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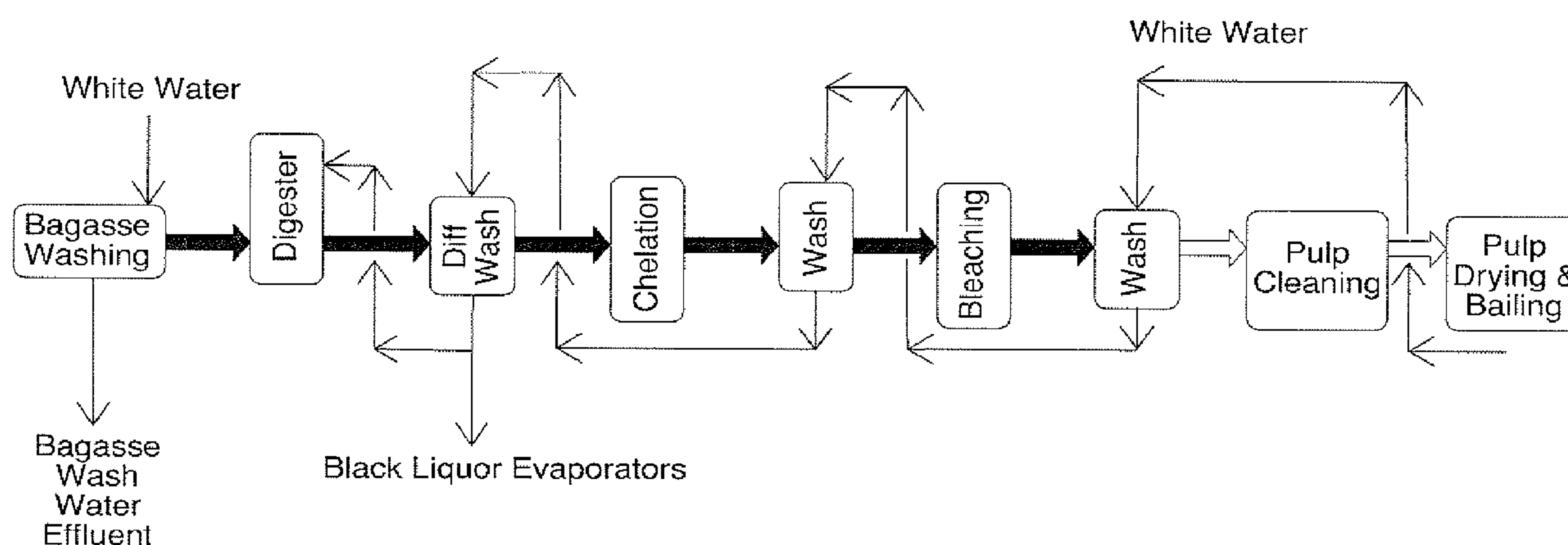


FIGURE 2

(57) **Abrégé/Abstract:**

One aspect of the invention relates to an article of manufacture made from a pulp composition comprising an ARF pulp. In one embodiment, the pulp composition made from agricultural renewable fibers (ARF) having low Kappa number with unexpected quality sufficient for papermaking (e.g., high strength parameters and high freeness). In another embodiment, the ARF pulp has ISO brightness of 60% or higher, and unexpected quality sufficient for papermaking (e.g. high strength parameters and high freeness). In another embodiment, the ARF pulp is made from a pulping process comprising using a high concentration of anthraquinone (AQ).



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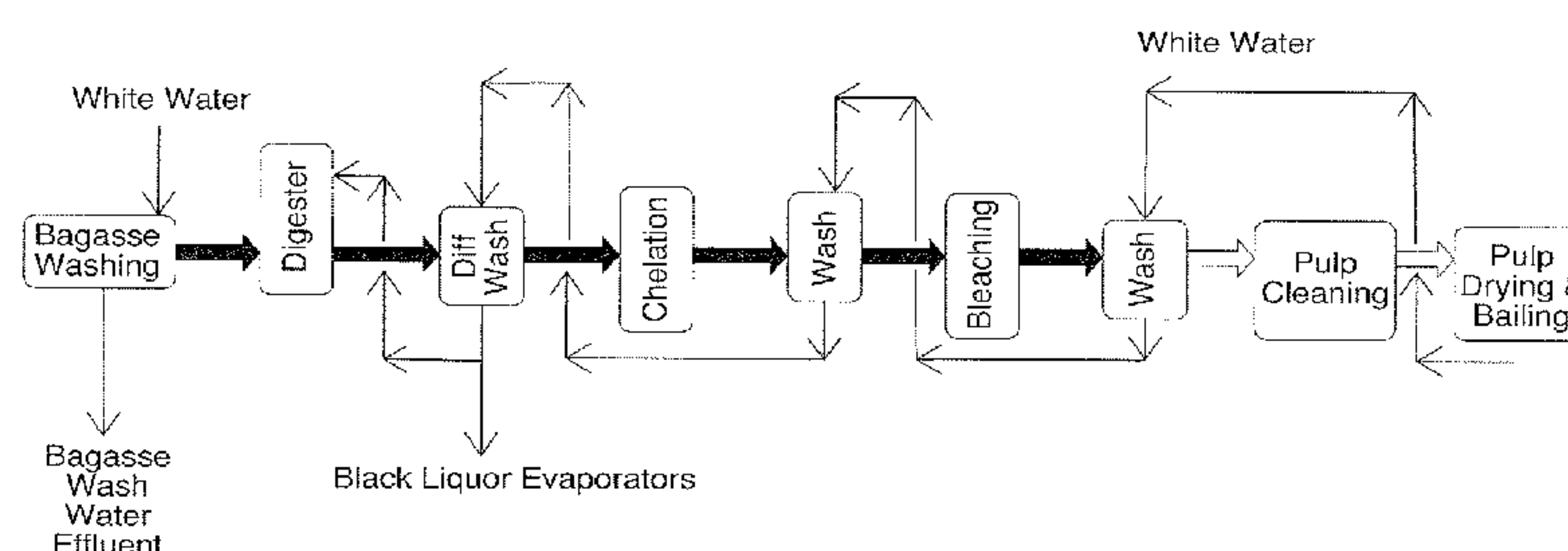


FIGURE 2

(57) **Abstract:** One aspect of the invention relates to an article of manufacture made from a pulp composition comprising an ARF pulp. In one embodiment, the pulp composition made from agricultural renewable fibers (ARF) having low Kappa number with unexpected quality sufficient for papermaking (e.g., high strength parameters and high freeness). In another embodiment, the ARF pulp has ISO brightness of 60% or higher, and unexpected quality sufficient for papermaking (e.g. high strength.parameters and high freeness). In another embodiment, the ARF pulp is made from a pulping process comprising using a high concentration of anthraquinone (AQ).

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ARTICLES OF MANUFACTURE MADE FROM PULP COMPOSITION

FIELD OF THE INVENTION

[0001] The disclosure relates to articles of manufacture made from pulp compositions.

BACKGROUND

[0002] Pulp is a lignocellulosic fibrous material prepared by chemically or mechanically separating cellulose fibers from wood, or non-wood fiber sources.

[0003] "Pulping" generally refers to the reduction of a bulk fiber source material into its component fibers. Wood and other plant materials used to make pulp generally contain three main components (apart from water): cellulose fibers (desired for papermaking), lignin (a three-dimensional polymer that binds the cellulose fibers together) and hemicelluloses (shorter branched carbohydrate polymers). The aim of pulping is to break down the bulk structure of the fiber source, be it chips, stems or other plant parts, into the constituent fibers.

[0004] Chemical pulping achieves this by degrading the lignin into small, water-soluble molecules which can be washed away from the cellulose and hemicellulose fibers without depolymerizing them. Depolymerizing the cellulose weakens the fibers and lowers the strength of the pulp obtained. Although lignin in pulp may enhance strength, a

pulp having a high degree of delignification may ease the bleaching process.

[0005] Generally, existing pulping processes do not provide pulps having a sufficient reduction in Kappa without the use of multiple delignification processes and/or unacceptable destruction or weakening of the cellulose in the pulp. Thus, there is a need for an improved pulping process that can achieve a pulp with desired characteristics and at the same time eliminate many of the steps necessary in the current art.

[0006] In addition, agricultural renewable fiber (ARF) is an environmentally-friendly alternative to the use of wood as a fiber source. ARF represents an economically-promising source of nonwood fibers. But, given the fragile nature of agricultural residues, ARF pulps currently available on the market do not have sufficient strength for many industrial uses, e.g., making printing and writing grade paper. Thus, there is a need for high quality, consistent ARF pulps that can substitute the pulps made from wood fibers for production of articles of manufacture.

SUMMARY OF THE INVENTION

[0007] One aspect of the disclosure relates to an article of manufacture made from a pulp composition comprising an ARF pulp.

[0008] In one embodiment, the ARF pulp has an unbleached Kappa number of about 15 or less, and strength parameters sufficient for papermaking.

[0009] In another embodiment, the ARF pulp made from a pulping method comprising cooking a first mixture comprising fibers, water, an alkali, and a delignification selectivity enhancing chemical for a cooking time and at a cooking condition sufficient to form a first pulp having a desired Kappa number of about 15 or less and strength parameters sufficient for papermaking.

DESCRIPTION OF THE DRAWINGS

[0010] Figure 1: Effect of anthraquinone (AQ) concentration applied in the cooking process on the Kappa number of obtained pulps for high H-factor and low H-factor processes.

[0011] Figure 2: Flowchart of a pulping process according to an embodiment of the present disclosure.

DETAILED DESCRIPTION

[0012] One aspect of the disclosure relates to articles of manufacture made from a pulp composition comprising an ARF pulp.

[0013] Examples of articles of manufacture produced from a pulp composition comprising an ARF pulp include, without limitation, tissue, printing and writing papers, communication papers, bleached board, food contact packaging papers such as OGR, bleached packaging grades, liquid packaging, the more exotic papers such as wet strength papers and release liner, recycled linerboard and molded packaging products.

[0014] The ARF pulp may be a bleached or an unbleached pulp.

Examples of articles of manufacture produced from a pulp composition comprising a bleached ARF pulp include, without limitation, tissue, printing and writing papers, communication papers, bleached board, food contact packaging papers such as oil and grease resistant ("OGR"), bleached packaging grades, liquid packaging and the more exotic papers such as wet strength papers and release liner. Examples of articles of manufacture produced from a pulp composition comprising an unbleached ARF pulp include, without limitation, recycled linerboard and molded packaging products. In certain embodiments, the use of the bleached or unbleached ARF pulp may improve the performance of the article of manufacture.

[0015] ARF includes fibers obtained from agricultural productions.

Examples of ARF include, without limitation, bagasse, wheat straw, rice straw, corn stover (stalks, leaves and husks), soy residuals, coconut tissues, cotton stalks, palm baskets, kenaf, industrial hemp, seed flax straw, textile flax straw, sisal, hesperaloe, rye grass, and mixtures thereof. In one embodiment, the ARFs are bagasse or corn stover.

[0016] The ARF pulp as disclosed herein exhibits exceptional bonding characteristics. Although the fibers in ARF pulp are generally short fibers, due to the superior bonding characteristics, the fibers unexpectedly perform more like long fibers, show physical dimensions similar to a hardwood fiber, and have a strength that allows them to

substitute in portion, if not entirely, for Northern bleached softwood kraft (NBSK) or similar. These bonding characteristics result in outstanding final paper sheet strength to meet today's demanding customer specifications. This sheet strength is achieved with a fraction of the usual refining energy required by wood fibers, a significant cost savings to tissue applications and others requiring refining wood pulps to develop strength. In certain embodiments, the fiber count per milligram is 19,000.

[0017] Premium grade bath tissue meeting North American Premium Specifications has been manufactured using minimal amounts of NBSK by directly substituting the ARF pulp without any further refining.

[0018] In one embodiment, the ARF pulp has an unbleached Kappa number of about 15 or less, and strength parameters sufficient for papermaking.

[0019] Kappa number reflects the hardness, bleachability, or degree of delignification of pulp. Generally, a pulp having a Kappa number of about 5 or lower can be bleached by chlorine dioxide (elemental chlorine free (ECF) techniques) or without chlorine compounds (totally chlorine free (TCF) techniques) to provide a bleached pulp having a desired brightness (e.g., ISO brightness of less than 50%, ISO brightness of about 60% or higher, about 70% or higher, about 80% or higher, about 84% or higher, about 88% or higher, about 80 to about 90%, or about 90% or higher). Generally, it takes more than one pulping step (sometimes referred to as cooking or delignification) to lower the Kappa

number while retaining the strength parameters of the pulp. A pulp having a higher Kappa number will make ECF or TCF bleaching difficult, requiring oxygen delignification and/or ozone, and/or far more peroxide. Alternatively, a pulp having a higher Kappa number can be bleached by chlorine. Therefore, an ARF pulp having a sufficiently low Kappa number and sufficiently high strength parameters will be appreciated in the art.

[0020] Many methods of measuring the degree of delignification have been developed in the art, but most are variations of the permanganate test. The normal permanganate test provides a permanganate or "Kappa number," which is the number of cubic centimeters of tenth normal (0.1N) potassium permanganate solution consumed by one gram of oven dried pulp under specified conditions. For example, it may be determined by TAPPI Standard Test T-236. The acceptable Kappa number range will vary depending upon the intended use of the pulp (e.g., the Kappa number requirements for brown paperboard may vary from about 50 to about 90, while the requirements for white paper stock may be less than 5).

[0021] Tensile, tear index, and burst index are examples of strength parameters of a pulp to be used to make articles, e.g., paper or paper products. Generally higher strength parameters of a pulp are desired to provide higher strength for the articles made therefrom. A pulp obtained from wood fibers usually shows better strength parameters compared to a pulp obtained from non-wood fibers (e.g., ARFs such as bagasse).

However, some of the strength parameters (e.g., tensile) of the pulp compositions disclosed herein are unexpectedly similar to or better than those of the pulp made from wood (see, e.g., Example 9, Table 2).

[0022] Examples of the strength parameters of a pulp that are sufficient for papermaking include, without limitation, a tensile of at least about 5.50 km, a tear index of at least about 6.00 mN.m²/g, a burst index of at least about 3.00 kPa.m²/g, and combinations thereof.

[0023] In certain embodiments, the pulp compositions have a Kappa number of about 15 or less, about 10 or less, or about 5 or less.

[0024] In certain embodiments, the pulp compositions also have a high freeness.

[0025] The term "freeness," as used herein refers to "pulp freeness," refers to the drainage rate of pulp, or how "freely" the pulp will give up its water. Freeness is important in papermaking in that, if the freeness is too low, it is not possible to remove enough water on the paper machine to achieve good sheet structure and strength. Often, mechanical pulps have low freeness due to harsh action imparted to the raw material, which produces fines and particles which plug up the draining paper mat. Many chemical pulping processes using whole-stalk (both bast and core) nonwood fiber source materials have problems with poor freeness, due to characteristics of the core fraction.

[0026] Some embodiments do not suffer from the freeness problems of prior art processes. Indeed, some ARF pulps disclosed herein have high freeness. The freeness is much higher than traditional nonwood pulps eliminating the concern about table capacity on the paper machine when substituting for wood based pulps. As used herein, the term "high freeness" is meant to refer to freeness of at least about 400 mL CSF and above.

[0027] In certain embodiments, the ARF pulp disclosed herein has freeness of at least about 400, 425, 450, 475, 500, 525, or 550 mL CSF.

[0028] In certain embodiments, the ARF pulp has an ISO brightness of about 60% or higher, and strength parameters sufficient for papermaking.

[0029] There are a number of methods of measuring pulp brightness. This parameter is usually a measure of reflectivity and its value is typically expressed as a percent of some scale. The International Standards Organization (ISO) brightness test is used herein. In certain embodiments, the ARF pulp of the disclosure has an ISO brightness of less than 50%. In certain embodiments, the ARF pulp of the disclosure should have an ISO brightness of about 60% or higher (suitable for use in the manufacture of printing and writing grade paper).

[0030] In certain embodiments, the ARF pulp has an ISO brightness of about 60% or higher, about 70% or higher, about 80% or higher, about

84% or higher, about 88% or higher, about 80 to about 90%, or about 90% or higher.

[0031] In another embodiment, the ARF pulp is made from a pulping method comprising cooking a first mixture comprising ARF fibers, water, an alkali, and a delignification selectivity enhancing chemical for a cooking time and at a cooking condition sufficient to form a first pulp having a desired Kappa number of about 15 or less, and strength parameters sufficient for papermaking. The cooking step can comprise a single cooking step to achieve the desired pulp.

[0032] In one embodiment, the fibers used in the pulping method are ARFs. In another embodiment, the ARFs are bagasse or corn stover. In another embodiment, the fibers used in the pulping method are wood fibers, e.g., hard or soft wood fibers.

[0033] Examples of the strength parameters sufficient for papermaking include, without limitation, a tensile of at least about 5.50 km, a tear index of at least about 6.00 mN.m²/g, a burst index of at least about 3.00 kPa.m²/g, where the starting material prior to cooking has a Kappa number of about 60 or greater, and combination thereof.

[0034] The concentration of the alkali in the first mixture may be from about 10% to 30% by weight, about 15% by weight to about 25% by weight, about 20% by weight to about 22% by weight, about 20% by weight to about 22.5% by weight, about 20% by weight, about 21% by

weight, about 22% by weight, about 22.5% by weight, about 24%, or about 27% by weight of the fiber feed (oven dried). An example of the alkali is, without limitation, sodium or potassium hydroxide, which may also contain sulfur chemistries. As used herein, "OD," and "O.D." are oven-dried. Other examples of suitable alkali additive include ammonia and ethanolamine or derivatives thereof.

[0035] Examples of a delignification selectivity enhancing chemical include, without limitation, anthraquinone (AQ) or derivatives thereof.

The concentration of AQ or a derivative thereof in the first mixture may be about 0.2% to about 1.0% by weight, at least about 0.1% by weight, at least about 0.17% by weight, at least about 0.2% by weight, at least about 0.25% by weight, at least about 0.27% by weight, at least about 0.3% by weight, at least about 0.35% by weight, at least about 0.4% by weight, at least about 0.45% by weight, at least about 0.5% by weight, at least about 0.55% by weight, at least about 0.6% by weight, at least about 0.65% by weight, at least about 0.7% by weight, at least about 0.75% by weight, at least about 0.8% by weight, or at least about 0.85% by weight of the OD fiber feed.

[0036] The liquid to dry fiber ratio (L/W) of the first mixture is the total liquid amount compared to completely dry fiber, e.g., the weight of liquor applied to a unit weight of oven dried digester feed. It includes all liquids involved in cooking, and can be from about 4, 5, 6, 7, 8, or 9 to about 10, about 7, or about 8.

[0037] The term "consistency", as used herein in referring to "reaction consistency," "mixture consistency" and to "pulp consistency," denotes percent (%) solids of the reaction mixture, the mixture, or the pulp slurry, e.g., the weight% of a fiber (usually pulp rather than raw fiber) in a pulp/water slurry.

[0038] The cooking conditions may be at a cooking temperature and a cooking pressure. The cooking temperature may be from about 120 °C to about 200 °C, about 150 °C to about 190 °C, or about 165 °C to about 185 °C, about 175 °C, lower than about 175 °C, no higher than 175 °C, about 165 °C, lower than about 165 °C, or no higher than 165 °C. The cooking pressure may be from about 60 psi/g to about 150 psi/g, 120 psi/g to about 150 psi/g, or about 130 psig to about 140 psig.

[0039] The cooking time sufficient to form the first pulp at a cooking condition depends on the condition, and may be from about 15 minutes to about 180 minutes, from about 15 minutes to about 120 minutes, from about 15 minutes to about 90 minutes, from about 30 to about 90 minutes, from about 30 to about 60 minutes, about 53 minutes, about 50 minutes, about 40 minutes, about 35 minutes, or about 34 minutes at the maximum cooking temperature.

[0040] In certain embodiments, the first mixture is heated from a lower temperature to a desired temperature during a first cooking time, and is maintained at the desired temperature for a second cooking time. For example, a desired temperature may be about 90 °C to about 200 °C,

about 120 °C to about 200 °C, about 150 °C to about 190 °C, or about 165 °C to about 185 °C, about 185 °C, about 175 °C, or about 165 °C. The lower temperature may be about room temperature, about 90 °C, about 120 °C, about 150 °C, or about 165 °C. The first cooking time may be about 1 minute to about 120 minutes, about 1 minute to about 90 minutes, about 1 minute to about 60 minutes, about 5 minute to about 120 minutes, about 5 minute to about 90 minutes, about 5 minute to about 60 minutes, or about 60 minutes. The second cooking time may be about 15 minutes to about 180 minutes, about 15 minutes to about 120 minutes, about 15 minutes to about 90 minutes, from about 30 to about 90 minutes, from about 30 to about 60 minutes, about 53 minutes, about 50 minutes, about 40 minutes, about 35 minutes, or about 34 minutes. In certain embodiments, the cooking condition is at a cooking pressure of about 130 psi/g to about 140 psi/g and the desired temperature is about 175 °C. The lower temperature is about 90 °C, the first cooking time is 60 minutes, and the second cooking time is about 40 minutes.

[0041] In certain embodiments, the cooking temperature is from about 120 °C to about 200 °C, and the cooking time is from about 15, 20, or 30 to about 45, 50, 60, 70, 80, or 90 minutes. In certain embodiments, the cooking temperature is from about 150 °C to about 190 °C, and the cooking time is from about 30 to 60 minutes. In certain embodiments, the cooking temperature is from about 165 °C to about 185 °C, and the cooking time is from about 35 to about 45 minutes.

[0042] In certain embodiments, the temperature of the first mixture is dropped in to a digester simulation at the desired temperature. For example, a second mixture having every ingredient of the first mixture except ARFs may be prepared at the desired temperature, then ARFs are added into the second mixture to form the first mixture. The cooking time at the desired temperature may be about 15 minutes to about 180 minutes, about 15 minutes to about 120 minutes, about 15 minutes to about 90 minutes, from about 30 to about 90 minutes, from about 30 to about 60 minutes, about 53 minutes, about 50 minutes, about 40 minutes, about 35 minutes, or about 34 minutes.

[0043] In the prior art, a pulp made from a first cooking step usually has a higher Kappa number or has damaged or destroyed the desired properties of the cellulose. For example, pulp made from bagasse known in the art generally has a Kappa number of about 20 or higher. Such pulp must be further delignified to reduce the Kappa number (e.g., oxygen delignification and/or ozone treatment), and/or bleached by chlorine. Such delignification and/or chlorine treatment are likely to damage the strength and other parameters of the obtained pulp and increase process costs.

[0044] The Kappa number of the first pulp is about 5 or lower, about 7 or lower, about 10 or lower, or about 15 or lower. The first pulp having a Kappa number of 5 or lower can be bleached by TCF or ECF to obtain pulp that is suitable for making paper with desired brightness (e.g. ISO

brightness of less than 50%, about 60% or higher, about 70% or higher, about 80% or higher, about 84% or higher, about 88% or higher, about 80 to about 90%, or about 90% or higher).

[0045] In certain embodiments, the Kappa number of the first pulp decreases as the amount of AQ applied to the cooking process increases (Figure 1).

[0046] H-factor indicates relative speed of lignin dissolution. It depends on cooking time and temperature. H-factor's dependency on temperature is very strong due to delignification temperature dependency. Even a difference of couple of degrees in cooking temperature can make a significant difference in pulp quality. H-factor has been defined so that 1 hour in 100 °C is equivalent with H-factor 1. Generally a higher H-factor in the cooking process is more likely to provide a lower Kappa number of the first pulp.

[0047] H-factor can be calculated by

$$H = \int_0^t e^{(43,2 - \frac{16115}{T})} dt$$

, wherein t is time and T is temperature (Kelvin degree).

[0048] In certain embodiments, the pulping process is performed at a H-factor of about 20 or higher, about 50 or higher, about 100 or higher, about 200 or higher, about 300 or higher, about 400 or higher, about

1000 or higher, about 200, about 300, about 400, about 1000, about 1100 or higher, about 1400 or higher, about 1700 or higher, about 2000 or higher, about 2500 or higher, about 3000 or higher, about 2000 to about 3000.

[0049] In another embodiment, the cooking condition is a pressurized cooking condition. The pulping method further comprises cooling the first pulp to lower than its boiling point before the first pulp is released from the pressurized cooking condition. Cellulose fibers in an alkaline matrix released to atmospheric pressure while still above the boiling point of weak black liquor will suffer damage. The damage may be severe. To avoid such damage, the first pulp may be cooled to within the temperature range of about 70 to about 95 °C before being released from the pressurized cooking condition. In certain embodiments, the blowline is cooled to lower than its boiling point before the first pulp is released from the pressurized cooking condition. In certain embodiments, the first pulp is diluted with cooled wash water to lower its temperature to lower than its boiling point before the first pulp is released from the pressurized cooking condition.

[0050] In another embodiment, the pulping method further comprises a cleaning step. In the cleaning step, unwanted materials (e.g. unwanted mineral material, unwanted cellulosic material, and burned or partially burned fibers) are removed from the fibers before addition of the fibers into the first mixture, from the first mixture, or from a pulp obtained after

one or more steps of the pulping process (e.g. the first pulp, a bleached pulp, and/or a pulp obtained from each stage of bleaching (e.g. chelation, oxygen enriched alkaline peroxide bleaching)).

[0051] Examples of the unwanted mineral material include, without limitation, rocks, sand, rust, soil, tramp metal, trash, and very fine (silicate) particles. These particles may wear out equipment, reduce brightness, affect freeness, and contribute to high ash content. The unwanted mineral material may be removed from the fibers before added into the first mixture, from the first mixture and/or from the pulp.

[0052] Examples of the unwanted cellulosic material include, without limitation, pith (parenchyma cells, and other nonfibrous cells). The unwanted cellulosic materials have little structural paper-making value, but they may use up chemicals and plug the sheet. The unwanted cellulosic materials may be difficult to remove from the pulp. Therefore, removal of the unwanted cellulosic materials as much as is practical from the fibers and/or from the first mixture is desired.

[0053] Examples of the burned or partially burned bagasse particles include, without limitation, carbon and char. Carbon, char, and partially burned bagasse particles may reduce finished pulp brightness if they are microscopic in size. If these particles are large, they will show up as dirt. Removal of these particles from the fibers before added into the first mixture, from the first mixture and/or from the pulp is desired.

[0054] The cleaning steps for raw fibers may comprise a single or multiple cleaning stages. For example, in a first cleaning stage gentle agitation is applied to the raw fibers to provide shear and release some of the pith attached to the fibers.

[0055] In a second cleaning stage, rocks and coarse sands are removed from the raw fibers by centrifugal cleaner.

[0056] In a third cleaning stage, the raw fibers are mixed at a first cleaning consistency in water for a first cleaning time to form a first cleaning mixture, then filtered with a first cleaning screen. A gentle agitation is optionally applied to the mixing step. The first cleaning consistency may be low to moderate, for example, from about 0.5% to about 10%, about 1%, or about 2% by weight. The water can be at a temperature of about 20 °C to about 100 °C, about 80 °C to about 100 °C, or about 60 °C. The first cleaning time can be from 1 minute to about 1 hour, or about 10 minutes. Optionally, a small quantity of detergent may be used to accelerate wetting. The first cleaning screen may be a coarse screen (about 0.5 cm or larger). The first cleaning mixture may be poured through the screen. The fibers which are retained on top of the screen are removed often to prevent forming a thick layer (about 1 cm or less in thickness). Much higher consistencies and much thicker layers prevent separation.

[0057] The fiber purification steps for the first pulp involve the separation of the spent chemicals and dissolved non-pulp materials in a

process known as washing. Washing is also used to denote using a surfactant then rinsing with water removing small unwanted particles both visible to the naked eye and those particles that are microscopic in size. Cleaning involves the separation of the desired fibers from the undesired fibers and other material such as sand, char or material that was not processed completely in the pulping step with systems known as screens and cleaners. Examples of process equipment of the first type would be rotary drum vacuum washers, wash presses and diffusion washing units. Examples of process equipment of the second type would be pressure pulp screens and centrifugal cleaners.

[0058] Additionally, for example, unwanted cellulosic and/or mineral materials may be removed from the pulp by actively rinsing the pulp with clean water. The pulp may be optionally diluted to form a lower consistency (e.g., about 1.0%) before the rinsing. The rinsing step may be carried out in a box with a screen mesh floor, wherein the pulp mat which forms on the mesh is not allowed to accumulate. As soon as a layer of washed pulp begins to form on the mash, it is removed and saved.

[0059] A diffusion washer is a multi stage diffusion unit operating at the cooking conditions to improve the washing efficiency. In certain embodiments, a diffusion unit has 5 or more stages of washing. Optionally, a pressure diffuser is used after each step of washing to allow energy reductions by never cooling the process.

[0060] To achieve good separation during cleaning, it is preferred to maintain a thinner pulp mat formed on the screen. In certain embodiments, the pulp mat has a thickness of less than 1 inch, or less than 0.5 inch before it is removed from the screen. The size of the holes on a screen may be about 1/8 inch, or about 3/8 inch.

[0061] Optionally, the screen may be vibrated during the separation. For example, without limitation, the vibration can be from about 0.1 to about 2 inch, about 0.1 to about 1 inch, about 0.1 to about 0.5 inch, about 0.25 to about 0.5 inch.

[0062] In certain embodiments, prior to digesting, the raw fibers, the first mixture, or the pulp is cleaned by dropping to a screen for separation of unwanted materials. The raw fibers, the first mixture, or the pulp is dropped at an angle other than 90° to prevent plugging. The angle may be about 45° or larger. It is desired to have a consistent pouring speed to feed the screen to keep the material distribution more level and consistent across the screen surface.

[0063] In certain embodiments, unwanted materials are separated from the raw fibers, the first mixture, or the pulp by a vertical hammermill or by a trammel screen. This is the first processing step of preparing the raw bagasse for shipment to the pulp mill and is called moist depithing.

[0064] In another embodiment, the pulping method further comprises bleaching the first pulp to provide a bleached pulp. In certain

embodiment, the pulp composition has an ISO brightness of about 60% or higher, about 70% or higher, about 80% or higher, about 84% or higher, about 88% or higher, about 80 to about 90%, or about 90% or higher.

[0065] The bleaching step may involve chlorine, chlorine dioxide (ECF techniques) or no chlorine compounds (TCF techniques). A bleaching step comprises one or multiple stages. Each stage may or may not include a bleaching agent. Each stage may be performed separately or be performed in combination with another stage at the same time. Optionally, a cleaning step is performed after each stage (e.g., via wash press, diffusion washer, or a diffuser washer). For example, in a C stage, chlorine is applied. In a PO, Ep, P, P1 or P2 stage, hydrogen peroxide is applied. In an E stage, an extraction with sodium hydroxide is applied. In a D, D1, or D100 stage, chloride dioxide is applied. In an Eop stage, sodium hydroxide is applied, and hydrogen peroxide and a small amount of oxygen gas is added. In an O stage, oxygen gas is applied. In a Q stage, a chelating agent is applied to remove metals. In a PO stage, alkaline peroxide and oxygen are applied at the same time to improve peroxide efficacy.

[0066] Optionally a wash is performed after each stage of reaction is completed.

[0067] Chelation is a step to protect peroxide used as a bleaching chemical in the next stage. Examples of chelating agent include, without

limitation, ethylenediaminetetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA), and diethylenetriamine penta(methylene phosphonic acid (DTPMPA). In certain embodiments, the pH of a pulp to be treated is adjusted to 4.0 to remove calcium and other metals. The pulp is treated with a chelating agent (e.g. EDTA, DTPA) and an acid (e.g. H_2SO_4) at a chelation temperature of 80 °C or higher, and for a chelation time of 10 minutes to 30 minutes or longer. When DTPMPA is used no pH adjustment is necessary. The target for all the chelants is primarily Mn, which causes catalytic loss of hydrogen peroxide. The chemicals may be added via a high shear chemical mixer or any other suitable equipment/method known in the art. In certain embodiments, the pulp is adjusted to a consistency of about 5 to about 30%, about 10 to about 30%, about 15 to about 20%, about 10%, about 15%, or about 20% before the chelation treatment. In certain embodiments, the pulp obtained from the chelation stage is washed before proceeding to the next stage. A wash may be performed in a wash press which presses then dilutes and represses the pulp for wash. The wash may be performed by other methods or equipments known in the art.

[0068] In certain embodiments, e.g., where the first pulp has a Kappa number of higher than about 5~15, a chlorine bleaching approach may be first applied to the first pulp to reduce the Kappa value to lower than about 5~15 (C stage), and then the less harmful hydrogen peroxide may substitute for hypochlorite if desired. For example, a C/Eop/PO or a

C/Ep/PO bleach sequence may be applied for the bleaching step replacing prior art sequence C/E/H or C/EOP/H or C/EP/H.

[0069] In certain embodiments, the first pulp has a Kappa number of about 5–15 or less, an ECF or TCF approach is applicable.

[0070] An ECF approach comprises one or more stages selected from the group consisting of D, D100, D1, Ep, D, PO, and Eop. ECF means that at least some chlorine dioxide is used. The “E” in ECF stands for “Elemental” meaning that no chlorine gas *per se* is applied. These replaced older sequences which were commonly C/E/H or its variants.

[0071] A TCF approach commonly comprises one or more stages selected from the group consisting of Q, P, PO, and O. The “T” in TCF stands for Totally. TCF sequences might also include a variety of other chemistries such as ozone “Z”, peracetic acid, Caro’s acid, sodium hydrosulfite, among others.

[0072] In certain embodiments, a TCF approach comprises a Q stage followed by multiple atmospheric peroxides stages or by a single atmospheric P stage followed by a PO stage. In the Q stage, chelation is performed as described supra, with 0.5% chelating agent and 0.4% H₂SO₄ at 80 °C for 30 minutes, and no H₂SO₄ but applying the same conditions if DTPMPA is used. In a PO stage, bleaching is accomplished in a single extreme alkaline peroxide bleaching stage that is enriched

with oxygen to improve peroxide efficacy. Most or even all the brightness gain may be accomplished in the P/PO stage. In certain embodiments, the pulp (e.g., about 5 to about 30%, about 10 to about 30%, about 15 to about 20%, about 10%, about 15%, or about 20%) is mixed with steam, caustic (NaOH, about 2.6% by weight of the dry pulp), oxygen (pressure of 60 psi/g), hydrogen peroxide (about 6.0% to about 9.0 percent, about 6.0% or about 7.0% by weight of the dry pulp), sodium silicate (about 4.0% by weight of the dry pulp), magsulfate (about 0.3% by weight of the dry pulp) at a temperature of about 120 °C for about 120 minutes. This stage may be performed in a high shear pulp/steam/chemical mixture, or any other suitable equipment/method known in the art. The ISO brightness of the bleached pulp is about 60% or higher, about 70% or higher, about 80% or higher, about 84% or higher, about 88% or higher, about 80 to about 90%, or about 90% or higher. The yield may be about 90% of feed fiber or higher, about 94% of feed fiber or higher, about 95% of feed fiber or higher.

[0073] In certain embodiments, a TCF approach has a sequence of Q/P1/Q/P2 and Q/P1/PO and Q/P1/Q/PO, and Q/PO wherein the Q stage and the P and PO stages are the same as described supra. In the P and PO stages, the pulp obtained from a first Q stage (optionally washed, consistency being about 5 to about 30%, about 10 to about 30%, about 15 to about 20%, about 10%, about 15%, or about 20%) is treated with caustic (NaOH, about 0.7% by weight of the dry pulp), hydrogen peroxide (about 1.0% by weight of the dry pulp), sodium silicate (about

4.0% by weight of the dry pulp), magnesium sulfate (about 0.3% by weight of the dry pulp) at a temperature of about 80 °C for about 30 minutes, and the final pH is about 10.6. The ISO brightness of the bleached pulp is about 60% or higher. The obtained pulp is then treated with another Q stage and a P2/PO stage as described supra.

[0074] In another embodiment, a pulping method is carried out as shown in the flow chart of Figure 2. In the bagasse washing step, the bagasse starting materials are washed with white water, i.e., the process water obtained from a paper making system such as process water obtained from different washes as shown in the figure, to provide washed bagasse (which is used for cooking in the digester step) and bagasse wash water effluent (which is lead to the drain), as described supra. After digestion, the resulted pulping mixture is sent for washes by different wash methods as described supra. The obtained wash water effluent is sent for further treatments. The washed bagasse is chelated as described supra, washed as described supra, and then bleached in the bleaching step. Although only one bleaching box is shown in the figure, a single or multiple stage of bleaching may be incorporated, as described supra. In certain embodiments, the washing between the steps may be optional. After the pulp is bleached, it is washed, cleaned, and dried & bailed.

[0075] EXAMPLES

[0076] Example 1. Cleaning of raw fibers

[0077] Bagasse was used as an example of raw fibers. Bagasse was first hydrated for 10 minutes with hot clean water (temperature of water was above room temperature, about 40 °C, or 60 °C), under moderate agitation, at a consistency of 0.5% to 2.0%. Pith and sand were separated from the fibers in a Trammel Screen, which was a rotating drum that lifted and dropped the material and accepted water and pith through 1/8th inch holes up to 1/2" holes. The rejected material was collected and removed from the screen to prevent accumulation, and disposed, and was dried before added into the pulping process. The washing yield was about 80% or higher, or about 85.9%, depending on quality of the bagasse starting material.

[0078] Example 2. Soda AQ pulping of bagasse

[0079] OD bagasse (cleaned as described in Example 1, Kappa number was 89) was treated with sodium hydroxide (20% by weight of the OD bagasse) and AQ (0.3% by weight to the dry weight of OD bagasse) at a liquid to dry fiber ratio of 7 (consistency of about 12.5%), at maximum temperature of about 175 °C for 35 or 40 minutes. Time to the maximum temperature was 60 minutes.

[0080] The target H-factor was 1060, as low as 20, and as high as 3000, and the temperature of the pulping reaction was 120 °C to 185 °C. The Kappa number of the obtained pulp was 4.5.

[0081] Example 3. Washing of pulp

[0082] A pulp obtained from Example 2 was washed in a pressure diffuser washer designed specifically to accomplish all washing with a single unit without introducing undesired modifications to the pulp. The temperature of the wash water was chosen to cool the pulp temperature to about 100 °C, 95 °C, 90 °C, 85 °C, 80 °C or lower. The output went to a bleaching step and was cooled to 100 °C or less to prevent flashing.

[0083] Example 4. Chelation stage of pulp (Q stage)

[0084] A pulp obtained from Example 3 was adjusted to a consistency of 15% and pH 4 by H₂SO₄ (about 0.4% by weight of the dry weight of pulp), then treated with DTPA (0.5% by weight of the dry weight of pulp) at 80 °C for 10 minutes. The pulp obtained was washed in a wash press before proceeding to the next stage.

[0085] Example 5. Alkaline peroxide bleaching of pulp (P2/PO stage)

[0086] The washed pulp obtained from Example 4 was adjusted to a consistency of 15% and proceeding to the P2/PO stage. The pulp (15% consistency) was mixed with steam, caustic (NaOH, 2.6% by weight of the dry pulp), oxygen (pressure of 60 psig), hydrogen peroxide (7.0% by weight of the dry pulp), sodium silicate (about 4.0% by weight of the dry pulp), magnesium sulfate (about 0.3% by weight of the dry pulp) at a temperature of about 120 °C for about 120 minutes in a high shear pulp/steam/chemical mixture. The ISO brightness of the bleached pulp

was 86% or higher, and was up to 89.2. The yield was about 94% of feed fiber or higher. The terminal pH was 10.2.

[0087] Example 6. Cleaning and drying of bleached pulp

[0088] The bleached pulp obtained from Example 5 was diluted to <2% consistency, and processed through centrifugal cleaners to remove sand, soil particles and other dirt and unwanted materials. These cleaners had a 20 psig differential at the cleaner. A 1% yield loss occurred at this stage.

[0089] After the bleached pulp was cleaned, it was formed into a sheet and pressed to 50% dry solid before drying in an air impingement dryer. The minimum dryness was 92%. The sheets were cut to desired size and stacked into bales of desired dimensions and weight. These bales were wrapped and tied and stored for shipment.

[0090] Example 7. ECF bleaching of a pulp obtained from Example 3

[0091] An ECF bleaching having a sequence of D100/E/D was performed on a pulp having Kappa number of 5 or lower.

[0092] D100 stage (low pH, about 2.4, ECF stage to delignify pulp): A pulp having consistency of 10% was treated at 50 °C for 60 minutes at a Kappa factor of 0.25. The final pH was 2.5, and residual chlorine was small to non-detectable.

[0093] Ep stage: The pulp obtained from the D100 stage was treated with hydrogen peroxide (0.50% to 0.8% by weight of the weight of the dry pulp) at 80 °C for 60 minutes. The final pH was 10.5-11.0, and the final ISO brightness of the obtained pulp was about 80-82%. The viscosity of the bleached pulp was high.

[0094] D stage: The pulp obtained from Ep stage was treated with chlorine dioxide (1.2% by weight of the weight of the dry pulp) at 80 °C for 150 minutes. The final pH was 3.5-4.0, the residual chloride dioxide was 0.05%, and the final ISO brightness of the bleached pulp was about 89%. The viscosity of the bleached pulp was high.

[0095] Example 8. TCF bleaching of a pulp obtained from Example 3

[0096] A TCF bleaching having a sequence of Q/P/PO having the following reaction condition was performed on a pulp having Kappa number of 5 or lower.

[0097] Q stage: A pulp having a consistency of 10% was treated with DTPMPA (0.5-0.7% by weight of the weight of the dry pulp) at 80 °C for 30 minutes. The final pH was 7.

[0098] P stage: The pulp obtained from the Q stage was treated with hydrogen peroxide (2.0% by weight of the weight of the dry pulp), sodium hydroxide (1.0-1.1% by weight of the weight of the dry pulp), DTPMPA (0.25% by weight of the weight of the dry pulp), MgSO_4 (0.60% by weight of the weight of the dry pulp), NaSiO_3 (0.50% by weight of the weight of

the dry pulp) at 85 °C for 60 minutes. The final pH was 10.5-11.0, and the final ISO brightness of the obtained pulp was about 80%. The residual was about 0.05%. The viscosity of the bleached pulp was high.

[0099] PO stage: The pulp obtained from the P stage can be treated with hydrogen peroxide (5% by weight of the weight of the dry pulp), DTPMPA (0.25% by weight of the weight of the dry pulp), MgSO_4 (0.60% by weight of the weight of the dry pulp), NaSiO_3 (0.50% by weight of the weight of the dry pulp) at 120 °C for 120 minutes. A final ISO brightness of the bleached pulp can be 88.00%. A viscosity of the bleached pulp can be high.

[00100] Example 9. Benchmark strength of a pulp product made from bagasse

[00101] I) Cleaning of the bagasse starting materials.

[00102] Bagasse # 11 was cleaned by the same procedure as described in Example 1 except that a 3/8" sieve was used instead of the 1/8" sieve.

[00103] II) Cooking

[00104] The cleaned bagasse was treated with sodium hydroxide (22% by weight of the OD bagasse) and AQ (0.2% by weight to the dry weight of OD bagasse) at a liquid to dry fiber ratio of 8.0 (consistency of about 12%), at a maximum temperature of about 165 °C for 35 minutes. Time to the maximum temperature from 90 °C was 60 minutes.

[00105] The target H-factor was 452. The Kappa number of the screened and quick dried pulp was 5.0, the cooking yield was 56.8%, the yield of the screened pulp was 55.8%, total rejects was 1.0% (+ 0.010"), and the viscosity of the pulp was 44.0 mPa.s.

[00106] The pulp obtained was box-washed pulp by first diluting the pulp to a consistency of 1.0%, and then rinsing the pulp in a box with a screen mesh floor, wherein the pulp mat which forms on the mesh was not allowed to accumulate of more than 1 inch. As soon as a layer of washed pulp began to form on the mash, it was removed and saved for the next step of process.

[00107] III) Bleaching

[00108] The washed pulp was bleached by an ECF sequence of D100/Ep/D1 to provide pulp A4420-1-D1 box washed. A duplicate washed pulp sample was bleached by a TCF sequence of Q/P1/PO to provide pulp A4420-2-PO box washed.

[00109] The ECF sequence of D100/Ep/D1 was carried out using the following conditions:

[00110] D100 stage: A pulp having consistency of 10% was treated with ClO_2 (1.15% as Cl_2) at 50 °C for 60 minutes using a Kappa factor of 0.25. The final pH was 2.0, and the residual chlorine was 0.02 g/L (as avail Cl_2).

[00111] Ep stage: The pulp obtained from the D100 stage was treated with hydrogen peroxide (0.5% by weight of the weight of the dry pulp), NaOH (0.7% by weight of the weight of the dry pulp), and MgSO_4 (0.1% by weight of the weight of the dry pulp), at 80 °C for 60 minutes. The final pH was 11.2, and the final ISO brightness of the obtained pulp was about 75.6%. The viscosity of the bleached pulp was very 21.4 mPa.s

[00112] D stage: The pulp obtained from Ep stage was treated with chlorine dioxide (1.5 to 1.7% by weight of the weight of the dry pulp) and NaOH (0.70% by weight of the weight of the dry pulp), at 80 °C for 150 minutes. The final pH was 4, the residual chloride dioxide was 0.09%, and the final ISO brightness of the bleached pulp was about 88.4%.

[00113] The TCF sequence of Q/PO was carried out using the following conditions.

[00114] Q stage: A pulp having a consistency of 10% was treated with DTPMPA (0.5% by weight of the weight of the dry pulp) at 80 °C for 30 minutes. The final pH was 6.6.

[00115] P1 stage. The pulp obtained from the Q stage was treated with hydrogen peroxide (2.0% by weight of the dry pulp), sodium hydroxide (1.1% by weight of the dry pulp), DTPMPA (0.5% by weight of the dry pulp), Magsulfate (0.6% by weight of the dry pulp), Sodium Silicate (1.0% by weight of the dry pulp) at 85C for sixty minutes. The

final pH was 11.2 and the ISO brightness of the pulp was about 67.7%.

The residual peroxide was 1.25%.

[00116] PO stage: The pulp obtained from the P1 stage was treated with hydrogen peroxide (6.0% by weight of the weight of the dry pulp), sodium hydroxide (2.8% by weight of the weight of the dry pulp), DTPMPA (0.5% by weight of the weight of the dry pulp), MgSO_4 (0.60% by weight of the weight of the dry pulp), NaSiO_3 (3.0% by weight of the weight of the dry pulp) at 120 °C for 120 minutes. The final pH was 11.2, and the final ISO brightness of the obtained pulp was about 86%. The residual hydrogen peroxide was about 0.39%.

[00117] Table 1 shows the Kappa number and ISO brightness of pulp A4420-1-D1 box washed (pulp 9-1) and pulp A4420-2-Po box washed (pulp 9-2).

Table 1. Kappa number and ISO brightness of pulp 9-1 and pulp 9-2.

Analysis	Unit	Pulp 9-1	Pulp 9-2
Kappa Number of the pulp before bleaching		4.57	4.57
ISO brightness	%	89	86.5
Overall yield	%	>50	>50

[00118] Table 2 shows benchmark strength of pulp A4420-1-D1 box washed (pulp 9-1) and pulp A4420-2-Po box washed (pulp 9-1) compared with bagasse pulp obtained from a Thailand mill (pulp 9-3), and standard pulps from bagasse (pulp 9-4, bleached bagasse pulp, pulp

atlas pulp #60) at 0 revolution in a TAPPI standard PFI analysis, and
 standard pulps from wood (pulp 9-5, eucalyptus bleached Kraft cenrtl.
 coastl. Brazil pulp, pulp atlas pulp #35) at revolutions of 0, 1000, and
 2000 in a TAPPI standard PFI analysis,.

**Table 2. Benchmark strength of pulps obtained from the
 embodiment, pulp from bagasse from another mill, standard pulp
 from bagasse, and standard pulp from wood**

Analysis	Unit	Pulp 9-1	Pulp 9-2	Pulp 9-3	Pulp 9-4	Pulp 9-5		
24 grams, 0.2 mm gap	Feed/mill gap							
PFI, TAPPI	Revolutions	0	0	0	0	0	1000	2000
C.S. Freeness	mL	538	571	488	484	500	399	362
Basis weight, conditioned	g/m ²	67.30	67.50	66.16	66.79	67.00	66.19	66.9
Bulk	cc/g	1.31	1.32	1.48	1.51	1.74	1.53	1.50
Burst factor		39	35	16				
Burst index	kPa.m ² /g	3.85	3.40	1.57	2.13	0.88	2.40	3.09
Tear factor		66	62	63				
Tear index	mN.m ² /g	6.49	6.09	6.17	6.15	4.40	9.39	9.84
Tensile strength	kN/m	4.37	4.10					
Tensile	km	6.61	6.20	3.26	4.018	2.161	4.568	5.69
Tensile index	N.m/g	64.9	60.8	32.0	39.4	21.2	44.8	55.9
Stretch	%	2.71	2.56	1.87	2.22	1.03	2.63	3.12
Tensile Energy Absorption	J/m ²	84.0	74.2	28.1	41.9	9.3	54.7	80.8
Porosity, Gurley	sec/100ml	32	27	12				
Fold, MIT	count	182	97					
Zero Span, Pulmac (dry)	km	11.0	10.8	8.18	8.94	13.87	15.13	15.5
Optical Properties								
Opacity	%	66.7	66.7		73.14	78.16		
Fiber Quality Analyzer:								
Population	fibers/mg	17,731	17,267	16,263	10,702*	21,943		
AFL, arithmetic	mm	0.51	0.51	0.42	0.522	0.580		
LWAFL	mm	1.04	1.05	0.87	1.14	0.76		
WWAFL	mm	1.77	1.81	1.53	1.90	0.94		
Coarseness	mg/m	0.111	0.113	0.146	0.179	0.079		
Curl, length weighted		0.099	0.109	0.078	0.076	0.102		
Kink index	1/mm	1.15	1.25	0.96	1.03	1.68		
Percent fines < 0.2 mm, arithmetic	%	32.16	30.93	42.39	37.01	17.77		
Percent fines < 0.2 mm, length weighted	%	8.78	8.40	12.62	9.43	3.59		

Bauer McNett Fiber Classification								
retained on + 28 mesh	%	18.6	19.0	11.0				
retained on + 65 mesh	%	37.3	36.5	41.2				
retained on + 100 mesh	%	19.9	19.8	16.5				
retained on + 200 mesh	%	10.3	10.3	12.9				
total retained	%	86.1	85.6	81.6				
finer through -200 mesh	%	13.9	14.4	18.4				

*most likely, an anomaly.

[00119] A standard PFI mill method (TAPPI Test Method T-248) was used to evaluate pulp quality for papermaking. A pulp was “beaten” or “refined” in a laboratory setting for certain revolutions to reflect further processing of the pulp in a mill. A zero revolution number meant no further process was done to the pulp. The data of a standard wood pulp (pulp 9-5) showed that further processing of the pulp lowers the freeness, but improves strength parameters such as burst, tear and tensile parameters. The bagasse pulps obtained from this embodiment (pulp 9-1 and pulp 9-2) with no revolutions had higher freeness, tensile and burst parameters than those of the standard hardwood pulp (pulp 9-5) with or without revolutions. The bagasse pulps obtained from this embodiment (pulp 9-1 and pulp 9-2) with no revolutions had higher tear and stretch parameters than those of the standard wood pulp (pulp 9-5) without revolutions. This showed that the bagasse pulps obtained from this embodiment had very good papermaking quality without further processing necessary for wood pulps.

[00120] Characters of the bagasse pulps obtained from this embodiment (pulps 9-1 and pulp 9-2) were also compared with those of known bagasse pulps (pulp 9-3 obtained from a Thailand mill and pulp 9-4, a standard bagasse pulp from the Pulp Atlas) at different revolutions (Table 3).

Table 3. Selected parameters of bagasse pulps obtained from Soda AQ pulping process

Analysis	PFI, TAPPI	C.S. Freeness	Burst index	Tear index	Tensile	Tensile index	Stre
Unit	Revolutions	mL	kPa.m ² /g	mN.m ² /g	km	N.m/g	%
Pulp 9-1	0	538	3.85	6.49	6.61	64.9	2.71
	200	389	4.49	6.21	7.55	74.0	2.76
	800	230	4.77	5.89	8.14	79.8	2.96
Pulp 9-2	0	571	3.40	6.09	6.20	60.8	2.56
	200	436	4.16	5.78	6.86	67.3	2.74
	800	294	4.49	5.37	7.65	75.3	2.84
Pulp 9-3	0	488	1.57	6.17	3.26	32.0	1.87
	250	362	2.37	6.36	4.38	42.9	2.71
	1000	244	2.90	6.33	5.00	49.0	2.99
Pulp 9-4	0	484	2.13	6.15	4.018	39.4	2.22
	250	344	3.05	5.84	4.819	47.3	2.98
	750	258	3.44	5.84	5.416	53.1	3.1

[00121] Table 3 shows selected parameters of bagasse pulps produced from different sources with different resolutions.

[00122] The freenesses of the pulps obtained from the embodiment (pulp 9-1 and pulp 9-2) were about 10% to about 18% higher than those of the bagasse pulps obtained from other sources (pulp 9-3 and pulp 9-4) when revolutions were 0.

[00123] The burst indexes of pulp 9-1 and pulp 9-2 were about 60% to 150% higher than those of pulp 9-3 and pulp 9-4 when revolutions were 0. Although the burst indexes of pulp 9-3 and pulp 9-4 increased at higher revolutions, the burst index of pulp 9-3 at 1000 revolutions and the burst index of pulp 9-4 at 750 revolutions were still lower than that of pulp 9-1 or pulp 9-2 at zero revolutions.

[00124] The tensile parameters of pulp 9-1 and pulp 9-2 were about 54% to about 100% higher than those of pulp 9-3 and pulp 9-4 when revolutions were 0. Although the tensile parameters of pulp 9-3 and pulp 9-4 increased at higher revolutions, the tensile parameters of pulp 9-3 at 1000 revolutions and the tensile parameters of pulp 9-4 at 750 revolutions were still lower than those of pulp 9-1 or pulp 9-2 at zero revolution.

[00125] The tear and stretch parameters of pulp 9-1 and pulp 9-2 were also higher than those of the pulp 9-3 and pulp 9-4.

[00126] The pulp obtained from the embodiment had significantly higher burst index than that of the reference bagasse pulps, about 60% to about 150% higher.

[00127] The improved strength parameters of pulp 9-1 and pulp 9-2 compared to the reference bagasse pulps were significant and unexpected, and were also found in other pulp produced by the pulping method disclosed in this disclosure from bagasse or other fiber sources (e.g., corn stover, Example 11 disclosed below).

[00128] Example 10. Effect of cleaning in the pulp process on benchmark strength of the final pulp products obtained from soda AQ process

[00129] I) Cleaning of bagasse

[00130] Bagasse # 6 was cleaned according to the procedure as described in Example 1.

[00131] II) Cooking

[00132] The cleaned bagasse was treated with sodium hydroxide (20% by weight of the OD bagasse) and AQ (0.3% by weight to the dry weight of OD bagasse) at a liquid to dry fiber ratio of 7.0 (consistency of about 12.5%), at a maximum temperature of about 175 °C for 34 minutes. Time to the maximum temperature was 60 minutes.

[00133] The target H-factor was 1056, temperature pulping reaction was 175 °C. The Kappa number of the screened pulp was 4.1, the cooking yield was 57.9%, the yield of the screened pulp was 56.6%, total rejects was 1.3% (+ 0.010"), and the viscosity of the pulp was 38.3 mPa.s.

[00134] III) Bleaching

[00135] Pulp A4354-1-P was obtained by bleaching the pulp obtained from the cooking step by a TCF bleaching having a sequence of Q/P having the following reaction condition.

[00136] Q stage: A pulp having a consistency of 10% was treated with DPTA (0.5-0.7% by weight of the weight of the dry pulp) at 80 °C for 30 minutes. The pH was 4.

[00137] P stage: The pulp obtained from the Q stage was treated with hydrogen peroxide (2.0% by weight of the weight of the dry pulp), sodium hydroxide (1.0-1.1% by weight of the weight of the dry pulp), DTPMPA (0.25% by weight of the weight of the dry pulp), MgSO_4 (0.60% by weight of the weight of the dry pulp), NaSiO_3 (0.50% by weight of the weight of the dry pulp) at 85 °C for 60 minutes. The final pH was 10.5-11.0, and the final ISO brightness of the obtained pulp was about 84.75%. The residual was about 0.05%.

[00138] Pulp A4354-2-P was obtained from the same process as the pulp A4354-1-P, further including cleaning the pulp obtained from the cooking step by box-washing before the TCF bleaching.

[00139] Box-washed pulp was obtained by first diluting the pulp to a consistency of 1.0%, and then rinsing the pulp in a box with a screen mesh floor, wherein the pulp mat which forms on the mesh was not allowed to accumulate of more than 1 inch. As soon as a layer of

washed pulp began to form on the mash, it was removed and saved for the next step of process.

[00140] Benchmark strength of pulp A4354-1-P (pulp 10-1) and pulp A4354-2-P (pulp 10-2) are shown in Table 4 below.

Table 4. Benchmark strength of pulp A4354-1-P (pulp 10-1) and pulp A4354-2-P (pulp 10-2)

Analysis	Unit	pulp 10-1	pulp 10-2
24 grams, 0.2 mm gap			
PFI, TAPPI	Revolutions	0	0
C.S.Freeness	mL	465	506
Basis weight, conditioned	g/m ²	66.50	66.43
Bulk	cc/g	1.45	1.41
Burst factor		33	33
Burst index	kPa.m ² /g	3.22	3.23
Tear factor		59	59
Tear index	mN.m ² /g	5.74	5.76
Tensile	km	5.88	6.00
Tensile index	N.m/g	57.7	58.8
Stretch	%	2.31	2.40
Tensile Energy Absorption	J/m ²	63.0	66.3
Porosity, Gurley	sec/100ml	27	24
Zero Span, Pulmac (dry)	km	10.3	10.0
Optical Properties:			
Brightness, ISO	%	84.75	85.6
Opacity	%	68.4	68.1
CIE Color			
L*		95.29	95.53
a*		-0.67	-0.67
b*		2.77	2.53
Hunter Color			
L		93.98	94.27
a		-0.69	-0.69
b		2.81	2.57

[00141] The results show that at 0 revolutions, both pulp A4354-1-P and pulp A4354-2-P have desired strength (e.g., tear, tensile, and burst), and desired C.S. freeness suitable for papermaking. The box-washing step increased C.S. Freeness of the final bleached pulp and provided a more desired product.

[00142] Example 11. Soda AQ pulping of corn stover

[00143] Pulp 11 (pulp L1503-2-Po) was made from corn stover by the following procedures:

[00144] I) Cleaning of corn stover

[00145] Aged damp corn stover was soaked in cold water for 1 hour, refined at 0.080" gap with standard plates, washed on a 4.75 mm sieve, and then washed on a 1.4 m screen.

[00146] II) Cooking

[00147] The cleaned corn stover was treated with sodium hydroxide (20% by weight of the OD corn stover) and AQ (0.2% by weight to the dry weight of OD corn stover) at a liquid to dry fiber ratio of 7.0 (consistency of about 12.5%), at a maximum temperature of about 165 °C for 8 minutes. Time to the maximum temperature was 48 minutes.

[00148] The target H-factor was 200, temperature pulping reaction was 165 °C . The Kappa number of the screened pulp was 5.0, the cooking yield was 56.8%, the yield of the screened pulp was 56.5%, total

rejects was 0.2% (+ 0.010" screen), and the viscosity of the pulp was 101.2 mPa.s.

[00149] III) Pulp cleaning

[00150] The pulp obtained from the cooking step was cleaned with a centricleaner using a consistency of 1.0%, 30 gpm flow, and pressure of 34 psi with lightning mixer. The cleaned pulp was further cleaned by water at a consistency of 0.05%, 30 gpm flow, and pressure of 34 psi with lightning mixer.

[00151] IV) Bleaching

[00152] Pulp L1503-2-Po was obtained by bleaching the cleaned pulp by a TCF bleaching having a sequence of QP1QPO having the following reaction condition.

[00153] Q stage: A pulp having a consistency of 10% was treated with DTPMPA (0.5% by weight of the weight of the dry pulp) and H₂SO₄ (0.35%) at 80 °C for 30 minutes. The initial pH was 4.0.

[00154] P1 stage: The pulp obtained from the Q stage was treated with hydrogen peroxide (1.0% by weight of the weight of the dry pulp), sodium hydroxide (0.8% by weight of the weight of the dry pulp), MgSO₄ (0.3% by weight of the weight of the dry pulp), NaSiO₃ (4.0% by weight of the weight of the dry pulp) at 85 °C for 60 minutes. ISO brightness of the obtained pulp was 73.5%, yield of P1 stage was 98.2%.

[00155] Q-Stage. The pulp obtained from the P1Stage having a consistency of 10% was treated with DTPMPA (0.5% by weight of the weight of the dry pulp) and H₂SO₄ (0.35%) at 80 °C for 30 minutes. The initial pH was 4.0.

[00156] PO stage: The pulp obtained from the Q Stage was treated with hydrogen peroxide (6.0% by weight of the weight of the dry pulp), sodium hydroxide (2.8% by weight of the weight of the dry pulp), NaSiO₃ (4.0% by weight of the weight of the dry pulp), O₂ (pressure measured as 60 psi) at 120 °C for 120 minutes. Final pH was 10.5, residual H₂O₂ was 0.37%, and ISO brightness was 90.8%, stage yield was 95.9%.

[00157] Benchmarking of Pulp 11 is shown below in Table 5.

Table 5. Benchmarking of Pulp 11

Analysis	Unit	L1503-2-Po		
24 grams, 0.2 mm gap				
PFI, TAPPI	Revolutions	0	200	700
C.S. Freeness	mL	486	352	270
Basis weight, conditioned	g/m ²	66.38	66.31	67.14
Bulk	cc/g	1.35	1.31	1.28
Density	g/cc	0.74	0.77	0.78
Burst factor		33	39	43
Burst index	kPa.m ² /g	3.23	3.82	4.17
Tear factor		66	61	60
Tear index	mN.m ² /g	6.43	6.02	5.92
Tensile	km	6.21	7.01	7.25
Tensile index	N.m/g	60.9	68.8	71.1
Stretch	%	2.48	2.56	2.64
Tensile Energy Absorption	J/m ²	71.5	81.7	88.8
Zero Span, Pulmac (dry)	km	11.7	12.1	12.5
Porosity, Gurley	sec/100ml	12	34	63
CIE color:				
L*		96.10	95.89	95.92

a*		-0.54	-0.54	-0.48
b*		1.89	1.74	1.67
Hunter color:				
L		95.01	94.73	94.77
a		-0.57	-0.57	-0.51
b		1.93	1.78	1.71
Fiber Quality Analyzer:				
Population	fibers/mg	23,277		
AFL, arithmetic	mm	0.45		
LWAFL	mm	0.98		
WWAFL	mm	1.80		
Coarseness	mg/m	0.095		
Curl, length weighted		0.152		
Kink index	1/mm	1.59		
Percent fines, < 0.2 mm, arithmetic	%	38.00		
Percent fines, < 0.2 mm, length weighted	%	11.66		
Bauer McNett Fiber Classification:		%		
• retained on + 28 mesh		12.3		
• retained on + 65 mesh		32.8		
• retained on + 100 mesh		17.4		
• retained on + 200 mesh		13.1		
• total retained		75.6		
• fines through - 200 mesh		24.4		

[00158] The results showed that a pulp having very high ISO brightness with desired strength parameters was obtained from corn stover.

[00159] Example 12. Effect of AQ concentration in the cooking process for ARF pulping

[00160] Raw bagasse was washed as described in Example 1 and cooked as described in Example 2 with the parameters summarized in Tables 6 (high H-factor, Cook Numbers L1483-1, L1483-2, L1483-3, L1484-3, A4385) and 7 (low H-factor, Cook Numbers L1486-2, L1488-2,

L1488-3, A4397, A4400) below. The effect of %AQ applied in the cooking process on the Kappa numbers of the obtained pulps shown in Tables 6 and 7 is reflected in Figure 1.

Table 6. Effect of AQ concentration in a soda AQ cooking process of bagasse (high H-factor (~ 1000))

Pulp Number	12-1	12-2	12-3	12-4	12-5
Cook Number	L1483-1	L1483-2	L1483-3	L1484-3	A4385
<u>Cooking:</u>					
NaOH, % on OD fiber weight	20	20	20	20	20
AQ, %	0	0.05	0.1	0.1	0.3
L/W	7.0	7.0	7.0	7.0	7.0
Max. Temperature, C°	175	175	175	175	175
Time to max., min from 90 C°	60	60	60	47	60
Time at max., min.	34	34	34	37	34
<u>End of Cook:</u>					
Residual EA, g/L as Na ₂ O	3.7	2.47	2.93	4.47	2.78
Residual AA, g/L as Na ₂ O	4.63	3.24	3.55	5.24	3.55
H-factor	1055	1067	1078	965	1080
<u>Unbleached Pulp:</u>					
Cooking yield, %	54.9	62*	56.6	52.7	57.3
Total rejects, +0.010", %	0.66	0.50	1.07	0.5	1.00
Screened yield, %	54.2		55.5	52.1	56.3
Kappa, screened, Quick Dry	8.4	6.0	5.5	5.3	5.2
Viscosity, mPa.s	32.1	30.5	26.8	28.7	30.6

Table 7. Effect of AQ concentration in the cooking process (low H-factor (~ 300))

Pulp Number	12-6	12-7	12-8	12-9	12-10
Cook Number	L1486-2	L1488-2	L1488-3	A4397	A4400
O.D. charge, g	400	372.6	400	1523	1513
O.D. solids, %	42.74	41.79	41.79	30.91	36.20

<u>Cooking:</u>					
NaOH, % on wood	20	20	20	20	20
AQ, %	0	0	0.1	0.2	0.2
L/W	7.0	7.0	7.0	8.0	8.0
Max. Temperature, C°	166	166	166	165	165
Time to max., min from 90 C°	47	"Drop-In" cooks		49	36
Time at max., min.	17	20	25	15	21
<u>End of Cook:</u>					
Residual EA, g/L as Na ₂ O	6.48	8.8	9.11	4.64	5.85
Residual AA, g/L as Na ₂ O	7.25	10.0	10.3	5.68	6.88
H-factor	300			308	300
<u>Unbleached Pulp:</u>					
Cooking yield, %	57.5	57.2	57.2	56.2	57.9
Total rejects, +0.010", %	4.5	9.2	4.6	3.2	3.1
Screened yield, %	53.0	48.0	52.6	53.0	54.8
Kappa, screened, Quick Dry	11.3	14.4	9.4	7.2	6.8
Viscosity, mPa.s	38.7	33.8	53.8	53.9	53.7

[00161] Example 13. Articles of Manufacture Made from Agricultural Renewable Fiber Pulp

[00162] An ARF pulp made as described supra was made having a fiber count per milligram of 19,000. A premium grade bath tissue meeting North American Premium Specifications was manufactured using the ARF Pulp by directly substituting minimal amounts of NBSK with the ARF pulp without any refining.

[00163] Examples of other articles of manufacture that can be made from the pulps set forth herein by partially or entirely substituting a prior art wood pulp with an ARF pulp or other pulp composition as described herein include, tissue, printing and writing papers, communication papers,

bleached board, food contact packaging papers such as OGR, bleached packaging grades, liquid packaging, the more exotic papers such as wet strength papers and release liner, recycled linerboard and molded packaging products.

[00164] Although the invention has been described with reference to preferred embodiments and specific examples, it will be readily appreciated by those skilled in the art that many modifications and adaptations of the invention are possible without deviating from the spirit and scope of the invention. Thus, it is to be clearly understood that this description is made only by way of example and not as a limitation on the scope of the invention. All references herein are hereby incorporated by reference.

Claims

1. An article of manufacture made from a pulp composition comprising:
fibers from an agricultural renewable fiber source, wherein the pulp
composition is unbleached and has a Kappa number of about 15 or less,
a high freeness, and a tensile of at least about 5.50 km, a tear index of at
least about 6.00 mN.m²/g, and a burst index of at least about 3.00
kPa.m²/g.
2. The article of manufacture of claim 1 selected from the group consisting
of tissue, printing and writing papers, communication papers, bleached
board, food contact packaging papers, OGR, bleached packaging grades,
liquid packaging, wet strength papers, release liner, recycled linerboard
and molded packaging products.
3. The article of manufacture of claim 1, wherein the Kappa number is about
10 or less.
4. The article of manufacture of claim 1, wherein the Kappa number is about
5 or less.
5. The article of manufacture of claim 1, wherein the agricultural renewable
fiber source is bagasse or corn stover.
6. The article of manufacture of claim 2, wherein the agricultural renewable
fiber source is bagasse or corn stover.

7. The article of manufacture of claim 3, wherein the agricultural renewable fiber source is bagasse or corn stover.
8. An article of manufacture made from a pulp composition comprising fibers from an agricultural renewable fiber source, wherein the pulp composition has an unbleached Kappa number of about 15 or less, a high freeness, and strength parameters sufficient for papermaking.
9. The article of manufacture of claim 8, wherein the pulp composition has a tensile of at least about 5.50 km, a tear index of at least about 6.00 mN.m²/g, and a burst index of at least about 3.00 kPa.m²/g.
10. The article of manufacture of claim 8, wherein the ISO brightness is less than 50% ISO.
11. The article of manufacture of claim 8, wherein the ISO brightness is about 70% or higher.
12. The article of manufacture of claim 8, wherein the ISO brightness is about 80% or higher.
13. The article of manufacture of claim 9, wherein the ISO brightness is about 80% or higher.
14. The article of manufacture of claim 8, wherein the ISO brightness is about 88% or higher.
15. The article of manufacture of claim 9, wherein the ISO brightness is about 88% or higher.

16. The article of manufacture of claim 8, wherein the ISO brightness is about 90% or higher.
17. The article of manufacture of claim 9, wherein the ISO brightness is about 90% or higher.
18. The article of manufacture of claim 8, wherein the agricultural renewable fibers are bagasse or corn stover.
19. The article of manufacture of claim 9, wherein the agricultural renewable fibers are bagasse or corn stover.
20. The article of manufacture of claim 13, wherein the agricultural renewable fibers are bagasse or corn stover.
21. The article of manufacture of claim 15, wherein the agricultural renewable fibers are bagasse or corn stover.
22. The article of manufacture of claim 18, wherein the agricultural renewable fibers are bagasse or corn stover.
23. The article of manufacture of claim 8 selected from the group consisting of tissue, printing and writing papers, communication papers, bleached board, food contact packaging papers, OGR, bleached packaging grades, liquid packaging, wet strength papers, release liner, recycled linerboard and molded packaging products.
24. The article of manufacture of claim 9 selected from the group consisting of tissue, printing and writing papers, communication papers, bleached

board, food contact packaging papers, OGR, bleached packaging grades, liquid packaging, wet strength papers, release liner, recycled linerboard and molded packaging products.

25. An article of manufacture made from a pulp composition comprising an agricultural renewable fiber pulp made from a pulping method comprising: providing a first mixture comprising the reaction products of:

agricultural renewable fibers,

water,

anthraquinone or derivative thereof having concentration of about 0.1% by weight or greater of the dry fiber, and
an alkali,

wherein the mixture has a liquid to dry fiber ratio from about 4 to about 10, and an initial Kappa number of about 60 or greater; and reacting the mixture for a cooking time and at a cooking condition sufficient to form a second mixture having a Kappa number of about 15 or less, high freeness, and strength parameters sufficient for papermaking.

26. The article of manufacture of claim 25, wherein the strength parameters sufficient for papermaking are selected from the group consisting of a tensile of at least about 5.50 km, a tear index of at least about 6.00 mN.m²/g, a burst index of at least about 3.00 kPa.m²/g, or a combination thereof.

27. The article of manufacture of claim 26, wherein the cooking condition and cooking time provides an H-factor of about 200 or higher.
28. The article of manufacture of claim 27, wherein the H-factor is about 1000 or higher.
29. The article of manufacture of claim 26, wherein the second mixture has a Kappa number of about 10 or less.
30. The article of manufacture of claim 26, wherein the second mixture has a Kappa number of about 5 or less.
31. The article of manufacture of claim 25, wherein the agricultural renewable fibers comprise bagasse or corn stover.
32. The article of manufacture of claim 26, wherein the pulping method further comprises bleaching the second mixture.
33. The article of manufacture of claim 25, wherein the agricultural renewable fiber pulp has an ISO brightness of about 60% or higher.
34. The article of manufacture of claim 25, wherein the agricultural renewable fiber pulp has an ISO brightness of about 70% or higher.
35. The article of manufacture of claim 25, wherein the agricultural renewable fiber pulp has an ISO brightness of about 80% or higher.
36. The article of manufacture of claim 25, wherein the agricultural renewable fiber pulp has an ISO brightness of about 85% or higher.
37. The article of manufacture of claim 25, wherein the agricultural renewable fiber pulp has an ISO brightness of about 90% or higher.

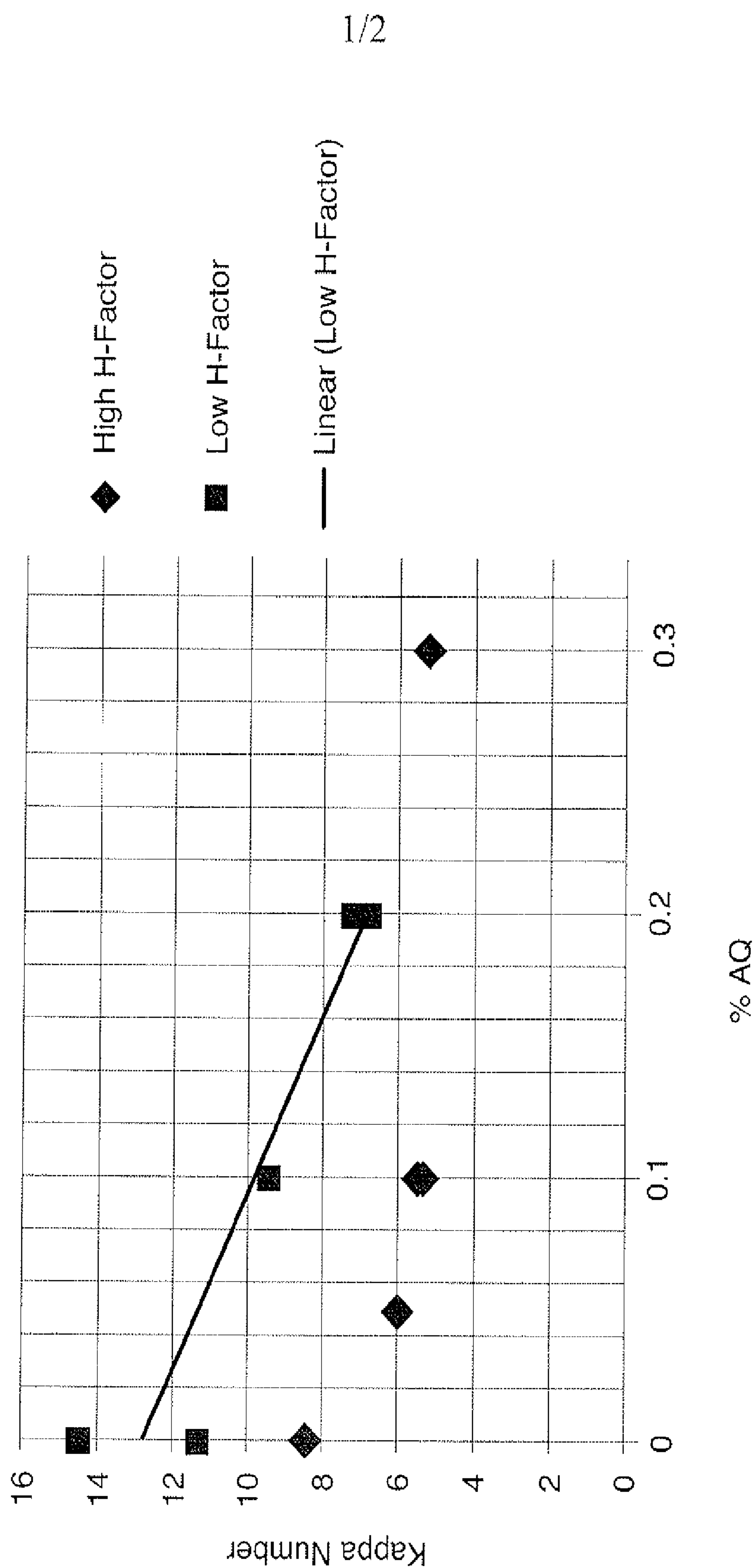


FIGURE 1

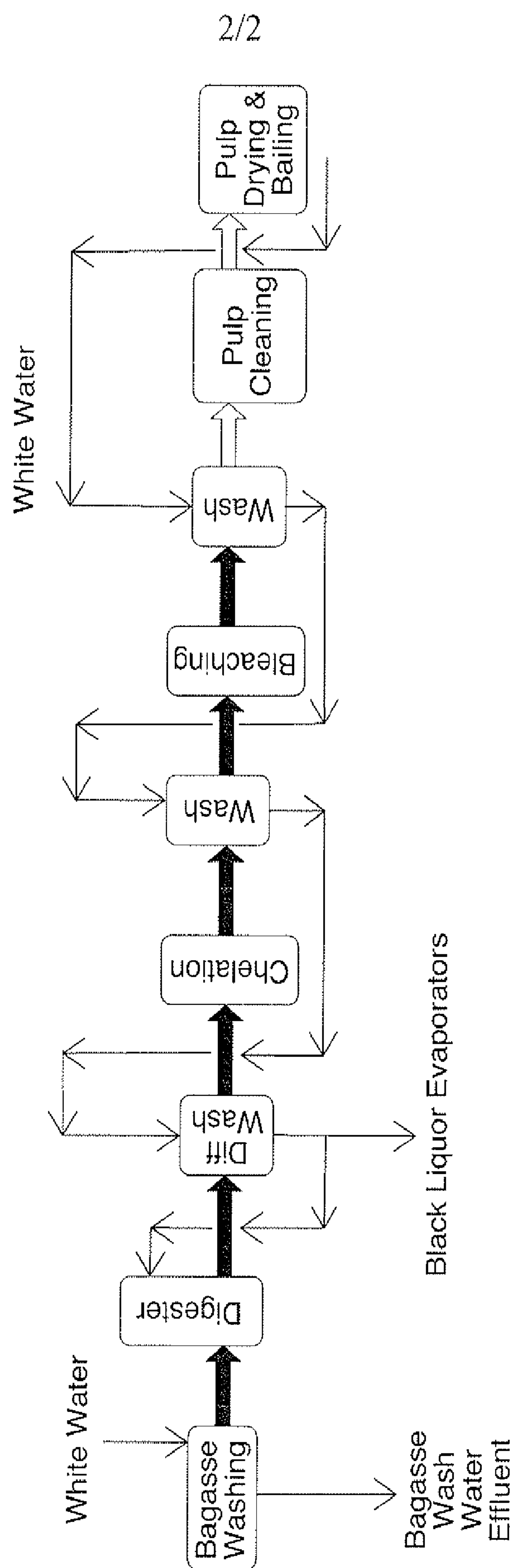


FIGURE 2

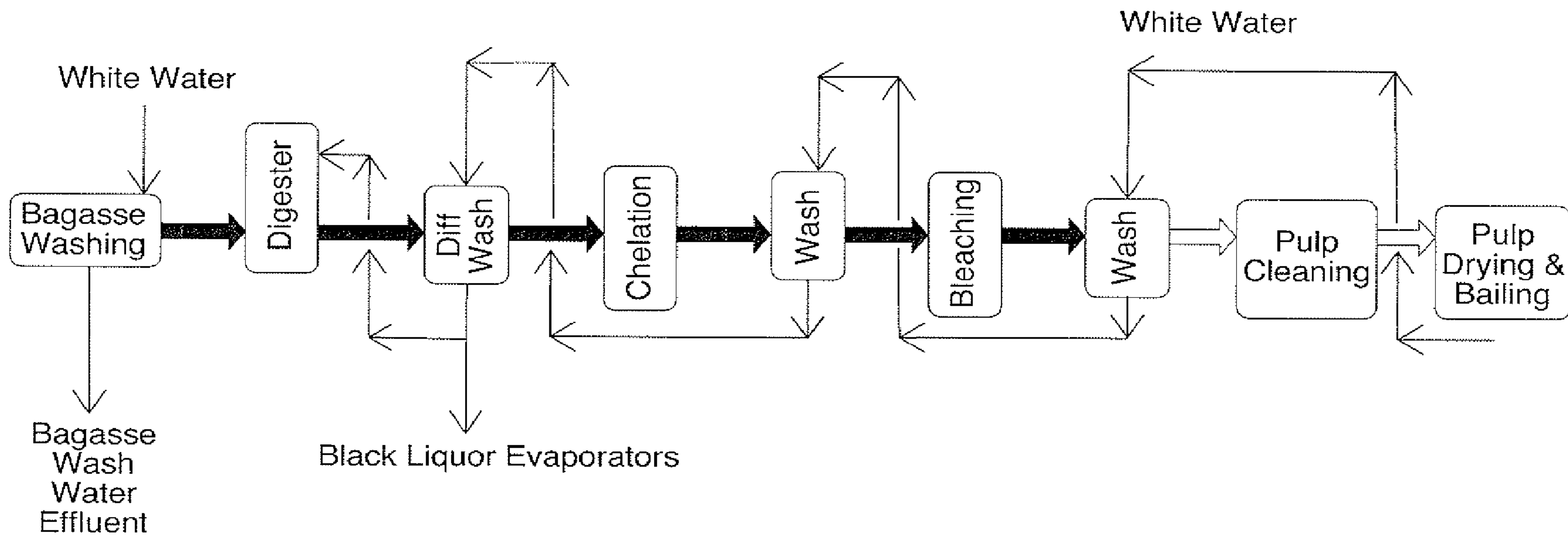


FIGURE 2