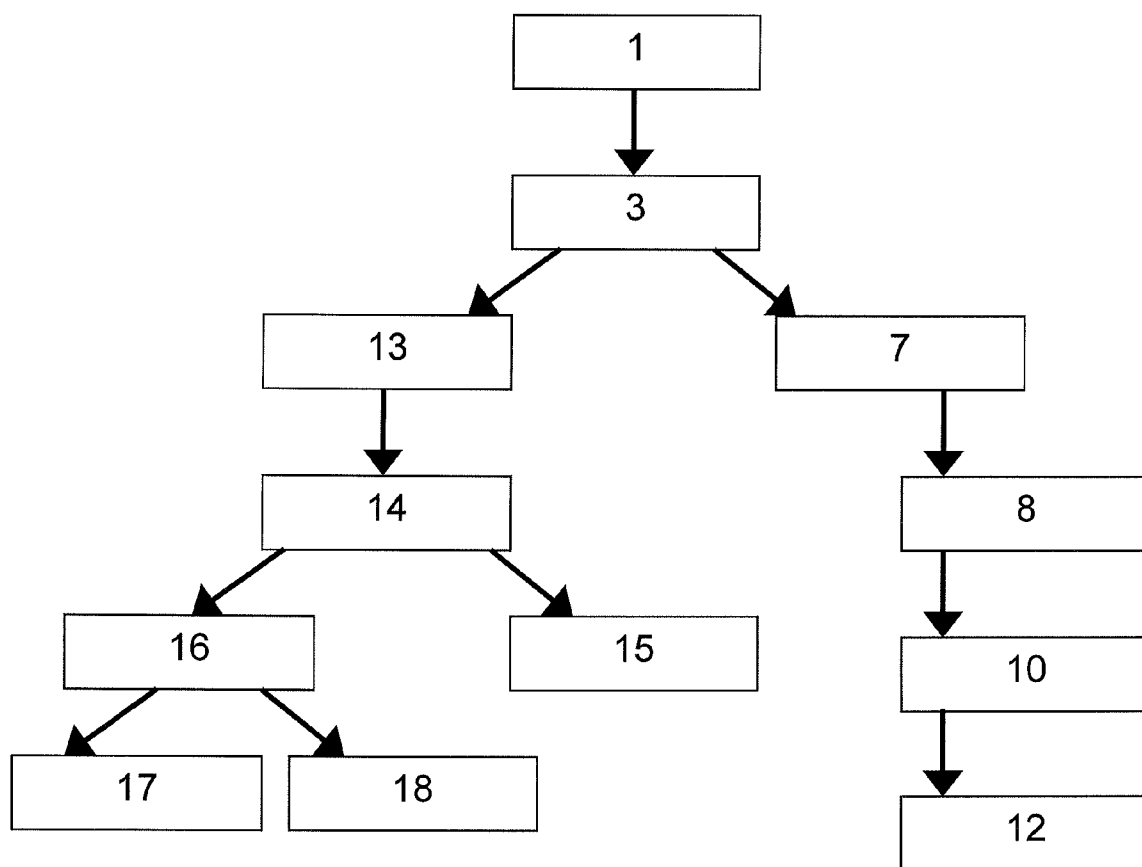




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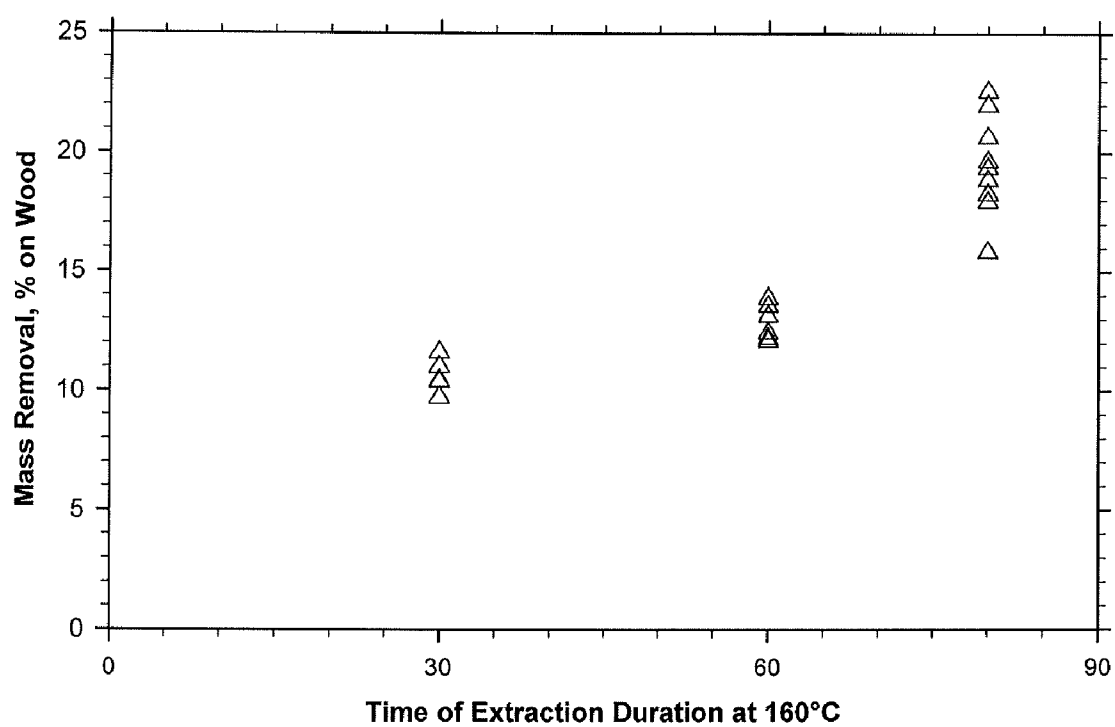
(19) **United States**(12) **Patent Application Publication**  
**Liu et al.**(10) **Pub. No.: US 2011/0073264 A1**(43) **Pub. Date: Mar. 31, 2011**(54) **KRAFT-PULPING OF HOT WATER  
EXTRACTED WOODCHIPS**(75) Inventors: **Shijie Liu**, Manlius, NY (US);  
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NY (US)(21) Appl. No.: **12/855,176**(22) Filed: **Aug. 12, 2010****Related U.S. Application Data**(60) Provisional application No. 61/233,704, filed on Aug.  
13, 2009.**Publication Classification**(51) **Int. Cl.**  
**D21C 1/02** (2006.01)  
**D21C 3/22** (2006.01)  
**D21C 3/02** (2006.01)  
(52) **U.S. Cl. .... 162/68; 162/70; 162/82; 162/90**  
(57) **ABSTRACT**

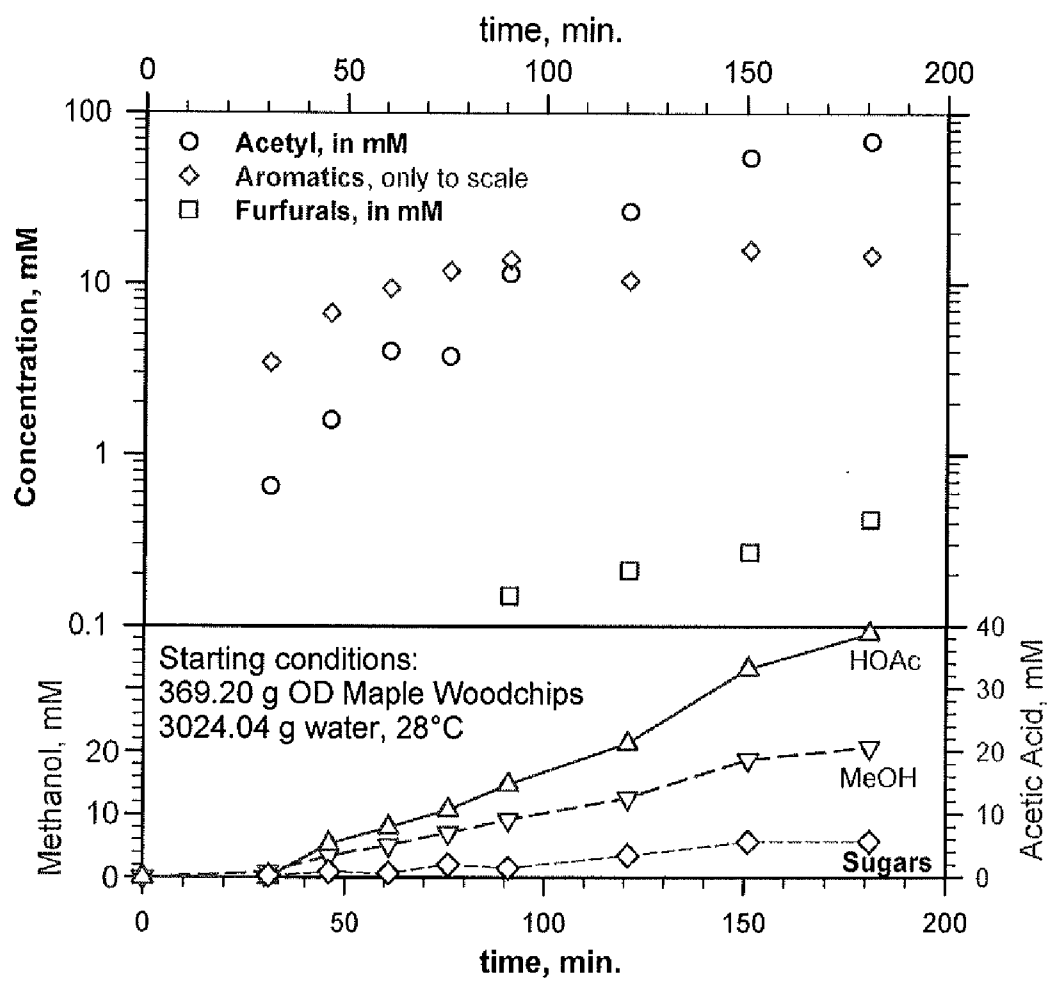
The method of the present invention is directed towards a method to increase the pulp yield of a lignocellulosic material, or increasing pulp bulk and/or pulp viscosity. This method comprises the following steps; preparing a lignocellulosic material, contacting the lignocellulosic material in a vessel with hot water or steam for a predetermined time, producing acetic acid from the reaction of the hot water or steam and the lignocellulosic material, lowering the pH to less than about 4, removing lignocellulosic material extracts including a large percentage of hemicellulose, acetic acid and metal ions, exposing contacted lignocellulosic material to pulping chemicals in a pulping reactor, forming a contacted lignocellulosic material pulp with a kappa number below about 19 after about 90 minutes of contact with the pulping chemicals, exposing the contacted lignocellulosic material pulp to whitening agents, and producing a whitened hot water contacted lignocellulosic material pulp.

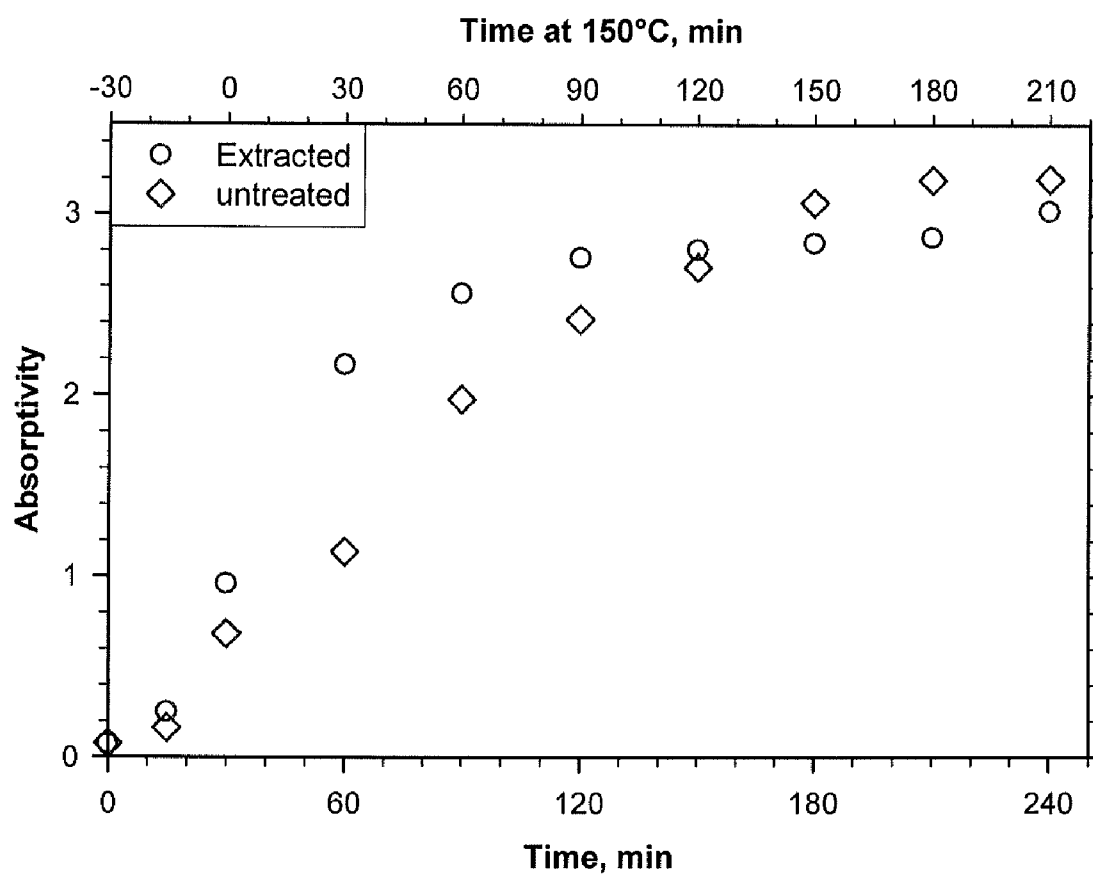
**FIGURE 1**

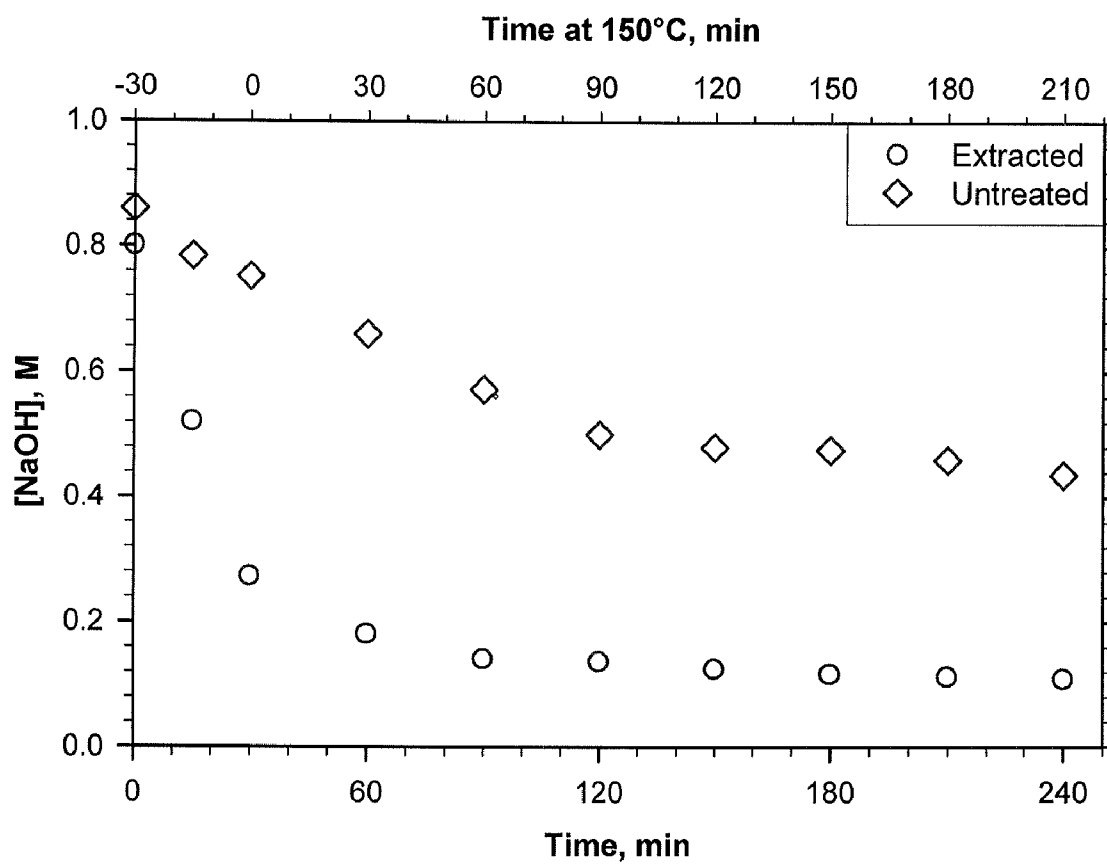
| Group   | Residence time<br>in extraction,<br>min | Mass Loss in<br>Extraction, % | Extraction,<br>Yield, % | Overall<br>Pulp<br>Yield, % | Digester<br>Yield,<br>% | Kappa<br>No.      | A.A,<br>% | S, % | Time at<br>temp.,<br>min |
|---------|-----------------------------------------|-------------------------------|-------------------------|-----------------------------|-------------------------|-------------------|-----------|------|--------------------------|
| Set I   | -----                                   | -----                         | -----                   | 56.14                       | 56.14                   | 28.73             | 16        | 18   | 210                      |
|         |                                         | -----                         | -----                   | 55.39                       | 55.39                   | 27.50             | 16        | 18   | 210                      |
|         | 30                                      | 10.42                         | 89.58                   | 45.71                       | 51.02                   | 14.47             | 16        | 18   | 210                      |
|         |                                         | 9.93                          | 90.07                   | 45.40                       | 50.41                   | 14.82             | 16        | 18   | 210                      |
|         | 60                                      | 12.44                         | 87.56                   | 41.89                       | 47.8                    | 11.64             | 16        | 18   | 210                      |
|         |                                         | 13.89                         | 86.11                   | 41.29                       | 47.95                   | 11.27             | 16        | 18   | 210                      |
|         | 80                                      | 18.28                         | 81.72                   | 39.79                       | 48.69                   | 10.82             | 16        | 18   | 210                      |
|         |                                         | 22.58                         | 77.42                   | 39.19                       | 50.61                   | 10.52             | 16        | 18   | 210                      |
|         |                                         | 20.00                         | 80.00                   | 39.51                       | 49.38                   | 10.96             | 16        | 18   | 210                      |
|         |                                         | 19.64                         | 80.36                   | 39.80                       | 49.52                   | 10.79             | 16        | 18   | 210                      |
| Set II  | -----                                   | -----                         | -----                   | 61.04                       | 61.04                   | No pulp<br>formed | 16        | 18   | 90                       |
|         | 30                                      | 11.6                          | 88.40                   | 48.33                       | 54.67                   | 18.79             | 16        | 18   | 90                       |
|         | 60                                      | 13.57                         | 86.43                   | 41.33                       | 47.82                   | 16.06             | 16        | 18   | 90                       |
|         | 80                                      | 19.37                         | 80.63                   | 40.74                       | 50.53                   | 14.10             | 16        | 18   | 90                       |
| Set III | -----                                   | -----                         | -----                   | 50.89                       | 50.89                   | 12.50             | 25        | 30   | 210                      |
|         |                                         | -----                         | -----                   | 50.12                       | 50.12                   | 12.20             | 25        | 30   | 210                      |
|         | 30                                      | 10.37                         | 89.63                   | 41.20                       | 45.97                   | 8.16              | 25        | 30   | 210                      |
|         |                                         | 11.00                         | 89.00                   | 40.96                       | 46.02                   | 9.12              | 25        | 30   | 210                      |
|         | 60                                      | 13.14                         | 86.86                   | 40.37                       | 46.48                   | 7.02              | 25        | 30   | 210                      |
|         |                                         | 12.22                         | 87.78                   | 41.14                       | 46.87                   | 7.53              | 25        | 30   | 210                      |
|         | 80                                      | 15.84                         | 84.16                   | 39.07                       | 46.42                   | 8.60              | 25        | 30   | 210                      |
|         |                                         | 18.86                         | 81.14                   | 37.24                       | 45.89                   | 6.60              | 25        | 30   | 210                      |
|         |                                         | 17.95                         | 82.05                   | 38.39                       | 46.79                   | 8.44              | 25        | 30   | 210                      |
| Set IV  | 30                                      | 9.71                          | 90.29                   | 44.45                       | 49.23                   | 10.24             | 25        | 30   | 150                      |
|         | 60                                      | 12.1                          | 87.90                   | 41.27                       | 46.95                   | 8.80              | 25        | 30   | 150                      |
|         | 80                                      | 20.67                         | 79.33                   | 39.25                       | 49.47                   | 10.77             | 16        | 18   | 150                      |
| Set V   | -----                                   | -----                         | -----                   | 49.05                       | 49.05                   | 11.36             | 35        | 37   | 210                      |
|         | -----                                   | -----                         | -----                   | 48.44                       | 48.44                   | 8.60              | 35        | 37   | 210                      |

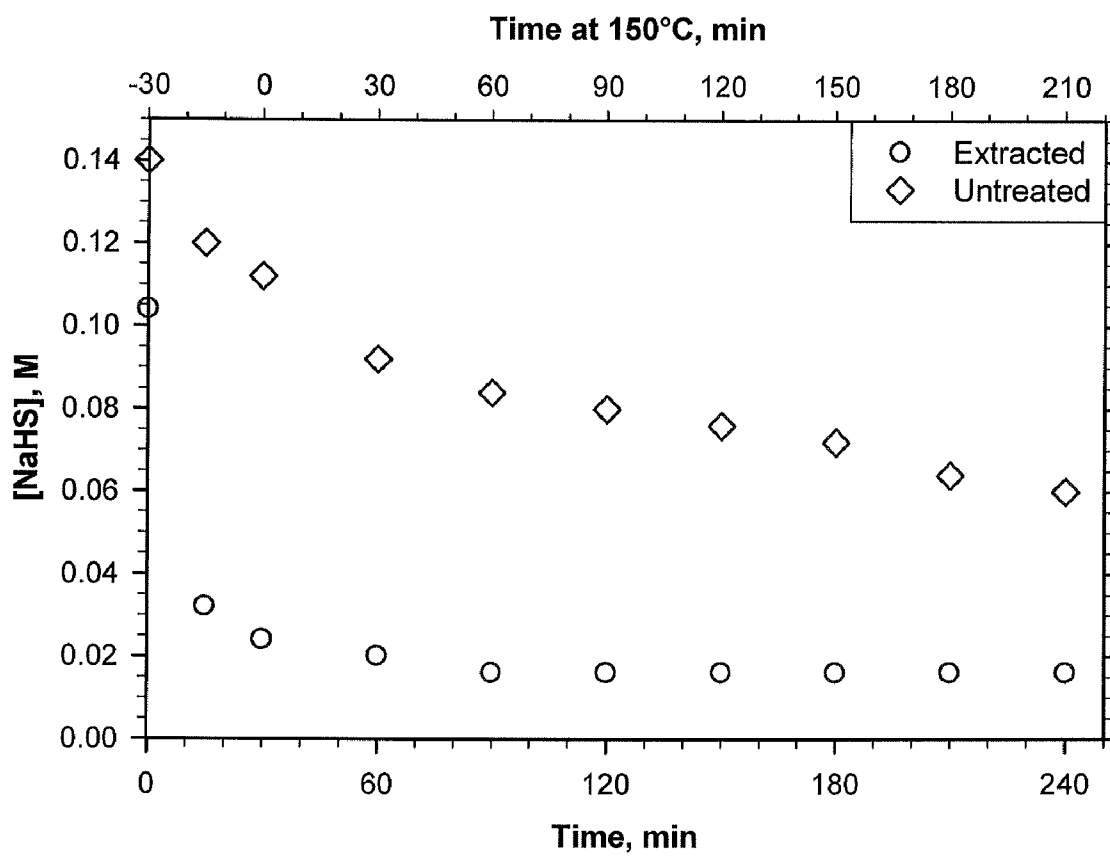
FIGURE 2

**FIGURE 3**

**FIGURE 4**

**FIGURE 5**

**FIGURE 6**

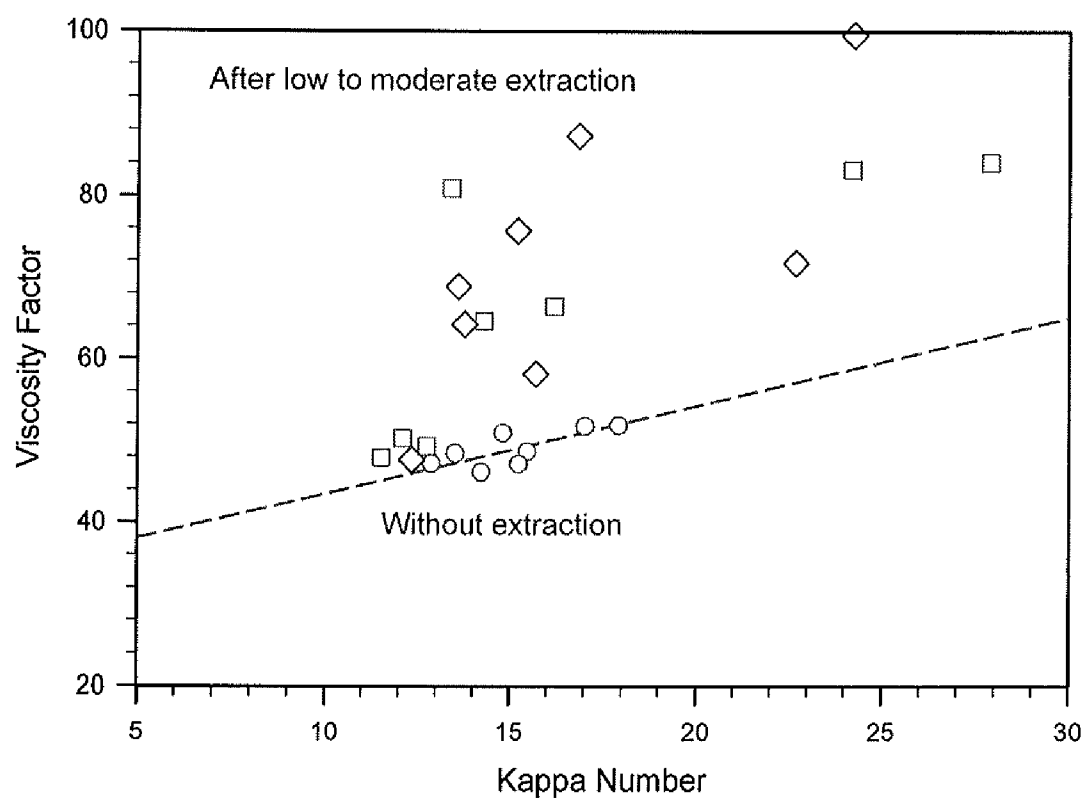
**FIGURE 7**

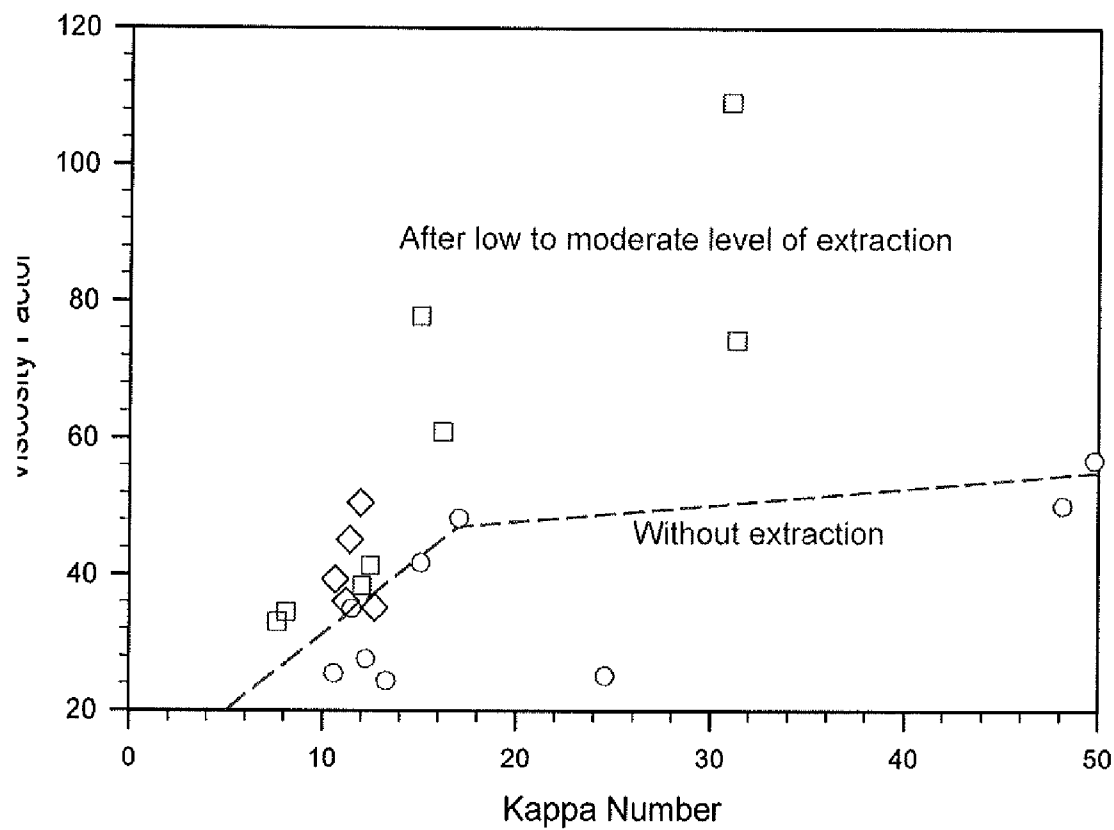
| No. | Residence time<br>in extraction,<br>min | Active alkali and<br>Sulfidity | Scott Bond,<br>J/m <sup>2</sup> | Tear, g-<br>cm | Burst Strength,<br>kPa | Bulk,<br>cm <sup>3</sup> /g |  |
|-----|-----------------------------------------|--------------------------------|---------------------------------|----------------|------------------------|-----------------------------|--|
| 1   | None                                    | 16% AA,<br>18% S               | 135.7                           | 2.5            | 160 - 144              | 1.96                        |  |
| 2   |                                         |                                | 132.5                           | 2.5            | 158 - 142              |                             |  |
| 3   | 30                                      |                                | 95.1                            | 2.5            | 100 - 96               | 2.06                        |  |
| 4   |                                         |                                | 88.9                            | 2.6            | 98 - 94                |                             |  |
| 5   | 60                                      |                                | 91.0                            | 2.3            | 79 – 76                | 2.02                        |  |
| 6   |                                         |                                | 93.2                            | 2.5            | 79 – 77                | 2.04                        |  |
| 7   | 80                                      |                                | 84.1                            | 2.3            | 87 – 84                | 2.00                        |  |
| 8   |                                         |                                | 77.3                            | 2.0            | 79 - 76                |                             |  |
| 9   |                                         |                                | 85.6                            | 2.1            | 82 – 80                |                             |  |
| 10  |                                         |                                | 86.7                            | 2.3            | 80 – 77                | 2.06                        |  |
| 11  | None                                    | 35% AA + 37% S                 | 93.2                            | 3.0            | 107 – 103              | 1.94                        |  |
| 12  | 60                                      | 25% AA + 30% S                 | 88.4                            | 2.0            | 59 - 58                | 2.16                        |  |

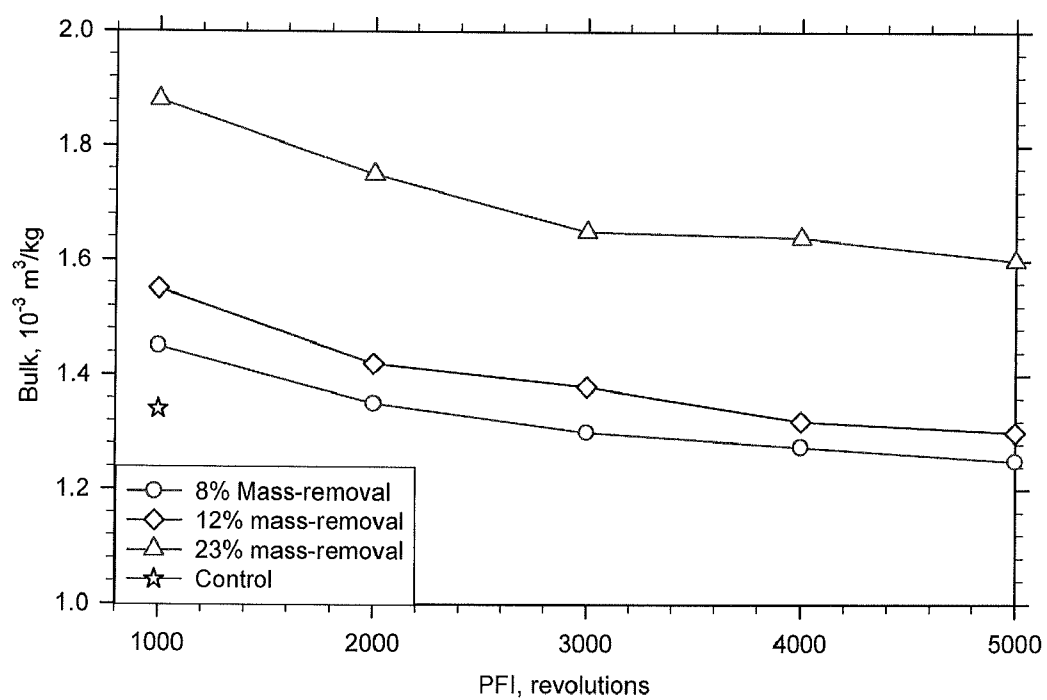
**FIGURE 8**

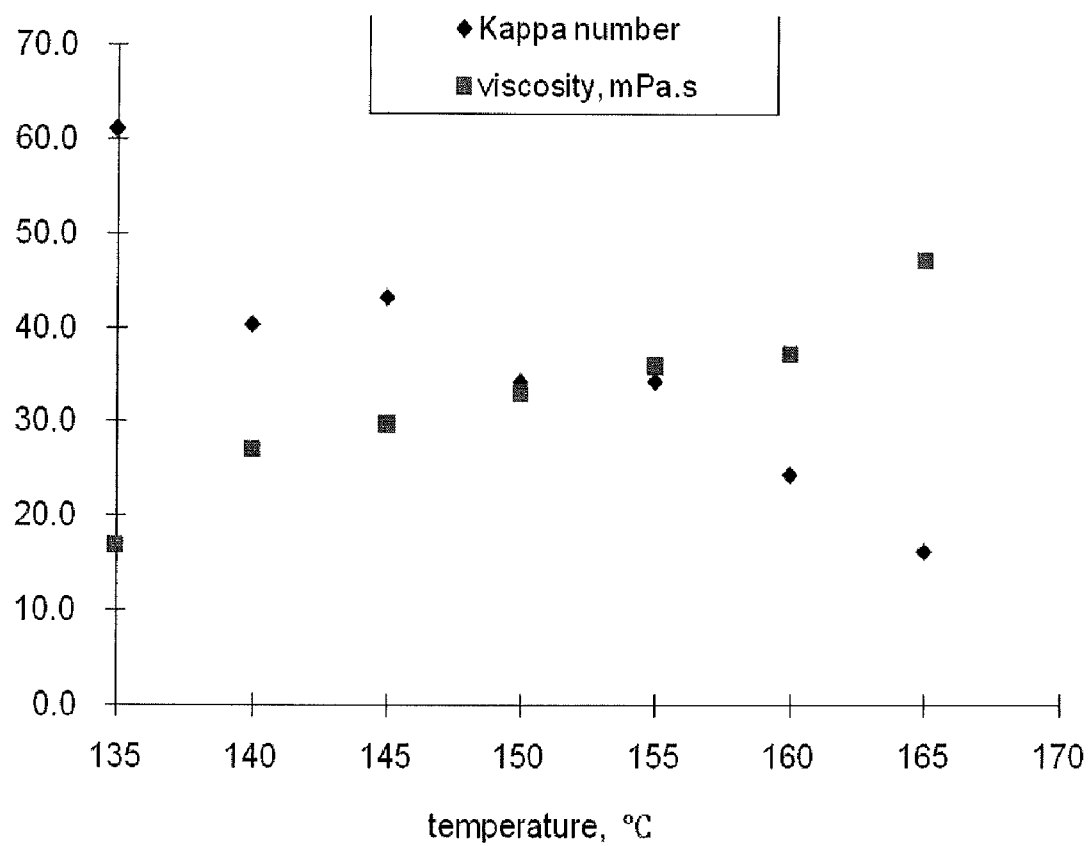
| Pulping conditions or pulp        | Untreated Chips            | Chips after hot-water extraction at 160°C for 2 hours |
|-----------------------------------|----------------------------|-------------------------------------------------------|
| Active Alkali, %                  | 16.0                       | 16.0                                                  |
| Sulfidity, %                      | 25.0                       | 25.0                                                  |
| H-Factor                          | 842                        | 453                                                   |
| Cooking temperature, °C           | 165                        | 155                                                   |
| Cooking time, minutes             | 75                         | 95                                                    |
| Anthraquinone, %                  | 0                          | 0.15                                                  |
| Digester yield, %                 | 52.4                       | 52.5                                                  |
| Overall yield, %                  | 52.4                       | 40.4                                                  |
| Kappa number                      | 18.0                       | 15.6                                                  |
| Bulk, cm <sup>3</sup> /g at (CSF) | 1.441 (393)<br>1.340 (363) | 1.608 (470)<br>1.520 (383)                            |
| Relative viscosity                | 1                          | 0.96                                                  |

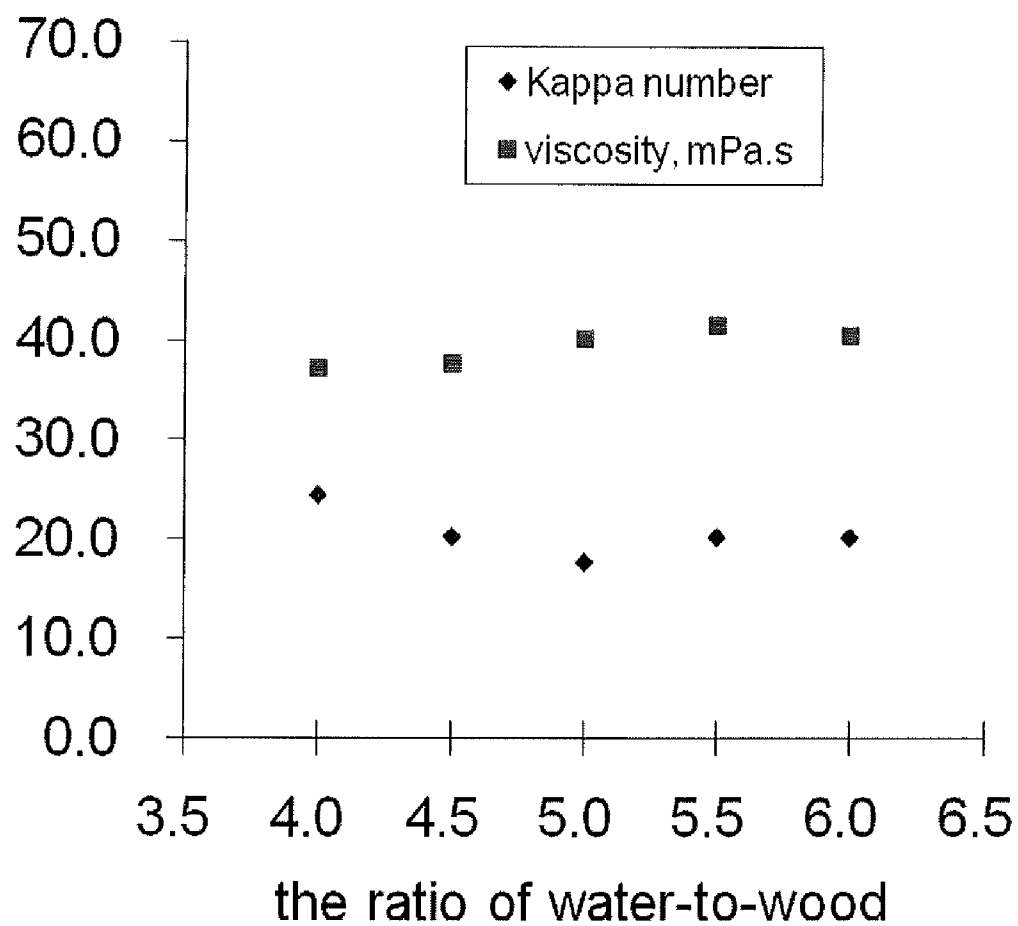
**FIGURE 9**

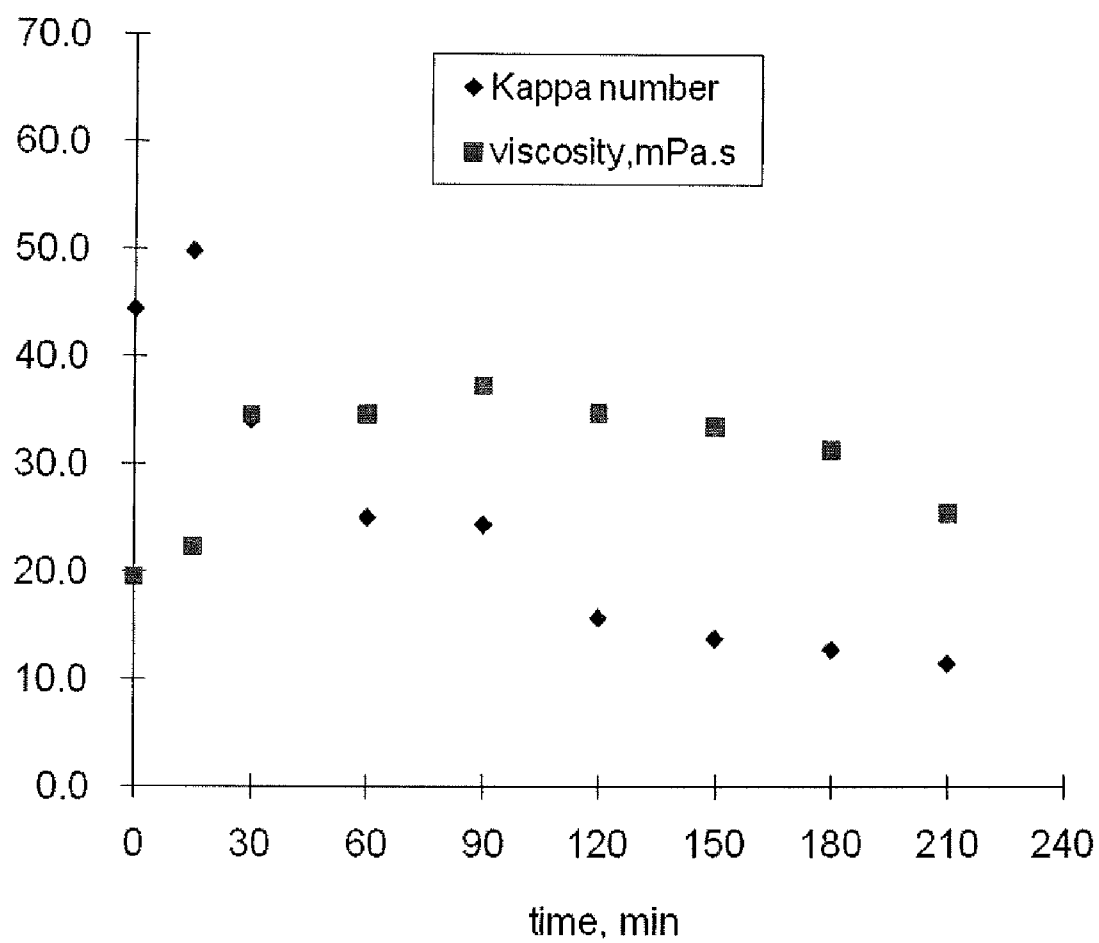
**FIGURE 10**

**FIGURE 11**

**FIGURE 12**

**FIGURE 13**

**FIGURE 14**

**FIGURE 15**

## KRAFT-PULPING OF HOT WATER EXTRACTED WOODCHIPS

### CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 61/233,704 filed on Aug. 13, 2009, the entire contents of which are incorporated herein by reference.

### FIELD OF THE INVENTION

[0002] The invention relates generally to the field of Kraft pulping of hot-water extracted wood chips. More specifically, the present invention is directed to treating lignocellulosic materials with a hot water extraction process to remove a substantial portion of hemicellulose, Kraft pulping the treated lignocellulosic material, thereby producing a lighter pulp with a lower lignin concentration, lower production time and/or lower chemical charge with lower residual chemical content.

### BACKGROUND OF THE INVENTION

[0003] There are a number of processes that convert lignocellulosic materials to pulp. Lignocellulosic materials comprise cellulose, lignin and hemicellulose, with conventional pulping operations recovering the cellulose in the form of long, flexible, natural linear homopolymer fibers. Lignin acts as a natural phenolic "glue" which holds the fibers of cellulose together, with the cellulose fibers and lignin being encrusted with the lower molecular weight hetero-sugar polymer, hemicellulose.

[0004] Pulp is the fibrous slurry of cellulosic fibers which is fed to a paper machine to produce paper. Mechanical, chemical and hybrid methods dominate commercial pulping plants. About 25% of worldwide pulp production is mechanical pulp. It is a high-yield process but suffers from high energy costs and damage to the lignocellulosic fibers. This damage produces lower strength paper. These disadvantages (cost and quality) limit the number of applications for pulp.

[0005] The chemical method of pulping lignocellulosic material produces a chemical pulp. The dominant chemical pulping process is the Kraft Process. The traditional Kraft Pulping process, introduced in 1879, is a process in which lignin is removed in the presence of a high concentration of sodium hydroxide and sodium sulfide. The Kraft process is the dominant chemical pulping process being used today. The popularity of the Kraft process is due to the process's insensitivity to the wood condition, favorable energy recovery and chemical recovery capabilities. One problem associated with the Kraft pulping process is non-uniformity of the pulp formed from the lignocellulosic material. Uniformity of the pulp formed from the lignocellulosic material is critical to improving the performances of cooking and downstream operations such as bleaching and papermaking. Incomplete penetration and inadequate diffusion of chemicals into lignocellulosic material remain the primary reasons for improper delignification and lower quality pulp.

[0006] Another problem associated with the Kraft pulping process is that the harsh chemicals used during the Kraft pulping process dissolve about 20-30% of the wood weight into the pulping liquor, this lost wood weight being in the form of lignin and hemicellulose. During commercial Kraft pulping, about 70% of the hemicellulose is removed from the

fibers. The removed hemicellulose and lignin is mostly burned in the boilers after the cellulose has been separated out for pulp production.

[0007] Hemicellulose is a mixture of sugar and sugar acids, a major component of which are xylans. The prior art has had difficulty in isolating hemicelluloses, with the majority of hemicelluloses being dissolved during Kraft pulping and discharged after pulping with the rest of the pulping liquor. The inability to capture a pure stream of a hemicellulose has limited the overall economic efficiency of the pulping process.

[0008] Hemicellulose is a relatively underutilized component of the wood during the traditional Kraft pulping process, and has commercial value beyond being burned in a furnace. Namely, hemicelluloses can be used as a raw material for production of furfural, ethyl alcohol, hydrogels, barrier films and for yeast nutrition. Thus, conventional pulping does not address at least one major aspect of commercial exploitation of lignocellulosic materials, mainly the use of extracted hemicellulose.

[0009] What is desired is a process which prepares lignocellulosic materials for a pulping process which will not require the addition of caustics, and will provide a benefit to the pulping, bleaching and fiber quality of the pulp produced. Further, what is desired is an improved pulping process to address the problem of non-uniform pulp caused by the lack of impregnation of chemicals used in traditional chemical pulping into the lignocellulosic material. Further, what is desired is an improved recovery for economically valuable products, the products being either a higher viscosity pulp, a lighter (bulkier) pulp, or pulp with a higher pulp yield.

[0010] Embodiments of the present application provide a method that addresses the above and other issues.

### SUMMARY OF THE INVENTION

[0011] The present invention is directed to an omnibus process of pulping lignocellulosic materials. The process is directed towards a method to 1) reduce pulp weight (increase bulk); 2) increase viscosity; or 3) increase the pulp yield of a lignocellulosic material. This method comprises the following steps; preparing a lignocellulosic material, contacting the lignocellulosic material in a vessel with hot water or steam for a predetermined time, producing acetic acid from the reaction of the hot water or steam and the lignocellulosic material, lowering the pH to less than about 4, removing lignocellulosic material extracts including a large percentage of hemicellulose, acetic acid and metal ions from the vessel, exposing contacted lignocellulosic material to pulping chemicals in a pulping reactor, forming a contacted lignocellulosic material pulp with a kappa number below about 19 after about 90 minutes of contact with the pulping chemicals, exposing the contacted lignocellulosic material pulp to whitening agents, and producing a whitened hot water contacted lignocellulosic material pulp.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The present invention will be better understood by reference to the following drawings of which:

[0013] FIG. 1 is a schematic flow diagram of the omnibus pulping process of the present application;

[0014] FIG. 2 is a table of corresponding fiber properties for exemplary sets of pulps;

[0015] FIG. 3 is a graphical representation of percentage mass removal during hot water contacting as a function of time;

[0016] FIG. 4 is a graphical representation of the dissolution of various components as measured in the hot water contacting vessel during hot water contact as a function of time;

[0017] FIG. 5 is a graphical representation of the light absorptivity of the liquid in the pulping reactor during pulping as a function of time;

[0018] FIG. 6 is a graphical representation of residual NaOH concentration of the liquid in the pulping reactor during pulping as a function of time;

[0019] FIG. 7 is a graphical representation of residual NaHS concentration of the liquid in the pulping reactor during pulping as a function of time;

[0020] FIG. 8 is a table displaying various properties of pulp obtained with 210 minutes of maintained temperature of 150° C. in an M/K digester for eucalyptus woodchips;

[0021] FIG. 9 is a table displaying various properties of hot water contacted, Kraft pulped sugar maple wood chips;

[0022] FIG. 10 is a graphical representation of the effect of hot water contact on the pulp viscosity of woodchips through variation of the H-factor for mixed northeast hardwoods;

[0023] FIG. 11 is a graphical representation of the effect of hot water contact on the pulp viscosity of woodchips through variation of the active alkali concentration for mixed northeast hardwoods; and

[0024] FIG. 12 is a graphical representation of the effect mass removal has on hot water contacted wood chips as a function of bulk and PFI revolutions, measuring the amount of refining required.

[0025] FIG. 13 is a graphical representation of the effect temperature during hot water extraction has on the kappa number and pulp viscosity.

[0026] FIG. 14 is a graphical representation of the effect liquor to wood ratio has on the kappa number and pulp viscosity during hot water extraction.

[0027] FIG. 15 is a graphical representation of the effect the length of time spent in hot water extraction has on kappa number and pulp viscosity.

#### DETAILED DESCRIPTION

[0028] The method of the present invention is an improvement over pulping methods which do not have a hot water contacting stage. The improvements are, inter alia, an increased pulp yield, pulp bulk and pulp viscosity, thereby producing a higher quality pulp. Initially an amount of lignocellulosic material is prepared for contact with hot water or steam in a vessel. Preparation could include chipping or cutting to reach a desired size and shape. The prepared lignocellulosic material is placed in a vessel and contacted with steam or hot water for a predetermined time, which could be any amount of time from 1 minute to 7 days. In one embodiment, the prepared lignocellulosic material is contacted with steam or hot water for about 90 minutes. The hot water in the vessel is between about 20° C. and 200° C. In one embodiment, the hot water in the vessel is about 150° C. This time period where the lignocellulosic material is being contacted with hot water causes a lowering of the pH level to less than about 5 because acetic acid is being produced from a reaction between the acetyl groups of the lignocellulosic material and the hot water or steam. In one embodiment the pH is lowered to about 3.5. In one embodiment, the acetic acid concentration reaches about 0.06 M. After the predetermined time for hot water or steam contact, the lignocellulosic material is removed and the remaining liquid is extracted from the vessel. This liquid contains hemicelluloses, the produced acetic acid, metal ions

among other extracts, which can be purified and commercialized. The liquid, metal ions and other extracts contain from about 2% to about 25% of the mass the lignocellulosic material had prior to hot water contact. In one embodiment, the liquid, metal ions and other extracts contain from about 8% to about 15% of the mass the lignocellulosic material had prior to hot water contact. At this point, the lignocellulosic material is exposed to pulping chemicals in a reactor which remove lignin. The pulping chemicals are consumed by about 80% within about 60 minutes by the treated lignocellulosic material. The residual concentration of the pulping chemicals in the contacted lignocellulosic material is about 10% of the initial concentration of pulping chemicals within the reactor. The pulping chemicals comprise sodium hydroxide and sodium sulfide. In one embodiment the initial concentration of sodium hydroxide within the reactor is 16% and the initial concentration of sodium sulfide within the reactor is 18%. In one embodiment, the pulping chemicals comprise sodium hydroxide. In one embodiment, the reactor is heated to between about 150° C. and about 180° C. The pulp formed from this exposure has a kappa number below about 19 after about 90 minutes of exposure to the pulping chemicals in a pulping reactor. This kappa number after 90 minutes is lower than a kappa number of an un-treated lignocellulosic material for the same amount of time because the de-lignification process occurs more quickly for hot water or steam treated lignocellulosic material. In one embodiment, the contacted lignocellulosic material pulp has a kappa number about 90% lower than a pulp which has not undergone hot water contact. Subsequent to pulping, the formed pulp is exposed to whitening agents, thereby producing a whitened hot water or steam contacted lignocellulosic material which can be made into a paper product. This whitened hot water or steam contacted lignocellulosic material has a bulk which is higher than a non-hot water contacted lignocellulosic material. In one embodiment this whitened hot water or steam contacted lignocellulosic material has a bulk of at least about 2.00 cm<sup>3</sup>/g after about 210 minutes of contact with the pulping chemicals. A more detailed description follows.

[0029] The process of the present application begins with the raw material utilized in the production of pulp and its by-products—lignocellulosic material. Some exemplary lignocellulosic materials utilized in pulping are woods, grasses and the like. Specific tree genus's which can provide lignocellulosic material for the pulping process include, among others, fir, hemlock, juniper, pine, spruce, larch, aspen, beech, alder, wattle, balsa, eucalyptus, maple, oak, birch and willow. Generally woods not suitable for use as lumber and certain species of grass are most commonly employed as raw materials in pulp and subsequent paper production.

[0030] Lignocellulosic materials 1 in accordance with the process depicted in FIG. 1, are subjected to hot water contact 3, where extraction of hemicelluloses from the lignocellulosic materials 1 takes place.

[0031] In hot water contact step 3, water, at temperature in the range of between about 50° C. and about 200° C. and a pH in the range of between about 1 and 7 contacts the lignocellulosic material 1 for a period in the range of between about 1 minute and about 7 days. More preferably, the water is at a temperature in the range of between about 140° C. and about 180° C., at a pH in the range of between about 3 and about 7 and a contact time between the lignocellulosic material 1 and the hot water is in the range of between about 30 minutes and about 120 minutes. As the wood is treated with hot water, acetic acid is produced. Acetic acid is produced as the acetyl

group (1-4.5% of the weight of the original lignocellulosic material 1) in lignocellulosic material 1 hydrates and dissociates, causing a subsequent reduction in pH levels. The acetic acid further catalyzes the de-acetylation and hydrolysis of lignocellulosic material 1, creating an autocatalytic reaction. The produced acetic acid also depolymerizes the hemicelluloses present in lignocellulosic material 1, for example the hemicellulose xylan to xylose and xylose oligomers, so that an un-damaged hemicellulose stream can be extracted as described, *supra*.

[0032] The hot water contacting step 3 mainly removes hemicelluloses, leaving a substantially uniform material which can be pulped. Hemicelluloses are extracted as their glycosidic bonds are broken by the absorption of protons and water molecules to the glycosidic bond sites during hot water extraction step 3. This autocatalytic hydrolysis leaves both cellulose and lignin intact as essentially un-degraded polymers and increases the lignin density at the surface of the hot water contacted lignocellulosic material 7.

[0033] The mass of the lignocellulosic material 1 which is lost due to hot water contacting step 3 can be seen in FIG. 3, which mainly represents the mass lost due to removal of hemicelluloses. An exemplary embodiment for a process for hot water contacting step 3 is described below in Example 1.

[0034] This hot water contacting step 3, which serves as an extraction step, represents an advance in the art insofar as this step not only enhances the quality of pulp for pulping, which is conducted subsequent to this step, but, in addition, the step that occurs downstream of the pulping step, pulp bleaching, requires fewer chemicals. Pulp quality and quantity is measured by several parameters, several of which the present process enhances. Mainly, the Kappa number of a pulp, which measures the lignin content or bleachability is enhanced by the present process. Kappa number is representative of the lignin content chemical requirement for bleaching, as the Kappa number decreases, so does the lignin content and chemical concentration required to achieve a desired level of whiteness in a paper product. Another pulp quality the present process enhances is pulp bulk. Pulp bulk is representative of the amount of volume a unit weight of a pulp will define. As pulp bulk increases so does the quantity of a paper product the pulp will be made into.

[0035] The hot water contacting step 3 is an example of autocatalytic hydrolysis which has advantages over other methods of extraction including no reduction in value due to caustic or metal hydroxides, there is no increase in corrosion from mineral acids, no sludges are generated, capital and operational costs are lowered and cellulose is not significantly degraded. Further, environmental and recovery side effects are avoided as caustic or sodium is not added to the process streams and no byproducts from mineral acid neutralization are produced. Because there is no caustic addition, hydrolyzed hemicelluloses produce acetic acid, in addition to sugars, with the acetic acid further catalyzing the extraction and hydrolysis reactions.

[0036] The aqueous extract 13 resulting from hot water contact step 3, an aqueous solution, is subject to further processing to recover chemical values present in the original lignocellulosic materials charged into the process. Aqueous extract 13 contains about 50% of the hemicellulose which was originally contained in the lignocellulosic material 1, which translates to about 8-25% of the dry weight of lignocellulosic material 1. The aqueous extract 13, in accordance with this aim is passed into a separation unit 14. Separation

unit 14 can recover the chemical values present in of aqueous extract 13 through fractionation or concentration with a membrane.

[0037] This separation permits recovery of material values inherent in lignocellulosic materials. Acetic acid is a commodity chemical with commercial value. Hemicellulose sugars, principally xylose, can, in the absence of the separated acetic acid, be used to produce other valuable products including processing for bioenergy applications. Xylose can also be converted polymers.

[0038] As depicted in FIG. 1, the aqueous extract 13 is separated in separation unit 14 into an acetic acid stream 15 and hemicellulose sugar aqueous solution stream 16. The hemicellulose sugar can, in the absence of acetic acid be treated to form valuable products 17 such as but not limited to ethanol, also the hemicellulose sugar aqueous solution stream 16 can be converted polymers 18.

[0039] The hot water extracted lignocellulosic material 7 is next subjected to chemical pulping step 8. The removal of hemicelluloses in hot water contact step 3 removes chromophors in fiber with chemical units such as uronic and hexenuronic acids that are resistant to pulping and bleaching. Further, because of hot water contacting step 3, there is an increase in internal porosity of the lignocellulosic material, rendering lignin bond sites more open and accessible to pulping chemicals, leaving pulping and bleaching requirements reduced. Internal porosity is increased because of the breaking of covalent bonds between lignin and carbohydrate as a result of hemicellulose removal.

[0040] The acidic conditions created during hot water contacting step 3 causes the removal of metal ions and carboxyl groups, especially those associated with hemicelluloses such as uronic acid in the lignocellulosic material 1. With a hydration transition pH of about 3.5 for polyvalent cationic species, the association or adsorption of these heavy metals on fibers is reduced when the woodchips or pulp is subject to an acidic environment with pH less than about 3.5.

[0041] This increased porosity and removal of metal ions and carboxyl groups allows lower chemical concentrations and shorter cooking times during pulping, in turn resulting in less fiber damage and a higher quality pulp 10. As an exemplary embodiment, the de-lignification process is described in Example 2 *supra*.

[0042] During chemical pulping 8, the hot water extracted lignocellulosic material 7 is added to a pulping reactor with water, active alkali and sulfide. Preferably, the initial concentration of active alkali is about 16%. Preferably, the initial concentration of sodium sulfide is about 18%. As one example of the exemplary method, the alkali and sulfide concentration change with respect to time is described in Examples 3 and 4 *supra*.

[0043] As can be seen in Example 3, alkali is consumed more quickly for hot-water extracted lignocellulosic material 7 as compared to untreated lignocellulosic material, and the residual concentration of alkali is lower in hot water extracted lignocellulosic material 7 as compared to untreated lignocellulosic material. Because of the fast consumption of alkali, a pulping facility can benefit by a higher throughput, which is the result of faster pulping times. Further, a lower load of alkali is required to reach the same consumption in a reasonable time, avoiding the use of a larger amount of costly chemicals.

[0044] As can be seen in example 4, sulfide is consumed more quickly by hot-water extracted lignocellulosic material 7 as compared to untreated lignocellulosic material, and the residual concentration of sulfide is lower in hot water extracted lignocellulosic material 7 as compared to untreated lignocellulosic material. Because of the fast consumption of sulfide, a pulping facility can benefit by a higher throughput, which is a result of faster pulping times. Further, a lower load of sulfide is required to reach the same consumption in a reasonable time, avoiding the use of a larger amount of costly chemicals.

[0045] After treatment in chemical pulping step 8, hot water extracted lignocellulosic material 7 becomes a pulp 10. The overall yield of pulp 10 can be similar to the yield of pulp received for untreated lignocellulosic material and pulp 10 has a lower kappa number. In one example, shown in FIG. 2, Pulp 10 has a lower kappa number and an increase in mass removal as compared to pulp which has not been hot water contacted. Non-hot water contacted pulp is referred to herein as control pulp. FIG. 2 shows that with an increase in length of hot water contact step 3, the kappa number decreases and mass removal increases. Kappa number is an indication of the lignin content, or bleachability of a lignocellulosic material pulp, with a lower number being associated with less lignin content and increased ability to be bleached with a lower chemical concentration. Pulp 10 has different properties than a control pulp, for example pulp 10 has a decreased burst strength and Scott bond, with an increase in bulk. The decrease in burst, tear, and Scott bond can be recovered by addition of a small amount of a bonding agent. A non-exhaustive list of examples of bonding agents includes starch, PHA, and PLA. Therefore, the strength is not an important factor for the hot-water extracted pulp.

[0046] In one example, shown in FIG. 8, bulk of pulp 10 is increased. Bulk of pulp 10 can be increased through either increasing the length of hot water extraction step 3 or increasing sulfidity. Scott bond, tear, burst strength and bulk are shown in FIG. 8, bulk is also shown in FIG. 12. As can be seen in FIG. 12, there is an increased bulk of pulp 10 as mass removal increases as compared to the bulk of control pulp. Further, the bulk of pulp 10 remains high as the amount of refining increases, which is measured in revolutions of a PFI mill.

[0047] Pulp 10 has further properties which differentiate it from control pulp, including viscosity and a lower H factor. FIG. 9 shows the decrease in H factor associated with pulp 10 as compared to control pulp. H factor is the effective cooking time (or the time duration if the pulping reaction were conducted at 100° C.). A lower H factor indicates a pulp which required a shorter time for lignocellulosic material to be converted to a pulp of a certain Kappa number.

[0048] FIG. 9 shows the effect of hot water contact step 3 on the pulping requirements for hot water extracted lignocellulosic material 7. As can be seen, hot water contacting step 3 results in viscosity increase of pulp 10. Example 5 below further describes FIG. 10 and FIG. 11 and the measure of viscosity of pulp 10.

[0049] FIG. 13 shows the effect of hot water contact temperature during hot water contact step 3 on the Soda pulping of Aspen woodchips. In this figure, there has been no sulfur addition to the soda pulping liquor. It can be seen that an increase in contact temperature increases the pulp viscosity while decreasing the kappa number.

[0050] FIG. 14 shows the effect of liquor to wood ratio during hot-water contact step 3 on the soda pulping of Aspen woodchips. In this figure, there has been no sulfur addition to the soda pulping liquor. It can be seen that the change in viscosity and kappa number is small as the liquor to wood ratio is changed during hot-water extraction step 3.

[0051] FIG. 15 shows the effect of extraction time during hot water contact step 3 on soda pulping of Aspen woodchips. In this figure, there has been no sulfur addition to the soda pulping liquor. It can be seen that while kappa number decreases with an increase of extraction time during hot water contact step 3, viscosity initially increases but subsequently begins to decrease. Because of hemicellulose removal and a subsequent reduced kappa number, there are positive benefits to pulping, bleaching and fiber quality.

[0052] Once hot water contacted lignocellulosic material 7 has just been pulped in chemical pulping step 8, it is bleached at bleaching step 13. In one preferred embodiment, it is preferred that bleaching step 13 be accomplished by contacting the pulp with a strong oxidizing agent. This strong oxidizing agent may be selected from the non-exhaustive group consisting of oxygen, hydrogen peroxide, ozone, peracetic acid, chlorine, chlorine dioxide, a hypochlorite anion and mixtures thereof. A particularly preferred oxidizing agent employed bleaching step 13 is hydrogen peroxide.

[0053] In another preferred embodiment, during bleaching step 13, pulp 10 is bleached in two oxygen-contacting stages. In this embodiment, it is desirable that there be a washing step between the two oxygen-contacting stages. Alternatively, that preferred embodiment with oxygen and sodium hydroxide between the two oxygen-contacting stages.

[0054] In another preferred embodiment, during bleaching step 13, pulp 10 is contacted with chlorine dioxide in the presence of at least one additional agent. In one preferred embodiment, the additional agent is oxygen. In another preferred embodiment, the additional agent is magnesium hydroxide or another magnesium containing compound. In yet another preferred embodiment the additional agents are oxygen and magnesium hydroxide or another magnesium containing compound. In still another preferred embodiment, the additional agent is potassium hydroxide or calcium hydroxide.

#### Example 1

[0055] In all of the following examples, the lignocellulosic material used was Eucalyptus wood chips, unless otherwise noted. Although Eucalyptus wood chips were used as the lignocellulosic source, any lignocellulosic material could be used.

[0056] A liquor (water) to lignocellulosic material ratio of 4:1 was added to a vessel capable of holding pressure, for example a high pressure laboratory M/K circulation digester and brought from about room temperature to about a temperature of 160° C. over about a 40 minute period. During this hot water contacting time, acetic acid was produced through an auto-hydrolysis reaction to reach a concentration of about 0.06M.

[0057] The vessel was maintained at this temperature for about 30 minutes to about 80 minutes. The extracted lignocellulosic material was then thoroughly washed with water to remove dissolved substances. The remaining liquor in the vessel was then separated into its constituents.

**[0058]** The mass which was removed during hot water contacting step accounts for the loss due to the hemicellulose and lignin removal, which depends on the length of time the lignocellulosic material was exposed to the hot water contact process. As can be seen in FIG. 3 below, mass removal, based on virgin, un-treated woodchip dry mass, or control wood chip dry mass, after about 30 minutes at peak temperature was about 10%, mass removal after 60 minutes was about 13%, with mass removal after about 80 minutes being about 20%.

**[0059]** The hot water contacting step produced a hot water extracted lignocellulosic material product and an aqueous extract. FIG. 4 is an example of components of the liquid which were within the reaction vessel as a function of time. The liquid in the reaction vessel became the aqueous extract.

#### Example 2

**[0060]** FIG. 5 shows the UV light absorptivities of the liquid, or black liquor, within the pulping reactor during the pulping process at 280 nm during the kraft pulping of hot-water extracted wood chips and control woodchips. Time zero represents when the reactor contents, including woodchips, water and an initial concentration of active alkali at 16% and sulfide at 18%, have been mixed for 15 minutes at room temperature, with the temperature about to be raised. The active alkali is the percentage of equivalent  $\text{Na}_2\text{O}$  in the solution and the sulfidity is the ratio of  $\text{Na}_2\text{S}$  (or specifically its equivalent in  $\text{Na}_2\text{O}$ ) to the total  $\text{Na}_2\text{O}$ . The temperature reached  $150^\circ\text{C}$ . in about 30 minutes, and was maintained at that temperature. Based on FIG. 5, there is a noticeable increase in UV light absorptivities at 280 nm during the initial de-lignification periods (from the start of the temperature raise to around 70 minutes), after which the absorptivity increased more slowly and leveled off towards the end. This initial increase in light absorptivity was mainly due to the concentration of lignin in the reactor liquid. The de-lignification process took a longer time to reach near completion (approximately 210 minutes) for control woodchips, as compared to hot-water extracted woodchips which reached near completion sooner (approximately 120 minutes). This difference in time is an advantage which reduces energy input into the pulping system, and increases throughput for a pulping facility.

#### Example 3

**[0061]** FIG. 6 shows the sodium hydroxide concentration in the black liquor as a function of time during chemical pulping for control and hot-water extracted wood chips. Initially sodium hydroxide was added to water in the pulping reactor at a concentration of about 0.956 Molar, followed by the addition of woodchips. The contents of the pulping reactor were mixed for 15 minutes at room temperature. The temperature was increased to about  $150^\circ\text{C}$ . over about 30 minutes. As can be seen in FIG. 6, during the first 30 minutes, the drop in alkali concentration in the black liquor was very rapid for hot-water extracted woodchips. More alkali was consumed at a faster rate for the pulping of hot-water extracted woodchips as compared to the control chips, and the residual concentration of alkali was much higher in the control wood chips as compared to the hot-water extracted wood chips.

#### Example 4

**[0062]** FIG. 7 shows the sodium sulfide concentration in the black liquor as a function of time during chemical pulping for control and hot-water extracted wood chips. Initially sodium sulfide was added to water in the pulping reactor at a concen-

tration of about 0.201 Molar, followed by the addition of woodchips. The contents of the pulping reactor were mixed for 15 minutes at room temperature. The temperature was increased to about  $150^\circ\text{C}$ . over about 30 minutes. As can be seen in FIG. 7, during the first 30 minutes, the drop in sulfide concentration in the black liquor was very rapid for hot-water extracted woodchips. More sulfide was consumed at a faster rate for the pulping of hot-water extracted woodchips as compared to the control chips, and the residual concentration of sulfide was much higher in the control wood chips as compared to the hot-water extracted wood chips.

#### Example 5

**[0063]** FIG. 9 shows the effect of hot water contact on the Kraft pulping requirements for sugar maple wood chips. To achieve similar pulp properties of control pulp properties, hot water contacted wood chips were beneficially exposed to reduced chemical concentrations and/or cooking times. FIG. 10 shows the effect of hot water contacting of woodchips on the pulp viscosity by varying the H factor for mixed northeast hardwoods. FIG. 11 shows the effect of hot water contacting of woodchips on the pulp viscosity by varying the active alkali charge for mixed northeast hardwoods. Pulp viscosity is a measure of chemical damage to the cellulose fibers of woodchips. A higher viscosity is indicative of less damage. For both FIG. 10 and FIG. 11 the hot water contacted woodchips were obtained by extracting mixed Northeast hardwood chips including maple, oak and birch with hot-water at about  $160^\circ\text{C}$ . for times less than 1 hour. Both hot water contacted and control woodchips were Kraft pulped with similar conditions. FIG. 10 shows the variation of pulp viscosity with Kappa number where H-factor, or effective pulping time, was altered while active alkali charge was maintained. FIG. 11 shows that the Kappa number changes were achieved by altering the active alkali charge, but maintaining the same H-factor during pulping. Based on FIG. 9, FIG. 10 and FIG. 11 it can be seen that hot water contacting results in viscosity increases of resultant pulp. A pulp with a high viscosity is an advantage because the pulp will produce a higher strength and quality paper.

#### Example 6

**[0064]** FIGS. 13 through 15 show the effect of hot water contact on the soda pulping for Aspen wood chips. Increase in hot-water contact time and temperature decreases the kappa number. Increase in hot-water contact temperature for 90 minutes increases the resulting pulp viscosity as seen in FIG. 13. A maximum viscosity is observed at 90 minutes contact when the pulping liquor is  $160^\circ\text{C}$ . as seen in FIG. 15. Water to liquor ratio during the hot-water contact prior to soda pulping has a minor impact on the kappa number and viscosity as shown in FIG. 14.

What is claimed is:

1. A method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material, the method comprising the steps of:
  - a. preparing a lignocellulosic material;
  - b. contacting the lignocellulosic material in a vessel with hot water or steam for a predetermined time;
  - c. lowering the pH to less than about 5 by producing acetic acid from the reaction of the hot water or steam and the lignocellulosic material;

- d. removing lignocellulosic material extracts including a percentage of hemicellulose, acetic acid and metal ions from the vessel;
  - e. exposing contacted lignocellulosic material to pulping chemicals in a pulping reactor;
  - f. forming a contacted lignocellulosic material pulp with a kappa number below about 19 after about 90 minutes of contact with the pulping chemicals;
  - g. exposing the contacted lignocellulosic material pulp to whitening agents; and
  - h. producing a whitened hot water contacted lignocellulosic material pulp.
2. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 1, wherein the hot water in the vessel is between about 20° C. and about 200° C.
3. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 2, wherein the hot water in the vessel is about 150° C.
4. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 1, wherein the lignocellulosic material is contacted for between about 1 minute and 7 days.
5. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 4, wherein the lignocellulosic material is contacted for about 90 minutes.
6. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 1, wherein the pH is lowered to about 3.5.
7. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 1, wherein the acetic acid reaches a concentration of about 0.06 M.
8. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 1, wherein the lignocellulosic material extracts are between about 2% and about 25% of the mass of the prepared lignocellulosic material.
9. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 1, wherein the lignocellulosic material extracts are between about 8% and about 15% of the mass of the prepared lignocellulosic material.
10. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 1, wherein the pulping chemicals are consumed by about 80% within about 60 minutes by the contacted lignocellulosic material.
11. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 1, wherein the residual concentration of pulping chemical in the contacted lignocellulosic material prior to exposing the contacted lignocellulosic material to whitening agents is about 10% of initial concentration within the pulping reactor.
12. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water

extracted lignocellulosic material of claim 9, wherein the pulping chemicals comprise sodium hydroxide and sodium sulfide.

13. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 10, wherein the pulping chemicals comprise sodium hydroxide and sodium sulfide.

14. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 1, wherein the contacted lignocellulosic material pulp has a kappa number about 90% lower than a pulp which has not undergone hot water contact.

15. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 13, wherein the pulping chemicals are sodium hydroxide at a concentration of 16% and sodium sulfide at a concentration of 18%.

16. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 13, wherein the pulping reactor is heated to between about 150° C. and 180° C.

17. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 1, wherein the contacted lignocellulosic material pulp has a bulk of at least about 2.00 cm<sup>3</sup>/g after about 210 minutes of contact with pulping chemicals.

18. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 1, wherein the contacted lignocellulosic material pulp has a bulk higher than an un-contacted lignocellulosic material pulp.

19. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 16, wherein the pulping chemicals are sodium hydroxide at a concentration of 16% and sodium sulfide at a concentration of 18%.

20. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 16, wherein the pulping reactor is heated to between about 150° C. and 180° C.

21. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 1, wherein about 50% of the hemicellulose content of the lignocellulosic material is extracted from the vessel during the removal of lignocellulosic material extracts step.

22. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 1, wherein the hot water contacted lignocellulosic material has a residual chemical concentration from about 25% to about 33% of the residual chemical concentration of a non hot water contacted lignocellulosic material.

23. The method of treating lignocellulosic material to increase pulp yield, pulp bulk and pulp viscosity of hot-water extracted lignocellulosic material of claim 1, wherein the pulping chemicals comprise sodium hydroxide.

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