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

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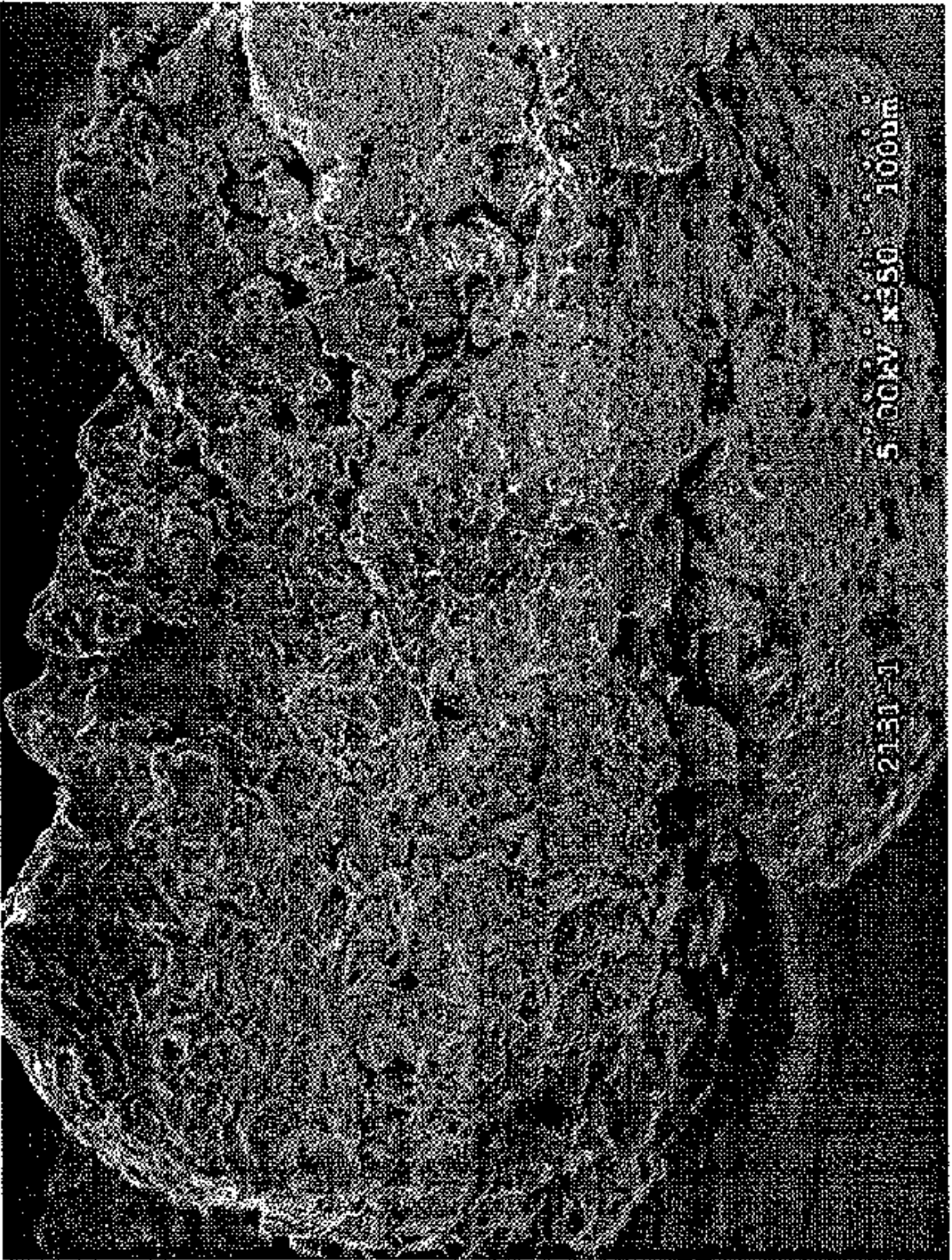
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(57) **ABSTRACT**

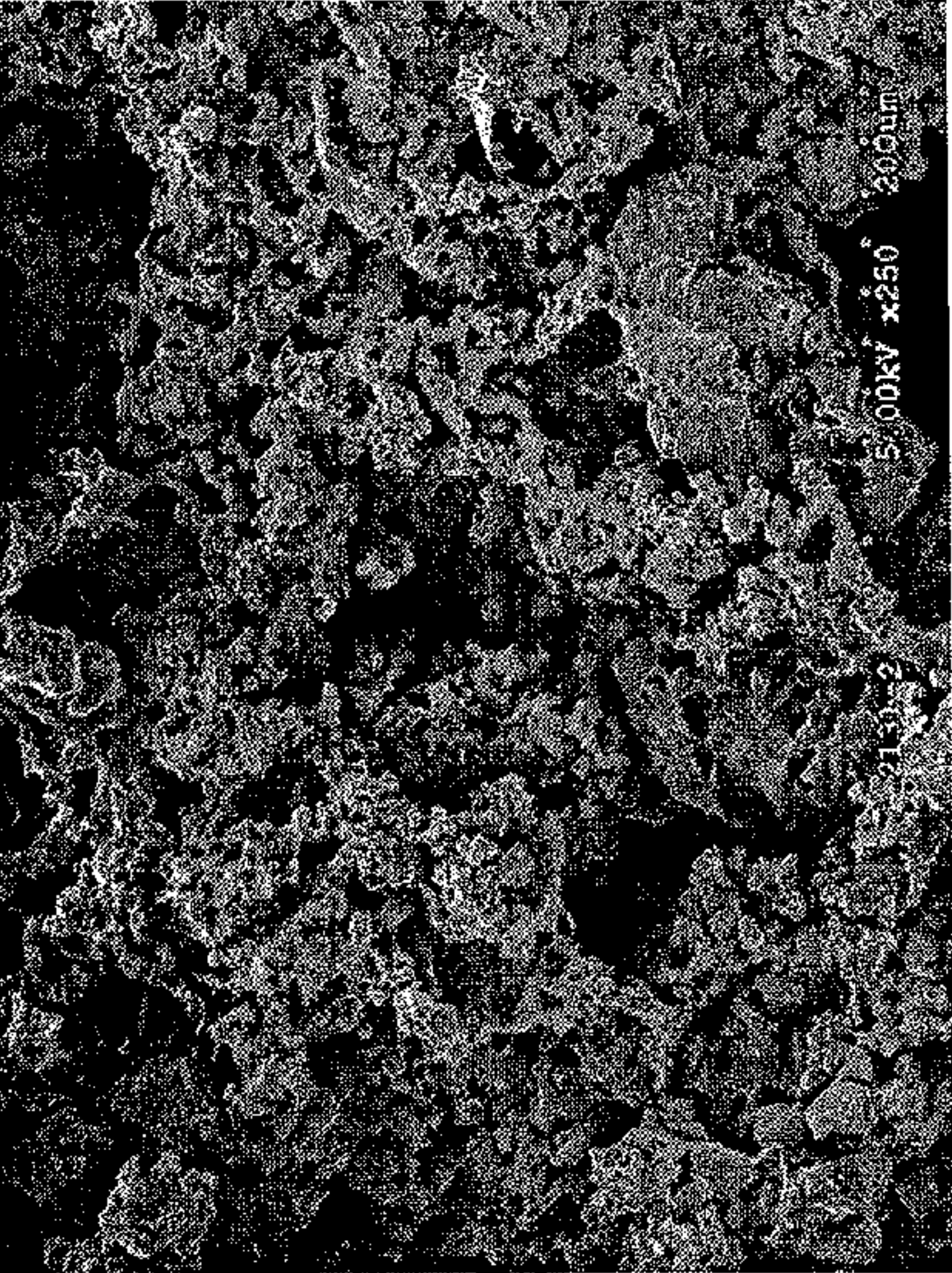
Synthetic coal, methods of producing synthetic coal, produced from fermentation residue, such as the residue from ethanol production, by subjecting the fermentation residue to hydrothermal carbonization in an aqueous solution at a temperature and a pressure sufficient to form a synthetic coal solid and a liquid component. The solid synthetic coal component has a low ash content and may be used as a carbon source for energy production, such as for combustive thermal energy generation, or for gassification for the production of synthesis gas.

Figure 1

Distiller's Grain



HTC Char



SYNTHETIC COAL AND METHODS OF PRODUCING SYNTHETIC COAL FROM FERMENTATION RESIDUE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Provisional Application entitled "Process for Making Products from Distiller grain Fermentation Residues" filed on Nov. 6, 2009. The contents of the previously mentioned provisional application is incorporated by reference herein.

BACKGROUND OF THE INVENTION

[0002] Natural coal is generally regarded as a non-renewable energy source in part because of the extreme amount of time needed for its formation. For instance, lignite coal requires hundreds of years, and anthracite coal requires hundreds of millions of years for their respective formation. The conditions for formation of natural coal are believed to be achieved through sediment of plant and animal materials accumulated, pressurized and heated under increased bed depth.

[0003] Rapid oxidation or burning of natural coal releases toxic agents, such as heavy metals (e.g., mercury, uranium) co-deposited as part of the sedimentation formation process. The toxic content of natural coal has been both a significant health concern as well as a global environmental concern. The effect of released carbon dioxide into the atmosphere and its association with global warming present increasing problems associated with the use of natural coal. Increased regulation in the form of emissions controls and carbon emission levels is expected.

[0004] Nitrogen fertilizers such as ammonium nitrate and urea require ammonia for their manufacture. Ammonia is chiefly manufactured from nitrogen and hydrogen at high temperature and pressure employing the Haber Bosch process. While nitrogen can be obtained relatively easily from the atmosphere, hydrogen is obtained by a process known as Steam Reforming from natural gas. Currently, 5% of the world's annual natural gas is utilized for that purpose. With continued use of natural gas as a fuel for home and commercial heating, hydrogen supply for fertilizer production and, increasingly, greater utilization of natural gas as a replacement of coal for generation of electricity, the world's reserves of natural gas will be depleted at an alarming rate. It would be desirable to generate an increased amount of nutrients for plants from biomass.

[0005] Hydrothermal carbonization is a process in which biomass is heated in water in a confined system. Two product streams are created: a coal-like char and an aqueous solution, with the two products being separated by filtration. Synthetic or artificial coals have been produced from lignocellulosic sources, such as wood and peat. Schuhmacher et al., *Fuel*, 39(3) pp. 223-234 (1960) describes a process involving heating lignocellulosic material in water at temperatures between 225° C. and 390° C. generally under alkaline conditions to prepare artificial coal-like products. According to this process, gaseous by-products include carbon dioxide and the residue ("artificial coal") is obtained in decreasing yield with increasing temperature. Woody (lignocellulosic) and higher plants contain many kinds of cells with specific functions. Cellulose, hemicellulose and lignin are products of specialized cells that provide structural stability and mechanical

strength allowing for passage of water and nutrients throughout the various parts of the plant. Antonietti, et al., *Chem. Mat.* 2007, 19, 4205-4212 and New J. Chem. 2007, 31, 787-789, have also subjected various kinds of terrestrial plant components such as sugar beet chips, pine cones, pine needles, oak leaves, and orange peels to hydrothermal carbonization at temperatures from 180-250° C. for periods from 4-24 hours.

[0006] In response to significantly increased crude oil prices and politically and economically uncomfortable dependence on imports of crude oil, ethanol has been utilized as an additive to gasoline since 1980 and has now commonly reached concentrations of 10 volume percent, with 20 volume percent being legislated to occur in Minnesota in 2013. Several states also currently offer E85 which contains 85% ethanol and 15% gasoline. 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 and yeast to convert the latter into ethanol, carbon dioxide and a solid residual product known as Distiller's Grains (DG). A bushel of corn can provide 2.8 gallons of ethanol, 18 pounds of DG (dried and known as Distiller's Dry Grains [DDG]) and 16 pounds of carbon dioxide. The DG fermentation residue is comprised of residual fermentable dextrins and yeast, unfermentable dextrins, protein, 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 monogastric animals such as swine and poultry. DG is most effectively utilized as the water-wet product (WDG or Wet Distiller's Grains) that can be shipped and utilized directly to farm sites within a relatively small radius, e.g., 30 miles, of the manufacturing site. In order to store, effectively transport, and minimize microbial growth, WDG must be dried and converted into DDG, and the drying process requires substantial amounts of heat energy adding considerable cost to the feed. As a consequence, ethanol manufacturers are often in a situation with a large surplus of WDG that must be dried at the manufacturing site. 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. There has been one report (Elliot, et. al., *Ind. Eng. Chem. Res.* 2004, 43:1999-2004) of hydrothermal gasification (with catalyst) conducted using Distiller's Dry Grains with Solubles (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] Production of coal and nutritive byproducts from fermentation residues using hydrothermal carbonization is unknown. There exists a need in the energy resource field for improved synthetic coal products and processes having enhanced energy efficiencies. There further exists a need for nutritive media that can be utilized as plant fertilizers and reduce the consumption of natural gas required for production of hydrogen and use in the manufacture of nitrogen

fertilizers. Additionally, there exists a need for innovative processes utilizing natural biological materials as carbon neutral energy resources, thereby not increasing the net amount of carbon dioxide in the atmosphere that utilizing fossil fuels causes.

SUMMARY OF THE INVENTION

[0008] The invention provides a coal-like product (herein after referred to as “coal”, “char”, or “coal product” in accordance with the definition below) 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. It has been discovered that hydrothermal carbonization can be performed upon fermentation residues, such as distiller’s grains, as a starting material to produce synthetic coal. It has also been discovered that despite the relatively large particle size of the fermentation residue starting biomass material, hydrothermal carbonization processing can efficiently produce a synthetic coal product. Furthermore, the invention can be applied to fermentation residues created from ethanol manufacturing.

[0009] The synthetic coal is prepared by an improved hydrothermal carbonization transformation process using fermentation residues as starting material. Unlike natural coal that occurs beneath the surface of the earth and is a “fossil fuel” formed over millions of years, because carbon dioxide from plant biomass is formed through photosynthesis, an advantage of the coals of the invention is that the carbon dioxide formed during oxidation results in a “carbon neutral” event with no “new” carbon dioxide being introduced into the earth’s atmosphere. Embodiments of the invention can also be used to sequester carbon for storage. 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 also 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 filtrate by-product from the process 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 the form of water-soluble compound by-products rather than being retained in the insoluble synthetic coal products, and these by-products can have separate uses.

[0010] Additionally, embodiments of the invention provide a hydrothermal carbonization process that increases the carbon-to-oxygen ratio of the resultant synthetic coal product primarily through dehydration rather than by loss of carbon dioxide and generates minimal gaseous products.

[0011] Embodiments of the invention further provide a process for preparing synthetic coal from fermentation residues, said process comprising the steps of: a) obtaining an aqueous fermentation residue; b) subjecting said fermentation residue to hydrothermal carbonization; c) separating solid char from liquid aqueous filtrate following said hydrothermal carbonization; wherein said solid char comprises solid synthetic coal.

[0012] The invention provides a 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; low or undetectable amounts of elemental sulfur content; low ash content; and an equivalent or greater heat of combustion per volume as compared to synthetic lignocellulosic coal and equivalent heat of combustion to bituminous coal. The invention further provides a filtrate from the process comprising an aqueous solution composition.

[0013] Furthermore, embodiments of the invention provide a method of using the synthetic coal prepared in accordance with the invention as an energy resource comprising employing said synthetic coal product as a carbon source within a combustive thermal energy generation system. In yet another embodiment, the coal product of the invention can be used in a coal gasification process. In some embodiments, the coal product can be used in a coal gasification process for preparing synthesis gas.

[0014] One advantage associated with embodiments of the invention is that the employment of a fermentation residue as a starting material to produce synthetic coal provides a carbon neutral energy source with reduced environmental impact. As a further advantage, the process generates significantly reduced or minimal gaseous output. This is especially the case for carbon dioxide output, since hydrothermal carbonization is conducted under reaction conditions that increase the carbon-to-oxygen ratio primarily by loss of water (dehydration) rather than by loss of carbon dioxide. The invention also affords a relatively low toxicity, e.g., low or undetectable sulfur, mercury and uranium contents, and a product with significantly higher nitrogen and hydrogen contents than natural bituminous coal. Embodiments of the invention also provide a low ash coal. These and other advantages will become apparent from the following disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] Embodiments of the invention are further illustrated by the following drawings—none of which is intended to be construed as necessarily limiting the invention.

[0016] 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

[0017] As used herein, “fermentation residues” are meant to refer to residues from various fermentation operations including ethanol production, whiskey and beer production, microbially-assisted antibiotics production, and other bacterial, yeast and fungal fermentation reactions.

[0018] 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.

[0019] The residue produced by the fermentation reactions is the remainder or residue of a fermentation reaction after the specific target material (e.g. biomass, biomaterial such as a

protein (e.g. an enzyme), carbohydrate, lipid or small molecule such as ethanol) is removed by distillation in the case of ethanol, followed by decantation, filtration or centrifugation.

[0020] 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, and which manifests itself as affirmatively present attributes and characteristics described within this specification and claims.

[0021] The term “coal” or “char” 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 state product outcome corresponding to the fermentation residue starting material input and the hydrothermal carbonization process of the invention. 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. 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.

[0022] The term “macroporous” comes from polymer science where it means a material that has pores with sizes ranging from 50 nm-1 μm . 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 quite high, i.e. in excess of 10 m^2/g .

[0023] 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; filtering the resulting solid materials to separate said solid material from the aqueous filtrate; and obtaining a fermentation residue-derived synthetic coal 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 or catalyst 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 6 hours, and a pressure up to about 2.41 MPa, for example. A solid or semi-solid fer-

mentation residue-derived coal product is obtained, along with an aqueous filtrate composition that can be further downstream processed.

[0024] 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, hydrogen, methane, carbon monoxide, ammonia, and the like. Under conditions employed in various embodiments of the present invention, the amount of carbon dioxide produced during hydrothermal carbonization is less than 10% of the reaction products.

[0025] 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 15-30% solids in water when centrifugation operations are employed, as is common in the corn ethanol manufacturing industry. These aqueous suspensions can be utilized 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 homogeneous mass.

[0026] The process of the invention optionally can include the use of buffers or catalysts. Buffers and catalysts can be added into the aqueous mixture prior to proceeding to the hydrothermal carbonization stage. Suitable buffers or catalysts 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.

[0027] 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 6 hours. For example, the process can be performed for a duration ranging from between about 0.5 hour up to about 6 hours, or between about 0.5 hour to about 2 hours.

[0028] 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.

[0029] 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. Carbonization and dewatering apparatuses similar to that described in Bodle et al. U.S. Pat. No. 4,632,731 can be used, the entire text of which is incorporated herein by reference.

[0030] In one embodiment, suitable apparatuses that can be used include those which can conduct a continuous process. For example, the apparatus can include commercially-available twin extruders of stainless steel construction. It is noted that continuous process systems may employ higher temperatures and conduct the process at shorter time periods (e.g., 1 to 5 minutes) and may achieve results similar to batch conditions. Such a system (for lignocellulosic processing) is described in Bobleter et al., *J. Appl. Polymer Sci.*, 20, pp. 2083-2093 (1976).

[0031] The 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.

[0032] 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 DDGS material or natural coal. In a number of applications of the present invention the ash content has been reduced an order of magnitude compared to the ash content of the starting DDGS 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 DDGS 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.

[0033] 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.

[0034] In yet 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.

[0035] 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, decantation and centrifugation. The separated solid or semi-solid component is the synthetic coal product and the remainder is a liquid filtrate.

[0036] 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.

[0037] 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 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

[0038] 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.

[0039] 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.

[0040] As is apparent to one skilled in the art, 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 may or may not be dried, and the concentration of solid material in an aqueous fermentation residue can be determined and its concentration adjusted accordingly.

Example 1

[0041] An experiment was conducted to illustrate the efficient transformation of a fermentation residue from dry distiller grain (DDG), into a high quality coal product comparable to natural bituminous coal. The transformation occurs employing DDG 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).

[0042] A mixture was prepared by combining DDGS (obtained from Chippewa Valley Ethanol Company (Benton, Minn.)) (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.

[0043] 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.

[0044] 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%.

[0045] 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 DDG have been liquefied or dissolved during the process and reformed into a solid, almost macroporous network as can be seen from the image on the right for the coal product.

Comparative Example 2

[0046] For purposes of illustrating the invention, hydrothermal carbonization of a lignocellulosic material was conducted for purposes of comparison. A monoculture prairie grass identified as “Little Bluestem” [having a lignin content of 20% and the following monosaccharide hydrolysis products: glucose (30%), xylose (15%), galactose (2%), arabinose (3%) and mannose (1%)] 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 product was only 59.0%.

[0047] 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

[0048]

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

[0049] 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.

Example 3

[0050] 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 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

[0051] 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

[0052] 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

[0053] 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 DG. 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% DDG 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

[0054] 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 % 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 % 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.

[0055] These observations were further confirmed by applying analysis of variance (ANOVA) methods to the data in Examples 7-18.

[0056] A linear regression equation was developed from the orthogonal factorial design:

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

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

[0057] where

[0058] X_1 =dimensionless temperature;

[0059] X_2 =dimensionless time and

[0060] 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

[0061] 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 DDG 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.

[0062] 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:

[0063]

26.5 g DDG	→	11.49 g Coal	+	10.69 g Solutes
% N = 4.9		% N = 4.1		% N = 6.9
1.3 g N		0.47 g N		0.74 g N = 1.21 Total
		36% in Coal		57% in Solution

[0064] Mass Balance=1.21/1.30=93%

Phosphorous Accounting:

[0065]

26.5 g DDG	→	11.49 g Coal	+	10.69 g Solutes
%P = 0.5		%P = n.d.		%P = 1.8
0.13 g P				0.19 g P
				146% in Solution**

**Data accuracy may have been hampered due to handling issues of the very sticky freeze-dried solute sample.

[0066] 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 phosphorous, as well as a significant concentration of potassium, are located in the aqueous solution and available as nutrients for plants.

Example 20

[0067] 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

[0068] 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 natural coal. The nitrogen content is elevated in both the DDG 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 at sufficiently low that normal remediation operations in effect at natural coal burning installations will 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.

[0069] 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 fermentation residues, the method comprising the steps of:

- obtaining a fermentation residue;
- subjecting said fermentation residue to hydrothermal carbonization in an aqueous medium at a temperature and a pressure sufficient to form a synthetic coal solid.

2. The method of claim 1 further comprising separating synthetic coal solid from the aqueous medium.

3. The method of claim 1 wherein the temperature is between about 170° C. and about 225° C.

4. The method of claim 1 wherein the pressure is between about 0.8 and about 2.41 MPa.

5. The method of claim 1 further comprising combining the fermentation residue with an acidic buffer.

6. The method of claim 1 wherein the fermentation residue is produced from corn based ethanol production.

7. A method of producing a synthetic coal from fermentation residues, the method comprising the steps of:

- obtaining an fermentation residue;
- subjecting said fermentation residue to hydrothermal carbonization in an aqueous solution at a temperature of between about 170° C. and about 225° C. and a pressure of between about 0.8 and about 2.41 MPa; and
- separating a synthetic coal solid from a liquid component.

8. The method of claim 7 further comprising combining the fermentation residue with an acidic buffer.

9. The method of claim 1 wherein the fermentation residue is a byproduct of corn based ethanol production.

10. The method of claim 7 further comprising employing the synthetic coal as a carbon source within a combustive thermal energy generation system.

11. The method of claim 7 further comprising gasifying the synthetic coal.

12. The method of claim 12 wherein gasifying the synthetic coal produces a synthesis gas.

13. The method of claim 7 further comprising providing the synthetic coal as a source of coke for the manufacture of steel.

14. A synthetic coal produced by the process comprising the steps of:

- obtaining an fermentation residue;
- subjecting said fermentation residue to hydrothermal carbonization in an aqueous solution at a temperature and a pressure sufficient to form a synthetic coal solid and a liquid component.

15. The synthetic coal of claim **14** wherein the process further comprises separating the synthetic coal solid from the liquid component.

16. The synthetic coal of claim **14** wherein the temperature is between about 170° C. and about 225° C.

17. The synthetic coal of claim **14** wherein the pressure is between about 0.8 and about 2.41 MPa.

18. The synthetic coal of claim **14** wherein the process further comprises combining the fermentation residue with an acidic buffer.

19. The synthetic coal of claim **14** wherein the fermentation residue is produced from corn based ethanol production.

20. The synthetic coal of claim **14** wherein the synthetic coal has an ash content of <1% by weight.

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