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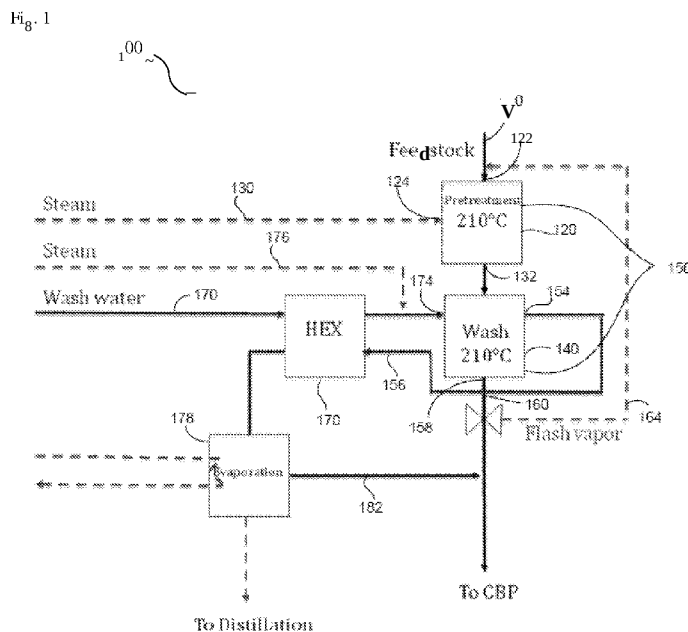
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(54) Title: SYSTEM AND METHOD FOR ENHANCING BIOMASS CONVERSION USING FLOW-THROUGH PRETREATMENT

(57) Abstract: A system and method are disclosed for pretreating biomass. High temperature flow-through pretreatment and an evaporation processes are used to provide digestible biomass for subsequent conversion to biofuels. Heat recycling helps reduce energy use in the processes.



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SYSTEM AND METHOD FOR ENHANCING BIOMASS CONVERSION USING FLOW-THROUGH PRETREATMENT

RELATED APPLICATION

[0001] This application claims priority of U. S. Provisional Application No. 61/579,968 filed on December 23, 2011, the content of which is hereby incorporated into this application by reference.

U.S. GOVERNMENT RIGHTS

[0002] This invention was made with government support under DE-AC05-00OR-22725 awarded by the Department of Energy. The government has certain rights in the invention.

BACKGROUND

I. Field of the Invention

[0003] This disclosure relates to treatment of biomass with a flow-through pretreatment process to enhance the conversion efficiency of biomass to biofuels.

II. Description of the Related Art

[0004] Fermentation derived fuels that come from plant biomass, including but not limited to ethanol, can be used as a substitute fuel for gasoline. While fermentation derived fuels are produced commercially today from the starch contained in grains such as corn and grain sorghum or from sugar rich feedstocks such as sugar cane or sugar beets, they can also be produced from lignocellulose, which is typically comprised primarily of cellulose, hemicellulose, and lignin. Cellulose is the main component of plant cell walls and is the most common organic compound on earth followed by hemicellulose. Making ethanol or other fermentation derived fuels from cellulose dramatically expands the types and amount of available material for fuel production while also providing a starting material with lower cost, and in many cases superior environmental performance, as compared to fermentation derived fuel produced from other sources. Examples of cellulosic materials include corn stover (stalks and leaves), rice straw, bagasse (residual fibrous stalks) from various plants, wood chips, fast-growing trees, grasses and recycled paper products.

[0005] Because cellulosic feedstocks are more difficult to convert into fermentable form than starch and sugar based feedstocks, the cellulosic biochemical conversion process requires additional steps. First, biomass may be subjected to a size reduction step to make it easier to handle and to make the ethanol production process more efficient. For example, agricultural residues go through a milling process and wood goes through a chipping process to decrease the particle size.

[0006] After the size reduction step, the biomass may then be subject to a pretreatment process. In this step, recalcitrant cellulosic fiber is converted into a form that is accessible to cellulase enzymes and/or cellulolytic microorganisms. There are a diversity of pretreatment processes described in the literature, and there is no complete, unified understanding of why various pretreatment processes are effective. In some but not all pretreatments, hemicellulose sugars are dissolved, yielding a mixture of five-carbon sugars, pentose sugars such as xylose and arabinose, and soluble six-carbon sugars, hexose sugars such as glucose, mannose and galactose, as well as soluble oligomers consisting of these compounds. Removal or redistribution of lignin (e.g. through dissolution and re-condensation) may also play a role. Cellulose is typically not solubilized to a significant extent during pretreatment.

[0007] Pretreated lignocellulose may be processed further to convert soluble oligomers to their monomeric components although this step is not necessary if either the pretreatment process produces primarily monomers or if the microbial system used for fermentation is capable of utilizing oligomers. After lignocellulose is pretreated to make lignocellulosic fiber accessible to cellulase enzymes and/or cellulolytic microbes, it is processed biologically. Four biologically mediated processes are involved: production of saccharolytic enzymes such as cellulases, solubilization of fiber into its component sugars as a result of the action of saccharolytic enzymes, fermentation of six-carbon sugars, and fermentation of five-carbon sugars. These processes may be combined and consolidated to varying degrees. When the four processing events are carried out in separate vessels, the biological processing is called separate hydrolysis and fermentation (SHF). Combining solubilization and hexose fermentation with separate steps for enzyme production and pentose fermentation is called simultaneous saccharification and fermentation (SSF). Combining solubilization with fermentation of both hexose and

pentose sugars with a separate step for enzyme production is referred to as simultaneous saccharification and cofermentation (SSCF). Combining all four biological processing events is called consolidated bioprocessing (CBP).

[0008] Yeast or bacteria may be employed in the fermentation processes to convert the sugars into ethanol or other fermentation derived fuels. Following fermentation, the ethanol or other fermentation derived fuel produced is separated from water by distillation or other separation processes.

[0009] Other components of the processed biomass also have utility. Lignin and other byproducts of the biomass conversion process can be used to produce other products, and lignin-rich process residues can be used to generate electricity and thermal energy via processes based on either combustion or gasification.

[00010] Various biomass pretreatment technologies have been developed. Examples of these developments include use of dilute acids or bases, steam explosion, autohydrolysis, controlled pH, ammonia fiber expansion (AFEX), and other aqueous ammonia pretreatment. Flow-through pretreatment, in which the liquid has a shorter residence time in the pretreatment reactor than the solids, has also been described in the literature, and performance advantages such as making fiber more reactive to enzymatic attack and increased recovery of sugars without degradation have been noted. However, the conversion of cellulose to ethanol using flow-through pretreatment has been regarded as impractical due to high energy requirements and high dilution of extracted sugars.

SUMMARY

[00011] The presently disclosed instrumentalities advance the art by providing a system and methods for pretreating biomass to enhance the conversion rate and efficiency from subsequent processing of biomass to biofuels using microbial and/or enzymatic processing. Flow-through pretreatment is distinguished from all other pretreatment configurations because the liquid phase has a shorter residence time in the reactor than does the solid phase. In one embodiment, the biomass may be held inside a pretreatment vessel. A high-temperature liquid (also referred to as "inflow") may be allowed to pass through the biomass (or feedstock) to generate a

flow-through mixture that exits the biomass (also referred to as "effluent"). In one aspect, the inflow may be pre-mixed with the biomass before entering the vessel. As the heated liquid passes through the biomass, the biomass and the inflow may be incubated for a period of time. In one aspect, the temperature of the incubation is at least 100°C, at least 120°C, or about 210-220°C.

[0010] Disclosed herein are methods and a system in which the wash water (i.e liquid phase) is recycled such that dilution is not excessive. In another embodiment, energy use is controlled. In one aspect, wash water is heated and cooled in a counter-current fashion. In another aspect, wash water is evaporated prior to fermentation to generate steam for distillation downstream. In one embodiment, the steam is not used for indirect "heating" during a distillation process via a reboiler, but rather for counter-current stripping and rectification of fermentation broth containing ethanol or some other volatile product via direct injection to the distillation column.

[0011] Counter-current embodiments (liquid flows one way, solids flow the other) are particularly advantageous in the methods disclosed herein. Steam may be added to heat the water, either in the reactor or outside the reactor. In another aspect, the solids are in contact with water. Liquids other than water may also be used.

[0012] In another embodiment, liquid-solid contact may be continuous. The solids are washed with inflow, whether added continuously or discontinuously. Flash vapor may be used to preheat the feed to the pretreatment vessel.

[0013] In one embodiment, the biomass that has been pretreated with hot liquid may be delivered into a wash vessel wherein the pretreated biomass is further washed and extracted by additional hot liquid, such as hot water. The wash vessel may have an outlet that allows hot wash to exit the wash vessel.

[0014] In another aspect, the pretreatment vessel is built such that it may function as both a vessel for pretreatment and a vessel for hot wash. For purposes of this disclosure, the term "pretreatment vessel" may refer to such a vessel that can be used for both pretreatment and wash (sometimes referred to as "pretreatment/wash vessel," or it may refer to the pretreatment vessel that is separate from a wash vessel. Similarly, the term "effluent" may refer to flow-through wash exiting either the pretreatment/wash vessel or the wash vessel. The pretreatment/wash vessel may contain an outlet that allows hot wash to exit the pretreatment/wash vessel.

[0015] The liquid or steam to be used for pretreatment/wash may be water or other fluids such as a solution.

[0016] In one embodiment, the effluent from the wash vessel or the pretreatment/wash vessel may contain one or more components of the biomass that have been solubilized or extracted from the biomass by the liquid. The first effluent may be guided through a heat exchanger, wherein at least a portion of the heat from the first effluent is transferred to a new incoming wash.

[0017] In another embodiment, a method for concentrating the effluent and for recycling heat in the process is disclosed. The effluent may be directed to an evaporator where at least one solvent in the effluent may be allowed to evaporate to obtain a first effluent concentrate and an evaporating steam.

[0018] In one embodiment, solids are washed with inflow added continuously or discontinuously. After the wash has been performed, the biomass may exit the pretreatment/wash vessel or wash vessel. Flash vapor released from the pretreatment/wash vessel or wash vessel may be used to preheat the feed to the pretreatment vessel. The biomass obtained after washing may be mixed with all effluent concentrates to form a reaction mixture that may be further subjected to hydrolysis and fermentation processes to generate alcohol or other products.

[0019] The steam generated during the evaporation step may be used for counter-current stripping and rectification of fermentation broth containing ethanol or other volatile products.

[0020] In one aspect, a method of processing cellulosic biomass into ethanol is disclosed wherein the amount of energy put into the process is less than the sum of the energy value of the ethanol created from the conversion of both liquid and solid process residues derived from the cellulosic biomass.

[0021] In another aspect, a method for processing cellulosic biomass into ethanol is disclosed whereby the amount of energy put into the process is less than about 47% of the heating value of the cellulosic biomass.

[0022] In another aspect, the cooled and pretreated cellulosic biomass is mixed with one or more effluent concentrates, and the mixture is subject to hydrolyzing and fermenting enzymes and/or organisms. In another aspect, about 4% to about 6% ethanol by volume is produced in the fermentation reactor. In another

step, the combination is separated into liquids and solids and then the liquids are distilled into a distillate having about 95% ethanol by volume.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] Figure 1 is a flow chart of flow-through pretreatment showing major components of the pretreatment system.

[0024] Figure 2 is a plot showing distillation feed ethanol concentration as a function of wash water usage with and without evaporation of wash water effluent.

[0025] Figure 3 is a plot showing process energy requirements as a function of the extent of washing.

[0026] Figure 4 shows comparison of SSF Conversion for flow-through (FT) and batch pretreated poplar and bagasse.

[0027] Figure 5 shows temperature-time contour plots on xylan solubilization and recovery for flow-through pretreated poplar.

[0028] Figure 6 is a temperature-time contour plot on glucan conversion by SSF for flow-through pretreated poplar.

[0029] Figure 7 shows the extraction sugars, acetyl, and pH profiles during FT pretreatment with increasing temperature.

[0030] Figure 8 shows the extraction organic carbon profile during FT pretreatment with increasing temperature.

[0031] Figure 9 shows comparison of the conversion of FT pretreated poplar by SSF and *C. thermocellum* with or without post-pretreatment particle size reduction.

[0032] Figure 10 shows comparison of SSF conversion for various flow-through pretreated feedstocks.

[0033] Figure 11 shows comparison of SSF conversion for poplar and bagasse after conventional (batch), FT, and partial FT (batch with wash) pretreatments.

DETAILED DESCRIPTION

[0034] The present disclosure provides systems and methods for pretreating biomass using a high temperature flow-through and an evaporation process to provide an improved separation of biomass components, improved

hemicellulose recovery, and improved cellulose digestibility. As used herein, "flow-through" refers to a process wherein a liquid is added to or mixed with a solid or a semi-solid material and is incubated with the material for a period of time before leaving the solid or semi-solid material. During the course of the flow-through, the liquid may solubilize, extract or otherwise bring along certain components of the biomass. Flow-through pretreatment is distinguished from all other pretreatment configurations because the liquid phase has a shorter residence time in the reactor than does the solid phase. Methods for reducing energy consumption and for effectively extracting usable sugar substrate from biomass are disclosed.

[0035] The term "biomass" generally refers to non-fossilized renewable materials that are derived from or produced by living organisms. For purpose of this disclosure, biomass may include animal biomass, plant biomass, human waste, and recycled materials, among others. Examples of animal biomass may include animal by-product and animal waste, etc. Plant biomass may be any plant-derived matter (woody or non-woody) that is available on a sustainable basis. Plant biomass may include, but is not limited to, agricultural crop wastes and residues such as corn stover, wheat straw, rice straw, sugar cane bagasse and the like, grass crops, such as switchgrass and the like. Plant biomass may further include, but is not limited to, woody energy crops, wood wastes and residues such as trees, softwood forest thinnings, barky wastes, sawdust, paper and pulp industry residues or waste streams, wood fiber, and the like. In urban areas, plant biomass may include yard waste, such as grass clippings, leaves, tree clippings, brush, etc., vegetable processing waste, as well as recycled cardboard and paper products.

[0036] The terms "vessel" refers to a container that holds the biomass and one or more other reactants, wash, or enzymes, among others.

[0037] In one embodiment, the energy penalty of flow-through pretreatment may be decreased by using a counter-current heat exchange. More specifically, the heat from the pretreatment wash water that exits the biomass (also called "effluent") may be transferred to incoming wash water (also called "inflow") that is about to enter the biomass. In one aspect, the dilution penalty resulting from the use of a large volume of wash water may be minimized by evaporating the effluent prior to hydrolysis and fermentation. In one embodiment, the evaporation

process employs a heating step to evaporate one or more solvent (e.g., water) from the effluent. The steam that is generated from such heating may be used for counter-current stripping and rectification of fermentation broth containing ethanol or other volatile products. Furthermore, evaporation via the heating step may also partially or completely remove volatile compounds from the liquid phase that are potentially inhibitory to downstream hydrolysis and/or fermentation. Examples of such volatile compounds may include by are not limited to furfural, phenol, among others.

[0038] For purpose of illustration only, Fig. 1 shows the flow of material and energy in the disclosed system **100**. Feedstock (or biomass) **110** is loaded into a pretreatment vessel **120**. Vessel **120** has at least one inlet and at least one outlet. In one embodiment, vessel **120** has two inlets. Inlet **122** allows the loading of feedstock **110**. Inlet **124** allows liquid **130** to enter into vessel **120**. In one embodiment, feedstock **110** is loaded into vessel **120** before liquid **130** is injected into vessel **120**. In another embodiment, liquid **130** may be pre-mixed with the feedstock **110** and loaded into the vessel **120** together. Liquid **130** is incubated with feedstock **110** inside the vessel **120** for a period of time such that one or more components of feedstock **110** may be solubilized or extracted by the liquid **130**. In one embodiment, the incubation takes place while liquid **130** passes through feedstock **110** inside vessel **120**. Note that the liquid **130** may be steam or water.

[0039] In one embodiment, the mixture of liquid **130** and feedstock **110** has a temperature of at least 100 °C, or at least 120 °C, or about 210-220 °C.

[0040] In one embodiment, pretreatment vessel **120** has one outlet **132**. Pretreated feedstock and the hot liquid exit vessel **120** through outlet **132** and enter into a wash vessel **140**. In another embodiment, pretreatment vessel **120** and wash vessel **140** are built as one vessel **150**. In one aspect, vessel **140** or **150** has two outlets. Outlet **154** allows the hot wash liquid to exit vessel **140** or **150** as effluent **156**. Outlet **158** allows the pretreated and washed feedstock **160** to leave vessel **140** or **150**. In one aspect, flash vapor **164** from feedstock **160** is used to preheat feedstock **110** before it enters pretreatment vessel **120**. In another aspect, effluent **156** enters a heat exchanger **166** through plumbing and has a direction of flow-through the plumbing within heat exchanger **166**. Incoming wash **170** enters heat exchanger **166** through different plumbing in a flow direction opposite to effluent **156** flow such that

a portion of the heat from effluent **156** is transferred to inflow **170**. Inflow **170** enters into vessel **140** or **150** through inlet **174**. Hot steam **176** may also be mixed with inflow **170** either inside or outside vessel **140** or **150** and then liquid inflow **170** enters through inlet **174**.

[0041] In one embodiment, after passing through heat exchanger **166**, effluent **156** is directed to an evaporator **178**, where effluent **156** is heated to allow solvent to evaporate. In one aspect, the steam from the evaporating solvent may be used for counter-current stripping and rectification of fermentation broth containing ethanol or some other volatile product.

[0042] In another embodiment, the concentrated effluent **182** leaving evaporator **178** is combined with the pretreated and washed feedstock **160** and are both subject to CBP processes.

[0043] In comparison to previous methods, the evaporation process disclosed herein considerably increases the amount of washing that can be employed within the energetic constraints imposed by dilution. Thus, the fermentable sugars from the biomass are obtained with higher concentration through pretreatment processes and the overall energy put into the system is less than using previous methods.

[0044] Fig. 2 examines the dilution constraint to flow-through pretreatment. In a typical CBP process, which features combining the pretreatment wash water with pretreated solids prior to fermentation, increased washing is accompanied by decreased ethanol titer. For example, given the hydrolysis and fermentation yields assumed here, the amount of washing compatible with a 5 wt.% ethanol titer is 4.3 kg water/kg dry solids. By comparison, when the presently disclosed evaporation process is incorporated into the process, the amount of washing compatible with a 5 wt.% ethanol titer is 7 kg/kg dry solids. Taking into account the economic optimum, the ethanol titer could be less than 5 wt.% ethanol. At 4 wt.% ethanol, for example, the allowable amount of washing becomes about 5.5 kg water/kg dry solids without the evaporation strategy and about 9 kg water/kg solids with the evaporation process.

[0045] Fig. 3 examines the process energy required for various purposes as a function of the extent of washing. The horizontal axis is the same as that of Fig. 2.

Results are expressed as a fraction of the feedstock heating value. The energy content of the liquid and solid process residues is about 47% of the heating value of the feedstock. Having process energy requirements higher than this value of energy would be problematic because the process would not be considered self-sufficient as far as energy is concerned. Processes for obtaining liquid, energetic fuels that require more energy than 47% of the heating value of the feedstock are not self-sufficient because they require more energy than they deliver. Such a non-self-sufficient process would have negative impacts on both economics and greenhouse gas emissions. Having process energy substantially less than that available in the feedstock is advantageous because the unused feedstock energy can be used to produce electricity or other revenue generating co-products.

[0046] The evaporation strategy disclosed herein decreases the amount of process energy required at a given extent of washing compared to the situation without implementing this strategy. This makes the benefits of flow-through pretreatment easier to realize by lowering the cost for a given extent of washing.

[0047] More washing may result in more solubilization/extraction of cellulose and hemicellulose and therefore, more ethanol may be produced. In one embodiment, the present method may generate more ethanol per unit of energy input into the system. In one aspect, this advantage may be achieved primarily through two heat recycling steps. The first step is through using a counter-current heat exchanger in which the heat from the post wash flow-through, namely, the effluent, is transferred to an incoming wash. The incoming wash then enters into the wash vessel and requires less heat input into the system to raise the wash to the temperature necessary for effective pretreatment. In another aspect, the now cooler effluent that just exchanged some of its heat with the incoming wash is then fed into an evaporator wherein the water evaporates forming a more concentrated wash (effluent) and a vapor. In another aspect, heating may be used in the evaporator to facilitate the evaporation. The concentrated wash may be fed into the consolidated bioprocessing (CBP) vessel where the solubilized cellulose and hemicellulose are hydrolyzed into their constituent sugars and then fermented into ethanol.

[0048] In another embodiment, the disclosed methods may provide higher solid reactivity because lignin and hemicellulose derivatives have much higher

solubility at pretreatment temperatures than at lower temperatures such as about 100 °C. In another aspect, by removing lignin and hemicellulose derivatives during pretreatment and wash, the disclosed methods help prevent the removed compounds from re-condensing on the surface of cellulose. Thus, the disclosed methods may increase access of enzymes to the substrate and may decrease non-productive cellulase binding.

[0049] In another embodiment, the disclosed methods may lead to less degradation of hemicellulose derivatives because the pretreatment can be quite effective at relatively mild conditions. The pretreatment is effective at milder conditions because under flow-through conditions, the fluid residence time is less than the solid residence time. Therefore, less time is available for degradation of dissolved compounds to take place.

[0050] In another embodiment, the biomass may be fractionated into various biomass components. These various biomass components may be solubilized at different temperatures and be recovered in different liquid fractions. Thus, the disclosed methods may allow selective capturing of biomass components, or selective exclusion of inhibitors or other unwanted products from subsequent processes. For instance, solubilized lignin may be used to for creating carbon fiber that is useful in the manufacturing of composite structures.

[0051] In another embodiment, according to the disclosed methods, less inhibition of hydrolyzing and fermenting enzymes and organisms may occur due to the milder pretreatment conditions. Under the milder pretreatment conditions, less inhibitors may form during the pretreatment process. Moreover, inhibitors may be separated by the fractionation of the wash.

[0052] In another embodiment, inhibitors present in the washate that are suitably volatile may be removed from the liquid phase via the evaporation step prior to downstream hydrolysis and/or fermentation.

[0053] For purpose of this disclosure, the term "flow-through" means a process wherein a fluid enters into a container that contains a biomass and the fluid is in contact with the biomass and then is removed through an outlet in a continuous manner. "Batch process" refers to a process having more than one step, wherein each step takes place in a discontinuous manner.

[0054] A counter-current heat exchanger refers to a device containing at least two pipes running parallel with respect to each other and are encased in a conductive material. The pipes contain liquids, gasses or other fluidics that have flows and/or temperature gradients that are opposite with respect to the other pipe. The pipe material is also conductive such that heat is exchanged from the liquid and/or gas in one pipe to the liquid and/or gas in the other.

[0055] Evaporator/Condenser: An evaporator/condenser is a device whereby the vapor phase of a liquid condenses and the heat from the condensing of the vapor is exchanged to an outside receiver.

[0056] The term "process energy" refers to the entire amount of energy that is put into the process that converts cellulosic biomass into ethanol. Heating value refers to the amount of heat that is generated through burning the cellulosic biomass.

[0057] The term "liquid process residue" is the fermentable carbon sources that are extracted into the wash.

[0058] The term "solid process residue" is the fermentable carbon sources from the cellulosic biomass that remain solid after being pretreated and washed.

EXAMPLES

[0059] The following examples are provided for purpose of illustrating the instant disclosure and are not limiting.

Example 1 SSF Conversion of Flow-through (FT) and Batch Pretreated Poplar and Bagasse

[0060] Both poplar and bagasse were pretreated using a FT or batch mode before being subjected to SSF process to generate ethanol. Fig. 4 shows the percentage of 4-day glucan conversion by SSF for poplar and sugarcane bagasse after FT or batch pretreatment. As shown in Fig. 4, the solids from the FT pretreatment have much higher reactivity relative to the conventional batch control, which is representative of continuous pretreatment without flow-through.

Example 2 FT Pretreatment and Hemicellulose Recovery

[0061] To examine the effect of high temperature pretreatment and wash on the recovery and degradation of hemicellulose, solubilization and recovery of

xylan was analyzed using temperature-time contour plots. Fig. 5 shows that FT pretreatment achieves high solids reactivity with little or no degradation of hemicellulose sugars, such as xylan. Recovery and conversion of glucan were analyzed under different temperatures and for different durations of pretreatment. Fig. 6 is a temperature-time contour plot showing that FT pretreatment achieves high solids reactivity with little or no degradation of glucan.

Example 3 Sugar Extraction Profile During FT Pretreatment

[0062] Fig. 7 shows the extraction profile during FT pretreatment with increasing temperature. The concentration of various sugars, acetic acid, and the pH are shown. Fig. 8 shows the organic carbon profile of the extracted during FT pretreatment with increasing temperature. As shown in Fig. 7 and Fig. 8, extractive components (carbohydrates, acetyl groups, and non-carbohydrate extractives) become soluble at defined temperature windows that are lower than the highest pretreatment temperature.

[0063] Various operating strategies may be designed involving temperature-staged pretreatment in order to minimize inhibitor formation or separate inhibitors from useful substances. Different temperature profiles may be used to maximize the capture value. For example, soluble lignin components may be recovered for making carbon fiber that can be used to manufacture composites. Different sugar or non-sugar extractives are solubilized/extracted at different temperatures. Thus, the disclosed FT pretreatment process may be used to fractionate different sugars or extractives based on their different extraction profiles.

Example 4 Conversion of FT-Pretreated Poplar by SSF and *C. thermocellum* with and without Post-Pretreatment Particle Size Reduction

[0064] As shown in Fig. 9, *C. thermocellum* showed much faster conversion of FT pretreated solids (e.g. 4 to 5 fold) as compared to SSF at the tested cellulase loadings. Particle size reduction is more effective to increase *C. thermocellum* conversion than to increase SSF conversion. In comparison to recombinant yeasts, *C. thermocellum* exhibits superior cellulose hydrolyzing capability and is also cheaper to use. However, in order to incorporate the faster

conversion capability of *C. thermocellum* into commercial processes, a much higher solids concentration is required.

Example 5 SSF Conversion of Various FT-Pretreated Feedstocks.

[0065] SSF Conversions of various FT-pretreated feedstocks are compared in Fig. 10. Fig. 10 shows that different feedstocks exhibit different reactivity to pretreatment under controlled conditions. In this case, poplar was shown to be less reactive than several herbaceous feedstocks. The difference between the reactivity of poplar and herbaceous feedstocks might have been underestimated by these data because the cellulase loading was very high and the extent of particle size reduction carried out for poplar was greater than the other feedstocks.

Example 6 SSF Conversion of Poplar and Bagasse after Batch, FT, and Partial FT Pretreatment.

[0066] Fig. 11 shows the results of a study calibrating FT pretreatment as a function of the extent of washing employed. High washing (30 kg water/kg dry solids), moderate washing (5 kg/kg dry solids), and no washing (batch control) were all used and their relative conversions are compared in Fig. 11. Conversion with moderate washing is as effective as high washing for poplar, and almost as effective for bagasse. It is noteworthy that the extraction efficiency in these studies was not optimized at a given level of washing. The level of washing for moderate washing falls within the feasible region as defined by the energy and dilution constraints depicted in Figs. 2 and 3.

CLAIMS

We claim:

1. A method for improving the pretreatment of biomass, said method comprising the steps of:
 - (a) mixing an amount of biomass with a first inflow, wherein said first inflow is a liquid,
 - (b) obtaining a first effluent after said first inflow passes through said biomass,
 - (c) allowing said first effluent to pass through a heat exchanger, wherein at least a portion of heat from said first effluent is transferred to a second inflow, wherein said second inflow is a liquid,
 - (d) mixing said second inflow with said biomass, said biomass having been in contact with said first inflow, and
 - (e) allowing a solvent in said first effluent to evaporate to obtain a first effluent concentrate and an evaporating steam,wherein said step (c) precedes step (d).
2. The method of claim 1, wherein said step (a) of mixing takes place in a vessel.
3. The method of claim 1, further comprising a step (g) of incubating said biomass and said first inflow at a temperature of at least 100°C, wherein said step (a) precedes step (g), and said step (g) precedes step (b).
4. The method of claim 3, wherein said biomass and said first inflow is incubated in step (g) at a temperature of at least 120°C.
5. The method of claim 3, wherein said biomass and said first inflow is incubated in step (g) at a temperature of about 210°C.
6. The method of claim 2, wherein said steps (b)-(e) are repeated for m cycles, m being an integer between 1-50.

7. The method of claim 6, further comprising a step of obtaining said biomass from said vessel after steps (b)-(e) have been repeated for m cycles.
8. The method of claim 7, wherein the biomass obtained after m cycles is mixed with all effluent concentrates collected in each cycle of the m cycles to form a reaction mixture.
9. The method of claim 8, wherein said reaction mixture is further subjected to a hydrolysis and fermentation process to generate alcohol.
10. The method of claim 1, wherein said evaporating steam is used for counter-current stripping and rectification of a fermentation broth containing ethanol.
11. The method of claim 6, wherein said inflow for all m cycles is aqueous.
12. The method of claim 6, wherein said solvent in step (e) is water.
13. The method of claim 2, wherein flash vapor released from said vessel is used to preheat a biomass feed to a pretreatment vessel.
14. A method for improving the pretreatment of biomass, said method comprising the steps of:
 - (a) mixing an amount of biomass with an Nth inflow, wherein said Nth inflow is a liquid, N being an integer between 1 and 50,
 - (b) obtaining a Nth effluent after said Nth inflow passes through said biomass,
 - (c) allowing said Nth effluent to pass through a heat exchanger, wherein at least a portion of heat from said Nth effluent is transferred to a Qth inflow, wherein said Qth inflow is a liquid, Q being an integer between 2 and 51, and $Q=N+1$.
 - (d) mixing said Qth inflow with said biomass, said biomass having been in contact with said Nth inflow, and
 - (e) allowing a solvent in said Nth effluent to evaporate to obtain a Nth effluent concentrate and an evaporating steam,

wherein said step (c) precedes step (d), and said steps (a)-(e) are repeated for 1-50 cycles.

15. A system for pretreating biomass, said system comprising:

- (a) a pretreatment vessel for holding said biomass, said pretreatment vessel comprising an inlet and an outlet, wherein said inlet allows for an inflow to enter into said pretreatment vessel, and said outlet allows for an effluent to exit said pretreatment vessel,
- (b) an evaporator for holding said effluent, said evaporator being connected to said pretreatment vessel, and
- (c) a heating means for heating said effluent and allowing at least one solvent in said effluent to evaporate from said effluent, thereby forming an effluent concentrate and an evaporating steam containing said at least one solvent.

16. The system of claim 15, further comprising a heat exchanger positioned between said pretreatment vessel and said evaporator, wherein at least a portion of heat from said effluent is transferred to a second inflow through said heat exchanger.

17. The system of claim 15, wherein said pretreatment vessel further comprises a second outlet, said second outlet allowing for the exit of pretreated biomass from said pretreatment vessel.

18. The system of claim 17, further comprising a reaction vessel wherein said pretreated biomass is subject to a hydrolysis and fermentation process to generate alcohol.

19. The system of claim 18, further comprising a conveying means for transporting said effluent concentrate from said evaporator to said reaction vessel.

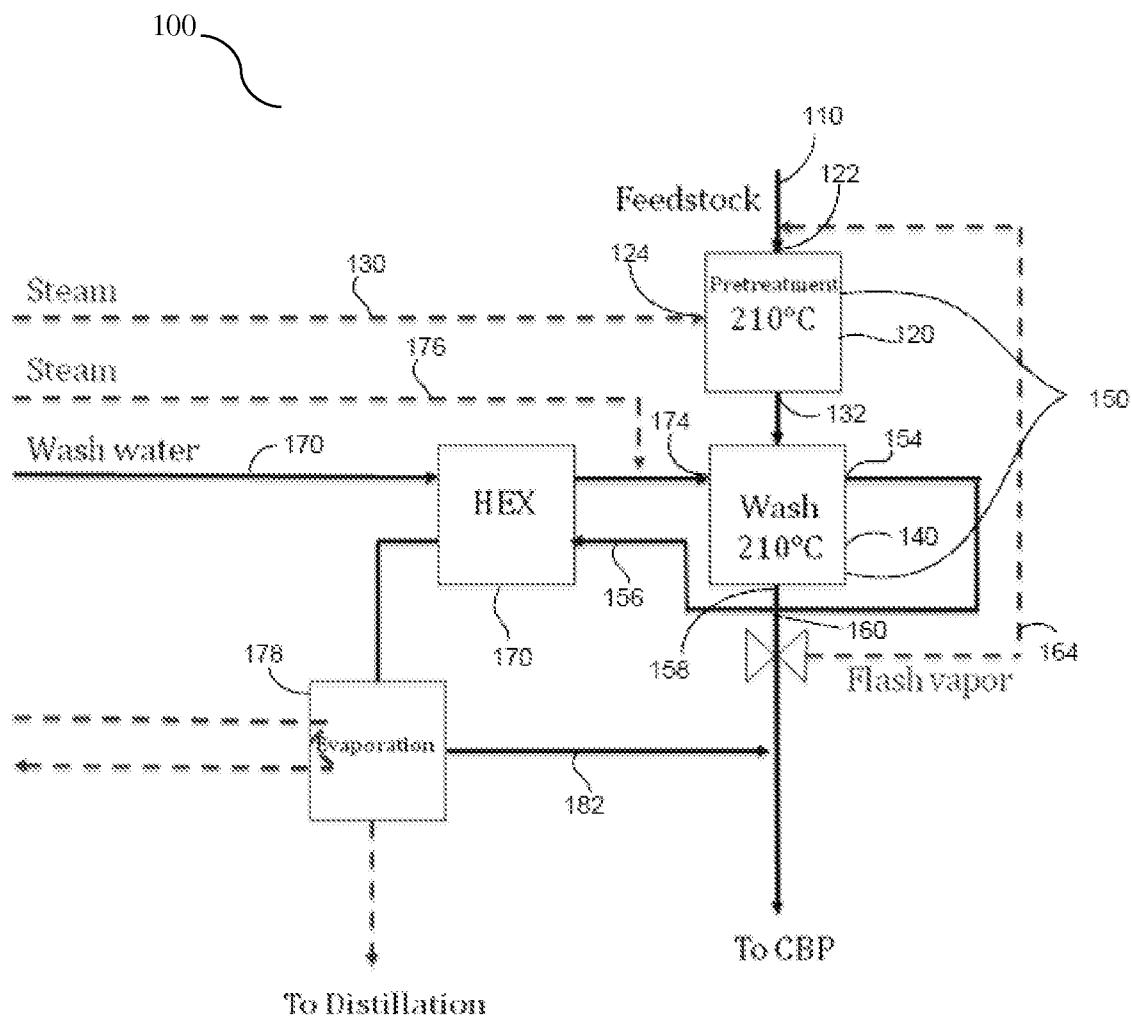
20. The system of claim 15, further comprising a second conveying means for transporting said evaporating steam to a distillation process.

21. A method for obtaining ethanol from a cellulosic biomass wherein the process energy for obtaining said ethanol is less than 47% of the heating value of said cellulosic biomass, said method comprising

- pretreatment of said cellulosic biomass in a reaction vessel with a flow-through input wash, and
- wherein effluent output from said reaction vessel comprises treated cellulosic biomass, and
- wherein said treated cellulosic biomass effluent exchanges heat in a heat exchanger with a flow-through input wash, and
- wherein said effluent is evaporated to produce steam, and
- wherein said steam is used for counter-current stripping of a fermentation broth containing ethanol.

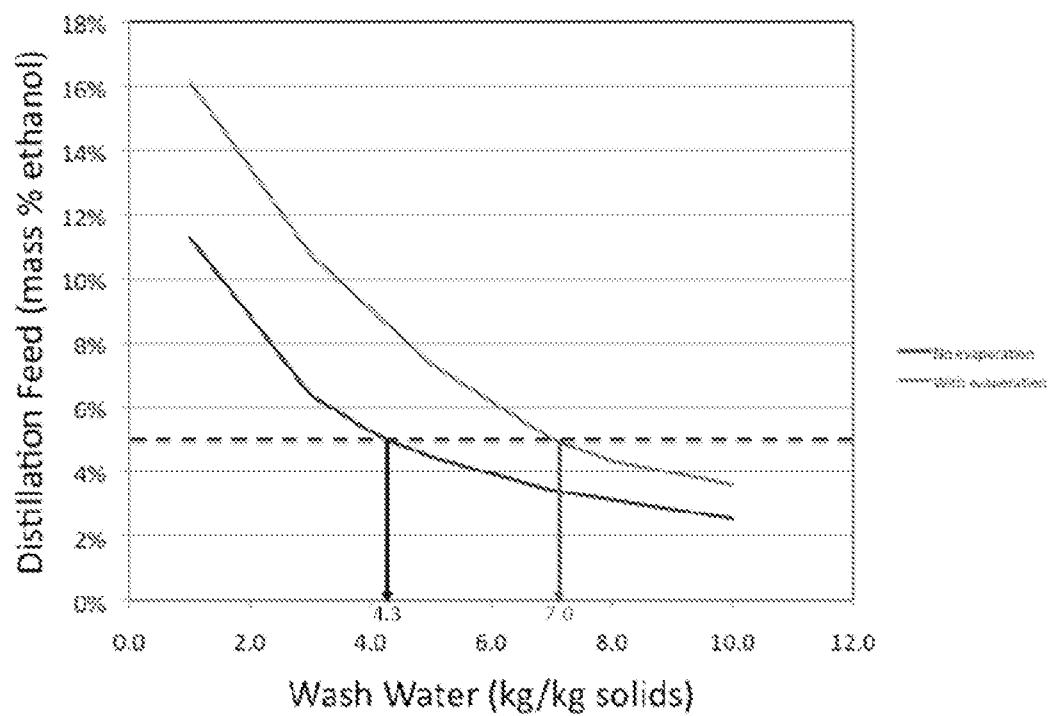
1/11

Fig. 1



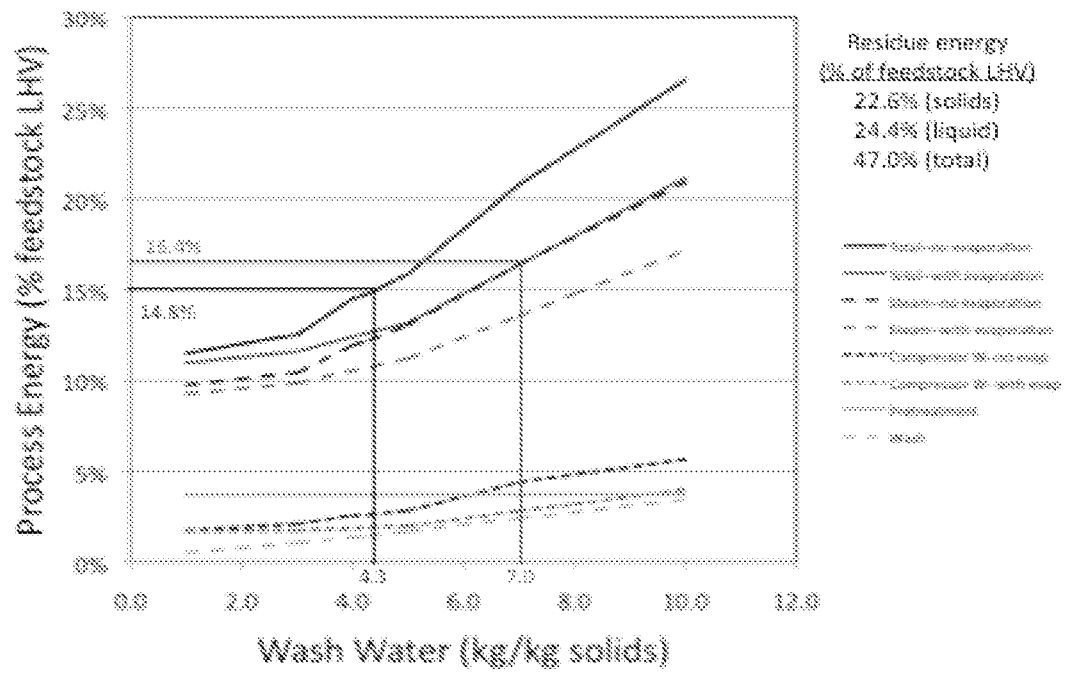
2/11

Fig. 2



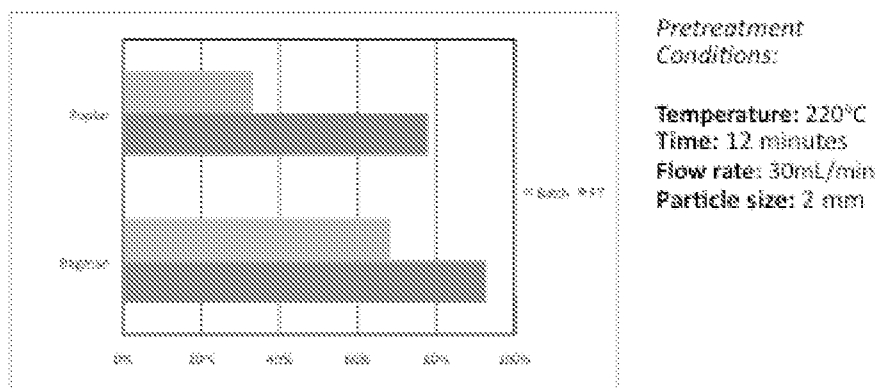
3/11

Fig. 3



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Fig. 4



Conversion system: SSF (yeast, added fungal cellulase), 96 hours

Pretreatments: Conventional aqueous (batch) and flow-through aqueous

Feedstocks: Poplar and bagasse

Enzyme loading: 11.7 mg enzymes/g solids (7FPU/g solids)

Initial substrate concentration: 20 g/L glucan*

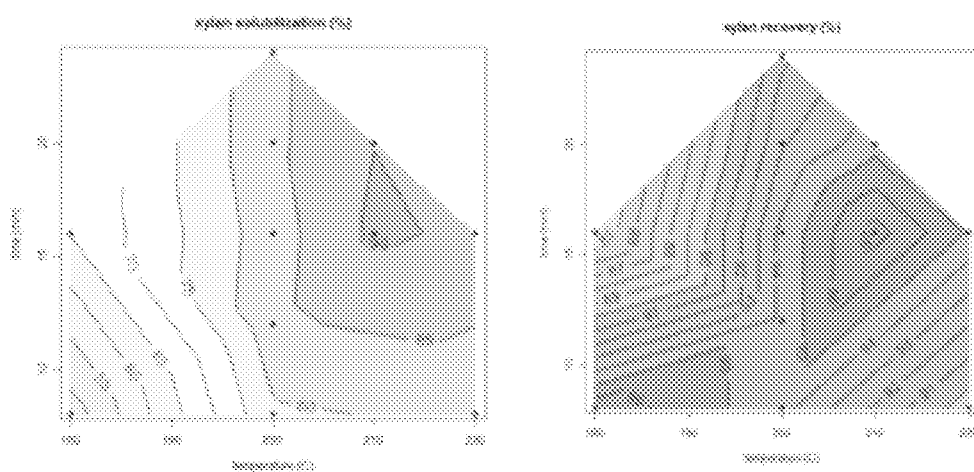
* Chosen to give an indication of solubilizing capability, not commercial

- FT pretreatment increases enzymatic digestibility at a given severity compared to conventional pretreatment (same residence time for solids, liquids)
- Bagasse is more reactive than poplar, at least under these conditions

Archambault-Leger, unpublished...

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Fig. 5



Conversion systems: SSF (10 FPU/g glucan), 96 hrs

Pretreatment: Flow through aqueous

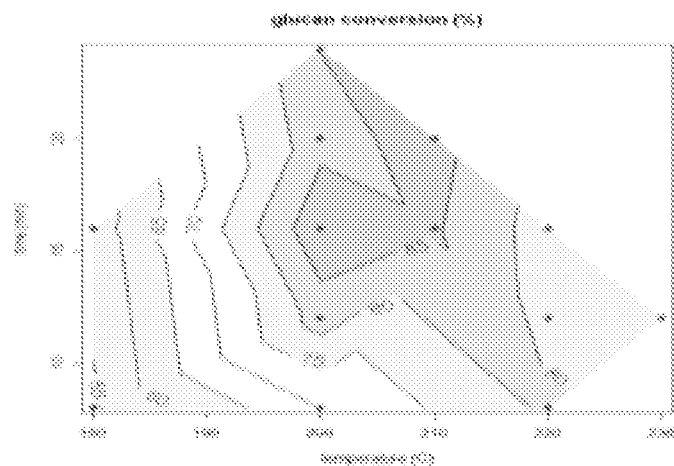
Feedstocks: Poplar (1 mm)

Initial substrate concentration: 20 g/L glucan

* Chosen to give an indication of solubilizing capability, not commercial

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Fig. 6



Conversion systems: SSF (10 FPU/g glucan), 96 hrs

Pretreatment: Flow through aqueous

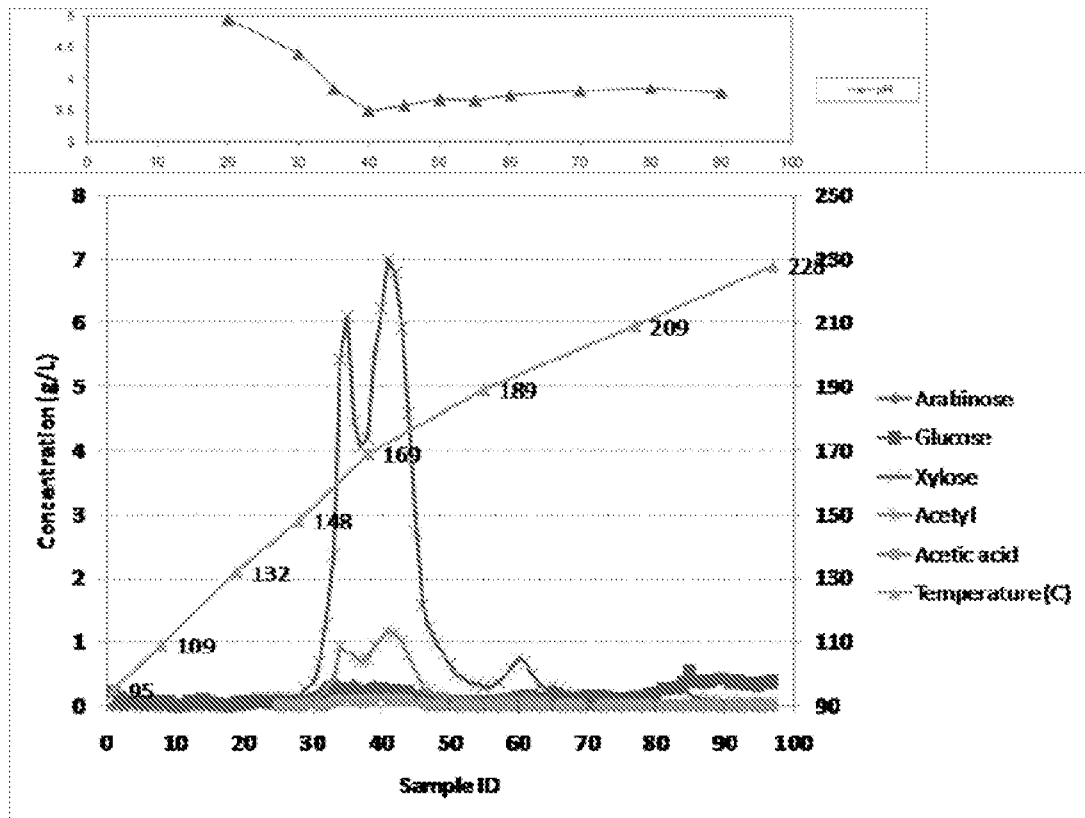
Feedstocks: Poplar (1mm)

Initial substrate concentration: 20 g/L glucan

* Chosen to give an indication of solubilizing capability, not commercial

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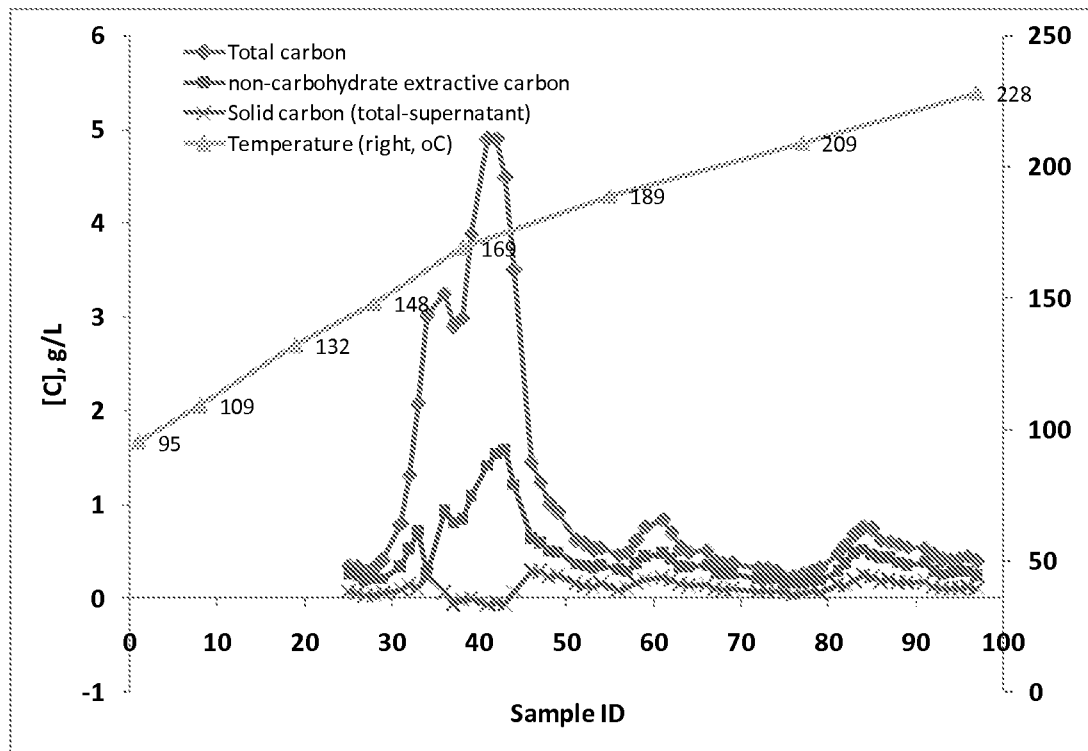
Fig. 7



Note: sugars are mostly in oligomers

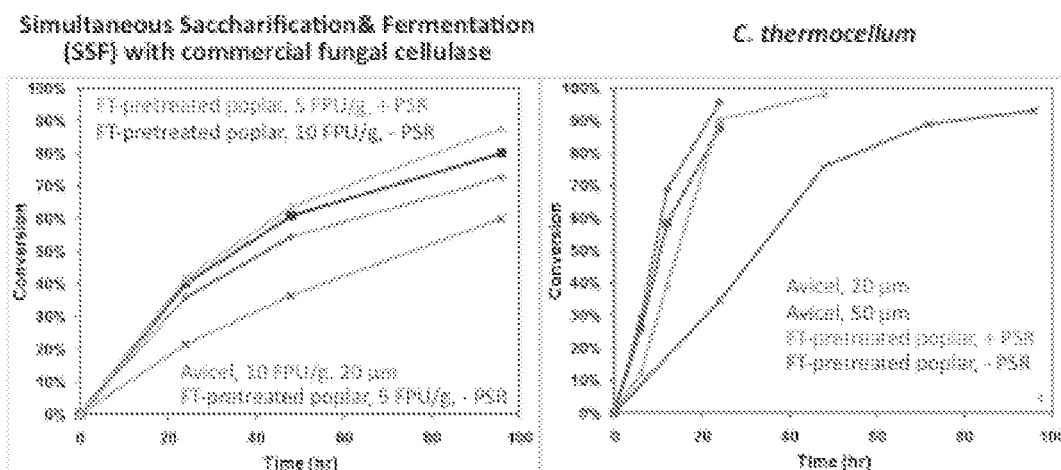
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Fig. 8



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Fig. 9



"PSR": Post-pretreatment particle size reduction; FPU/gglucan $\rightarrow$ mg/g solids: $\times 1.12$ for poplar, $\times 1.67$ for Avicel
 All experiments at 5 gglucan/L, chosen to give an indication of solubilization capability (not commercial)

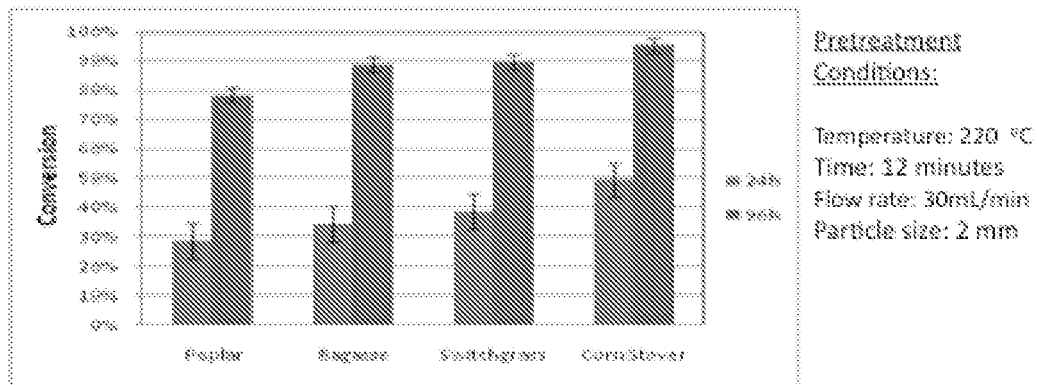
***C. thermocellum*:** > 90% conversion for Avicel (1 day), pretreated poplar with particle size reduction (1 day), pretreated poplar without particle size reduction (4 days)

SSF: Maximum conversion < 90% for all conditions after 4 days, 60% conversion for pretreated poplar without particle size reduction at 5 FPU/g

Post-pretreatment particle size reduction: 2-fold reduction in enzyme loading for SSF, 3-fold reduction in reaction time for *C. thermocellum*

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Fig. 10



Conversion systems: SSF (16.7 mg/g glucan), 96 hrs

Pretreatment: Flow through aqueous

Feedstocks: Poplar, bagasse, switchgrass, corn stover

Initial substrate concentration: 20 g/L glucan

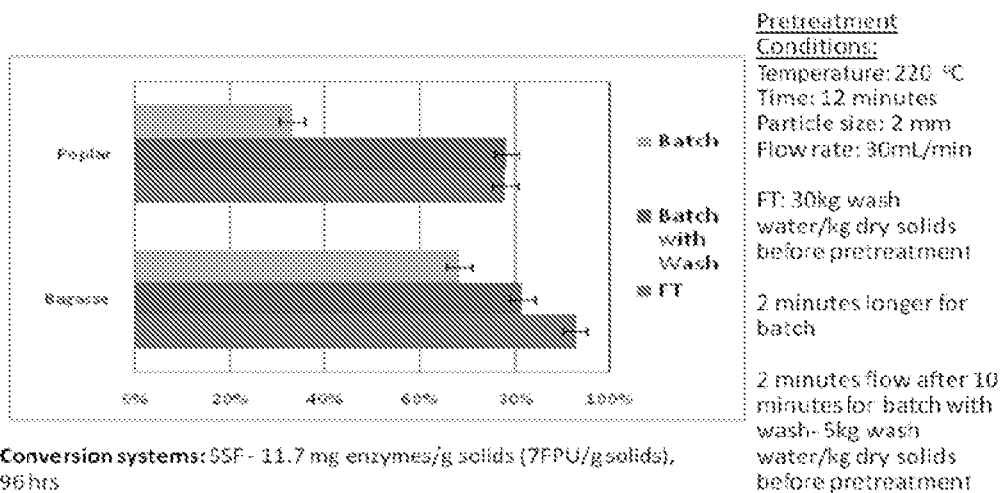
* Chosen to give an indication of solubilizing capability, not commercial

- Some feedstocks are more reactive than others, at least under these conditions
- Herbaceous feedstocks are more easily pretreated than poplar

Archambault-Leger, unpublished...

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Fig. 11



Conversion systems: SSF - 11.7 mg enzymes/g solids (7FPU/g solids), 96 hrs

Pretreatment: Aqueous FT with: continuous wash, wash at end of cycle, and without wash

Feedstocks: Poplar, bagasse

Initial substrate concentration: 20 g/L glucan

* Chosen to give an indication of solubilizing capability, not commercial

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/071367**A. CLASSIFICATION OF SUBJECT MATTER****CIOG 3/00(2006.01)i, B09B 3/00(2006.01)1, CIOL 1/04(2006.01)1**

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

CIOG 3/00; C07C 29/80; C07H 1/08; C12P 7/10; C12P 19/00; C13K 1/02; B01D 3/16; C12P 7/06; C12P 19/02

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: biomass, pretreatment, heat exchange, evaporate, ethanol

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009-0017503 A1 (ZHANG, Y. H. P. et al.) 15 January 2009 See abstract ; paragraphs [0025] -[0029] ; figure 1; and claims 1-11 , 13 , 15 .	1-21
Y	US 4522920 A (THORSSON, C. R. et al.) 11 June 1985 See abstract ; figures 4-5 ; and claims 1 , 8 .	1-21
A	US 4822737 A (SAIDA, T.) 18 April 1989 See abstract ; columns 2-6 ; figures 1-2 ; and claims 1 , 4 .	1-21
A	US 2009-0221042 A1 (DALE, B. E. et al.) 3 September 2009 See abstract ; paragraphs [0043] -[0044] ; figures 1-2 ; and claims 1 , 5 , 8 .	1-21
A	US 2011-0076725 A1 (YANG, B. et al.) 31 March 2011 See abstract ; figure 1; and claims 1-3 , 7-10 .	1-21

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

23 April 2013 (23.04.2013)

Date of mailing of the international search report

25 April 2013 (25.04.2013)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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