Bergius work mentioned above that very high temperatures were required for conversion of cellulose into a char.

[0012] A continuous flow reactor system was disclosed in 1976 capable of achieving temperatures up to 300° C. with reaction volumes of 0.5 mL for the slurries examined. See, Bobleter O., Niesner R., Rohr M. *J. Appl. Polym. Sci.* 1976; 20:2083. It was also shown that finely ground wheat straw which contained mostly cellulose and hemicellulose was initially degraded by hydration of these polysaccharides, resulting in the formation of soluble carbohydrates, glucose and cellobiose, from the cellulose and xylose and arabinose from the hemicellulose. At the lower temperature of 218° C., only carbohydrates were formed from the hemicellulose but the cellulose was unaffected. Cellulose responded to provide the soluble carbohydrates only when reaction temperatures were greater than 260° C. This study established that hydration of polysaccharides was the initial step in the reaction mechanism of hydrothermal carbonization production of char materials and confirmed to those of skill that any breakdown of cellulose required high heat and pressure.

[0013] Further research examined the hydrothermal carbonization of other high cellulose content materials, including; sugar beet chips, pine cones, pine needles, oak leaves, and orange peels that contained cellulose, hemicellulose and up to 35% lignins. See, Titirici M. M., Thomas A., Yu S. H.,

Muller J. O., Antonietti M., *Chem. Mater.* 2007; 19:4205. These materials in the presence of suitable catalysts such as citric acid or Fe⁺² ions provided hydrochars containing from 68-73% carbon contents at 200° C. for 16 hours. That carbonization occurred at this somewhat lower temperature under the condition of substantially increased reaction time can be attributed to a Boltzmann distribution of energy states. Often this concept is represented by a bell-shaped curve of energy states with a small fraction of molecules possessing sufficient energy for reaction to occur, thus requiring longer reaction times for efficient conversion to hydrochar. However, those of skill will appreciate that 8 hour reaction times, let alone 16 hours, make continuous processing of a char from cellulosic materials commercially infeasible. With temperatures below 180° C. only small or no conversions were detected. This lack of carbonization of cellulose is further illustrated in applicant's publication seen in *Biomass & Bioenergy*, vol 35 pp 2526-2533 2011, Heilmann, et al, which article is incorporated herein by reference thereto, wherein microcrystalline cellulose was subjected to the reaction conditions of the present invention and the solid recovered unchanged and having the same carbon content by weight as the starting material

[0014] What is understood by the person of skill relative to the technology and purpose of HTC as illustrated above is that the production of chars requires the use of wood or other wood like materials having a high cellulosic content, i.e. cellulose, hemicellulose and lignins. In addition, any char production required relatively high pressures and temperatures well in excess of 225° C. be applied for a period of several hours.

[0015] Thus, it was surprisingly discovered in the present invention that HTC could be applied to fermentation residues and result in a char product. This was surprising because the prior art taught that the production of chars required the use of high cellulosic content substrates. It was also surprising that a char was formed because the makeup of WDG, for example, is completely unlike that of wood, or other cellulosic biomass that consist primarily of cellulose, hemicelluloses and lignins. For example, as stated above, corn based WDG consists of a small amount of residual fermentable dextrans and yeast, less than 20% by dry weight of cellulose, unfermentable dextrans, protein, fat, low concentrations of metal salts, and water.

[0016] The invention herein produces a coal-like char product that is similar to natural bituminous coal in terms of percent carbon content and energy equivalency while at the same time containing relatively low levels of sulfur and contaminant heavy metals. The char produced by the process of the present invention can be used as a fuel and burned to provide an energy source comparable to bituminous coal in terms of BTU's produced per unit weight. However, unlike natural coal and other fossil fuels that are formed by the sequestration of carbon over millions of years, when the char of the present invention is burned no “new” carbon is added to the atmosphere. As is well understood, carbon dioxide from plant biomass is formed through photosynthesis. Thus, as the particular substrate is grown, e.g. corn, the carbon is extracted from the atmosphere and that same carbon is then returned to the atmosphere when the ethanol is burned. That carbon returned to the atmosphere is then extracted again in a subsequent corn growing season resulting in a carbon neutral process having no net addition of carbon thereto. The process of the present invention can also include the step of seques-

tering the char produced thereby by burying or storage thereof. Alternatively, the coal product of the invention can also be utilized as a soil additive to improve moisture retention and provide nutrients for plant growth. The coal product of the invention may also be useful for the production of industrial chemicals such as methanol, acetic acid and ethylene glycol, as well as preparing hydrocarbon fuels through gasification. The coal or char can further be utilized as a carbonaceous starting material for the production of coke used for the manufacture of steel. The coal/water mixture could also be employed directly into a fuel cell operated at low temperature. Furthermore, the aqueous solution by-product from the process herein can be used as a nutritive fermentation supplement and as a fertilizer. Furthermore, it has been discovered that much of the nitrogen and phosphorous contents of the fermentation residue processed through hydrothermal carbonization becomes transformed into water-soluble compounds. These compounds are found dissolved in the aqueous solution after the char has been separated therefrom. The phosphorous and nitrogen can then be used as a nutrient source for the growing of further grain crops that provide fermentable substrate materials such as corn. The aqueous solution can also be combined with a fermentation substrate prior to its fermentation thereby recycling and reducing the amount of water used in the production of ethanol.

[0017] Additionally, it was found that the invention herein provides a hydrothermal carbonization process that increases the carbon-to-oxygen ratio of the resultant char advantageously and primarily through dehydration rather than by loss of carbon dioxide, although minor amounts (<15%) of carbon dioxide may also be formed. A similar value for carbon loss was also reported by applicant relative to the HTC treatment of a noncellulosic algal biomass. See, Biomass & Bioenergy (volume 34, pp. 875-882, 2010, Heilmann et al.) which article is incorporated herein by reference thereto. The invention herein produces a synthetic coal or char product having the following characteristics: a substantially macroporous microstructure; a substantially higher hydrogen and nitrogen content as compared to bituminous coal and synthetic lignocellulosic coal; low or undetectable amounts of elemental sulfur content; low ash content; and an equivalent or greater heat of combustion per unit weight as compared to both synthetic lignocellulosic coal and fossil fuel bituminous coal.

[0018] The char of the invention is also low in mercury and uranium and other toxic heavy metals. These and other advantages will become apparent from the following disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] Embodiments of the invention are further illustrated by the following drawings—none of which is intended to be construed as necessarily limiting the invention.

[0020] FIG. 1 is a collection of four scanning electron micrographs (SEM) at 25× (macro sense images) and 300× (micro sense images) employing an accelerating voltage of 5000 volts, with the first pair of images being distiller's dry grain starting material and the second pair of images being the resultant coal product as prepared according to a process similar to that set forth in Example 1 below.

DETAILED DESCRIPTION OF THE INVENTION

[0021] As used herein, “fermentation residues” are meant to refer to residues from various fermentation operations

including ethanol production, whiskey and beer production, microbially-assisted antibiotic production, and other bacterial, yeast and fungal fermentation reactions.

[0022] Examples of fermentation processes which produce fermentation residues include ethanol production from grains, cereal and brewing. Examples of grains which may be used in such fermentation processes resulting in a fermentation residue include corn, wheat, rice, barley and other grains.

[0023] The residue produced by the fermentation reactions is the remainder or residue of a fermentation reaction after the specific target material, such as, a protein (e.g. an enzyme), a carbohydrate, a lipid, ethanol or the like, is removed.

[0024] “Hydrothermal carbonization” means heating an insoluble, low cellulosic biomass material or substrate suspended in an aqueous medium in a confined system under the temperature and time conditions specified.

[0025] The phrase “synthetic coal” is meant to refer to the fact that the synthetic coal-like product was prepared according to embodiments of the invention utilizing fermentation residues as starting material (the term fermentation residues as defined above) and having a substantially predominant non-lignocellulosic content.

[0026] The term “coal” or “char” or “hydrochar” as used within the context of the synthetic or artificial output product of the invention, is meant to refer to the solid or semi-solid product of the resulting from the HTC process of the present invention as applied to a corresponding fermentation residue starting material. The term is not meant to necessarily indicate the employment of the product as an ignited energy source, although the ability of such usage is an important aspect of the invention.

[0027] The term “carbon neutral” as used herein refers to the achievement of net zero carbon emissions by balancing a measured amount of carbon released with an equivalent amount sequestered through formation by photosynthesis. As used herein, the term “comprising” means the elements recited, or their equivalent in structure or function, plus any other element(s) which are not recited. The terms “having” and “including” are also to be construed as open ended unless the context suggests otherwise. Terms such as “about”, “generally”, “substantially” and the like are to be construed as modifying a term or value such that it is not an absolute, but does not read on the prior art. Such terms will be defined by the circumstances and the terms that they modify are understood by those of skill in the art. This includes at the very least the degree of expected experimental error, technique error, and instrument error for a given technique used to measure a value.

[0028] The term “macroporous” comes from polymer science where it means a material that has pores with sizes ranging from 50 nm-1 μ m. For purposes of this invention, the term has been broadened in scope to include materials with surfaces that have channels and crevices of small scale that can be accessed by suspending media such as aqueous solutions. Surface areas of these materials are generally in excess of 1 m²/g.

[0029] The invention provides a process for preparing a fermentation residue-derived synthetic coal product, said process comprising the steps of: obtaining a starting fermentation residue material comprising a fermentation residue-containing aqueous composition; subjecting said starting material to hydrothermal carbonization; separating the resulting materials into a fermentation residue derived synthetic coal/char product. In some embodiments, the concentration

of aqueous fermentation residue may be from between about 5% phw to about 40% phw. In some embodiments, the process further comprises the step of adding an acidic buffer to the aqueous suspension prior to the hydrothermal carbonization step. The hydrothermal carbonization process may be performed using a temperature ranging from between about 170° C. and about 225° C., for a duration ranging from a period of about 0.5 hour to about 4 hours, and a pressure up to about 2.41 MPa, for example. A solid or semi-solid fermentation residue-derived synthetic coal product is obtained, along with an aqueous solution that can be further downstream processed.

[0030] Another important aspect of the process of the invention is that the process conditions reduce or minimize the generation of gaseous products such as carbon dioxide. Under conditions employed in various embodiments of the present invention, and as was exemplified in our U.S. Non-provisional application Ser. No. 12/715,595 dealing with microalgal substrates, the amount of carbon released as carbon dioxide gas produced during the HTC process is approximately equal to or less than 15% of the carbon in the initial fermentation residue reaction products.

[0031] The concentration of the fermentation residue in water is important to the invention. It is believed that particle-to-particle reactions occur and create the agglomerated synthetic coal product of the invention. Starting fermentation residues having high surface areas and agglomeration characteristics can be associated with shorter processing times. In general, the higher particle concentration per unit volume of water, the more agglomeration and bulk mass creation can occur, and a larger yield of the synthetic coal product can be obtained. Thus, the concentration of fermentation residue in the aqueous suspension of the starting material can affect the output quality and yield of the process. Concentrations of fermentation residues in the starting suspension can be between about 5% to about 40% phw, such as between about 5% to about 30% phw, or between about 5% to about 15% phw. Fermentation operations are conducted in water, and residue concentrations vary depending on the particular microbe and substrate employed. The residue obtained may be a moist material that is at least 15-40% solids in water when centrifugation operations are employed, as is common in the corn ethanol manufacturing industry. These aqueous suspensions can be utilized directly as the undiluted centrifugate or diluted with water to achieve a desired solids level such that the overall suspension can be moved as a relatively homogenous (though not a solution) mass.

[0032] The process of the invention optionally can include the use of buffers. Buffers can be added into the aqueous mixture prior to proceeding to the hydrothermal carbonization stage. Suitable buffers that can be employed in the process include those compounds that afford an acidic pH to the mixture. Polyacidic pH buffers that can be used include, but are not limited to, citric acid and oxalic acid. For example, polyacidic pH buffers which contain significant concentrations of carboxylate (basic) and carboxyl (acidic) functional moieties may be used in embodiments of the invention.

[0033] Another important aspect of the invention resides in the process parameters and conditions—particularly relating to temperature, time and pressure during hydrothermal carbonization. The process of the invention can be performed at temperatures between about 170° C. and about 225° C., such as between about 190° C. and about 215° C. The process of the invention can be generally performed within a time period

of less than about 4 hours. For example, the process can be performed for a duration ranging from between about 0.5 hour up to about 4 hours, or between about 0.5 hour to about 2 hours.

[0034] In addition to the advantages of relatively low temperature parameters and associated reduced energy usage of the process, the pressure conditions needed for the process of the invention are also relatively low and conservative. The process can be conducted at a pressure of about 2.41 MPa and less, such as between about 0.8 and 2.41 MPa. When a pressure of 2.41 is used, about 70% of the pressure, or 1.55 MPa, is due to H₂O vapor pressure.

[0035] The hydrothermal carbonization step of the process can be conducted within a pressure-sustaining batch reaction apparatus. Batch reactor apparatuses that can be used include commercially available vessels capable of generating the temperatures (up to about 225° C.) and sustaining the pressure conditions (<2.41 MPa) in aqueous process conditions associated with the invention.

[0036] It is contemplated that the HTC process of the present invention can be conducted on a continuous basis. Examples of continuous process hardware that could be adapted for use in the present invention include commercially-available twin extruders of stainless steel construction, and as described in Bobleter et al., *J. Appl. Polymer Sci.*, 20, pp. 2083-2093 (1976) and as seen in Bodle et al., U.S. Pat. No. 4,632,731.

[0037] The product of the process of the present invention includes a fermentation residue-derived synthetic coal product having the following characteristics: a substantially macroporous microstructure; a substantially higher hydrogen and nitrogen content as compared to bituminous coal and synthetic lignocellulosic coal; relatively low or undetectable amounts of elemental sulfur content; comparable heat of combustion as compared to bituminous coal; significantly reduced ash content; and generally higher heat of combustion as compared to synthetic lignocellulosic coal. For example, the coal product may have a hydrogen content of about 6% to about 8% by weight, a nitrogen content of about 3% to about 4% by weight, an elemental sulfur content of about <1% by weight, and an ash content of about <1% by weight. The coal product may have a heat of combustion of about 10,000 BTU/lb to about 17,000 BTU/lb; in other embodiments a heat of combustion of about 11,000 BTU/lb to about 13,000 BTU/lb; in yet other embodiments a heat of combustion of about 13,000 BTU/lb to about 15,000 BTU/lb.

[0038] It is noted that in various embodiments of the present invention, the macroporous microstructure of the coal product of the present invention exhibits cavities greater than 50 nanometers in diameter. It is further noted that the ash content of the coal product of the present invention is significantly reduced in comparison to the ash content of starting fermentation residue material or natural coal. In a number of applications of the present invention the ash content has been reduced by an order of magnitude compared to the ash content of the starting fermentation residue material. For example, in various embodiments of the present invention, the reduction levels of ash in the coal product of the present invention compared to the ash content of the starting fermentation residue material is >20%, preferably >55%, more preferably >90% reduction. Such a reduction is very important for applications such as conversion into synthesis gas and coal coke replacement.

[0039] Embodiments of the invention include methods of using the fermentation residue-derived synthetic coal prepared as described herein as an energy resource comprising employing said fermentation residue-derived synthetic coal product as a carbon source within a combustive thermal energy generation system. Examples of combustive thermal generation systems in which the product of the invention can be employed include, but are not limited to, boiler plus furnace systems, supercritical turbine systems, combined cycle power systems, combined heat and power cogeneration systems, and the like. In addition to the synthetic coal product being separately utilized, the process of the invention can be modified for large industrial scale operation and incorporated as part of a unified combustion thermal generation system with a fossil fuel to reduce the overall amount of “new” carbon dioxide introduced into the atmosphere.

[0040] In another method, the fermentation residue-derived coal product of the invention can be used in a gasification process. In one embodiment, the coal product of the invention can be used in a steam reforming gasification process for preparing synthesis gas or syngas (a mixture of carbon monoxide and hydrogen gas). Syngas can, in turn, be converted into transportation fuels or industrial chemicals such as methanol, ethylene glycol, acetic acid, and the like. The material can also be utilized to prepare an alternative to coal coke used in the manufacture of steel.

[0041] Following the hydrothermal carbonization step, the reaction mixture is cooled and the insoluble content of the mixture can be separated from the water-soluble contents by filtration. Other methods that may be used for separation of the insoluble content include, but are not limited to, compression, decantation and centrifugation. The separated solid or semi-solid component is the synthetic coal product and the remainder is a liquid (aqueous) solution product.

[0042] The fermentation residue-derived synthetic coal product prepared in accordance with the hydrothermal carbonization processes described herein contains chemical and physical attributes unique to the solid or semi-solid product and which are attributable to the particular process steps described herein. The above descriptions for the product and process are both set forth in the above summary of the invention and described in detail within this specification.

[0043] Another very significant product of the invention is the aqueous filtrate obtained during filtration unit operation conducted to separate the synthetic coal from the water-soluble products of the invention. Among the solutes present in the solution are significant concentrations of potassium (K), ammonium (N), and phosphate (P) ions that make up the important KNP components of plant fertilizers. This solution is therefore useful in fertilizing terrestrial plants such as corn, soybeans, and wheat. In various embodiments, the solution is generally a concentrate that may be diluted with water prior to application. Development of useful fertilizer alternatives to ammonia based commercial products (urea and ammonium nitrate) is very important to minimize our national consumption of natural gas. At stoichiometric efficiency, $\frac{3}{8}$ of a mole of natural gas is required to make each mole of ammonia, with additional natural gas being required to heat the reaction system to temperature. Reserves of natural gas are important for our national security and are finite.

EXAMPLES

[0044] The invention is further illustrated by the following examples, none of which are intended to be construed as

necessarily limiting the claimed invention to the particular embodiments described therein but help to better illustrate the present invention to those of skill.

[0045] For each of the examples below, the HTC reactor employed was a 450 mL stirred stainless steel reactor (purchased from Parr Instruments, Inc., Moline, Ill.). Heating methods were of two types: an induction heating system (available from LC Miller, Co., Monterey Park, Calif.) and a resistive heating mantle arrangement (available from Parr Instruments, Inc.). Rates of heating varied between the two arrangements, with the inductively heated system achieving the desired temperature more rapidly, but no differences in products were detected with the two methods.

[0046] As is apparent to one skilled in the art, many of the examples were conducted by rehydrating DDGS samples. This was done for research purposes in order to employ accurate and reproducible masses of starting materials. In actual practice of the invention, the starting material is preferably not dried, and the concentration of solid material in an aqueous fermentation residue can be determined and its concentration adjusted accordingly.

Example 1

[0047] An experiment was conducted to illustrate the efficient transformation of a fermentation residue from dry distillers' grains with solubles (DDGS), into a high quality coal product comparable to natural bituminous coal. The transformation occurs employing DDGS at about 20% solids content at a temperature of about 200° C. for a period of about 2 hours in the presence of oxalic acid (2% by weight).

[0048] A mixture was prepared by combining DDGS (obtained from Chippewa Valley Ethanol Company (Benton, Minn.) having the following elemental analysis: % C=48.1, % H=7.1, and % N=4.9) (46.5 g), distilled water (186 g) and oxalic acid (0.93 g) in a 500 mL round-bottomed flask and shaken vigorously to create a homogeneous suspension. The suspension was then transferred (98% of the mass) into a 450 mL Parr reactor and stirred at 88 rpm. The reactor was heated to a temperature of 200° C. using the rapid induction heating system, with the initial reaction pressure at about 1.72 MPa.

[0049] After a period of about 2 hours, heating was discontinued and the unit was cooled employing a fan to expedite process. At ambient temperature, the residual pressure was measured at 0.76 MPa. The reaction product was filtered, and the char product was washed well with water. The freeze-dried char product weighed 18.07 g (40% mass yield based on starting DDGS). Elemental analysis of the char gave the following elemental content amounts: % C=67.0; % H=7.8%; and % N=4.2%.

[0050] Images of starting DDGS material and DDGS-derived synthetic coal are shown in FIG. 1. Relatively macroscopic images of the two solids are shown in images on the left side, with microscopic images on the right. These images demonstrate the drastic changes that occur during the hydrothermal carbonization process. The starting DDGS consists of chunks of various sizes with some approaching 1 mm in cross section. Microscopically, DDGS has an organized, almost cellular, structure appearance. The corresponding synthetic coal made from DDGS, in contrast, is quite different. Components of the DDGS have been liquefied or dissolved during the process and reformed into a solid, macroporous network as can be seen from the image on the right for the coal product. These images further confirm that a char resulted from the HTC of DDGS at a combination of temperature,

pressure and time parameters that were not seen in or suggested by the prior art to form a char let alone from a substrate having less than 20% by dry weight of cellulose. The cellulose that was originally present in the DDGS was essentially unaffected under the HTC conditions and is present in the hydrochar as a “filler” or inert material.

[0051] This example demonstrated that a fermentation residue having less than 20% by weight cellulose could be transformed under unexpectedly mild conditions into a char product wherein the carbon content had increased 21% and possessed a significantly increased energy content compared to starting DDGS, natural coal and a lignocellulosic coal (Example 20). Furthermore, the char possessed a macroporous structure.

Comparative Example 2

[0052] HTC of a lignocellulosic material was conducted for purposes of comparison to the process of the present invention. A monoculture prairie grass identified as “Little Bluestem” having a seasonally variable cellulose content from 32-36% (Allen L J, Harbers L H, Schalles R R, Wensby C E, Smith E F, J Range Management 1976; 29(4):306-308) was selected as starting material. A sun and air dried, brown colored sample of the grass was obtained and ground thoroughly into a powder having components with primarily linear aspect and sizes less than 1 mm. The material was then subjected to a reported (Antonietti, et al., *Chem. Mater.* 2007, 19, 4205-4212) hydrothermal carbonization condition for lignocellulosic materials, i.e., 10% solids, with added oxalic acid, at 200° C. for 17 hours. The freeze-dried brown filtered synthetic coal product was obtained in 57% yield. Elemental analysis of the synthetic coal gave: % C=62.3; % H=5.6; and % N=<0.5%. When the reaction was repeated and the reaction time halved, i.e., 8.5 h, the isolated yield was 70% but the % C in the coal produced was only 59.0%.

[0053] The following characterization information was obtained regarding the aqueous solution and its solutes obtained in the 17 h reaction: 1) the % solids of freeze-dried material was 1.28%; 2) elemental analysis gave: % C=44.3; % H=5.2; and % N=not detected; 3) the salt content was 17.3 mM; 4) the pH was 3.38 and 5) the metal analysis was determined in Inductively Coupled Plasma (ICP) analysis provided the following list of metals:

Lignocellulosic Filtrate Metal Content													
Content (ppm)													
	738	688	234	110	102	46	36	22	12	8	6	2	2
Element	Si	K	Ca	P	Mg	Fe	S	Na	Mn	Ni	B	Ba	Zn

[0054] For purposes of employment as a fertilizer, relatively high concentrations of the elements K, N and P are particularly important. As can be seen from the above table, Si and Ca are among the top three elements present with the lignocellulosic material, and no detectable nitrogen was found in the system. This solution would not be a promising fertilizer solution. In contrast, the results of Example 19 conducted using DDGS indicate an aqueous filtrate that should provide an excellent fertilizing material.

[0055] This Comparative Example teaches that despite substantially decreasing the particle size of the Little Blue

Stem substrate and increasing the reaction time to overnight duration (17 h) only a modest level of carbonization (62%) had occurred and the fuel quality of the char was correspondingly reduced compared to the fermentation residue-based chars of the invention (Example 20). The aqueous solution product of the Comparative Example was significantly reduced in KNP to be used as a fertilizer.

Example 3

[0056] This Example teaches that employment of reaction conditions comparable to reported conditions for lignocellulosic materials are not necessary and less efficient than those required for fermentation residues. The conditions were the same as Example 1 except that a 14 h reaction time was employed. The mass yield of char product obtained from DDGS was 39%. Elemental analysis gave: % C=69.2; % H=7.8; and % N=4.4. The increased reaction time gave a slightly greater level of carbonization (2.2%), but not sufficiently greater to warrant the substantially increased reaction time.

Examples 4-6

[0057] These Examples examine multiple DDGS samples of varying composition. The results obtained indicate that DDGS, in general, can be converted efficiently into a high quality coal product, with accompanying aqueous solution byproducts. Samples were obtained from the University of Minnesota Swine Center (Professor Gerald Shurson) and the DDGS web site collection. Three samples were received having the following compositions given in weight percent:

ID#	% Fat	% Protein	% Carbohydrate	% Ash
S022	8.79	29.88	57.59	3.74
S037	11.34	31.34	52.32	5.00
S026	12.29	32.56	39.18	15.96

[0058] Each of the DDS samples was subjected to hydrothermal carbonization at 200° C., 15% solids, 2 h reaction time, and with 2% oxalic acid present. Yields and elemental analyses of freeze-dried coals were as follows:

Example	% Yield	% C	% H	% N
4(S022)	42.4	66.7	7.7	3.8
5(S037)	37.1	67.4	8.1	4.0
6(S026)	37.2	66.6	7.8	4.1

These examples show that despite compositional differences in DDGS samples similar synthetic coals are obtained.

Examples 7-18

[0059] The following Examples constitute a three-variable, two-level factorial experiment with replicated centerpoints examining the importance and interdependence of reaction temperature, reaction time and concentration of the DDGS. Temperatures examined were: 190, 200, and 210° C.; reaction times: 0.50, 1.25, and 2.00 hours; and % solids levels: 5, 15, and 25% DDGS by weight. Water also containing oxalic acid (2.0 wt %) was the HTC medium in all experiments.

Example	Temp. (° C.)	Time, h	[DDGS] % Solids	% Yield	Char % C
7	190	0.5	5	31.1	61.6
8	190	0.5	25	45.6	61.2
9	190	2	5	31.7	65.0
10	190	2	25	44.4	64.3
11	200	1.25	15	38.9	65.5
12	200	1.25	15	39.1	66.0
13	200	1.25	15	39.0	65.2
14	200	1.25	15	39.1	65.7
15	210	0.5	5	30.2	65.2
16	210	0.5	25	41.9	65.9
17	210	2	5	30.4	67.1
18	210	2	25	39.6	68.1

[0060] Examples 11-14 are replicate experiments in which standard deviations for % yield and % C were computed to be 0.1 and 0.3, respectively. The data show a strong dependence on % solids, with high % char mass yields being achieved at 25% solids at both 190 (Examples 8 and 10) and 210° C. (Examples 16 and 18). Carbonization was favored at higher temperature as evidenced by % C levels being greater at 210° C. at both solids levels at 0.5 h (Examples 15 and 16) compared to those obtained at 190° C. where % C values were reduced by over 4% at the 0.5 h reaction time (Examples 7 and 8). Higher temperatures and longer reaction times were also somewhat deleterious to % char yield. Comparison of 2 h reaction times and 25% solids concentrations at 190° C. (Example 10) and 210° C. (Example 18) showed a decrease in % yield of about 5% at the higher temperature. The reaction condition of Example 16 really points toward optimum conditions. In this experiment, the greatest mass of DDGS was converted in the shortest amount of time into a highly carbonized coal obtained in virtually the highest yield observed in the study. This result suggests that possibly shorter reaction times, higher solids and slightly higher reaction temperatures may approach a condition in which batch processing operations can give way to continuous processing operations.

[0061] These observations were further confirmed by applying analysis of variance (ANOVA) methods to the data in Examples 7-18.

[0062] A linear regression equation was developed from the orthogonal factorial design:

$$\text{For \% Carbon } y_1 = 65.05 + 1.78X_1 + 1.32X_2 + 0.08X_3 \text{ and}$$

$$\text{For \% Yield } y_2 = 35.08 - 1.34X_1 - 0.34X_2 + 6.01X_3$$

[0063] where

[0064] X_1 = dimensionless temperature;

[0065] X_2 = dimensionless time and

[0066] X_3 = dimensionless % solids

From these equations and the sizes of the coefficients therein, it is apparent that % solids is extremely important for % yield but not so important for carbonization (% C). This is an

important and desirable result because, within the reaction condition space examined, efficient carbonization of the bulk DDGS material at the highest % solids was achieved regardless of temperature and time.

Example 19

[0067] This Example considers the characteristics and utility of the aqueous solution product of the hydrothermal carbonization of DDGS. The aqueous filtrate examined in this Example was the combined aqueous filtrates of the designed experiment centerpoint replicates (Examples 11-14). The pH was 4.62 and % solids of the solution was 6.29%. Elemental analysis of the freeze-dried solute material gave: % C=35.9; % H=6.7; % N=6.9; % P=1.8; and % S=1.5. Corresponding values from the starting DDGS were: % C=48.1; % H=7.1; % N=4.9; % P=0.5; and % S=0.7. ICP analysis of the filtrate solution (diluted 1:50 with deionized water) gave the following values in ppm: K=36, Ca=1, Mg=11, Na=4, Fe=0.4, Zn=0.1, Cu=<0.01, Mo=0.02 and B=0.03. No detectable nitrate ion was recorded, and the ionic nitrogen solutes in the filtrate were almost exclusively ammonium.

[0068] In the replicate experiments, 29.4 grams of DDGS (minus 10% residual moisture=26.5 g) gave an average of 11.49 g of coal and 10.69 g of solutes in the aqueous solution.

Nitrogen Accounting:

[0069]

26.5 g DDGS % N = 4.9 1.30 g N	→	11.49 g Coal % N = 4.1 0.47 g N 36% in Coal	+	10.69 g Solutes % N = 6.9 0.74 g N = 1.21 Total 57% in Solution
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$$\text{Mass Balance} = 1.21/1.30 = 93\%$$

Phosphorous Accounting:

[0070]

26.5 g DDGS % P = 0.5 0.13 g P	→	11.49 g Coal % P = n.d.	+	10.69 g Solutes % P = 1.8 0.19 g P 146% in Solution**
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**Data accuracy may have been hampered due to handling issues of the very sticky freeze-dried solute sample.

Carbon Accounting:

[0071]

26.5 g DDGS % C = 48.1 12.75 g	→	11.49 g Coal % C = 65.7 7.55 g	+	10.69 g Solute % C = 35.9 3.24 g
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85% of the carbon in coal and solution.

[0072] Clearly, the lack of detection of any significant phosphorous content in the coal indicates that essentially all of the phosphorous ends up in the aqueous filtrate. These results indicate that the majorities of nitrogen and phospho-

rous, as well as a significant concentration of potassium, are located in the aqueous solution and available as nutrients for plants.

[0073] That 85% of the carbon present in the substrate DDGS can be accounted for by the carbon contents of the coal and aqueous solution products formed indicates that decarboxylation is not a major carbonization pathway. This conclusion was also supported by construction of a Van Krevelen Diagram in Example 23.

Example 20

[0074] This Example compares the heats of combustion, elemental analysis and ash content of starting DDGS with that of coal produced from DDGS (Example 1), a natural coal [Powder River Basin coal obtained from Xcel Energy, Inc. (St. Paul, Minn.)] and a synthetic coal obtained from a lignocellulosic plant source (Comparative Example 2).

Sample	Heat of Combustion in BTU/lb	% C	% H	% N	% S	% P	Ash
DDGS	8,652	48.1	7.1	4.9	0.7	0.5	4.1
DDGS Coal	12,752	67.0	7.8	4.2	<0.5	<0.001	0.4
Natural Coal	12,293	69.6	5.7	0.9	0.6	nd	5.6
Synthetic Lignocellulosic Coal	10,482	62.3	5.6	<0.5	nd	nd	nd

nd = not determined

[0075] The heat of combustion for the DDGS coal product is substantially greater than that for starting DDGS, greater than the synthetic coal obtained from a lignocellulosic plant source (Comparative Example 2) that required 17 hours of heating, and comparable to or higher than natural coal. The nitrogen content is elevated in both the DDGS starting material and the coal produced from it, albeit with the majority of the nitrogen in the starting DDGS being “removed” in the filtrate (Example 19). Nitrogen levels present in the DDGS coal are sufficiently low that normal remediation operations in effect at natural coal burning installations can effectively remove any NOX materials formed during combustion. Ash content of the char has also been substantially reduced compared to starting DDGS and greatly reduced compared to natural coal.

Examples 21 and 22

[0076] These examples teach that stillage fermentation residues that are essentially intermediate products in the dry-grind ethanol manufacturing process are useful substrates in the invention. Both thin and whole stillage materials were received from Al-corn Clean Fuels (Claremont, Minn.). % Solids levels of the two stillages were 7.2% for thin stillage and 12.0% for whole stillage, and the fatty acid contents of the two stillages were 17.5% and 14.8%, respectively. Elemental analyses for thin stillage were % C=44.3, % H=7.9, and % N=2.8; and for whole stillage % C=46.0, % H=7.6, and % N=4.0.

[0077] Thin stillage (255.4 g containing 18.38 g of solid material) was poured into the reactor, stirred at 88 rpm, and heated to 220° C. for 75 minutes. The pressure in the reactor after the reaction period was 2.34 MPa, and the apparatus was cooled using a fan. When the unit had cooled to ca. 35° C., the

reactor was disassembled, and the contents were filtered and the hydrochar was washed thoroughly with distilled water. The moist hydrochar (4.04 g) was freeze-dried to obtain 2.95 grams of dry hydrochar. Extraction of fatty acids from the hydrochar was accomplished by shaking with eight volumes of methyl t-butyl ether (MTBE) on a rotating shaker for 30 minutes, followed by filtration and washing with an additional three volumes of MTBE. The extracted hydrochar was dried overnight at room temperature at 40° C. and additionally for one hour at <1 Torr. The mass of the dry extracted hydrochar was 1.12 g (6.1% based on starting solids). Removal of the MTBE from the extract to constant weight using a rotary evaporator gave 1.81 g of a black oil (9.8% based on starting solids). IR analysis of the oil was consistent with a fatty acid with broad OH stretching absorptions between 3300-2500 cm⁻¹ and strong C=O stretching absorption bands at 1760 cm⁻¹. ¹H-NMR analysis of the extract indicated that fatty acids comprised 84% of the mass of the extract, and the corresponding actual yield of fatty acids was 1.52 g (8.6% based on starting solids).

[0078] Similarly, whole stillage (245.5 g containing 29.5 g of solid material) was stirred and heated to 215° C. for 75 minutes. Pressure in the reactor was 2.10 MPa, and the reaction mixture was cooled to 45° C. before filtration and workup. The extracted hydrochar mass was 5.24 g (17.8% yield), and the fatty acid extract mass was 4.02 g. The NMR analysis, again, indicated that the fatty acids comprised 84% of the extract, and the % yield of isolated fatty acids was 12.8% based on starting solids. Results obtained with the two stillage substrates are contained in the Table below:

Example	Extd. Hydrochar				Fatty Acid ^a
	% C	% H	% N	% Yield	% Yield
21 (Thin Stillage)	62.5	6.2	6.3	6.1	47
22 (Whole Stillage)	65.3	6.5	5.5	17.8	87

^a = % Yield is based on total amount of fatty acids present in the starting material.

Example 23

[0079] This Example teaches that the principal mode of carbonization occurring during hydrothermal carbonization under the reaction conditions of the invention is by dehydration and that decarboxylation to form carbon dioxide is a minor reaction. This proposition was explored by construction of a Van Krevelen Diagram (Van Krevelen D W. Fuel 1950, 29, 269-284). This approach is a graphical statistical method of analyzing reaction mechanisms that occur during carbonization processes. The method involves determining the H/C and O/C atomic ratios, i.e., weight percent divided by atomic weight, for starting materials and hydrochar products. For this example, the % O values were determined independently at Huffman Laboratories, Inc. (Golden, Colo.) and were 37.1% for starting freeze-dried thin stillage and 17.4% for the hydrochar of Example 21. Corresponding H/C and O/C atomic ratios for starting thin stillage were 7.9 and 2.31, while for the hydrochar were 6.2 and 1.08. With this technique, a slope of 2.0 of the line connecting starting biomass and carbonized products identifies a perfectly dehydrative process, while slopes <2.0 provide evidence for decarboxy-

lation. When these values were plotted on an X/Y graph depicting H/C as the y axis and O/C as the x axis, a line connecting the two points had a slope of 2.0. This result supports the hypothesis that the principal mode of carbonization is by loss of water (dehydration) and not by loss of carbon dioxide (decarboxylation).

[0080] The entire texts of patents, publications and other documents referred to herein above are fully incorporated herein by reference. The invention herein above has been described with reference to various and specific embodiments and techniques. It will be understood by one of ordinary skill in the art, however, that reasonable variations and modifications may be made with respect to such embodiments and techniques without substantial departure from either the spirit or scope of the invention defined by the following claims.

What is claimed is:

1. A method of producing a synthetic coal from a fermentation residue having a low lignocellulosic content, the method comprising the steps of:

subjecting the fermentation residue to hydrothermal carbonization in an aqueous suspending medium at a temperature of between about 170° C. and about 225° C., at a pressure of between about 0.8 and about 2.41 MPa, for a period of time of less than 4 hours, and separating the resulting synthetic coal from a liquid component.

2. The method of claim **1** and further including the step of adding an acidic buffer to the fermentation residue prior to subjecting said residue to hydrothermal carbonization.

3. The method as defined in claim **1** and wherein the fermentation residue is thin stillage obtained from the corn based ethanol manufacturing process.

4. The method as defined in claim **1** and wherein the fermentation residue is whole stillage obtained from the corn based ethanol manufacturing process.

5. The method as defined in claim **1** and wherein the lignocellulosic content is less than 20% by dry weight of the fermentation residue.

6. The method of claim **1** and the fermentation residue based synthetic coal produced thereby having an ash content less than both lignocellulosic substrate derived synthetic coals and fossil fuel bituminous coals.

7. The method of claim **1** and the fermentation residue based synthetic coal produced thereby having both a nitrogen and hydrogen content greater than both lignocellulosic substrate derived synthetic coals and fossil fuel bituminous coals.

8. The method of claim **1** and the fermentation residue based synthetic coal produced thereby having a heat of combustion greater than 10,000 BTU's per pound.

9. The method of claim **1** and the fermentation residue based synthetic coal produced thereby having a sulfur content

less than both lignocellulosic substrate derived synthetic coals and fossil fuel bituminous coals.

10. The method of claim **1** and the fermentation residue based synthetic coal produced thereby having a macroporous structure.

11. The method of claim **1** and the liquid component thereof containing an amount of phosphorous comprising substantially all the phosphorous present in the fermentation residue.

12. A method of producing a synthetic coal from a fermentation residue having a lignocellulosic content less than 20% by dry weight of the fermentation residue, the method comprising the steps of:

subjecting the fermentation residue to hydrothermal carbonization in an aqueous suspending medium at a temperature of between about 170° C. and about 225° C., at a pressure of between about 0.8 and about 2.41 MPa, for a period of time of less than 4 hours, and

separating the resulting synthetic coal from a liquid component.

13. The method of claim **12** and further including the step of adding an acidic buffer to the fermentation residue prior to subjecting said residue to hydrothermal carbonization.

14. The method as defined in claim **12** and wherein the fermentation residue is obtained from a corn based ethanol manufacturing facility.

15. The method of claim **12** and the fermentation residue based synthetic coal produced thereby having an ash content less than both lignocellulosic substrate derived synthetic coals and fossil fuel bituminous coals.

16. The method of claim **15** and the fermentation residue based synthetic coal produced thereby having both a Nitrogen and Hydrogen content greater than both lignocellulosic substrate derived synthetic coals and fossil fuel bituminous coals.

17. The method of claim **16** and the fermentation residue based synthetic coal produced thereby having a heat of combustion greater than 10,000 BTU's per pound.

18. The method of claim **17** and the fermentation residue based synthetic coal produced thereby having a sulfur content less than both synthetic lignocellulosic substrate derived coals and fossil fuel bituminous coals.

19. The method of claim **18** and the fermentation residue based synthetic coal produced thereby having a macroporous structure.

20. The method of claim **12** and the liquid component thereof containing phosphorous comprising substantially all the phosphorous present in the fermentation residue.

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