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(54) Title: ELECTROCHEMICAL OXIDATION OF ORGANIC MATTER

(57) Abstract: Carbonaceous feedstock is at least partially oxidized using a concentrated metal ion solution that is regenerated in an electrochemical hydrogen gas producing process. The at least partially oxidized feedstock and/or hydrogen are then advantageously used as an energy carrier in a downstream process.



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ELECTROCHEMICAL OXIDATION OF ORGANIC MATTER

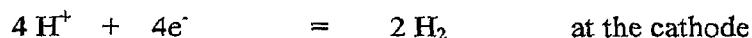
This application claims priority to our copending U.S. provisional patent applications with the serial number 60/797873, filed May 5, 2006, and serial number 60/909677, filed April 2, 2007, both of which are incorporated by reference herein.

Field of The Invention

The field of the invention is oxidation of carbonaceous feedstocks, especially as it relates to chemical oxidation of cellulosic materials to prepare yeast fermentable materials for ethanol production.

Background of The Invention

Electrochemical oxidation of various organic materials, and particularly coal was studied by numerous groups to generate hydrogen and useful organic products in aqueous medium. The exemplary reaction for aqueous combustion of coal below illustrates such process:



Remarkably, it was found that presence of iron ions in coal significantly accelerated this reaction, and in most cases even acted as a redox reagent in which ferric iron (*i.e.*, Fe^{+3}) lowered the required voltage by about 0.7 V. While such acceleration provides at least some cost reduction of electrochemically produced hydrogen, the benefits of the catalyzed reaction in heretofore known systems are limited by the rather poor solubility of the iron ions in the (commonly sulfuric acid) electrolyte. For example, ferric sulfate has a solubility maximum of about 0.5M in aqueous systems, which negatively impacts the current density of the electrochemical process and/or the low temperature rate of oxidation required to make useful quantities of desired products. Thus, electrochemical generation of hydrogen from carbon in aqueous systems is under most circumstances impractical and economically not attractive.

Further related electrochemical processes are described, for example, in R.W. Coughlin and M. Farooque, *Nature* 249, 301 (1979), R.L. Clarke, P.C. Foller, R.J. Vaughan Paper 587, 163 Meeting of Electrochemical Society. San Francisco (1983), P.M. Dooge, S.M. Park, J. Electrochem. Soc 130, 1029 (1983), and S. Lavani, M. Pata, R. Coughlin; *Fuel* 62, 427 (1983)

14. Electrochemical hydrogen production configurations and methods are described in U.S. Pat. Nos. 4,279,710 and 4,268,363, and iron-assisted electrochemical hydrogen production is described in U.S. Pat. Nos. 4,592,814, 4,608,136, 4,412,893, and 4,608,137.

Electrochemical oxidation processes using iron ions as redox carrier can also be used to generate a variety of organic products. For example coal and/or petroleum coke can be partially oxidized to humic acid at temperatures of 150 °C, or completely oxidized to carbon dioxide at temperatures in excess of 300 °C (*e.g.*, Electrochemical Hydrogen Technologies, Clarke and Foller p.345-371; Elsevier 1990). Thus, it should be recognized that oxidation of carbonaceous fuels using an iron redox carrier is impacted by both the temperature of the electrolyte and the concentration of the ferric ions. Unfortunately, while the temperature can be raised, solubility problems will remain even at high temperatures. Furthermore, especially where partially oxidized byproducts are desired, higher temperatures often thermally destroy such products.

Therefore, while numerous configurations and methods of electrochemical oxidation of organic matter are known in the art, all or almost all of them suffer from one or more disadvantages. Thus, there is still a need to provide improved configurations and methods for efficient electrochemical oxidation of organic matter.

Summary of the Invention

The present invention is directed to compositions and methods of oxidizing various organic materials, and especially carbonaceous feedstock using highly concentrated metal ion solutions. Most preferably, the metal ion is a transition metal ion, and high concentrations of the metal are achieved by an additive that is stable under conditions at which the metal ion is regenerated after oxidation of the feedstock.

In one aspect of the inventive subject matter, a method of oxidizing a carbonaceous feedstock includes a step of combining a metal and a solubility-enhancing compound to form a metal-containing solution. Most preferably, the solubility-enhancing compound is present at a concentration and has a composition effective to increase solubility of the metal over solubility of the same metal in sulfuric acid in an amount of at least 10%, and wherein the solubility-enhancing compound has a composition effective to resist oxidation under conditions at which the metal is electrochemically oxidized from a reduced form. In another step, the carbonaceous

feedstock is combined with the metal-containing solution to thereby at least partially oxidize the feedstock and form the reduced form of the metal, and optionally, the metal is electrochemically regenerated from the reduced form of the metal, wherein the step of regenerating is carried out under conditions effective to produce hydrogen. In a still further
5 step, the hydrogen and/or the oxidized feedstock are then used as an energy carrier in a subsequent reaction.

Most preferably, the carbonaceous feedstock is a cellulosic material, lignocellulosic material, paper, cotton, plant materials, coal, tar, and/or coke, and the metal is a transition metal ion (preferably a period 4 transition metal ion, and particularly an iron ion, a copper ion,
10 and/or a manganese ion). With respect to the solubility-enhancing compound it is generally preferred that the compound is an acid, and especially an organic acid comprising a sulfur atom (but not sulfuric acid). Most preferably, the solubility-enhancing compound is an optionally substituted alkyl sulfonic acid or an optionally substituted alkyl sulfamic acid, and present at a concentration effective to increase solubility of the metal over solubility of the
15 same metal in sulfuric acid in an amount of at least 50%, and more typically at least 100%. While contemplated reactions can be carried out at various temperatures, it is preferred that the step of at least partially oxidizing the feedstock is performed at a temperature between 20 °C and 50 °C, and more typically between 50 °C and 300 °C. Regeneration of the metal is preferably carried out via electrochemical oxidation of the reduced metal, preferably under
20 conditions such that hydrogen is produced in only one side of the cell without or at reduced oxygen production (e.g., at least 10%, more typically at least 30%, and most typically at least 50% less as compared to same setup but without metal in electrolyte) in another side of the cell.

Therefore, in another aspect of the inventive subject matter, a liquid intermediate in the
25 oxidation of a carbonaceous feedstock comprises an organic acid other than sulfuric acid, a transition metal ion, and a carbonaceous feedstock selected from the group consisting of an oligosaccharide, a polysaccharide, coal, tar, and coke. Most typically, the organic acid includes an optionally substituted alkyl sulfonic acid or an optionally substituted alkyl sulfamic acid, optionally further comprising a complexing agent, and/or the transition metal ion is
30 selected from the group consisting of an iron ion, a copper ion, and a manganese ion.

Various objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of preferred embodiments of the invention.

Detailed Description

5 The inventors have discovered that electrochemical oxidation of organic matter in aqueous media using ionic species of metals, and especially iron ions as redox agents can be dramatically improved by using in the electrolyte an acid or corresponding salt of the acid that increases solubility of the metal ion. Additionally, or alternatively, a complexing agent may be added that increases solubility of the metal ion. In especially preferred aspects, the metal ion is
10 an iron ion (*e.g.*, ferric iron $[\text{Fe}^{+3}]$ and/or ferrous iron $[\text{Fe}^{+2}]$).

 In one preferred exemplary aspect of the inventive subject matter, the metal ion is a ferric and/or ferrous iron, and the electrolyte is a 1.5M aqueous ferrous methane sulfonate solution that is electrochemically oxidized in a standard divided cell (*e.g.*, with NAFION™ [sulfonated tetrafluorethylene copolymer] separator) on a platinum coated titanium electrode
15 to generate a ferric methane sulfonate solution.

 Carbonaceous feedstock is then combined with the ferric methane sulfonate solution and reacted at a desired temperature for a time appropriate to generate the desired product or to exhaust the ferric iron. While the nature of the feedstock is generally not limiting to the inventive subject matter, it is typically preferred that where hydrogen and/or carbon dioxide is
20 the desired product, coal, coke, tar, and/or other high-carbon content materials are used as a feedstock, while in applications where fermentable carbohydrates are the desired products, suitable feedstocks include various processed (*e.g.*, cotton, paper, pulp, etc.) or unprocessed (*e.g.*, plant fibers, leaves, etc.) cellulosic materials. High-carbon content materials typically include those in which at least 25 wt%, and more typically at least 30 wt% of the materials are
25 carbon (in elemental form and/or bonded to other atoms). For example, suitable high-carbon content materials include oligo- and polysaccharides, which may be linear, branched, and/or chemically modified, lignin and lignaceous materials, combustion and/or pyrolysis products, coke, tar, coal, hydrocarbons, etc.

 Depending on the particular nature of the feedstock, desired reaction endpoint, and
30 molar ratio between the ferric iron and oxidizable atoms or groups, the reaction temperature

may be elevated (*e.g.*, between 30-300 °C, more typically between 50-150 °C, and most typically between 60-90 °C) for at least part of the reaction time. Furthermore, preferred reaction times will typically be chosen such that the ferric iron concentration will remain above 0.2-0.3M, more preferably above 0.3-0.5M, and most preferably above 0.5-0.7M. On the other hand, and especially in batch operations, the processing time may be less critical and the reaction can be driven to exhaustion of the ferric iron and/or the oxidizable material. Thus, the ratio of the ferric iron to oxidizable material may vary considerably. For example, where relatively fast reaction is desired, the ferric iron may be in molar excess over the oxidizable material (*e.g.*, up to 2-fold molar excess, more typically up to 5-fold molar excess, even more typically up to 10-fold molar excess, and in some instances up to 20-fold molar excess and even higher). Similarly, where complete oxidation of the oxidizable material is less critical (or even undesirable), the oxidizable material may be in molar excess over the ferric iron (*e.g.*, up to 2-fold molar excess, more typically up to 5-fold molar excess, even more typically up to 10-fold molar excess, and in some instances up to 20-fold molar excess and even higher).

It should be further recognized that numerous compounds other than methane sulfonic acid (and its corresponding salts) are also suitable as compounds to increase the solubility of the metal ion. For example, suitable compounds include various alkylsulfonic acids (*e.g.*, ethane sulfonic acid) and/or an alkylsulfamic acids (*e.g.*, methylsulfamic acid), which may entirely replace sulfuric acid of previously known systems. However, where needed (*e.g.*, to adjust the pH of the aqueous solution) sulfuric acid and/or other organic or inorganic acids (*e.g.*, hydrochloric acid, phosphoric acid, nitric acid, etc.) may be added. More generally, it should be recognized suitable compounds increase solubility of the metal ions over solubility of the same metal ions in sulfuric acid in an amount of at least 10%, more typically at least 25%, even more typically at least 50%, and most typically at least 100% absolute. Thus, appropriate compounds can be easily identified by their solubilizing properties using various protocols well known in the art. Most preferably, contemplated compounds will be include (typically substituted) organic or inorganic acids, but may also include polymeric materials (soluble or insoluble) with cationic and/or anionic groups (which may be part of the polymer backbone or be pendant groups). Alternatively, in less preferred aspects of the inventive subject matter, suitable compounds also include bases and neutral compositions.

Similarly, with respect to oxidation resistance of suitable compounds, the person of ordinary skill in the art is well equipped to recognize appropriate alternative acids. It is generally preferred that the compounds will resist oxidation under conditions at which the metal ion is electrochemically (or chemically) oxidized from the reduced form. Thus, in most preferred aspects, at least 85 mol%, more typically at least 95 mol%, and most typically at least 98 mol% of contemplated compounds will remain chemically unchanged in the electrolyte after 10 cycles of re-oxidation. Furthermore, suitable compounds will be heat stable at temperatures of between 10-150 °C (and even higher), more typically between 20-100 °C, and most typically between 30-90 °C. Therefore, and among other choices, suitable compounds may also be fluorinated (*e.g.*, fluorinated methylsulfonic and/or fluorinated methylsulfamic acid).

It is still further preferred that contemplated compounds (or mixture thereof) are present in the aqueous electrolyte at a concentration of at least 5-10 wt%, more typically at least 20 wt%, even more typically at least 40 wt%, and most typically at saturation. Depending on the particular compound, the compound will be present in concentrations between about 0.1 M to 0.5 M, more typically 0.5 M to 1.0 M, even more typically between 1.0 M and 1.5 M, and most typically above 1.5-2.0 M. Therefore, the solubility of the metal ion (*e.g.*, ferrous and ferric iron) in the electrolyte at 25 °C may be between 0.2 M and 0.5 M, more preferably between 0.5 M and 1.0 M, even more preferably between 1.0 M and 2.0 M, and most preferably above 2.0 M. Consequently, it should be recognized that the electrolyte will have an acid pH of between pH 0 and pH 6.7, and more typically between pH 2.0 and pH 6.0.

With respect to metal- and especially iron complexing agents, it is contemplated that all compounds suitable for complexing iron ions are suitable for use in conjunction with the teachings presented herein. Thus, suitable complexing agents include various oligodentate compounds, crown ethers, exchange resins, etc. For example, especially preferred compounds that complex iron ions include desferrioxamine and desferrioxamine analogs, bacterial or synthetic siderophores, humates (including *in situ* electrochemically generated humates), EDTA (ethylenediaminetetraacetic acid), EDMA (ethylenediiminobis (2-hydroxy-4-methyl-phenyl) acetic acid), and DTPA (diethylenetriamine-pentaacetic acid). Depending on the particular reaction conditions, temperature, pH, and other parameters, the complexing agents may be present at a concentration of between about 0.1 M to 1.0 M, and more preferably

between 1.0 M to 2.0 M (and higher). Most preferably, one or more complexing agents are combined with contemplated compounds (*e.g.*, with methane sulfonic acid), but they may also be used separately.

It is particularly preferred that the metal ion is an iron ion, and especially ferric iron in the oxidized state and ferrous iron in the reduced state. However, it should be recognized that various alternative metals and/or oxidation states are also deemed suitable, and especially contemplated metals and metal ions include transition metals, lanthanides (and particularly cerium), and metals of the fourth (*e.g.*, titanium, chromium, copper, etc.) and fifth (*e.g.*, molybdenum, indium, tin, etc.) period. Depending on the particular metal, it should be recognized that the ionic charge may therefore be between +1 and +7, and more typically between +1 and +4 (or the metal may be elemental in one state). Where the metal is in a complex (*e.g.*, with an organic ligand or inorganic component), ionic charges may also be between -1 and typically -4. Still further, it should be recognized that mixtures of various metals may also be appropriate.

In a typical exemplary process in which coal and/or coke were oxidized to CO₂, the inventors discovered that the concentration of ferrous ions created by the reaction between ferric ions and the organic matter (here: coal and coke) was a critical parameter. In presently contemplated electrochemical cells (see below), the ferrous ion was oxidized at the anode. Remarkably, in such systems, oxygen evolution was not favored, and the current increased with increasing concentration of ferrous ions before the voltage increased. In stark contrast, heretofore known devices needed to flow the electrolyte as quickly as possible to overcome mass transfer limitations of low iron solubility in sulfuric electrolytes. Moreover, it should be noted that in configurations and methods according to the inventive subject matter presented herein the reaction rate between the ferric ions and the carbon fuel increased with higher temperatures, which is particularly advantageous as iron sulfates reach their maximum solubility at 80 °C. Still further, it should be appreciated that methane sulfonic acid not only considerably increased solubility of ferrous and ferric iron, but also enhanced the reaction by the compatibility of methane sulfonic acid with the carbon and carbon oxidized surface, possibly via a detergent-like effect.

Depending on the particular metal, feedstock, electrolyte composition (aqueous or non-aqueous, type of compound, etc.) and other factors, it should be appreciated that the

(preferably metal-mediated) oxidation can be carried out in a reactor that is separate from the electrochemical cell in which the electrolyte is regenerated, or that the oxidation of the feedstock and the regeneration can be carried out in the same reactor. Similarly, under certain conditions, (preferably metal-mediated) oxidation of the feedstock and regeneration of the electrolyte may be carried out at the same time.

Remarkably, the configurations and methods according to the inventive subject matter were substantially inert to sulfur in the coal and did not impact the purity of carbon dioxide that issued from the reactor as sulfur compounds were oxidized to sulfuric acid that remained in the electrolyte. Similarly, the carbon dioxide was also free of oxides of nitrogen as all nitrogen compounds were oxidized to nitrates. Furthermore, hydrogen produced in such electrolytic cells was free of oxygen as the catholyte was separated from the anolyte by an ion exchange membrane. Thus, heretofore known problems with gas separation can be entirely avoided and substantially pure hydrogen is created as the hydrogen is produced in only one side of the cell without oxygen production (*i.e.*, less than 10) in another side of the cell. It was also observed that heavy metals were separated from the gaseous stream and collected on the cathode or in the oxidized coke product.

Consequently, it should be appreciated that contemplated systems and methods will not only generate partially oxidized feedstock but also produce hydrogen. Such products can be used (alone or in combination) as an energy carrier in downstream reactions. For example, the at least partially oxidized feedstock can be employed in a fermentation reaction as nutrient for the fermenting microorganism. In another example, hydrogen may be employed as a direct fuel in a hydrogen fuel cell for energy production, or as an indirect fuel in which hydrogen is a component for fuel production (*e.g.*, via Fischer-Tropsch reaction of CO and H₂ produced in such systems [CO can be produced from CO₂ in a reverse shift reaction]), wherein that fuel then provides energy. Thus, the term "energy carrier" as used herein refers to compounds that are either used as a fuel in combustion or feed component in a fermentation and/or used as precursor(s) in the synthesis of a hydrocarbon fuel (and especially methane). Consequently, subsequent reactions may be catalyzed or uncatalyzed in a reactor, or performed in an *in vitro* or *in vivo* enzyme-containing system.

In heretofore known studies it was shown that wood flour, corn husk, and sewage sludge (mainly cellulose) could be completely solubilized at temperatures below 100 °C. It was

assumed that some of the organic material had been oxidized to carbon dioxide but some remained as organic materials like sugars. Therefore, it is now contemplated that with more concentrated iron redox carriers it is now possible at temperatures lower than 100 °C to consider (preferably selective) oxidation of cellulose like materials to products that are more easily converted to benign or useful products. For example, cellulose can be converted to sugars that are then biologically converted to alcohol. The first part of such process is the breaking of the cellulose polymer into smaller molecules and then to individual sugars by hydrolysis with strong acids. In another example, ferric ions are used to convert aniline to polyaniline for example, one very toxic the other relatively benign. Of course, it should be recognized that all of the contemplated processes herein can be applied with or without the electrochemical recycling of the metal redox carriers and/or attempts to electrochemically produce hydrogen. Therefore, suitable temperatures for oxidation reactions will be between 20 °C and 50 °C, more typically between 50 °C and 80 °C, even more typically between 80 °C and 100 °C, and in some cases between 50 °C and 300 °C.

It should further be recognized that by changing the temperature and/or the feed stock (e.g., wood, husk, fiber, stalks, etc.) various products will be formed in various ratios. Thus, the organic materials can be broken down to smaller molecules (e.g., cellulose and lignins present in plant materials into polysaccharides and sugars) that may be converted to biofuels by subsequent biological processes, and especially fermentation (see below). As it will be much easier to control the breakdown process without use of aggressive mineral acids, it is expected that the overall processing costs will significantly drop. Furthermore, the impact on the cost of generating hydrogen electrochemically at high current density is easily forecast from extrapolation from the results of Clarke and Foller.

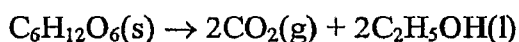
In a further especially contemplated aspect, it should be recognized that pure H₂ and CO₂ (essentially free from NO_x and SO_x) can be prepared at a substantially lower price than in conventional electrolysis processes. Moreover, these products can be combined to make carbon monoxide and hydrogen (syngas), which is an ideally suitable feedstock for Fischer-Tropsch synthesis as the so produced gas mixture is free of interfering sulfur compounds and/or nitrogen oxides.

Examples

The following examples and calculations are provided as exemplary guidance for a person of ordinary skill in the art to illustrate various advantages and benefits of the inventive concept presented herein.

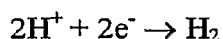
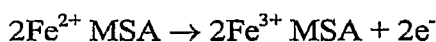
Energy Balance In Typical Iron-Mediated Reaction For Ethanol Production

A typical reaction is started with 50 kg of lignocellulosic material to obtain water soluble materials of about 40 kg. The typical fermentable sugar content is in the range of 70%, which translates to about 30 kg fermentable sugar. According to the below net equation for the fermentation process, 180 g of sugar will give 46 g of ethanol.



With an approximate 30 % fermentation efficiency, about 2.5 kg of ethanol are being produced. Theoretical Energy density of ethanol is 26.8 MJ/Kg, which will produce 65 MJ total energy from ethanol. Assuming about 90% purity of the ethanol, total energy available from ethanol is about 60 MJ.

(a) Energy Consumption During Electrolysis



A typical electrolysis of 100 A for 10 hrs at 2 V for a 2 electron reaction needs,

$$100 \times 10 \times 3600 \times 2 = 720,000 \text{ Coulombs}$$

That will give an energy consumption for the electrolysis about 15 MJ. Assuming 50 % current efficiency for the process this will need an energy of 30 MJ.

(b) By-Product Credit : Hydrogen Energy Produced

720,000 Coulombs will produce 37 moles of H_2 . Energy density of H_2 is 120 MJ/kg. 37 moles of H_2 = 74 g of H_2 which gives an energy of 8.8 MJ assuming 50% efficiency for electrolysis the net energy from hydrogen is 4 MJ.

(c) Energy Consumed For Heating

The reaction is carried out at 80°C. Energy required to keep water at that temperature for the electrolysis time is (assuming only the heat capacity of water and if all the energy supplied is used to heat the water) specific heat capacity of water is 4180 J kg⁻¹ K⁻¹. The energy needed to heat 5 kg of water at 80°C for 100 hrs is 2 MJ.

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(d) Energy Equation

Total energy produced = 60 MJ + 4 MJ = 64 MJ; Total energy consumed = 30 MJ + 2 MJ = 32 MJ. Energy needed to produce ethanol = 12.8 MJ/ kg = 35000 BTU/gal (1 BTU = 1054 J)

If one uses state of the art technology, the net energy ratio for the ethanol production will be better than 2:1. That is, if 100 BTU's of energy is used for the overall process, 200 BTU's of energy is available in the fuel ethanol. This is a very rough estimate of the energy content in the process and we are confident that as processing technologies improve ethanol production will become less and less energy intensive. It should be noted that the Fe-MSA used in the above process is not consumed and is 100% recyclable. The process has further advantages associated with of electrochemical processes, including lack of thermal energy loss, and simplicity of operation. With the anticipated development of new fermentation processes, the overall yield of the process should further significantly increase.

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Comparison Corn Ethanol Versus Cellulosic Ethanol

Currently, corn is the primary raw material for ethanol production, accounting for about 92% of the total feedstock in the ethanol industry. Most ethanol in the United States is produced by either a wet milling or a dry milling process and utilizes shelled corn as the principal feedstock. According to most generally accepted energy calculations, about 70 percent more energy is required to produce corn-based ethanol than the energy that is actually available in ethanol. The corn based ethanol has a net energy value of about ~5000 BTUs. As the production of ethanol from corn is a relatively mature technology, it is not likely that significant reductions in production costs will be achieved using conventional technology. Another major drawback of the corn-based ethanol technology is the potential environmental damage during the process. The environmental system in which corn is being produced is being rapidly degraded. The use of croplands to grow corn for ethanol production will also eventually affect the food industry. It is at this point that alternative ethanol production from

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widely available materials gains significant interest. Clearly, what is needed is configurations and methods to produce ethanol in an energetically and economically favorable manner, which has been achieved by the inventors by combining electrochemistry, organic chemistry, and biotechnology.

5 Cellulosic ethanol is an alternative fuel made from a wide variety of nonfood plant materials (or feedstocks), including agricultural wastes such as corn stover and cereal straws, industrial plant waste like saw dust and paper pulp, and energy crops grown specifically for fuel production like switch grass. By using a variety of regional feed stocks for refining cellulosic ethanol, the fuel can be produced in nearly every city of the country. With the
10 current status of corn price as the dominant cost factor, the development of low-cost feedstock is the key to further reduce the cost.

Still further, lignocellulosic biomass is the earth's most attractive alternative among fuel sources and most sustainable energy resource and is reproduced by the bioconversion of carbon dioxide. Lignocellulosic biomass is the most abundant biodegradable substance with an
15 annual net yield of 1.8×10^{15} kg which can give about 10^{14} Kg of cellulose and 10^{13} Kg of ethanol using current technologies, which is sufficient to meet current gasoline consumption in America (200 Billion Gallons = 10^{12} Kg). The low cost of lignocellulosic materials makes them a promising feedstock for ethanol production. Although lignocellulosic materials often require a more complex refining process, cellulosic ethanol contains more net energy and
20 results in lower greenhouse emissions than traditional corn-based ethanol. E85, an ethanol fuel blend that is 85% ethanol, is already available in more than 1,000 fueling stations nationwide and can power millions of flexible fuel vehicles already on the roads. The high cost of cellulose enzymes is the key barrier to economic production of cellulosic ethanol.

Exemplary Ethanol Process with Ferric Iron

25 In contrast to currently known systems and methods, the unique aspect of the ethanol processes contemplated herein is the use of a redox system that can act in a manner similar to a surface active reagent and as an electron source at the same time. While not limiting to the inventive subject matter, it is thought that the hydrophobic part of the methane sulfonic acid facilitates the solubilizing of the rigid cellulose molecules while the Fe^{3+} provides the energy to
30 break down the organic material to fermentable sugars. Thus, use of costly and unstable

enzymes is reduced, or even entirely avoided, and contemplated processes can be integrated in a simple manner into known yeast fermentation processes. Remarkably, the methods and processes contemplated herein also produce two desirable side products, lignin and hydrogen. The following table exemplarily illustrates some of the advantages of contemplated methods and configurations:

	Cellulosic Ethanol	Corn Ethanol	Gasoline	Contemplated Ethanol process
Current Price	\$0.74/Kg	\$ 0.60/Kg	1.07 \$/Kg	\$0.5 \$/Kg
Density	0.8 g/ml	0.8 g/ml	0.74 g/ml	0.8 g/ml
Energy Content	25443 BTU/Kg	25443 BTU/Kg	44642 BTU/Kg	25443 BTU/Kg
Energy Cost	34382 BTU/\$	34382 BTU/\$	41721 BTU/\$	50886 BTU/\$
Cost matching	\$0.61 /kg to match the price of gasoline			
Octane Number	129	129	95	129
CO ₂ Emission	10	75	100	10
Energy Balance	60,000 Btu per gallon	25,000 Btu per gallon		
Capital Cost	0.85 \$/Kg	0.6\$/Kg		0.3 \$/Kg
Capital Charge@ 10%	\$0.085/kg	0.06\$/Kg		0.03 \$/Kg
Feed Cost	\$0.05/Kg	\$0.3/Kg		\$0.01/Kg
Production cost	\$0.5/Kg	\$0.4/Kg	\$0.35/Kg (total)	\$0.1/kg

Thus, it should be appreciated that the methods and configurations presented herein are the first reported ethanol producing process in which hydrogen is being produced as a side product. The lignin produced can be used to enhance the net energy value or as source for producing biodiesel and other valuable organic chemicals.

The exemplary ethanol process contemplated herein includes five different stages: (1) Optional digestion of the biomass to separate lignin and cellulose from raw materials such as wood and straw to make it amenable to hydrolysis. (2) An optional pretreatment with dilute sulfuric acid at 80°C to make the material more porous. (3) Electrochemically controlled acid hydrolysis of the cellulosic material (preferably in a flow reactor at about 80 °C) to produce a fermentable carbohydrate solution. (4) Yeast fermentation of the carbohydrate solution to produce ethanol. (5) Optional purification (e.g., passing through molecular sieves) to produce 99.5 % pure alcohol.

It should also be recognized that metal-mediated electrochemical oxidation is also a promising technology for the destruction of other organic waste material, and/or for the remediation of mixed wastes containing transuranic components. The combination of a powerful oxidant and an organic sulfonic acid solution allows the conversion of nearly all organics, whether present in hazardous or in mixed waste. Moreover, insoluble transuranics are dissolved in this process and may be recovered by separation and precipitation. The oxidant, or metal mediator, is preferably a multivalent transition metal ion, which is cleanly recycled in a number of charge transfer steps in an electrochemical cell. It should be noted that the mediated electrochemical oxidation technique offers several advantages: First, the oxidation/dissolution processes are accomplished at near ambient pressures and temperatures (30-90°C). Second, all waste stream components and oxidation products (with the exception of evolved gases) are contained in an aqueous environment. The electrolyte therefore acts as an accumulator for inorganics, which were present in the original waste stream, and the large volume of electrolyte provides a thermal buffer for the energy released during oxidation of the organics. Third, the generation of secondary waste is minimal, as the process needs no additional reagents. Finally, the entire process can be shut down by simply turning off the power, affording a level of control unavailable in many other techniques.

Experiments

(a) Iron powder is dissolved in commercially available 70% methane sulfonic acid. The ferrous ion solution is diluted with water to produce 1.5 molar ferrous methane sulfonate in excess methane sulfonic acid. The solution is treated in a divided electrochemical cell fitted with an iridium oxide or platinum coated titanium electrode. Current is applied until the ferrous iron is converted to ferric ion. Wood flour is added to form a suspension. The mixture is heated to 80 °C and stirred for one hour or until all the iron is converted to the ferrous state. The mixture is filtered to remove any unreacted wood flour. The solution is then treated by liquid/liquid extraction to remove organic materials formed, and regenerated in the electrochemical cell to form ferric ion for treatment with more wood flour.

(b) In a second example, powdered coal (100 mesh) is treated in a reactor with ferric methane sulfonic acid in excess methane sulfonic acid at 180 °C. The solution after reaction is fed to the anode compartment of an electrochemical cell. The cell has an ion exchange membrane made from NAFION™. The cathode is made from stainless titanium, the

anode is iridium oxide coated titanium. The product from the cathode is hydrogen and the anodic products are oxidized coal, carbon dioxide, and a small amount of sulfuric acid. Oxidized coal can be further oxidized by repeated cycling of the process, or the solution is mixed with further quantities of coal to top up the available fuel. At even higher temperatures
5 (e.g., 300 °C and higher) complete oxidation of the coal to carbon dioxide is possible.

(c) In a third example, a solution of Fe^{+3} was made up in methane sulfonic acid at a concentration of 100 gm/l Fe^{+3} to which was added cotton muslin that had been previously soaked in sulfuric acid 80 °C for 2 hours, then washed and dried. The color of the ferric MSA solution changed immediately to a color characteristic of a ferrous MSA solution, indicating
10 that significant oxidation had taken place. The resultant reaction products (cellulose, starch, and possibly other oxidized carbohydrate species) were washed and appeared as a white powder similar to starch. Most preferably, the acid treatment and oxidation is carried out under conditions that will only partially hydrolyze the feedstock. The best degree of partial oxidation can be readily determined by a person of ordinary skill in the art based on energy
15 consumption and ethanol yield. This starch-like material was added to a small quantity of water, brewers yeast was added, and the mixture left over two days, during and after which the mixture vigorously evolved CO_2 and had a clear odor of ethanol. Thus, it should be recognized that contemplated compositions and processes allow for efficient conversion of materials otherwise not amenable to yeast fermentation.

Of course, it should be noted that numerous other cellulosic materials may be employed
20 as a feedstock for the oxidation process provided herein, and exemplary alternative feedstocks include switchgrass, lignocellulosic materials, paper products, cotton products, agricultural waste products, and other plant-derived polysaccharides that are ordinarily not fermentable by microorganisms. Suitable feedstocks are described in EP 0091221 and WO 02/12529, which
25 are incorporated by reference herein. Furthermore, it should be noted that additional and/or alternative oxidizing species may be employed, and particularly suitable alternative oxidizing species include aluminum ions and manganese ions in various oxidation states.

Still further, it should be appreciated that the hydrogen evolved in such systems can be used as fuel component to regenerate the oxidizing species (e.g., using electrochemical
30 regeneration of Fe^{+3} from Fe^{+2} in a hydrogen powered fuel cell). Therefore, it should be particularly noted that the partial oxidation of the feedstock will not only provide fermentable

materials for ethanol production, but also reduce overall energy consumption by energetic coupling of the hydrogen byproduct with the regeneration of the oxidant. Moreover, as the MSA significantly increases solubility of the oxidant and, reaction time and temperature can be further reduced. Additional configurations, contemplations and details suitable for use herein
5 are described in U.S. Pat. No. 3,939,286, which is incorporated by reference herein.

Thus, specific embodiments and applications of electrochemical oxidation of organic matter have been disclosed. It should be apparent, however, to those skilled in the art that many more modifications besides those already described are possible without departing from the inventive concepts herein. The inventive subject matter, therefore, is not to be restricted
10 except in the spirit of the appended claims. Moreover, in interpreting both the specification and the claims, all terms should be interpreted in the broadest possible manner consistent with the context. In particular, the terms "comprises" and "comprising" should be interpreted as referring to elements, components, or steps in a non-exclusive manner, indicating that the referenced elements, components, or steps may be present, or utilized, or combined with other
15 elements, components, or steps that are not expressly referenced. Furthermore, where a definition or use of a term in a reference, which is incorporated by reference herein is inconsistent or contrary to the definition of that term provided herein, the definition of that term provided herein applies and the definition of that term in the reference does not apply.

CLAIMS

What is claimed is:

1. A method of oxidizing a carbonaceous feedstock, comprising:
combining a metal and a solubility-enhancing compound to form a metal-containing solution;
wherein the solubility-enhancing compound is present at a concentration and has a composition effective to increase solubility of the metal over solubility of the same metal in sulfuric acid in an amount of at least 10%;
wherein the solubility-enhancing compound has a composition effective to resist oxidation under conditions at which the metal is electrochemically oxidized from a reduced form;
combining the carbonaceous feedstock with the metal-containing solution to thereby at least partially oxidize the feedstock and form the reduced form of the metal;
optionally electrochemically regenerating the metal from the reduced form of the metal, wherein the step of regenerating is carried out under conditions effective to produce hydrogen; and
using at least one of the hydrogen and the at least partially oxidized feedstock as an energy carrier in a subsequent reaction.
2. The method of claim 1 wherein the carbonaceous feedstock comprises a material selected from the group consisting of a cellulosic material, lignocellulosic material, paper, cotton, plant materials, coal, tar, and coke.
3. The method of claim 1 wherein the metal is a transition metal ion.
4. The method of claim 3 wherein the transition metal ion is a period 4 transition metal ion.
5. The method of claim 3 wherein the transition metal ion is selected from the group consisting of an iron ion, a copper ion, and a manganese ion.

6. The method of claim 1 wherein the solubility-enhancing compound comprises an organic acid that comprises a sulfur atom, and wherein the solubility-enhancing compound is not sulfuric acid.
7. The method of claim 1 wherein the solubility-enhancing compound is an optionally substituted alkyl sulfonic acid or an optionally substituted alkyl sulfamic acid.
8. The method of claim 1 wherein the solubility-enhancing compound is present at a concentration effective to increase solubility of the metal over solubility of the same metal in sulfuric acid in an amount of at least 50%.
9. The method of claim 1 wherein the solubility-enhancing compound is present at a concentration effective to increase solubility of the metal over solubility of the same metal in sulfuric acid in an amount of at least 100%.
10. The method of claim 1 wherein the metal-containing solution has an acid pH of between pH 2.0 and pH 6.0.
11. The method of claim 1 wherein the step of at least partially oxidizing the feedstock is performed at a temperature between 20 °C and 50 °C.
12. The method of claim 1 wherein the step of at least partially oxidizing the feedstock is performed at a temperature between 50 °C and 300 °C.
13. The method of claim 1 wherein the metal is electrochemically regenerated.
14. The method of claim 1 wherein the metal is electrochemically regenerated in a divided cell under conditions such that the hydrogen is produced in only one side of the cell without oxygen production in another side of the cell.
15. The method of claim 1 wherein the hydrogen is used in a fuel cell to generate energy.
16. The method of claim 1 wherein the at least partially oxidized feedstock is used as a feed component in a fermentation.
17. A liquid intermediate in the oxidation of a carbonaceous feedstock comprising (1) an organic acid other than sulfuric acid, (2) a transition metal ion, and (3) a carbonaceous

feedstock selected from the group consisting of an oligosaccharide, a polysaccharide, coal, tar, and coke.

18. The intermediate of claim 17 wherein the organic acid comprises an optionally substituted alkyl sulfonic acid or an optionally substituted alkyl sulfamic acid, optionally further comprising a complexing agent.
19. The intermediate of claim 17 wherein the transition metal ion is selected from the group consisting of an iron ion, a copper ion, and a manganese ion.
20. The intermediate of claim 17 wherein the intermediate is an aqueous intermediate having a pH between 2.0 and 6.0.