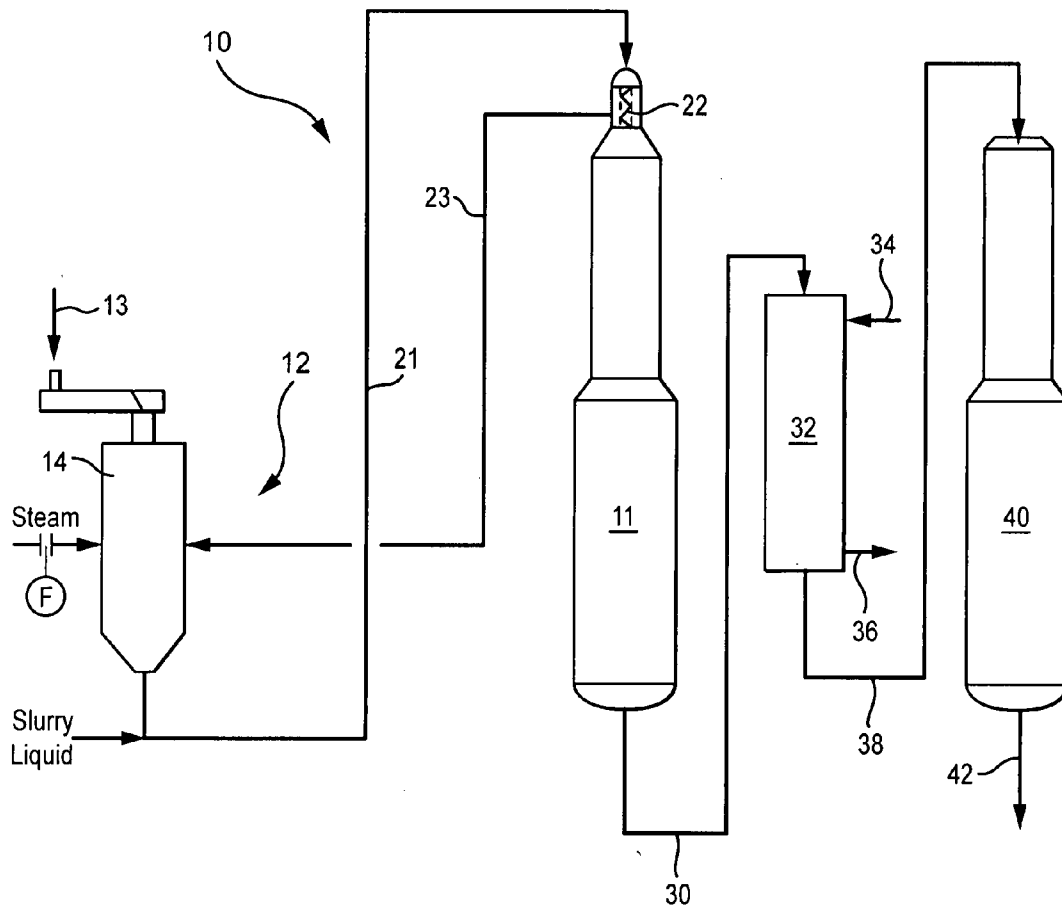




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(19) **United States**(12) **Patent Application Publication****Shin et al.**(10) **Pub. No.: US 2007/0240837 A1**(43) **Pub. Date: Oct. 18, 2007**(54) **HARDWOOD ALKALINE PULPING
PROCESSES AND SYSTEMS**(52) **U.S. Cl. 162/76**(75) Inventors: **Nam Hee Shin**, Clifton Park, NY
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NY (US)(21) Appl. No.: **11/709,278**(22) Filed: **Feb. 22, 2007****Related U.S. Application Data**(60) Provisional application No. 60/791,431, filed on Apr.
13, 2006.**Publication Classification**(51) **Int. Cl.**
D21C 1/04 (2006.01)(57) **ABSTRACT**

Hardwood pulp rejects at a given Kappa number can be reduced by subjecting the hardwood pulp to specified cooking conditions at the end of cooking. In this regard, it has been discovered that s-lignin reacts faster than g-lignin and that there exists a higher proportion of g-lignin at the end of a hardwood cook as compared to the g-lignin present at the beginning of the cook. Thus, when cooking hardwoods, relatively harsher cooking conditions (e.g., higher cooking temperatures) at the end of the cooking have been discovered to decrease the g-lignin content which in turn decreases the percentage of pulp rejects at a given Kappa number. In preferred embodiments, methods and systems are provided for continuously producing chemical cellulose pulp from a slurry of comminuted hardwood material by subjecting the slurry of comminuted hardwood material to a first cooking stage under conditions sufficient to reduce syringyl lignin (s-lignin) content in the hardwood material as compared to guaiacyl lignin (g-lignin) content therein, and thereafter subjecting the slurry of comminuted hardwood material to a second cooking stage under conditions sufficient to reduce the g-lignin content remaining therein after the first cooking stage.



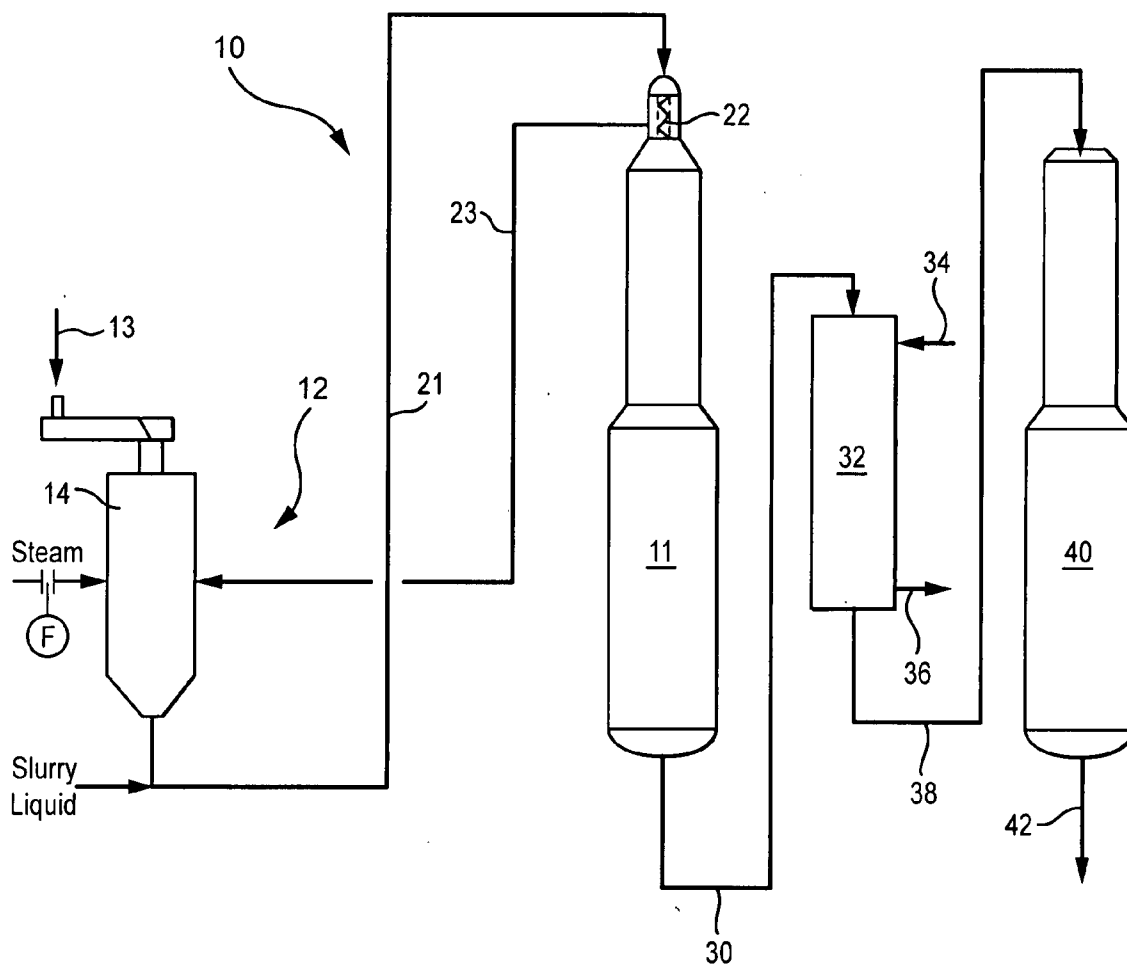


Fig. 1

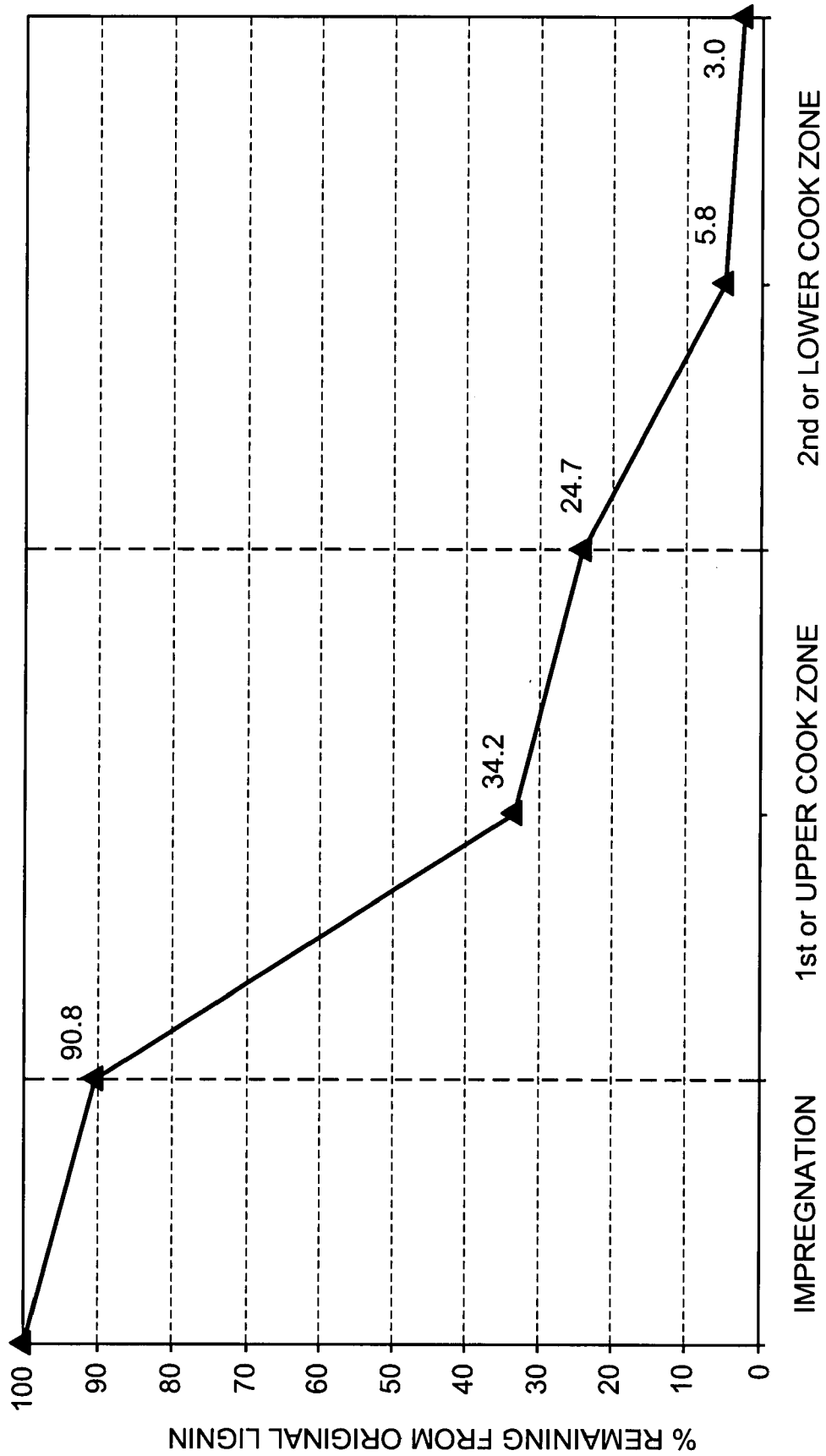


Fig. 2

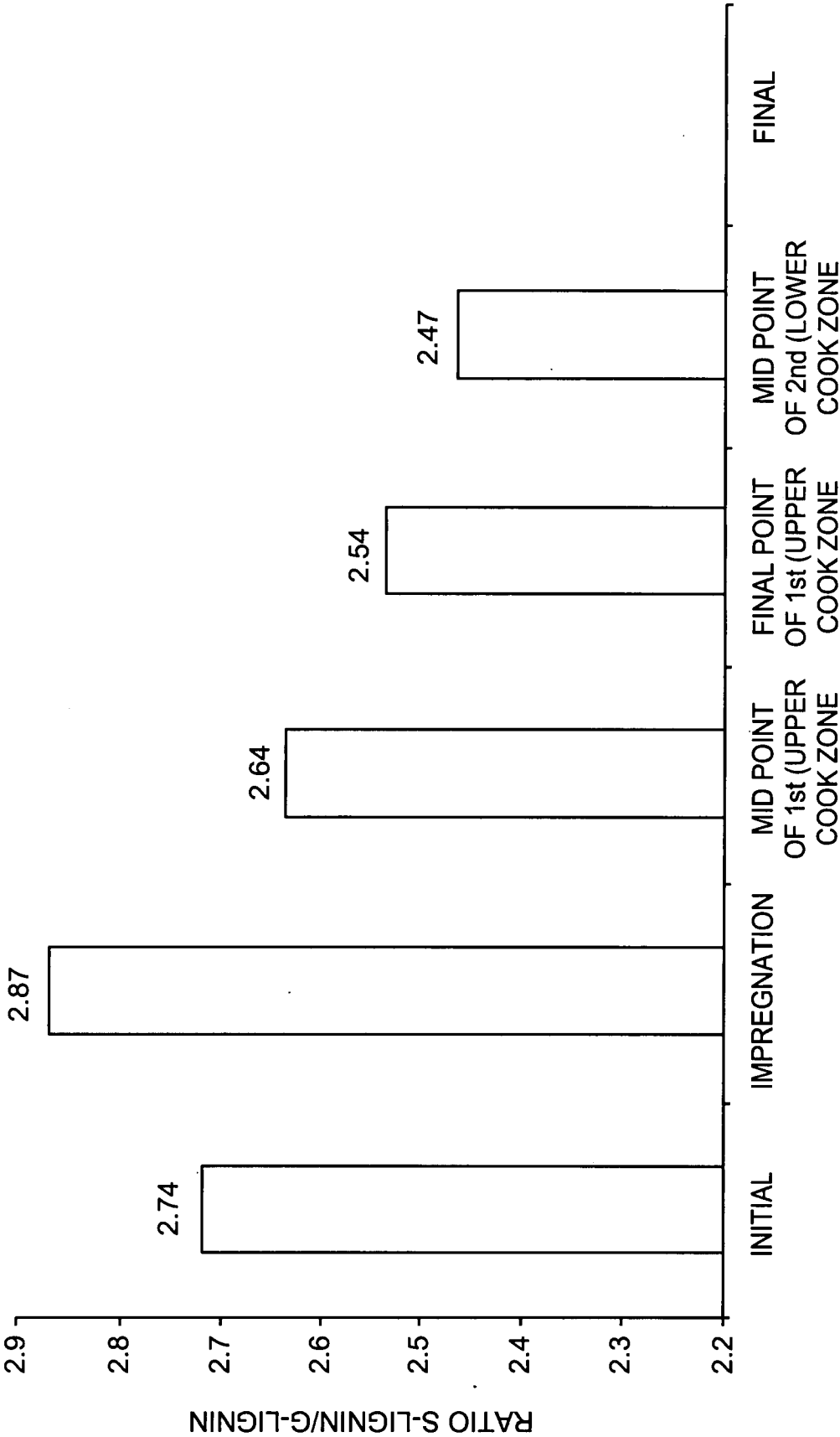


Fig. 3

HARDWOOD ALKALINE PULPING PROCESSES AND SYSTEMS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is based on and claims domestic priority benefits under 35 USC §119(e) from U.S. Provisional Application Ser. No. 60/791,431 filed on Apr. 13, 2006, the entire content of which is expressly incorporated hereinto by reference.

FIELD OF THE INVENTION

[0002] The present invention relates generally to the field of chemical treatments of comminuted cellulosic fibrous material. In especially preferred embodiments, the present invention relates to processes and apparatus for the alkaline pulping of comminuted hardwoods.

BACKGROUND AND SUMMARY OF THE INVENTION

[0003] Chemical cooking of hardwoods can typically result in greater pulp rejects as compared to pulp obtained from the chemical cooking of softwoods at Kappa numbers of 17 and greater. In this regard, the present applicants have discovered that the middle lamella in hardwoods have substantial amounts of guaiacyl lignin (g-lignin) on a cellular level in the middle lamella as compared to the presence of syringyl lignin (s-lignin). Specifically, the lignin in the middle lamella of hardwoods is predominantly g-lignin. The middle lamella of softwood cells will typically be substantially entirely comprised of g-lignin.

[0004] Since s-lignin is predominantly found in the secondary walls of hardwoods and is more easily dissolved during the cooking process, the cooking conditions to obtain the same Kappa number pulp from hardwoods tends to be less harsh as compared to the cooking conditions to obtain pulp from softwoods. In order to increase pulp yield it would be desirable to cook hardwoods to a higher Kappa number but such a practice is conventionally not possible since the amount of rejects would increase to a point that would not be commercially feasible. By way of comparison, while softwoods may be cooked under relatively harsh conditions using higher temperature and higher alkali charge to obtain the same Kappa number as hardwood (e.g., due to the presence of substantially all g-lignin in the middle lamella and well as secondary walls), this harsh cooking condition which promotes the degradation of g-lignin in the middle lamella result in producing substantially lower rejects level than when cooking hardwoods to a Kappa number of about 30. At a Kappa number of about 30, softwoods have a reject level less than 1% while hardwoods show a rejects level of higher than 20%. Thus, for hardwoods, conventional cooking conditions are selected so as to achieve a Kappa number of less than about 20, and typically less than about 17 so as to achieve an acceptably low amount of rejects.

[0005] It has now been discovered that rejects from cooking hardwoods at a given Kappa number can be reduced by subjecting the hardwoods to specific cooking conditions at the end of cooking. According to the present invention, therefore, alkaline cooking processes and apparatus, especially those useful for hardwoods, are provided which aim to increase the Kappa number of the hardwood pulp at the end of cook to levels above 17, but with much lower rejects

levels. The present invention may be combined with an effective oxygen delignification stage to reduce the kappa number below 17. The present invention therefore contributes to benefits in respect to overall pulping yield and pulp strength.

[0006] It has been discovered that s-lignin reacts faster than g-lignin and that there exists a higher proportion of g-lignin at the end of a hardwood cook as compared to at the beginning of the cook. Thus, when cooking hardwoods, relatively harsher cooking conditions (e.g., higher cooking temperatures) at the end of the cooking have been discovered to decrease the percentage of pulp rejects at a given Kappa number as a result of g-lignin breakdown.

[0007] According to certain aspects of this invention, methods and systems are provided for continuously producing chemical cellulose pulp from a slurry of comminuted hardwood material by subjecting the slurry of comminuted hardwood material to a first cooking stage under conditions sufficient to reduce syringyl lignin (s-lignin) content in the hardwood material as compared to guaiacyl lignin (g-lignin) content therein, and thereafter subjecting the slurry of comminuted hardwood material to a second cooking stage under conditions sufficient to reduce the g-lignin content remaining therein after the first cooking stage.

[0008] In some embodiments, the first stage of cooking of the hardwood material (that is the treatment stage after pretreatment or impregnation) is practiced so as to subject the hardwood material to a temperature of between about 120° C. to about 170° C. at about 2 to about 10% effective alkaline charge as (EA) NaOH on wood and/or so that the Kappa number for the cooked hardwood material which exits the first cooking stage is between about 30 to about 100.

[0009] According to other preferred embodiments, the first cooking stage is conducted under a low sulfidity condition of less than about 20% sulfidity. Such a low sulfidity condition of the first cooking stage may be performed, if necessary, by adding a sufficient amount of preferably anthraquinone and/or polysulfide.

[0010] The second cooking stage according to some embodiments of the invention is practiced so as to subject the slurry of hardwood material to a temperature of between about 130° C. to about 180° C. at about 2 to about 10% effective alkaline charge as (EA) NaOH on wood and/or so that the Kappa number for the cooked hardwood material which exits the second cooking stage is between about 15 to about 30.

[0011] It is preferred in some embodiments of the invention that the second cooking stage be conducted under a higher sulfidity condition of greater than about 20% sulfidity with or without the addition of anthraquinone and/or polysulfide.

[0012] The comminuted hardwood material may optionally be pretreated. If employed, the pretreatment occurs prior to the first cooking zone at about 20 to about 70% of the total effective alkaline charge as (EA) NaOH on wood at a temperature between about 80 to about 120° C.

[0013] These and other aspects and advantages will become more apparent after careful consideration is given to the following detailed description of the preferred exemplary embodiments thereof.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS

[0014] Reference will hereinafter be made to the accompanying drawings, wherein like reference numerals throughout the various FIGURES denote like structural elements, and wherein;

[0015] FIG. 1 is a schematic presentation of exemplary apparatus for practicing the method according to the present invention, and comprising an exemplary system according to the present invention;

[0016] FIG. 2 is a graph of the percent lignin from the original lignin of the cellulose material remaining at each of the sample points during a hardwood cook; and

[0017] FIG. 3 is a graph representing the ratio of s-lignin to g-lignin at various stages of a hardwood cook.

DETAILED DESCRIPTION OF THE INVENTION

[0018] Accompanying FIG. 1 illustrates one preferred embodiment of the present invention. In this regard, FIG. 1 illustrates a comminuted cellulosic fibrous material treatment system 10 consisting essentially of or comprising a continuous digester 11 having a continuous digester feed system 12. Feed system 12 may be a LO-LEVEL® feed system or a TURBOFEED® system both as sold by Andritz Inc. but any conventional feed system for introducing, steaming, and slurrying comminuted cellulosic fibrous material may be used; and/or one or more separate impregnation vessels may be used; and/or unconventional systems, such as those including equipment and/or a chip bin in the wood yard with pumping to the digester. Also in some circumstances a plurality of impregnation vessels may be used, with slurry pumped from a particular vessel once impregnation with, or without, cooking additive is complete (or will complete during pumping).

[0019] Comminuted cellulosic fibrous material, for example, in the form of hardwood chips 13, are introduced to feed system 12, as described in U.S. Pat. Nos. 5,763,075; 6,106,668; 6,325,890; 6,551,462; 6,336,993; 6,841,042 (the entire content of each patent being expressly incorporated hereinto by reference), and marketed by Andritz Inc. under the trademark TURBOFEED®; or a feed system as described in U.S. Pat. Nos. 5,476,572; 5,700,355; 5,968,314 (the entire content of each patent being expressly incorporated hereinto by reference), and marketed by Andritz Inc. under the trademark LO-LEVEL® which may include forwarding the chips to steam treatment in a vessel 14, which is preferably a vessel as described in U.S. Pat. Nos. 5,500,083; 5,617,975; 5,628,873; 4,958,741; and 5,700,355 (the entire content of each patent being expressly incorporated hereinto by reference), and marketed by Andritz Inc. under the trademark DIAMONDBACK®, though other types of steaming vessels may be used. From the vessel the chips pass through equipment such as a metering device connected to a conduit, which is preferably a Chip Tube provided by Andritz Inc. The slurry of chips and liquid is fed to the impregnation vessel (if used) or to the digester 11 via a pressurizing means.

[0020] The slurry pressurized, typically, to a pressure of between about 5 and 15 bar and propels the slurry via conduit 21 to the top of the continuous digester 11. Excess liquor contained in the slurry is removed from the slurry at the inlet of the digester 11 by a separating device 22, typically a conventional Top Separator, and the excess liquid is removed and returned to feed system 12 via conduit 23. During treatment within vessel 14, the slurry of hardwood material may be pretreated at an alkaline charge of between about 20 to about 70% of total effective alkaline (EA) NaOH charge on wood at a temperature between about 80 to about 120° C., preferably between about 100 to about 110° C.

[0021] Feed system 12 also typically includes conventional non-illustrated devices such as in-line drainer, level tank, and make-up liquor pump. Cooking liquor, for example, kraft white liquor (WL) is typically provided to the level tank (not shown) as is conventional.

[0022] The pretreated hardwood material (which may, but not necessarily, have been treated in an impregnation vessel) fed via line 21 is subjected to a first cooking stage in digester 11. However, in accordance with the present invention, the pretreatment of the hardwood material as described above is not absolutely necessary as the hardwood material may be fed directly into the digester 11. Whether or not the hardwood material is pretreated, the first cook within digester 11 is conducted under low sulfidity conditions (i.e., 0-20% sulfidity) using a beneficial additive such as anthroquinone (AQ) and/or polysulfide. The first cooking stage in digester 11 is conducted at temperatures of between about 120 to about 170° C. using an alkaline charge of between about 2 to about 10% effective alkaline (EA) NaOH charge on wood. The cooked hardwood material exits digester 11 via line 30 having a Kappa number of between about 30 to about 100 (preferably between about 40 to about 60).

[0023] The hardwood material after the first cooking stage in digester 11 has a higher proportion of g-lignin relative to s-lignin than at the beginning of the first cooking stage. High concentration of s-lignin in surrounding liquor may interfere with the dissolution of g-lignin remaining in the hardwood material. To reduce this interference, it may be necessary to wash the hardwood material following the first cooking stage in digester 11. Thus, the hardwood material may optionally be transferred to a wash vessel 32 via line 30 and subjected to wash conditions with a wash liquor introduced via line 34. Spent wash liquor is removed from the wash vessel 32 via line 36. Since the wash stage within wash vessel 32 reduces the s-lignin in surrounding liquor, any cooking additives which could later be used would not be detrimentally consumed by the already dissolved s-lignin in the surrounding liquor.

[0024] The washed pulp which exits the optional wash vessel 32 via line 38 is directed to a digester 40 where a second cooking stage is conducted so as to further breakdown and reduce the g-lignin content in the hardwood material. Breakdown of g-lignin can be accomplished by use of high sulfidity cooking liquor (i.e., greater than about 20% sulfidity, and preferably between about 25 to about 40% sulfidity) with or without AQ and/or polysulfide. (See for example U.S. Pat. No. 6,576,084, the entire content is expressly incorporated hereinto by reference). Other cooking chemicals that work well under cooking conditions, such as sulfite, could also be used alone or in conjunction with AQ and/or polysulfide as mentioned above.

[0025] The second cooking stage in digester 40 is conducted at a temperature between about 130 to about 180° C., preferably between about 140 to about 180° C., with an alkali charge of between about 2 to about 10% EA charge on wood (original wood charge) and a Kappa number at the beginning of the second cooking stage of between about 30 to about 100 (preferably between about 40 to about 60). During this phase, it may be advantageous (but not always necessary) to increase the temperature to above that of the first cooking stage.

[0026] If sufficient alkali has not been provided initially at the beginning of the second cooking stage, it may be necessary to introduce additional white liquor to digester 40

during the second cook stage prior to removal from digester **40** in a second location. If this second addition of white liquor is made at the end of the second cook stage, it is preferred that the hardwood material be allowed to continue to cook at a temperature of at least about 130°. At the point where the hardwood cellulosic material exits the digester **40** via line **42**, the Kappa number will preferably be between 15 to 30, more preferably between about 17 to about 30.

[0027] Important to the present invention is that the hardwood material is divided into two distinct cooking stages. The H-factor achieved at the end of the second cooking stage is at least 50% of the total H-factor that is achieved for the entire cook. Stated another way, the H-factor achieved through the first cooking stage is less than 50% of the H-factor achieved for the entire cook (i.e., at the end of the second cooking stage).

[0028] It is also possible that the cooking stages, and washing stage if used, are preformed in a single digester vessel. If a single vessel is used the same operating parameters for each stage as described would be used and end of stage would not require intermediate transfer of material to multiple vessels.

[0029] The first and second cooking stages conducted in digesters **11** and **40**, respectively, or in a single digester vessel, is preferably conducted in accordance with one or more of the processes described more fully in U.S. Pat. Nos. 5,489,363; 5,536,366; 5,547,012; 5,575,890; 5,620,562; and 5,662,775 (the entire contents of each such patent being expressly incorporated hereinto by reference). The processes and apparatus disclosed in these patents are marketed under the trademark LO-SOLIDS® Cooking by Andritz Inc. of Glens Falls, N.Y.

[0030] The processes and apparatus of the present invention produce a pulp low in HexA content as a result of the relatively high temperature of the new treatment and/or cooking in the second cooking stage. This low HexA pulp favors oxygen delignification conditions which in turn provides for a low Kappa number pulp to a subsequent bleaching process. See in this regard, U.S. Pat. Nos. 6,776,876 and 6,475,338, the entire content of each being expressly incorporated hereinto by reference. The low Kappa number pulp may therefore be bleached using less chemicals thereby resulting in lower effluent loading. The following non-limiting example further illustrates the present invention.

EXAMPLE 1

[0031] A hardwood cooking cycle was performed using a total EA (effective alkaline as NaOH) charge of 18% introduced during the impregnation, first cook and second cook stages. The following conditions were used during each of the stages:

[0032] Impregnation:

[0033] 60% of the total EA or 10.8% EA charged

[0034] Impregnation temperature of 110° C.

[0035] Time to impregnation temperature=15 minutes

[0036] Time at impregnation temperature=30 minutes

[0037] 1st Cook Stage:

[0038] 25% of the total EA or 4.5% EA added at beginning of cook

[0039] Cook temperature=140° C.

[0040] Time to heat to cook temperature=15 minutes

[0041] Time at cook temperature=60 minutes

[0042] 2nd Cook Stage:

[0043] 15% of total EA or 2.7% EA added at beginning of cook

[0044] Cook temperature=158° C.

[0045] Time at cook temperature=76 minutes

[0046] From this set of cooking conditions, the high temperature in the second stage of the cook gave lower Kappa number and at least 30% lower reject rate than the set of cooking conditions using 140° C. cooking temperature in both cook stages under the same alkali charge and the same H-factor.

EXAMPLE 2

[0047] A hardwood cooking cycle was performed using a total EA (effective alkaline as NaOH) charge of 17.5% introduced during the impregnation, first (or upper) cook and second (or lower) cook sequences. The following conditions were used during each of the cook sequences:

[0048] Impregnation:

[0049] 50% of the total EA or 8.75% EA charged

[0050] Impregnation temperature of 110° C.

[0051] Time to impregnation temperature=15 minutes

[0052] Time at impregnation temperature=30 minutes

[0053] 1st (Upper) Cook:

[0054] 30% of the total EA or 5.25% EA added at beginning of cook

[0055] Cook temperature=155° C.

[0056] Time to heat to cook temperature=15 minutes

[0057] Time at cook temperature=60 minutes

[0058] 2nd (Lower) Cook:

[0059] 20% of total EA or 3.5% EA added at beginning of cook

[0060] Cook temperature=156° C.

[0061] Time at cook temperature=120 minutes

[0062] A sample of the cellulosic material (wood chips) was taken after impregnation was complete and tested for s-lignin and g-lignin in the laboratory using the method described in Lin et al, "Methods in Lignin Chemistry", Springer-Verlag, Berlin (1992) (the entire content of which is expressly incorporated hereinto by reference). In addition, samples of the cellulosic material (wood chips) were taken at the midpoint of cook (e.g., about 90 minutes from the beginning of impregnation and at the end of the 1st (upper) cook (e.g., about 120 minutes from the beginning of impregnation). Each such sample was likewise analyzed for s-lignin and g-lignin content. Finally, a sample was also taken at the mid point of the 2nd (lower) cook (e.g., about 180 minutes from the beginning of impregnation). No analysis for s-lignin and g-lignin in the final pulp produced was made since the lignin content generally is so low that it is difficult to accurately analyze for the s-lignin and g-lignin species.

[0063] Accompanying FIG. 2 is a plot of the percent of lignin from the original cellulosic material remaining at each of the sample points. At the beginning of impregnation, 100% of the lignin is present, but by the end of the 2nd (lower) cook zone only about 3% of the lignin remains. As a general rule, wood chips prior to treatment contain about 24% lignin which means from the data of FIG. 2 the amount of lignin is only about 0.72% of the wood chips and thus any analysis of s-lignin and g-lignin content would not be accurate.

[0064] FIG. 3 present data that shows the change in the ratio of s-lignin to g-lignin as the cook described above progressed. The first ratio of 2.74 is the initial ratio before

the addition of any liquor or any treatment. The second ratio of 2.87 is at end of impregnation. The third and fourth ratios of 2.64 and 2.54 are respectively at the middle of the first cook stage and at the end of the first cook stage. The fifth and final ratio of 2.47 is at the middle of the second cook stage. [0065] The data of FIG. 3 thus suggests that the s-lignin is being broken down or dissolved at a faster rate than that of the g-lignin. As a result, the g-lignin content remains present on a cellular level which requires a different set of conditions to cause it to break apart and be destroyed or dissolved. In order to destroy the g-lignin, therefore, operating conditions in the digester must change in the later stages of the cook. Specifically, according to the present invention, the later stages of the cook require a higher temperature as compared to the early stages to ensure that the g-lignin is destroyed and to improve the yield (thereby reducing the rejects) and physical properties of the pulp.

[0066] While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiments, it is to be understood that the invention is not to be limited to the disclosed embodiment, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

What is claimed is:

1. A method of continuously producing chemical cellulose pulp from a slurry of comminuted hardwood material, comprising:

- (a) subjecting the slurry of comminuted hardwood material to a first cooking stage under conditions sufficient to reduce syringyl lignin (s-lignin) content in the hardwood material as compared to guaiacyl lignin (g-lignin) content therein; and thereafter
- (b) subjecting the slurry of comminuted hardwood material to a second cooking stage under conditions sufficient to reduce the g-lignin content remaining therein after the first cooking stage.

2. The method of claim 1, wherein step (a) comprises subjecting the slurry of hardwood material to a temperature of between about 120° C. to about 170° C. at about 2 to about 10% effective alkaline charge as (EA) NaOH on wood.

3. The method of claim 2, wherein step (a) is practiced so that the Kappa number for the cooked hardwood material which exits the first cooking stage is between about 30 to about 100.

4. The method of claim 1, wherein step (a) is conducted under a low sulfidity condition of less than about 20% sulfidity.

5. The method of claim 4, wherein the low sulfidity condition of the first cooking stage is achieved by adding a sufficient amount of anthroquinone and/or polysulfide.

6. The method of claim 4, wherein the low sulfidity condition of the first cooking stage is achieved without adding anthroquinone and/or polysulfide.

7. The method of any one of claims 1-6, wherein step (b) comprises subjecting the slurry of hardwood material to a temperature of between about 130° C. to about 180° C. at about 2 to about 10% effective alkaline charge as (EA) NaOH on wood.

8. The method of claim 7, wherein step (b) is practiced so that the Kappa number for the cooked hardwood material which exits the second cooking stage is between about 15 to about 30.

9. The method of claim 1, wherein step (b) is conducted under a high condition of greater than about 20% sulfidity.

10. The method of claim 9, wherein the high sulfidity condition of the second cooking stage is achieved by adding a sufficient amount of anthroquinone and/or polysulfide.

11. The method of claim 9, wherein the high sulfidity condition of the second cooking stage is achieved without adding anthroquinone and/or polysulfide.

12. The method of claim 1, further comprising prior to step (a), the step of pretreating the slurry of comminuted hardwood material at about 20 to about 70% of total effective alkaline charge as (EA) NaOH on wood at a temperature between about 80 to about 120° C.

13. A system for continuously producing chemical cellulose pulp from a slurry of comminuted hardwood material, comprising:

- (a) a first digester for subjecting the slurry of comminuted hardwood material to a first cooking stage under conditions sufficient to reduce syringyl lignin (s-lignin) content in the hardwood material as compared to guaiacyl lignin (g-lignin) content therein; and
- (b) a second digester downstream from the first digester for subjecting the slurry of comminuted hardwood material to a second cooking stage under conditions sufficient to reduce the g-lignin content remaining therein after the first cooking stage.

14. The system of claim 13, wherein the first digester subjects the slurry of hardwood material to a temperature of between about 120° C. to about 170° C. at about 2 to about 10% effective alkaline charge as (EA) NaOH on wood.

15. The system of claim 14, wherein the cooked hardwood material which exits the first cooking stage is between about 30 to about 100.

16. The system of claim 13, wherein the first digester is operated under a low sulfidity condition of less than about 20% sulfidity.

17. The system of claim 16, wherein the low sulfidity condition of the first cooking stage is achieved by adding a sufficient amount of anthroquinone and/or polysulfide.

18. The system of claim 16, wherein the low sulfidity condition of the first cooking stage is achieved without adding anthroquinone and/or polysulfide.

19. The system of any one of claims 13-18, wherein the second digester subjects the slurry of hardwood material to a temperature of between about 130° C. to about 180° C. at about 2 to about 10% effective alkaline charge as (EA) NaOH on wood.

20. The system of claim 19, wherein the cooked hardwood material which exits the second cooking stage is between about 15 to about 30.

21. The system of claim 13, wherein the second digester is conducted under a high condition of greater than about 20% sulfidity.

22. The system of claim 13, wherein the high sulfidity condition of the second cooking stage is achieved by adding a sufficient amount of anthroquinone and/or polysulfide.

23. The system of claim 13, wherein the high sulfidity condition of the second cooking stage is achieved without adding anthroquinone and/or polysulfide.

24. The system of claim 13, further comprising prior to the first digester, a pretreatment vessel for pretreating the slurry of comminuted hardwood material at an alkaline charge of between about 20 to about 70% of total effective alkaline charge as (EA) NaOH on wood at a temperature between about 80 to about 120° C.