PROCESSING BIOMASS

RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application Serial No. 61/139,473 filed December 19, 2008. The complete disclosure of this provisional application is hereby incorporated by reference herein.

BACKGROUND

Various carbohydrates, such as cellulosic and lignocellulosic materials, e.g., in fibrous form, are produced, processed, and used in large quantities in a number of applications. Often such materials are used once, and then discarded as waste, or are simply considered to be waste materials, e.g., sewage, bagasse, sawdust, and stover.

Various cellulosic and lignocellulosic materials, their uses, and applications have been described, for example, in U.S. Patent Nos. 7,307,108, 7,074,918, 6,448,307, 6,258,876, 6,207,729, 5,973,035 and 5,952,105.

SUMMARY

Generally, this ~~invention~~disclosure relates to carbohydrate-containing materials (e.g., biomass materials or biomass-derived materials, such as starchy materials and/or cellulosic or lignocellulosic materials), methods of making and processing such materials to change their structure and/or their recalcitrance level, and products made from the changed materials. For example, many of the methods described herein can provide cellulosic and/or lignocellulosic materials that have an oxygen-rich functionality, a lower molecular weight and/or crystallinity relative to a native material. Many of the methods, such as Fenton oxidation methods, provide materials that can be more readily utilized by a variety of microorganisms (with or without enzymatic hydrolysis) to produce useful products, such as hydrogen, alcohols (e.g., ethanol or butanol), organic acids (e.g., acetic acid), hydrocarbons, co-products (e.g., proteins) or mixtures of any of these. Many of the products obtained, such as ethanol or n-butanol, can be utilized as fuel, e.g., as an internal combustion fuel or as a fuel cell feedstock. In addition, the products described herein can

be utilized for electrical power generation, e.g., in a conventional steam generating plant or in a fuel cell plant.

In one aspect, there is provided a method of enhancing oxidative recalcitrance reduction in cellulosic or lignocellulosic materials, the method comprising:

providing a first cellulosic or lignocellulosic material that has been exposed to an ion beam to impart about 10 to about 50 Mrad of ionizing radiation the first cellulosic or lignocellulosic material having a first level of recalcitrance, and one or more functional groups formed by the ion beam exposure; and oxidizing the first cellulosic or lignocellulosic material in water or an aqueous medium together with one or more compounds comprising one or more naturally-occurring, non-radioactive group 5, 6, 8, 9, 10 or 11 elements, the one or more elements substantially dissociating as cations in the water or aqueous medium, and the cations participating in a Fenton-type reaction while oxidizing, to produce a second cellulosic or lignocellulosic material having a second level of recalcitrance lower than the first level of recalcitrance, wherein the functional groups enhance the effectiveness of the oxidizing reaction.

In another aspect, there is provide a composition comprising a pretreated cellulosic or lignocelllulosic material having a modified level of recalcitrance, the composition having been formed by:

providing a first cellulosic or lignocellulosic material that has been exposed to an ion beam, the cellulosic or lignocellulosic material having a first level of recalcitrance that is greater than the modified level of recalcitrance, and one or more functional groups formed by the ion beam exposure; and

oxidizing the first cellulosic or lignocellulosic material in water or an aqueous medium together with one or more compounds comprising one or more naturally-occurring, non-radioactive group 5, 6, 8, 9, 10 or 11 elements, the one or more elements substantially dissociating as cations in the water or aqueous medium, and the cations participating in a Fenton-type reaction while oxidizing, wherein the functional groups enhance the effectiveness of the oxidizing reaction, thereby enhancing oxidative recalcitrance modification of the first cellulosic or lignocellulosic material.

~~In one aspect,~~ tThe ~~invention~~disclosure features methods of changing molecular structures and/or reducing recalcitrance in materials, such as hydrocarbon-containing materials and/or biomass materials, e.g., cellulosic or lignocellulosic materials, such as any one or more unprocessed (e.g., cut grass), semi-processed (e.g., comminuted grass) or processed materials (e.g., comminuted and irradiated grass) described herein.

The methods can feature oxidative methods of reducing recalcitrance in cellulosic or lignocellulosic materials that employ Fenton-type chemistry. Fenton-type chemistry is discussed in Pestovsky et al., Angew. Chem., Int. Ed. 2005, 44, 6871-6874, the entire disclosure of which is hereby incorporated by reference herein. The methods can also feature combinations of Fenton oxidation and any other pretreatment method described herein in any order.

Without wishing to be bound by any particular theory, it is believed that oxidation increases the number of hydrogen-bonding groups on the cellulose and/or the lignin, such as hydroxyl groups, aldehyde groups, ketone groups carboxylic acid groups or anhydride groups, which can increase its dispersability and/or its solubility.

~~In one aspect, t~~The ~~invention~~disclosure features methods that include contacting, in a mixture, a first cellulosic or lignocellulosic material having a first level of recalcitrance with one or more compounds comprising one or more naturally-occurring, non-radioactive metallic elements, e.g., non-radioactive group 5, 6, 7, 8, 9, 10 or 11 elements, and, optionally, one or more oxidants capable of increasing an oxidation state of at least some of said elements, to produce a second cellulosic or lignocellulosic material having a second level of recalcitrance lower than the first level of recalcitrance.

Other methods include combining a hydrocarbon-containing material with one or more compounds including one or more naturally-occurring, non-radioactive metallic elements, e.g., non-radioactive group 5, 6, 7, 8, 9, 10 or 11 elements to provide a mixture in which the one or more compounds contact the hydrocarbon-containing material; and maintaining the contact for a period of time and under conditions sufficient to change the structure of the hydrocarbon-containing material.

In some embodiments, the method further includes combining the first cellulosic, lignocellulosic, or hydrocarbon-containing material with one or more oxidants capable of increasing an oxidation state of at least some of the elements. In such instances, the one or more oxidants contact the material with the one or more compounds in the mixture. In some embodiments, the one or more oxidants include ozone and/or hydrogen peroxide.

In some embodiments, the one or more elements are in a 1+, 2+, 3+, 4+ or 5+ oxidation state. In particular instances, the one or more elements are in a 2+, 3+ or 4+ oxidation state. For example, iron can be in the form of iron(II), iron(III) or iron(IV).

In particular instances, the one or more elements include Mn, Fe, Co, Ni, Cu or Zn, preferably Fe or Co. For example, the Fe or Co can be in the form of a sulfate, e.g., iron(II) or iron(III) sulfate.

In some embodiments, the one or more oxidants are applied to the first cellulosic or lignocellulosic material and the one or more compounds as a gas, such as by generating ozone *in-situ* by irradiating the first cellulosic or lignocellulosic material and the one or more compounds through air with a beam of particles, such as electrons or protons.

In some embodiments, the mixture further includes one or more hydroquinones, such as 2,5-dimethoxyhydroquinone and/or one or more benzoquinones, such as 2,5-dimethoxy-1,4-benzoquinone. Such compounds, which have similar molecular entities as lignin, can aid in electron transfer.

In some desirable embodiments, the one or more oxidants are electrochemically or electromagnetically generated *in-situ*. For example, hydrogen peroxide and/or ozone can be electrochemically or electromagnetically produced within a contact or reaction vessel or outside the vessel and transferred into the vessel.

The methods may further include contacting the second cellulosic or lignocellulosic material with an enzyme and/or microorganism. Products produced by such contact can include any of those products described herein, such as food or fuel, e.g., ethanol, or any other products described in U.S. Provisional Application Serial No. 61/139,453, which is hereby incorporated by reference herein in its entirety.

~~In another aspect, t~~The ~~invention~~disclosure also features systems that include a structure or carrier, e.g., a reaction vessel, containing a mixture including 1) any material described herein,

such as a cellulosic or lignocellulosic material and 2) one or more compounds comprising one or more naturally-occurring, non-radioactive metallic elements, e.g., non-radioactive group 5, 6, 7, 8, 9, 10 or 11 elements. Optionally, the mixture can include 3) one or more oxidants capable of increasing an oxidation state of at least some of the elements.

~~In another aspect, t~~The ~~invention~~disclosure also features compositions that include 1) any material described herein, such as a cellulosic or lignocellulosic material and 2) one or more compounds comprising one or more naturally-occurring, non-radioactive group 5, 6, 7, 8, 9, 10 or 11 elements. Optionally, the composition can include one or more oxidants capable of increasing an oxidation state of at least some of the elements.

~~In another aspect, t~~The ~~invention~~disclosure also features methods of changing molecular structures and/or reducing recalcitrance in biomass materials, such as cellulosic or lignocellulosic materials. The methods include combining a first lignocellulosic material having a first level of recalcitrance with one or more ligninases and/or one or more biomass-destroying, e.g., lignin-destroying organisms, in a manner that the one or more ligninases and/or organisms contact the first cellulosic or lignocellulosic material; and maintaining the contact for a period of time and under conditions sufficient to produce a second lignocellulosic material having a second level of recalcitrance lower than the first level of recalcitrance. The method can further include contacting the second cellulosic or lignocellulosic material with an enzyme and/or microorganism, e.g., to make any product described herein, e.g., food or fuel, e.g., ethanol or butanol (e.g., n-butanol) or any product described in U.S. Provisional Application Serial No. 61/139,453.

The ligninase can be, e.g., one or more of manganese peroxidase, lignin peroxidase or laccases.

The biomass-destroying organism can be, e.g., one or more of white rot, brown rot or soft rot. For example, the biomass-destroying organism can be a Basidiomycetes fungus. In particular embodiments, the biomass-destroying organism is *Phanerochaete chrysoporium* or *Gleophyllum trabeum*.

In certain embodiments, the first material is in the form of a fibrous material that includes fibers provided by shearing a fiber source. Shearing alone can reduce the crystallinity of a fibrous material and can work synergistically with any process technique that also reduces crystalliinity and/or molecular weight. For example, the shearing can be