(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 December 2004 (09.12.2004)

PCT

(10) International Publication Number
WO 2004/106624 A1

(51) International Patent Classification[7]: D21C 1/04, 3/02, 11/04

(21) International Application Number: PCT/CA2003/001901

(22) International Filing Date: 5 December 2003 (05.12.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/474,961	3 June 2003 (03.06.2003)	US
60/508,308	6 October 2003 (06.10.2003)	US

(71) Applicant and
(72) Inventor: **TARASENKO, David** [CA/CA]; 313 - 3185 Via Centrale, Kelowna, British Columbia V1V 2A7 (CA).

(74) Agents: **ASH, Craig** et al.; Oyen Wiggs Green & Mutala, 480 - The Station, 601 West Cordova Street, Vancouver, British Columbia V6B 1G1 (CA).

(81) Designated States *(national)*: AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, EG, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK (utility model), SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:
— *of inventorship (Rule 4.17(iv)) for US only*

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR PRODUCING PULP AND LIGNIN

(57) Abstract: The invention provides for methods for producing pulp (comprising cellulose) and lignin from lignocellulosic material, such as wood chips. The methods involve acid catalyzed hydrolysis. Lignocellulosic material having a relatively high moisture concentration can be used as the starting material. The lignocellulosic material is impregnated with an acid (preferably nitric acid) and heated. During the heating lignin is depolymerized at relatively low temperatures, and the acid catalyst is distilledoff. The acid catalyst can be collected and recycled after impregnation and heating. The lignocellulosic material is then digested in an alkaline solution under heat, dissolving the lignin and allowing the pulp to be removed. Acid is added to the black liquor to precipitate the lignin which is then removed. The resultant amber liquor can be further processed into other ancillary products such as alcohols and/or unicellular proteins.

WO 2004/106624 A1

METHOD FOR PRODUCING PULP AND LIGNIN

Technical Field

This invention pertains to a method for producing pulp (comprising cellulose) and lignin from lignocellulosic material such as wood chips.

Background

Wood is a composite material comprising cellulose, lignin and hemicellulose. Cellulose is the strong, fibrous component which consists of long chains of glucose molecules and which is used to make paper. Lignin is a phenolic polymeric matrix which holds the cellulose fibres together. Hemicellulose is the component comprised of short, branched chains of glucose and other like molecules.

In general terms, pulping processes involve converting wood chips (or other suitable vegetative material) into a fibrous form in order to produce pulp. Pulp refers to cellulose fibres or material containing cellulose fibres which may be used in the production of paper or paper containing products.

The two main types of pulping processes in use today are mechanical pulping and chemical pulping though there are other pulping processes, such as chemi-thermal mechanical pulping, which are a combination thereof.

Mechanical pulping involves the physical separation of individual fibres of the wood by forcing debarked logs and hot water between large rotating steel discs with teeth that tear the wood apart, or alternatively, by pressing logs against grindstones. Generally, pulps produced by mechanical pulping are of lower quality than pulps produced according to chemical pulping, and thus are used to produce newsprint and cardboard type products.

On the other hand, chemical pulping involves subjecting wood to heat and chemicals in order to dissolve the lignin and hemicellulose binding materials, thereby separating the cellulosic fibres. Kraft pulping is an example of a chemical pulping process, and involves involves cooking wood chips in a pressurized vessel known as a digester in the presence of hot caustic soda (NaOH) and sodium sulfide (Na_2S). Kraft pulping is a variation of the soda process where only NaOH is used to break down and remove the lignin. Relative to the soda process, the addition of the

sodium sulfide in the Kraft process assisted in dissolving the lignin with less damage to cellulosic fibres.

In Kraft pulping, the digestion process dissolves the lignin that "glues" the cellulosic fibers to each other in the wood. The resultant solution containing the dissolved ligneous material is referred to as a "black liquor". After digestion, the cellulose-containing pulp is separated from the black liquor and washed. At this stage, the resultant colored slurry of cellulose fibres is referred to as "brownstock". The color of the slurry is the result of some residual lignin remaining within the slurry with the cellulosic fibres. If desired, a further step of bleaching the slurry can be carried out to remove some additional components of the lignin, thereby brightening the pulp. Typically, the pulp is bleached in multiple stages with various combinations of oxygen, hydrogen peroxide and sodium hydroxide. Chelation stages can be utilized in the bleaching process to remove transition metals in the pulp which may otherwise interfere with peroxide bleaching.

One disadvantage with Kraft pulping is that it is carried out under extreme conditions which adversely affect yields. Kraft pulping typically involves pressures of approximately 120 p.s.i., temperatures of approximately 160 - 180 °C and initial pH values over 12 in the digestion stage. In part, these reaction conditions are required by the fact that reactions carried out in Kraft pulping are oxidation reactions. These harsh conditions result in a loss of some cellulose and the destruction of much of natural form lignin from the wood chips.

Lignin typically is not recovered as an end-product in typical Kraft pulping processes. Instead, in Kraft pulping processes the black liquor is typically condensed in recovery boilers in the process of recovering chemicals such as sodium hydroxide for reuse. Solids such as lignin are burned as fuel to run the pulp mill utilizing the Kraft process. It would be advantageous to recover as much lignin as possible in a pulping process since lignin is a valuable component in its own right, having a wide range of industrial applications such in the manufacture of fertilizers, asphalt emulsifiers, soil stabilizers, wood products (such as plywood and particle board), oil well drilling fluids and dispersing agents for preparing concrete.

Summary of Invention

In one aspect the invention provides for methods for producing pulp and lignin from lignocellulosic material, the pulp comprising cellulose. The methods comprise: (a) contacting the lignocellulosic material with an aqueous acid solution to impregnate the lignocellulosic material, the aqueous acid solution comprising from about 10% to about 40% by weight of the acid; (b) heating the lignocellulosic material in two stages, the first heating stage being carried out for a period of time which is sufficient to depolymerize lignin within the lignocellolosic material without substantially degrading the cellulose or lignin in the ligncellulosic material, the second heating stage being carried out at or above the boiling point of the acid to distill off the acid; (c) contacting the lignocellulosic material with an aqueous alkaline solution under heat to solubilize lignin in the alkaline solution, leaving a black liquor; (d) removing the pulp from the black liquor; (e) adding sufficient acid to the black liquor to precipitate the lignin; and (f) removing the lignin from the liquor.

The acid in step (a) may be nitric acid. The aqueous acid solution in step (a) may comprise, without limitation, from about 10% to about 30%, from about 15% to about 30%, from about 20% to about 25%, or from about 10% to about 15%, by weight of the acid.

The lignocellulosic material may be contacted with the aqueous acid solution in step (a) for at least 30 minutes, including without limitation, from about 12 hours to about 24 hours. The lignocellulosic material may be contacted with the aqueous acid solution in step (a) under heat. The lignocellulosic material may be contacted with the aqueous nitric acid solution in step (a) at a temperature from about 50 °C to below the boiling point of the nitric acid.

The temperature during the second heating stage of step (b) may be, without limitation, from about 73 °C to below 100 °C or from about 90 °C to about 95 °C. The temperature during the first heating stage of step (b) may be, without limitation, up to about 75 °C, from about 50 °C to about 75 °C, from about 60 °C to about 70 °C, from about 50 °C to about 60 °C, or from about 70 °C to about 75 °C. The first heating stage in step (b) may be carried out for at least 15 minutes.

The aqueous alkaline solution may comprise sodium hydroxide or potassium hydroxide or a combination of sodium hydroxide and potassium hydroxide. The aqueous alkaline solution may comprise an amount of alkali solute which is at least the normal equivalent of the nitric acid in the aqueous acid solution in step (a). The

aqueous alkaline solution may comprise an amount of alkali solute which is at least the molar equivalent of the nitric acid in the aqueous acid solution in step (a).

The acid used in step (e) may be sulfuric acid. The amount of acid added in step (e) may be at least the molar amount of the alkali in the aqueous alkaline solution in step (c). The amount of acid added in step (e) may be at least the normal amount of the alkali in the aqueous alkaline solution in step (c).

The black liquor may cooled from the temperature in step (c) before the acid is added in step (e). The temperature of the black liquor when the acid is added in step (e) may be, without limitation, up to about 75 °C, from about 5 °C to about 75 °C, from about 5 °C to about 50 °C, from about 25 °C to about 50 °C, or from about 50 °C to about 75 °C.

Any aqueous acid solution not absorbed by the lignocellulosic material in step (a) may be removed prior to heating the lignocellulosic material in step (b). The methods may comprise collecting any aqueous acid solution which is removed prior to step (b) and recycling the collected aqueous acid solution for use in step (a), and comprising collecting any acid which is distilled off in step (b) and recycling the collected acid for use in step (a).

The starting moisture content of the lignocellulosic material may be from about 30% to about 55% by weight of water. The method may comprise contacting the lignocellulosic material with water before step (a) to increase the moisture content in the lignocellulosic material. The starting lignocellulosic material may comprise, without limitation, wood chips, wood shavings, sawdust, pieces of rye, wheat, hemp and combinations of two or more of the foregoing. The starting lignocellulosic material may comprise undigested lignocellulosic material previously subjected to the method.

An amber liquor may be left following the removal of the lignin, and the method may comprise processing the amber liquor after the lignin has been removed, for example, to produce unicellular proteins or alcohols or both. Any water which is produced as a reaction byproduct in one or more of the steps in the method may be collected and recycled for use in the method.

Steps (a) and (c) and the first heating stage in step (b) may each carried out at a temperature from about 50 °C to about 75 °C. One or more of the heating of the impregnated lignocellulosic material in step (b), the contacting the lignocellulosic material with the aqueous alkaline solution in step (c) and the adding the acid in step (e) may be carried out with agitation. The methods may be carried out at atmospheric pressure.

The pulp removed in step (d) may be washed, pressed, bleached and dried. Similarly, the lignin removed in step (f) may be dried. Any residual liquor that is removed from the pulp by pressing may be collected and added to the black liquor prior to adding the acid in step (e). Similarly, any residual liquor which is removed from the lignin during drying may be collected and added to the liquor after step (f), and wherein the liquor is processed after the lignin has been precipitated and removed.

Enough acid may be added to the solution in step (e) to lower the pH of the solution to an acidic pH.

Without limitation, step (c) may be carried out at a temperature up to about 75°C, from about 5 °C to about 75 °C, from about 50 °C to about 75 °C, from about 20 °C to about 50 °C, from about 30 °C to about 40 °C, or from about 40 °C to about 50 °C.

Step (a) may comprise immersing the lignocellulosic material in the aqueous acid solution in step (a), or spraying the lignocellulosic material with aqueous nitric acid solution.

In another aspect the invention provides for methods for producing pulp and lignin from lignocellulosic material, the pulp comprising cellulose, the methods comprise: (a) contacting the lignocellulosic material with an aqueous nitric acid solution to impregnate the lignocellulosic material, the aqueous nitric acid solution comprising from about 10% to about 40% by weight of the nitric acid; (b) heating the impregnated lignocellulosic material in two stages, the first heating stage being carried out a temperature from about 50 °C to about 75 °C for a period of time which is sufficient to depolymerize lignin within the lignocellolosic material without substantially degrading the cellulose or lignin in the lignocellulosic material, the second heating stage being carried out at or above the boiling point of the nitric acid to

distill off the nitric acid; (c) contacting the lignocellulosic material with an aqueous alkaline solution at a temperature from about 50 °C to about 75 °C to solubilize lignin in the alkaline solution, leaving a black liquor, the aqueous alkaline solution comprising an amount of alkali which is at least the normal amount of the nitric acid in the aqueous acid solution in step (a); (d) removing the pulp from the black liquor; (e) cooling the black liquor and then adding an acid to the black liquor to acidify the solution to precipitate the lignin; (f) removing the lignin, leaving an amber liquor; and (g) processing the amber liquor to produce unicellular proteins or alcohols or both, wherein any aqueous nitric acid not absorbed by the lignocellulosic material in step (a) is removed and collected following step (a) prior to heating the lignocellulosic material in step (b) and then recycled for use in step (a), and wherein any nitric acid which is distilled off is collected prior to contacting the lignocellulosic material with the alkaline solution in step (c) and then recylcled for use in step (a), and wherein the heating of the lignocellulosic material in step (b), the contacting the lignocellulosic material with the aqueous alkaline solution in step (c) and the addition of the acid in step (e) are each carried out with agitation.

In yet another aspect the invention provides for methods for producing pulp and lignin comprising the steps of contacting lignocellulosic material with an acid and, after removing any acid not absorbed by the lignocellulosic material, heating the lignocellulosic material at a temperature up to about 75 °C to effect the acid-catalyzed hydrolytic depolymerization of the lignin in the lignocellulosic material without substantially degrading the cellulose or lignin in the lignocellulosic material, the acid-contacting and heating steps being carried out before the lignocellulosic material is digested in an alkaline liquor, the pulp being removed following the digestion of the lignocellulosic material in the alkaline liquor, the lignin being removed after being precipitated out with the addition of an acid to the black liquor produced following the digestion of the lignocellulosic material in the alkaline liquor, wherein the pulp comprises cellulose. The acid-contacting step may comprise immersing the lignocellulosic material in an aqueous solution of the acid, and wherein the acid is nitric acid and the aqueous solution comprises from about 10 % to about 40 % by weight of nitric acid. The lignocellulosic material may be heated, after depolymerizing the lignin but before digesting the lignocellulosic material, at a temperature above the boiling point of the acid in order to distill off the acid.

In yet another aspect the invention provides methods for treating lignocellulosic material comprising: (a) contacting the lignocellulosic material with an aqueous acid solution to impregnate the lignocellulosic material, the aqueous acid solution comprising from about 10% to about 40% by weight of the acid; (b) heating the lignocellulosic material in two stages, the first heating stage being carried out for a period of time which is sufficient to depolymerize lignin within the lignocellolosic material without substantially degrading the cellulose or lignin in the ligncellulosic material, the second heating stage being carried out at or above the boiling point of the acid to distill off the acid, wherein any aqueous acid solution not absorbed by the lignocellulosic material in step (a) is removed prior to heating the lignocellulosic material in step (b); (c) contacting the lignocellulosic material with an aqueous alkaline solution under heat to solubilize lignin in the alkaline solution, leaving a black liquor; and (d) removing the pulp from the black liquor, the pulp comprising cellulose.

In yet another aspect the invention provides methods for producing pulp and lignin from lignocellulosic material, the pulp comprising cellulose, the methods comprising: (a) contacting the lignocellulosic material with an aqueous nitric acid solution to impregnate the lignocellulosic material, the aqueous acid solution comprising from about 10% to about 40% by weight of the nitric acid; (b) heating the lignocellulosic material in two stages, the first heating stage being carried out for a period of time which is sufficient to depolymerize lignin within the lignocellolosic material without substantially degrading the cellulose or lignin in the ligncellulosic material, the second heating stage being carried out at or above the boiling point of the acid to distill off the acid, wherein any aqueous acid solution not absorbed by the lignocellulosic material in step (a) is removed prior to heating the lignocellulosic material in step (b); (c) contacting the lignocellulosic material with an aqueous alkaline solution under heat to solubilize lignin in the alkaline solution, leaving a black liquor; (d) removing the pulp from the black liquor; (e) adding sufficient acid to the black liquor to precipitate the lignin; and (f) removing the lignin from the liquor.

Further aspects of the invention and features of specific embodiments of the invention are described below.

Brief Description of Drawings

Figure 1 is an illustration of the mechanism of acid-catalyzed hydrolysis of an ester; and

Figure 2 is a schematic illustration of a method according to the present invention.

Description

Throughout the following description specific details are set forth in order to provide a more thorough understanding of the invention. However, the invention may be practiced without these particulars. In other instances, well known elements have not been shown or described in detail to avoid unnecessarily obscuring the present invention. Accordingly, the specification and drawings are to be regarded in an illustrative, rather than a restrictive, sense.

Most existing pulping processes involve high pressure and/or high temperature conditions or concentrated chemicals. Not only do these factors increase costs, but they also reduce the yield and purity of cellulose-containing pulp and lignin end-products since the cellulose and lignin can be degraded or destroyed during the pulping processes. The present invention addresses these deficiencies by utilizing the acid catalyzed hydrolysis of lignocellulosic material in methods for producing pulp and lignin from lignocellulosic material. The hydrolysis reaction allows the controlled de-polymerization of lignin within the starting lignocellulosic material, utilizes much lower concentrations of pulping chemicals and lower temperatures than existing Kraft pulping processes and may be carried out at atmospheric pressure. These modest reaction conditions not only result in reduced costs relative to existing Kraft pulping processes, but also increase the yield and purity of the cellulose-containing pulp and lignin since there is less degradation and and destruction of these components during the pulping process relative to existing Kraft pulping processes.

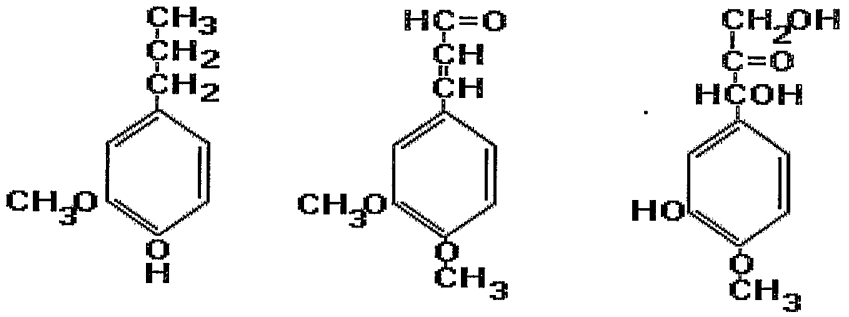
The invention includes methods involving contacting lignocellulosic material with an acid, preferably nitric acid, in order to impregnate the lignocellulosic material and then heating the lignocellulosic material to de-polymerize the lignin within the lignocellulosic material prior to digesting the lignocellulosic material in an alkaline solution to solubilize lignin in the alkaline solution, leaving a black liquor (comprising the solubilized lignin) and pulp. The pulp is then removed and processed (e.g. pressing, washing, bleaching, drying). The solubilized lignin is precipitated out of

the black liquor with the addition of an acid and then removed for processing. The remaining solution can be further processed to produce other useful by-products such as unicellular proteins, alcohols or both.

As used herein, "lignocellulosic material" refers to any material which contains cellulose and lignin and, without limitation, includes pieces or particles (for example wood chips, wood shavings, sawdust) from any type of tree (for example pine, oak, maple, fir, spruce) and other vegetative material (for example rye, wheat , hemp) and combinations thereof.

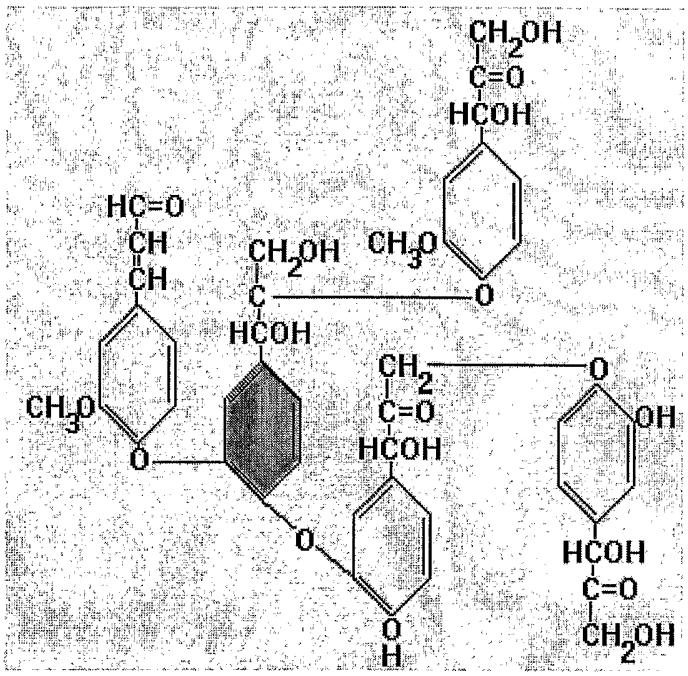
As used herein, "impregnation" refers to the absorption of an impregnating material by lignocellulosic material. For example, impregnating wood chips can be accomplished by immersing or soaking the wood chips in a sufficient volume of the impregnating material (e.g. nitric acid solution) to saturate all or part of the wood chips. Other methods such as spraying could also be used to accomplish the impregnation.

The separation of lignin and cellulose in their natural forms has proven difficult in practice. Many existing pulping processes are inefficient, with valuable cellulose and lignin being degraded, modified or destroyed during pulping, or less than optimal separation between cellulose and lignin being achieved in the pulping process. The difficulty in separating lignin and cellulose arises from the inherent instability and fragile nature of pure lignin. Lignins are formed by removal of water from sugars to create aromatic structures and these reactions are irreversible. There are many possible monomers of lignin, and the types and proportions depend on the source in nature. Some typical monomers of lignin are shown below:



(I) (II) (III)

The hydroxyl (-OH) groups, either the hydroxyl groups on the chains or the hydroxyl groups on the aromatic rings, can react with each other or with the aldehyde or ketone groups. A ether linkage is formed when a hydroxyl group reacts with another hydroxyl group, a hemiacetal is formed when a hydroxyl group reacts with an aldehyde and a ketal is formed when a hydroxyl group reacts with a ketone. An early stage in the condensation of various monomers to form lignin is shown below, wherein there are several groups shown that can react further:



(IV)

Some monomers will simply extend the polymer while others will establish cross-linking. The shaded monomer has three of its functional groups linked to other monomers, so it is starting a branch or cross-link. Lignin molecules are three-dimensional and heavily cross-linked. A typical lignin molecule can have a molecular weight of about 15,000 amu. Lignin molecules are susceptible to harsh chemical concentrations and temperature exposure. A lignin polymeric matrix may be broken down at temperatures as low as 100°C. Lignin is unstable, light sensitive, and breaks down into acid compound as it ages, and its presence in paper items contributes to their degradation over time.

As mentioned above, the present invention utilizes the acid-catalyzed hyrolysis of lignocellulosic material. The lignin within lignocellulosic material includes ester functional groups. Figure 1 illustrates the mechanism of the acid-catalyzed hydroly-

sis of an ester. The rate of ester hydrolysis is very slow because their leaving groups are basic. The rate can be increased by the presence of a catalyst, such as an acid. In such an acid catalyzed reaction all organic reactants, intermediates, and products are positively charged. The following steps take place within the hydrolysis of the ester:

(A) An acid/base reaction is illustrated. Since there is only a weak nucleophile and a poor electrophile the ester needs to be activated. The acid protonates the ester carbonyl, making it more electrophilic.

(B) The oxygen atom in the water molecule functions as the nucleophile, attacking the electrophilic carbon atom in the C=O. Electrons move towards the oxonium ion, thereby creating a tetrahedral intermediate.

(C) Another acid/base reaction is illustrated. The oxygen atom in the water molecule is deprotonated to neutralize the charge.

(D) Another acid/base reaction is illustrated. The $-OCH_3$ must leave, but first must be converted into a more stable group by being protonated.

(E) The electrons from the adjacent oxygen atom assist the formation of the leaving group, a neutral methanol molecule CH_3OH.

(F) Another acid/base reaction. The oxonium ion is deprotonated, which exposes the carbonyl C=O carboxylic acid product and regenerates the acid catalyst.

The carboxylic acid product obtained in (F) is a de-polymerized form of lignin. Because water (H_20) and methanol (CH_3OH) have approximately the same basicity, it will be equally easy for the tetrahedral intermediates to collapse to reform the ester as it would be for the formation of the carboxylic acid. Hence, at equilibrium both the ester and the carboxylic acid will be obtained. However, an excess of water will shift the equilibrium towards the formation of the carboxylic acid product, de-polymerized lignin. Thus, methods of the present invention will render higher yields with the addition of water and, for this reason, it is possible to use lignocellulosic material which has a relatively high moisture content (e.g. "green" wood chips) or which has been previously contacted with water in order to increase

the moisture content prior to impregnating the lignocellulosic material with the acid.

The ability to use lignocellulosic materials with a relatively high moisture content in the present invention is an advantage compared to existing Kraft type pulping processes. In many existing processes it is necessary to dry wood chips prior to pulping in order to remove or reduce moisture to meet stringent requirements. In fact, chips are preferred in many existing processes on a BDU (bone dry unit) basis. Requiring a drying step adds expense to such processes. The present invention overcomes this disadvantage since "wet" starting materials can be used, thus removing the need to dry the wood chips or other starting materials. Moreover, as explained above in relation to Figure 1, since excess water drives the depolymerization reaction to favor the formation of a carboxylic acid instead of collapsing to reform an ester, additional moisture in the chips improves yields in methods according to this invention.

Following depolymerization of lignin, the lignocellulosic material is digested in the presence of an alkali such as sodium hydroxide (NaOH) and/or potassium hydroxide (KOH). The positive cations (K^+ or Na^+ or another suitable ion) then attacks the exposed -OH on the lignin product (carboxylic acid) bumping out the hydrogen cation (H^+). The hydrogen cation then bonds with the negatively charged hydroxyl ion to form water. The lignin is then water-soluble and drops into solution, thereby separating the dissolved lignin from the cellulose-containing pulp. Due to more modest temperature, pressure and reactant concentrations involved, the lignin and cellulose produced are subject to less degradation than products obtained through a Kraft type process, thereby providing increased yield and purity.

Figure 2 is a schematic illustration of a method 10 according to the present invention. Lignocellulosic material, such as wood chips (not shown), is used as the starting raw material in an impregnating tank 12. The wood chips are prepared by chipping wood into a convenient size, for example, chips of roughly 0.5 - 2.0 inches in diameter. This can be done with a standard mill. Other sizes and shapes of lignocellulosic material can be used. Given the hydrolysis involved in the method, preferably "green" wood chips are used, or in other words, chips having a starting moisture content of approximately 30 - 55%, or even higher, by weight of water. A pre-treatment stage could be utilized wherein the wood chips were immersed or otherwise contacted with water prior to being placed in the impregnating tank in order to increase the moisture content within the chips up to or beyond

30 - 55% by weight of water, though this step is not necessary to produce lignin, pulp and other ancillary products according to this invention. Impregnating bone dry chips with an acid solution could be done, but this will result in higher consumption rates of the acid impregnant, thereby increasing costs.

Wood chips are loaded into impregnating tank 12 where they are contacted with an acid in order to impregnate the wood chips with the acid. The acid is preferably provided within an aqueous solution, and in such a case, the acid impregnates the wood chips as part of the solution. That is, the wood chips absorb both acid and water. According to one aspect of the invention, the aqueous solution comprises from about 10% to about 40% by weight of the acid. The invention also includes utilizing other, narrower acid concentration ranges within this range. For example, the aqueous acid solution may comprise from about 15% to about 30%, from about 10% to about 25%, from about 10% to about 15%, or from about 20% to about 25%, by weight of the acid.

The aqueous acid solution is provided to impregnating tank 12 from acid solution tank 14 in a sufficient volume to immerse the wood chips. The acid used is preferably nitric acid, but those skilled in the art will appreciate that other acids could instead be used within the scope of the present invention. Nitric acid is used herein for illustration purposes.

The wood chips are impregnated by allowing them to soak in the aqueous nitric acid solution in the impregnating tank 12. The impregnation time may last for as little as 30 minutes or less and may extend for any length of time before the degradation of the wood chips begins to occur. For example, impregnation may last from about 2 hours and 45 minutes to about 48 hours. It is contemplated that the impregnation time may fall within a narrower time ranges such as, for example, from about 12 to about 24 hours and ranges within this range.

Heating the chips during the impregnation step may decrease the impregnation time. For example, impregnation of the wood chips could occur from about 30 minutes or less to about 13 hours with the addition of heat, or up to 48 hours or longer, without the addition of heat. Heating during impregnation can be achieved by any number of well known techniques that could be used to heat the wood chips within impregnating tank 12. For example, the exterior of impregnating tank could be heated with steam to heat the tank 12. After sufficient time has passed to complete

impregnation, any excess nitric acid solution is removed from the wood chips, by drainage for example, and passed to spent solution tank 16. Any collected excess nitric acid solution may then be recycled for use in the impregnating tank 12. Preferably any excess nitric acid solution is filtered and purified using conventional techniques before being reconstituted back up to strength. Filtration and/or purification could be accomplished by passing any spent nitric acid solution from spent acid solution tank 16 to a conventional filtration and/or purification apparatus (not shown) before the solution is passed to acid solution tank 14. However, it may not be necessary to filter and purify the excess nitric acid solution if there are not significant amounts of contaminants present.

The impregnated wood chips are then passed to a heating tank 18. This transfer can be accomplished by gravity feed, if impregnating tank 12 is located above the heating tank 18, or by a suitable transfer mechanism if not. The impregnated chips are heated within heating tank 18. The exterior of heating tank 18 is heated with steam produced by steam boiler 20, thereby heating the chips within heating tank 18. Many other known apparatus or techniques could alternatively be used to heat heating tank 18. Heating of the chips in heating tank 18 may be carried out in two heating stages; the first heating stage to depolymerize the lignin within the wood chips without substantially degrading the cellulose or lignin, and the second heating stage to distill off the acid following depolymerization of the lignin. The distilled off nitric acid is recycled for use in the impregnation stage. In particular, the distilled off nitric acid is collected and passed to a condenser 22 and then to spent solution tank 16 to be reconstituted to a desired strength and then passed back to nitric acid tank 14 for eventual use in impregnating tank 12.

The nitric acid attacks the cross-links or ester groups of the lignin polymeric matrix during the first heating stage. The first heating stage is carried out for a period of time which is sufficient to depolymerize the lignin within the wood chips without substantially degrading the cellulose or lignin. When nitric acid is used as the impregnating acid, preferably the first heating stage is carried out at a temperature up to about 75 °C, but above the freezing point of the aqueous acid solution It is within the scope of the invention for the first heating stage to be carried out within a narrower temperature range, for example from about 50 °C to about 75 °C, from about 50 °C to about 60 °C, from about 70 °C to about 75 °C, or from about 60 °C to about 70 °C, when nitric acid is used as the impregnating acid. It is desirable to maintain these more modest temperatures (relative to Kraft pulping

temperatures) in order to prevent the unwanted degradation and destruction of the lignin and cellulose within the wood chips, thus providing improved product yield and purity.

Preferably heating tank 18 is fitted with an agitator 24 to provide agitation during the heating of chips within heating tank 18. Aggressive agitation by agitator 24 helps to both bring about a homogeneous temperature within heating tank 18 and to begin breaking apart the fibers in the wood chips.

During the second heating stage, the temperature is then brought above the boiling point of the acid for a sufficient time (for example, 30 minutes) to distill off the nitric acid. It is important to note that the temperature of the boiling point of the acid in this stage may depart slightly from the temperature that one would expect the acid to boil. This discrepancy results from various factors including the interaction of the acid with the wood, the moisture content within the wood, and, for nitric acid, the formation of azeotropes with water. For example, whereas some scientific literature establishes the boiling point of nitric acid to be 83 °C, the inventor has observed boiling for nitric acid with wood chips as low as 73 °C. Thus, it is preferred for the temperature of the second heating stage within heating tank 18 be at least about 73 °C where nitric acid is utilized. Similarly, it is also preferred to maintain the temperature during the second heating stage below the boiling point of water, 100 °C, to avoid the accidental distilling off of wood chip moisture, which would initiate the burning of the wood chips. Thus, according to one aspect of the invention, the second heating stage could be carried out from about 73 °C to below 100 °C. Again, it is within the scope of the invention to utilize narrower ranges, for example from about 90 °C to about 95 °C, within this larger range.

The amount of time for the first and second heating stages will vary depending upon a number of factors, including the particular temperatures involved. For example, the first heating stage may be carried out for as little as 15 minutes, and could be carried out for a longer period of time.

Following the heating in the heating tank 18, the wood chips are then transferred to a digester 26. There the wood chips are digested by being contacted with a caustic solution, or in other words, an aqueous alkaline solution wherein the solute is an alkali such as sodium hydroxide, potassium hydroxide, or a combination of these.

Those skilled in the art will appreciate that other bases having similar chemical properties as these bases could be used. The wood chips are contacted with the aqueous alkaline solution under heat to solubilize the lignin in the solution. The resultant solution is darker in color due to the solubilized lignin and is thus referred to as black liquor. This digestion step thereby separates the lignin and the black liquor from the pulp. The alkaline solution is provided to digester 26 from caustic solution tank 28. The concentration of the alkaline solution is such to just make the lignin water soluble. This is accomplished by the positive cations (K^+ or Na^+ or another suitable ion) attaching to the exposed cleavage sites on the lignin monomers and the lignin then dissolving into the water.

The temperature during the digestion stage is preferably up to about 75 °C, but above the freezing point of the aqueous alkaline solution. It is however within the scope of the invention to increase the temperature above 75 °C up to the boiling point of the alkaline solution. For example, where the alkaline solution comprises an aqueous sodium hydroxide solution, it is possible for the temperature during the digestion step to be from about 75 °C to about 95 °C. It is also within the scope of the invention for the digestion stage to be carried out within a narrower temperature range, for example, from about 5 °C to about 75 °C, from about 50 °C to about 75 °C, from about 20 °C to about 50 °C, from about 30 °C to about 40 °C, or from about 40 °C to about 50 °C. Heat is provided to digester 26 by heater 30, which may be any conventional apparatus or arrangement for providing heat to the digester 26.

Digester 26 may be fitted with an agitator 32 to provide agitation during the digestion of the chips. Aagitation helps to bring about a homogeneous temperature within the digester 26 and to break up the wood chips. Agitation also increases the rate that the cation (e.g. K^+, Na^+, etc.) binds to the exposed lignin cleavage sites thus minimizing any possible caustic action on the cellulose.

For cost and yield reasons, it is desirable to use as little alkali as possible within the caustic solution in the digestion of the wood chips. In one aspect of the invention, the alkaline solution may include an amount of alkali which is at least the normal equivalent of the nitric acid in the solution used in the impregnation stage. Adding excess alkali will increase costs by requiring more acid to be added at a later step. Further, the alkali concentration in the aqueous alkaline solution should be main-

tained below 17.5% by weight of the solution since beta and gamma cellulose dissolve at this level.

Following digestion, the resultant pulp (containing cellulose) and black liquor (containing solubilized lignin) is transferred to pulp tank 34 . The black liquor is removed, for example by drainage, and transferred to black liquor tank 36. The cellulose-containing pulp is then processed according to the user's needs. Typically, processing would involve washing, pressing, bleaching and drying the pulp following the separation from the black liquor. For example, in Figure 2, the pulp would be pressed in a pulp press 38 to remove any residual black liquor (which would also be transferred to black liquor tank 36), and then bleached and dried with bleaching apparatus 40 and dryer 42. Bleaching apparatus 40 and dryer 42 could be any conventional known apparatuses for these purposes.

The lignin is precipitated out of the black liquor in black liquor tank 36 after the addition of an acid from acid solution tank 44. Preferably the acid added is a mineral acid, such as sulfuric acid. The acid added to the black liquor strips off the cation from the caustic solute, thereby precipitating out the lignin and a caustic salt (e.g. where sulfuric acid is used, the salts Na_2SO_4, K_2SO_4, or other similar salts depending upon the alkali solute used in digestion, would result). Addition of the acid to the black liquor lowers the pH of the liquor until it is just slightly acidic. The acid may be added to the black liquor within an aqueous solution. For cost and yield reasons, it is advantageous if the acid solution is as dilute a solution as possible. Black liquor tank 36 may be fitted with an agitator 46 to provide agitation during the addition of the acid from tank 44. The contents of black liquor tank 36 may be cooled, for example by cooler 48, in order to faciliate the precipitation of lignin. Cooler 48 can be any known apparatus for cooling purposes. The black liquor may be cooled from the digestion temperature before the addition of the acid. Preferably the temperature is up to about 75 °C, but above the freezing point of the black liquor. Other narrower temperature ranges could be used at this step such as from about 5 °C to about 75 °C, 5 °C to about 75 °C, from about 50 °C to about 75 °C, or from about 25 °C to about 50 °C.

The precipitated lignin can then be removed from the resultant amber liquor (which is lighter in color than the black liquor due to the removal of the lignin) and processed using any conventional technique. For example, the resultant amber liquor and lignin slurry may be passed from black liquor tank 36 through a lignin

filter 50, with the lignin then being transferred to a lignin dryer 52 and dried at temperatures that will not degrade the lignin. The resultant lignin contains natural form lignin.

The filtrate passing through lignin filter 50 is the amber liquor, which is then transferred to an amber liquor tank 54. Any residual amber liquor removed during the drying of lignin in lignin dryer 52 is also transferred to amber liquor tank 54, as illustrated in Figure 2. Amber liquor is an aqueous solution containing starches, sugars, and other minerals and compounds found in plants that are not cellulose or lignin. In amber liquor tank 54, the amber liquor can be processed to yield various other products of value including alcohols, unicellular proteins or both. For example, the amber liquor could be used as a starting culture for various bacteria to produce various products, such as animal feeds and alcohols. Amber liquor tank 54 may be fitted with an agitator 56 to provide agitation if desired. Any proteins produced during the processing of the amber liquor may be removed by filtration (via protein filter 58) and dried (via protein dryer 60). Suitable apparatus modifications and/or additions could be made to accommodate alcohol processing and/or the production of other desired end products. The final filtrate can be recovered and treated in water treater 62 to remove any contaminants, thereby allowing the recycling of water within various steps in the method, for example in reuse in washing in pulp tank 34, preparation of the alkaline solution in caustic solution tank 28 and in steam boiler 20. Any recovered water could also be used in steam boiler 20 or in the preparation of the aqueous acid solutions in acid solution tank 14 and/or acid solution tank 44.

Without limitation, the present invention provides the following benefits:

1) Wet starting materials can be used. Since water is essential to the hydrolysis of the lignocellulosic material, this removes the need to dry the starting materials prior to the pulping process, thus resulting in lower costs relative to certain existing pulping methods.

2) The method of the present invention does not require added pressure, but may be carried out at atmospheric pressure. This reduces costs relative to certain existing pulping methods, as does the fact that the method of the present invention does not require the addition of heat at temperatures approaching those used in typical Kraft type pulping processes.

3) Weak concentrations of strong acids and strong bases may be used, thereby minimizing raw material costs and degradation of final products.

4) The acid catalyst can be recovered and recycled for reuse, allowing improved cost efficiency. These factors also allow a closed system, minimize pollution, and therefore environmental impact. Very little pollution is caused by methods according to this invention.

5) Only small amounts of chemicals are needed to bring back to strength each recovered chemical before being reused in the method. Moreover, unlike recovery stages in certain Kraft type processes, external energy (and the resultant expense) is not required during the recovery of chemicals in methods according to the present invention.

6) Water used in the method may be recovered in saleable byproducts (such as alcohols and animal feeds) treated and reused or vented as steam, with suitable apparatus and process modifications. The vented steam could be used in providing energy for the method, thereby eliminating even this small loss of water.

7) The method is flexible in terms of starting materials. The ability to process a wide variety of lignocellulosic material without retooling any apparatus or changing the methods involved gives flexibility in pulp production. Currently, mills are typically designed to produce specific pulp types and utilize specific wood species as raw materials. Furthermore, most Kraft mills require chips meeting stringent quality specifications to remain economically viable. The present method may utilize not only any number of differently sized chips, but also sawdust, and also chips that would be considered "green" and unusable by current pulp mill standards. The flexibility provided by methods of this invention eliminates or simplifies the need for chip mills designed to produce chips of stringent standards, thereby offering the potential for lower operating and capital costs.

8) The yield of alpha cellulose is high using the method, while the method also allows for a high yield of lignin, which is a valuable component itself.

9) Aside from cellulose and lignin, other useful and potentially valuable by-products may be recovered using methods of this invention. For example, the amber liquor is suitable for fermentation of unicellular protein following precipitation and removal of lignin. The protein can be used in animal feeds or for research purposes.

10) Methods of the invention may be applied to different sized and configured apparatuses, thereby improving the flexibility of use.

11) Mills utilizing a method of the present invention will be highly efficient, with lower operating costs than mills using typical Kraft pulping processes.

The following examples are presented by way of illustration and not by way of limitation.

Example 1

This example comprises 19 trials which were run to illustrate the yields of pulp and lignin obtained using methods according to this invention, and also to illustrate the recovery of the acid used in the impregnation stage.

The starting lignocellulosic material in Trials 1 - 18 comprised 200 grams of a mixture of hardwood and softwood wood chips obtained from a sawmill and chip mill operation in Kelowna, British Columbia, Canada. 600 grams of wood chips were used as the starting material in Trial 19. All of the different species of trees that the chips originated from were not ascertained, but at least some of the chips came from Ponderosa Pine, Douglas Fir, Maple, Oak and Spruce.

The moisture content of the wood chips was between 35 - 50 % water by weight. The moisture content was calculated by drying separate samples of the wood chips (which were not subjected to the steps of the method) and measuring the weight difference in the wood chips following the drying step.

The acid used in the impregnating step was nitric acid (HNO_3). Nitric acid solutions were prepared by diluting an amount (chosen depending upon the strength of solution desired) of 70% (w/w) nitric acid with distilled water. In each trial, 1 L of an aqueous nitric acid solution was used in the impregnating step, with the

exception that Trials 17 and 18 each used 750 mL, and Trial 19 used 2250 mL. A 2500 mL beaker sealed with laboratory film was used as the impregnating tank.

Following the impregnation step, excess nitric acid solution was removed from the wood chips before they were heated in the heating step. The heating step was carried out in a 2000 ml round bottom triple neck boiling flask, which was fitted with a distillation setup so that nitric acid distilled out in the heating step would be collected.

In order to calculate the efficiency of the method in recovering the nitric acid, samples from the excess acid solution collected following the impregnating step and from the distilled nitric acid which was collected during the heating step were each titrated using a 10% (w/w) % solution that was prepared by dissolving 100 g NaOH in distilled water and topped up in a 1 L volumetric flask. Titration of the excess nitric acid solution collected from after the impregnation step permitted the calculation of the number of moles of nitric acid recovered after the impregnating step, which in turn permitted the calculation of the number of moles of nitric acid which were absorbed by the wood chips, since the moles of nitric acid in the initial 1 L solution was known. After titrating the nitric acid that was distilled out and collected from the heating step, it was possible to calculate the total moles of nitric acid recovered in the method. By comparing this number to the amount of moles in a particular starting nitric acid solution allowed the calculation of the percentage of starting nitric acid which was recovered by the method. Also, it was found that red fuming nitric acid (RFNA) and nitrogen dioxide (NO_2) formed during the heating step and these vapors were lost to the atmosphere. These vapors could have been retained with better equipment, and if that were the case, the amount of nitric acid actually recovered would have greatly increased. To account for this, the amount of mass lost from the heating tank was determined by weighing the tank before and after the heating stage, with the difference which was lost as RFNA and NO_2. On the assumption that this amount could be recoverable as HNO_3 with appropriate equipment modifications, it is then possible to calculate what the total moles of HNO_3 which would be recoverable using the method by adding the amount actually recovered with the amount lost as RFNA and NO_2, and expressing this as a percentage of the starting moles of HNO_3. This is shown in Tables 1-5 for Trials 1 - 19. All titrations used 2 drops phenolphthalein as an indicator.

Following the heating step, the chips were digested in a round stainless steel tank with a 9.283 liter capacity (22.86 cm diameter, 11.43 cm height). The alkaline solution used in digestion was prepared by diluting an amount of 2.5 molar sodium hydroxide (NaOH) solution, 2.5 molar potassium hydroxide (KOH) solution, or a combination thereof, with distilled water. Various volumes of the initial 2.5 molar solutions were added to make the final alkaline solution used in digestion and various volumes of the final alkaline solution prepared were used for the various trials. The moles of each alkali solute(s) and the total volume of the aqueous alkaline solution prepared for Trials 1 - 19 are found in Tables 1 - 5.

In each of Trials 1 - 19 it took about 10 minutes or less to digest approximately 95% or more of the wood chips. In certain trials, a portion of the chips remained undigested, and the amounts are indicated in Tables 1 - 5 for such trials, as are the total digestion time for each trial.

Following the digestion step, the black liquor (containing solubilized lignin) was vaccum filtered in a buchner funnel without filter paper to remove the pulp, which was washed with distilled water and then air-dried at room temperature and weighed. The black liquor was transferred to a 2500 mL beaker, where the lignin was precipitated with the addition of a sulfuric acid (H_2SO_4) solution. The sulfuric acid solution was prepared by diluting an volume (depending upon the concentration sought) of pure sulfuric acid in a 1 L volumetric flask with distilled water. In most cases, the temperature of the black liquor was allowed to cool from the digestion step for the lignin precipitation step. The various temperatures are shown in Tables 1 - 5.

The lignin was vacuum filtered in a buchner funnel without filter paper and thus removed from the amber liquor. The lignin was air-dried at room temperature and weighed. The lignin was not however dried and weighed for Trials 17 and 18. In these trials, the lignin did precipitate and was, by visual inspection, found to have a similar relative amount and appearance as the lignin produced in Trials 1 - 16.

As set out below, heat was applied during the heating and digestion steps and in five trials, during the impregnation step. Where so indicated, the heat was supplied in various steps by using a heating mantle made by Glas-Col Apparatus Co., Cat 10 0-410, having 465 total watts and 110 volts. The mantle controller was a Powerstat variable autotransformer, Type 3PN116B, made by The Superior Electric Co. of

Bristol, Conn. Agitation was provided during the digestion step by a cold steel impeller which was 8 inches in diameter with 1/2 inch separation between 45 ° offset blades. A 18 volt DEWALT™ XRP cordless drill was used to power the agitator. Agitation was provided during the lignin precipitation step by manual stirring using a glass stir rod for approximately 30 - 45 seconds in each trial.

The conditions and results of Trials 1 - 19 are found in Tables 1 - 5.

Table 1

	Trial 1	Trial 2	Trial 3	Trial 4
IMPREGNATION STEP				
% HNO_3 (w/w)	15	24.15	25	30
Impregnating Time (hours)	24	48	48	13
HEATING STEP				
Time to reach 50 °C (min.)	55	41	40	30
Time between 50 - 75 °C (min.)	76	91	30	75
Time above 75 °C (min.)	59	19	35	32
Minimum HNO_3 Distillation Temp. (°C)	85	81	81	73
Distillation time (min.)	59	19	35	32
DIGESTION STEP				
Alkaline Solution				
moles NaOH	0.425	0.625	0	0.435
moles KOH	0	0.125	0.625	0.19
Vol. of Alkaline Solution (mL)	2670	3300	3000	3000
Digestion Temp. (°C)	60	63	50	70
Digestion Time (min.)	30	50	40	25
Amount of Undigested Chips (g)	0	0	5.4	0
LIGNIN PRECIPITATION STEP				
% H_2SO_4 Solution added to black liquor (v/v)	20	10	10	20
Vol. of Acid Sol'n added to black liquor (mL)	35	140	140	75
Temp. during Addition of Acid (°C)	25	45	45	25
RESULTS				
Pulp recovered (g)	92.1	104.6	99.6	94.5
Pulp recovered (%)	46.05	52.3	49.8	47.25
Lignin recovered (g)	41.4	42.1	39.8	43.1
Lignin recovered (%)	20.7	21.05	19.9	21.55
HNO_3 recoverable (%)	98.44	93.2	91.7	77.7

Table 2

	Trial 5	Trial 6	Trial 7	Trial 8
IMPREGNATION STEP				
% HNO_3 (w/w)	15	15	11.5	15
Impregnating Time (hours)	24	21	48	13, at 75-80°C
HEATING STEP				
Time to reach 50 °C (min.)	15	19	31	35
Time between 50 - 75 °C (min.)	20	90	65	25
Time above 75 °C (min.)	45	12	15	20
Minimum HNO_3 Distillation Temp. (°C)	83	81	83	83
Distillation time (min.)	45	12	15	20
DIGESTION STEP				
Alkaline Solution				
moles NaOH	0.55	0	0.25	0.3125
moles KOH	0	0.625	0.3	0.3
Vol. of Alkaline Solution (mL)	3220	3250	3220	3245
Digestion Temp. (°C)	50	50	60	70
Digestion Time (min.)	30	60	15	30
Amount of Undigested Chips (g)	7	8.6	14.2	7
LIGNIN PRECIPITATION STEP				
% H_2SO_4 Solution added to black liquor (v/v)	10	10	10	10
Vol. of Acid Sol'n added to black liquor (mL)	90	132	150	125
Temp. during Addition of Acid (°C)	40	32	34	61
RESULTS				
Pulp recovered (g)	92.2	90.1	88.6	101.4
Pulp recovered (%)	46.1	45.1	44.3	50.7
Lignin recovered (g)	37.9	39.1	38.3	42.2
Lignin recovered (%)	19	19.6	19.2	21.1
HNO_3 recoverable (%)	93.4	92.1	93.4	88.1

Table 3

	Trial 9	Trial 10	Trial 11	Trial 12
IMPREGNATION STEP				
% HNO_3 (w/w)	15	20	15	24.15
Impregnating Time (hours)	17 at 75-80 °C	2:45 at 75°C	31	30
HEATING STEP				
Time to reach 50 °C (min.)	35	19	37	41
Time between 50 - 75 °C (min.)	24	85	32	105
Time above 75 °C (min.)	22	12	114	30
Minimum HNO_3 Distillation Temp. (°C)	83	75	80	83
Distillation time (min.)	22	12	20	30
DIGESTION STEP				
Alkaline Solution				
moles NaOH	0.625	0.625	0	0.3125
moles KOH	0	0	0.625	0.3125
Vol. of Alkaline Solution (mL)	3000	3000	2500	2250
Digestion Temp. (°C)	50 - 63	70	55	60
Digestion Time (min.)	30	15	15	20
Amount of Undigested Chips (g)	0	20.3	24.4	0
LIGNIN PRECIPITATION STEP				
% H_2SO_4 Solution added to black liquor (v/v)	10	10	20	10
Vol. of Acid Sol'n added (mL)	150	150	65	125
Temp. during Addition of Acid (°C)	29	38	27	31
RESULTS				
Pulp recovered (g)	85.6	87.1	77.1	103.5
Pulp recovered (%)	42.8	43.6	38.6	51.75
Lignin recovered (g)	38.9	43.9	33.9	44.1
Lignin recovered (%)	19.5	22	17	22.05
HNO_3 recoverable (%)	93.4	92.61	93.8	65.05

Table 4

	Trial 13	Trial 14	Trial 15	Trial 16
IMPREGNATION STEP				
% HNO_3 (w/w)	20	30	15	15
Impregnating Time (hours)	13	15	12	14
HEATING STEP				
Time to reach 50 °C (min.)	19	23	14	6
Time between 50 - 75 °C (min.)	95	55	48	57
Time above 75 °C (min.)	15	20	35	18
Minimum HNO_3 Distillation Temp. (°C)	81	80	81	79
Distillation time (min.)	15	20	45	25
DIGESTION STEP				
Alkaline Solution				
moles NaOH	0.625	0	0.5	0.5
moles KOH	0	0.625	0	0
Vol. of Alkaline Solution (mL)	2500	2750	2700	2700
Digestion Temp. (°C)	55	61	73	41
Digestion Time (min.)	20	25	10	13
Amount of Undigested Chips (g)	4.9	11.6	28.7	102.3
LIGNIN PRECIPITATION STEP				
% H_2SO_4 Solution added to black liquor (v/v)	10	10	20	20
Vol. of Acid Sol'n added to black liquor (mL)	150	150	110	130
Temp. during Addition of Acid (°C)	26	36	18	5
RESULTS				
Pulp recovered (g)	96.4	87	71.2	35.2
Pulp recovered (%)	48.2	43.5	35.6	17.6
Lignin recovered (g)	47	38.6	27.2	17.8
Lignin recovered (%)	23.5	19.3	13.6	8.9
HNO_3 recoverable (%)	91.1	90.6	83.7	84.1

Table 5

	Trial 17	Trial 18	Trial 19
IMPREGNATION STEP			
% HNO_3 (w/w)	15	15	15
Impregnating Time (hours)	1:25 at 50 - 55 °C	2:10 at 50 - 55 °C	12
HEATING STEP			
Time to reach 50 °C (min.)	12	10	20
Time between 50 - 75 °C (min.)	60 (held between 70 - 75 °C)	55 (held between 60 - 70 °C)	35
Time above 75 °C (min.)	11	22	27
Minimum HNO_3 Distillation Temp. (°C)	83	82	83
Distillation time (min.)	11	15	32
DIGESTION STEP			
Alkaline Solution moles NaOH moles KOH	 0.5 0	 0.475 0	 1.2625 0
Vol. of Alkaline Solution (mL)	2500	2690	3050
Digestion Temp. (°C)	70	63	83
Digestion Time (min.)	10	3	10
Amount of Undigested Chips (g)	31.6	37.8	166
LIGNIN PRECIPITATION STEP			
% H_2SO_4 Solution added to black liquor (v/v)	20	20	20
Vol. of Acid Sol'n added to black liquor (mL)	130	115	300
Temp. during Addition of Acid (°C)	7	10	32
RESULTS			

Pulp recovered (g)	71	67.6	169.3
Pulp recovered (%)	35.5	33.8	28.2
Lignin recovered (g)	Not Weighed	Not Weighed	72.5
Lignin recovered (%)	Not Weighed	Not Weighed	12.1
HNO_3 recoverable (%)	80.2	83.2	78.8

Example 2

This example comprised a trial that was similar to Trials 1 - 19 in example 1 except that the starting lignocellulosic material was 150 grams of shavings and sawdust from Hemlock, Oak and Pine tree species. Impregnation was done for 30 minutes in 15% (w/w) HNO_3 solution under heat of 50 °C. The impregnated shavings and sawdust were heated for 60 minutes between 50 - 75 °C, and then for 10 minutes over 80 °C. Following the heating step, the shavings and sawdust were contacted with an alkaline solution having 1.25 moles of NaOH and 2600 mL total volume at a temperature of 52 °C for 7 minutes. Following pulp removal, lignin was precipitated with the addition of 20 % (v/v) H_2S0_4. The pulp and lignin were not weighed, but a visual inspection showed satisfactory appearance and yield for each, proving that the method of this invention can be carried out with relatively small pieces of lignocellulosic material such as shavings and sawdust.

Example 3

The pulp samples produced in Trials 5, 7 and 2 from example 1 were subsequently analyzed to determine the relative amounts of alpha cellulose, beta cellulose and gamma cellulose therein. The results are found in Table 6 below.

Table 6

	Trial 5	Trial 7	Trial 2
Alpha Cellulose (%)	81.3	79.6	79.2
Beta Cellulose (%)	4.4	3.7	7.5
Gamma Cellulose (%)	14.3	16.7	13.3

In addition to the methods herein, the present invention also includes pulp produced according to the methods herein, as well as paper products comprising cellulose from pulp produced according to the methods herein. Similarly, the present invention also includes lignin produced according to the methods herein, as well as numerous other products and compositions comprising lignin produced according to the methods herein, including for example, fertilizers, asphalt emulsifiers, soil stabilizers, wood products (such as plywood and particle board), oil well drilling fluids and dispersing agents for preparing concrete.

As will be apparent to those skilled in the art in the light of the foregoing disclosure, many alterations and modifications are possible in the practice of this invention without departing from the scope thereof. Accordingly, the scope of the invention is to be construed in accordance with the substance defined by the following claims.

WHAT IS CLAIMED IS:

1. A method for producing pulp and lignin from lignocellulosic material, the pulp comprising cellulose, the method comprising:

(a) contacting the lignocellulosic material with an aqueous acid solution to impregnate the lignocellulosic material, the aqueous acid solution comprising from about 10% to about 40% by weight of the acid;

(b) heating the lignocellulosic material in two stages, the first heating stage being carried out for a period of time which is sufficient to depolymerize lignin within the lignocellolosic material without substantially degrading the cellulose or lignin in the lignocellulosic material, the second heating stage being carried out at or above the boiling point of the acid to distill off the acid;

(c) contacting the lignocellulosic material with an aqueous alkaline solution under heat to solubilize lignin in the alkaline solution, leaving a black liquor;

(d) removing the pulp from the black liquor;

(e) adding sufficient acid to the black liquor to precipitate the lignin; and

(f) removing the lignin from the liquor.

2. A method according to claim 1 wherein the acid is nitric acid.

3. A method according to claim 1 or 2 wherein the lignocellulosic material is contacted with the aqueous acid solution in step (a) for at least 30 minutes.

4. A method according to any one of claims 1 to 3 wherein the lignocellulosic material is contacted with the aqueous acid solution in step (a) from about 12 hours to about 24 hours.

5. A method according to any one of claims 1 to 4 wherein the lignocellulosic material is contacted with the aqueous acid solution in step (a) under heat.

6. A method according to claim 2 wherein the lignocellulosic material is contacted with the aqueous nitric acid solution in step (a) at a temperature from about 50 °C to below the boiling point of the nitric acid.

7. A method according to claim 2 wherein the aqueous nitric acid solution in step (a) comprises from about 10% to about 30% by weight of the nitric acid.

8. A method according to claim 7 wherein the aqueous nitric acid solution comprises from about 15% to about 30% by weight of the nitric acid.

9. A method according to 8 wherein the aqueous nitric acid solution comprises from about 20% to about 25% by weight of the nitric acid.

10. A method according to claim 2 wherein the aqueous nitric acid solution comprises from about 10% to about 15% by weight of the nitric acid.

11. A method according to any one of claims 2 and 7 to 10 wherein the temperature during the second heating stage of step (b) is from about 73 °C to below 100 °C.

12. A method according to claim 11 wherein the temperature during the second heating stage of step (b) is from about 90 °C to about 95 °C.

13. A method according to any one of claims 2 and 7 to 12 wherein the temperature during the first heating stage of step (b) is up to about 75 °C.

14. A method according to claim 13 wherein the temperature during the first heating stage of step (b) is from about 50 °C to about 75 °C.

15. A method according to claim 14 wherein the temperature during the first heating stage of step (b) is from about 60 °C to about 70 °C.

16. A method according to claim 14 wherein the temperature during the first heating stage of step (b) is from about 50 °C to about 60 °C.

17. A method according to claim 14 wherein the temperature during the first heating stage of step (b) is from about 70 °C to about 75 °C.

18. A method according to any one of claims 1 to 17 wherein the first heating stage in step (b) is carried out for at least 15 minutes.

19. A method according to any one of claims 1 to 18 wherein the aqueous alkaline solution comprises sodium hydroxide or potassium hydroxide or a combination of sodium hydroxide and potassium hydroxide.

20. A method according to any one of claims 1 to 19 wherein the aqueous alkaline solution comprises an amount of alkali solute which is at least the normal equivalent of the nitric acid in the aqueous acid solution in step (a).

21. A method according to any one of claims 1 to 19 wherein the aqueous alkaline solution comprises an amount of alkali solute which is at least the molar equivalent of the nitric acid in the aqueous acid solution in step (a).

22. A method according to any one of claims 1 to 21 wherein the acid added in step (e) is sulfuric acid.

23. A method according to any one of claims 1 to 22 wherein the amount of acid added in step (e) is at least the molar amount of the alkali in the aqueous alkaline solution in step (c).

24. A method according to any one of claims 1 to 23 wherein the black liquor is cooled from the temperature in step (c) before the acid is added in step (e).

25. A method according to any one of claims 2 and 7 to 17 wherein the temperature of the black liquor when the acid is added in step (e) is up to about 75 °C.

26. A method according to claim 25 wherein the temperature of the black liquor when the acid is added in step (e) is from about 5 °C to about 75 °C.

27. A method according to claim 26 wherein the temperature of the black liquor when the acid is added in step (e) is from about 5 °C to about 50 °C.

28. A method according to claim 27 wherein the temperature of the black liquor when the acid is added in step (e) is from about 25 °C to about 50 °C.

29. A method according to claim 25 wherein the temperature of the black liquor when the acid is added in step (e) is from about 50 °C to about 75 °C.

30. A method according to any one of claims 1 to 29 wherein any aqueous acid solution not absorbed by the lignocellulosic material in step (a) is removed prior to heating the lignocellulosic material in step (b).

31. A method according to claim 30 comprising collecting any aqueous acid solution which is removed prior to step (b) and recycling the collected aqueous acid solution for use in step (a), and comprising collecting any acid which is distilled off in step (b) and recycling the collected acid for use in step (a).

32. A method according to any one of claims 1 to 31 wherein the starting moisture content of the lignocellulosic material is from about 30% to about 55% by weight of water.

33. A method according to any one of claims 1 to 32 comprising contacting the lignocellulosic material with water before step (a) to increase the moisture content in the lignocellulosic material.

34. A method according to any one of claims 1 to 33 wherein the starting lignocellulosic material comprises undigested lignocellulosic material previously subjected to the method.

35. A method according to any one of claims 1 to 34 wherein the starting lignocellulosic material comprises wood chips, wood shavings, sawdust or a combination of two or more wood chips, wood shavings and sawdust.

36. A method according to any one of claims 1 to 35 wherein the starting lignocellulosic material comprises pieces of rye, wheat, hemp or a combination of two or more of rye, wheat and hemp.

37. A method according to any one of claims 1 to 36 wherein an amber liquor is left following the removal of the lignin, and comprising processing the amber liquor after the lignin has been removed.

38. A method according to claim 37 wherein the amber liquor is processed to produce unicellular proteins or alcohols or both.

39. A method according to any one of claims 1 to 38 wherein any water which is produced as a reaction byproduct in one or more of the steps is collected and recycled for use in the method.

40. A method according to any one of claims 2, 7 to 17 and 25 to 29 wherein steps (a) and (c) and the first heating stage in step (b) are each carried out at a temperature from about 50 °C to about 75 °C.

41. A method according to any one of claims 1 to 40 wherein at least one of the heating of the impregnated lignocellulosic material in step (b), the contacting the lignocellulosic material with the aqueous alkaline solution in step (c) and the adding the acid in step (e) is carried out with agitation.

42. A method according to any one of claims 1 to 41 wherein the heating of the impregnated lignocellulosic material in step (b), the contacting the lignocellulosic material with the aqueous alkaline solution in step (c) and the addition of the acid in step (e) are each carried out with agitation.

43. A method according to any one of claims 1 to 42 wherein the method is carried out at atmospheric pressure.

44. A method according to any one of claims 1 to 43 comprising washing, pressing, bleaching and drying the pulp removed in step (d).

45. A method according to any one of claims 1 to 44 comprising drying the lignin removed in step (f).

46. A method according to any one of claims 2, 7 to 17, 25 to 29 and 40 wherein step (c) is carried out at a temperature up to about 75°C.

47. A method according to claim 46 wherein step (c) is carried out at a temperature from about 5 °C to about 75 °C.

48. A method according to claim 47 wherein step (c) is carried out at a temperature from about 50 °C to about 75 °C.

49. A method according to claim 46 wherein step (c) is carried out at a temperature from about 20 °C to about 50 °C.

50. A method according to claim 47 wherein step (c) is carried out at a temperature from about 30 °C to about 40 °C.

51. A method according to claim 47 wherein step (c) is carried out at a temperature from about 40 °C to about 50 °C.

52. A method according to any one of claims 1 to 51 wherein the lignocellulosic material is immersed in the aqueous acid solution in step (a).

53. A method according to any one of claims 1 to 52 wherein the lignocellulosic material is sprayed with the aqueous acid solution in step (a).

54. A method for producing pulp and lignin from lignocellulosic material, the pulp comprising cellulose, the method comprising:

(a) contacting the lignocellulosic material with an aqueous nitric acid solution to impregnate the lignocellulosic material, the aqueous nitric acid solution comprising from about 10% to about 40% by weight of the nitric acid,

(b) heating the impregnated lignocellulosic material in two stages, the first heating stage being carried out a temperature from about 50 °C to about 75 °C for a period of time which is sufficient to depolymerize lignin within the lignocellolosic material without substantially degrading the cellulose or lignin in the ligncellulosic material, the second heating stage being carried out at or above the boiling point of the nitric acid to distill off the nitric acid;

(c) contacting the lignocellulosic material with an aqueous alkaline solution at a temperature from about 50 °C to about 75 °C to solubilize lignin in the alkaline solution, leaving a black liquor, the aqueous alkaline solution comprising an amount of alkali which is at least the normal amount of the nitric acid in the aqueous acid solution in step (a);

(d) removing the pulp from the black liquor;

(e) cooling the black liquor and then adding an acid to the black liquor to acidify the solution to precipitate the lignin;

(f) removing the lignin, leaving an amber liquor; and

(g) processing the amber liquor to produce unicellular proteins or alcohols or both,

wherein any aqueous nitric acid not absorbed by the lignocellulosic material in step (a) is removed and collected following step (a) prior to heating the lignocellulosic material in step (b) and then recycled for use in step (a), and wherein any nitric acid which is distilled off is collected prior to contacting the lignocellulosic material with the alkaline solution in step (c) and then recylcled for use in step (a), and wherein the heating of the lignocellulosic material in step (b), the contacting the lignocellulosic material with the aqueous alkaline solution in step (c) and the addition of the acid in step (e) are each carried out with agitation.

55. A method for producing pulp and lignin comprising the steps of contacting lignocellulosic material with an acid and, after removing any acid not absorbed by the lignocellulosic material, heating the lignocellulosic material at a temperature up to about 75 °C to effect the acid-catalyzed hydrolytic depolymerization of the lignin in the lignocellulosic material without substantially degrading the cellulose or lignin in the lignocellulosic material, the acid-contacting and heating steps being carried out before the lignocellulosic material is digested in an alkaline liquor, the pulp being removed following the digestion of the lignocellulosic material in the alkaline liquor, the lignin being removed after being precipitated out with

the addition of an acid to the black liquor produced following the digestion of the lignocellulosic material in the alkaline liquor, wherein the pulp comprises cellulose.

56. A method according to claim 55 wherein the acid-contacting step comprises immersing the lignocellulosic material in an aqueous solution of the acid, and wherein the acid is nitric acid and the aqueous solution comprises from about 10 % to about 40 % by weight of nitric acid.

57. A method according to claim 55 or 56 comprising heating the lignocellulosic material after depolymerizing the lignin but before digesting the lignocellulosic material, at a temperature above the boiling point of the acid in order to distill off the acid.

58. A method according to claim 44 wherein any liquor that is removed from the pulp by pressing is collected and added to the black liquor prior to adding the acid in step (e).

59. A method according to claim 45 wherein any liquor which is removed from the lignin during drying is collected and added to the liquor after step (f), and wherein the liquor is processed after the lignin has been precipitated and removed.

60. A method according to any one of claims 1 to 53, 57 and 58 wherein enough acid is added to the solution in step (e) to lower the pH of the solution to an acidic pH.

61. A method for treating lignocellulosic material comprising:

(a) contacting the lignocellulosic material with an aqueous acid solution to impregnate the lignocellulosic material, the aqueous acid solution comprising from about 10% to about 40% by weight of the acid;

(b) heating the lignocellulosic material in two stages, the first heating stage being carried out for a period of time which is sufficient to depolymerize lignin within the lignocellolosic material without substantially degrading the cellulose or lignin in the ligncellulosic

material, the second heating stage being carried out at or above the boiling point of the acid to distill off the acid, wherein any aqueous acid solution not absorbed by the lignocellulosic material in step (a) is removed prior to heating the lignocellulosic material in step (b);

(c) contacting the lignocellulosic material with an aqueous alkaline solution under heat to solubilize lignin in the alkaline solution, leaving a black liquor; and

(d) removing the pulp from the black liquor, the pulp comprising cellulose.

62. A method according to any one of claims 1 to 53, 57, 58 and 60 wherein the amount of acid added in step (e) is at least the normal amount of the alkali in the aqueous alkaline solution in step (c).

63. A method for producing pulp and lignin from lignocellulosic material, the pulp comprising cellulose, the method comprising:

(a) contacting the lignocellulosic material with an aqueous nitric acid solution to impregnate the lignocellulosic material, the aqueous acid solution comprising from about 10% to about 40% by weight of the nitric acid;

(b) heating the lignocellulosic material in two stages, the first heating stage being carried out for a period of time which is sufficient to depolymerize lignin within the lignocellolosic material without substantially degrading the cellulose or lignin in the ligncellulosic material, the second heating stage being carried out at or above the boiling point of the acid to distill off the acid, wherein any aqueous acid solution not absorbed by the lignocellulosic material in step (a) is removed prior to heating the lignocellulosic material in step (b);

(c) contacting the lignocellulosic material with an aqueous alkaline solution under heat to solubilize lignin in the alkaline solution, leaving a black liquor;

(d) removing the pulp from the black liquor;

(e) adding sufficient acid to the black liquor to precipitate the lignin; and

(f) removing the lignin from the liquor.

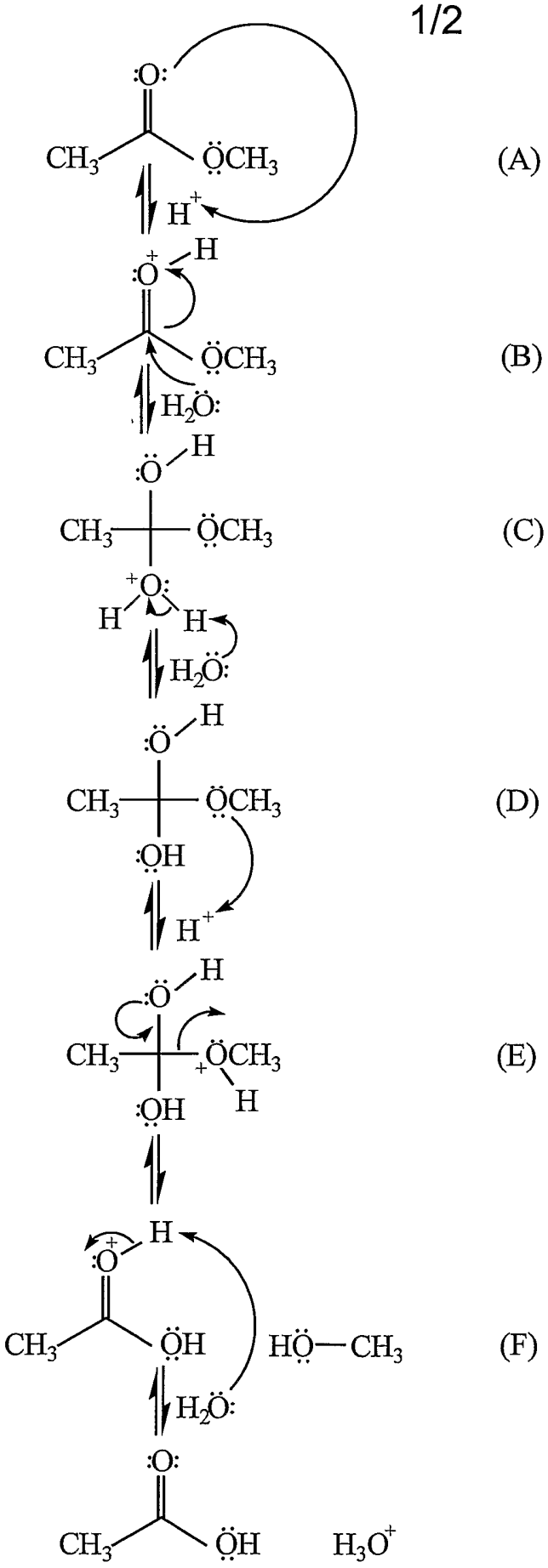
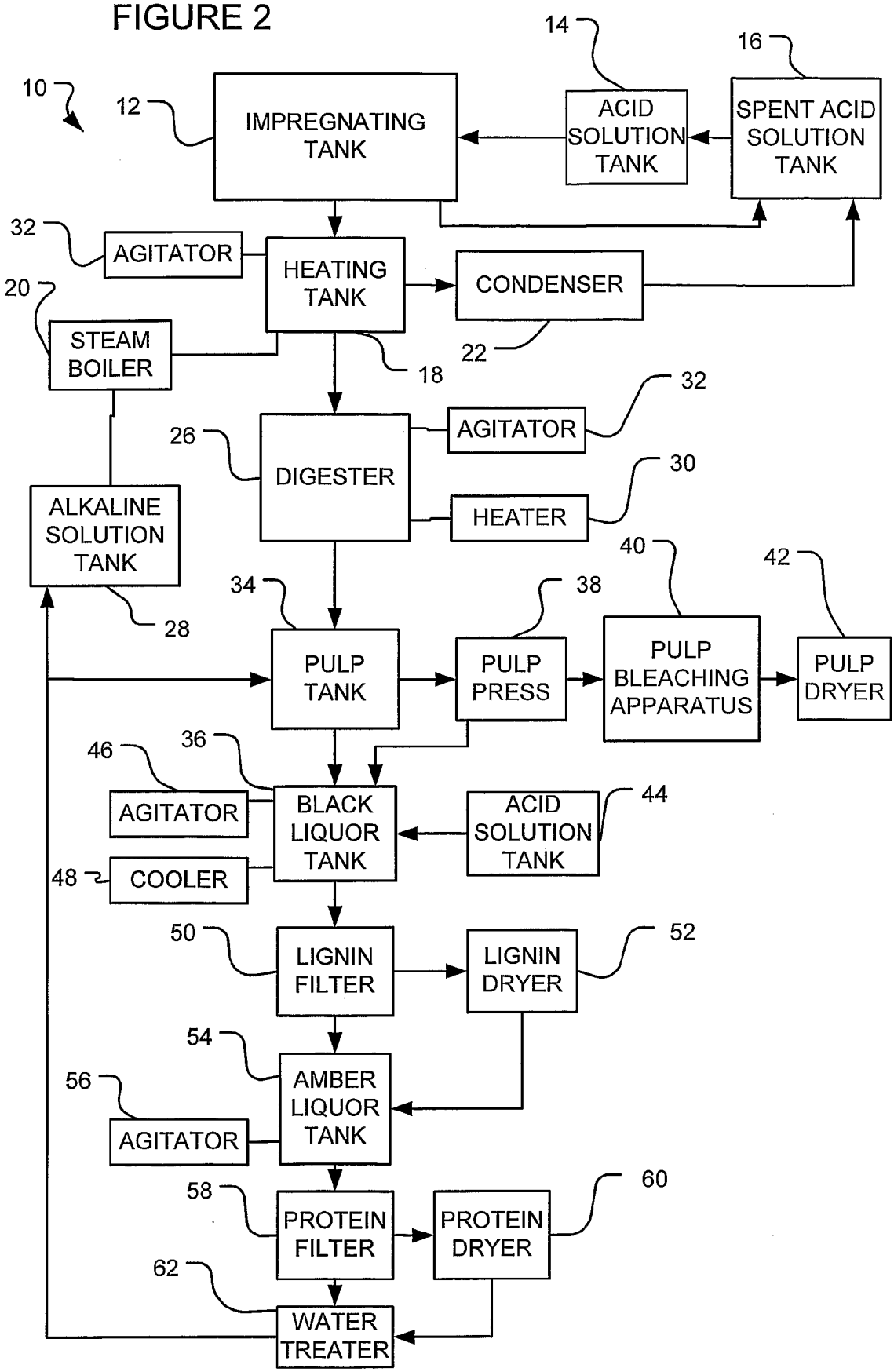


FIGURE 1

FIGURE 2


10
12
IMPREGNATING TANK
14
ACID SOLUTION TANK
16
SPENT ACID SOLUTION TANK
32
AGITATOR
HEATING TANK
CONDENSER
20
STEAM BOILER
18
22
32
AGITATOR
26
DIGESTER
30
HEATER
ALKALINE SOLUTION TANK
28
34
38
40
42
PULP TANK
PULP PRESS
PULP BLEACHING APPARATUS
PULP DRYER
46
36
AGITATOR
BLACK LIQUOR TANK
ACID SOLUTION TANK
44
48
COOLER
50
LIGNIN FILTER
LIGNIN DRYER
52
54
AMBER LIQUOR TANK
56
AGITATOR
58
PROTEIN FILTER
PROTEIN DRYER
60
62
WATER TREATER

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 03/01901

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D21C1/04 D21C3/02 D21C11/04

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D21C

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/041982 A1 (PRIOR ERIC S) 6 March 2003 (2003-03-06) claims 1-28; example 1	1,54,55, 61,63
Y	US 6 533 896 B1 (FANT THOMAS ET AL) 18 March 2003 (2003-03-18) claims 1-8; examples 1-9	1,54,55, 61,63
Y	US 5 944 953 A (LAVOIE PIERRE ET AL) 31 August 1999 (1999-08-31) claims 1-4; example 1	1,54,55, 61,63
Y	US 4 602 982 A (SAMUELSON HANS O) 29 July 1986 (1986-07-29) claims 1-16; figure 1	1,54,55, 61,63

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 April 2004	28/04/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Karlsson, L

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 03/01901

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 012 775 A (PRIOR ERIC S) 9 July 1980 (1980-07-09) claims 1-10	1,54,55, 61,63
Y	EP 0 364 632 A (ICI PLC) 25 April 1990 (1990-04-25) claims 1-10; example 1	1,54,55, 61,63
A	GB 1 366 252 A (KILBORN ENG LTD) 11 September 1974 (1974-09-11) the whole document	1-63
A	GB 583 074 A (ENGLISH CELLULOSE DERIVATIVES;GUSTAV ULLMANN) 6 December 1946 (1946-12-06) the whole document	1-63
A	US 4 456 750 A (MARTTALA TAPANI ET AL) 26 June 1984 (1984-06-26) the whole document	1-63

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/CA 03/01901

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 2003041982	A1	06-03-2003	NONE		
US 6533896	B1	18-03-2003	FI	974455 A	09-06-1999
			BR	9805237 A	09-11-1999
			EP	0921228 A2	09-06-1999
			JP	11241285 A	07-09-1999
US 5944953	A	31-08-1999	CA	2171681 A1	13-09-1997
US 4602982	A	29-07-1986	SE	434283 B	16-07-1984
			AT	384252 B	27-10-1987
			AT	418483 A	15-03-1987
			AU	560978 B2	30-04-1987
			AU	2085883 A	07-06-1984
			CA	1205959 A1	17-06-1986
			DE	3343403 A1	07-06-1984
			FI	834382 A ,B,	02-06-1984
			FR	2537176 A1	08-06-1984
			JP	1002715 B	18-01-1989
			JP	1519599 C	29-09-1989
			JP	59106592 A	20-06-1984
			NO	834407 A ,B,	04-06-1984
			NZ	205971 A	23-01-1987
			SE	8206859 A	02-06-1984
EP 0012775	A	09-07-1980	EP	0012775 A1	09-07-1980
			DE	2862405 D1	20-06-1984
EP 0364632	A	25-04-1990	EP	0364632 A1	25-04-1990
			BR	8805568 A	05-06-1990
			CA	1313865 C	23-02-1993
			US	4946946 A	07-08-1990
GB 1366252	A	11-09-1974	DE	2215739 A1	26-10-1972
			FR	2136259 A5	22-12-1972
			JP	58022597 B	10-05-1983
			PH	13234 A	14-02-1980
GB 583074	A	06-12-1946	NONE		
US 4456750	A	26-06-1984	FI	63790 B	29-04-1983
			SE	455708 B	01-08-1988
			SE	8300687 A	12-08-1983