**Title:** CONVERSION OF LIGNIN TO PHENOLIC AND CARBOXYLATE COMPOUNDS

**Abstract:** A method of converting lignin to phenolic compounds and dicarboxylates in high yield is described. The method involves the use of peroxy acids to react with lignin at a moderated treatment conditions. The peroxy acids can be used alone or in combination of other catalysts that have the capability to lower the molecular weight of lignin. A phenolic compounds yield is achieved (60%) and these phenolic compounds represents high value precursors for various applications including but not limited to antioxidants, health improvement agents, anticorrosive agents, liquid fuel components and performance enhancing agents, resin and adhesives. Dicarboxylic acids can be used for polymer applications or hydrodeoxygenation to hydrocarbon fuel.

**FIG. 4**
CONVERSION OF LIGNIN TO PHENOLIC AND CARBOXYLATE COMPOUNDS

BACKGROUND

[0001] Lignin is a major constituent of plant biomass and represents the second largest organic polymer on our planet. A large quantity of lignin is generated from pulp and papermaking processes. The upcoming biomass biorefinery industry will bring in an enormous amount of lignin. However, despite significant efforts in the past few decades, the commercial lignin market has stagnated at about one million tons per year. Catalytic degradation of biorefinery lignin to low molecular weight phenolic compounds is an area which has not been well studied.

[0002] It is clear that there is a lack of efficient method to convert polymeric lignin at a moderate condition to phenolic compounds in high yield. Most of the processes either lack the selectivity to obtain target products in high yield or require high temperature and high pressure conditions.

SUMMARY

[0003] Lignin is the largest source of renewable material with an aromatic skeleton. Depolymerizing lignin to low molecular weight aromatic and phenolic compounds offers an attractive opportunity to produce a range of potential high value products/chemicals. Lignin can be chemically and/or biologically depolymerized into smaller molecular weight phenolic compounds. Phenolic compounds have been applied as anti-oxidants to reduce the amount of dissolved oxygen in biofuel, and hence to prevent metal corrosion. Another area permitting large quantity application of lignin derived phenolic compounds is in biofuels. Conventional fossil fuels contain a significant amount of aromatics (up to 50% by volume) either derived from petroleum or blended as additives. Besides providing energy value, fuel aromatics also function as antioxidants and anti-corrosive agents. Most biofuel products (e.g.
biodiesel form plant oil, bio-alcohols from ligno-cellulosic biomass) are expected to have low aromatics content, due to either the nature of the feedstock or process configurations. Supplementing lignin derived phenolic compounds to biofuels will not only increase the energy content but also improve the quality of biofuels.

[0004] Disclosed are processes to produce both phenolic and dicarboxylate compounds comprising oxidative depolymerizing a lignin thereof with a peroxy acid at a temperature of not greater than about 160 °C to give a mixture of dicarboxylic acid compounds and a mixture of phenolic compounds. The mixture of dicarboxylic acid compounds may be formed in at least about 10% total weight yield, and the mixture of phenolic compounds may be at least about 28% total weight yield, wherein the total weight yield is calculated from the lignin on a contained lignin basis. Processes disclosed may further comprise formation of one or more organic solvents or combination thereof in at least about 5% total weight yield. In some embodiments, the oxidative depolymerizing is at a temperature of not less than about 60 °C to not greater than about 90 °C for about 10 minutes to about 3 hours. In other embodiments, the reaction is at least 3 hours. Shorter times favor the formation of phenolic products, while longer reaction time favors formation of dicarboxylic acids. Peak yields of phenolic products may be obtained at about 1-2 hours.

[0005] Also disclosed are antimicrobial mixtures of compounds comprising benzoic acid, vanillin, vanillic acid, gallic acid, and at least one substituted aryl ether. In addition, antibacterial agents may be produced by providing a lignin; decomposing the lignin with a peroxy acid for at least ten minutes and not greater than 3 hours at a temperature of not less than 40 °C to not greater than 120 °C to give a decomposition product; and extracting decomposition product with an organic solvent to give a solution of the antibacterial agent. Further, an antibacterial agent may be produced by providing a lignin; decomposing the lignin with a peroxy acid to give a decomposition product; partitioning the decomposition
product between aqueous phase and an organic phase; and concentrating the antibacterial agent.

[0006] The use of synthetic antibiotics in animals is a controversial practice in animal agriculture. Overuse of antibiotics has led to antimicrobial resistant microbes. There is significant movement toward prohibiting and reduce the use of synthetic antibacterial agents. Biobased antibacterial derived from lignin has a potential to replace synthetic antibiotics. Further, adhesives derived from biomass lignin have the potential to be cost competitive and to reduce petroleum consumption.

DESCRIPTION OF DRAWINGS

[0007] For a fuller understanding of the nature and advantages of the present technologies, reference should be had to the following detailed description taken in connection with the accompanying drawings, in which:

[0008] Figure 1: Lignin to phenolic compounds conversion yield during peracetic acid treatment.

[0009] Figure 2: Phenolic compound yield obtained from different lignin feedstock.

[0010] Figure 3: Types of phenolic compounds identified by GC/MS analysis of silylated samples.

[0011] Figure 4: Catalytic conversion of lignin to bioproducts and biofuel.

[0012] Figure 5: A non-limiting example of a method to fractionation reaction mixture.

[0013] Figure 6: The antibacterial activity of fraction B obtained from peroxyacetic acid depolymerization of alkaline lignin. Square symbols represent 0.1 g/mL, round symbols represent 0.05 g/mL, triangle symbols represent 0.01 g/mL.
**Figure 7:** A graph demonstrating conversion of an agriculture biomass lignin to phenolic compounds and dicarboxylic acids as a percent fraction of the total identified compounds. The graph is interpreted from bottom to top as: open boxes represent malonic acid, the vertical line boxes represent succinic acid, the diagonal square boxes represent maleic acid, dashed diagonal line boxes represent malic acid, diagonal brick boxes represent hydroquinone, heavier dot boxes represent vanillin, bold forward slash boxes represent parahydroxybenzaldehyde, lighter dot boxes represent vanillic acid, back slash boxes represent parahydroxybenzoic acid, and forward slash boxes represent para-coumaric acid.

**DETAILED DESCRIPTION**

**[0015]** Before the present compositions and methods are described, it is to be understood that they are not limited to the particular compositions, methodologies or protocols described, as these may vary. It is also to be understood that the terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit their scope which will be limited only by the appended claims.

**[0016]** It must also be noted that as used herein and in the appended claims, the singular forms "a", "an", and "the" include plural reference unless the context clearly dictates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. Any methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments disclosed.

**[0017]** "Optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where the event occurs and instances where it does not.
"Substantially no" means that the subsequently described event may occur at most about less than 10% of the time or the subsequently described component may be at most about less than 10% of the total composition, in some embodiments, and in others, at most about less than 5%, and in still others at most about less than 1%.

The term "alkyl" or "alkyl group" refers to a branched or unbranched hydrocarbon or group of 1 to 20 carbon atoms, such as but not limited to methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, octyl, decyl, tetradecyl, hexadecyl, eicosyl, tetracosyl and the like. "Cycloalkyl" or "cycloalkyl groups" are branched or unbranched hydrocarbons in which all or some of the carbons are arranged in a ring, such as but not limited to cyclopentyl, cyclohexyl, methylcyclohexyl and the like. The term "lower alkyl" includes an alkyl group of 1 to 10 carbon atoms.

The term "aryl" or "aryl group" refers to monovalent aromatic hydrocarbon radicals or groups consisting of one or more fused rings in which at least one ring is aromatic in nature. Aryls may include but are not limited to phenyl, naphthyl, biphenyl ring systems and the like. The aryl group may be unsubstituted or substituted with a variety of substituents including, but not limited to, alkyl, alkenyl, halide, benzylic, alkyl or aromatic ether, nitro, cyano and the like and combinations thereof.

"Substituent" refers to a molecular group that replaces a hydrogen in a compound and may include, but are not limited to, trifluoromethyl, nitro, cyano, C1-C2 alkyl, aromatic or aryl, halide (F, Cl, Br, I), C1-C2 alkyl ether, benzyl halide, benzyl ether, aromatic or aryl ether, hydroxy, alkoxy, amino, alkylamino (-NHR), dialkylamino (-NR'R") or other groups which do not interfere with the formation of the diaryl alkylphosphonate.

Methods to convert lignin to phenolic compounds in high yield at moderate conditions are described herein. The produced phenolics compounds can be applied as antioxidant, adhesive, animal feed fuel additives, or any other known applications of...
phenolic compounds. Methods are also described to further convert phenolic compounds to aromatic fuel components.

[0023] Peroxy acids, such as peracetic acid or persulfuric acid, are a group of selective delignification agents. Oxygen insertion is a characteristic step in peroxy acids catalyzed reaction with lignin. Due to their high oxidation potential, peroxy acids depolymerization of lignin can be performed at moderate conditions to minimize aromatic ring opening reactions.

[0024] Process embodiments include methods to produce both phenolic and dicarboxylate compounds comprising oxidative depolymerizing a lignin thereof with a peroxy acid at a temperature of not greater than about 160 °C to give a mixture of dicarboxylic acid compounds and a mixture of phenolic compounds. In some embodiments, the mixture of dicarboxylic acid compounds is in at least about 10% total weight yield, and the mixture of phenolic compounds is in at least about 28% total weight yield, wherein total weight yield is calculated from the lignin on a contained lignin basis. The solutions may include one or more organic solvents or combination thereof in at least about 5% total weight yield.

[0025] Various embodiments of the method include substantially separating one or more dicarboxylic acid compounds or combination thereof from the mixture of phenolic compounds; reducing at least one of the dicarboxylic acid compounds to a saturated dicarboxylic acid; recovering one or more dicarboxylic acids or combination thereof in at least about 10% total weight yield.

[0026] Various other embodiments include substantially separating one or more dicarboxylic acid compounds or combination thereof from the mixture of phenolic compounds; esterifying at least one of the dicarboxylic acid compounds to a dicarboxylate
ester; recovering one or more dicarboxylate esters or combination thereof in at least about 10% total weight yield.

[0027] The lignin may be any available lignin. The lignin may be an alkaline lignin, a steam exploded lignin, or a steam exploded lignin having an enzyme treatment, a pyrolytic lignin, or combination thereof. **Figure 2** shows alkaline lignin has surprisingly higher yields of phenolic conversion as compared to steam exploded lignin. Steam exploded lignin gave surprisingly higher yields than pyrolytic lignins.

[0028] The Klason lignin assay may be used to determine lignin content of a sample. Klason lignin is obtained. In the Klason lignin assay method, polysaccharides are hydrolyzed by treating wood with sulfuric acid to provide water-soluble sugars, and the lignin is recovered as an insoluble residue. The Klason content of the lignin used, expressed as a weight percentage, is about 50% by weight to about 100% by weight or a range within that range. As used herein, the term "percent (or %) by weight" or "weight percentage", when applied to the lignin content of treated pulp, means weight percentage relative to the dry weight of the treated pulp. Lignin content is measured by a sugar content assay based on Technical Association of Pulp and Paper Industries (TAPPI) standard method T249 cm-00 and lignin content is estimated from the solid residue after filtration of sugar solution from hydrolyzed samples. In a summary of the method, samples are hydrolyzed with sulfuric acid using a two-step technique. The precipitate is isolated and dried. In embodiments, the Klason lignin assay is at least 50%, at least 60%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, at least 95%, at least 99%, or greater. "Contained lignin basis" are calculated using a Klason lignin assay result on the dried the lignin utilized. Yields and total weight yields are calculated from the dried lignin utilized using a Klason lignin assay result.

[0029] The oxidative depolymerization is performed at moderate temperatures. The oxidative depolymerization can be performed at a reaction temperature of not less than
about 5 °C to not greater than about 160 °C. In some embodiments, the reaction is performed
at a temperature of about 40 °C to not greater than about 120 °C. In other embodiments, the
reaction is performed at a temperature of about 60 °C to not greater than about 90 °C. In
certain other embodiments, the reaction is performed at about 30 °C, about 40 °C, about 50
°C, about 60 °C, about 70 °C, about 80 °C, about 90 °C, about 100 °C, about 120 °C, about
140 °C, about 160 °C, or a range between any two of the specified temperatures. Specific
embodiments have ranges of about 25-120 °C, about 40-120 °C, about 40-90 °C, about 50-80
°C, and about 60-90 °C.

[0030] In some reactions, the reaction is performed for about 10 minutes to about
3 hours. In other reactions the minimum temperature of the temperature range is held for at
least three hours. As a non-limiting example, an embodiment has the oxidative
depolymerization performed at not less than 60 °C for 10 minutes to three hours, with an
upper temperature of not more than 90 °C. In another embodiment, the depolymerization is
performed at not less than 60 °C for about 150 minutes, with an upper temperature of not
more than 90 °C. In yet another embodiment, the oxidative depolymerization is performed at
not less than 60 °C for at least three hours. Figure 1 shows an unexpected result wherein a
maximum phenolic compounds yield was reached at about 1.5 hours of reaction at about 60
°C. Longer reaction times favored dicarboxylic acid formation.

[0031] The peroxy acid may include any organic peroxy acid. In some
embodiments, the peroxy acid includes peracetic acid, performic acid, or combinations
thereof. In other embodiments, the peroxy acid is a peroxyaryloic acid. In certain
embodiments, the peroxyaryloic acid is a peroxybenzoic acid. In still other embodiments, the
peroxy acid is a m-chloroperoxybenzoic acid (MCPBA). The peroxy acid may be generated
in situ from an organic acid and hydrogen peroxide. The formation of a peroxy acid may be
catalyzed by an organic catalyst or inorganic catalyst in the presence of hydrogen peroxide.
When the oxidizing agent includes a peroxyl acid prepared in situ, it may be prepared in any manner, such as by combining a peroxide and an acid. Any peroxide or combination of peroxides that can provide a peroxyl acid be used, such as hydrogen peroxide, for example, aqueous hydrogen peroxide. Any acid or combination of acids that can provide a peroxyl acid can be used, such as formic acid, or acetic acid, for example, aqueous solutions of formic and/or acetic acid. Performic acid may be obtained, for example, by combining hydrogen peroxide and formic acid. Peracetic acid may be obtained by combining hydrogen peroxide with acetic acid.

The peroxyl acid may include a peroxysulfuric acid. The peroxyl acid may include peroxymonosulfuric acid, peroxysulfuric acid, peroxysulfonic acid, or a mixture thereof. Most of peroxyl acids can be decomposed to simple acid, oxygen and water. Using peroxyl acids for lignin conversion to phenolic compounds provides a green process for lignin conversion.

The peroxyl acid may be added or prepared in a quantity dependent upon the weight of the contained lignin. In some embodiments, the quantity of added or in situ prepared peroxyl acid is 0.01 - 0.5:1 weight:weight ratio. Thus, in that embodiment for each 100 grams of lignin, the would be added or prepared one to fifty grams of peroxyl acid. In other embodiments, the quantity of peroxyl acid is 0.001 - 0.5:1 w/w%, is 0.001 - 0.25:1 w/w%, 0.01 - 0.5:1 w/w%, 0.01 - 0.25:1 w/w%, 0.01 - 0.15:1 w/w%, or 0.05 - 0.25:1 w/w%. In situ preparation may be achieved by a hydrogen peroxide or an alkali metal peroxide.

The depolymerizing may be performed in an aqueous medium, a non-aqueous medium, or a biphasic mixture of an aqueous medium and a non-aqueous medium. The depolymerizing reaction may be performed at any pH. Lower pH reactions favor higher yields of the phenolic compounds, while higher pH reactions favor higher yields of dicarboxylates. Peroxyacids are sometimes less stable at the highest pH ranges. Higher pH
reactions. In various non-limiting examples, the depolymerizing is performed in an aqueous solution at a pH of about 2 to about 4, about 2 to about 7, about 3.5 to about 10.5, about 7 to about 10.5, about 7 to about 12, and about 9 to about 11. Specific examples of pH values include about 2, about 3, about 4, about 5, about 6, about 7, about 8, about 9, about 10, about 11, and ranges between any two of these values (including endpoints).

[0036] The method may further include recovering phenolic compounds. The recovery may include an organic solvent extraction. The recovery may include a low temperature distillation. The recovery may include a steam distillation. The distillation may use reduced pressure and/or azeotropic distillations or similar distillations known to those of skill in the art. The recovered phenolic compounds may include vanillin, vanillic acid, gallic acid, or combinations thereof.

[0037] The method may further include substantial deoxygenating of the recovered phenolic compounds to give hydrocarbon fuel components. The deoxygenating may include substantial dehydration and hydrogenation of the recovered phenolic compounds to give hydrocarbon fuel components.

[0038] The method may further include recovering dicarboxylic acid compounds from a dicarboxylic acid fraction. The recovery may include extracting the dicarboxylic acid compounds into an aqueous solvent at a pH of about 3.5 or greater. In some embodiments, the extraction is into an aqueous mixture of about 3.5 pH to about 10.5 pH. The recovered dicarboxylic acid compounds may include muconic acid, succinic acid, maleic acid, or a combination thereof.

[0039] The method may further include esterifying the dicarboxylic acid fraction. The esterification may include formation of dialkyl esters, monoacid monoalkyl esters, and combinations thereof. In certain embodiments, the dialkyl esters may include a dialkyl muconate, a dialkyl succinate, a dialkyl maleate, or a combination thereof.
In various embodiments, the mixture of phenolic compounds is in at least 28% total weight yield. In certain embodiments, the mixture of phenolic compounds is in at least about 28%, about 35%, about 40%, about 45%, about 50%, about 55%, about 60%, about 70%, about 80% weight yield, or a weight yield between or including any two of the stated weight yields.

In various embodiments, the mixture of dicarboxylic acid and/or derivative ester compounds is in at least 10% total weight yield. In certain embodiments, the mixture of carboxylate compounds is in at least about 15%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, about 50%, about 60% weight yield, or a weight yield between or including any two of the stated weight yields.

Other embodiments are an antimicrobial mixture of compounds. The mixture of compounds may include benzoic acid, vanillin, vanillic acid, gallic acid, and at least one substituted bisaryl ether. In some embodiments, the mixture is bactericidal at a concentration of 0.1 g/mL. In other embodiments, the mixture is bacteriostatic at a concentration of 0.01 g/mL.

In certain embodiments, the antibacterial agent may be produced by providing a lignin; decomposing the lignin with a peroxy acid for at least ten minutes and not greater than 3 hours at a temperature of not less than 40 °C to not greater than 120 °C to give the antibacterial agent. The antibacterial agent may be produced by providing a lignin; decomposing the lignin with a peroxy acid for at least ten minutes and not greater than 3 hours at a temperature of not less than 60 °C to not greater than 90 °C. The antibacterial agent may be produced by decomposing a lignin with a peroxy acid, partitioning between aqueous phase and an organic phase, and further eluting the aqueous fraction through a chromatographic material. The chromatographic material may be a reverse-phase material.
The antibacterial agent may be isolated. Isolation may include an organic solvent extraction.

The isolation may include concentrating the antibacterial agent.

[0044] Other embodiments are an adhesive mixture of compounds. The adhesive mixture may be produced by providing a lignin; decomposing the lignin with a peroxy acid to give a decomposition product; partitioning the decomposition product between an aqueous phase and an organic phase; eluting the water fraction through a reverse-phase material with an acidic alkanol; and concentrating the adhesive product.

[0045] These technologies and embodiments illustrating the method and materials used may be further understood by reference to the following non-limiting examples.

EXAMPLES

EXAMPLE 1: Depolymerization of Lignin

[0046] An alkaline lignin (Sigma) was treated by peracetic acid (PAA) at 60°C. The production of phenolic compounds from lignin was measured during 24 hours of reaction. As shown in Figure 1, lignin was quickly depolymerized to low molecular weight phenolic compounds after peroxyacetic acid addition with a maximum phenolic compounds yield reached at approximately 62% following 1.5 hours of reaction. Extending the reaction time led to further disruption of the aromatic structure and formation of dicarboxylate compounds. The ratio between phenolic compounds and carboxylic acids depends on the lignin and reaction conditions. Varying the lignin source and reaction conditions, allowed yields of phenolic compounds of about 28% to 63% and carboxylic acids yield to about approximately 10% to 40%, as shown in Figure 2.

EXAMPLE 2: Depolymerization of Lignin to form Phenolics

[0047] Dried lignin, 100 grams, having 80% contained lignin by Klason assay, is reacted with 15 grams of aqueous peracetic acid in 100 ml of hexane at a pH of about 4.
Depolymerizing lignin in hexane led to an in-situ separation of polar and non-polar products in the respective water and hexane layers. The hexane layer contained mostly hydrocarbon compounds such as benzene and benzene derivative while the phenolic compounds were enriched in the aqueous layer. The reaction is stopped at 1.5 hours at about 50 °C by cooling to room temperature and phase separation.

[0048] The phenolic compounds were isolated by HPLC and identified by GC/MS. The major phenolic constituents were vanillin, gallic acid, vanillic acid, benzoic acid, and phenolic dimers (Figure 3). The weight yield of the phenols is about 65%.

[0049] The dicarboxylate compounds were identified in the aqueous fraction. The identified dicarboxylic acids included muconic acid, succinic acid, and maleic acid. These acids result from peroxy acid ring opening reactions. The weight yield of the dicarboxylates is about 10%.

[0050] Besides phenolic compounds and dicarboxylic acids, benzene, furan, and their derivatives are identified by GC/MS (5-15% weight yield). The benzene, furan, and derivatives are used or fuel components.

EXAMPLE 3: Depolymerization of Lignin to form Dicarboxylates

[0051] Peroxy acids depolymerization of lignin can be performed in aqueous media. 100 grams of dried lignin, having 50% contained lignin by Klason assay, is reacted with 25 grams of aqueous peracetic acid in water at a pH of about 9. The reaction is performed for 12 hours at about 80 °C. The weight yield of the dicarboxylates is about 40%.

EXAMPLE 4: Preparation of Polymer Precursors from Dicarboxylates

[0052] Besides achieving high phenolic compounds yield, oxidative depolymerization of lignin also provides a new pathway to convert lignin to aliphatic compounds for hydrocarbon fuel and polymer productions. The carboxylic acids of Example
3 are converted to polymer precursors. Hydrogenation (Figure 4) of the dicarboxylate mixture converts muconic acid to the monomer adipic acid.

EXAMPLE 5: Test of Antimicrobial Properties of Lignin Derivatives

[0053] The depolymerization reaction of Example 1 was extracted with ethyl acetate (see Figure 5). The ethyl acetate fraction (B) was tested for antimicrobial effect (using Salmonella enteritidis) at 0.1 gm/mL, 0.05 gm/mL, and at 0.01 gm/mL. As shown in Figure 6, the ethyl acetate fraction (B) was an effective antimicrobial agent. The ethyl acetate fraction inhibited the growth of Salmonella at a concentration of 0.1 g/ml. When the ethyl acetate fraction was used at a concentration of 0.05 g/ml it took between 8 and 12 hours to eliminate the bacteria. At a concentration of 0.01 g/ml the solution was a bacteriostatic agent, significantly reducing the number of bacteria colony units. Testing of the water fraction (A) showed similar antimicrobial effects as the ethyl acetate fraction (B).

EXAMPLE 6: Test of Adhesive Properties of Lignin Derivatives

[0054] The various fractions of Example 1 (see Figure 5) were tested for adhesive ability. Methanol Fraction C has shown good adhesive properties.

EXAMPLE 7: Depolymerization of Lignin by in-situ Produced Peroxyacid to form Dicarboxylates

[0055] An agricultural biomass lignin was depolymerized to phenolic compounds and dicarboxylic acids by a mixture of hydrogen peroxide and a transition metal catalyst, the ratios monitored by time as shown in Figure 7. In the first half hour, phenolic compounds were the predominant compounds. Longer reaction time favors a higher yield of carboxylic acids.
Although the present technology has been described in considerable detail with reference to certain embodiments thereof, other versions are possible. Therefore the spirit and scope of the appended claims is not be limited to the description and the versions contained within this specification.
CLAIMS

What Is Claimed Is:

1. A process to produce both phenolic and dicarboxylate compounds comprising oxidative depolymerizing a lignin thereof with a per oxy acid at a temperature of not greater than about 160 °C to give a mixture of dicarboxylic acid compounds and a mixture of phenolic compounds.

2. The process of claim 1, wherein the mixture of dicarboxylic acid compounds is in at least about 10% total weight yield, and the mixture of phenolic compounds is in at least about 28% total weight yield, wherein total weight yield is calculated from the lignin on a contained lignin basis.

3. The process of claim 2, further comprising one or more organic solvents or combination thereof in at least about 5% total weight yield.

4. The process of any one of claims 1-3, further comprising substantially separating one or more dicarboxylic acid compounds or combination thereof from the mixture of phenolic compounds; reducing at least one of the dicarboxylic acid compounds to a saturated dicarboxylic acid; recovering one or more dicarboxylic acids or combination thereof in at least about 10% total weight yield.

5. The process of any one of claims 1-3, further comprising substantially separating one or more dicarboxylic acid compounds or combination thereof from the mixture of phenolic compounds; esterifying at least one of the dicarboxylic acid compounds to a dicarboxylate ester; recovering one or more dicarboxylate esters or combination thereof in at least about 10% total weight yield.
6. The process of claim 1, wherein the mixture of phenolic compounds is in at least about 35% total weight yield.

7. The process of claim 1, wherein the mixture of phenolic compounds is in at least about 60% total weight yield.

8. The process of claim 1, wherein the mixture of dicarboxylic acids is at least about 25% total weight yield.

9. The process of claim 1, wherein the mixture of dicarboxylic acids is at least about 40% total weight yield.

10. The process of any one of claims 1-9, wherein the lignin is an alkaline lignin.

11. The process of any one of claims 1-9, wherein the lignin is a steam exploded lignin.

12. The process of any one of claims 1-9, wherein the lignin is a steam exploded lignin from steam explosion and enzyme treatment.

13. The process of any one of claims 1-12, wherein the lignin is at least about 50% weight on a contained lignin basis.

14. The process of any one of claims 1-12, wherein the lignin is at least about 60% weight on a contained lignin basis.

15. The process of any one of claims 1-12, wherein the lignin is at least about 80% weight on a contained lignin basis.

16. The process of claim 1, wherein the oxidative depolymerizing is at a temperature of not less than about 40 °C to not greater than about 120 °C.
17. The process of claim 1, wherein the oxidative depolymerizing is at a temperature of not less than about 60 °C to not greater than about 90 °C.

18. The process of claim 1, wherein the oxidative depolymerizing is at a temperature of not less than about 60 °C to not greater than about 90 °C for about 10 minutes to about 3 hours.

19. The process of claim 1, wherein the reaction is at least 3 hours.

20. The process of any one of claims 1-19, wherein the peroxy acid comprises an organic peroxy acid.

21. The process of any one of claims 1-19, wherein the peroxy acid comprises peracetic acid, performic acid, or combinations thereof.

22. The process of any one of claims 1-19, wherein the peroxy acid is a peroxyaryloic acid.

23. The process of any one of claims 1-19, wherein the peroxy acid is a per oxybenzoic acid.

24. The process of any one of claims 1-19, wherein the peroxy acid is a metachloro-per oxybenzoic acid.

25. The process of any one of claims 1-19, wherein the peroxy acid is generated in-situ from an organic acid and hydrogen peroxide.

26. The process of claim 25, wherein the organic acid is acetic acid, formic acid, benzoic acid, or combinations thereof.
27. The process of any one of claims 1-19, wherein the peroxy acid comprises peroxymonosulfuric acid.

28. The process of any one of claims 1-19, wherein the peroxy acid is a peroxysulfonic acid.

29. The process of any one of claims 1-28, wherein the oxidative depolymerizing comprises an aqueous medium.

30. The process of any one of claims 1-28, wherein the oxidative depolymerizing comprises a non-aqueous medium.

31. The process of any one of claims 1-28, wherein the oxidative depolymerizing comprises biphasic mixture of aqueous media and non-aqueous media.

32. The process of claim 1, further comprising substantial deoxygenation of the recovered phenolic compounds to give hydrocarbon fuel components.

33. The process of claim 32, wherein deoxygenation comprises substantial dehydration and hydrogenation of the recovered phenolic compounds to give hydrocarbon fuel components.

34. The process of claim 1, wherein the recovering phenolic compounds comprises an organic solvent extraction.

35. The process of claim 1, wherein the mixture of phenolic compounds comprises vanillin, vanillic acid, and gallic acid.

36. The process of any one of claims 27-33, wherein the dicarboxylic acid fraction comprises muconic acid, succinic acid, maleic acid, or a combination thereof:
37. The process of claim 5, wherein the dicarboxylate ester fraction comprises a dialkyl muconate, a dialkyl succinate, a dialkyl maleate, or a combination thereof:

38. The process of any one of claims 4-5, wherein substantially separating the dicarboxylic acid compounds comprises an aqueous solvent extraction at a pH of about 3.5 to about 10.5.

39. The process of any one of claims 1-38, wherein the peroxide is added at least 0.01 grams peroxo acid to about 0.5 grams peroxo acid per gram of lignin on a contained lignin basis.

40. The process of any one of claims 1-38, wherein the peroxide is added at least 0.05 grams peroxo acid to about 0.25 grams peroxo acid per gram of lignin on a contained lignin basis.

41. An antimicrobial mixture of compounds comprising benzoic acid, vanillin, vanillic acid, gallic acid, and at least one substituted bisaryl ether.

42. The antimicrobial mixture of claim 41, wherein the mixture is bactericidal at a concentration of 0.1 g/mL.

43. The antimicrobial mixture of claim 41, wherein the mixture is bacteriostatic at a concentration of 0.01 g/mL.

44. An antibacterial agent produced by providing a lignin; decomposing the lignin with a peroxo acid for at least ten minutes and not greater than 3 hours at a temperature of not less than 40 °C to not greater than 120 °C to give a decomposition product; and extracting decomposition product with an organic solvent to give a solution of the antibacterial agent.
45. The antibacterial agent of claim 44, further comprising substantially isolating the antibacterial agent from the organic solvent.

46. The antibacterial agent of any one of claims 44-45, wherein the decomposing is performed at a temperature of not less than 60 °C to not greater than 90 °C.

47. An antibacterial agent produced by providing a lignin; decomposing the lignin with a peroxy acid to give a decomposition product; partitioning the decomposition product between aqueous phase and an organic phase; and concentrating the antibacterial agent.

48. The antibacterial agent of claim 47, wherein the method further comprises eluting the water fraction through a reverse-phase material with water.
FIG. 1

FIG. 2
Lignin

Oxidative depolymerization

Phenolic Compounds

Separation/Fractionation

Antioxidants, Adhesives,
Fuel Additives, Animal
Feed, Antibiotics, and so on

Dicarboxylic Acids

Catalytic Hydrogenation
Hydrodeoxygenation

Aliphatic Hydrocarbons,
Polymer Precursors

FIG. 4
Mixture after PAA reaction with lignin

Extract with Ethyl Acetate

Ethyl Acetate fraction (B)

Water fraction

Water fraction (A) ← Elute with water

Solid phase extraction (C18 column)

Elute with methanol (0.01% HCL)

Methanol fraction (C)

FIG. 5
FIG. 6
INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 13/45927

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) : C07C 37/54, 51/285; C12P 1/04 (2013.01)
USPC - 204/912; 564/151; 524/191

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): C12P 1/04, 7/20, 7/22, 7/42; C07C 37/54, 51/285, 1/02, 4/06, 29/149, 39/11; A01P 1/00, 3/00; A01N 25/00, 65/00 (2013.01)
USPC: 204/912; 564/151; 524/191; 504/339; 435/146; 562/407, 523; 424/769, 771, 770, 405

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)


C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>WO 2010/141499 A2 (ALBIZATI, K et al.) 09 December 2010; figure 5; paragraphs [0009], [00104], [00115], [00132], [00151], [00193]</td>
<td>3, 4/1-3, 5-1-3, 32-35, 37/5/1-3, 44-45, 46/44.45, 47-48</td>
</tr>
<tr>
<td>Y</td>
<td>WO 2013/015895 A2 (CHEN, JG et al.) 31 January 2013; paragraphs [04], [16], [18]</td>
<td>32-33</td>
</tr>
<tr>
<td>Y</td>
<td>US 3663712 A (SCHMELING, BV et al.) 16 May, 1972; page 1, lines 31-36</td>
<td>41-43</td>
</tr>
<tr>
<td>Y</td>
<td>US 2069185 A (HIBBERT, H et al.) 26 January 1937; page 1, column 2, lines 25-25</td>
<td>47-48</td>
</tr>
</tbody>
</table>

Date of the actual completion of the international search
25 November 2013 (25.11.2013)

Date of mailing of the international search report
Q8 JAN 2014

Name and mailing address of the ISA/US
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-3201

Authorized officer:
Shane Thomas
PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)
This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.; because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.; because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 10-15, 20-31, 36, 38-40 because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 

Remark on Protest
☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/2 10 (continuation of first sheet (2)) (July 2009)