

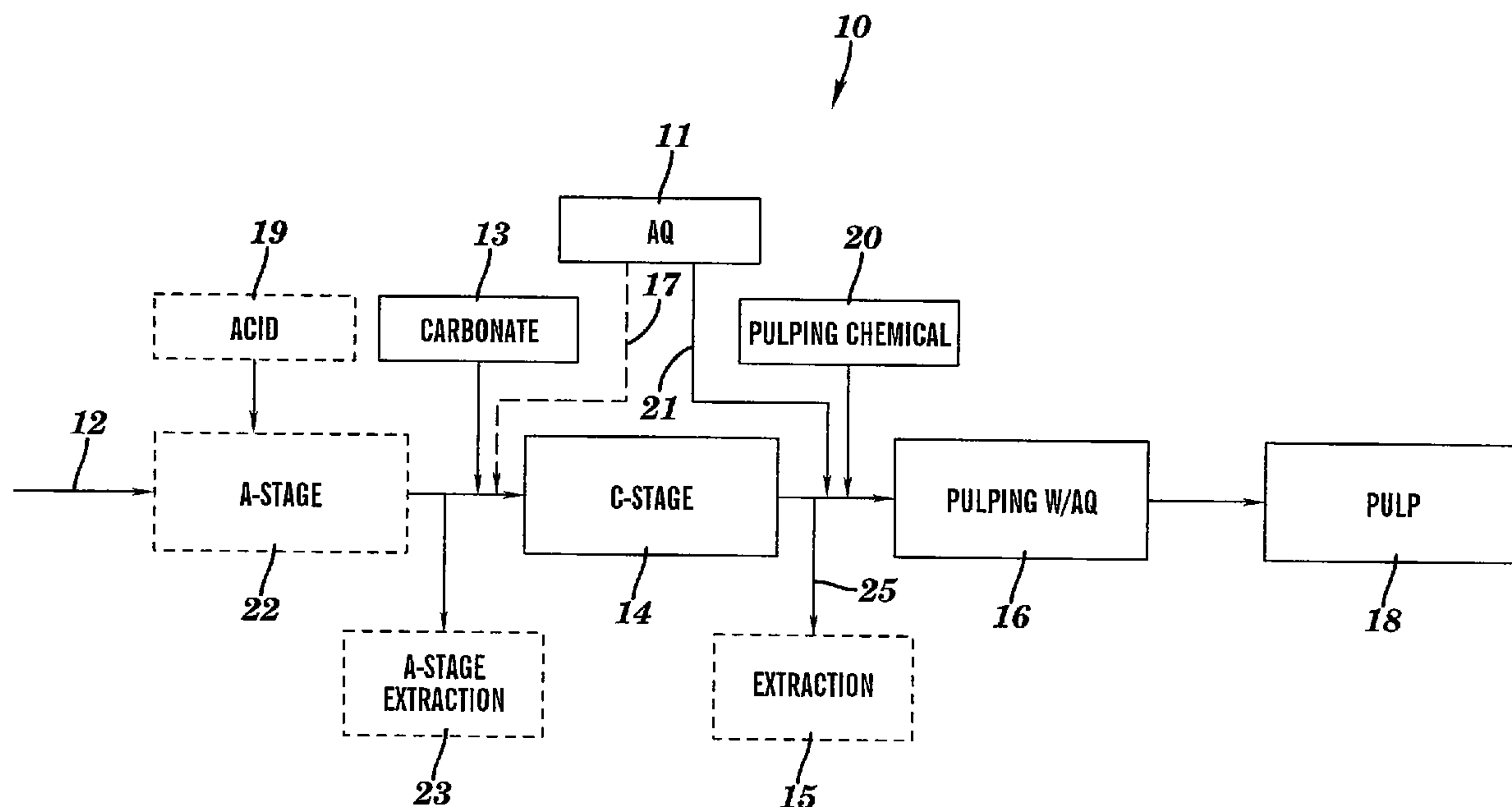


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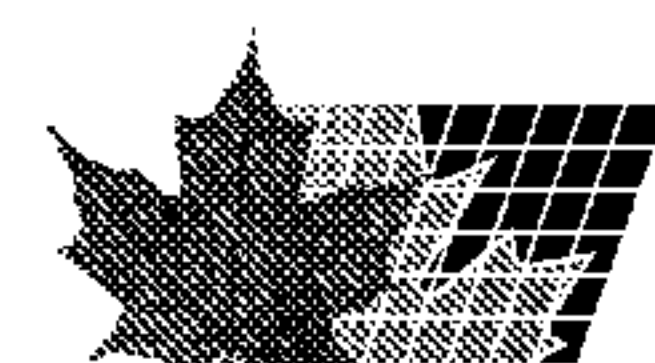
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(54) Title: METHODS FOR CARBONATE PRETREATMENT AND PULPING OF CELLULOSIC MATERIAL



(57) Abrégé/Abstract:

A method of pretreating comminuted fibrous material with sodium carbonate and then cooking the pretreated material in the presence of anthraquinone (AQ) is provided. The resulting pulp produced has a higher yield, enhanced strength, and better bleachability compared to pulp produced by prior art methods. AQ may also be introduced to the carbonate pretreatment stage. The method may further include an acid pretreatment providing further enhanced properties to the pulp produced.



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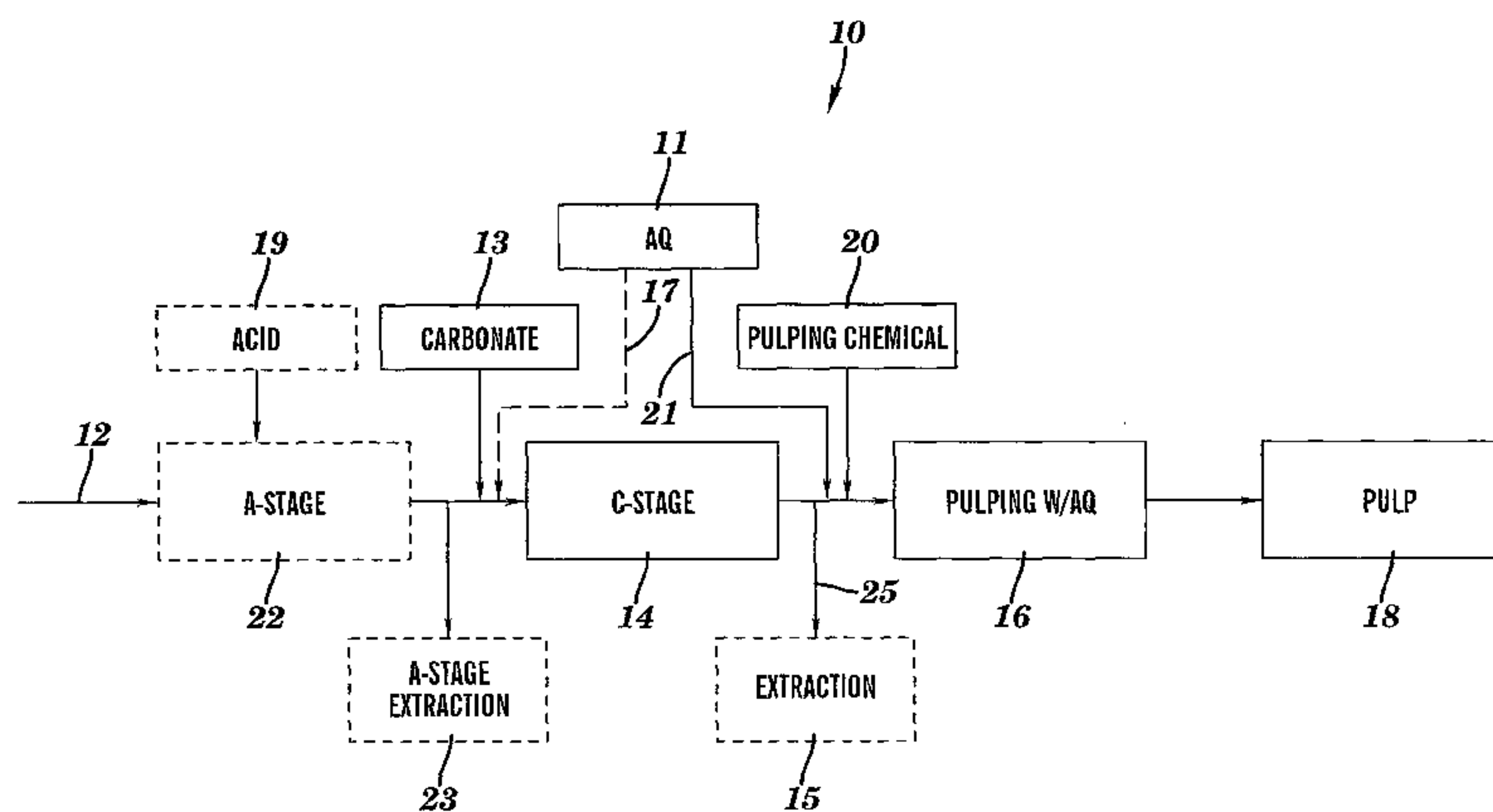
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(54) Title: METHODS FOR CARBONATE PRETREATMENT AND PULPING OF CELLULOSIC MATERIAL



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METHODS FOR CARBONATE PRETREATMENT AND PULPING OF CELLULOSIC MATERIAL

FIELD OF THE INVENTION

[0001] The present invention relates to a process for treating comminuted cellulosic fibrous material, for example, wood chips, with a carbonate pre-treatment prior to cooking the cellulosic material with a cooking chemical in the presence of an anthraquinone (AQ).

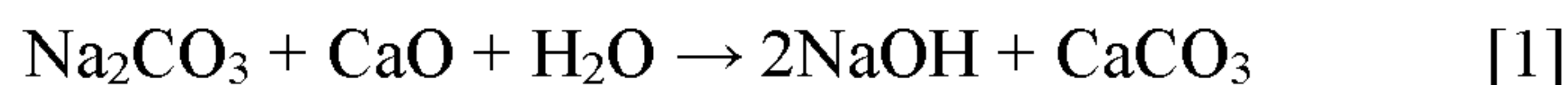
BACKGROUND OF THE INVENTION

[0002] In the art of chemical pulping, cellulosic material, such as wood chips, is treated with pulping chemicals to produce pulp for use in the manufacture of paper and other products. It is well known in this art to use caustic soda (that is, sodium hydroxide [NaOH] as a pulping chemical), referred to as soda cooking, in both batch and continuous digesters. There are many advantages to soda cooking, including the ability to raise the design pressure of the recovery boiler to improve the recovery boiler efficiency and the elimination of sulfur in the process. Among other benefits, the elimination of sulfur in the cooking process allows for the use of black liquor gasification systems. The use of black liquor gasification results in a power generation increase that is multiple times the power generated using a sulfur-based system.

[0003] One disadvantage of soda cooking includes a lower pulp yield (for both softwoods and hardwoods) than realized by kraft cooking, that is, cooking using sodium hydroxide (NaOH) and sodium sulfide (Na₂S) as the pulping chemicals. However, the addition of anthraquinone (AQ) to soda cooking has shown to improve the pulp yield and therefore make the pulp yield comparable to that of kraft cooking. Even with AQ addition, however, pulp from soda cooking processes exhibits weaker pulp strength and poorer bleaching compared to kraft cooking.

[0004] However, disadvantages also exist with soda anthraquinone (SAQ) cooking as compared to kraft cooking. For instance, SAQ cooking requires higher amounts of NaOH and it is more difficult to bleach pulp produced from a SAQ pulping process.

For example, the more NaOH required, the more recausticizing required. As known in the art, recausticizing of sodium carbonate to regenerate NaOH proceeds as outlined in equations 1 and 2 below.



[0005] The volume of NaOH per ton of wood pulp required is higher for SAQ cooking compared to the NaOH required for kraft cooking. This higher volume of NaOH required in SAQ cooking is needed to compensate for the sodium sulfide present in kraft cooking which is not present in SAQ cooking. As is known in the art, sodium sulfide (Na_2S) present in kraft cooking hydrolyzes to NaSH and NaOH and therefore impacts the cooking of the cellulosic material during kraft cooking. The volume of NaOH required in soda AQ cooking is about 20% to 40% higher than in kraft cooking. The higher requirement for NaOH results in higher energy requirements to convert, or causticize, the sodium carbonate (Na_2CO_3) from the recovery boiler to NaOH used in the digester and other parts of the fiber line.

[0006] For instance, when an active alkali ($\text{AA} = \text{NaOH} + \text{Na}_2\text{S}$ on a Na_2O basis) of 16.0% Na_2O and 30% sulfidity is used for kraft pulping, 11.2% of the AA comes from NaOH and 4.8% of the AA from Na_2S . In kraft recovery, where all of the sulfur is recovered as Na_2S , re-causticizing would be required to convert to NaOH so that the desired 11.2% Na_2O on new chips is achieved. SAQ pulping of hardwoods requires approximately the same effective alkali ($\text{EA} = \text{NaOH} + \frac{1}{2} \text{Na}_2\text{S}$ on a Na_2O basis) as kraft pulping. In the kraft pulping example above, the EA was 13.6% Na_2O and a similar amount of alkali would be required for SAQ pulping but all of it would come from NaOH.

[0007] Further, it is well known that hemicelluloses are quickly dissolved in soda, kraft, and SAQ pulping, and that a significant fraction of the applied NaOH is consumed in degrading the hemicelluloses to low molecular weight (MW) products. These low MW organics are difficult to recover from the pulping effluent, referred to in the art as “black liquor,” and they do not have high calorific values. It is also

known that the green liquor from the recovery furnace is primarily Na_2CO_3 when the SAQ process is used.

[0008] It has been shown that pulps from hardwood material processed using Lo-Solids® Cooking methods (as described in U.S. Patents 5,489,363; 5,536,366; 5,547,012; 5,620,562; 5,662,775; 5,824,188; 5,849,150; 5,849,151; 6,086,712; 6,132,556; 6,159,337; 6,280,568; 6,346,167)

and soda-AQ (SAQ) as the cooking chemicals result in pulp with better strength than that produced by conventional kraft cooking. Additionally, the pulp produced from hardwood material processed using the Lo-Solids® Cooking method with soda-AQ as a cooking chemical can obtain a better terminal brightness than conventional Soda-AQ, but not as bright as pulp produced from kraft cooking. Although the bleach chemical consumption with Lo-Solids Soda-AQ is better than conventional Soda-AQ for a given final brightness, the pulp still requires a greater quantity of bleaching chemicals than pulp produced by kraft cooking.

[0009] For these and other reasons, kraft cooking (and its many sulfur related problems) is the prevailing pulping process in the industry. However, the applicants have found that by pretreating the cellulosic material with an substantially sulfur-free (<1 g/l total Sulfur) carbonate solution and then practicing SAQ, the disadvantage of SAQ pulping can be overcome.

[0010] U.S. Patent No. 1, 887,241

discusses pre-treating, also referred to as pre-cooking, a cellulosic material with sodium carbonate, followed by treating the resulting material with either soda or kraft cooking. In the process disclosed in the '241 patent, wood chips that have been steamed may undergo this carbonate pretreatment stage at a temperature of about 330 degrees Fahrenheit, that is, about 165 degrees Celsius (C). According to the '241 patent, the pretreatment stage using sodium carbonate reduces the quantity of NaOH required. For instance, as disclosed in US patent No. 1,887,241, a quantity of 10% sodium carbonate on wood is used along with 15% NaOH, compared to about 25% NaOH added to conventional soda cooking. Though pretreatment with sodium carbonate at about 165 degrees C is disclosed in the above-referenced patent, the high temperature treatment disclosed in the '241 patent (published in 1932), for various reasons, has not been accepted in the pulping industry, and is typically not practiced

today. The treatment disclosed in '241 patent also does not involve the use of an anthraquinone in any processing step.

[0011] Recent advantages in the pulping industry include methods for removing silica from cellulosic material using a sodium carbonate containing solution. (See US Application No: 2006/0225852) The methods disclosed in the 0225852 application relate to almost 100% removal of silica contained in cellulosic material, such removal occurring prior to the processing of the fibrous material using conventional methods.

[0012] Aspects of the present invention provide a method for processing cellulose material that overcomes the disadvantages and drawbacks of the prior art methods. For example, some aspects of the present invention provide an avenue for minimizing or eliminating the presence of sulfur from the pulp mill while producing a commercially viable product – a long left, but unresolved need of the Pulping Industry.

SUMMARY OF THE INVENTION

[0013] The present invention, in its many aspects, relates to the pretreatment of cellulosic material with carbonate, such as a substantially sulfur-free (<1 g/l total Sulfur) sodium carbonate (Na_2CO_3), followed by cooking the pretreated cellulosic material in the presence of a pulping chemical, such as, sodium hydroxide alone (that is, the “soda” process), but also sodium hydroxide and sodium sulfide (that is, the “kraft” process), or a combination of soda and kraft, and additionally and at least one anthraquinone, i.e. anthraquinone or a substituted anthraquinone, such as 2-methylantraquinone. The AQ may be added at anytime during the process. For instance, an AQ may be added to the pretreatment stage, the cooking stage, or even both the pretreatment stage and the cooking stage, as well as before or after each stage. (Addition of AQ to the cooking stage can be performed as described in US patent 6,569,289.)

[0014] One aspect of the invention is a method of treating comminuted cellulosic fibrous material according to: a) treating the cellulosic fibrous material with a carbonate-containing solution, such as, a substantially sulfur-free carbonate

containing solution, to produce a pretreated cellulosic material; b) treating the pretreated cellulosic material with a pulping chemical for a sufficient time and at a sufficient temperature to produce a cellulose pulp, wherein, in at least one of a) and b), the cellulosic fibrous material is treated with at least one anthraquinone. In this method, the cellulosic fibrous material may be treated with an anthraquinone in a), b), or both a) and b). In one aspect, the carbonate-containing solution may comprise a sodium carbonate containing solution. In another aspect, the pulping chemical may comprise sodium hydroxide. Further, the active pulping chemical may consist substantially of sodium hydroxide.

[0015] One aspect of the above method includes additional steps, prior to a), the comminuted fibrous material may be c) treated with an acidic solution, and after c), d) extracting at least some of the acidic solution from the cellulose fibrous material may take place.

[0016] In another aspect, the method produces a pulp having a lower rejects percent and a higher screened yield percent compared to a pulp produced where a) is not practiced.

[0017] One aspect of the invention may further include an oxygen delignification treatment as well as at least one bleaching stage, where the method produces a cellulosic pulp having a brightness greater than 88% elrepho. When an oxygen delignification treatment is provided, the method may produce a pulp having a lower kappa number after the oxygen delignification treatment at a predetermined screened yield compared to a pulp produced without practicing a). As known in the art, kappa number is used to define the degree of delignification. It refers to the modified permanganate test value of pulp that has been corrected to 50 percent consumption of the chemical. Kappa number has the advantage of a linear relationship with lignin content over a wide range, for example $\text{Kappa Number} \times 0.15\% = \% \text{ lignin in pulp}$.

[0018] An additional aspect of the present invention relates to a method of treating comminuted cellulosic fibrous material by treating the cellulosic fibrous material with a carbonate containing solution to produce a pretreated cellulosic material, treating the pretreated cellulosic material with a pulping chemical for a sufficient time and at a sufficient temperature to produce a cellulose pulp and a liquid containing spent

pulping chemical, treating the liquid containing spent pulping chemical to produce a carbonate-containing solution from the spent pulping chemical, and using the carbonate-containing solution produced from the spent pulping chemical as the carbonate containing solution in a) of the method described above.

[0019] A further aspect of the invention includes a method of treating comminuted cellulosic fibrous material comprising a) treating the cellulosic fibrous material with an acid solution, b) treating the cellulosic fibrous material with a carbonate-containing solution to produce a pretreated cellulosic material, and c) treating the pretreated cellulosic material with a sulfur-containing pulping chemical for a sufficient time and at a sufficient temperature to produce a cellulose pulp, where in at least of one of b) and c), the cellulosic fibrous material is treated with an anthraquinone. The sulfur-containing pulping chemical may typically contain sodium hydroxide and sodium sulfide.

[0020] A still further aspect of the invention comprises a pulp produced from one of the above methods wherein the pulp has a greater yield than produced from prior art methods. These and other aspects and advantages of the invention can be more completely understood in view of the following descriptions of the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] The present invention will be better understood from the detailed description given herein below and the accompanying drawings which are given by way of illustration only, and thus are not a limitative of the present invention and wherein:

[0022] **Figure 1** is a schematic diagram of a pulping process according to aspects of the present invention.

[0023] **Figure 2** is a schematic illustration of a chemical recovery system that can be used in aspects of the invention.

[0024] **Figure 3** is a plot comparing the screened yield of pulps produced by aspects of the present invention to pulps produced by the prior art.

[0025] **Figure 4** is a plot comparing light absorption coefficient values of pulps produced by aspects of the present invention to pulps produced by the prior art.

[0026] **Figure 5** is a schematic illustration of the catalysis of lignin and carbohydrate reactions by anthraquinone as enhanced by aspects of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0027] The applicants have found that by treating comminuted cellulosic fibrous material, such as wood chips, in a first pretreatment stage with a carbonate compound, for example, substantially sulfur-free sodium carbonate, and then in a second pulping stage, for example, soda pulping in the presence of an anthraquinone (AQ used to symbolize any anthraquinones), - an improved pulp can be produced. An improved pulp is also produced if the pulp undergoes an acid treatment prior to a first pretreatment stage, followed by kraft pulping in the presence of an anthraquinone. For example, the pulp produced may be characterized by increased pulp yield, increased bleachability, higher strength, and lower rejects, among other beneficial properties.

[0028] Moreover, by treating the chips with a solution containing carbonate prior to treating the chips with pulping chemical, the amount of pulping chemical required in the pulping process for a desired treatment may be reduced. This development can have a significant impact on attempts to reduce or eliminate the content of sulfur containing pulping chemicals, most notably, sodium sulfide (Na_2S). As noted above, non-sulfur pulping processes, such as, the soda process and the SAQ process, have received limited acceptance in the industry due the relatively poor quality of pulp produced compared to the sulfur-bearing kraft process. Further, typically soda and SAQ processes require a larger amount of pulping chemical, that is, sodium hydroxide (NaOH) compared to the kraft process. As will be discussed below, aspects of the present overcome these limitations while producing an economically viable pulp.

[0029] An additional aspect of the present invention relates to a method of treating comminuted cellulosic fibrous material includes: treating the cellulosic fibrous material with a substantially sulfur-free carbonate containing solution to produce a pretreated cellulosic material, treating the pretreated cellulosic material with a pulping

chemical, such as, an alkaline pulping chemical, for a sufficient time and at a sufficient temperature to produce a cellulose pulp and a liquid containing spent pulping chemical, treating the liquid containing spent pulping chemical to produce a carbonate-containing solution from the spent pulping chemical, and using the carbonate-containing solution produced from the spent pulping chemical as the carbonate containing solution in a) as described above in paragraph 16. The carbonate containing solutions may contain sodium carbonate comprising about 1% to about 12% sodium carbonate as Na_2O on chips. The above method may also include an oxygen delignification treatment.

[0030] In one aspect, treating the liquid containing spent pulping chemical includes concentrating the liquid sufficiently to support combustion, burning the concentration liquid to produce a smelt containing carbonate, and, introducing a liquid to the smelt to provide the carbonate containing solution from the spent pulping chemical.

[0031] A further aspect of the invention includes a method of treating comminuted cellulosic fibrous material comprising a) treating the cellulosic fibrous material with an acid solution, b) treating the cellulosic fibrous material with a carbonate-containing solution, such as sodium carbonate, to produce a pretreated cellulosic material, and c) treating the pretreated cellulosic material with a pulping chemical for a sufficient time and at a sufficient temperature to produce a cellulose pulp, where in at least of one of b) and c), the cellulosic fibrous material is treated with an anthraquinone.

[0032] Using processes and methods according to aspects of the invention several surprising results from laboratory tests have been found. These improvements include: a decrease in the H-factor in the cooking stage which is greater than would be expected (the total H-factor from first stage treatment plus the H-factor from cooking is lower than the H-factor without the first stage carbonate treatment at the same kappa number; this is shown in **Tables 2** and **3** below; an increase in pulp yield; enhanced bleachability; increased strength; and lower rejects). As known in the art and for the purpose of this application, H-factor refers to a method of expressing cooking time and temperature as a single variable for delignification.

[0033] **Figure 1** is a schematic diagram of a pulping process 10 employing aspects of the present invention in which comminuted cellulosic fibrous material 12, for

example, wood chips, is treated by a carbonate pretreatment stage 14 and a cooking or pulping stage 16. It will be understood by those of skill in the art that though the term “wood chips” is used to facilitate discussion of the invention, aspects of the invention are not limited to treating chips, but may be used to treat any form of comminuted cellulosic fibrous material, including, but not limited to, hardwood chips, softwood chips, sawdust, recycled fibers, recycled paper, agricultural waste, such as bagasse, and other fibrous cellulosic material.

[0034] As is typical in the art, prior to being introduced to process 10, chips 12 may typically be conditioned for treatment, for example, steamed, to moisten the chips, heat the chips, and remove as much air and other gases as possible to enhance penetration of the treatment solutions. Steaming of chips 12 may be practiced, for example, in a horizontal steaming vessel or in a Diamondback® steaming vessel, both provided by Andritz Inc. of Glens Falls, NY, prior to treatment. According to aspects of the invention, in the carbonate stage 14 (also referred to as c-stage, pretreatment stage, or first stage) of treatment, chips 12 are treated with carbonate-containing solution 13, typically a sodium carbonate solution, although potassium and magnesium carbonate solutions may also be applicable. In one aspect of the invention, this carbonate containing solution may be substantially free of sulfur. A person of skill in the art would appreciate that such absence of sulfur may not mean that no sulfur is present in the carbonate solution in the absolute sense, but that the solution would be "substantially" sulfur-free. After treatment in first stage 14, chips 12 are then treated in a second or pulping stage 16, that is, a cooking stage, with pulping chemical 20 for a sufficient time and at a sufficient temperature to produce a cellulose pulp 18. Pulp 18 may typically be forwarded for further treatment, for example, to washing, bleaching, or screening, among other conventional treatments. The carbonate-containing solution 13 may be provided by a variety of sources, including, but not limited to, commercially available carbonate and carbonate recovered from a related process, such as, from a chemical recovery cycle (for example, as illustrated in and discussed with respect to **Figure 2** below).

[0035] According to aspects of the present invention, the carbonate-containing solution 13 may have a concentration of from about 1% to about 12% carbonate (expressed as Na₂O) on wood. For example, the carbonate containing solution may

have a concentration of from about 2% to about 9% as Na_2O on wood. The carbonate containing solution may typically be provided as an aqueous solution, that is, as a solution of carbonate in water, though other compounds may be present. A person of ordinary skill in the art would understand the use of the term “about” when describing percent carbonate and will appreciate that it is difficult to have absolute measurements and the use of the term about when describing percent carbonate is ubiquitous in the art. One kg mole of Na_2CO_3 (106 kg) is equivalent to one kg mole of Na_2O (62 kg). Other carbonates such as potassium and magnesium may to be added as Na_2O molar equivalence. The carbonate treatment 14 is typically practiced at a temperature of greater than 100 degrees C, for example, between about 120 degrees C and about 200 degrees. In one aspect, carbonate treatment 14 may be practiced at between about 120 degrees C and about 170 degrees C, for example, between about 120 degrees C and about 150 degrees C. A person of ordinary skill in the art would understand the use of the term “about” when describing temperature ranges and will appreciate that it is difficult to have absolute measurements and the use of the term “about” when describing temperature is ubiquitous in the art. Such use of the term “about” is understood by a person of skill in the art to define measurement ranges for any parameter of the treatment process throughout this disclosure, including pressure, time, temperature, percentage of components used in the pulping process and other related measurements. At such temperatures, treatment 14 may typically be practiced at superatmospheric pressure of about 50 psig to about 150 psig. Pretreatment stage 14 is typically practiced for a sufficient time to provide at least some benefit to the resulting pulp produced in process 10. For example, pretreatment stage 14 may be practiced for at least 5 minutes, but may be practiced from about 15 minutes to about 6 hours, depending upon the nature of the furnish, that is, the nature of chips 12, but is typically practiced from about 15 minutes to about 120 minutes.

[0036] In one aspect of the invention, after pretreatment 14 and before pulping stage 16, at least some of the liquid present may be removed or extracted from the chips 12, as indicated by 25. In one aspect, the extracted carbonate-containing liquid 15 may be treated, for example, in a recovery system, disposed of, or otherwise re-used. For example, in one aspect, the carbonate-containing liquid may be recirculated and re-used as the source of or supplement to carbonate 13.

[0037] After pretreatment stage 14, the carbonate pretreated chips 12 are then treated in pulping stage 16 with a pulping chemical for a sufficient time and at a sufficient temperature to produce a cellulose pulp 18. Though a single stage 16 is shown in **Figure 1**, according to one aspect of the invention, however, one or more pulping stages 16 may be provided. According to one aspect of the invention, the pulping chemical 20 used in pulping stage 16 may be primarily sodium hydroxide (NaOH), that is, the pulping stage 16 may be “soda” pulping stage. In another aspect of the invention, the pulping chemical 20 may comprise NaOH and sodium sulfide (Na₂S), that is, the pulping stage may be a “sulfate” treatment or “kraft” treatment. When the pulping stage comprises a kraft pulping stage, in one aspect, the carbonate stage 13 may be preceded by an acid stage 22 (as discussed below). However, according to aspects of the present invention, the pulping of pretreated chips 12 is practiced in pulping stage 16 in the presence of at least one anthraquinone (AQ) 11.

[0038] In one aspect, the pulping of chips 12 in the presence of AQ may be performed as described in U.S. Patent 6,569,289.

The applicants have found that the pretreatment of chips 12 with carbonate, in particular with Na₂CO₃, followed by SAQ pulping, provides a pulp 18 having enhanced properties, for example, improved yield, reduced lignin, and improved bleachability, compared to pulps provided by prior art treatments. For example, the experiments performed by the applicants suggest that there may be some synergistic effects in the carbonate or carbonate-AQ pretreatment and pulping process of the present invention that are typically not predictable from the prior art treatments with AQ.

[0039] According to aspects of the present invention, at least one AQ, or its derivatives or equivalents, is introduced to pretreatment stage 14, pulping stage 16, or both stages 14 and 16. In one aspect, AQ may be provided in its reduced form (that is, a chemical commonly referred to as AHQ, see **Figure 5**). In one aspect, an aqueous solution of AQ may be introduced to the carbonate pretreatment stage 14 (as indicated by phantom line 17 in **Figure 1**), for example, provided prior to, at the beginning, middle, near the end of pretreatment stage 14, or some combination thereof. The concentration of the aqueous AQ introduced during stage 14 may range from between about 0.01 weight percent to about 0.20 weight percent on chips, but is

typically from between about 0.05 and about 0.10 weight percent. For the purpose of this application, AQ can be added anytime during the pulping process as described in **Figure 1**.

[0040] In one aspect, the AQ may be introduced to the pulping stage 16 (as indicated by line 21 in **Figure 1**), for example, at the beginning, middle, near the end of the stage, or some combination thereof. The concentration of the aqueous AQ introduced during pulping stage 16 may range from between about 0.01 weight percent to about 0.20 weight percent on chips, but is typically between from about 0.05 and about 0.1 weight percent on chips. In one aspect, AQ may be introduced to carbonate stage 14, and omitted from pulping stage 16; in another aspect, AQ may be introduced to both carbonate stage 14 and pulping stage 16.

[0041] According to aspects of the invention, when a first treatment stage 14 using a sodium carbonate solution as the carbonate-containing solution, for example, a sulfur-free carbonate solution, is followed by a second pulping stage 16 employing NaOH (for example, at a charge of about 13 % NaOH on wood) and AQ (that is, a SAQ cooking stage), surprising results have been identified in laboratory testing. A NaOH dose of 13% on wood correspond to about 10% Na₂O, i.e., two kg moles or 80 kg of NaOH are equivalent to one kg mole or 62 kg of Na₂O. For example, in laboratory testing, when a first carbonate stage 14 is followed by a second soda pulping stage 16 (with 13% NaOH on wood) in the presence of AQ, the pulping treatment had significantly lower NaOH requirements and produced a pulp with a yield closer to that produced by kraft pulps, without increasing the rejects produced.

[0042] In another aspect of the invention, before the pretreatment stage 14, the chips 12 may be treated with an acidic solution 19 in an acid stage 22 (shown in phantom in **Figure 1**). When kraft pulping in the presence of AQ is the pulping method used, acid pretreatment 22 may be followed by carbonate treatment 14. Any acid containing solution may be used for acid 19, but in one aspect, acid 19 is preferably a non-sulfur containing acid solution, for example, an organic acid (such as, acetic acid) or an inorganic acid (such as, nitric or hydrofluoric acid). In one aspect, stage 22 may be practiced in the presence of a naturally occurring acid, that is, a naturally occurring

wood acid. The acid solution 19 may be provided to produce an aqueous environment about chips 12 having a pH of about 6 or below, for example, having a pH of between about 4 and about 6. The acid treatment may be practiced at a temperature greater than 50 degrees C, for example, at about 80 degrees C to about 160 degrees C. Acid treatment stage 22 is typically practiced for a sufficient time to provide at least some benefit to the resulting pulp produced in process 10. For example, acid treatment stage 22 may be practiced for at least 5 minutes, but may be practiced from about 30 minutes to about 6 hours, and is typically practiced from about 30 minutes to about 90 minutes, depending upon the nature of the furnish, for example, the pH of chips 12. The quantity of acid needed may include any amount needed to produce the same effect as 2 to 6% acetic acid at 120°C.

[0043] As shown in **Figure 1**, in one aspect of the invention, after acid treatment 22, and before carbonate pretreatment 14, at least some of the liquid present after acid treatment 22 may be removed or extracted from the chips 12, as indicated by extraction stage 23 (shown in phantom in **Figure 1**). In one aspect, the extracted acid-containing liquid 23 may be treated, for example, in a recovery system, disposed of, or re-used. For example, in one aspect, the acid-containing liquid may be re-circulated and re-used as the source of or supplement to acid 19.

[0044] The acid treatment may be provided by chips 12, for example, the acid in stage 22 may be an acid resulting from mature wood (that is, wood which has been in storage for a period of time sufficient to produce an acidic liquor naturally occurring from the wood itself). In another aspect, the acid in stage 22 may be provided by a conventional acid hydrolysis process, for example, a process used to remove metals and other contaminants from the chips 12. One such process is disclosed in U.S. Patent 5,338,366 (the disclosure of which is incorporated by reference herein in its entirety).

[0045] According to aspects of the invention, by combining the acid treatment stage 22 with the carbonate pretreatment stage 14 and pulping stage 16 having either NaOH (soda) and AQ, or NaOH and Na₂S (kraft) and AQ, or a combination of soda and AQ and kraft and AQ, the chemical consumption (for example, the amount of NaOH required) may be reduced and the bleachability of the resulting pulp 18 enhanced. That is, the amount of bleaching chemical required to achieve a desired brightness, may be

reduced compared to prior art treatments. In some aspects of the invention, it is also possible to see improvements in pulp yield when using the process of acid treatment 22 followed by carbonate treatment 14 followed by SAQ. An improvement in bleachability is observed if pulping stage 16 is the kraft process. The chemical consumption disadvantages in SAQ cooking can be addressed by the carbonate treatment stage 14 and aspects of the invention may also improve pulp bleachability by oxygen and most likely by other one-electron transfer oxidants, such as, chlorine dioxide, as well. Acid treatment stage 22 (A) may further improve the bleachability of both soda-AQ and kraft pulps, particularly, after an oxygen (O) delignification stage. A kraft green liquor ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{S}$) may be used as the source of carbonate 13 if the pulping process 16 comprises a kraft process.

[0046] **Figure 2** is a schematic illustration of a chemical recovery system 100 that can be used in aspects of the invention. Chemical recovery system 100 includes a conventional recovery furnace or gasifier 110 for burning concentrated spent cooking liquor 112, for example, black liquor, to produce a chemical smelt (not shown) containing sodium carbonate and sodium sulfide (when the black liquor comprises kraft black liquor), among other products of combustion of black liquor known in the art. According to conventional practice, the carbonate containing smelt is dissolved in water in vessel 114, that is, the green liquor tank, to produce an aqueous solution (known as “green liquor”) containing carbonate. In one aspect, green liquor containing sulfide may be used for the carbonate containing solution when the pulping stage comprises kraft pulping. The carbonate treatment with green liquor may be preceded by an acid treatment (stage 22 of **Figure 1**) prior to kraft pulping. Vessel 114 may be a green liquor tank or other appropriate vessel as is known in the art. According to prior art practice, the aqueous sodium carbonate in vessel 114 is typically forwarded for further processing 120, that is, causticization, to regenerate NaOH to be used for cooking or bleaching, for example, for oxygen delignification. According to aspects of the invention, the carbonate in the green liquor in vessel 114 may be used as one source of the carbonate 13 for pretreatment stage 14 described in **Figure 1**.

[0047] The improvements and advantages provided by aspects of the present invention were investigated by the applicants in laboratory batch treatment vessels,

that is, in laboratory batch digesters. The results of one such laboratory trial are summarized in **Table 1**. Such vessels are commonly used to develop processes for continuous and batch digesters. In the present invention, a continuous or batch digester may be used.

[0048] **Table 1** summarizes the treatment conditions and the results obtained by a series of laboratory trials using batch digesters. The present invention corresponds to trials 1, 3, and 4 in **Table 1** where at least some sodium carbonate is provided in a first treatment stage followed by a soda-AQ (SAQ) pulping stage. Run number 2 is a reference trial which corresponds to a conventional SAQ pulping stage with no carbonate pretreatment and run number 5 is a reference trial which corresponds to a conventional kraft cook without AQ.

Table 1

Effect of Carbonate Pretreatment on Soda/AQ Pulping
as Evidenced by Laboratory Batch Pulping Trials

Run Number	Na ₂ CO ₃ in CPC ¹	H Factor in CPC	CPC End pH	H Factor in SAQ	SAQ End pH	Screened Yield ³	Rejects ³	Kappa No. ⁴
1	4.0%	312	7.6	1027	12.5	54.1	3.9	25.7
2	0	0	-	1506 ²	11.0	28.4	27.0	48.1
3	6.0%	544	8.9	1027	12.6	53.4	6.7	33.9
4	4.0	665	-	1027	12.6	55.3	0.3	22.8
5	-	-	-	Kraft-1300		51.8	0.1	17.9

¹As Na₂O on chips

²10% Na₂O from NaOH + 6% Na₂O from Na₂CO₃. The other SAQ cooks were with 10% Na₂O from NaOH only. The kraft cook used 12% Na₂O from NaOH.

³Percent on chips

⁴Kappa number of screened pulp

[0049] In these laboratory trials, a 0.8 kg of sugar maple (*Acer saccharum*) chips (a hardwood) were loaded into a laboratory digester. The carbonate pre-treatment summarized in **Table 1** were performed at 165°C and 170°C using a Na₂CO₃ dose of 4.0 – 6.0% as Na₂O on chips, that is, a 6.8 – 10.3% Na₂CO₃. In runs 1, 3, and 4, the carbonate pretreatment (CPC = Carbonate Pre-Cook) was followed by soda –AQ pulping with a NaOH dose of only 10% as Na₂O on chips. The initial testing approach, after the carbonate pretreatment, depressurizing the batch digester (that is,

“blowing the digester”) and condensing the carbonate stage off-gases (that is, the effluent). The NaOH and AQ were added to the condensed effluent and the effluent with NaOH and AQ was re-loaded to the digester with the chip sample. The digester was then heated back up to pulping temperature.

[0050] **Table 1** includes the “H Factor” for the pretreatment and for the cooking stages of the trials. As is known, in the art, H factor normalizes alkaline delignification rates with temperature of a treatment. Typically, the higher the H factor the more rigorous the treatment. The H factor during the second heat-up is included in the total for the SAQ cooks. **Table 1** also provides the pH of the liquor in the digester after the carbonate pretreatment and after the soda-AQ treatment.

[0051] The benefits of the present invention are reflected in the “screened yield,” “rejects,” and “Kappa number” data that appear in **Table 1**. As known in the art, screened yield is the percent of the original chips present in the pulped chips after treatment and after the pulp has been screened to remove chips, fines, pins, etc, that were not sufficiently pulped in the process and other non-fibrous debris. As is known in the art, a higher relative screened yield is preferred. The rejects are an indication of how much of the original chips were not fully cooked by the process, for example, as isolated by screening. The lower the rejects the less wood is discarded or re-treated. As is also known in the art, kappa number provides a relative indication of the amount of undesirable lignin present in the resulting pulp. Typically, the higher the kappa number, the more lignin present in the pulp and the more bleaching chemical required to achieve a desired bleached brightness. Thus, a lower kappa number is preferred.

[0052] The data in **Table 1** supports advantages of the present invention. The data provided in **Table 1** illustrate that the method shown in **Figure 1** offers a dramatic improvement in conventional soda-AQ pulping. For example, as shown in **Table 1**, the reject values are the clearest indication of the advantage of aspects of the present invention. According to **Table 1**, run number 4 - corresponding to carbonate pretreatment and soda-AQ pulping - provides a value of 0.3 for rejects and a screened yield of 55.3%. In comparison, run number 2 - representing the prior art SAQ pulping –provides a value of 27.0% for rejects and a significantly lower screen yield of 28.4%. This implies that aspects of the present invention more efficiently cook more of the chips to produce a pulp while retaining a significant portion of the cellulose as

evidenced by the high yield. That is, the lower the rejects the more efficient the cooking process. Also, the data in **Table 1** indicate that run number 2 (corresponding to the prior art SAQ process) provides a lower SAQ end pH than runs 1, 3, and 4 (representing aspects of the invention) even though the NaOH application was 10% Na₂O on wood in all four cases. The applicants theorize that the lower pH of the prior art SAQ process is due to NaOH, a stronger base, out-competing Na₂CO₃ in wasteful carbohydrate degradation reactions. The Na₂CO₃ remains in solution in SAQ cooking and is not a strong enough base to cause the alkaline rearrangements necessary for lignin depolymerization and solubilization. When Na₂CO₃ is added by itself in a pretreatment, the reactive carbohydrates react with it because it is the only alkali present. Aspects of the present invention allow for more of the NaOH added to stage 16 to go towards lignin depolymerization or degradation and thus may provide a more effective pulping process.

[0053] Cooking without carbonate pretreatment was also investigated in laboratory trials to provide a basis for comparison with the aspects of the present invention. The results of these trials are summarized in **Table 2**. In these trials, a series of kraft and SAQ pulps were prepared from sugar maple chips without carbonate pre-cooking. One of the kraft pulping trials was made with a higher sulfidity and lower effective alkali (10% Na₂O on chips from NaOH and 5% Na₂O on chips from Na₂S), see the second line of data in **Table 2**. This kraft pulping trial (second line in **Table 2**) provided a higher screened yield (approximately 1.0% higher screened yield on chips) compared to a kraft trial with a higher EA, that is, 12% Na₂O on chips from NaOH and 4% Na₂O on chips from Na₂S (see the first line of data in **Table 2**). Both pulps had approximately the same unbleached kappa number (that is, 17.4 and 17.8). However, the pulp produced using the lower EA (that is, 10% NaOH and 5% Na₂S, in the second line of **Table 2**) appeared to be less responsive to oxygen (O₂) delignification than the pulp produced with higher EA (12% NaOH and 4% Na₂S), as will be discussed below. The applicants understand that the difference in post -O₂ kappa numbers between these pulps to be significant. As also shown in **Table 2**, a series of SAQ trials were also performed. As shown, trials with varying EA and AQ charges of 0.1 percent on chips produced pulps having kappa numbers as low as 15.2 with relatively low rejects.

Table 2.
Typical Properties of Treatment of Control Pulps
by Prior Kraft and Soda-AQ Pulping
(that is, without Carbonate Pretreatment)

Pulping Process	NaOH ¹	Na ₂ S ¹	Cooking Temp, °C ²	H Factor	Screened Yield ³	Rejects ³	Kappa No. ⁴
Kraft	12.0%	4.0%	165	1297	51.9	0.1	17.4
Kraft	10.0%	5.0%	165	1602	52.8 (52.9) ⁵	0.2	17.8 (18.2) ⁵
SAQ	11.0%	0 ⁶	165	1602	51.7	8.0	42.0
SAQ	12.5	0 ⁶	165	1602	52.3	1.1	21.5
SAQ	14.0	0 ⁶	165	1602	52.8	0.6	19.3
SAQ	14.0	0 ⁶	170	1969	51.1	0.2	15.2

¹ As Na₂O on chips

² 90 minutes to temperature

³ Percent on chips

⁴ Kappa number of screened pulp

⁵ Repeat experiment at a later date

⁶ 0.1% AQ on chips

[0054] Carbonate precooking according to one aspect of the invention was investigated in lab trials. The results of these trials are summarized in **Table 3**. **Table 3** provides the treatment conditions for pretreating chips with carbonate followed by a SAQ treatment (runs 1-5) and by a kraft treatment (runs 6 and 7). The advantages of carbonate precooking according to aspects of the invention are evident by comparing the results presented in **Table 2** (the prior art) to those presented in **Table 3**. For instance, if run 1 in **Table 3** is compared to the conventional SAQ in **Table 2** (the fifth line of **Table 2**) it can be seen that a 30 minute carbonate stage at 165°C (the “C₁ condition,” see footnotes 2 and 3 of **Table 3**) decreased alkali requirement in the SAQ stage from 14.0% (in **Table 2**) to 10% (in **Table 3**) as Na₂O. A comparison of the kappa numbers produced shows that the unbleached pulp produced with carbonate pretreatment was slightly lower in kappa number (18.4 vs. 19.3) while the screened yield produced with carbonate pretreatment was slightly higher (53.1% vs. 52.8%). If carbonate-SAQ according to aspects of the invention (for example, run 5 in **Table 3**) is compared to carbonate-kraft (for example, run 7 of **Table 3**), it can be seen that a higher yield (1.0% on chips) is obtained for carbonate-

SAQ compared to carbonate-kraft treatment. A higher yield results in a more efficient process and thus a high screened yield is desired.

[0055] Aspects of the present invention may also result in an H-factor decrease in the cooking stage that is greater than would be expected. When comparing the result as describe in **Table 2** to those of **Table 3**, it is evident that the H-factor provided in the treatment performed without carbonate pretreatment is higher than the total H factor for carbonate pretreatment plus cooking to the same kappa number. For instance, the H factor for pulp that was not pretreated (lines 3-5 in **Table 2**) was over 1600 for SAQ. The H factor for the SAQ stage for the first two carbonate (C₁) pretreated pulp (runs 1-2 in **Table 3**) was 1239, and the C₁ stage H factor was 358 for a total of 1597 for the combined carbonate and SAQ treatments. The resulting carbonate pretreated pulp with kappa number 18.4 (line 1 of **Table 3**) had an improved pulp screened yield, improved bleachability, and resulted in a lower amount of rejects than the unpretreated pulps. A further comparison illustrating the benefits of aspects of the present invention may be found in **Figure 3**, as discussed below.

Table 3.
Effect of Carbonate Pretreatment on Soda-AQ
and Kraft Pulping of Sugar Maple Chips

Run Number	C-Stage End pH	H Factor in Pulping	Process ¹	Screened Yield	Rejects	Kappa No. ²
1	8.4 (C ₁) ³	1239	SAQ	53.1	0.1	18.4
2	7.9 ⁴ (C ₁)	1239	SAQ	52.7	0.1	17.2
3	8.4 (C ₁)	1239	SAQ ⁵	54.7	0.8	26.4
4	9.8 (C ₁)	1445	SAQ ⁵	53.9	0.2	22.7
5	~7.0 (C ₂)	1239	SAQ	52.2	0.1	16.7
6	8.4 (C ₁)	1027	Kraft	52.1	0.3	18.0
7	~7.0 (C ₂)	1239	Kraft	50.8	0.1	15.6

¹10% Na₂O for SAQ; 8.5% and 3.0% from NaOH and Na₂S in kraft

² Kappa number of screened pulp

³ C₁= 30 minute at 165°C; C₂= 60 minutes, 4.0% Na₂O on chips for all runs except run 4 where 5.0% was used.

⁴ AQ added to C-stage instead of SAQ

⁵ Only 9% Na₂O in SAQ

[0056] Following the cooking trials discussed above and summarized in **Table 2** and **Table 3**, the cellulosic material was bleached. The bleaching sequence used in

the laboratory test was an OD₀EpD₁ (where O is alkaline O₂ stage; D₀ is chlorine dioxide delignification with an end pH of 2-3; Ep is alkaline extraction with sodium hydroxide and hydrogen peroxide for incremental delignification; D₁ is a chlorine dioxide brightening with an end pH of 3.4-4.5). The chlorine dioxide application in the D₀ stage is based on the formula: wt% chlorine dioxide on pulp = 0.076 x kappa number of O₂ pulp. According to laboratory test performed, the applicants found that the 21.5 kappa number pulp produced in the soda-AQ pulp trial (that is, the data in the fourth line of **Table 2**) could be produced with 12.5% Na₂O; however, this pulp was more difficult to bleach than the pulp produced when 14.0% Na₂O was used (that is, the data in the fifth and sixth lines of **Table 2**). The kappa number decrease due to O₂ is typically an indicator of the ease of bleachability. According to aspects of the invention, the bleachability of a soda-AQ pulp is improved by the carbonate pretreatment. It will be understood by those with skill in the art that, though this specific bleaching sequence was used in this investigation, according to aspects of the invention, any suitable known bleaching process can be used, including bleaching processes that eliminate chlorinated compounds, that is, totally chlorine free (TCF) bleaching processes a eliminatel elemental chlorine, that is, elemental chlorine free (ECF) bleaching processes.

[0057] **Figure 3** provides a plot of a comparison of screen yield as a function of post oxygen delignification kappa number for aspects of the present invention and the prior art. As shown, aspects of the invention provide a pulp that is more easily bleached compared to conventional prior art methods. As known in the art, screen yield percent is a ratio of the weight of the output pulp of the process over the weight of the input wood to the process after the output pulp has been screened to remove knots, shives, and other unwanted material. A higher screen yield is preferred. The O₂ kappa number relates to the lignin content of the cooked and oxygen-delignified pulp. As is known in the art, a lower kappa number is preferred. With regard to **Figures 3 and 4**, the following notations are used: A = Acid; C = carbonate pretreatment; Kr= kraft treatment; SAQ= soda anthraquinone treatment. The designation “(M + N)” means that the treatment was performed at M % NaOH on wood as Na₂O and N % Na₂S on wood as Na₂O. Methods of the present invention further include an oxygen delignification treatment resulting in a pulp having a lower kappa number after the oxygen delignification treatment at a predetermined screened

yield compared to a pulp produced by the method without practicing a pretreatment stage 14.

[0058] As shown in **Figure 3**, there is a dramatic improvement for carbonate pretreated Soda-AQ (“X” C-SAQ) as compared to soda-AQ pulp without pretreatment (“▲” SAQ). According to the results presented in **Figure 3**, the kappa number which has been produced by carbonate pretreatment followed by soda AQ (“X” C-SAQ) cooking achieves a lower post O₂ bleaching kappa number than the kappa number for soda-AQ pulp without pretreatment (“▲” SAQ). For instance, the O₂ kappa number for C-SAQ (“X”) is just over 8 kappa with a screened yield percent of over 52% and the O₂ kappa number for SAQ (“▲”) is approximately 10.5 kappa with a comparable screened yield of approximately 52.5%. That is, at comparable screened yields, an aspect of the present invention provides a lower kappa number compared to the prior art. Therefore, the carbonate treatment decreases the kappa number (both unbleached and after the O stage).

[0059] In these laboratory trials, yield loss in all the oxygen stages was approximately 1.4-1.8% on pulp. The small differences in yield loss during O stages are insignificant when converted to a “percent on chips” basis. Carbonate treatment or acid treatment followed by carbonate pretreatment (that is, “AC-pretreatment”) did not improve the fiber yield of kraft pulping. However, as shown in **Figure 3**, carbonate and acid + carbonate pretreatments (“X” C-SAQ and “*” AC_SAQ) clearly improved the yield of SAQ pulping (“▲”). That is, according to aspects of the invention, a higher screened yield is provided compared to conventional SAQ pulping methods.

[0060] **Figure 4** provides a plot of a comparison of fully bleached pulp as a function of post oxygen delignification kappa number for aspects of the present invention and the prior art. The ordinate in **Figure 4** is the light absorption coefficient (LAC) value for the fully bleached pulp after OD₀EpD₁ bleaching and the abscissa is the post O₂ kappa number. A review of **Figure 4** reveals that the conventional soda-AQ pulps (“▲”) contain more color (that is, have a higher LAC values) than kraft pulps (“closed diamond”). However, the soda-AQ pulp after acid (A) and carbonate (C) pretreatments (“open triangle” and “open diamond”) according to aspects of the

invention had equal or slightly lower color content than kraft pulps without pretreatments.

[0061] Further laboratory tests were performed to compare properties of bleached kraft, bleached acid carbonate kraft, and bleach acid carbonate soda anthraquinone pulps. Several properties of bleached kraft pulp according to the prior art, Acid Carbonate (AC)-kraft pulp according to an aspect of the invention, and Acid Carbonate (AC)-SAQ pulps according to an aspect of the invention from sugar maple chips are documented in **Table 4**. As shown in **Table 4**, the soda AQ pulp pretreated with both acid and carbonate treatments resulted in an improved yield. The screen yields were highest for AC-SAQ, a value of 53.2, compared to a yield under 52 for both the prior art kraft and AC-kraft pulps. The AC pretreatment increased the final brightness of the kraft pulp from 91.0 to 92.6.

Table 4
Properties of Bleached Pulp Produced by Prior Art Kraft Process
and by AC-Kraft and AC-SAQ Pulping Processes According to Present
Invention

	Kraft	AC-Kraft	AC-SAQ
Unbl. Kappa Number	17.4	17.8	19.3
Screened Yield ¹	51.8	51.4	53.2
Rejects ¹	0.1	0.1	0.1
Post O ₂ Kappa Number	9.2	8.7	9.8
O ₂ Brightness ²	~55.0	57.4	54.1
ODEp Brightness	82.8	83.5	82.3
Final Brightness	91.0	92.6	91.2
Final LAC ³ , m ² /kg	0.182	0.121	0.173
Bleached Pulp Yield ¹	49.8	49.5	51.2

¹% on chips

² % Elrepho

³ Light scattering coefficient = 40.8 m²/kg for all three pulps

[0062] When cooking in accordance to aspects of the invention, as illustrated in **Figure 1**, at least some of the A-stage (acid stage) effluent may be displaced, for example, 50% to 75% of the total A stage effluent, with the carbonate-containing solution. In one aspect, at least some and possibly all of the carbonate stage effluent may be transferred with the chips into the kraft or SAQ stage. In the laboratory trials reported on so far, the carbonate stage effluent was recovered after passing through a condenser. The NaOH was introduced to the effluent as pellets and AQ powder was

dissolved in the condensed effluent. The carbonate and AQ containing effluent was then returned to the lab digester for the SAQ stage. Sodium sulfide solution and NaOH pellets are added to the carbonate stage effluent in the case of kraft pulping. For the purpose of this application, brightness is percent elrepho.

[0063] The applicants surmise that the use of some or all of the carbonate stage effluent may be important to aspects of the invention, for example, to the carbonate-SAQ process. The applicants believe that this may be because it is likely that the carbonate effluent may contain many low molecular weight carbohydrates with reducing end groups. It is estimated that carbohydrate dissolution during the carbonate stage may be approximately 5% of the original chip mass (oven dry basis). The applicants believe that random hydrolysis of the carbohydrates would be expected and formation of a new reducing end group is likely with each hydrolysis. The higher concentration of reducing end groups would reduce AQ at a higher rate to form AHQ (anthrahydroquinone), that is, the active delignification catalyst. The AQ/AHQ catalytic cycle is shown schematically in **Figure 5**. Also, when a reducing end group in the solid phase is oxidized to a carboxylic acid it becomes resistant to the alkaline peeling reaction that lowers the molecular weight of carbohydrates and decreases pulp yield. The hypothesis above may explain why the carbonate stage improves pulp yield for SAQ pulping, but not for kraft pulping. The oxidation of reducing end groups to carboxylic acids is not known to be a significant reaction (or even occur) in the kraft process, or the soda process without AQ addition.

[0064] In further support of the benefits of aspects of the invention, further laboratory research was performed with chips from a mixture of woods. For instance, a chip mixture comprising approximately 60% eastern cottonwood (*Populus deltoids*) clone, approximately 20% white birch (*Betula papyrifera*), and approximately 20% sugar maple was used. The results for prior art kraft pulping, prior art soda-AQ pulping and pulping according to aspects of the invention, that is, with acid and acid/carbonate pretreatments are presented in **Table 5**. The acid pretreatment conditions were:

A₁: 20 min. at 150°C with 1.5% acetic acid on chips (end pH~3.5); and

A₂: 60 min. at 120°C with 3.0% acetic acid (end pH 3.2).

[0065] As indicated in **Table 5**, the A₁ pretreatment provided a soda-AQ pulp with higher bleached (that is, “Final”) brightness (90.8) than kraft (89.9), but pulp yield was somewhat lower. The milder A₂ pretreatment with an acid carbonate-SAQ provided a higher pulp yield (54.2%) than both conventional kraft pulping and SAQ pulping. The A₂C-SAQ treatment also afforded a higher bleached brightness (89.2) than SAQ pulping (88.4) but less than kraft pulping (89.9). In one aspect of the invention, the applicants believe that that the severity of the acid (A) stage may preferably be higher than the A₂ acid treatment, but lower than the A₁ acid treatment for this chip furnish. As also indicated in **Table 5**, the rate of tensile strength development after 2,000 PFI revolutions of refining, as indicated by “tensile index,” for acid-kraft pulping (78.3) and acid-SAQ pulping (86.1) was lower than for kraft pulping (94.4). However, acid-carbonate-SAQ had the highest rate (that is, 100.2), further underscoring the benefits of aspects of the invention. From the results that appear in **Table 5**, it appears that a pulp with a higher yield and probably more hemicelluloses required less refining. There were no significant differences in the tensile-tear curves.

Table 5
Effect of Acid and Acid/Carbonate Pretreatments on Kraft and Soda-AQ Pulping
of Mixed Hardwoods

	Kraft	A ₁ -Kraft	SAQ	A ₁ -SAQ	A ₂ C ₁ -SAQ ¹
Screened Yield	53.2	51.1	53.0	52.7	54.2
Rejects	0.2	0.1	0.3	0.1	0.2
Unbleached Kappa	16.7	17.1	16.6	15.9	18.9
O ₂ Kappa	9.6	9.6	9.8	9.4	9.5
Final Brightness (% elrepho)	89.9	91.8	88.4	90.8	89.2
CSF ²	412	487		429	375
Tensile Index ²	94.4	78.3		86.1	100.2

¹EA=10% Na₂O; 14.0% for other cooks

²Canadian Standard Freeness and tensile index at 2000 PFI revolutions (light load) for O₂ delignified pulps

[0066] Further, milder carbonate stage conditions were studied to fully understand the benefits of carbonate-SAQ pulping and to further differentiate the present

invention from the earlier research in '241 where no anthraquinones were involved. The results of this investigation are summarized in **Table 6**. A chip furnish was prepared consisting of 50% sugar maple, 40% eastern cottonwood and 10% white birch. Carbonate treatment stages according to aspects of the invention were performed at 130°C and 140°C with either 3.0 or 5.0% Na₂CO₃ charge (as Na₂O) on wood and for a time period of either 30 or 60 minutes. In these trials it took approximately 30-35 minutes to achieve maximum temperature. About 70% of the carbonate stage effluent was drained off and discarded after the carbonate treatment. The carbonate effluent was replaced by distilled water when the pulping chemicals were added for SAQ or kraft cooking.

Table 6
Effect of Carbonate Pre-Cooking at 130 degrees C and 140 degrees C

Run Number	C Temp, °C	Time, Min.	End pH ¹	H Factor in S or K ²	Screened Yield ³	Rejects ³	Kappa No. ⁴
1	130 (3.0%) ⁵	30	8.0	816 (S)	55.1	2.8	28.8
2	130 (3.0%)	60	7.8	816 (S)	55.8	1.4	27.6
3	130 (5.0%)	30	9.1	816 (S)	55.1	1.1	23.4
4	140 (3.0%)	30	8.2	816 (S)	55.0	1.5	24.4 (12.3)
5	140 (3.0%)	60	7.9	816 (S)	55.8	0.6	23.1 (10.7)
6	140 (3.0%)	60	7.5	816 (K)	54.4	0.4	20.9
7	140 (5.0%)	30	8.6	816 (S)	54.5	0.3	19.3 (10.2)
8	-		-	992 (K) ⁶	53.5	0.5	17.3 (9.0)
9	-		-	992(S)	54.2	1.0	22.6

¹ End pH of C stage

² S = SAQ; K= Kraft

³ Percent on chips

⁴ Kappa number of screened pulp; O₂ value in parentheses

⁵ Na₂CO₃ applied as % Na₂O on chips

[0067] According to the result presented in **Table 6**, the best results were obtained with a carbonate-SAQ treatment having a carbonate stage of 60 minutes in duration at 140 degrees C with 3% Na₂CO₃ on chips (as Na₂O) (for example, see run 5). The pulp from run 5 had a screened yield on chips of approximately 2.0% higher than run 8 (the reference kraft cook) and only a 1.7 kappa unit disadvantage after oxygen delignification as compared to run 8. When comparing the kraft pulp with pretreatment (run 6) the carbonate-SAQ pulp (run 5) had a yield advantage of

approximately 1.0% on chips. Such a yield advantage would translate to a net increase in profit of approximately \$4M/annum for a typical chemical pulp mill.

[0068] In addition, the combined H factor for the carbonate (C) and soda-AQ stages in run 5 is 897 (81+816) produced a pulp having approximately the same kappa number (23.1 vs. 22.6), higher yield (55.8 vs. 54.2) and lower rejects (0.6 vs. 1.0) compared to a prior art SAQ produced pulp without the pretreatment but with a H factor of 992 (run 9). Time spent in the carbonate stage may have a significant impact on the resulting pulp. In laboratory tests, an additional 30 minutes in the carbonate stage at pH ~ 8 (see run 4 vs. run 5) resulted in a 1.6 kappa unit advantage after soda-AQ and oxygen delignification. Further, the extra 30 minutes in the carbonate stage afforded a higher screened yield. Additionally, it is believed that more reducing end groups were generated in the extra 30 minutes spent in the carbonate stage, and the longer overall cooking time converted more rejects to screened fibers.

[0069] Aspects of the invention can be performed in equipment for a batch (such as but not limited to conventional, SuperBatch® or Rapid Displacement Heating) or continuous (such as but not limited to conventional soda, conventional kraft, Lo-Solids® Cooking, EMCC® Cooking, ITC® Cooking, and Compact Cooking) where pressurized equipment (as required for the carbonate treatment) is used for any or all of the stages of acid, carbonate and cooking. Aspects of the invention are also amenable to pretreatment during transport or storage of comminuted fibrous material, for example, as described in U.S. Patent 6,55,462, the disclose of which is incorporated by reference herein. For batch systems, conventional means such as pumping of liquor into the vessel can be used to displace the liquid in the digester, or the liquor can be discharged from the digester by inherent pressure or pump-out means, before the new cooking liquor is added to the digester. All liquids can be preheated using methods known in the art, such as extracted liquor from SuperBatch or RDH methods. Further, heating of the liquid can be accomplished in the vessel by circulation loops or direct steam addition.

[0070] As described herein, aspects of the present invention provide cellulosic material pretreatment process and pulping process that provides advantageous improvements to prior art treatments of wood chips, and related comminuted cellulosic materials. As made clear from the test data presented herein, pretreatment

of wood chips with a carbonate solution, with or without the presence of an anthraquinone can produce cellulose pulps that are higher in yield, lower in rejects, greater in strength, and require less chemical to both produce and bleach.

[0071] While several aspects of the present invention have been described and depicted herein, alternative aspects may be provided by those skilled in the art to accomplish the same objectives.

* * * * *

WHAT IS CLAIMED IS:

1. A method of treating comminuted cellulosic fibrous material comprising:
 - a) treating the cellulosic fibrous material with a sulfur-free sodium carbonate-containing solution to produce a pretreated cellulosic material and, at the end of a), a solution having a pH from 7.0 to 9.1; and
 - b) treating the pretreated cellulosic material with sodium hydroxide or a combination of sodium hydroxide and sodium sulfide as a pulping chemical to produce a cellulose pulp;

wherein, in at least one of a) and b), the cellulosic fibrous material is treated with an anthraquinone.
2. The method as recited in claim 1, wherein the cellulosic fibrous material is treated with an anthraquinone in a).
3. The method as recited in claim 1 or claim 2, wherein the pretreated cellulosic fibrous material is treated with an anthraquinone in b).
4. The method as recited in any one of claims 1 to 3, wherein the sodium carbonate-containing solution comprises 1% to 5% sodium carbonate as Na_2O on wood and the treatment a) is for 15 to 120 minutes, at 120 degrees C to 200 degrees C.
5. The method as recited in claim 4, wherein the sodium carbonate-containing solution comprises 2% to 4% sodium carbonate as Na_2O on wood and the treatment a) is for 15 to 120 minutes, at 120 degrees C to 170 degrees C.
6. The method as recited in anyone of claims 1 to 3, wherein a) is practiced at a temperature between 120 degrees C and 170 degrees C.

7. The method as recited in anyone of claims 1 to 3, wherein a) is practiced at a temperature between 120 degrees C and 150 degrees C.
8. The method as recited in anyone of claims 1 to 3, wherein the treatment with anthraquinone comprises an aqueous anthraquinone having a concentration between 0.01 weight percent to 0.20 weight percent on wood.
9. The method as recited in anyone of claims 1 to 3, wherein the treatment with anthraquinone comprises an aqueous anthraquinone having a concentration between 0.05 weight percent to 0.10 weight percent on wood.
10. The method as recited in anyone of claims 1 to 3, wherein an anthraquinone is introduced after a) and comprises a concentration of aqueous anthraquinone 0.01 weight percent to 0.20 weight percent on wood.
11. The method as recited in claim 1 or claim 2, wherein the method further comprises, prior to a), c) treating the comminuted fibrous material with an acidic solution.
12. The method as recited in claim 11, wherein the method further comprises, after c) and before a), d) extracting at least some of the acidic solution from the cellulosic fibrous material.
13. The method as recited in anyone of claims 1 to 3, wherein treating the pretreated cellulosic material with a pulping chemical further comprises producing a liquid containing spent pulping chemical; and wherein the method further comprises:

treating the liquid containing spent pulping chemical to produce a sulfur free sodium carbonate-containing solution from the spent pulping chemical; and

using the sulfur free sodium carbonate-containing solution produced from the spent pulping chemical as the sodium carbonate containing solution in a).

14. The method as recited in claim 13, wherein treating the liquid containing spent pulping chemical comprises:

concentrating the liquid sufficiently to support combustion;

burning the concentrated liquid to produce a smelt containing sodium carbonate;
and

introducing a liquid to the smelt to provide the sulfur free sodium carbonate-containing solution from the spent pulping chemical.

15. The method as recited in claim 1 or claim 2, wherein, at the end of a), the solution has a pH from 7.0 to 8.9.

16. The method as recited in anyone of claims 1 to 3, wherein the method is practiced continuously.

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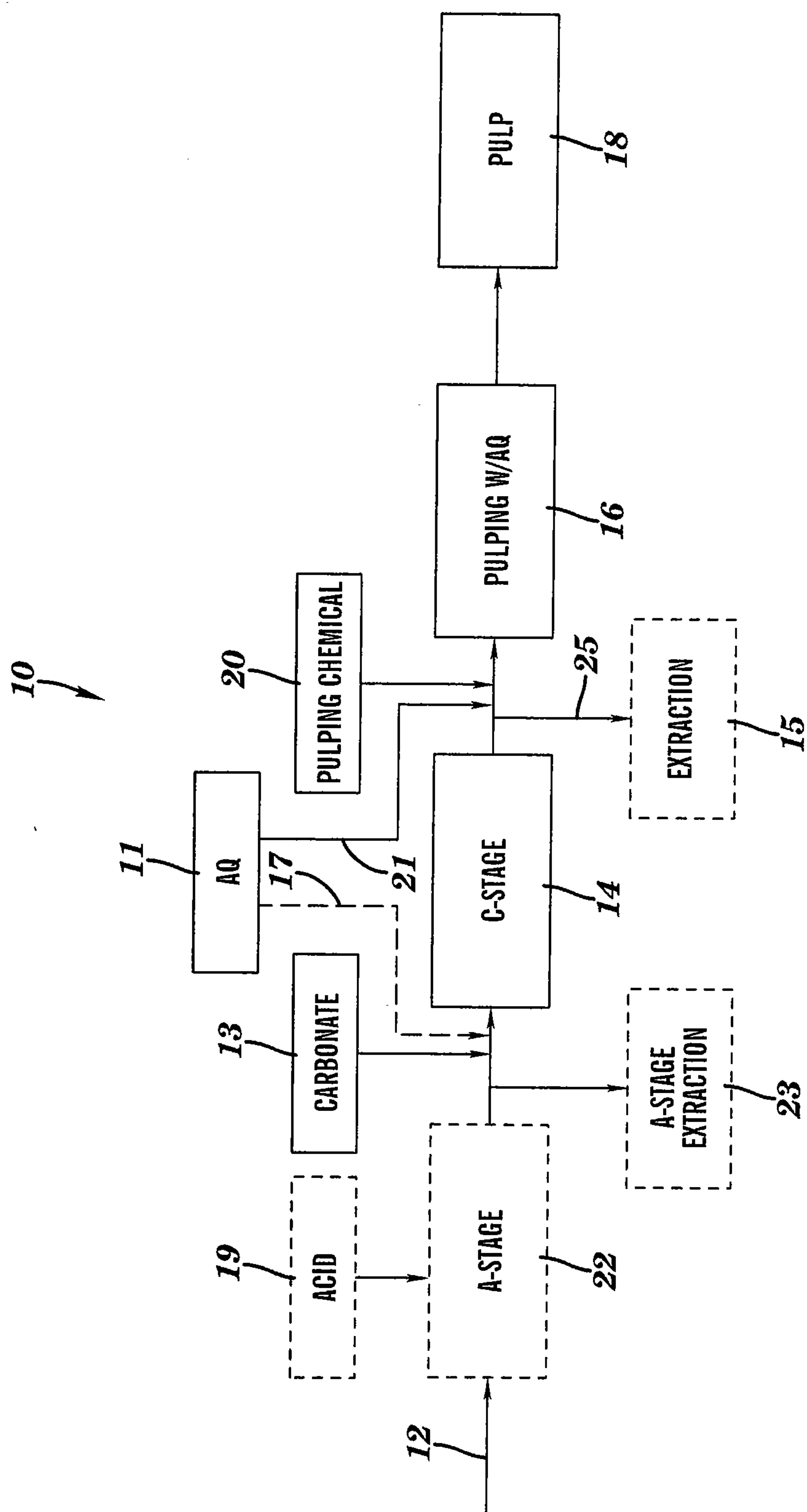
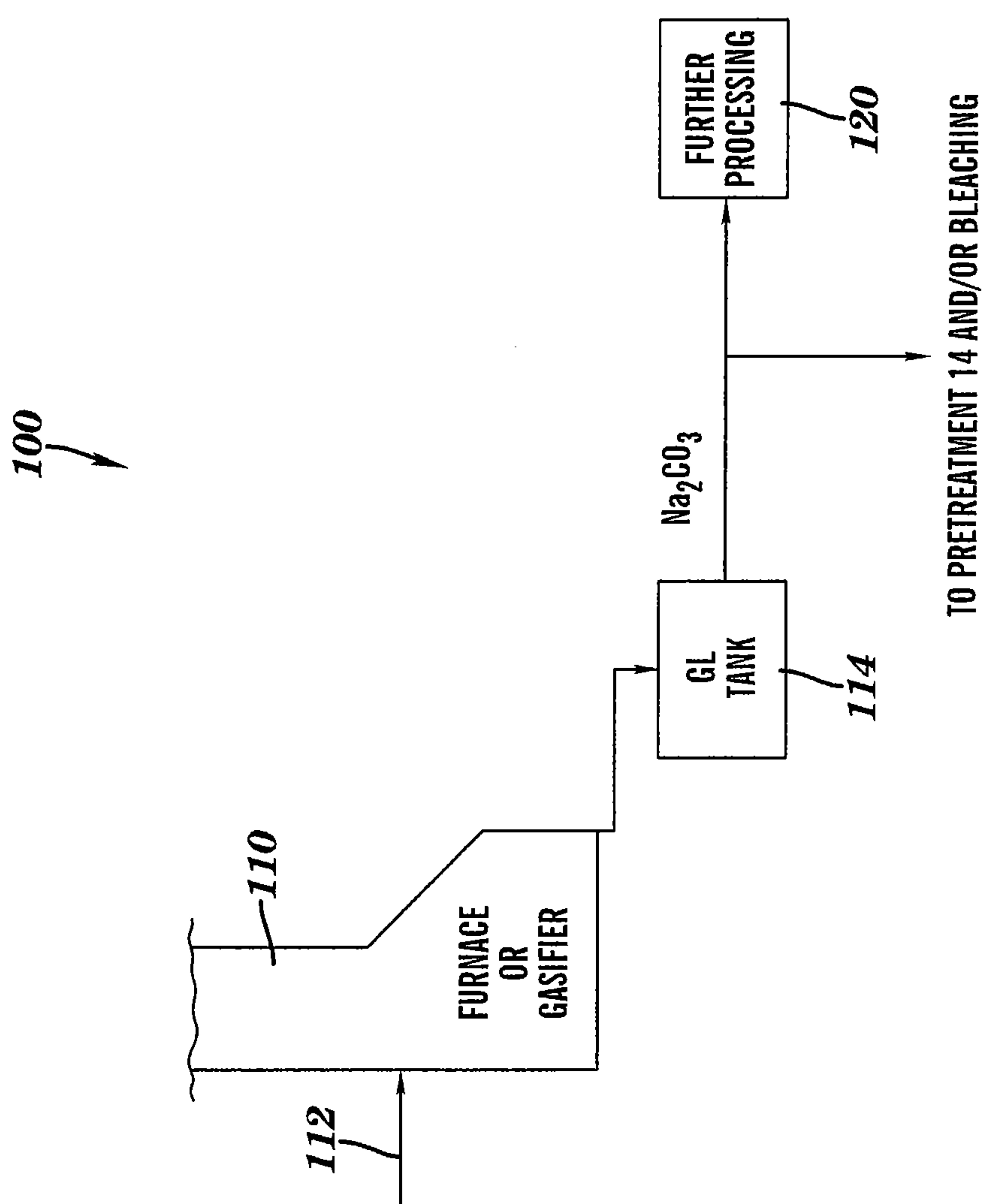


FIG. 1

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**FIG. 2**

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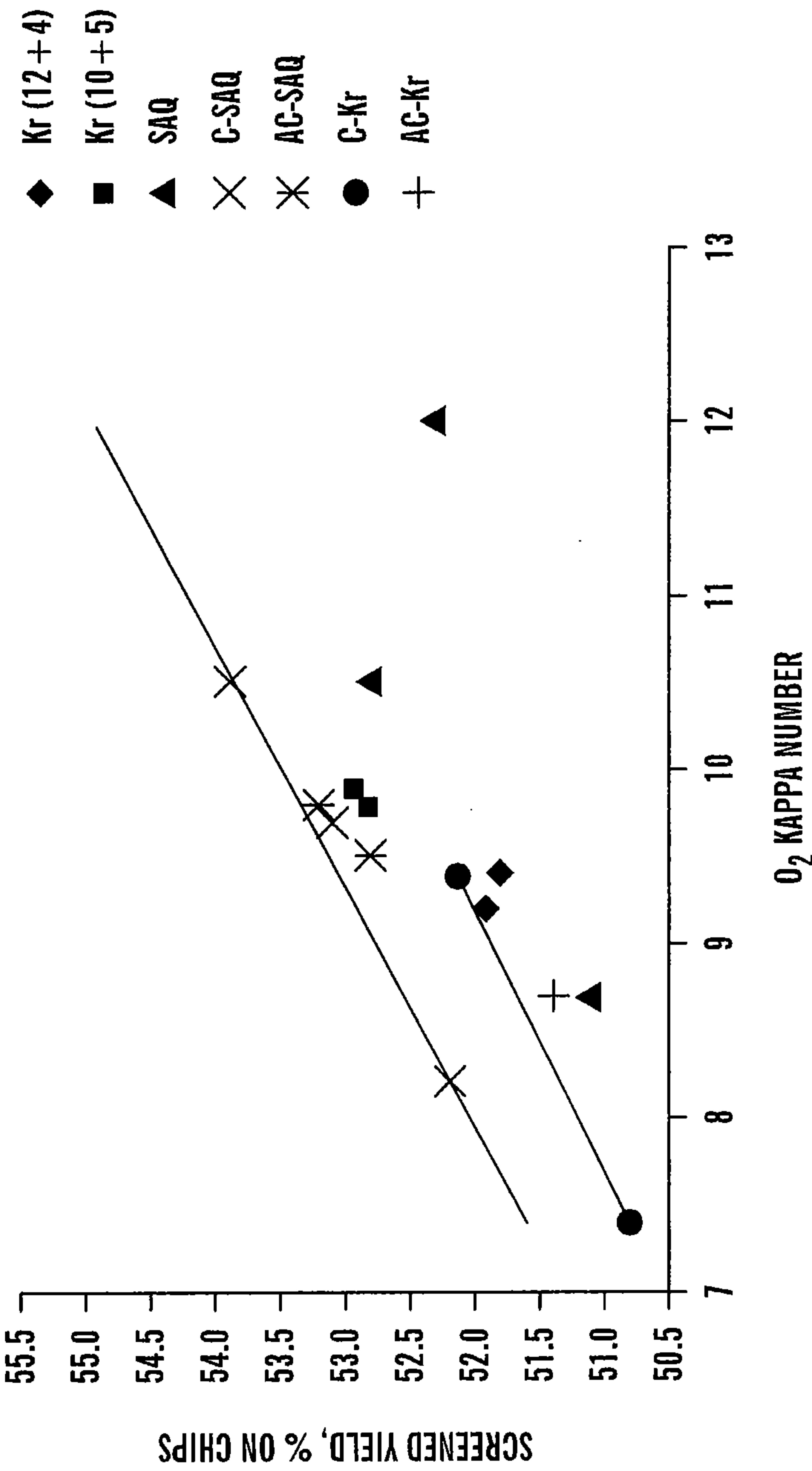
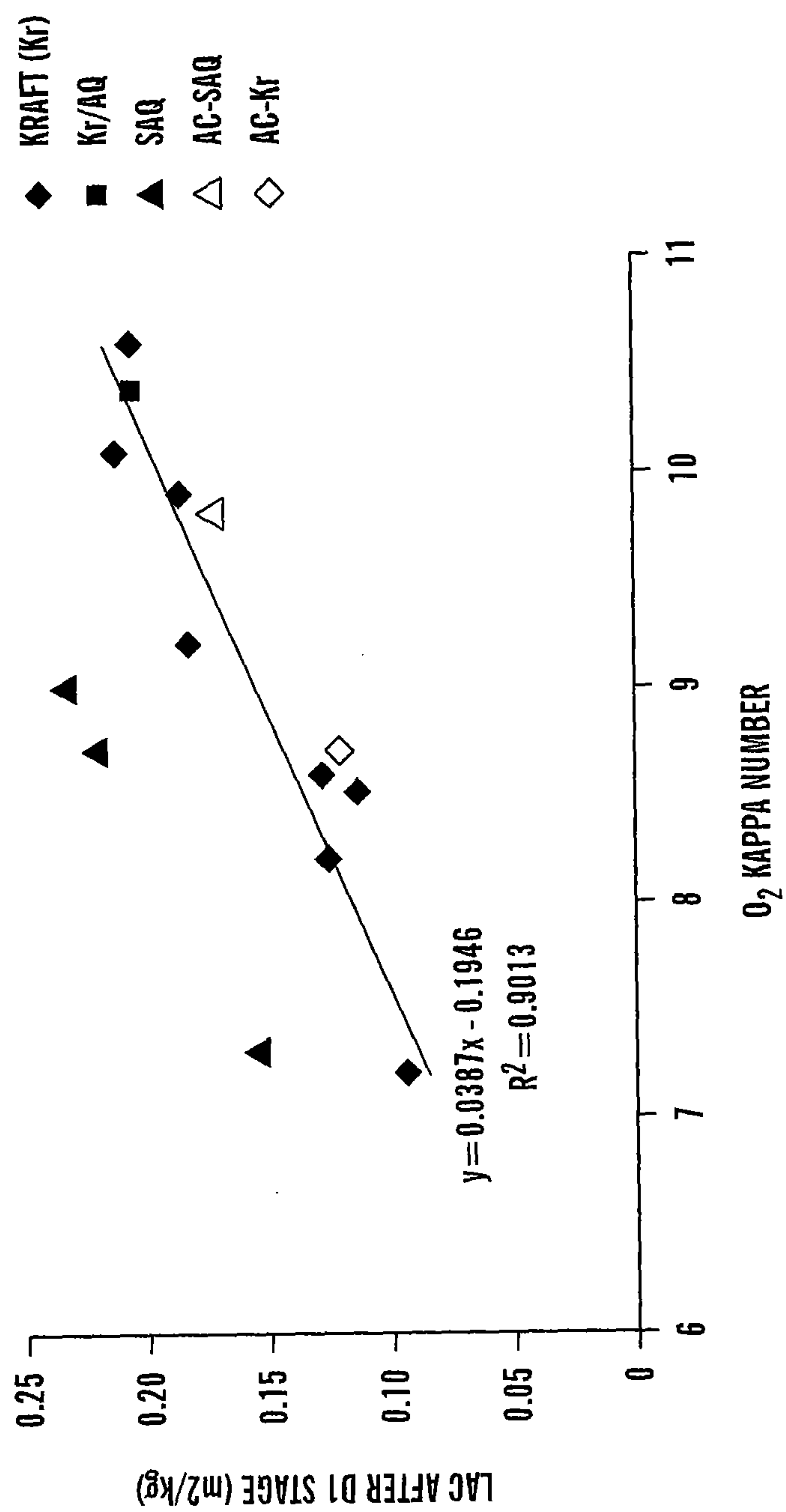


FIG. 3

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**FIG. 4**

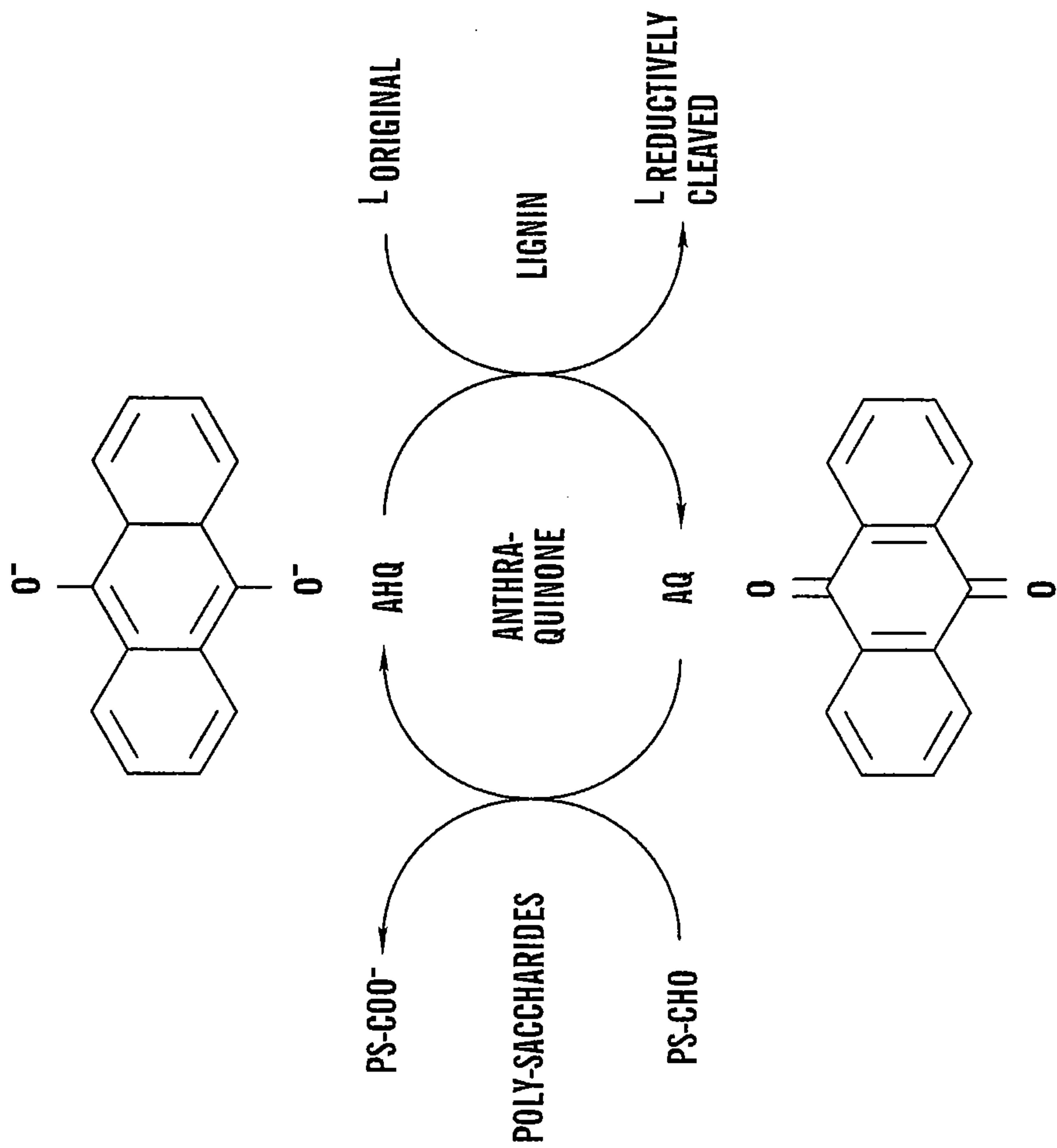


FIG. 5

