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**CARR et al.**(10) **Pub. No.: US 2009/0008049 A1**(43) **Pub. Date: Jan. 8, 2009**(54) **NON-SCALING CHIP CONDITIONING  
SYSTEM FOR ENERGY REDUCTION IN  
MECHANICAL PULPING**(22) Filed: **Jul. 2, 2008****Related U.S. Application Data**(75) Inventors: **MICHAEL A. CARR,**  
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**D21C 3/20** (2006.01)(52) **U.S. Cl. .... 162/76**(57) **ABSTRACT**

A method for pulping a fibrous lignocellulosic material includes a pretreatment step wherein the lignocellulosic material is reacted with a chelating agent selected from the group consisting of amino acids, monocarboxylic acids and polycarboxylic acids preferably having from two to six carbon atoms. The chelating agent reacts with calcium ions in the material to form stable, water-soluble calcium complexes so as to avoid scaling, and the treated material requires a significantly lower energy input to undergo refining using either a mechanical or thermomechanical pulping method.

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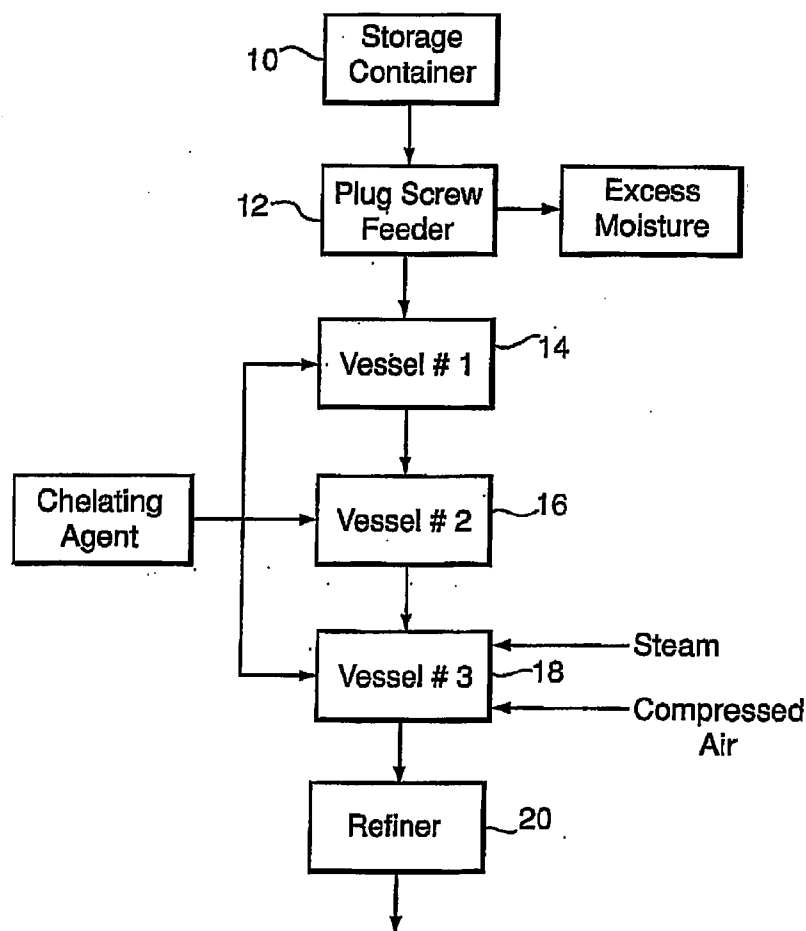
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Fig.1

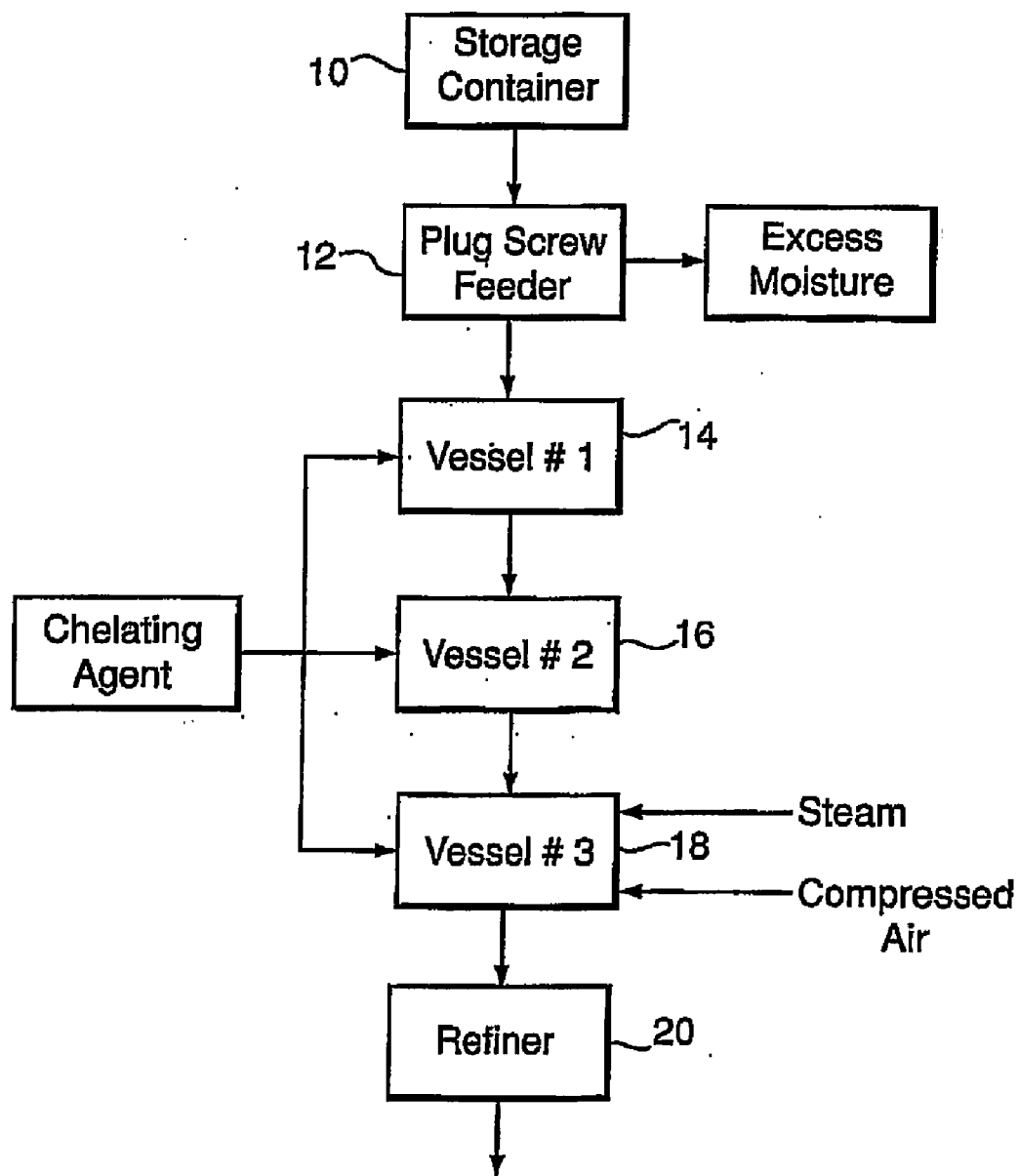
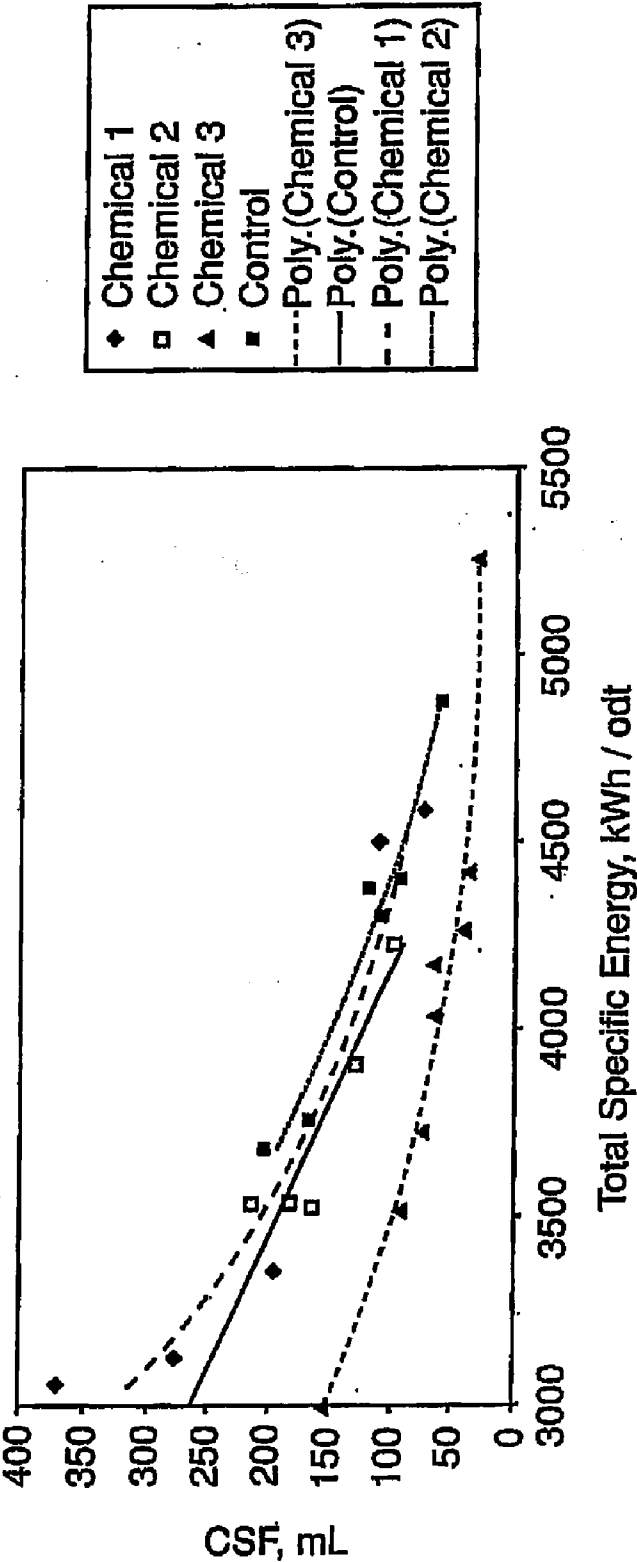


Fig.2

Canadian Standard Freeness vs Total Specific Energy Two Stage Refining



CSF SE Reduction - Chemical 3 Relative to Control

mL  
100 22%  
150 25%

## NON-SCALING CHIP CONDITIONING SYSTEM FOR ENERGY REDUCTION IN MECHANICAL PULPING

### RELATED APPLICATION

[0001] Pursuant to 35 U.S.C. § 119(e), this application claims the benefit of the filing date of U.S. Provisional Patent Application No. 60/948,144, filed on Jul. 5, 2007, the entire disclosure of which is incorporated herein by reference.

### FIELD OF THE INVENTION

[0002] The present invention relates to methods for pretreatment of lignocellulosic materials in order to reduce energy consumption in pulp mills.

### BACKGROUND OF THE INVENTION

[0003] In the production of paper products, lignocellulosic materials such as wood are converted to a viscous liquid suspension called pulp. There are two main categories of wood pulps for papermaking, namely chemical or kraft pulps and mechanical or high yield pulps. In the production of chemical pulps, cellulose fibers are separated by chemically dissolving away the lignin that binds them together. In the production of mechanical pulps, the fibers are physically torn apart, leaving the lignin attached to the fibers.

[0004] In the early days of mechanical pulping, logs were pressed against turning stones to produce ground wood pulp. In the early 1970's, metal disk refiners were introduced as a replacement process for ground wood pulping. These refiners used large horsepower motors to drive disk refiners that grind wood chips under steam pressure to the desired fiber size. This process is called thermo-mechanical pulping (TMP). TMP permits the use of wood chips from sawmills as the lignocellulosic feed material, thereby reducing labor and material costs. One disadvantage of TMP, and mechanical pulping in general, is that large amounts of energy are required to drive the disk refiners which tear the fibers apart. It is estimated that TMP requires 2500 to 3000 Kwhr to refine one ton of pulp, with a typical mill processing about 1000 tons per day. The rising cost of electrical energy threatens the economic viability of TMP mills.

[0005] In recent years, considerable attention has turned to improving energy efficiency of mechanical pulp mills. Some of these efforts have focused on pretreatments which "soften" the lignocellulosic materials and make the fibers easier to separate, thereby reducing energy requirements during refining. Some of these processes have focused on biochemical pretreatment of the lignocellulosic materials by enzymes or microorganisms. One such pretreatment utilizes naturally occurring white rot fungi to pretreat wood. These fungi are believed to preferentially attack the lignin in wood, thereby facilitating the separation of the cellulose fibers in the refiners. Initial tests showed promising results and significant energy reductions were observed when using fungi-treated wood in the refiners. However, pretreatments based on white rot fungi are limited in their commercial usefulness by the fact that treatment times are very long, ranging from two days to two weeks, thereby requiring the mill to stock and treat large inventories of material. Furthermore, the fungal treatment tends to degrade the brightness of the pulp, resulting in increased bleaching costs.

[0006] It was subsequently discovered that the active agent produced by the white rot fungus is oxalic acid, a strong

organic acid. This discovery resulted in the development of pretreatment processes using oxalic acid and oxalic acid derivatives. Examples of these processes are described in International Publication No. WO 02/075043 A1, published on Sep. 26, 2002, and International Publication No. WO 2007/008689 A2, published on Jan. 18, 2007. Oxalic acid pretreatment processes are more controllable, have much shorter treatment times, and result in better pulp quality and brightness as compared to biochemical pretreatment processes. One major disadvantage of oxalic acid pretreatment is, however, the formation of insoluble oxalate salts which form a tenacious scale on inner surfaces of plant piping and vessels. To date, this deficiency has not been overcome, and rising energy costs continue to threaten the viability of mechanical pulping mills.

[0007] Therefore, the need exists for a process for pretreatment of lignocellulosic materials which is non-scaling and which improves the energy efficiency of mechanical pulp mills.

### SUMMARY OF THE INVENTION

[0008] The present invention provides a method for pulping a fibrous lignocellulosic material. The method comprises: (a) reducing the material to a size appropriate for pulping; (b) contacting the material with at least one chelating agent selected from the group consisting of amino acids, monocarboxylic acids and polycarboxylic acids, wherein the chelating agent contains from two to six carbon atoms; (c) reacting the material with the chelating agent at a temperature and for a time sufficient such that the chelating agent reacts with calcium ions in the material to form stable, water-soluble calcium complexes; and (d) mechanically refining the material so as to produce a pulp suspension. In the process of the invention, a lower energy input is required to pulp the material, after the material is reacted with the chelating agent, than if the material was refined without first being contacted with and reacted with the chelating agent. Also, the calcium complexes are sufficiently soluble throughout the entire pulping process so as to substantially avoid the formation of scale on process equipment and piping.

[0009] In a preferred aspect of the present invention, the amino acids are selected from the group consisting of glycine, alanine, valine, serine, threonine, cysteine, asparagine, glutamine, aspartic acid, glutamic acid and gamma-aminobutyric acid.

[0010] In another preferred aspect of the present invention, the monocarboxylic and polycarboxylic acids are selected from the group consisting of citric acid, succinic acid, fumaric acid, malic acid, oxaloacetic acid, propionic acid, valeric acid, acrylic acid, butyric acid, pyruvic acid, malonic acid, glutaric acid, lactic acid and tartaric acid.

[0011] In yet another preferred aspect of the present invention, the chelating agent is added in combination with one or more additional chelating agents selected from ethylenediamine tetraacetate (EDTA) and diethylenetriaminepentaacetate (DTPA).

[0012] In yet another preferred aspect of the present invention, the chelating agent is contacted with the lignocellulosic material in the form of an aqueous solution.

[0013] In yet another preferred aspect of the present invention, step (b) is conducted in a first vessel and wherein step (c) is conducted in a second vessel, and the chelating agent is preferably added to both the first and second vessels.

**[0014]** In yet another preferred aspect of the present invention, the solubility of the calcium complexes is at least one order of magnitude greater than the solubility of calcium oxalate.

**[0015]** In yet another preferred aspect of the present invention, the calcium complexes remain substantially dissolved in the pulp suspension throughout a pH range of from about 5 to about 9.

**[0016]** In yet another preferred aspect of the present invention, the chelating agent and the lignocellulosic material are reacted at a temperature in the range from about 50 to about 150 degrees Celsius.

**[0017]** In yet another preferred aspect of the present invention, the chelating agent and the lignocellulosic material are reacted for a time of 5 minutes or longer, for example about 5 minutes to about 2 hours, more preferably from about 10 to 20 minutes although, as further discussed below, the reaction time can be as long as several days under certain process conditions.

**[0018]** In yet another preferred aspect of the present invention, the chelating agent and the lignocellulosic material are reacted at an elevated pressure and temperature.

**[0019]** In yet another preferred aspect of the present invention, the method further comprises the step of reacting the lignocellulosic material at an elevated pressure in a third vessel, wherein the third vessel comprises a pressure vessel which is pressurized by compressed air and steam.

**[0020]** In yet another preferred aspect of the present invention, the lignocellulosic material is in the form of wood chips.

**[0021]** In yet another preferred aspect of the present invention, the lignocellulosic material is refined using either a mechanical pulping method or a thermo-mechanical pulping method.

**[0022]** In yet another preferred aspect of the present invention, the energy input required to pulp the material, after the material is reacted with the chelating agent, is at least 20 percent lower than if the material was refined without first being contacted with and reacted with the chelating agent.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0023]** The invention will now be described, by way of example only, with reference to the accompanying drawings in which:

**[0024]** FIG. 1 is a flow chart illustrating the preferred apparatus and process steps for use in a mechanical pulping process according to the invention; and

**[0025]** FIG. 2 is a graph of Canadian Standard Freeness v. Total Specific Energy derived from the refining trial data set out in Table 1.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

**[0026]** The present invention provides a method for pre-treating lignocellulosic materials for the production of pulp, and also relates to pulp-producing processes using the pre-treatment according to the invention.

**[0027]** According to the pretreatment method of the present invention, a lignocellulosic material is treated with a chelating agent which removes minerals from the lignocellulosic material in the form of water-soluble mineral salts. The water-soluble salts do not form a scale on the process equipment, but rather remain soluble in the white water system throughout the pulping and papermaking processes and are removed in

the plant effluent. After pre-treating the lignocellulosic material with one of the chelating agents according to the present invention, it may be refined using any one of several pulping methods to produce a pulp product. The inventors have observed that pretreated lignocellulosic materials according to the present invention are refined with decreased electrical energy input, and in some cases the decrease in energy input during refining exceeds about 20 percent.

**[0028]** In the above-mentioned International Publication No. WO 2007/008689 A2, it is believed that the removal of hemicellulose from the lignocellulosic material is responsible for providing electrical energy savings in the production of pulp. In contrast, the inventors of the present invention believe that oxalic acid and other chelating agents provide energy savings because they promote the removal of calcium and other minerals which help to bind the cellulosic fibers together through ionic bonding. The removal of these minerals through chelation is believed by the inventors to weaken the bonds between the cellulosic fibers, thereby reducing the amount of energy required to separate the fibers during refining. The inventors have also appreciated that the oxalate scale formed during oxalic acid pretreatment predominantly comprises calcium oxalate, which is water-insoluble. Based on these observations, the inventors have discovered that certain chelating agents which have water-soluble calcium salts can be substituted for oxalic acid and its derivatives in the pre-treatment of lignocellulosic materials, with significant savings in energy and with a reduced level of scale formation.

**[0029]** Without being bound by theory, it is known that calcium in wood is usually associated with pectin, which is found in the tori of pit membranes, the middle lamella, cell corners and ray cell parenchyma. Calcium is an important cross-linking agent in plant cell walls. Calcium ions in pectin are interleaved between polygalacturonic chains in an "egg-box" arrangement, binding to carboxyl groups of opposing chains and providing structural support. Pectin is a good chelating agent for  $\text{Ca}^{2+}$  in such an environment. Cell wall separation occurs when the  $\text{Ca}^{2+}$  is sequestered by a superior chelating agent such as ammonium oxalate, sodium hexametaphosphate, ethylenediamine tetraacetate (EDTA) and cyclohexanediamine tetraacetate (CDTA). Therefore, the inventors believe that treatment of the lignocellulosic material with a chelating agent which will effectively sequester the calcium ions and remove them from between the cellulosic fibers of the material will result in easier separation of the fibers, and more energy-efficient production of pulp in mechanical pulp mills.

**[0030]** The lignocellulosic materials treated by the process of the present invention generally include materials containing cellulose polymers and lignin, and typically include matter capable of being processed into pulp for making paper products. Such materials may include wood, either in the form of whole trees or wood products, such as wood chips or other wood scraps resulting from forest and sawmill operations, or recovered paper. Recovered paper may include both pre-consumer recovered paper, such as trimmings and scraps from printing, carton manufacturing, or other converting processes, or post-consumer paper such as corrugated boxes, newspapers, magazines and office paper.

**[0031]** The preferred chelating agents for use in the method of the present invention preferably are of a relatively low molecular weight so as to effectively penetrate between the fibers of the lignocellulosic material to sequester calcium ions located between the cellulosic fibers, and preferably contain

from two to six carbon atoms. As mentioned above, the chelating agents for use in the method of the present invention must also produce stable, water-soluble mineral salts so as to avoid scaling, and in particular produce stable, water-soluble calcium salts. The mineral salts produced by the chelating agents are preferably stable and water-soluble under acidic, neutral and basic conditions so as to avoid scaling under all pH conditions which may be encountered in the pulping and papermaking processes. Preferably, the mineral salts are stable and water-soluble within the pH range of from about 5 to about 9.

**[0032]** Preferred chelating agents according to the present invention are amino acids and organic monocarboxylic and polycarboxylic acids containing from two to six carbon atoms and which produce stable, water-soluble calcium salts so as to avoid scaling. Some examples of chelating agents which may be used in the method of the present invention include the following:

calcium citrate complexes is such that they do not undergo ligand exchange with EDTA, which forms a highly stable complex with  $\text{Ca}^{2+}$ . Furthermore, the water solubility of calcium citrate ( $9.5 \times 10^{-2}$  g/100 mL) is about 1-2 orders of magnitude greater than the water solubility of calcium oxalate ( $6.7 \times 10^{-4}$  g/100 mL). In addition, citric acid has a relatively low molecular weight (192.12) and contains six carbon atoms. Although EDTA and DTPA are better chelating agents for calcium, it is believed by the inventors that the large size of these agents may prevent them from entering the spaces between the cellulosic fibers and accessing  $\text{Ca}^{2+}$  ions located between the fibers. For this reason the inventors believe that smaller, lighter molecules such as citric acid will be more successful in extracting minerals such as calcium from between the fibers.

**[0035]** The process of the present invention is now described with reference to FIG. 1. The apparatus and process steps illustrated in FIG. 1 are similar to those illustrated and

| NAME                               | IUPAC   | FORMULA                                       |
|------------------------------------|---|---|
| <u>AMINO ACIDS</u>                 |   |   |
| Glycine                            | aminoethanoic acid  | $\text{C}_2\text{H}_5\text{NO}_2$             |
| Alanine                            | 2-aminopropanoic acid                                     | $\text{C}_3\text{H}_7\text{NO}_2$             |
| Valine                             | (S)-2-amino-3-methyl-butanoic acid                        | $\text{C}_5\text{H}_{11}\text{NO}_2$          |
| Serine                             | (S)-2-amino-3-hydroxypropanoic acid                       | $\text{C}_3\text{H}_7\text{NO}_3$             |
| Threonine                          | (2S,3R)-2-amino-3-hydroxybutanoic acid                    | $\text{C}_4\text{H}_9\text{NO}_3$             |
| Cysteine                           | (2R)-2-amino-3-sulfanyl-propanoic acid                    | $\text{C}_3\text{H}_7\text{NO}_2\text{S}$     |
| Asparagine                         | (2S)-2-amino-3-carbamoyl-propanoic acid                   | $\text{C}_4\text{H}_8\text{N}_2\text{O}_3$    |
| Glutamine                          | (2S)-2-amino-4-carbamoyl-butanoic acid                    | $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_3$ |
| Aspartic acid                      | (2S)-2-aminobutanedioic acid                              | $\text{C}_4\text{H}_7\text{NO}_4$             |
| Glutamic acid                      | (2S)-2-aminopentanedioic acid                             | $\text{C}_5\text{H}_9\text{NO}_4$             |
| Gamma-aminobutyric acid            | 4-aminobutanoic acid                                      | $\text{C}_4\text{H}_9\text{NO}_2$             |
| <u>ORGANIC ACIDS (KREBS CYCLE)</u> |   |   |
| Citric acid                        | 2-hydroxypropane-1,2,3-tricarboxylic acid                 | $\text{C}_6\text{H}_8\text{O}_7$              |
| Succinic acid                      | butanedioic acid, ethane-1,2-dicarboxylic acid            | $\text{C}_4\text{H}_6\text{O}_4$              |
| Fumaric acid                       | (E)-butenedioic acid, trans-1,2-ethylenedicarboxylic acid | $\text{C}_4\text{H}_4\text{O}_4$              |
| Malic acid                         | 2-hydroxybutanedioic acid                                 | $\text{C}_4\text{H}_6\text{O}_5$              |
| Oxaloacetic acid                   | Oxobutanedioic acid                                       | $\text{C}_4\text{H}_4\text{O}_5$              |
| <u>CARBOXYLIC ACIDS</u>            |   |   |
| Propionic acid                     | ethanecarboxylic acid                                     | $\text{C}_2\text{H}_4\text{O}_2$              |
| Valeric acid                       | butane-1-carboxylic acid                                  | $\text{C}_5\text{H}_{10}\text{O}_2$           |
| Acrylic acid                       | ethylenecarboxylic acid                                   | $\text{C}_3\text{H}_4\text{O}_2$              |
| Butyric acid                       | propane-1-carboxylic acid                                 | $\text{C}_4\text{H}_8\text{O}_2$              |
| Pyruvic acid                       | 2-oxopropanoic acid                                       | $\text{C}_3\text{H}_4\text{O}_3$              |
| Malonic acid                       | methanedicarboxylic acid                                  | $\text{C}_3\text{H}_4\text{O}_4$              |
| Glutaric acid                      | pentanedioic Acid   | $\text{C}_5\text{H}_8\text{O}_4$              |
| Lactic acid                        | 2-hydroxypropanoic acid                                   | $\text{C}_3\text{H}_6\text{O}_3$              |
| Tartaric acid                      | 2,3-dihydroxybutanedioic acid                             | $\text{C}_4\text{H}_6\text{O}_6$              |

**[0033]** It will be appreciated that the present invention also includes methods in which a lignocellulosic material is pretreated with combinations of two or more of the above-listed chelating agents. It will also be appreciated that the present invention includes methods in which a lignocellulosic material is pretreated with one or more of the above-listed chelating agents and another, higher molecular weight chelating agents such as EDTA or diethylenetriaminepentaacetic acid (DTPA), both of which are commercially used in the removal of minerals from pulp prior to bleaching.

**[0034]** One of the preferred chelating agents for use in the present invention is citric acid, which forms stable, water-soluble complexes with  $\text{Ca}^{2+}$ . In particular, the stability of

described in U.S. Pat. No. 4,599,138 (Lindahl), issued on Jul. 8, 1986, which is incorporated herein by reference in its entirety. In the method of the present invention, a particulate lignocellulosic material, which is preferably wood in the form of wood chips, is fed from a storage container **10** to a first vessel **14** by a plug screw feeder **12**. The feeder **12** compresses the wood chips to remove some of the absorbed and excess moisture as it conveys the wood chips to the first vessel **14**. As described by the Lindahl patent, the plug screw feeder **12** may comprise a tapered screw which operates within a perforated housing through which moisture is drained.

**[0036]** The first vessel **14** is also known as an impregnation vessel. Inside vessel **14**, the wood chips are impregnated by a

pretreatment solution which preferably contains one or more chelating agents according to the present invention. The pretreatment solution is preferably an aqueous solution. As in the Lindahl patent, the first vessel **14** may be provided with screws for conveying the chips through the vessel.

**[0037]** From the first vessel **14**, the wood chips are transferred to a second vessel **16** in which the chips are heated to an elevated temperature within a range from about 50 to about 130° C. for a desired reaction time. The second vessel **16** is also known as a reaction vessel. Optionally, additional pretreatment solution containing one or more chelating agents according to the present invention is injected into the second vessel **16**. As described by Lindahl, the elevated temperature within the second vessel **16** may be maintained by a steam jacket (not shown).

**[0038]** Following treatment in the second vessel, the lignocellulosic material is optionally, and preferably, transferred to a third vessel **18**, also known as a pressure vessel. The interior of the third vessel **18** is preferably maintained under pressure by injection of pressurized steam and/or air, preferably with a pretreatment solution containing at least one chelating agent according to the present invention. The wood chips are optionally transferred from the second vessel **16** to the third vessel **18** by a second plug screw feeder (not shown). The inventors have found that the optional pressure treatment of the wood chips with the pretreatment solution according to the invention provides additional softening of the wood chips, so as to produce energy savings which may be in excess of 20% during the subsequent refining stage. It will be appreciated, however, that pressure treatment of the wood chips with at least one chelating agent according to the present invention is optional, and not essential. In processes where the pressure pretreatment step in pressure vessel **18** is eliminated, the energy savings during refining may be somewhat more modest, for example on the order of 5 to 10%. Given the amount of electrical energy used in mechanical pulping mills, even a 5 to 10% reduction in power consumption is significant and should result in improved profitability.

**[0039]** Although the pressure pretreatment in the vessel **18** is described above as being conducted in combination with the steps conducted in vessels **14** and **16**, it will be appreciated that in some embodiments of the invention either one or both vessels **14** and **16** can be eliminated. In other embodiments of the invention, the pressurized pretreatment step in vessel **18** may be the only step in the pretreatment method.

**[0040]** Preferably, the lignocellulosic material is reacted with the chelating agent at an elevated temperature and pressure, and for a time sufficient, that the chelating agent reacts with calcium ions in the material to form stable, water-soluble calcium complexes, and such that a lower energy input is required to pulp the resulting treated material than if the material was refined without being reacted with the chelating agent. In some preferred embodiments of the invention, the reaction time is about 5 minutes or longer, for example from about 5 minutes to two hours, more preferably from about 10 to about 20 minutes. The pressure vessel is preferably pressurized by saturated steam and/or compressed air at a pressure of about 30-60 psig, with the saturated steam at these pressures being at a temperature of about 275-400 degrees Celsius. During the pressurized pretreatment step the lignocellulosic material is preferably heated to a temperature in the range from about 50-150 degrees Celsius. It will be appreciated that the reaction time is variable and depends on a number of factors, such as chip size, wood species, moisture level

and processing conditions. For example, chips containing high moisture levels are slow to take up the solution of chelating agent. Also, large chips require a longer period of time to become impregnated with the solution. Under some conditions, the reaction time can be as long as several days.

**[0041]** Following the optional pretreatment stage in the pressure vessel **18**, the lignocellulosic material is fed, optionally by a plug screw feeder (not shown), to a disk refiner **20**, in which the fibers of the lignocellulosic material are separated. Bleaching chemicals may optionally be charged to the refiner although, as discussed above, the amount of bleaching chemicals used in the method of the present invention are expected to be considerably less than those used in biochemical treatment processes. The apparatus according to the invention may optionally include additional disk refiners (not shown) where the defibration and refining are completed. The pulp produced by the process may then be screened in a pressure screen (not shown) and cleaned in a hydrocyclone (not shown), following which the finished pulp is separated from the system.

**[0042]** The invention is further described by reference to the following non-limiting examples.

#### EXAMPLE 1

##### Pretreatment of Wood Chips

**[0043]** Twenty four barrels of commercial wood chips were collected for treatment. The following is a description of the treatment process used for the batches treated with EDTA, DTPA and citric acid.

**[0044]** The wood chips were washed to remove sand and grit and 70 liters of the washed wood chips were placed in a 130 liter autoclave. The chips were then steamed for 30 minutes in the autoclave to remove air, and the pressure in the vessel was repeatedly raised and decreased in order to accelerate the de-aeration process.

**[0045]** After completing the de-aeration process, the pressure in the autoclave was released by opening the vent and 90 liters of impregnation solution was added to the mass of chips in the autoclave. The impregnation solution contained between 0.5-2.5 kg of chelating agent, depending on which specific chelating agent was used. The temperature of the impregnation solution was about 80 degrees Celsius.

**[0046]** Following the addition of the impregnation solution, the autoclave was pressurized to 40 psig for 105 minutes using compressed air. The vessel was subsequently depressurized and the excess impregnation solution was drained from the mass of wood chips and collected for analysis and reuse or disposal.

**[0047]** The wood chips were subsequently heated to 130 degrees Celsius and held in the autoclave for 30 minutes using saturated steam at 40 psig. The vessel was then depressurized and the chips were washed with 90 liters of hot water. The chips were flushed for another 30 minutes before being placed in 100 liters of water for 24 hours, following which the chips were drained and stored in sealed plastic bags in a walk-in refrigerator at 4 degrees Celsius.

**[0048]** A first batch was pretreated with EDTA (also referred to below as "Chemical 1"), a second batch was pretreated with DTPA (also referred to below as "Chemical 2") and a third batch was pretreated with citric acid (also referred

to below as "Chemical 3"). Finally, a batch of wood chips was left untreated and used as a control.

### EXAMPLE 2

#### Refiner Trials

[0049] Treated wood chips produced in Example 1, and the untreated control chips, were run through a refiner equipment set-up and refiner power consumption was monitored in relation to the freeness measurement of the resulting pulp discharged from the refiner. Freeness, also referred to herein as "Canadian Standard Freeness" or "CSF", is a measure of the degree of separation of the fibers of the lignocellulosic material, i.e. the higher the freeness the higher the degree of separation.

[0050] The refining was performed in two passes to simulate primary and secondary refining in a TMP mill. Three drums each of the treated chips and the control chips were subjected to refining. Prior to refining, the chips were

screened on a radar thickness screen to remove chips that were more than 6 mm thick. The chips were then washed to remove sand and grit. The chips were then dumped into a plug screw feeder and fed to a pressurized pre-heater. Once heated, the chips were refined in a pressurized conical disc refiner. The refined pulp was collected and weighed to determine the consumption of electrical energy per kg of pulp produced during first stage refining. Following the first stage refining the pulp samples were collected and tested for various quality parameters.

[0051] Second stage refining was performed using the same disc refiner, but was conducted at atmospheric pressure. The second stage refined pulp was collected and weighed to determine the consumption of electrical energy per kg of pulp produced during second stage refining.

[0052] The following Table sets out the data obtained during the refining trials, and which is graphically depicted in FIG. 2.

TABLE 1

|                          | Wet<br>Mass | Cons   | Ref    | Prod'n<br>Rate<br>od | Gap  | Time | Energy |      | Prim SE | Second<br>SE | Total SE | CSF |
|--------------------------|-------------|--------|--------|----------------------|------|------|--------|------|---------|--------------|----------|-----|
| Run                      | kg          | (7L) % | Cons % | kg/min               | mm   | min  | kW     | kWh  | kWh/odt | kWh/odt      | kWh/odt  | mL  |
| Control - Untreated      |             |        |        |                      |      |      |        |      |         |              |          |     |
| 1                        | 4.272       |        |        |                      | 0.7  |      | 29.8   |      |         |              |          |     |
| 2                        | 3.452       | 0.41   | 8.2    | 0.28                 | 0.6  | 1    | 40.9   | 0.68 | 1958    | 2408         | 4366     | 325 |
| 3                        | 3.006       | 0.45   | 9.0    | 0.27                 | 0.55 | 1    | 59     | 0.98 | 1958    | 3635         | 5593     | 195 |
| 4                        | 3.746       | 0.6    | 12.0   | 0.45                 | 0.52 | 1    | 46.6   | 0.78 | 1958    | 1728         | 3686     | 206 |
| 5                        | 3.458       | 0.6    | 12.0   | 0.41                 | 0.5  | 1    | 44.9   | 0.75 | 1958    | 1803         | 3761     | 167 |
| 6                        | 3.258       | 0.66   | 13.2   | 0.43                 | 0.48 | 1    | 62.3   | 1.04 | 1958    | 2414         | 4372     | 122 |
| 7                        | 3.359       | 0.66   | 13.2   | 0.44                 | 0.45 | 1    | 62.3   | 1.04 | 1958    | 2342         | 4300     | 110 |
| 8                        | 3.319       | 0.65   | 13.0   | 0.43                 | 0.40 | 1    | 63.4   | 1.06 | 1958    | 2449         | 4407     | 96  |
| 9                        | 3.078       | 0.71   | 14.2   | 0.44                 | 0.35 | 1    | 76.6   | 1.28 | 1958    | 2921         | 4879     | 62  |
| Ave                      |             |        |        | 0.35                 |      |      |        |      |         |              |          |     |
| s.d.                     |             |        |        | 0.10                 |      |      |        |      |         |              |          |     |
| Chemical 1 - EDTA        |             |        |        |                      |      |      |        |      |         |              |          |     |
| 1                        | 3.544       |        |        |                      | 0.7  | 1    | 49.8   | 0.83 |         |              |          |     |
| 2                        | 3.45        | 0.57   | 11.4   | 0.39                 | 0.6  | 1    | 50.4   | 0.84 | 918     | 2136         | 3053     | 372 |
| 3                        | 3.24        | 0.59   | 11.8   | 0.38                 | 0.55 | 1    | 59.4   | 0.99 | 918     | 2589         |          |     |
| 4                        | 3.719       | 0.61   | 12.2   | 0.45                 | 0.52 | 1    | 60.1   | 1.00 | 918     | 2208         | 3125     | 277 |
| 5                        | 2.944       | 0.77   | 15.4   | 0.45                 | 0.5  | 1    | 81.3   | 1.36 | 918     | 2989         |          |     |
| 6                        | 3.447       | 0.71   | 14.2   | 0.49                 | 0.48 | 1    | 71.6   | 1.19 | 918     | 2438         | 3356     | 197 |
| 7                        | 3.379       | 0.71   | 14.2   | 0.48                 | 0.45 | 1    | 65.9   | 1.10 | 918     | 2289         |          |     |
| 8                        | 2.472       | 0.7    | 14     | 0.35                 | 0.40 | 1    | 74.4   | 1.24 | 918     | 3583         | 4501     | 112 |
| 9                        | 2.459       | 0.86   | 17.2   | 0.42                 | 0.35 | 1    | 93.0   | 1.55 | 918     | 3665         | 4582     | 75  |
| Ave                      |             |        | 13.8   | 0.43                 |      |      |        |      |         |              |          |     |
| s.d.                     |             |        | 2.0    | 0.05                 |      |      |        |      |         |              |          |     |
| Chemical 2 - DPTA        |             |        |        |                      |      |      |        |      |         |              |          |     |
| 1                        | 4.063       |        |        |                      | 0.7  | 1    | 36.7   | 0.61 |         |              |          |     |
| 2                        | 3.362       | 0.49   | 9.8    | 0.33                 | 0.6  | 1    | 46.8   | 0.78 | 1083    | 2367         | 3450     | 425 |
| 3                        | 3.33        | 0.54   | 10.8   | 0.36                 | 0.55 | 1    | 55.6   | 0.93 | 1083    | 2577         | 3659     | 300 |
| 4                        | 4.174       | 0.69   | 13.8   | 0.58                 | 0.52 | 1    | 65.7   | 1.10 | 1083    | 1901         | 2984     | 270 |
| 5                        | 3.097       | 0.69   | 13.8   | 0.43                 | 0.5  | 1    | 62.9   | 1.05 | 1083    | 2453         | 3536     | 215 |
| 6                        | 3.368       | 0.68   | 13.6   | 0.46                 | 0.48 | 1    | 67.6   | 1.13 | 1083    | 2460         | 3542     | 183 |
| 7                        | 3.526       | 0.67   | 13.4   | 0.47                 | 0.45 | 1    | 69.4   | 1.16 | 1083    | 2448         | 3531     | 165 |
| 8                        | 3.203       | 0.7    | 14.0   | 0.45                 | 0.40 | 1    | 76.1   | 1.27 | 1083    | 2828         | 3911     | 130 |
| 9                        | 3.066       | 0.77   | 15.4   | 0.47                 | 0.35 | 1    | 89.2   | 1.49 | 1083    | 3149         | 4231     | 100 |
| Ave                      |             |        | 13.1   | 0.44                 |      |      |        |      |         |              |          |     |
| s.d.                     |             |        | 1.8    | 0.08                 |      |      |        |      |         |              |          |     |
| Chemical 3 - Citric Acid |             |        |        |                      |      |      |        |      |         |              |          |     |
| 1                        | 4.048       | 0.47   | 10.97  | 0.44                 | 0.7  | 1    | 49.3   | 0.82 | 1299    | 1851         | 3150     | 295 |
| 2                        | 3.521       | 0.51   | 11.90  | 0.42                 | 0.6  | 1    | 42.8   | 0.71 | 1299    | 1702         | 3001     | 154 |
| 3                        | 3.466       | 0.69   | 16.10  | 0.56                 | 0.55 | 1    | 74.3   | 1.24 | 1299    | 2219         | 3518     | 94  |
| 4                        | 3.065       | 0.6    | 14.00  | 0.43                 | 0.52 | 1    | 62.6   | 1.04 | 1299    | 2431         | 3730     | 74  |



TABLE 1-continued

| Run  | Wet<br>Mass<br>kg | Cons<br>(7L) % | Ref<br>Cons % | Prod'n<br>Rate<br>od<br>kg/min | Gap<br>mm | Time<br>min | Energy |      | Prim SE<br>kWh/odt | Second<br>SE<br>kWh/odt | Total SE<br>kWh/odt | CSF<br>mL |
|------|-------------------|----------------|---------------|--------------------------------|-----------|-------------|--------|------|--------------------|-------------------------|---------------------|-----------|
|      |                   |                |               |                                |           |             | kW     | kWh  |                    |                         |                     |           |
| 5    | 2.988             | 0.66           | 15.40         | 0.46                           | 0.5       | 1           | 75.5   | 1.26 | 1299               | 2735                    | 4033                | 67        |
| 6    | 2.869             | 0.56           | 13.07         | 0.37                           | 0.48      | 1           | 64.7   | 1.08 | 1299               | 2876                    | 4175                | 67        |
| 7    | 2.729             | 0.66           | 15.40         | 0.42                           | 0.45      | 1           | 74.8   | 1.25 | 1299               | 2966                    | 4265                | 42        |
| 8    | 2.734             | 0.65           | 15.17         | 0.41                           | 0.40      | 1           | 77.5   | 1.29 | 1299               | 3115                    | 4414                | 38        |
| 9    | 2.34              | 0.6            | 14.00         | 0.33                           | 0.35      | 1           | 77.7   | 1.30 | 1299               | 3953                    | 5252                | 33        |
| Ave  |                   |                | 14.0          | 0.43                           |           |             |        |      |                    |                         |                     |           |
| s.d. |                   |                | 1.7           | 0.06                           |           |             |        |      |                    |                         |                     |           |

A number of the abbreviated terms used above in Table 1 are explained as follows:

"Cons" = Consistency;

"Prim SE" = Specific Energy of Primary Stage Refining;

"Second SE" = Specific Energy of Secondary Stage Refining;

"Total SE" = Total Specific Energy of Primary and Secondary Stage Refining; and

"od" is used in the units "od kg/min" and "kWh/odt" to signify that the Production Rate and the Specific Energy are defined on a dry basis, i.e. in terms of pulp which has been dried to remove water.

**[0053]** As can be seen from Table 1 and FIG. 2, the refiner trials using wood chips pretreated with citric acid showed a significant reduction in total refiner energy over two stages. After adjusting for freeness, refiner energy reductions on the order of 20-23% were achieved with the citric acid pretreated chips. In contrast, the results achieved after two refiner passes with EDTA and DTPA pretreated wood chips were similar to those achieved by the control. This observation supports the inventors' belief that the relatively large EDTA and DTPA molecules do not penetrate between the cellulosic fibers of the wood chips as effectively as the relatively small citric acid molecule.

**[0054]** Some of the refined pulp products obtained in the refiner trials were tested to determine their suitability for papermaking. In particular, a comparison of a pulp prepared from citric acid pretreated wood chips showed similar strength, optical and fiber length properties to the control sample, and the 0.004 Pulmac shives were 50% higher for the pulp pretreated with citric acid, indicating that the number of fiber bundles present in the pulp pretreated with citric acid was not significantly greater than the control. Visual inspection of the pulp samples also indicated that the pulp prepared from citric acid pretreated wood chips did not have any physical properties different from those of industry standard pulp. In particular, the pulp produced from citric acid pretreated wood chips appears to have the same or better brightness than the control samples. It is believed that the improved brightness results from the removal of metal ions which decrease the brightness of the pulp.

**[0055]** Although the invention has been described in connection with certain preferred embodiments, it is not limited thereto. Rather, the invention includes all embodiments which may fall within the scope of the following claims.

What is claimed is:

1. A method for pulping a fibrous lignocellulosic material, the method comprising:

- reducing the material to a size appropriate for pulping;
- contacting the material with at least one chelating agent selected from the group consisting of amino acids, monocarboxylic acids and polycarboxylic acids, wherein the chelating agent contains from two to six carbon atoms;

- reacting the material with the chelating agent at a temperature and for a time sufficient such that the chelating agent reacts with calcium ions in the material to form stable, water-soluble calcium complexes; and

- mechanically refining the material so as to produce a pulp suspension;

wherein a lower energy input is required to pulp the material, after the material is reacted with the chelating agent, than if the material was refined without first being contacted with and reacted with the chelating agent; and

wherein the calcium complexes are sufficiently soluble throughout the entire pulping process so as to substantially avoid the formation of scale on process equipment and piping.

2. The method of claim 1, wherein the amino acids are selected from the group consisting of glycine, alanine, valine, serine, threonine, cysteine, asparagine, glutamine, aspartic acid, glutamic acid and gamma-aminobutyric acid.

3. The method of claim 1, wherein the monocarboxylic and polycarboxylic acids are selected from the group consisting of citric acid, succinic acid, fumaric acid, malic acid, oxaloacetic acid, propionic acid, valeric acid, acrylic acid, butyric acid, pyruvic acid, malonic acid, glutaric acid, lactic acid and tartaric acid.

4. The method of claim 1, wherein the chelating agent is citric acid.

5. The method of claim 1, wherein the chelating agent is added in combination with one or more additional chelating agents selected from ethylenediamine tetraacetate (EDTA) and diethylenetriaminepentaacetic acid (DTPA).

6. The method of claim 1, wherein the chelating agent is contacted with the lignocellulosic material in the form of an aqueous solution.

7. The method of claim 1, wherein step (b) is conducted in a first vessel and wherein step (c) is conducted in a second vessel.

8. The method of claim 7, wherein the chelating agent is added to both the first and second vessels.

9. The method of claim 1, wherein the solubility of the calcium complexes is at least one order of magnitude greater than the solubility of calcium oxalate.

10. The method of claim 1, wherein the calcium complexes remain substantially dissolved in the pulp suspension throughout a pH range of from about 5 to about 9.

11. The method of claim 1, wherein the chelating agent and the lignocellulosic material are reacted at a temperature in the range from about 50 to about 150 degrees Celsius.

12. The method of claim 1, wherein the chelating agent and the lignocellulosic material are reacted for a time of about 10 to 20 minutes.

13. The method of claim 1, wherein the chelating agent and the lignocellulosic material are reacted at an elevated pressure and temperature.

14. The method of claim 7, further comprising the step of reacting the lignocellulosic material at an elevated pressure in

a third vessel, wherein the third vessel comprises a pressure vessel which is pressurized by compressed air and steam.

15. The method of claim 1, wherein the lignocellulosic material is in the form of wood chips.

16. The method of claim 1, wherein the lignocellulosic material is refined using either a mechanical pulping method or a thermo-mechanical pulping method.

17. The method of claim 1, wherein the energy input required to pulp the material, after the material is reacted with the chelating agent, is at least 20 percent lower than if the material was refined without first being contacted with and reacted with the chelating agent.

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