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(71) Applicant *(for all designated States except US)*: **NORTH CAROLINA STATE UNIVERSITY** [US/US]; 920 Main Campus Drive, Venture Building II, Suite 400, Raleigh, NC 27695 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **CUOMO, Jerome, J.** [US/US]; 108 Kinnard Lane, Cary, NC 27511 (US). **OLDHAM, Christopher, J.** [US/US]; 700 Mial. St., Raleigh, NC 27608 (US). **KING, Matthew, R.** [US/US]; 3411 Melrose Ridge Ct., Apt. 116, Raleigh, NC 27603 (US).

(74) Agents: **GLOEKLER, David, P.** et al.; The Eclipse Group LLP, 10605 Balboa Blvd., Suite 300, Granda Hills, CA 91344 (US).

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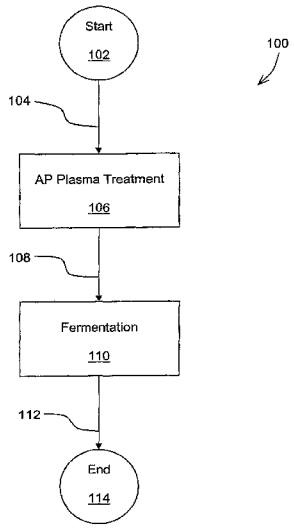
(54) **Title:** PROCESSING CELLULOSIC MATERIAL UTILIZING ATMOSPHERIC-PRESSURE PLASMA



(57) **Abstract:** Cellulosic material is treated by atmospheric-pressure (AP) plasma to enhance processes for extracting sugars from cellulosic material and fermenting sugars into alcohol's or other chemicals. In one example, the AP plasma treatment is utilized to improve the release, activation or production of glucose and conversion of glucose to ethanol. The AP plasma treatment may be performed in conjunction with other processes such as depolymerization or degradation, for example hydrolysis, as well as fermentation. The AP plasma treatment may be performed as a substitute for pretreatment processes such as steam explosion, and in some implementations is sufficiently effective to serve as a substitute for hydrolytic processes or at least as an enhancement to hydrolytic processes or other depolymerization or degradation processes.

WO 2007/136843 A2

PROCESSING CELLULOSIC MATERIAL UTILIZING ATMOSPHERIC-PRESSURE PLASMA

RELATED APPLICATIONS

[001] This application claims the benefit of U.S. Provisional Patent Application Serial No. 60/801,442, filed May 18, 2006, titled "PROCESSING CELLULOSIC MATERIAL UTILIZING ATMOSPHERIC-PRESSURE PLASMA;" the content of which is incorporated by reference herein in its entirety.

BACKGROUND OF THE INVENTION

[002] **1. Field of the Invention.**

[003] This invention relates generally to the processing of biomass such as cellulosic material to produce sugars and the fermentation of such sugars to produce alcohols and other chemicals. More particularly, the invention relates to the utilization of atmospheric-pressure plasma to enhance such processing.

[004] **2. Related Art.**

[005] Cellulosic materials, including lignocellulosic materials, biomass, etc., occur abundantly in nature and constitute a significant source of sugars from which alcohols and other industrial chemicals may be derived. Cellulose, hemicellulose, and lignin are three primary components of cellulosic materials. Cellulose forms the primary structural component of plant cell walls. The secondary cell wall of green plants contains lignin as well as cellulose. Lignocellulose (cellulose and lignin) such as wood is the most common terrestrial biopolymer, by some accounts comprising approximately 50% of the biomass in the world. *See* M. Galbe & G. Zacchi, "A review of the production of ethanol from softwood," *Appl. Microbiol. Biotechnol.*, Vol. 59, pp. 618-628, Springer-Verlag (2002). Cellulose holds particular interest because it can be processed to yield glucose monomers. Glucose can be converted to fuel-grade alcohols such as ethanol (CH_3CH_2OH, or C_2H_6O) by fermentation (i.e., bioethanol).

[006] Galbe, *supra*, and others have investigated the merits of bioethanol as a renewable energy source. Rendering bioethanol commercially available is considered to be a viable way for reducing the environmental effects of and dependence on fossil fuels. The combustion of

bioethanol results in low emissions of carbon dioxide (CO_2), as well as carbon monoxide (CO), non-combusted hydrocarbons (HCs), nitrogen oxides (NO_x), and volatile organic compounds (VOCs). Moreover, the mixing of ethanol and gasoline is advantageous in that the higher octane number of ethanol (96-113) increases the octane number of the mixture and thereby reduces the need for toxic, octane-enhancing additives, the ethanol supplies oxygen for the fuel and thus enables cleaner combustion, and ethanol is believed to be about 15% more efficient than gasoline. Accordingly, although ethanol has only about two-thirds of the volumetric energy content of gasoline, it would still be possible to drive 75-80% of the distance on a given volume of ethanol. *See* Galbe, *supra*. For reasons such as the foregoing, cellulosic materials are considered to be an important potential renewable source—particularly a domestic source of alternative fuels—and thus the efficient conversion of cellulosic components to alcohols, particularly ethanol, is the subject of ongoing research.

[007] Cellulosic materials exist in nature in a variety of different compositions and structures. As a general example, a typical cellulosic material may be considered as being a heterogeneous, three-dimensional composite or complex of cellulose fibers wrapped in a sheath of hemicellulose and lignin. The cellulosic material typically includes crystalline regions as well as less ordered amorphous regions. The ratios of the three primary components of the cellulosic material—cellulose, hemicellulose, and lignin—relative to each other depend on the species of the cellulose-containing material (e.g., various woods, grains, corn stover, etc.). In addition to the three primary components, the cellulosic material may include lower organic components and mineral components of lesser immediate interest for the purposes of the present disclosure.

[008] Cellulose and hemicellulose are carbohydrate polymers. Cellulose is a long-chain polysaccharide carbohydrate of β-glucose monomers, which may be chemically represented as $(C_6H_{10}O_5)_n$. More specifically, cellulose is a polymer of D-glucose ($C_6H_{12}O_6$) with β [1→4] linkages (glycosidic bonds) between each of the about 500 to 10,000 glucose units. Cellulose is a straight-chain polymer that exhibits a rod-like conformation, unlike starch which exhibits coiling. Cellulose constitutes about 35-60% by weight of typical cellulosic materials. Hemicellulose is a non-cellulosic, heteropolymer polysaccharide of primarily D-xylose ($C_5H_{10}O_5$) and other pentoses and some hexoses with β [1→4] linkages. Hemicellulose may be found as a branched polymer of glucose or xylose, substituted with

arabinose, xylose, galactose, fucose, mannose, glucose, or glucuronic acid. The molecular weights of hemicellulose polymers are usually lower than that of cellulose, and hemicellulose polymers have a weak undifferentiated structure compared to crystalline cellulose. Hemicellulose, however, binds with pectin (a heterosaccharide) to cellulose to form a network of cross-linked fibers that serves as the structural backbone of plant cell walls. Hemicellulose constitutes about 20-35% by weight of typical cellulosic materials. Lignin may be characterized as a complex, cross-linked, random, amorphous, three-dimensional polyphenolic polymer that typically is based on variously substituted p-hydroxyphenlypropane units. Lignin generally permeates the matrix of cellulose fibers and largely fills in the interstices between the cellular structures (cellulose, hemicellulose and pectin components) of the cellulosic material. However, lignin appears to be more intimately cross-linked or otherwise associated with hemicellulose than with the distinct crystalline phase of cellulose. Lignin constitutes about 10-30% by weight of typical cellulosic materials.

[009] Cellulosic materials are converted to alcohols by releasing the component sugars of the cellulosic materials, and fermenting the sugars to alcohols. The carbohydrate polymers of cellulosic materials are typically depolymerized (degraded or broken down) into fermentable monomeric sugars by hydrolysis. Component sugars may include six-carbon sugars (hexoses) such as glucose, galactose, and mannose, and five-carbon sugars (pentoses) such as xylose and arabinose. Both chemical and enzymatic hydrolytic processes have been utilized.

[010] Chemical hydrolysis typically entails the use of an acid such as sulfuric acid as a catalyst. Generally, microcrystalline cellulose is relatively resistant to typical acid hydrolysis, amorphous cellulose is less resistant, hemicellulose (which is also amorphous) is even less resistant, and lignin is highly resistant but may be dissolved by certain organic solvents. Acid hydrolysis utilizes either concentrated acids or diluted acids. Acid hydrolysis generally is around 10-40% efficient in terms of sugar recovery, depending on process conditions. Concentrated acid hydrolysis involves short reaction times, but requires a large amount of expensive acid(s), corrosion-resistant equipment, and energy-demanding means for recycling the acid. Moreover, concentrated acid hydrolysis requires significant control over the reaction to avoid degrading the desired sugars and forming toxic byproducts. Dilute acid hydrolysis is a lower cost process involving a relatively low consumption of acid(s), but

requires longer reaction times and results in a decreased glucose yield as compared to concentrated acid hydrolysis. Moreover, dilute acid hydrolysis requires high temperatures to attain acceptable rates of conversion of cellulose to sugar monomers. High temperatures require a high input of energy, promote equipment corrosion, and increase the rates of hemicellulose-derived sugar decomposition. For example, the products of decomposing hemicellulose may include furfural and hydroxymethylfurfual. It is known that sugar decomposition products can inhibit the subsequent fermentation process.

[011] To reduce sugar decomposition, a two-stage acid hydrolysis process has been employed. The first stage is carried out under relatively mild conditions to release sugars as a result of hydrolysis of the hemicellulose, and the second stage is carried out under relatively harsher conditions to hydrolyze the cellulose fraction. The first stage enables the second stage to proceed under the harsher conditions without decomposing the hemicellulose into undesired by-products, but the glucose yield is still unacceptably low (e.g., 50%). *See* Galbe, *supra.*

[012] Enzymatic hydrolysis (e.g., biodegradation) may entail the use of a variety of microorganisms, which may be naturally occurring or genetically engineered. Enzymes include carbohydrases such as cellulases and hemicellulases. More than one type of enyzme may be employed, and their combined effect may be synergistic. For example, the combined action of the three cellulase enzymes endo-β-glucanase, exo-β-glucanase, and β-glucosidase (cellobiase) has been employed to convert cellulose into the glucose monomer. The endocellulase breaks internal bonds to disrupt the crystalline structure of cellulose and expose individual cellulase polysaccharide chains. The exocellulase cleaves two to four units from the ends of the exposed chains produced by the endocellulase, resulting in tetrasaccharides or disaccharide such as cellobiose. The glucosidase hydrolyzes the endocellulase product into individual monosaccharides. Similarly, mixtures of hemicellulases such as xylases have been employed to hydrolyze the xylose component of hemicellulose. Also, certain enzymes may be effective in cleaving lignin. Due to the specific activity of enzymatic catalysts, enzymatic hydrolysis has been thought to have the potential for higher monomeric sugar yields and reduced formation of toxic compounds as compared to acid hydrolysis. However, the efficiency of enzymatic hydrolysis is typically low (less than 20%), although may be improved by employing an excessive amount of enzyme. Moreover, the rates of conversion

of cellulose to sugar is typically very slow due to the cellulose being protected by the matrix of hemicellulose and lignin.

[013] Fermentation of hydrolyzate sugars involves the use of digesting or metabolizing agents such as yeast. Yeast readily metabolizes glucose, which is the predominant hydrolyzate of many types of cellulosic materials. Yeast, however, cannot metabolize other hydrolyzates such as xylose, and thus other organisms such as certain species of bacteria (e.g., *Zymonmonas* sp. and *E. coli*) have been employed for this purpose, including organisms genetically engineered to consume a specific type of hydrolyzate such as xylose. The stoichiometric expressions for the conversion of glucose and xylose into ethanol are, respectively:

[014] $C_6H_{12}O_6 \rightarrow 2C_2H_6O + 2CO_2$ and

[015] $3C_5H_{10}O_5 \rightarrow 5C_2H_6O + 5CO_2$.

[016] Hydrolysis may be performed separately from fermentation in processes termed separate hydrolysis and fermentation (SHF), or may be performed simultaneously with fermentation in processes termed simultaneous saccharification and fermentation (SSF). Cellulose and hemicellulose may be fermented separately, or may be fermented together in processes termed simultaneous saccharification co-fermentation (SSCF).

[017] Once fermentation is completed, the resulting alcohols may be separated (e.g., distilled) and purified according to any suitable processes. Residual components of the fermentation process may include lignin, unreacted cellulose and hemicellulose, ash, enzymes, microorganisms, etc.

[018] Due to its crystalline structure, cellulose is generally water-insoluble and resistant to depolymerization. The highly packed and crystalline structure of cellulose also means that the surface area available for hydrolytic and fermentative activity is low. Moreover, as noted above, the presence of hemicellulose and lignin impedes hydrolysis of the cellulose. Hemicellulose hydrogen-bonds to cellulose to form the afore-mentioned cross-linked network. Lignin, as a large and complex macromolecule, is difficult to degrade, which renders it an effective physical barrier to plant pathogens and pests but at the same time a detrimental protection against the desired depolymerization of cellulose. Moreover, in the case of enzymatic hydrolysis, lignin is thought to bind to cellulase and thereby interfere with its ability to digest cellulose. As a result, the efficiency and costs associated with the

conversion of cellulosic material into alcohols are less than desirable. In view of this, various pre-treatment methods have been proposed that endeavor to disrupt the cellulose-hemicellulose-lignin complex, expose the cellulose, and/or modify the pores of the matrix, and thereby make the cellulose more available for hydrolysis such as by allowing enzymes to penetrate into the fibers of the matrix. Pre-treatment methods have included comminution (e.g., milling, chopping, etc.), uncatalyzed steam explosion, catalyzed steam explosion (e.g., using H_2SO_4 or SO_2), hydrothermolysis (the addition of liquid hot water), the addition of acids (e.g., H_2SO_4, HCl), bases or alkalis (e.g., NaOH, lime), solvents (e.g., organosolv, ethylene glycol) and ammonia, wet oxidation (e.g., treatment of biomass with water and air or oxygen at temperatures above 120 °C, sometimes also adding an alkali catalyst), ammonia fiber/freeze explosion (AFEX), ammonia recycled percolation (ARP), and other known techniques. Pre-treatment methods such as these have been summarized in Mosier et al., "Features of promising technologies for pretreatment of lignocellulosic biomass," *Bioresource Technology*, Vol. 96, pp. 673-686, Elsevier (2005); M. Galbe & G. Zacchi, "A review of the production of ethanol from softwood," *Appl. Microbiol. Biotechnol.*, Vol. 59, pp. 618-628, Springer-Verlag (2002); as well as in other literature. Many of these pre-treatment methods require high pressures, temperatures and energy inputs, and are costly.

[019] Therefore, in view of the foregoing, despite some advances in pre-treatment and hydrolytic methods, it is well-recognized by persons skilled in the art that an ongoing need exists for providing improved methods, apparatus and systems for the conversion of cellulosic materials to sugars and further conversion of sugars into alcohols and other chemicals. Higher efficiency is desired in terms of yield, energy consumption, and cost.

SUMMARY

[020] According to one implementation, a method is provided for treating a cellulosic material. The method includes subjecting the cellulosic material to an atmospheric-pressure plasma.

[021] According to another implementation, a method is provided for treating a cellulosic material. According to the method, the cellulosic material is subjected to an atmospheric-pressure plasma to produce a plasma-treated cellulosic material. One or more components of the plasma-treated cellulosic material are subjected to a degradation process.

Examples of the degradation process include, but are not limited to, various acid hydrolysis and enzymatic hydrolysis processes.

[022] According to another implementation, a method is provided for treating a cellulosic material. According to the method, the cellulosic material is subjected to a first degradation process to produce a first degradation-processed cellulosic material. One or more components of the first degradation-processed cellulosic material are subjected to an atmospheric-pressure plasma to produce a plasma-treated cellulosic material. One or more components of the plasma-treated cellulosic material are subjected to a second degradation process. Examples of the first and second degradation processes include, but are not limited to, various acid hydrolysis and enzymatic hydrolysis processes.

[023] According to another implementation, a method is provided for treating a cellulosic material. According to the method, the cellulosic material is subjected to a pretreatment process, an atmospheric-pressure plasma treatment, and a degradation process. Examples of the pretreatment process include, but are not limited to, comminution, steam explosion, hydrothermolysis, the addition of acids, bases, solvents, or ammonia, wet oxidation, ammonia fiber/freeze explosion (AFEX), ammonia recycled percolation (ARP), hydrolysis, and combinations of two or more of the foregoing.

[024] According to implementations disclosed herein, the atmospheric-pressure plasma treatments and/or the degradation processes may produce sugars. According to some implementations, one or more of these sugars may be further processed as needed to produce sugars of commercial-grade quality. According to other implementations, one or more of these sugars may be subjected to one or more fermentation processes as desired to produce one or more types of alcohols or other chemicals.

[025] According to implementations disclosed herein, atmospheric-pressure plasma treatment may include introducing the cellulosic material to a plasma-generating apparatus, and operating the apparatus to generate the atmospheric-pressure plasma from a plasma medium provided to the apparatus. In some implementations, the atmospheric-pressure plasma treatment may include operating a dielectric barrier discharge apparatus. In some implementations, the atmospheric-pressure plasma treatment may include operating a plasma-generating apparatus configured as, for example, a parallel-plate reactor, a drop-tube reactor,

a fluidized-bed reactor, or a liquid-bath reactor, a plasma jet apparatus, or a microplasma-generating apparatus.

[026] According to other implementations, devices, apparatus, structures, systems and/or materials are provided for practicing methods or processes disclosed herein.

[027] According to another implementation, a sugar such as, for example, glucose is provided that is produced according to one or more implementations disclosed herein.

[028] According to another implementation, a fermentation product is provided that is produced according to one or more implementations disclosed herein. Examples of fermentation products include, but are not limited to, organic compounds such as, for example, alcohols, examples of which include ethanol among other compounds.

[029] Other devices, apparatus, systems, methods, features and advantages of the invention will be or will become apparent to one with skill in the art upon examination of the following figures and detailed description. It is intended that all such additional systems, methods, features and advantages be included within this description, be within the scope of the invention, and be protected by the accompanying claims.

BRIEF DESCRIPTION OF THE FIGURES

[030] The invention can be better understood by referring to the following figures. The components in the figures are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention. In the figures, like reference numerals designate corresponding parts throughout the different views.

[031] Figure 1 is a flow diagram illustrating an example of a method for treating cellulosic material according to one or more implementations of the invention.

[032] Figure 2 is a flow diagram illustrating an example of another method for treating cellulosic material according to one or more other implementations of the invention.

[033] Figure 3 is a flow diagram illustrating an example of another method for treating cellulosic material according to one or more other implementations of the invention.

[034] Figure 4 is a flow diagram illustrating an example of another method for treating cellulosic material according to one or more other implementations of the invention.

[035] Figure 5 is a schematic diagram illustrating an example of an atmospheric-pressure (AP) plasma apparatus provided in accordance with one or more implementations of the invention.

[036] Figure 6 is a schematic diagram illustrating an example of another AP plasma apparatus provided in accordance with one or more other implementations of the invention.

[037] Figure 7 is a schematic diagram illustrating an example of another AP plasma apparatus provided in accordance with one or more other implementations of the invention.

[038] Figure 8 is a schematic diagram illustrating an example of another AP plasma apparatus provided in accordance with one or more other implementations of the invention.

[039] Figure 9 is a schematic diagram illustrating an example of another AP plasma apparatus provided in accordance with one or more other implementations of the invention.

[040] Figure 10 is a flow diagram illustrating an experimental procedure performed in conjunction with studying the effects of AP plasma treatment on cellulosic material.

[041] Figure 11 is a bar graph illustrating data acquired as a result of performing the experimental procedure illustrated in Figure 9.

[042] Figure 12 is a top plan view of container employed to hold samples of cellulosic material in conjunction with another experimental procedure performed to study the effects of AP plasma treatment on cellulosic material.

DETAILED DESCRIPTION

[043] As used herein, the term "cellulosic material" generally encompasses any cellulose-containing material, including lignocellulosic material and biomass, either living or existing as a waste product of industry or nature. Examples of cellulosic material include, but are not limited to, the following: forestry products, including forestry wastes, such as woods of various species of trees, including softwoods (e.g., gymnosperms such as conifers, pine, spruce, etc.), hardwoods (e.g., angiosperms such as maple, poplar, etc.), etc., including in the form of log slash, bark, trunks, stumps, branches, twigs, and the like, as well as grasses (e.g., angiosperms); agricultural products, including agricultural wastes, such as corn stover, corn cobs, rice straw, orchard and vineyard trimmings, manure, etc.; biomass crops such as grasses (e.g., switch grass), woods (e.g., poplar trees), crop residue, etc.; municipal/industrial wastes such as paper, gardening and yard refuse, etc.; and the outer coverings of various fruits,

vegatables, seeds, and other plant matter such as maize (e.g., corn), straw, cereals, rye, rape-seed, cotton-seed, sunflower seed, alfalfa, oats, barleys, wheat, millet, sorghum, buckwheat, bagasse, etc.; sawdust, wood chips, wooden plant material, non-wooden plant material, etc. Generally, wooden and non-wooden plant material may be in any form, including, but not limited to, stems, stalks, shrubs, foliage, leaves, bark, roots, shells, rinds, pods, nuts, husks, hulls, fibers, vines, straws, hay, grasses, bamboo, reeds, etc. Wooden material may include heartwood (e.g., duramen) as well as outer wood (e.g., xylem). Moreover, the cellulosic material may be a mixture or combination of one or more of the foregoing items.

[044] As used herein, the term "degradation" generally encompasses any process that results in a molecule being broken down into simpler molecules, radicals, and/or charged species. For example, the term "degradation" may encompass the breaking down of a polymer into smaller polymers (e.g., oligomers, trimers, dimers, etc.) and/or monomers such as, for example, the breaking down of a cellulose into glucose units. The term "degradation" may also encompass the breaking up or removal of physical and/or chemical bonds among different types of components of a complex material, and/or bonds internal to such components. For example, degradation may encompass the breaking up of bonds between cellulose, hemicellulose, and/or lignin, and/or the breaking down of polymeric cellulose or hemicellulose into component sugars. The term "degradation" may also encompass the removal, in whole or in part, of a component from a complex material. For example, in a complex of cellulose, hemicellulose and lignin, degradation may encompass the removal of at least some of the lignin from the complex, thereby providing greater access to the cellulose and hemicellulose components. The term "degradation" may also encompass the alteration or modification of the structure of a biomaterial. For example, degradation may encompass the opening up of interstices, voids, recesses or pores (more generally, spatial features) existing within the structure of a complex of cellulose, hemicellulose and lignin, and/or the creation of new interstices, voids, recesses or pores in such material. Degradation may entail physical, chemical, and/or biological work. Degradation may entail processes that are aided or unaided by catalytic activity. In view of the foregoing, the term "degradation" encompasses such terms as depolymerization, hydrolysis, dissociation, dissolution, disruption, delignification, removal of material, conversion of a complex material into simpler components, and release or extraction of components from a complex material.

[045] In general, the term "communicate" (for example, a first component "communicates with" or "is in communication with" a second component) is utilized in the present disclosure to indicate a structural, functional, mechanical, electrical, optical, magnetic, ionic or fluidic relationship between two or more components (or elements, features, or the like). As such, the fact that one component is said to communicate with a second component is not intended to exclude the possibility that additional components may be present between, and/or operatively associated or engaged with, the first and second components.

[046] According to implementations of the invention, described by way of example in the present disclosure, cellulosic material or other biomass is treated by atmospheric-pressure (AP) plasma. In some implementations, the treatment by AP plasma is employed as a substitute for conventionally known degradation or depolymerization processes such as acid hydrolysis and enzymatic hydrolysis. That is, the treatment by AP plasma is in some implementations sufficient to activate, expose, and/or even release or produce fermentable sugars from the cellulosic material. In other implementations, the treatment by atmospheric plasma is utilized to improve or enhance other processes for converting the cellulosic material to sugars (e.g., hydrolysis), including processes for converting the cellulosic material to fermentable sugars followed by converting the sugars to alcohols as well as other industrial chemicals. As compared to conventional hydrolytic techniques, AP plasma treatment is less harsh or rigorous in terms of its effects on cellulosic material and the process conditions required. Accordingly, the AP plasma treatment of cellulosic materials may be characterized as a "soft" degradation technique (e.g., soft depolymerization, soft hydrolysis, etc.). The treatment by AP plasma renders the cellulosic material more susceptible or accessible to methods for breaking down the cellulosic material into constituent sugars—such as glucose in the case of cellulose, and xylose and/or other pentoses in the case of most hemicelluloses—such methods including chemical hydrolysis and enzymatic hydrolysis. Moreover, the treatment by AP plasma renders fermentation techniques for producing chemicals of interest (e.g., ethanol) more effective, including techniques entailing co-fermentation of more than one type of sugar and techniques entailing simultaneous depolymerization and fermentation. Accordingly, the treatment by AP plasma facilitates not only the extraction of sugars but also the conversion of the hydrolyzate sugars into ethanol and/or other alcohols and chemicals of

interest. As such, the treatment by AP plasma is a low-cost, low-energy (e.g., low-temperature, low electrical demand) alternative to conventional treatments. Moreover, in at least some implementations, AP plasma treatment enables the conversion of cellulosic material to sugars or further to alcohols or other chemicals to be performed as a continuous process.

[047] The structure and composition of typical cellulosic materials is briefly summarized above and described in more detail in readily available literature. Without wishing to be bound by any particular theory, it is believed that the application of AP plasma in accordance with the invention degrades the coating (e.g., lignin) protecting the cellulose and opens up the cellulose-hemicellulose-lignin complex by enlarging spatial features existing in the complex and/or creating new spatial features, thereby creating greater access to internal structures of value, i.e., saccharide components. It is also believed that the AP plasma treatment prevents further interference from secondary protective coatings such as lignin and other binders in biomass material. Additionally, or alternatively, it is believed that the AP plasma disrupts at least some of the bonds or linkages existing within the complex, including bonds between the cellulose, hemicellulose and lignin (e.g., delignification) and/or at least some of the bonds or linkages existing within one or more individual components of the cellulose, hemicellulose and lignin. As a result, the treatment by AP plasma renders the cellulose component of the cellulosic material more amenable to hydrolytic cleavage or other types of depolymerization and, more generally, increases both the chemical and biochemical reactivity of the cellulose. The AP plasma-treated cellulosic material provides greater surface area available for hydrolyzing, solubilizing and fermenting activity, and greater access and contact with hydrolyzing, solubilizing and fermenting agents, thereby improving the efficiency of yield as well as the effectiveness and rates of reaction.

[048] Figures 1 – 4 illustrate examples of methods for treating cellulosic material. In some implementations, such methods may be practiced for at least partially converting the cellulosic materials into sugars. In other implementations, such methods may be practiced for at least partially converting the sugars into alcohols, such as ethanol, or other desired chemicals.

[049] Figure 1 is a flow diagram **100** illustrating an example of a method for treating cellulosic material. Depending on the cellulosic material being processed and the process

conditions, the treatment of the cellulosic material by AP plasma according to the method may, in and of itself, result in degradation of at least some of the biopolymeric components of the cellulosic material such that monomeric sugars are released (or oligomeric compounds readily convertible to monomeric sugars). In such implementations, the AP plasma treatment may be performed in conjunction with enzymatic treatment for producing alcohols or other desired chemicals, or may be directly followed by such enzymatic treatment. In other implementations, the AP plasma treatment at least may result in conditioning the cellulosic material in a manner that optimizes or facilitates a subsequent degradation process such as, for example, hydrolysis. The flow diagram **100** may also represent an apparatus or system capable of performing the illustrated method.

[050] The method begins at starting point **102**. In implementations where the cellulosic material is initially provided as a raw feedstock, the starting point **102** may be representative of any suitable preliminary steps that may be taken to prepare the cellulosic material for treatment by AP plasma. For instance, if the cellulosic material is initially provided in the form of large pieces of wood, the wood may be further comminuted into wood chips or sawdust. As another example, the cellulosic material may be washed to remove dirt or other undesired substances. As another example, the cellulosic material may be dried by any suitable means to remove moisture if desired. The cellulosic material **104** (raw feedstock, or feedstock prepared such as by the afore-mentioned preliminary steps) is introduced to an apparatus for generating an AP plasma (AP plasma apparatus). The AP plasma apparatus may be adapted for either batch processing or continuous processing, and therefore the term "introduced" is used to indicate any manner by which the cellulosic material **104** is exposed to the AP plasma such as, for example, loading or feeding the cellulosic material **104** into the AP plasma, apparatus directing an AP plasma plume or jet toward the cellulosic material, etc. At block **106**, the AP plasma apparatus is operated to generate and maintain a suitable AP plasma, thereby subjecting the cellulosic material **104** to the AP plasma.

[051] Examples of AP plasma apparatus or systems are described below with reference to Figures 5 – 9. Generally, the plasma utilized in accordance with the invention may be characterized as an ionized gas stream or cloud that may be generated in, for example, a radio frequency (RF), direct current (DC), pulsed DC, asymmetrical pulsed, or alternating current (AC) electromagnetic field, or by microwave energy. The input current for the generation of

a suitable plasma may typically range from about 30 to about 300 mA, although the invention is not limited to this range. The voltage applied to the plasma may typically range from about 500 to about 50,000 V, although the invention is not limited to this range. The working frequency of the plasma may typically range from about 0.050 to about 150 kHz, although the invention is not limited to this range. The power density of the plasma may typically range from about 0.1 to about 500 W/cm^3, although the invention is not limited to this range. Any suitable working gases for the AP plasma may be utilized. Examples of working gases include, but are not limited to, air, oxygen, hydrogen, helium, water-saturated helium, neon, argon, hydrogen, nitrogen, xenon, carbon dioxide, SF_6, CF_4, NH_3, and combinations of two or more of the foregoing. Flow rates may typically range from about 100 to about 50,000 standard cubic centimeters per minute (sccm), although the invention is not limited to this range. The particular species of the AP plasma that serve an active role in altering the structure or chemistry of the cellulosic material to attain the beneficial effects described herein will generally depend on the type of working gases employed. Examples of active species of the plasma may include, but are not limited to, oxygen radicals, hydroxide radicals, NOx, and ozone. For purposes of the present disclosure, the term "atmospheric pressure" is not limited to the exact value of 760 Torr but may range from, for example, about 100 to about 1000 Torr. Accordingly, as used herein, the term "atmospheric" encompasses the term "near atmospheric." The temperature in the chamber of the apparatus containing the AP plasma may range from about 25 to about 150 °C, although the invention is not limited to this range. The duration of the AP plasma treatment may range from about 1 to about 30 minutes, although the invention is not limited to this range.

[052] The treatment of the cellulosic material **104** by AP plasma at block **106** results in an AP plasma-treated cellulosic material **108**. The plasma-treated cellulosic material **108** may include oligosaccharide and/or monosaccharide species released from components of the cellulosic material (cellulose and/or hemicellulose) as a result of the AP plasma treatment **106**, as well as residual polysaccharide species, lignin and other components of the cellulosic material not appreciably affected by the AP plasma treatment **106**. As described previously, however, the AP plasma treatment may have the effect of removing lignin or at least disrupting the structure of lignin and its bonds so as to reduce interference of the lignin with the treatment of the cellulose. The released monosaccharide species may include hexose

sugars such as, for example, glucose, galactose and/or mannose, and/or pentose sugars such as, for example, xylose and/or arabinose, and/or other monosaccharides.

[053] At this stage, if desired, the sugars (particularly the monosaccharides) may be recovered and separated from the plasma-treated cellulosic material **108** by any suitable means such as, for example, cyclone separation, centrifugation, decanting, filtration, washing, etc. If desired, the sugars may then be subjected to any suitable purification and/or refinement processes as necessary to provide commercial-grade sugars. In the case where sugars are the intended end product, the method ends at **114**.

[054] Generally, the sugars (particularly the monosaccharides) produced or released as a result of the AP plasma treatment **106** are microbially fermentable and hence may be utilized as a fermentation medium to produce desired alcohols and/or any other desired chemicals or organic compounds such as various ketones and organic acids. Accordingly, in other implementations, as illustrated in Figure 1, the process may continue by subjecting AP plasma treatment-derived sugars to any suitable fermentation processing **110** to produce a fermentation product **112** that includes alcohols such as ethanol or other chemicals.

[055] Generally, the fermentation process **110** may entail the use of any microorganisms capable of converting the sugars (e.g., oligosaccharides, monosaccharides, and the like) into the desired alcohols or other chemicals. As examples, the fermenting microorganisms may be mesophilic (which grow optimally at a temperature in the range of about 20-40 °C) or thermophilic (which grow optimally at an elevated temperature above about 50 °C). The fermenting microorganisms may be naturally occurring or alternatively may be genetically engineered to effect a desired fermentation pathway. Generally, in the case of producing ethanol, any suitable ethanologenic strains of microorganisms may be employed. As an example, to convert glucose to ethanol, suitable fermenting microorganisms include yeast species such as baker's yeast, a further non-limiting example of which is *Saccharomyces cerevisiae*. As another example, *Zymomonas mobilis* may be employed to ferment glucose to ethanol. As compared to *S. cerevisiae*, *Z. mobilis* has been thought to produce higher yields of ethanol but is less robust. As another example, to convert xylose to ethanol, suitable fermenting microorganisms include Thermoanaerobacter species (e.g., *T. mathranii*), Zymomonas species (e.g., *Z. mobilis*), and certain yeast species (e.g., *Pichia*). It may be possible to genetically engineer microorganisms such as *S. cerevisiae*, *Z. mobilis*, and the

bacteria *Eschericihia coli* to improve fermenting performance. As appreciated by persons skilled in the art, more than one fermentation step may be required, depending on the desired chemical(s) to be produced (e.g., ethanol, xylitol, etc.), the type(s) of sugars to be fermented (e.g., glucose, xylose, etc.), and other factors. Moreover, different fermentation processes may be carried out in the same reaction vessel or in different reaction vessels. Furthermore, fermentation may be carried out as a batch process or as a continuous process. Still further, the fermentation of different types of components of the plasma-treated cellulosic material **108** may be carried out sequentially or simultaneously.

[056] It will be understood that the fermentation process **110** may be preceded by any suitable pre-conditioning steps deemed necessary in preparation for fermentation, such as neutralization or other pH adjustment, removal of any components deemed to act as fermentation inhibitors, and the like. In addition, the fermentation product **112** may be subjected to any suitable post-fermentation processes as needed, such as distillation and/or adsorption to separate the desired alcohols or other chemicals from the fermentation medium and concentrate and purify the alcohols or other chemicals for commercially-acceptable uses. In addition, residual materials such as lignin may be recovered for utilization as an energy source, as appreciated by persons skilled in the art. The method ends at **114**.

[057] As noted above, Figure 1 may also represent an example of an apparatus or system **100** for treating cellulosic material. Accordingly, block **106** may be considered as depicting a means for subjecting cellulosic material to AP plasma. An example of such means is a plasma-generating apparatus or system and associated components and materials required for its operation. Specific examples of plasma-generating apparatus or systems are described elsewhere in this disclosure and are illustrated in Figures 5 – 9. Block **110** may be considered as depicting a means for fermenting plasma-treated cellulosic material. An example of such means is one or more vessels, tanks or the like suitable for carrying out fermentation, as well as associated components and materials required for its operation, as appreciated by persons skilled in the art. The apparatus or system **100** may be configured for continuous processing or batch processing, or partially for continuous processing and partially for batch processing. Accordingly, in the context of an apparatus or system **100** for treating cellulosic material, one or more of the arrows shown in Figure 1 may represent physical components (e.g., pipes, conduits, containers, or the like) employed for holding the

cellulosic material being processed or transporting the cellulosic material from one location or device to another, or may otherwise represent the direction of process flow between locations or devices of the apparatus or system **100**.

[058] Figure 2 is a flow diagram **200** illustrating another example of a method for treating cellulosic material. The flow diagram **200** may also represent an apparatus or system capable of performing the illustrated method.

[059] The method begins at the starting point **202**. As in the case of the method illustrated in Figure 1, the starting point **202** may be representative of any suitable preliminary steps taken to prepare the cellulosic material for treatment by AP plasma. The raw or prepared cellulosic material **204** is introduced to an AP plasma apparatus. At block **206**, the AP plasma apparatus is operated to generate and maintain a suitable AP plasma that interacts with the cellulosic material **204**. The process conditions (pressure, temperature, duration, etc.) of the AP plasma treatment **206** may be the same as or similar to those described above for the method illustrated in Figure 1.

[060] The treatment of the cellulosic material **204** by AP plasma at block **206** results in an AP plasma-treated cellulosic material **208**. As described above, the plasma-treated cellulosic material **208** may include oligosaccharide and/or monosaccharide species released from components of the cellulosic material (cellulose and/or hemicellulose) as a result of the AP plasma treatment **206**, as well as residual polysaccharide species and lignin not affected by the AP plasma treatment **206**. At this stage, if desired, the released sugars may be recovered and separated from the plasma-treated cellulosic material **208** by any suitable means and then subjected to further processing as necessary to provide commercial-grade sugars. Alternatively, as indicated by the schematic process line **210** in Figure 2, the released sugars may be recovered for subsequent fermentation.

[061] The portion of the plasma-treated cellulosic material **208** that has not been degraded by the AP plasma treatment step **206** is nevertheless, as a result of the AP plasma treatment step **206**, optimally conditioned for subsequent degradation processing. Accordingly, at block **212**, the plasma-treated cellulosic material **208** may then be subjected to any suitable cellulosic material degradation or depolymerization process. The degradation process **212** may be any process suitable for yielding desired sugars such that the sugars may then be subsequently processed for commercial consumption or fermented for producing

alcohols or other chemicals. Examples of suitable degradation processes **212** include, but are not limited to, acid hydrolysis processes and enzymatic hydrolysis processes. Acid hydrolysis generally entails reacting the plasma-treated cellulosic material **208** with water and employing a suitable acid or acidic compound as a catalyst. Examples of suitable acids and acidic or acid-like compounds include, but are not limited to, mineral acids such as sulfuric acid, sulfurous acid, hydrochloric acid, hydrofluoric acid, phosphoric acid, formic acid and nitric acid, and acidic salts such as aluminum sulfate, ferric sulfate, ferrous sulfate, magnesium sulfate, ferric chloride, aluminum chloride, aluminum nitrate, and ferric nitrate. More generally, a variety of organic and inorganic acids may be employed as appreciated by persons skilled in the art, but particularly toxic or corrosive acids should be avoided. Enzymatic hydrolysis generally entails reacting the plasma-treated cellulosic material **208** with one or more appropriate carbohydrase enzymes such as various known cellulases and hemicellulases. For instance, a cellulase enzyme complex may be employed for the saccharification of the cellulose of the plasma-treated cellulosic material **208** to yield glucose.

[062] The degradation process **212** results in (at least partially) degraded cellulosic material **214**. The degraded (or degradation-processed) cellulosic material **214** may include oligosaccharide and/or monosaccharide species released from components of the cellulosic material (cellulose and/or hemicellulose) as well as residual polysaccharide species and lignin not affected by the degradation process **212**. Due to the preceding AP plasma treatment **206**, the degradation process **212** may result in a much higher yield of monosaccharides than had the degradation process **212** been carried out alone without the AP plasma treatment **206** or had the degradation process **212** been preceded by a conventional pre-treatment process. At this stage, if desired, the released sugars may be recovered and separated from the degraded cellulosic material **214** by any suitable means and then subjected to further processing as necessary to provide commercial-grade sugars. In the case where sugars are the intended end product, the method ends at **220**.

[063] In other implementations, as illustrated in Figure 2, the process may continue by subjecting the sugars obtained from the degraded cellulosic material **214** to any suitable fermentation processing **216** to produce a fermentation product **218**. The fermentation product **218** may include alcohols such as ethanol and/or other desired chemicals. As described above in conjunction with the method exemplified in Figure 1, the fermentation

process **216** may entail the use of any microorganisms capable of converting the sugars (e.g., oligosaccharides, monosaccharides, and the like) into the desired alcohols or other compounds. Moreover, it will be understood that the fermentation process **216** may be preceded by any suitable pre-conditioning steps deemed necessary in preparation for fermentation, such as neutralization, removal of any components deemed to act as fermentation inhibitors, and the like. Furthermore, the fermentation product **218** may be subjected to any suitable post-fermentation processes as needed, such as distillation to separate the desired alcohols or other chemicals from the fermentation medium and purify the alcohols or other chemicals for commercially-acceptable uses. The method ends at **220**.

[064] As noted above, Figure 2 may also represent an example of an apparatus or system **200** for treating cellulosic material. Accordingly, block **206** may be considered as depicting a means for subjecting cellulosic material to AP plasma. Examples of such means are referred to above in connection with the apparatus or system **100** illustrated in Figure 1. Block **212** may be considered as depicting a means for degrading cellulosic material to produce sugars. An example of such means is one or more vessels, tanks or the like suitable for carrying out a degradation process such as, for example, acid or enzymatic hydrolysis, as well as associated components and materials required for its operation, as appreciated by persons skilled in the art. Block **216** may be considered as depicting a means for fermenting plasma-treated cellulosic material. As previously noted, an example of such means is one or more vessels, tanks or the like suitable for carrying out fermentation, as well as associated components and materials required for its operation. The apparatus or system **200** may be configured in whole or part for continuous processing or batch processing, as noted above in connection with the apparatus or system **100** illustrated in Figure 1.

[065] Prior to fermentation, more than one iteration of AP treatment and/or degradation may be performed. For example, Figure 3 is a flow diagram **300** illustrating another method for treating a cellulosic material. The flow diagram **300** may also represent an apparatus or system capable of performing the illustrated method. This example entails a two-stage degradation process that is enhanced by one or more AP plasma treatment steps.

[066] The method begins at the starting point **302**. Raw or prepared cellulosic material **304** is subjected to a first-stage degradation process at block **306**, in which at least some of the components of the cellulosic material **304** are degraded or depolymerized without the aid

of AP plasma treatment. For example, the first-stage degradation process **306** may entail dilute acid hydrolysis. The first-stage degradation process **306** may serve as a relatively mild process that acts on certain polysaccharide components of the cellulosic material **304** that, due to their initial structure (e.g., degree of crystallinity or amorphousness) or accessibility (e.g., exposure, freedom from lignin binding, etc.), are readily degradable without the aid of a pre-treatment step. Alternatively, or additionally, the first-stage degradation process **306** may serve as a pre-treatment process in and of itself, for example to break down the hemicellulose for removal, and/or more generally to at least partially disrupt the cellulose-hemicellulose-lignin complex, in preparation for hydrolyzing or otherwise degrading the cellulose (and particularly the crystalline phase) in a subsequent degradation step.

[067] The first-stage degradation process **306** produces (at least partially) degraded cellulosic material **308**, which may be a mixture of sugar solution and residual cellulosic material such as unreacted cellulose and lignin. At this stage, if desired, any suitable separation process may be performed to separate the sugar solution from the residual cellulosic material. The sugars obtained at this stage may be processed for commercial use or, as indicated by line **310** in Figure 3, recovered for subsequent fermentation. At block **312**, the unreacted cellulosic material is subjected to AP plasma treatment as described elsewhere in this disclosure. The process conditions (pressure, temperature, duration, etc.) of the AP plasma treatment **312** may be the same as or similar to conditions described above.

[068] The treatment of the cellulosic material by AP plasma at block **312** results in an AP plasma-treated cellulosic material **314**. As described above, the plasma-treated cellulosic material **314** may include oligosaccharide and/or monosaccharide species released from components of the cellulosic material (cellulose and/or hemicellulose) as a result of the AP plasma treatment **312**, as well as residual polysaccharide species and lignin not affected by the AP plasma treatment **312**. At this stage, if desired, the released sugars may be recovered and separated from the plasma-treated cellulosic material **314** by any suitable means and then subjected to further processing as necessary to provide commercial-grade sugars. Alternatively, as indicated by the schematic process line **316** in Figure 3, the released sugars may be recovered for subsequent fermentation.

[069] The portion of the plasma-treated cellulosic material **314** that has not been degraded by the AP plasma treatment step **312** is, as a result of the AP treatment step **312**,

optimally conditioned for subsequent degradation processing. Accordingly, at block **318**, the plasma-treated cellulosic material **314** may then be subjected to a second-stage cellulose degradation or depolymerization process. To the extent that the cellulosic material undergoing the second-stage degradation **318** was not degraded into sugars in the first-stage degradation process **306** or AP plasma treatment process **312** and hence is more difficult to degrade, the second-stage degradation process **318** may be a more rigorous process in comparison to the first-stage degradation process **306**. For example, the second-stage degradation process **318** may entail an acid hydrolysis process in which a higher concentration of acid is employed as compared with the first-stage acid hydrolysis. For example, the first-stage hydrolysis may be carried out in a 0.5M (4.9% w/w) H_2SO_4 (sulfuric acid) solution, and the second-stage hydrolysis may be carried out in a 1.0M (9.8% w/w) H_2SO_4 solution. Alternatively, depending on the nature of the cellulosic material being processed, the effectiveness of the AP treatment process **312** may be such that the second-stage degradation process **318** need not be more rigorous, or may even be less rigorous, than the first-stage degradation process **306**. As another example, the second-stage degradation process **318** may be an enzymatic process that employs enzymes (e.g., cellulases) specifically selected to hydrolyze the more difficultly hydrolyzable components of the cellulosic material such as crystalline cellulose.

[070] The processing of the plasma-treated cellulosic material **314** by the second-stage degradation process **318** yields further degradation-processed cellulosic material **320** that includes sugars. At this stage, the sugars may be subjected to any post-degradation processes such as purification and refinement as necessary to provide commercial-grade sugar. Alternatively, at block **322**, the process may continue by subjecting the sugars to any suitable fermentation process to produce alcohols or other desired chemicals. As noted previously, any sugars produced from the first-stage degradation process **306** and the AP plasma treatment process **312** may likewise be fermented. In some implementations, the sugars produced from the first-stage degradation process **306** and/or the AP plasma treatment process **312** may be combined with the sugars produced from the second-stage degradation process **318**, and all sugars co-fermented simultaneously. The process illustrated in Figure 3 ends at **324**.

[071] As noted above, Figure 3 may also represent an example of an apparatus or system **300** for treating cellulosic material. Accordingly, block **306** may be considered as depicting a means for degrading cellulosic material to produce sugars. An example of such means is one or more vessels, tanks or the like suitable for carrying out a degradation process such as, for example, acid or enzymatic hydrolysis, as well as associated components and materials required for its operation. Block **312** may be considered as depicting a means for subjecting cellulosic material to AP plasma. Examples of such means are referred to above in connection with the apparatus or system **100** illustrated in Figure 1. Block **318** may be considered as depicting a separate degrading means, or may be the same means as means **306**. Block **322** may be considered as depicting a means for fermenting plasma-treated cellulosic material. As previously noted, an example of such means is one or more vessels, tanks or the like suitable for carrying out fermentation, as well as associated components and materials required for its operation. The apparatus or system **300** may be configured in whole or part for continuous processing or batch processing, as noted above in connection with the apparatus or system **100** illustrated in Figure 1.

[072] Depending on the composition of the cellulosic material to be processed, one or more AP plasma treatment steps may be combined with one or more degradation processes, as well as with "pre-treatment" processes traditionally associated with conventional degradation processes such as acid hydrolysis and enzymatic hydrolysis. The pre-treatment process may be any chemical, biological, biochemical, physical, or physio-chemical process or processes now known or later developed that is effective in enhancing conventional degradation processes. Examples of pre-treatment processes include, but are not limited to, comminution, uncatalyzed steam explosion, hydrothermolysis, the addition of acids, bases, solvents, or ammonia, ammonia fiber/freeze explosion (AFEX), ammonia recycled percolation (ARP), etc. An example of a process that combines pre-treatment with AP plasma treatment is illustrated in Figure 4, which is a flow diagram **400** illustrating another method for treating a cellulosic material. The flow diagram **400** may also represent an apparatus or system capable of performing the illustrated method.

[073] The method begins at the starting point **402**. Raw or prepared cellulosic material **404** is introduced to a suitable AP plasma apparatus and subjected to a first-stage AP plasma treatment at block **406**, which yields plasma-treated cellulosic material **408** as previously

described. As also previously described, the plasma-treated cellulosic material **408** may include sugars as a result of the AP plasma treatment **406**, as well as residual polysaccharide species and lignin not affected by the AP plasma treatment **406**. At this stage, if desired, the released sugars may be recovered and separated from the plasma-treated cellulosic material **408** by any suitable means and then subjected to further processing as necessary to provide commercial-grade sugars. Alternatively, as indicated by the process schematic line **410** in Figure 4, the sugars resulting from the first-stage AP plasma treatment **406** may be recovered for subsequent fermentation. At block **412**, the plasma-treated cellulosic material **408** is subjected to any suitable pre-treatment process to enhance a subsequent degradation technique or techniques. The pre-treatment process **412** yields pre-treated cellulosic material **414**.

[074] In other implementations, as indicated by the process schematic line **416**, raw or prepared cellulosic material **404** is subjected directly to the pre-treatment process **412** without an intervening AP plasma treatment **406**.

[075] The pre-treated cellulosic material **414** is then subjected to a second-stage AP plasma treatment at block **418**, which yields further plasma-treated cellulosic material **420**. The second-stage AP plasma treatment **418** may serve to enhance the role of the pre-treatment step **412** (and the first-stage AP plasma treatment **406**, if employed) in optimizing the cellulosic material for a subsequent degradation process or processes. On the other hand, the pre-treatment step **412** may be considered as enhancing the role of the first-stage AP plasma treatment **406** and/or the second-stage AP plasma treatment **418** in optimizing the cellulosic material for subsequent degradation. Moreover, as in the case of the first-stage AP plasma treatment **406**, the second-stage AP plasma treatment **418** may yield sugars as a result of second-stage AP plasma treatment **418**. At this stage, if desired, these sugars may be recovered and separated from the plasma-treated cellulosic material **420** by any suitable means and then subjected to further processing as necessary to provide commercial-grade sugars. Alternatively, as indicated by the process schematic line **422** in Figure 4, the sugars resulting from the second-stage AP plasma treatment **418** may be recovered for subsequent fermentation.

[076] After the second-stage AP plasma treatment **418**, at block **424**, the plasma-treated cellulosic material **420** is subjected to any suitable degradation process such as, for example,

acid hydrolysis or enzymatic hydrolysis to break down remaining polysaccharide components of the plasma-treated cellulosic material **420** into sugars. The degradation process **424** yields a mixture **426** of sugar solution and residual cellulosic material such as lignin.

[077] In other implementations, as indicated by the process schematic line **428**, the pre-treated cellulosic material **414** is subjected directly to the degradation process **424** without an intervening AP plasma treatment **418**.

[078] At this stage, any suitable separation process may be performed to separate the sugar solution from the residual cellulosic material. The sugars obtained at this stage may be processed for commercial use. Alternatively, as indicated at block **430**, the resulting sugars may be subjected any suitable fermentation process to produce a fermentation product **432** that includes alcohols or other desired chemicals. As noted previously, any sugars produced from the first-stage AP plasma treatment **406** and/or the second-stage AP plasma treatment **418** may likewise be fermented, together with or separately from the sugars derived from the degradation process **424**. The process illustrated in Figure 4 ends at **434**.

[079] As noted above, Figure 4 may also represent an example of an apparatus or system **400** for treating cellulosic material. Accordingly, block **406** may be considered as depicting a means for subjecting cellulosic material to AP plasma. Examples of such means are referred to above in connection with the apparatus or system **100** illustrated in Figure 1. Block **412** may be considered as depicting a means for pre-treating cellulosic material in preparation for a degradation process. Examples of pre-treatment processes are noted above, and the devices and systems for implementing such pre-treatment processes are known to persons skilled in the art. Block **418** may be considered as depicting a separate AP plasma treatment means, or may be the same means as means **406**. Block **424** may be considered as depicting a means for degrading cellulosic material to produce sugars. An example of such means is one or more vessels, tanks or the like suitable for carrying out a degradation process such as, for example, acid or enzymatic hydrolysis, as well as associated components and materials required for its operation. Block **430** may be considered as depicting a means for fermenting plasma-treated cellulosic material. As previously noted, an example of such means is one or more vessels, tanks or the like suitable for carrying out fermentation, as well as associated components and materials required for its operation. The apparatus or system

400 may be configured in whole or part for continuous processing or batch processing, as noted above in connection with the apparatus or system 100 illustrated in Figure 1.

[080] Any of the methods, apparatus and systems described by example above and illustrated by example in Figures 1 – 4, in implementations involving fermentation, may be adapted for separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), and/or simultaneous saccharification co-fermentation (SSCF).

[081] Figures 5 – 9 illustrate examples of AP plasma apparatus or systems that may be employed in the AP plasma treatment processes performed in methods according to the invention, including the methods described by above example and illustrated by example in Figures 1 – 4. It will be understood that implementations of AP plasma apparatus or systems other than those illustrated in Figures 5 – 9 may also be suitable in the practice of the invention.

[082] Referring now to Figure 5, an AP plasma apparatus or system 500 is illustrated. The AP plasma apparatus 500 may be provided as a dielectric barrier discharge (DBD) apparatus. The AP plasma apparatus 500 may include a housing or enclosure 504 in which AP plasma treatment of cellulosic material 508 is performed. It will be understood, however, that because the plasma operates at atmospheric pressure, an enclosure 504 is not required, at least not one of the type required in evacuated or pressurized systems. The AP plasma apparatus 500 has a parallel-plate configuration, and thus includes a first electrode 512 and a second electrode 516 spaced at a distance from the first electrode 512. The first and second electrodes 512 and 516 may be positioned or mounted within the enclosure 504 by any suitable means. Although in the present example the electrodes 512 and 516 are illustrated as having a planar geometry (i.e., plates), any other suitable geometry may be employed for the electrodes 512 and 516. For example, a cylindrical or rectangular symmetry may be employed. The electrodes 512 and 516 may be composed of any suitable electrically conductive material such as, for example, aluminum (Al). One or both of the electrodes 512 and 516 may be coated, covered, or otherwise isolated by a dielectric element (e.g., a layer, film, or the like). In the present example, the first electrode 512 is covered by a first dielectric element 520 and the second electrode 516 is covered by a second dielectric element 524. The dielectric elements 520 and 524 may be composed of any suitable electrically insulating material such as, for example, a silica glass. A high-voltage power supply 528

electrically communicates with the first and second electrodes **512** and **516** via suitable conductive elements **532** and **536**, respectively. The electrodes **512** and **516** are separated by some distance, typically less than 25.4 mm. The gap is filled with suitable gas at a pressure at or near 760 Torr but may range from 100 to 1000 Torr as noted previously. Due to the presence of one or more dielectric elements **520** and **524** between the electrodes **512** and **516**, the high-voltage power supply **528** is an AC (alternating current) source. Although in this configuration two dielectric elements **520** and **524** are employed, it is not required that both electrodes **512** and **516** be covered in this manner. It has been shown that materials with a high resistivity can also act as a barrier for plasma formation. Additionally, in other implementations the power source can be operated in other modes such as a DC, pulsed DC, or RF voltage (up to and including the Ghz range in frequency), etc. as previously noted. In the present configuration, the high-voltage power supply **528** may operate at an amplitude ranging from about 500 V to about 50,000 V and a frequency ranging from about 0.050 kHz to about 150 kHz.

[083] In operation, a mass of cellulosic material **508** is introduced into the AP plasma apparatus **500** by any means and positioned between the electrodes **512** and **516** and dielectric barrier(s) **520** and **524**. The cellulosic material **508** introduced into the AP plasma apparatus **500** may be dry, moist or combined with a liquid medium (e.g., water). In the example illustrated in Figure 5, the cellulosic material **508** is provided on or in a suitable holder **540**. The holder **540** may, for example, be any container, planar surface or platter utilized for conventional applications (e.g., semiconductor or micro-electro-mechanical fabrication) of plasma-generating apparatus. One non-limiting example of a holder **540** is a fluoroware container. One or more working gases suitable for generating a plasma such as, for example, argon and/or helium, are then introduced into the interior of the enclosure **504**. Alternatively, ambient air may be employed as the plasma medium, in which case a specific gas introduction step is not required. The high-voltage power supply **528** is then operated to strike a bulk plasma **544** between the electrodes **512** and **516** and dielectric barrier(s) **520** and **524**. In the present context, the term "bulk" indicates a wide-beam or non-directional plasma **544** that maximizes contact with the cellulosic material **508**. That is, a focused narrow plasma beam is not required in this implementation but may be employed in other implementations utilizing an AP plasma. As appreciated by persons skilled in the art, the

high-voltage power supply **528** may be operated according to a voltage profile suitable for the design of the AP plasma apparatus **500** and the working gas employed under conditions suitable for generation of an AP plasma. For instance, the amplitude of the voltage applied to the electrodes **512** and **516** is typically relatively high to strike the plasma **544**, and subsequently is lowered to maintain the plasma **544**. It will also be noted that the plasma **544** may be generated prior to introduction of the cellulosic material **508** into the AP plasma apparatus **500**. Other operating conditions of the AP plasma apparatus **500**, such as temperature and time duration of the treatment, may fall within the ranges noted above in conjunction with the method illustrated in Figure 1. The exposure of the cellulosic material **508** to the energetic AP plasma **544** results in a plasma-treated cellulosic material, the effects of which are described above in conjunction with the examples of methods illustrated in Figures 1 – 4.

[084] Figure 6 illustrates another AP plasma apparatus or system **600**, which may be provided as a DBD apparatus. The AP plasma apparatus **600** includes a housing, container or enclosure **604** in which AP plasma treatment of cellulosic material **608** is performed. Moreover, the enclosure **604** may be composed of a glass or other suitable electrically insulating material such as Pyrex® glass or other silicate or borosilicate glass, quartz or alumina, thereby serving as a dielectric barrier as well as a plasma reaction chamber. It will be understood, however, that implementations of the invention are not limited to operation in a reaction chamber, as the plasma may be operated under atmospheric pressure as previously noted. The enclosure **604** may be generally cylindrical or have some other hollow geometry. As illustrated in Figure 6, the enclosure **604** may be vertically oriented as a drop tube and thus elongated along the vertical dimension. Accordingly, the AP apparatus **600** may be referred to herein as having a drop-tube configuration. In other implementations, the enclosure **604** may be horizontally oriented or oriented at an angle relative to a vertical or horizontal plane. The AP plasma apparatus **600** also includes a first electrode **612** and a second electrode **616** spaced at a distance from the first electrode **612**. The electrodes **612** and **616** may be composed of any suitable electrically conductive material such as, for example, aluminum (Al). The electrodes **612** and **616** are coaxially disposed around the outside surface of the enclosure **604** and fixed in position by any means. The electrodes **612** and **616** may be entirely or partially formed as annular or ring-shaped members. A high-

voltage AC power supply **628** electrically communicates with the first and second electrodes **612** and **616** via suitable conductive elements **632** and **636**, respectively. The high-voltage power supply **628** may operate at an amplitude ranging from about 500 to about 50,000 V and a frequency ranging from about 0.05 to about 150 kHz.

[085] The enclosure **604** has an opening at one end or, in the flow-through implementation illustrated in Figure 6, has an inlet opening **652** at one end and an outlet opening **654** at the opposite end. In the illustrated vertically-oriented implementation, the AP plasma apparatus **600** may additionally include a container or holder **672** such as a hopper or other suitable design that is positioned above the inlet opening **652** of the enclosure **604** for initially containing untreated cellulosic material **608** and thereafter dropping the cellulosic material **608** by gravity feed into the interior of the enclosure **604** via the inlet opening **652**. The AP plasma apparatus **600** may also include another holder or container **674** positioned below the outlet opening **654** of the enclosure **604** for collecting AP plasma-treated cellulosic material **608**. Alternatively, opening **654** may serve as the inlet opening and opening **652** may serve as the outlet opening, or one of openings **652** or **654** may serve as both the inlet opening and the outlet opening.

[086] In operation, one or more working gases suitable for generating a bulk plasma **644** such as, for example, argon and/or helium, are introduced into the interior of the enclosure **604**. Alternatively, ambient air may be employed as the plasma medium. The high-voltage power supply **628** is operated to strike the bulk plasma **644** within the chamber defined by the enclosure **604**. The operating conditions of the AP plasma apparatus **600**, such as the voltage profile of the high-voltage power supply **628**, the temperature within the enclosure **604**, and the time duration of the treatment, may be as noted above in conjunction with the method illustrated in Figure 1 and the apparatus **500** illustrated in Figure 5. A mass of cellulosic material **608** is introduced into the enclosure **604** such as by unloading the holder **672** and allowing the cellulosic material **608** to flow through the inlet opening **652** by gravity feed. The cellulosic material **608** introduced into the AP plasma apparatus **600** may be dry or moist. In this implementation, it is desirable in many cases that the cellulosic material **608** be comminuted sufficiently to maximize the duration of travel through the enclosure **604** during operation of the AP plasma **644**. The cellulosic material **608** is thus treated by the energetic AP plasma **644** as it flows down through the plasma **644** along the elongated dimension of

the enclosure **604**. At the bottom of the enclosure **604**, the resulting plasma-treated cellulosic material **608** flows through the outlet opening **654** and into the holder **674** for collection.

[087] Figure 7 illustrates another AP plasma apparatus or system **700**, which may be provided as a DBD apparatus. The AP plasma apparatus **700** includes a housing, container or enclosure **704** in which AP plasma treatment of cellulosic material **708** is performed. Similar to the apparatus **600** shown in Figure 6, the enclosure **704** may be composed of a glass or other suitable electrically insulating material and hence function as a dielectric barrier as well as a plasma reaction chamber. The enclosure **704** may be generally cylindrical or have some other hollow geometry, and may be vertically oriented and elongated. The AP plasma apparatus **700** also includes a first electrode **712** and a second electrode **716** spaced at a distance from the first electrode **712**. The electrodes **712** and **716** may be composed of any suitable electrically conductive material such as, for example, aluminum (Al), and may be elongated members. The first electrode **712** is helically wound as a coil around the outside surface of the enclosure **704** or otherwise coaxially disposed about the enclosure **704**. The second electrode **716** extends as a rod or wire into the enclosure **704** generally along the central longitudinal axis of the interior of the enclosure **704**. A high-voltage AC power supply **728** electrically communicates with the first and second electrodes **712** and **716** via suitable conductive elements **732** and **736**, respectively. The high-voltage power supply **728** may operate at an amplitude ranging from about 500 to about 50,000 V and a frequency ranging from about 0.05 to about 150 kHz.

[088] The enclosure **704** has an opening at one end or, in the flow-through implementation illustrated in Figure 7, has an inlet opening **752** at one end and an outlet opening **754** at the opposite end. The AP plasma apparatus **700** may additionally include a container or holder (not shown, but see Figure 6) such as a hopper or other suitable design that is positioned above the inlet opening **752** of the enclosure **704** for initially containing untreated cellulosic material **708** and thereafter dropping the cellulosic material **708** by gravity feed into the interior of the enclosure **704** via the inlet opening **752**. The AP plasma apparatus **700** may also include another holder or container (not shown, but see Figure 6) positioned below the outlet opening **754** of the enclosure **704** for collecting AP plasma-treated cellulosic material **708**. Alternatively, as described below, the opening **754** may serve

as the inlet opening and the opening **752** may serve as the outlet opening, or one of the openings **752** or **754** may serve as both the inlet opening and the outlet opening.

[089] Additionally, a gas distributor **782** is positioned by any means in the bottom region of the enclosure **704** near the outlet opening **754**. The gas distributor **782** may have any configuration suitable for flowing a gas up through the interior of the enclosure **704**. For example, the gas distributor **782** may include a manifold and a plurality or orifices or jets (not shown) for this purpose. The gas distributor **782** may be annular or toroidal in shape, or have a plurality of passages extending from the upper side of the gas distributor **782** to the lower side, to facilitate a flow-through implementation of the AP plasma apparatus **700**, i.e., to allow plasma-treated cellulosic material **708** to flow through a center opening or plurality of passages provided by the gas distributor **782**. The gas distributor **782** communicates with a suitable gas source **784**. By this configuration, the AP plasma apparatus **700** may be considered as operating as a fluidized-bed reactor. For this purpose, any suitable gas may be supplied to the gas distributor **782**. Examples of gases include, but are not limited to, air, oxygen, hydrogen, helium, water-saturated helium, neon, argon, hydrogen, nitrogen, xenon, carbon dioxide, SF_6, CF_4, NH_3 and combinations of two or more of the foregoing.

[090] In operation, one or more working gases suitable for generating a bulk plasma **744** such as, for example, argon and/or helium, are introduced into the interior of the enclosure **704**. The gas distributor **782** may be employed for this purpose, or additional, dedicated working gas supply and delivery means (not shown) may be provided. Alternatively, ambient air may be employed as the plasma medium. The high-voltage power supply **728** is operated to strike the bulk plasma **744** within the chamber defined by the enclosure **704**. The operating conditions of the AP plasma apparatus **700**, such as the voltage profile of the high-voltage power supply **728**, the temperature within the enclosure **704**, and the time duration of the treatment, may be as noted above in conjunction with the method illustrated in Figure 1 and the apparatus **500** illustrated in Figure 5. A flow of gas is established through the gas distributor **782** into the interior of the enclosure **704**, with the gas being directed generally in the upward vertical direction. A mass of cellulosic material **708** is introduced into the enclosure **704** such as by unloading a holder (not shown) and allowing the cellulosic material **708** to flow through the inlet opening **752** by gravity feed. Alternatively, the cellulosic material **708** may be introduced at some flow rate into the enclosure **704** through opening **754**

(if provided) or some other opening near the bottom of the enclosure **704**, and conducted upward through the enclosure **704** with the assistance of the gas flow. The cellulosic material **708** introduced into the AP plasma apparatus **700** may be dry or moist. In this implementation, it is desirable in many cases that the cellulosic material **708** be comminuted sufficiently to maximize the duration of travel through the enclosure **704** during operation of the AP plasma **744**. In such a case, however, the cellulosic material **708** need not be comminuted to the same degree as in the case of the apparatus **600** shown in Figure 6, because the gas distributor **782** establishes a fluidized-bed condition in the enclosure **704** by which the cellulosic material **708** is suspended for a suitable working time due to a balancing of forces from gravity and the gas flow. Moreover, the fluidized-bed condition may cause the components of the cellulosic material **708** to flow along turbulent or tumbling pathways, thereby enabling more effective interaction between the cellulosic material **708** and the plasma **744**. The cellulosic material **708** is thus treated by the energetic AP plasma **744** as it is effectively suspended in and flows through the plasma **744**. At the bottom of the enclosure **704**, the resulting plasma-treated cellulosic material **708** flows through or around the gas distributor **782**, through the outlet opening **754**, and optionally into a holder (not shown) for collection. In other implementations, the flow of gas through the gas distributor **782** may be increased so as to over-pressurize the enclosure **704** and thereby conduct the plasma-treated cellulosic material **708** out through the inlet opening **752** of the enclosure **704** and into a suitable collector.

[091] Figure 8 illustrates another AP plasma apparatus or system **800**. The AP plasma apparatus **800** includes a housing, container or enclosure **804** in which AP plasma treatment of cellulosic material **808** is performed. The enclosure **804** may be provided as a container with an open or closed top **810** and contain a volume of liquid **888** thereby serving as a liquid bath. Accordingly, the AP plasma apparatus **800** may be referred to as having a liquid-bath configuration. Examples of liquids **888** include, but are not limited to, water, acids, bases, and solvents. The enclosure **804** may be generally cylindrical or have some other hollow geometry suitable for holding the volume of liquid **888**. The AP plasma apparatus **800** also includes one or more electrodes **812** and **816** spaced at distances from each other. The distance intervals between adjacent electrodes **812** and **816** may be equal or non-equal. The electrodes **812** and **816** may be composed of any suitable electrically conductive material

such as, for example, aluminum (Al). The electrodes **812** and **816** may be elongated members such as wires or rods, may be plates, or may have any other suitable shapes. The electrodes **812** and **816** may be fixed in position within the interior of the enclosure **804** by any means, and thus in practice are immersed in the liquid bath. The electrodes **812** and **816** may be vertically oriented as in the illustrated example or positioned in any other orientation. As illustrated in the inset portion of Figure 8, one or more of the electrodes **812** and **816** may be coated or otherwise covered with a dielectric layer **820** composed of any suitable electrically insulating material such as, for example, Pyrex® glass or other silicate or borosilicate glass, quartz, or alumina. A high-voltage AC power supply **828** electrically communicates with the first set of electrodes **812** and second set of electrodes **816** via suitable conductive elements **832** and **836**, respectively. The conductive elements **832** and **836** may be passed through a sidewall **811** of the enclosure **804** such as by employing sealed feed-through members (not shown). Alternatively, in the case where the top **810** of the enclosure **804** is open, the conductive elements **832** and **836** may be routed into the interior of the enclosure **804** via the open top **810**. The high-voltage power supply **828** may operate at an amplitude ranging from about 3000 to about 50,000 V and a frequency ranging from about 1 to about 150 kHz.

[092] In operation, the enclosure **804** is partially or completely filled with a volume of liquid **888**, which serves as the plasma medium. A mass of cellulosic material **808** is introduced into the liquid bath by any means and permitted to become distributed through the volume of liquid **888**, at least in the region of the electrodes **812** and **816** where the plasma is generated The high-voltage power supply **828** is operated to strike a bulk plasma **844** within the enclosure **804**. The operating conditions of the AP plasma apparatus **800**, such as the voltage profile of the high-voltage power supply **828**, the temperature within the enclosure **804**, and the time duration of the treatment, may be as noted above in conjunction with the method illustrated in Figure 1 and the apparatus **500** illustrated in Figure 5. In some implementations, the plasma **844** may be generated prior to introducing the cellulosic material **808**, but it may desirable to first introduce the cellulosic material **808** to allow the cellulosic material **808** to become distributed prior to treatment by the plasma **844**. The cellulosic material **808** is thus treated by the energetic AP plasma **844** for a desired period of time (e.g., 5 minutes or thereabouts). The resulting plasma-treated cellulosic material **808** is

thereafter removed from AP plasma apparatus **800**, and may be subjected to further processing in accordance with any of the methods of the invention.

[093] Figure 9 illustrates another AP plasma apparatus or system **900**. The AP plasma apparatus **900** includes a first electrode **912** and an encasement or enclosure **916**. At least a portion of the enclosure **916** serves as a second electrode. The first electrode **912** and the enclosure **916** (or at least the electrode portion of the enclosure **916**) may be composed of any suitable electrically conductive material such as, for example, aluminum. A high-voltage AC power supply **928** electrically communicates with the first electrode **912** and the enclosure **916** via suitable conductive elements **932** and **936**, respectively. The enclosure **916** provides an internal volume for containing cellulosic material **908**, which may be fed into the enclosure **916** via an inlet opening **952** typically located at or near the top of the enclosure **916**. The first electrode **912** extends through the top of the enclosure **916** and into the interior volume, typically along the central, longitudinal axis of the enclosure **916**. The first electrode **912** terminates at some point within the enclosure **916** and is radially spaced from an annular or hollow, conductive portion of the enclosure **916**. The cross-section of the enclosure **916** may be generally circular, elliptical, or polygonal. The lower region of the enclosure **916** may be tapered so as to form a nozzle section **920** that terminates at an outlet opening **954**.

[094] In operation, the cellulosic material **908** is fed into the enclosure **916** through the inlet opening **952**. A source gas for generating AP plasma is fed through a source gas inlet opening **984** of the enclosure **916**. The cellulosic material **908** and source gas flow generally from the top of the enclosure **916** toward the nozzle section **920**. The high-voltage power supply **928** is operated to ignite the source gas, thereby creating an ignited plasma **944** in the nozzle section **920** of the enclosure **916** in the form of a plasma jet, which is directed out from the outlet opening **954** of the nozzle section **920**. The cellulosic material **908** is treated by the plasma **944** as it flows with the plasma **944** out from the outlet opening **954**. The treated cellulosic material **908** is collected at a suitable collector **974**, which may be positioned at some distance from the outlet opening **954**.

[095] In at least some implementations and for at least some types of cellulosic materials, the apparatus **600, 700, 800** and **900** respectively illustrated in Figures 6, 7, 8 and 9 may be more effective at treating cellulosic materials as compared with the apparatus **500**

illustrated in Figure 5, due to the three-dimensional exposure of the cellulosic material to the plasma.

[096] In addition to the implementations described above and illustrated in Figures 6-9, another type of plasma-generating apparatus that may be employed is one configured for generating a microplasma. The design and operation of microplasma-generating apparatus, outside of the context of treating cellulosic materials, are known to persons skilled in the art. One of the above-described apparatus **500, 600, 700, 800** and **900** may be configured to produce a microplasma.

[097] EXAMPLE 1

[098] Figure 10 is a schematic diagram **1000** illustrating an experimental implementation carried out to determine the impact of treatment by AP plasma on the process of acid hydrolysis of cellulosic material. In this experiment, the cellulosic material studied was biomass, specifically maple sawdust. In Figure 10, the samples are designated Sample #1, Sample #2, and Sample #3. Each of Sample #1, Sample #2, and Sample #3 consisted of 1 gram (g) of dry maple sawdust. The diagram **1000** illustrates three experimental pathways **1002, 1004** and **1006** to which the three separate but identical samples of maple sawdust were respectively subjected. In the experimental pathways **1002, 1004** and **1006**, Sample #1, Sample #2, and Sample #3 were respectively subjected to a conventional, relatively dilute acid hydrolysis process, at block **1022**. Each hydrolysis process **1022** entailed placing Sample #1, Sample #2, or Sample #3 in a respective glass container containing a 19 mL mixture of 0.5-M H_2SO_4 (sulfuric acid) and water. An identical container was employed for each of Sample #1, Sample #2, and Sample #3. For each hydrolysis process **1022**, the mixture, including the acid, water, and Sample #1, Sample #2, or Sample #3, was heated at 100 °C for 75 minutes. Thereafter, at block **1024**, the respective hydrolyzate sugar solutions were removed from each of Sample #1, Sample #2, and Sample #3 for analysis. As expected, the data (e.g., glucose and xylose concentrations) from this analysis was essentially identical for each of Sample #1, Sample #2, and Sample #3. The portions of Sample #1, Sample #2, and Sample #3 not affected by the initial hydrolysis process **1022**, designated sample portions **1032, 1034** and **1036**, respectively, were subjected to further experimental processing as described below.

[099] Experiment **1002** was carried out to determine the effect of temperature on the process being studied in comparison to AP plasma treatment. Accordingly, after the initial hydrolysis process **1022**, the sample portion **1032** was then subjected to an oven treatment at block **1042**. Specifically, the sample portion **1032** was placed in a laboratory oven and baked at 100 °C and ambient pressure for 20 minutes, yielding an oven-treated sample portion **1044**. Experiment **1004** was continued under comparable thermal and temporal conditions by subjecting the sample portion **1032** to an AP plasma treatment **1052** for 20 minutes, yielding a plasma-treated sample portion **1054**. The AP plasma treatment **1052** was implemented by utilizing an apparatus similar to the apparatus **500** described above and illustrated in Figure 5. The working gases employed to generate and maintain the plasma were oxygen (O_2), helium (He) and neon (Ne). Experiment **1006** served as a control and therefore the sample portion **1036** was not subjected to any type of treatment other than hydrolysis.

[0100] Subsequently, in each of experimental pathways **1002**, **1004** and **1006**, the oven-treated sample portion **1044**, plasma-treated sample portion **1054**, and untreated control sample portion **1036** were respectively subjected to a second conventional, relatively concentrated acid hydrolysis process, at block **1062**. Each hydrolysis process **1062** entailed placing the oven-treated sample portion **1044**, plasma-treated sample portion **1054**, or untreated control sample portion **1036** in a respective glass container containing a 19 mL mixture of 1.0-M H_2SO_4 and water. An identical container was employed for each of the oven-treated sample portion **1044**, plasma-treated sample portion **1054**, and untreated control sample portion **1036**. For each hydrolysis process **1062**, the mixture, including the acid, water, and the oven-treated sample portion **1044**, plasma-treated sample portion **1054**, or untreated control sample portion **1036**, was heated at 100 °C for 75 minutes. Thereafter, at block **1064**, the respective hydrolyzate sugar solutions were removed from each of the oven-treated sample portion **1044**, plasma-treated sample portion **1054**, and untreated control sample portion **1036** for analysis.

[0101] The six sugar solutions (derived from Sample #1, Sample #2, and Sample #3 and the two hydrolysis stages **1022** and **1062**) were analyzed by an employing HPLC (high-performance liquid chromatography) technique, with particular emphasis on measuring the glucose and xylose concentrations of the sugar solutions. Figure 11 illustrates data acquired from this analysis. In Figure 11, the ordinate values represent sugar concentration (in μg/mL

solution), and three pairs of bars are presented along the abscissa. The first pair corresponds to experimental pathway **1002** (oven treatment **1042** in Figure 10), the second pair corresponds to experimental pathway **1004** (AP plasma treatment **1052** in Figure 10), and the third pair corresponds to experimental pathway **1006** (control). For each pair, the left bar depicts glucose concentration and the right bar depicts xylose concentration. It will be noted that data obtained from the first-stage hydrolysis process **1022** (Figure 10) was omitted due to the identical nature of each sample resulting from that stage. It was determined that sugar concentrations in liquid obtained from the second-stage hydrolysis process **1062** (Figure 10) would adequately provide good indications of the effect each experiment **1002, 1004** and **1006** had on the maple sawdust Samples #1, #2 and #3.

[0102] It can be seen from Figure 11 that Sample #2, the plasma-treated sample, produced significantly higher concentrations of both glucose and xylose as compared to that of Sample #1 (oven-treated sample) and Sample #3 (control sample). The AP treatment showed improvement in xylose and glucose concentrations of approximately 80% ((0.92 – 0.51)/0.51) and 88% ((0.30 – 0.16)/0.16), respectively, when compared to the closest data of the other two experiments. In view of the foregoing, Figures 10 and 11 demonstrate that AP plasma treatment of maple sawdust provides an improvement over current practices of acid hydrolysis treatment.

[0103] EXAMPLE 2

[0104] This experiment utilized the reduction of potassium permanganate ($KMnO_4$) with glucose as a purple-pink indicator in conjunction with acid hydrolysis of pure cellulose. Deep purple-colored permanganate (MnO_4^-) can be reduced to the faintly pink Mn^{+2} cation in an acidic solution, where Mn is in a +2 oxidation state, as represented by the following stoichiometric expression:

[0105] $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O$.

[0106] The permanganate reacts with the glucose in solution, so as the process of acid hydrolysis is breaking down the cellulose into glucose, the permanganate is consumed, thus precipitating the loss of the purple or pink color over time. The amount of time required for the solution to lose its color indicates how effective the acid hydrolysis process is at breaking down the cellulose. Therefore, the effectiveness of AP plasma treatment as a precursor to

acid hydrolysis will be indicated in the case where the permanganate/glucose reactions of plasma-treated samples run to completion faster than those of untreated cellulose.

[0107] In this experiment, two plastic wafer holders were employed as containers and configured to hold eight individual samples of pure cellulose such that each sample was isolated from the other seven samples. Figure 12 is a top plan view of one of the containers **1200**. The container **1200** includes eight individual samples **1204** physically separated by gaps **1208** that radially extend from the center **1212** of the container **1200** to its peripheral region **1214**, at equal angles to each other, such that the samples **1204** have the appearance of pie slices in Figure 12. Sixteen 0.25-g samples of pure cellulose were prepared for treatment by an AP plasma apparatus, similar to the apparatus **500** described above and illustrated in Figure 5, by placing each sample **1204** in the container **1200** and separated from the other samples **1204** in the manner illustrated in Figure 12 Two containers **1200** were employed, each holding eight samples **1204**. Four more 0.25-g samples of pure cellulose were prepared as controls for the experiment.

[0108] The first container **1200** of eight samples **1204** was placed into the AP plasma apparatus, which was then closed off. The background gas for the plasma was water-saturated helium. Specifically, a He gas line routed to the AP plasma apparatus was opened and allowed to bubble (percolate) through deionized (DI) water to produce a constant He/H_2O vapor gas flow. The gas lines and chamber of the AP plasma apparatus were allowed to purge for five to eight minutes. Once the system had purged, the voltage source of the AP plasma apparatus was engaged, thereby producing a pink-purple plasma. The samples **1204** were treated by the plasma generated in the AP plasma apparatus for five minutes. The container **1200** was then removed from the chamber and four of the eight samples **1204** were transferred into four other individual containers for subsequent hydrolysis. The AP plasma apparatus was prepared again in the same way as before, and the four remaining samples were treated for five more minutes, and thus for a total of ten minutes. This procedure was performed again for another eight samples, four of which were treated for twenty minutes and the other four for thirty minutes.

[0109] All plasma-treated samples were then subjected to dilute-acid hydrolysis, employing 1M H_2SO_4 (diluted from 18M H_2SO_4). After hydrolysis of the samples was completed, the effectiveness of the AP plasma treatment as an enhancement to the hydrolysis

was analyzed according to the following procedure. Each 0.25-g sample was placed in a 100-mL round-bottom flask and 10 mL of tap water was added. The flask was then held in a boiling water bath (100 °C) by a ring stand, and a magnetic stir bar was operated to ensure proper mixing throughout the experiment. Five mL of 1M H_2SO_4 was added, followed by 2 mL of $KMnO_4$ ($0.4g_{KMnO4}$ / L_{H20} concentration). As soon as the permanganate was added, a timer was started. The reaction was allowed to run until the solution lost all of the pink color, at which point the timer was stopped. The flask and stir bar were thoroughly washed and the experiment was then repeated for the remaining samples.

[0110] The TABLE below tabulates the reaction times for each sample (20 total) with H_2SO_4 ans $KMnO_4$. The row of the TABLE providing the data for zero-minute treatment times corresponds to the untreated control samples. There appeared to be some degree of variation with the reaction times, which was determined to be due to the error involved in "eyeballing" when exactly the solutions lose all their color. However, the TABLE evidences that the times required for each reaction to run to completion were consistently shorter for all plasma-treated samples when compared to the untreated samples.

[0111] TABLE

Treatment Time	1st Run	2nd Run	3rd Run	4th Run
0 Min	1:43	1:35	1:32	1:22
5 min	0:50	1:04	1:15	0:56
10 min	1:12	1:15	1:17	1:03
20 min	1:01	0:57	0:49	0:49
30 min	0:54	0:43	0:51	0:50

[0112] The consistency of the shorter reaction times for treated samples indicates that the AP plasma treatment of the cellulose facilitates the hydrolysis of cellulose into glucose.

[0113] EXAMPLE 3

[0114] This experiment was conducted to determine whether AP plasma treatment itself was capable of producing glucose from cellulose. Three samples of pure cellulose were provided, weighing 225.1 mg, 231 mg and 226.9 mg, respectively. Each sample was dried in a vacuum oven under 30 mm Hg of pressure at a temperature of 110 °C for two and one half hours. This allowed for full evaporation of the water in the cellulose, using knowledge

gained from previous experiments that determined the time to dry 200 mg of cellulose was approximately one hour. After the drying cycle, the dry weights of the three samples were measured to be 203, 210.9 and 206.9 mg, respectively. Each sample was then treated by AP plasma by placing the sample in an AP plasma apparatus, similar to the apparatus **500** described above and illustrated in Figure 5, and exposing the sample to a plasma generated by the AP plasma apparatus. The AP plasma apparatus was operated at a voltage of 5 kV and a current of 50 mA. Alumina dielectrics were employed between the two electrodes of the apparatus, and were spaced apart by a one-inch gap. The plasma medium was water vapor in helium, similar to that described above in connection with EXAMPLE 2. The three samples were plasma-treated for ten, twenty and thirty minutes, respectively.

[0115] During the plasma treatments, the three samples were analyzed with an optical spectrometer that was integrated with the AP plasma apparatus. Peak emissions were observed at 309.56-314.92 (molecular peak), 336.48, 353.64, 357.69, 380.43, 389.13, 587.84, 656.36, 667.90, 706.72, and 728.22 nm.

[0116] After the plasma treatments, the three samples were then placed into respective 100-mL beakers with 50 mL of DI water. Using a hotplate and magnetic stir bars, the three samples were boiled and stirred in the beakers for one hour. This step was completed to ensure that if glucose was produced by the AP plasma treatment, then the glucose would dissolve in the water leaving behind only the cellulose not converted by the plasma treatment. After the boiling/stirring cycle, the solutions of the three samples were each separated from the unconverted residual material by employing a syringe with a 1-micron filter paper.

[0117] After separation, the three samples were placed into the vacuum oven under the same conditions described above prior to the AP plasma treatment. After two hours of drying, the dry weights of the treated samples were found to be 188.3, 193.4 and 190.0 mg for the 10-min, 20-min and 30-min treatments, respectively. These weights represent the amount of cellulose not converted by the AP plasma treatment for each sample. By taking the original, pre-treatment dry weights and subtracting the post-treatment dry weights for each sample, it was determined that the amounts of glucose produced as a result of the AP plasma treatment were 14.7, 17.6 and 15.2 mg, respectively. This demonstrates 7.2%, 8.3% and 7.4% conversion of cellulose to glucose for the 10-min, 20-min and 30-min treatments, respectively. Therefore, the foregoing data indicate that the AP plasma treatment itself is

capable of releasing glucose from cellulose, without the use of conventional techniques such as hydrolysis, and further demonstrates the ability of AP plasma treatment to promote conversion of cellulose and cellulose-containing materials to alcohol.

[0118] The foregoing results of the EXAMPLES are significant as they relate to the long felt need related to economic and ecological aspects of this invention. Fewer steps are required, and expensive acids, high temperatures, high pressures, and costly enzymes are bypassed by providing a direct pathway to the sugars through plasma-enhanced soft degradation as taught in the present disclosure.

[0119] While the foregoing disclosure has focused primarily on the treatment of cellulose, the invention may also be applicable to the treatment of starch. As readily appreciated by persons skilled in the art, starch is a water-insoluble, complex carbohydrate containing around 2500 glucose monomer units. In general, starches have the formula $(C_6H_{10}O_5)n$, where "n" denotes the total number of glucose monomer units. More specifically, starch is a combination of the two polysaccharides amylose and amylopectin. Amylose constitutes a straight chain of glucose units joined to one another by α-1,4 linkages. Amylopectin, on the other hand, includes branches, with an α-1,6 linkage every 24-30 glucose units. That is, starch forms clusters of linked linear polymers, where the α-1,4 linked chains form columns of glucose units which branch regularly at the α-1,6 links. As previously noted, a starch molecule as a result has a coiled conformation unlike a straight-chain cellulose molecule. Starches can be digested by hydrolysis into simpler saccharide units. The hydrolysis may be catalyzed by enzymes known as amylases, which break the glycosidic bonds between the α-glucose components of the starch polysaccharide molecule.

[0120] The foregoing description of implementations has been presented for purposes of illustration and description. It is not exhaustive and does not limit the claimed inventions to the precise form disclosed. Modifications and variations are possible in light of the above description or may be acquired from practicing the invention. The claims and their equivalents define the scope of the invention.

CLAIMS

What is claimed is:

1. A method for treating a cellulosic material, comprising subjecting the cellulosic material to an atmospheric-pressure plasma to produce a plasma-treated cellulosic material.

2. The method of claim 1, wherein subjecting includes introducing the cellulosic material to a plasma-generating apparatus, and operating the apparatus to generate the atmospheric-pressure plasma from a plasma medium present in the apparatus.

3. The method of claim 2, wherein operating the apparatus includes operating a plasma-generating apparatus selected from the group consisting of a dielectric barrier discharge apparatus, a microplasma-generating apparatus, a plasma-generating apparatus including a parallel-plate configuration, a plasma-generating apparatus including a drop-tube configuration, a plasma-generating apparatus including a fluidized-bed configuration, a plasma-generating apparatus including a liquid-bath configuration, and a plasma-generating apparatus including a plasma-jet configuration.

4. The method of claim 2, wherein the atmospheric-pressure plasma is generated from a plasma medium selected from the group consisting of air, oxygen, hydrogen, helium, water-saturated helium, neon, argon, and combinations of two or more of the foregoing.

5. The method of claim 1, wherein the plasma-treated cellulosic material includes one or more degraded species.

6. The method of claim 5, wherein the one or more degraded species include one or more sugars.

7. The method of claim 6, wherein the one or more sugars include glucose.

8. The method of claim 5, further including separating one or more of the degraded species from a remaining portion of the plasma-treated cellulosic material.

9. The method of claim 1, further including fermenting one or more components of the plasma-treated cellulosic material.

10. The method of claim 9, wherein fermenting includes allowing the one or more components to interact with one or more fermentative enzymes at a temperature at which the one or more enzymes exhibit fermenting activity.

11. The method of claim 10, wherein the one or more enzymes include microorganisms.

12. The method of claim 10, wherein the one or more enzymes include yeast.

13. The method of claim 9, wherein fermenting produces a fermentation product including an organic compound.

14. The method of claim 13, wherein the organic compound includes an alcohol.

15. The method of claim 14, wherein the alcohol includes ethanol.

16. The method of claim 1, further including subjecting the cellulosic material to an additional treatment process selected from the group consisting of comminution, steam explosion, hydrothermolysis, acid addition, alkali addition, solvent addition, ammonia addition, wet oxidation, ammonia fiber/freeze explosion (AFEX), ammonia recycled percolation (ARP), hydrolysis, acid-assisted hydrolysis, enzyme-assisted hydrolysis, and combinations of two or more of the foregoing.

17. A sugar produced according to the method of claim 1.

18. The sugar of claim 17, wherein the sugar includes glucose.

19. A fermentation product produced by fermenting one or more components of a cellulosic material treated according to the method of claim 1.

20. The fermentation product of claim 19, wherein the fermentation product includes an organic compound.

21. The fermentation product of claim 20, wherein the organic compound includes ethanol.

22. A method for treating a cellulosic material, comprising:

subjecting the cellulosic material to an atmospheric-pressure plasma to produce a plasma-treated cellulosic material; and

subjecting one or more components of the plasma-treated cellulosic material to a degradation process to produce a degradation-processed cellulosic material.

23. The method of claim 22, wherein subjecting the cellulosic material to the atmospheric-pressure plasma includes introducing the cellulosic material to a plasma-generating apparatus, and operating the apparatus to generate the atmospheric-pressure plasma from a plasma medium present in the apparatus.

24. The method of claim 22, wherein the plasma-treated cellulosic material includes one or more degraded species.

25. The method of claim 24, further including separating one or more of the degraded species from a remaining portion of the plasma-treated cellulosic material, wherein the remaining portion includes the one or more components of the plasma-treated cellulosic material subjected to the degradation process.

26. The method of claim 24, further including fermenting one or more components of the degraded species.

27. The method of claim 26, wherein fermenting produces a fermentation product including ethanol.

28. The method of claim 22, wherein subjecting the one or more components of the plasma-treated cellulosic material to the degradation process includes performing hydrolysis.

29. The method of claim 28, wherein performing hydrolysis includes performing acid hydrolysis.

30. The method of claim 29, wherein performing acid hydrolysis includes combining the one or more components of the plasma-treated cellulosic material with a liquid and an acidic component, at a temperature sufficient for the acidic component to catalyze hydrolysis.

31. The method of claim 30, wherein the acidic component is selected from the group consisting of mineral acids, acidic salts and combinations of the foregoing.

32. The method of claim 28, wherein performing hydrolysis includes performing enzymatic hydrolysis.

33. The method of claim 32, wherein performing enzymatic hydrolysis includes combining the one or more components of the plasma-treated cellulosic material with a liquid and an enzyme, at a temperature sufficient for the enzyme to catalyze hydrolysis.

34. The method of claim 33, wherein the enzyme is selected from the group consisting of cellulases, hemicellulases, and combinations of the foregoing.

35. The method of claim 22, wherein the degradation-processed cellulosic material includes one or more monomeric sugars.

36. The method of claim 22, further including fermenting one or more components of the degradation-processed cellulosic material.

37. The method of claim 36, wherein fermenting produces a fermentation product including ethanol.

38. The method of claim 22, further including:

separating a first portion of the plasma-treated cellulosic material from a second portion of the plasma-treated cellulosic material, wherein the second portion includes the one or more components of the plasma-treated cellulosic material subjected to the degradation process;

fermenting one or more components of the first portion to produce a first fermentation product; and

fermenting one or more components of the degradation-processed cellulosic material to produce a second fermentation product.

39. The method of claim 38, wherein at least one of the first and second fermentation products includes ethanol.

40. The method of claim 38, wherein the one or more components of the first portion of the plasma-treated cellulosic material are fermented together with the one or more components of the degradation-processed cellulosic material.

41. The method of claim 22, further including subjecting the cellulosic material to an additional treatment process selected from the group consisting of comminution, steam explosion, hydrothermolysis, acid addition, alkali addition, solvent addition, ammonia fiber/freeze explosion (AFEX), ammonia recycled percolation (ARP), and combinations of two or more of the foregoing.

42. A method for treating a cellulosic material, comprising:

subjecting the cellulosic material to a first degradation process to produce a first degradation-processed cellulosic material;

subjecting one or more components of the first degradation-processed cellulosic material to an atmospheric-pressure plasma to produce a plasma-treated cellulosic material; and

subjecting one or more components of the plasma-treated cellulosic material to a second degradation process to produce a second degradation-processed cellulosic material.

43. The method of claim 42, wherein subjecting the one or more components of the first degradation-processed cellulosic material to the atmospheric-pressure plasma includes introducing the one or more components of the first degradation-processed cellulosic material to a plasma-generating apparatus, and operating the apparatus to generate the atmospheric-pressure plasma from a plasma medium present in the apparatus.

44. The method of claim 42, wherein at least one of the first and second degradation processes includes hydrolysis.

45. The method of claim 42, wherein subjecting the cellulosic material to the first degradation process includes performing a first hydrolysis, and subjecting the one or more components of the plasma-treated cellulosic material to the second degradation process includes performing a second hydrolysis.

46. The method of claim 45, wherein performing the first hydrolysis includes performing a first acid hydrolysis and performing the second hydrolysis includes performing a second acid hydrolysis.

47. The method of claim 46, wherein the first acid hydrolysis is performed at a lower acidic concentration than the second acid hydrolysis.

48. The method of claim 45, wherein performing the first hydrolysis includes performing an acid hydrolysis and performing the second hydrolysis includes performing an enzymatic hydrolysis.

49. The method of claim 45, wherein performing the first hydrolysis includes performing an enzymatic hydrolysis and performing the second hydrolysis includes performing an acid hydrolysis.

50. The method of claim 42, wherein the first degradation-processed cellulosic material includes one or more monomeric sugars.

51. The method of claim 50, further including fermenting one or more of the monomeric sugars.

52. The method of claim 51, wherein fermenting produces a fermentation product including ethanol.

53. The method of claim 42, wherein the plasma-treated cellulosic material includes one or more monomeric sugars.

54. The method of claim 53, further including fermenting one or more of the monomeric sugars.

55. The method of claim 54, wherein fermenting produces a fermentation product including ethanol.

56. The method of claim 42, wherein the second degradation-processed cellulosic material includes one or more monomeric sugars.

57. The method of claim 56, further including fermenting one or more of the monomeric sugars.

58. The method of claim 57, wherein fermenting produces a fermentation product including ethanol.

59. The method of claim 42, wherein the first degradation-processed cellulosic material includes one or more monomeric sugars and the plasma-treated cellulosic material includes one or more monomeric sugars, and the method further includes fermenting the one or more monomeric sugars of the first degradation-processed cellulosic material, and fermenting the one or more monomeric sugars of the plasma-treated cellulosic material.

60. The method of claim 42, wherein the first degradation-processed cellulosic material includes one or more monomeric sugars, the plasma-treated cellulosic material includes one or more monomeric sugars, and the second degradation-processed cellulosic material includes one or more monomeric sugars, and the method further includes fermenting the one or more monomeric sugars of the first degradation-processed cellulosic material, fermenting the one or more monomeric sugars of the plasma-treated cellulosic material, and fermenting the one or more monomeric sugars of the second degradation-processed cellulosic material.

61. The method of claim 42, wherein the plasma-treated cellulosic material includes one or more monomeric sugars and the second degradation-processed cellulosic material includes one or more monomeric sugars, and the method further includes fermenting the one or more monomeric sugars of the plasma-treated cellulosic material, and fermenting the one or more monomeric sugars of the second degradation-processed cellulosic material.

62. The method of claim 61, wherein the one or more monomeric sugars of the plasma-treated cellulosic material are fermented together with the one or more monomeric sugars of the second degradation-processed cellulosic material.

63. The method of claim 42, wherein at least one of the first degradation-processed cellulosic material, the plasma-treated cellulosic material, and the second degradation-processed cellulosic material includes one or more monomeric sugars, and the method further

includes fermenting the one or more monomeric sugars to produce a fermentation product including ethanol.

64. The method of claim 42, further including subjecting the cellulosic material to an additional treatment process selected from the group consisting of comminution, steam explosion, hydrothermolysis, acid addition, alkali addition, solvent addition, ammonia fiber/freeze explosion (AFEX), ammonia recycled percolation (ARP), and combinations of two or more of the foregoing.

65. A method for treating a cellulosic material, comprising:
subjecting the cellulosic material to a pretreatment process;
subjecting the cellulosic material to an atmospheric-pressure plasma; and
subjecting the cellulosic material to a degradation process.

66. The method of claim 65, wherein subjecting the cellulosic material to the atmospheric-pressure plasma includes introducing the cellulosic material to a plasma-generating apparatus, and operating the apparatus to generate the atmospheric-pressure plasma from a plasma medium present in the apparatus.

67. The method of claim 65, wherein subjecting the cellulosic material to the pretreatment process produces a pretreated cellulosic material, and subjecting the cellulosic material to the atmospheric-pressure plasma occurs after the pretreatment process and includes subjecting one or more components of the pretreated cellulosic material to the atmospheric-pressure plasma.

68. The method of claim 65, wherein subjecting the cellulosic material to the atmospheric-pressure plasma produces a plasma-treated cellulosic material, and the pretreatment process occurs after producing the plasma-treated cellulosic material and includes subjecting one or more components of the plasma-treated cellulosic material to the pretreatment process.

69. The method of claim 65, wherein:

subjecting the cellulosic material to the atmospheric-pressure plasma includes subjecting the cellulosic material to at least a first plasma treatment and a subsequent second plasma treatment, the pretreatment process occurring between the first and second plasma treatments;

subjecting the cellulosic material to the first plasma treatment produces a first plasma-treated cellulosic material, and subjecting the cellulosic material to the pretreatment process includes subjecting one or more components of the first plasma-treated cellulosic material to the pretreatment process to produce a pretreated cellulosic material;

subjecting the cellulosic material to the second plasma treatment includes subjecting one or more components of the pretreated cellulosic material to the second plasma treatment to produce a second plasma-treated cellulosic material; and

subjecting the cellulosic material to the degradation process includes subjecting one or more components of the second plasma-treated cellulosic material to the degradation process.

70. The method of claim 65, wherein the pretreatment process is selected from the group consisting of comminution, steam explosion, hydrothermolysis, acid addition, alkali addition, solvent addition, ammonia fiber/freeze explosion (AFEX), ammonia recycled percolation (ARP), and combinations of two or more of the foregoing.

71. The method of claim 65, wherein subjecting the cellulosic material to an atmospheric-pressure plasma produces a plasma-treated cellulosic material, and the method further includes fermenting one or more components of the plasma-treated cellulosic material.

72. The method of claim 71, wherein fermenting produces a fermentation product including ethanol.

73. The method of claim 65, wherein subjecting the cellulosic material to a degradation process produces a degradation-processed cellulosic material, and the method further

includes fermenting one or more components of the degradation-processed cellulosic material.

74. The method of claim 73, wherein fermenting produces a fermentation product including ethanol.

75. The method of claim 65, wherein subjecting the cellulosic material to an atmospheric-pressure plasma produces a plasma-treated cellulosic material and subjecting the cellulosic material to a degradation process produces a degradation-processed cellulosic material, and the method further includes fermenting one or more components of the plasma-treated cellulosic material to produce a first fermentation product and fermenting one or more components of the degradation-processed cellulosic material to produce a second fermentation product.

76. The method of claim 75, wherein at least one of the first and second fermentation products includes ethanol.

77. A cellulosic material treatment apparatus, comprising:

a first electrode;

a second electrode;

means for providing a cellulosic material between the first and second electrodes; and

means for subjecting the cellulosic material to an atmospheric-pressure plasma between the first and second electrodes.

78. The cellulosic material treatment apparatus of claim 77, wherein the first electrode and the second electrode comprise an electrode arrangement selected from the group consisting of a first plate and a second plate spaced from the first plate, a first annular electrode and a second annular electrode coaxially disposed about a container, a first electrode disposed in a container and a second electrode coaxially disposed about the container, a first electrode and a second electrode spaced from the first electrode in a

container, and an elongated electrode and a hollow electrode coaxially disposed about the elongated electrode.

79. The cellulosic material treatment apparatus of claim 77, wherein the providing means is selected from the group consisting of a planar surface, a container, an enclosure having an opening, a flow-through conduit having an inlet and an outlet, a liquid-bath container, and a plasma-jet enclosure.

80. The cellulosic material treatment apparatus of claim 77, wherein the subjecting means includes a plasma-generating apparatus selected from the group consisting of a dielectric barrier discharge apparatus, a microplasma-generating apparatus, a plasma-generating apparatus including a parallel-plate configuration, a plasma-generating apparatus including a drop-tube configuration, a plasma-generating apparatus including a fluidized-bed configuration, a plasma-generating apparatus including a liquid-bath configuration, and a plasma-generating apparatus including a plasma-jet configuration.

81. The cellulosic material treatment apparatus of claim 77, wherein the subjecting means includes a plasma-generating apparatus utilizing a plasma medium selected from the group consisting of air, oxygen, hydrogen, helium, water-saturated helium, neon, argon, and combinations of two or more of the foregoing.

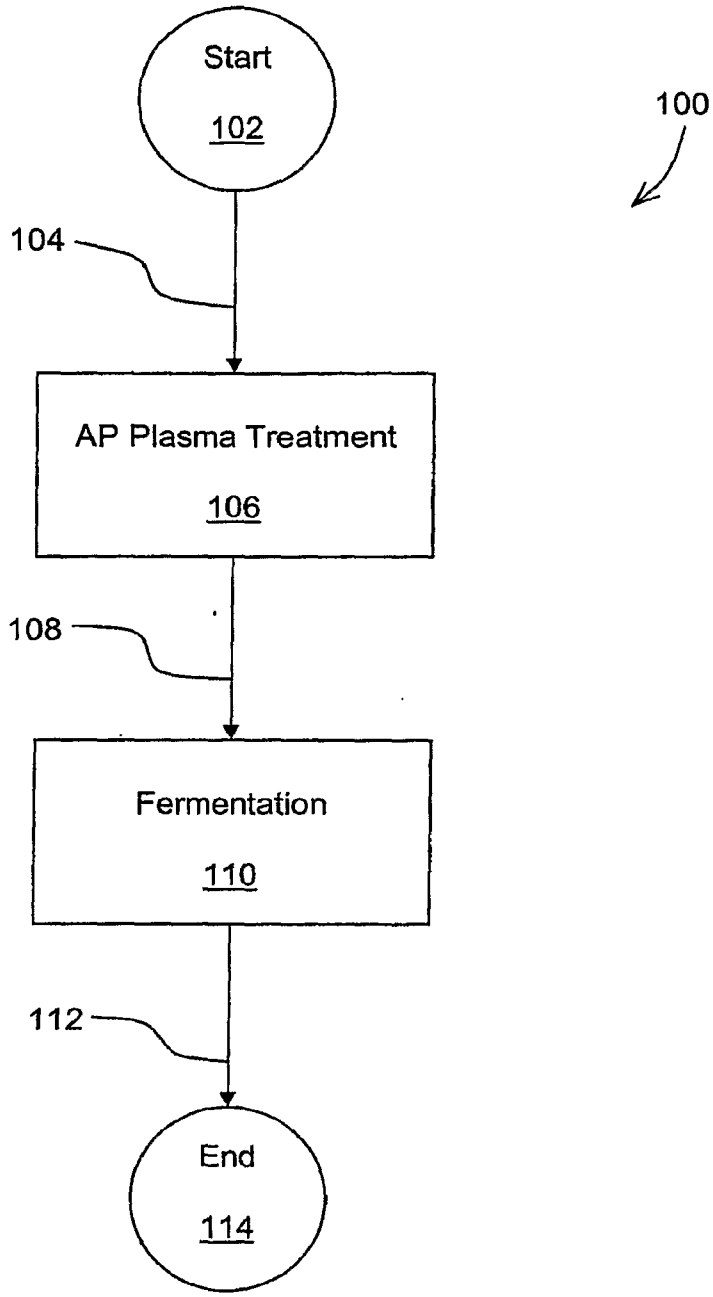

Start
102
100
104
AP Plasma Treatment
106
108
Fermentation
110
112
End
114

Fig. 1

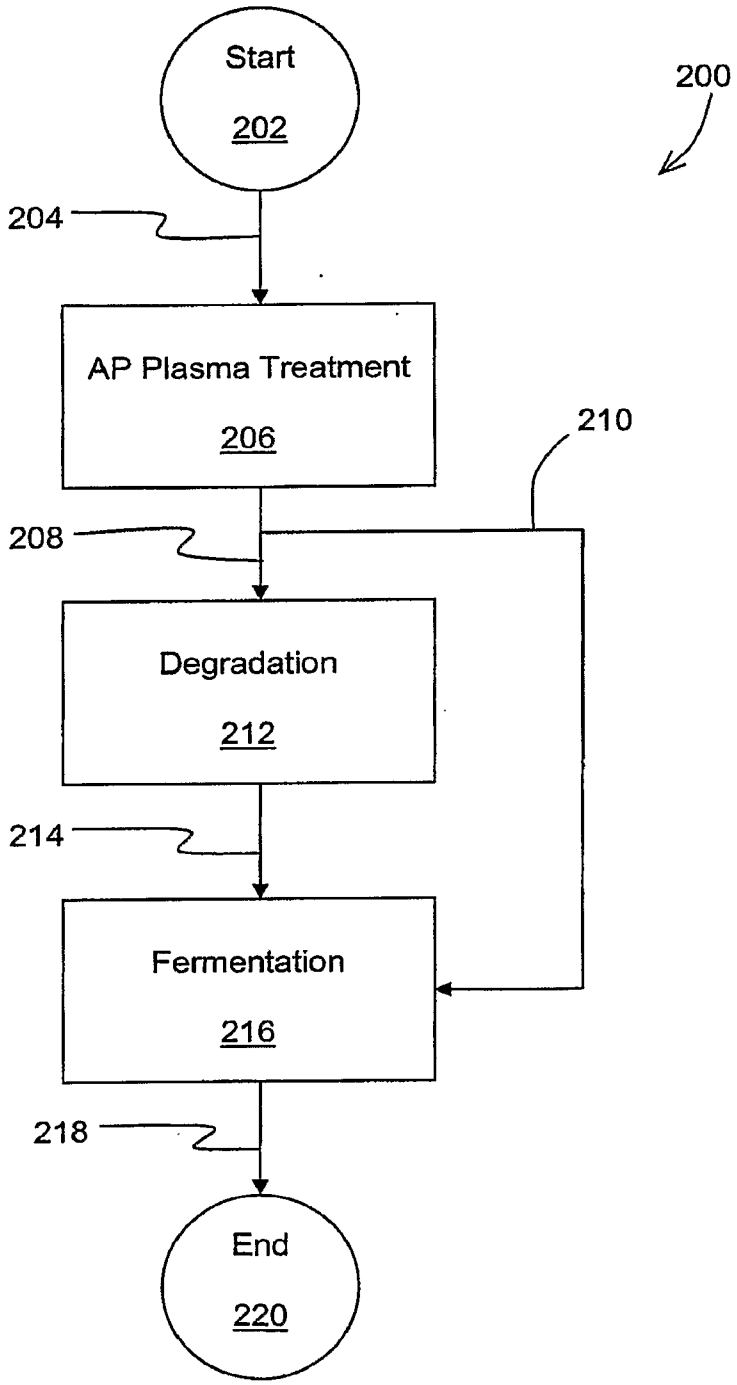

Start
202
200
204
AP Plasma Treatment
206
210
208
Degradation
212
214
Fermentation
216
218
End
220

Fig. 2

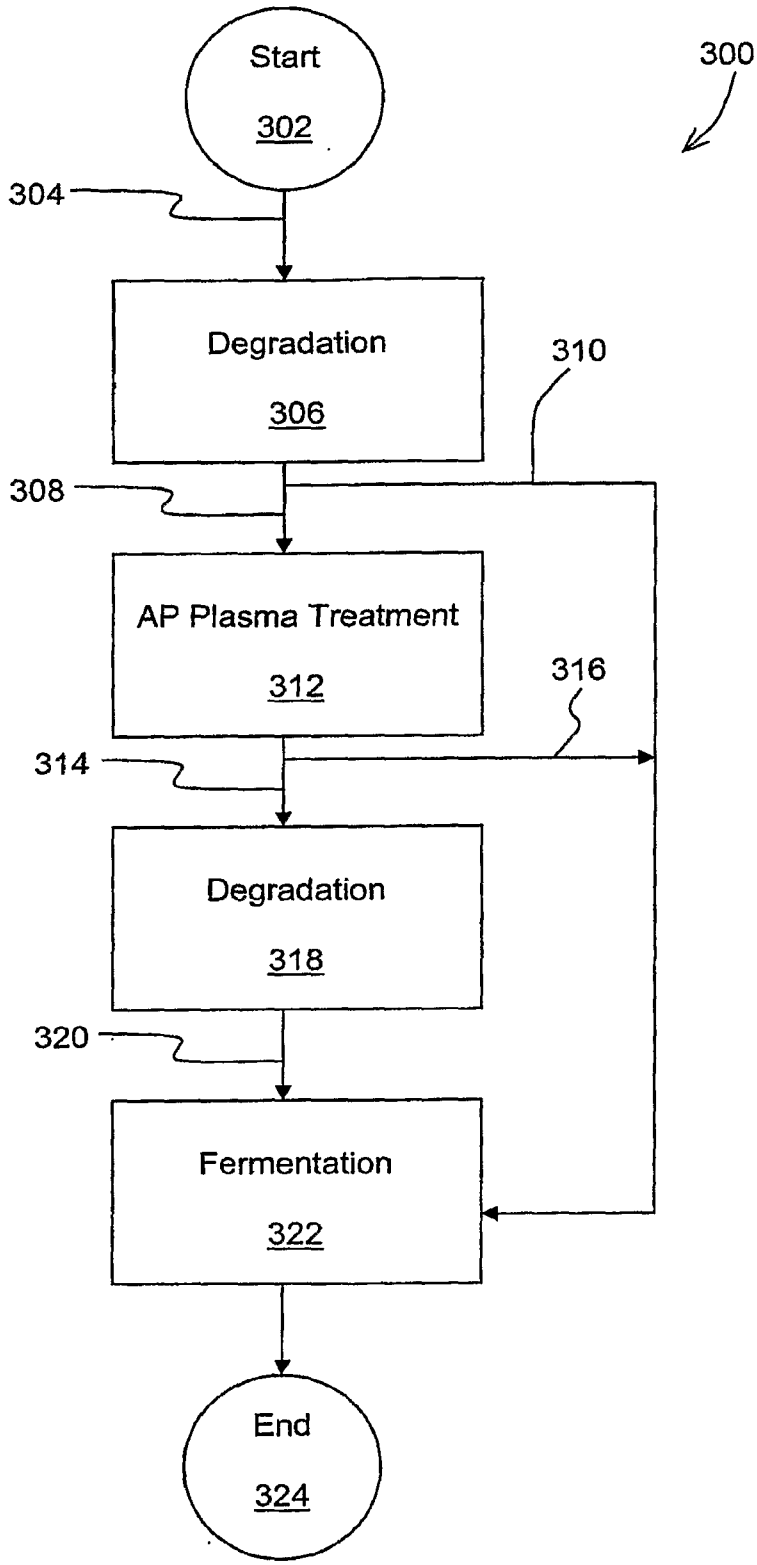

Start
302
300
304
Degradation
306
310
308
AP Plasma Treatment
312
316
314
Degradation
318
320
Fermentation
322
End
324

Fig. 3

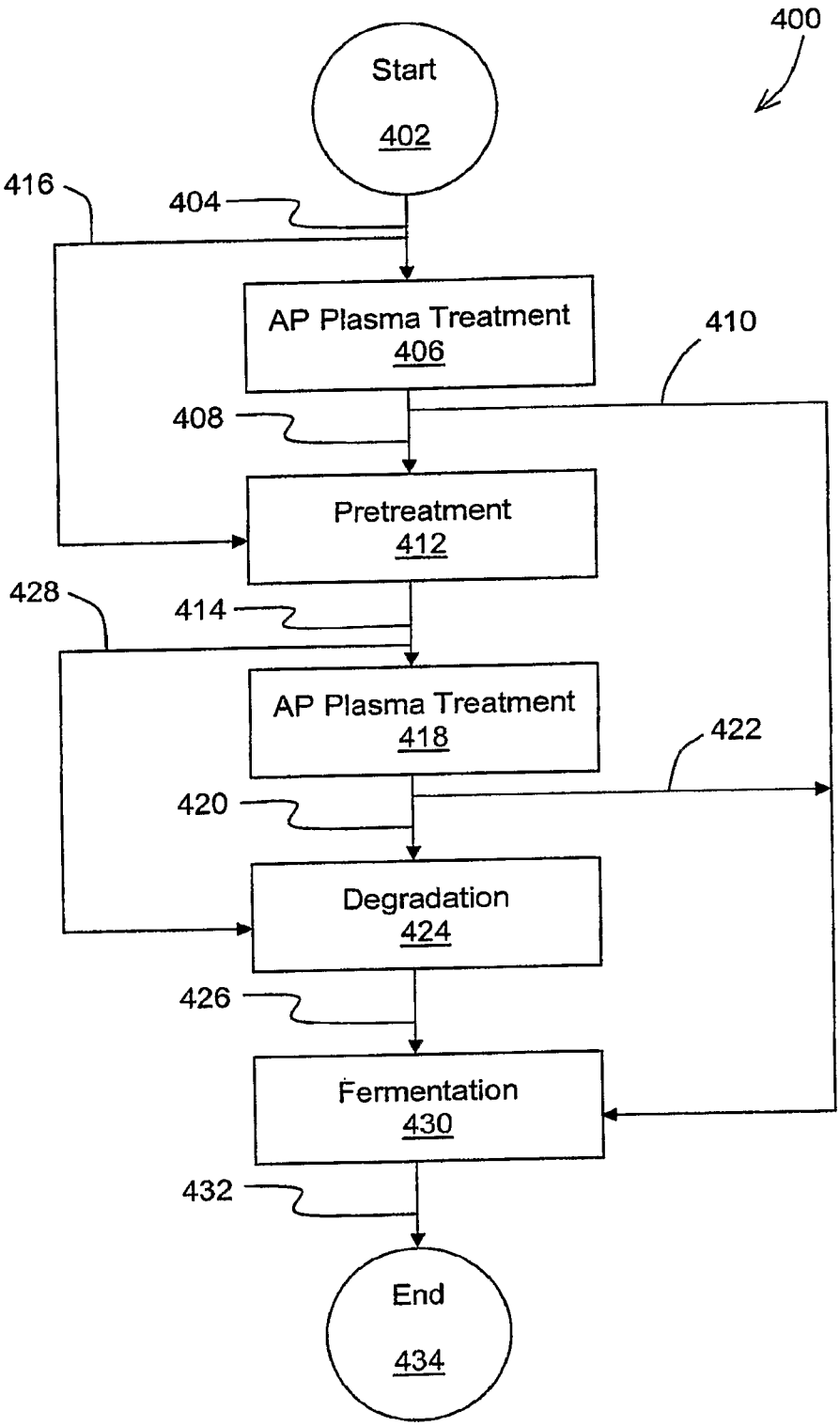

400
Start
402
416
404
AP Plasma Treatment
406
410
408
Pretreatment
412
428
414
AP Plasma Treatment
418
422
420
Degradation
424
426
Fermentation
430
432
End
434

Fig. 4

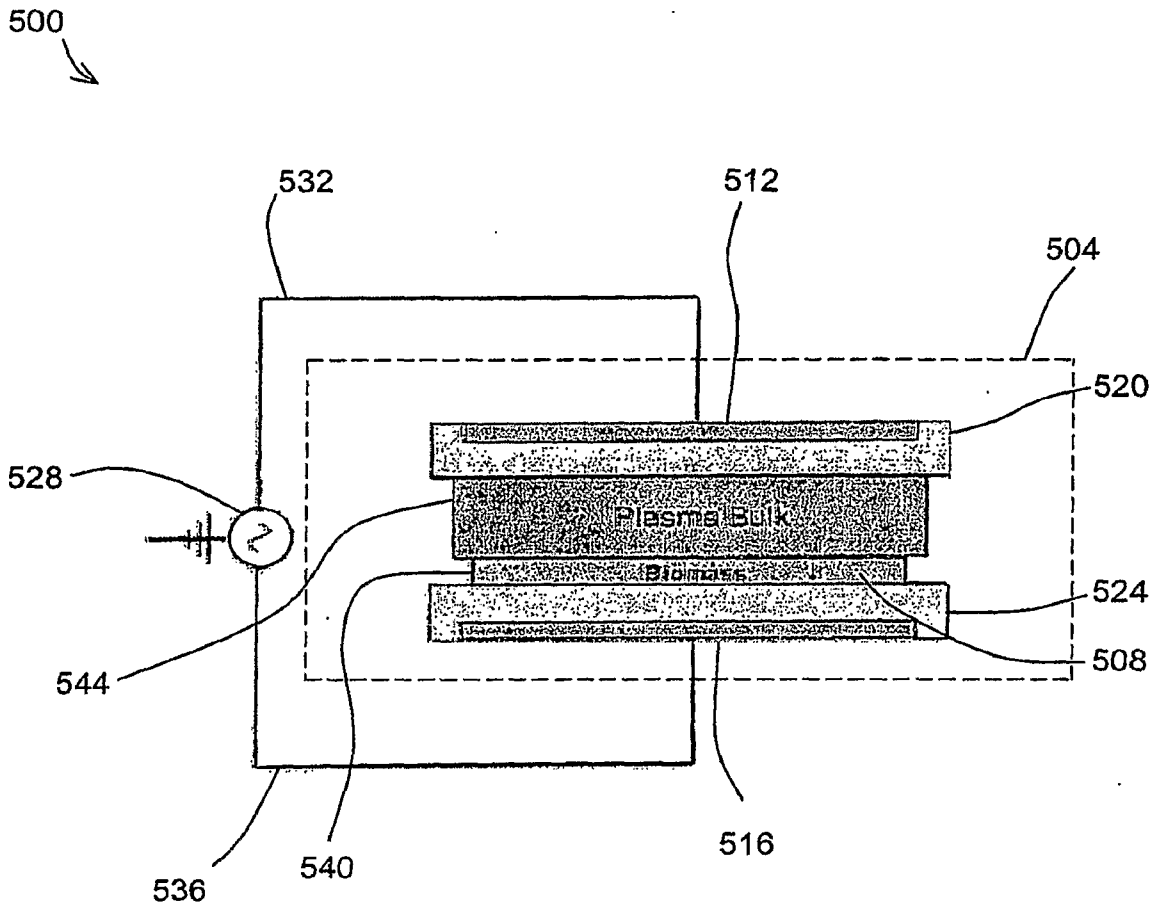


Fig. 5

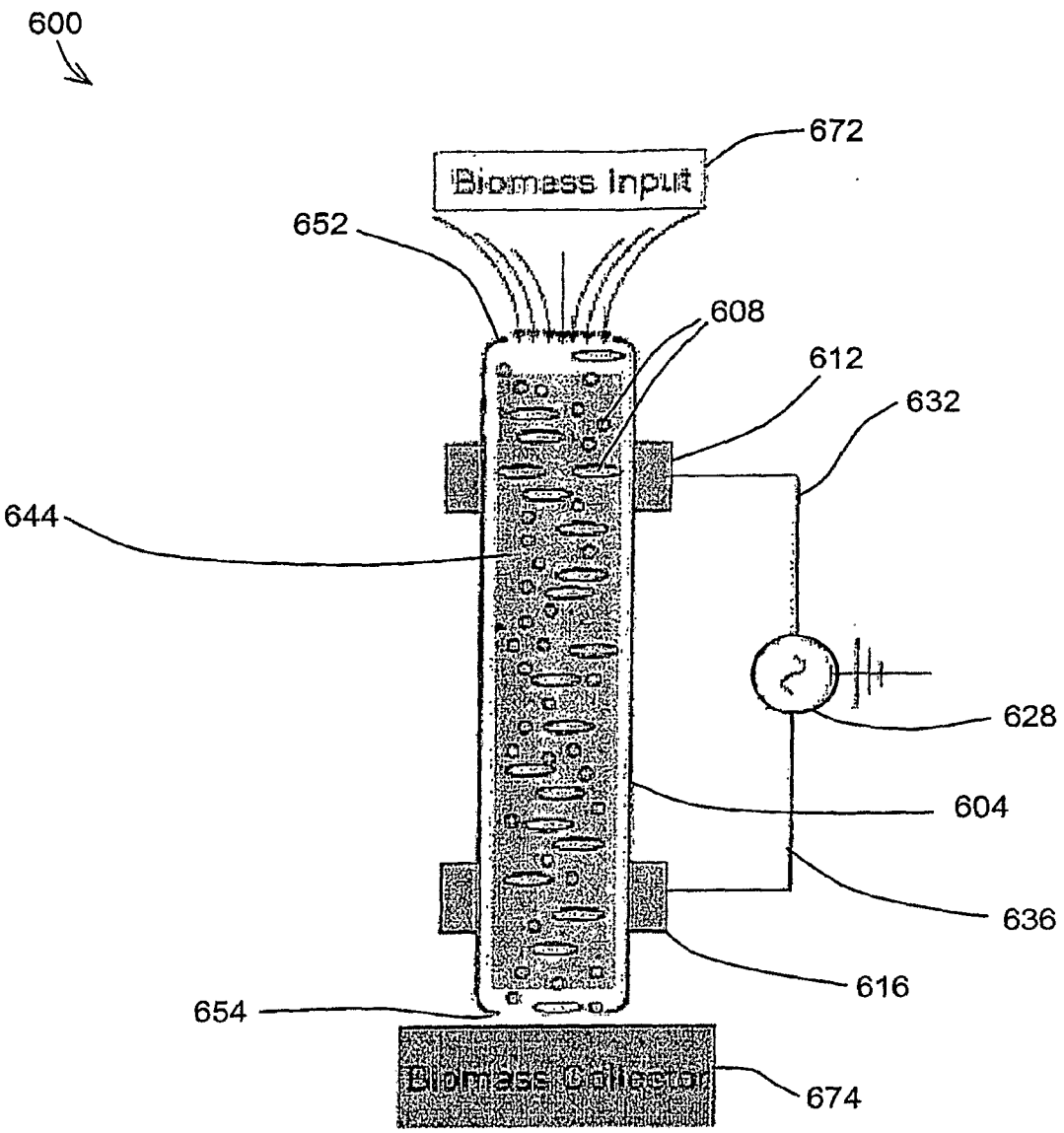

600
672
Biomass Input
652
608
612
632
644
628
604
636
616
654
Biomass Collector
674

Fig. 6

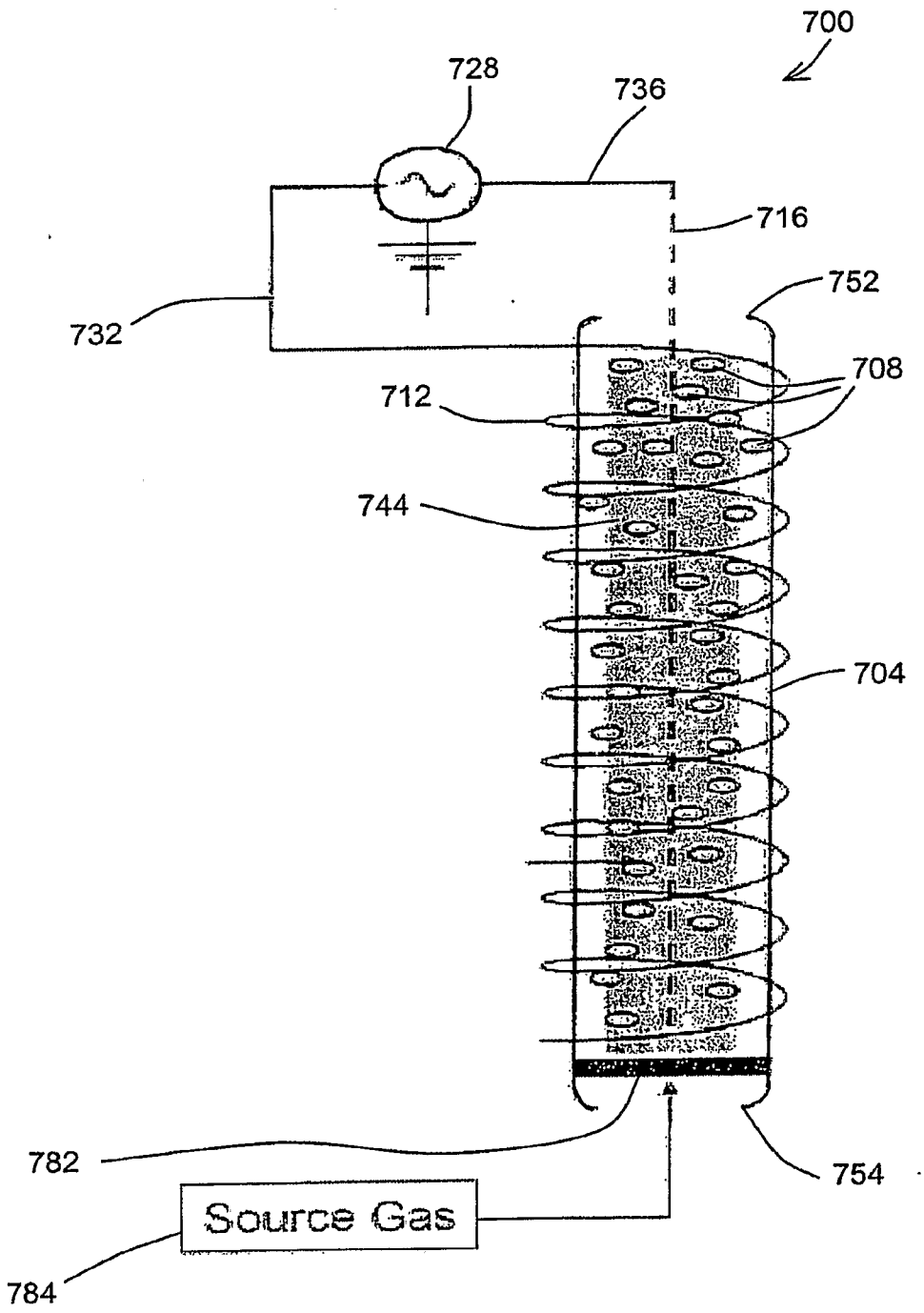


Fig. 7

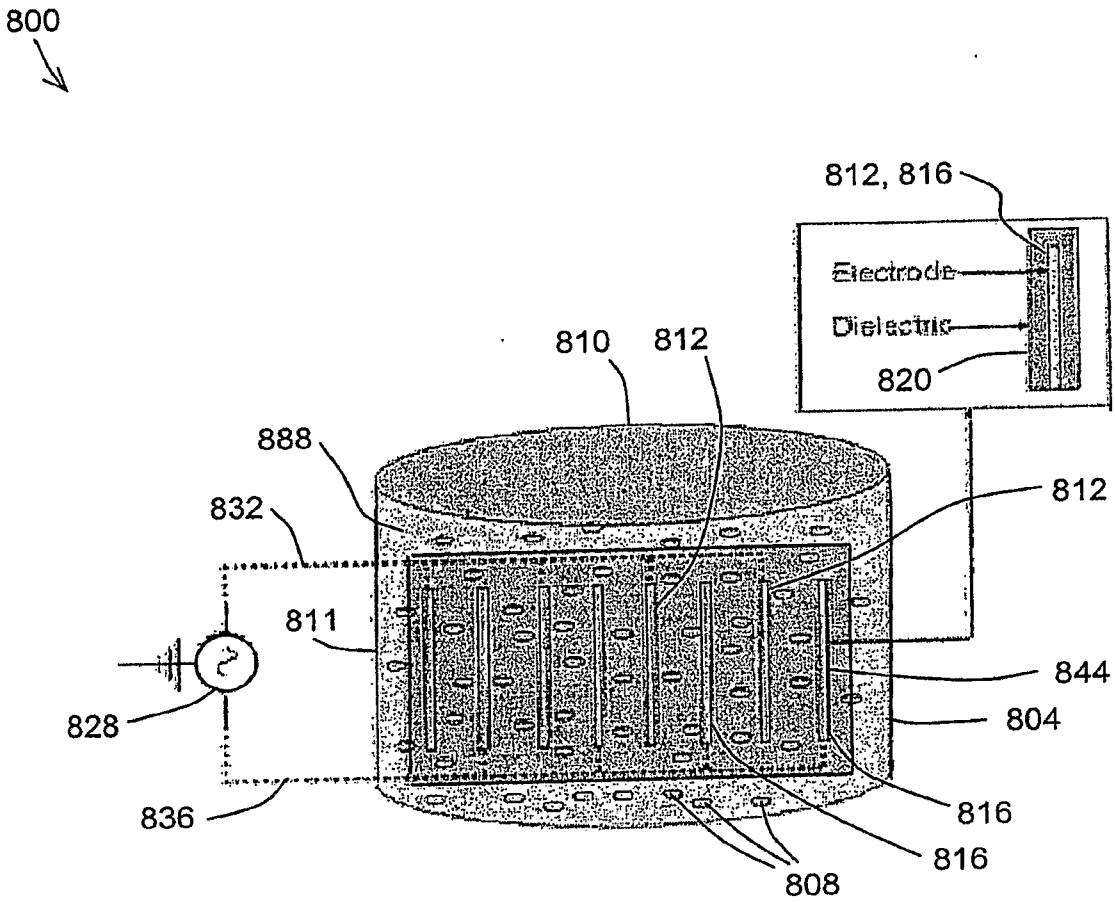

800
812, 816
Electrode
Dielectric
820
810
812
888
832
812
811
844
804
828
836
816
816
808

Fig. 8

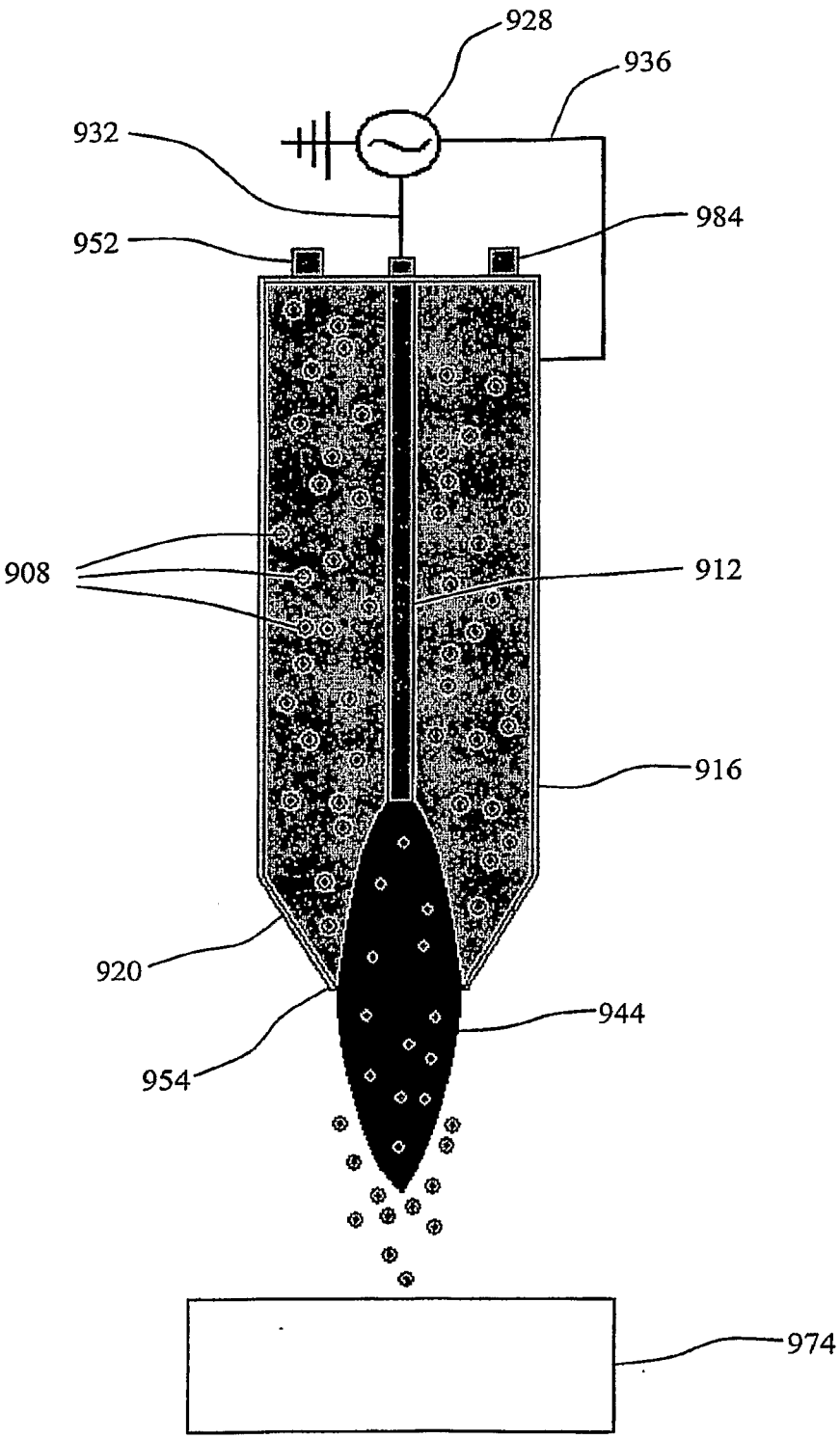


Fig. 9

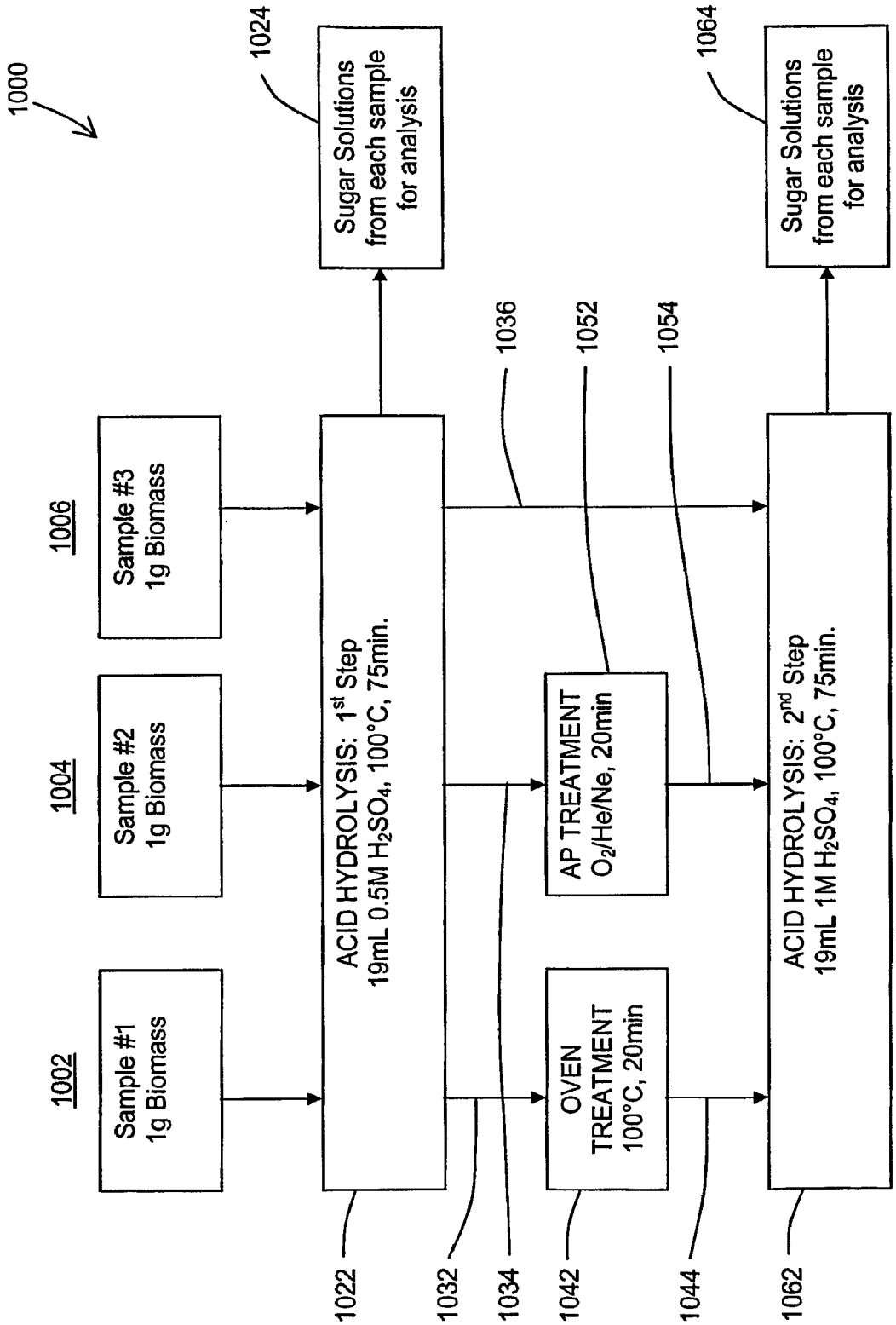

1000
1002
Sample #1
1g Biomass
1004
Sample #2
1g Biomass
1006
Sample #3
1g Biomass
ACID HYDROLYSIS: 1st Step
19mL 0.5M H2SO4, 100°C, 75min.
1022
1024
Sugar Solutions
from each sample
for analysis
1032
1034
1036
OVEN
TREATMENT
100°C, 20min
1042
AP TREATMENT
O2/He/Ne, 20min
1052
1044
1054
ACID HYDROLYSIS: 2nd Step
19mL 1M H2SO4, 100°C, 75min.
1062
1064
Sugar Solutions
from each sample
for analysis

FIG. 10

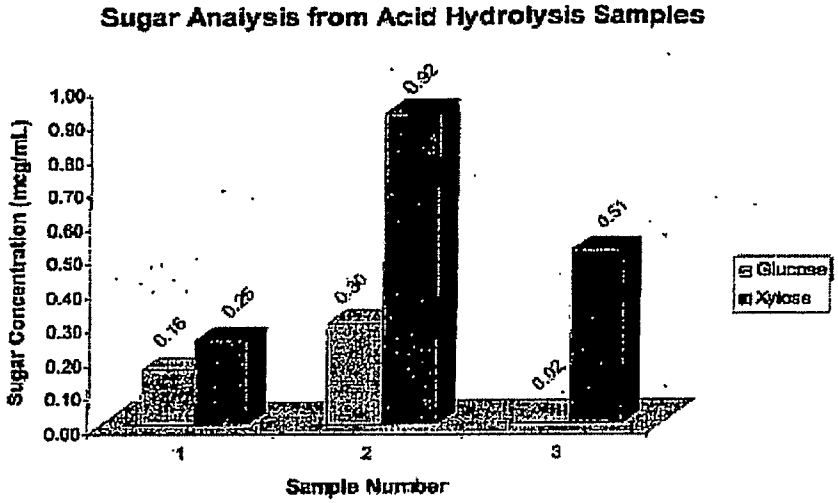

Sugar Analysis from Acid Hydrolysis Samples
Sugar Concentration (mg/mL)
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0.16
0.26
0.30
0.92
0.02
0.51
1
2
3
Sample Number
Glucose
Xylose

Fig. 11

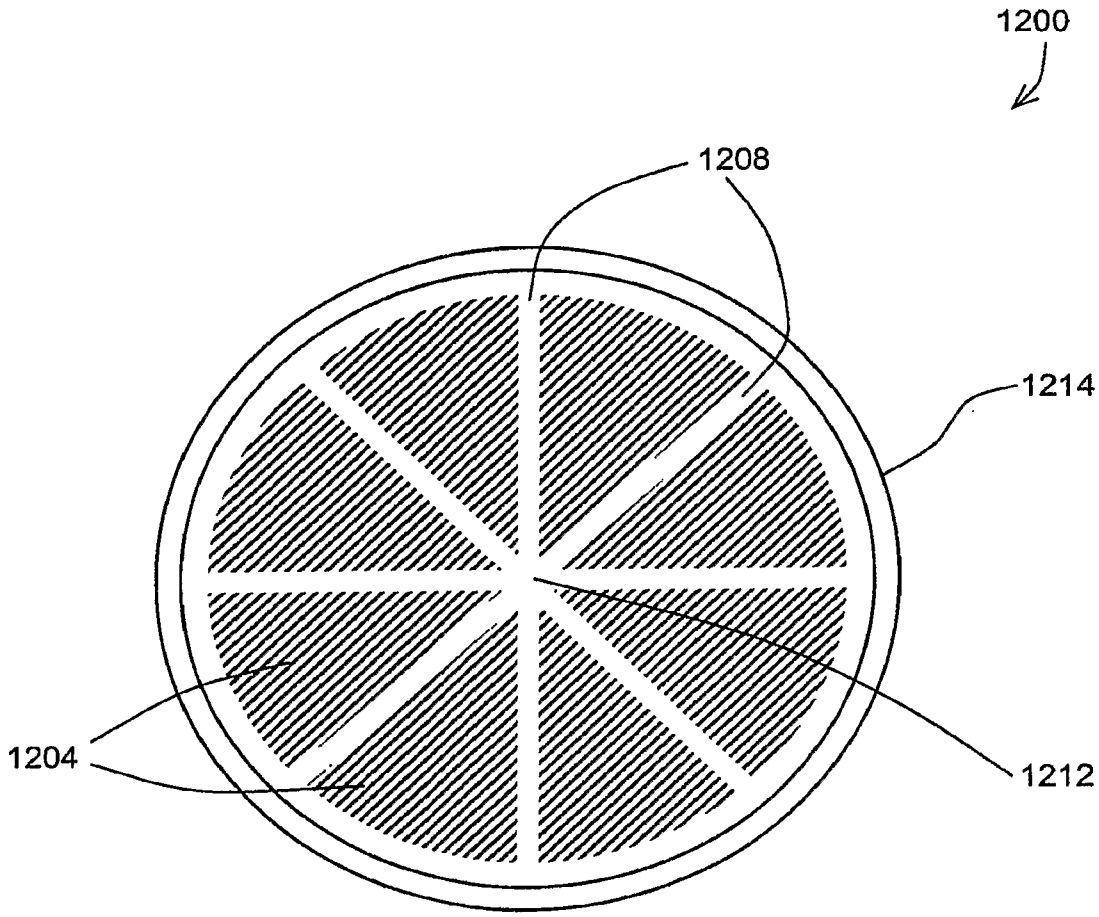


Fig. 12