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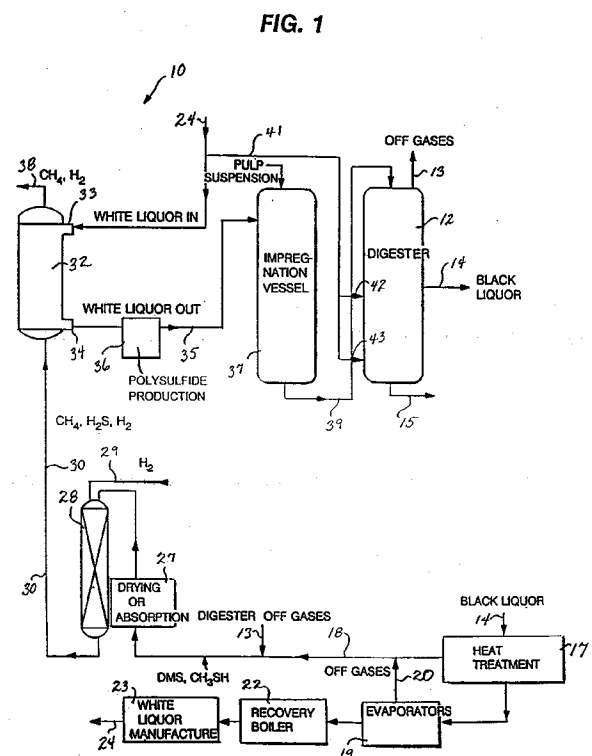
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Multi-level sulfide content.

Paper pulp (e.g. kraft pulp or sulfite pulp) is produced utilizing at least two different supplies (35, 41) of cooking liquor (e.g. white liquor), having different percentages of lignin reaction enhancing or carbohydrate degradation slowing chemicals (e.g. one having low sulfide content, and the other high sulfide content). The high sulfide content supply is typically used to impregnate the pulp (in 37), while the second supply is used in other cooking stages (e.g. digester 12), whether co-current or countercurrent. At least 60% of the sulfide of the cooking chemicals may be provided in the first supply (35). Some of the sulfide in the first supply is desirably provided in the form of polysulfide or elemental sulfur. When about 2% polysulfide on wood is utilized yield is significantly increased. Utilizing multiple chemical (e.g. sulfide) content supplies results in an optimum viscosity/kappa ratio and/or pulp strength properties for the pulp produced.



For many years it has been known that a higher sulfide concentration in white liquor for kraft pulping in the pulp and paper industry (i.e. higher white liquor sulfur content) could produce kraft pulp with higher viscosity and better physical properties. It has also been known that the beneficial effect of higher white liquor sulfur content is more profound in the early stages of the kraft cook than in the later stages. However in the past there have been a number of technical and practical concerns and conditions which have precluded practical utilization of these concepts. Similarly maximum utilization has not been commercially made of the known ability of polysulfide to stabilize carbohydrates and wood against degradation during chemical pulping by oxidatively converting the reducing end groups in celluloses and hemi-cellulose to carboxylic groups. (See U.S. patent 2,944,928.)

According to the most specific aspects of the present invention, the concepts described above are utilized in a practical manner to provide kraft pulp that has an optimum viscosity/kappa ratio, and/or good strength properties, and with good yield. The invention is applicable to a wide variety of different kraft cooking processes, both batch and continuous. For example the invention can be utilized in continuous digesters having an impregnation zone, or in cooking systems utilizing a separate impregnation vessel from the continuous digester, or in batch digesters. The invention can also be utilized in association with co-current movements of white liquor with the pulp, or countercurrent movements, such as are provided in the commercial digesting process marketed by Kamy, Inc. of Glens Falls, New York under the trademark "MCC".

White liquor is that treatment liquid in a kraft process which contains the active cooking chemicals, sodium hydroxide (NaOH) and sodium sulfide (Na₂S); or white liquor in an extreme situation may contain substantially only NaOH as active ingredient. According to standard practice, the white liquor cooking sulfur content is maintained in the range of 25-35% (this overall sulfur content ratio is the amount of sodium sulfide to the sum of sodium sulfide and sodium hydroxide applied to the whole cooking process), and according to standard practice in the art, a sulfur content level below 15% results in a deterioration in the cooking rate and pulp quality. During the production of kraft pulp, residual or "black liquor" containing the reaction products of lignin solubilization is withdrawn from the digester, concentrated, and burned in a recovery furnace to yield an inorganic smelt of sodium carbonate and sodium sulfide. The smelt is dissolved to form green liquor which is reacted with quick lime (CaO) to convert the sodium carbonate into sodium hydroxide and thereby regenerate the original white liquor.

According to the present invention, it has been found that by making two (or more) supplies or streams of white liquor, with different sulfur contents, and applying them to different portions in the kraft cycle, significantly improved results can be achieved. In fact it has been found that it is highly desirable to add the majority of the sulfide in the total white liquor (total cooking chemical) -- at least about 60-90%, in fact even almost all the sulfide -- at the initial stages (e.g. impregnation) of the kraft cycle, while adding white liquor with primarily only sodium hydroxide at the later stages (e.g. co-current or countercurrent cooks). Practicing the invention, it is possible to optimize the viscosity/kappa ratio of the produced pulp for any given level of sulfur content, and/or to optimize pulp strength properties. The increase can be dramatic, easily on the order of 25% for conventional cooks with multiple white liquor additions (co-current), about the same increase for modified continuous cooking (MCC™), and 15% or more for extended modified continuous cooking (EMCC™). Comparable increases occur for batch treatment too.

When about 2% polysulfide on wood, expressed as elemental sulfur, is provided in the white liquor, a yield equal to kappa 18-20 for a conventional kraft cook is produced with a kappa of about 12.5, and pulp with a viscosity comparable to conventional cook kraft pulp at a kappa of about 26 is produced. Elemental sulfur (in dry or slurry form) may be used instead of polysulfide; elemental sulfur is about 60-75% as effective as polysulfide.

While the exact source of the sulfur for producing the high sulfur content stream or supply of white liquor according to the invention is not critical, one exceptionally good source that allows a practical, industrial scale process to be practiced is that shown in U.S. patent 4,929,307 wherein sulfate black liquor is heated to above the cooking temperature so as to split the macro-molecular lignin fraction, to produce sulfur containing off gases. Those off gases may be reacted to produce primarily methane and hydrogen sulfide, and then brought into contact with sulfur depleted white liquor from the normal chemical manufacturing facility of the pulp mill, to produce an extremely high sulfur content white liquor, the hydrogen sulfide being selectively absorbed into the white liquor. That high sulfur content white liquor may then be acted upon to produce at least some significant portions of polysulfide, and then utilized in early stages of the kraft cook.

According to one specific aspect of the present invention, a method of producing kraft pulp from cellulosic comminuted fibrous material utilizing white liquor, is provided. It comprises the following steps: (a) Making at least two streams of white liquor, including a second stream having relatively low sulfur content, and a first stream having relatively high sulfur content, substantially higher than the sulfur content of the second stream. (b) Impregnating the cellulosic comminuted fibrous material with the first stream of white liquor. (c) Cooking the cellulosic comminuted fibrous material under kraft cooking conditions, in a cooking zone with cooking chem-

icals to produce kraft pulp. (d) Supplying the second stream of white liquor to the cooking zone as cooking chemicals. And, (e) washing the kraft pulp produced.

According to another specific aspect of the present invention there is provided a method of producing kraft pulp comprising the following steps: (a) Treating a slurry of cellulosic fibrous material in a plurality of consecutive stages with white liquor, including at least first and second stages, using a first supply of white liquor to the first stage and a second supply to the second stage. (b) Subjecting the material treated with white liquor to cooking conditions in at least one stage of the stages to effect kraft cooking thereof, and producing black liquor. (c) Recovering sulfur from the black liquor. And, (d) adding the recovered sulfur to the first supply of white liquor to significantly increase the sulfur content thereof so that it is greater than the sulfur content of the second supply.

According to still another specific aspect of the present invention there is provided a method of producing kraft pulp comprising the steps of: (a) Treating cellulosic comminuted fibrous material in a first stage with a first supply of white liquor. (b) Treating the material in a second stage with a second supply of white liquor. And, (c) controlling the relative sulfur contents of the first and second supplies of white liquor so as to optimize the viscosity/kappa ratio and/or physical strength properties of the kraft pulp produced.

While the invention will primarily be described in this application with respect to kraft cooking, there is a broader aspect of the present invention. According to the broadest aspect of the present invention, any lignin reaction enhancing or carbohydrate degradation slowing chemicals are targeted to one or more specific parts of the cook, such as the impregnation, co-current, or countercurrent stages. Thus the invention is applicable not just to kraft white liquor, but to sulfite process cooking liquors (containing a cationic base), anthraquinone, derivatives of or equivalents to anthraquinone, or the like. The anthraquinone may replace all or some of the sodium sulfide in a cooking liquor containing NaOH, or may be used in other liquor compositions.

According to the broadest aspect of the present invention, a method of treating comminuted cellulosic fibrous material with cooking liquor to obtain cellulosic pulp, is provided. The method comprises the following steps: (a) Providing at least first and second cooking liquors, including a first cooking liquor having a first concentration of lignin enhancing or carbohydrate degradation slowing chemical, and a second cooking liquor having a second concentration of that lignin enhancing or carbohydrate degradation slowing chemical, the second concentration being from zero to much less than the first concentration. (b) Cooking the comminuted cellulosic fibrous material in several cook stages. (c) Targeting the first cooking liquor to one or more, but less than all, of the cook stages, to provide cooking liquor for that one or more stages; and (d) utilizing the second cooking liquor in at least one cook stage in which the first cooking liquor is not utilized.

The cooking liquor utilized above may be a kraft cooking liquor, sulfite cooking liquor, or the like. It may contain a cationic base, sodium sulfide, anthraquinone or its derivatives or equivalents, or the like, and the first liquor may be targeted to an impregnation stage, co-current cook stage, or countercurrent cook stage.

It is the primary object of the present invention to provide a substantially improved cook cycle for the production of paper pulp. This and other objects of the invention will become clear from an inspection of the detailed description of the invention, and from the appended claims.

BRIEF DESCRIPTION OF THE DRAWING

FIGURE 1 is a schematic view of exemplary apparatus for practicing an exemplary method according to the present invention.

DETAILED DESCRIPTION OF THE DRAWING

FIGURE 1 illustrates exemplary apparatus for use in a kraft pulping process. However, as indicated above, the invention is applicable to other processes for the production of paper pulp from comminuted cellulosic fibrous material in which any lignin reaction enhancing or carbohydrate degradation slowing chemicals are targeted to one or more specific parts of the cook, such as the impregnation, co-current, or countercurrent stages.

In a typical kraft pulping process, as illustrated in FIGURE 1, a digester 12 -- which preferably is a continuous digester such as that sold by Kamy, Inc. of Glens Falls, New York, but may be a batch digester -- has a stream of off gases 13, and black liquor (residual white liquor containing the reaction products of lignin solubilization) is withdrawn at an intermediate position as indicated at 14, while the kraft pulp produced is discharged at 15. When the black liquor in line 14 is discharged, it may be passed directly to black liquor evaporators, and preferably it is subjected, somewhere in the evaporator chain, to a heat treatment process at step 17 to produce off gases in line 18. The heat treatment of block 17 is preferably that described in U.S. patent 4,929,307. After heat treatment at 17 the black liquor passes to evaporators 19 (evaporators 19' may concentrate the black liquor before heat treatment 17 too), which also produce off gases in line 20, then to a conventional recovery boiler 22, with conventional white liquor manufacture at block 23, to produce white liquor in line 24 having depleted

sulfur content.

The off gases in line 18 -- which may include only those from the heat treatment 17, or also those from the digester line 13, only and from the black liquor evaporators in line 20, or a combination of any two of them -- are preferably first subjected to a drying or absorption stage (as indicated schematically at 27 in FIGURE 1) in order to remove a majority of the water vapor. The removal of the water vapor increases the concentration of organic sulfur gases. Step 27 is accomplished by drying the gas stream by any conventional means and/or by absorbing or adsorbing the organic portion of the gas onto a solid, or additionally by absorbing the off gas into one of any non-polar liquids (e.g. kerosene or mineral oil). Treatment may be provided of a liquid mixture, but preferably according to the invention further treatment is of the concentrated gas.

The next steps in the treatment of the off gases as illustrated in FIGURE 1 are to add hydrogen, and then pass the gas in the presence of the added hydrogen past a hydrogen desulfurization catalyst. This may be accomplished, for example, in the hydrogen desulfurization (HDS) unit 28, with the hydrogen gas from line 29 added to the unit 28 along with the gas in line 18. The hydrogen gas in line 29 can come from any source (e.g. be purchased, from water electrolysis, etc.). It is preferred that the hydrogen desulfurization catalyst consist essentially of a transition metal-molybdenum alloy, particularly a nickel molybdenum or cobalt molybdenum alloy.

Typically, in gaseous processing, the product gas stream in line 30 is further acted upon. The gas stream in line 30 contains primarily methane, and hydrogen sulfide, with hydrogen also present. Preferably the hydrogen sulfide is then separated out from the gas in stream 30. While the hydrogen sulfide may be separated as a gas and then used in its gaseous form in conventional pulping techniques, it may be fed to a scrubber 32 in which it is brought into contact with a caustic solution, preferably kraft white liquor, which contains sodium hydroxide and most likely at least some sodium sulfide. While in the preferred embodiment illustrated in the drawings white liquor is utilized, under some circumstances green liquor may be advantageously utilized, with white liquor subsequently made from the green liquor.

White liquor from line 24 is passed into inlet 33 of scrubber 32, the hydrogen sulfide being absorbed in the white liquor and thereby significantly enhancing its sulfur content. The significantly enhanced sulfur content white liquor then passes through the outlet 34 of the scrubber into line 35, to be used in the pulping process. Desirably, the white liquor in line 35 passes through a polysulfide treatment stage, as illustrated at 36, and then to the impregnation vessel 37 (if a separate impregnation vessel is used) or the like, to be utilized in the pulping cycle. Elemental sulfur may be added at 36 instead of polysulfide.

The gas stream that remains, in line 38, contains primarily methane, but also some hydrogen. Ultimately, the gas in line 38 may become the source of the hydrogen for line 29.

According to the invention, the high sulfur content white liquor in line 35 is provided at an early stage of the cook, e. g. at the beginning of the impregnation vessel 37, or impregnation stage if impregnation takes place in the digester 12 itself, or at multiple-places in the impregnation zone and/or vessel 37. A countercurrent impregnation flow may be provided, in which case the higher sulfur content liquor is added near the end of the impregnation stage. Part of the sulfide depleted white liquor in line 24 is passed into line 41, and it is then introduced into the cook, preferably at multiple locations, as indicated at 42 and 43 in FIGURE 1.

According to the invention, where the low sulfur content white liquor in line 41 is introduced into the kraft cook may vary widely. For example, it may be added to the middle of the impregnation vessel 37, at one, two, or more co-current stages in the digester 12, or at one, two, or more countercurrent stages in the digester 12 (e.g. for modified continuous cooking, or extended modified continuous cooking). Of course, the liquor in line 41 may also be utilized in a batch process.

While the drawing illustrates only two streams or supplies of white liquor, 35, 41, having different sulfur content, as many different sulfur content streams as desired may be produced. For example two series connected units 32 may be utilized, the first producing the highest sulfur content level white liquor, while the second produces an intermediate (between lines 35 and 41) sulfur content level white liquor. The intermediate sulfidity white liquor is added earlier in the cook than the white liquor in line 41.

The relative amount of sulfur content of the white liquor added at various stages within the kraft cycle may also be varied widely according to the invention. For example, if the kraft pulping process is to be a multi-level conventional cook, that is white liquor is added at two or more points in the cook and flows co-currently with the pulp, then about 60% of the total cooking chemical is added to the impregnation vessel (e.g. in line 35), while about 25% is added to the first co-current stage (e.g. at 42) and about 15% to the second co-current stage (e.g. at 43). In this procedure, preferably the amount of sulfide provided in line 35 is about 60-90%, and if practical may be almost 100% of the total sulfide in all of the white liquor streams, that is the white liquor in stream 41 is substantially fully sulfide depleted. The stream in line 35 in this embodiment may be made by manufactured by passing 35-65% of the total volume of white liquor through the unit 32, the remaining 65-35% of the white liquor being added through line 41. According to another embodiment, about 35% of the total volume of white

liquor is passed through unit 32, and this high sulfur content white liquor is then added to the top circulation in the conventional impregnation vessel 37. The sulfide-depleted white liquor in line 41 is added to middle circulation in the vessel 37 in the amount of about 25-35% of the total cooking chemical from white liquor, while about 20-25% of the total cooking chemical, in the sulfide depleted white liquor in line 41, is added to the continuous digester 12 first cooking circulation.

The low sodium sulfide content liquor in line 41 may also be added at 44 to an oxygen delignification or bleaching stage 45 as a source of sodium hydroxide.

When utilizing the multiple level sulphitity white liquors according to the invention in modified continuous cooking and extended modified continuous cooking sequences, the viscosity to kappa ratio may be increased by about 0.2-0.3 units if almost all sulfide is added to the impregnation stage (e.g. in line 35 to vessel 37). Preferably at least about 60% (e.g. 60-90%) of the total sulfur content is added in the impregnation stage (line 35), the total volume of white liquor added in line 35 being about 40-65% of the total volume of white liquor used in the pulping process.

In stage 36, polysulfide is added to the white liquor. For example, this can be done by the MOXY (TM) process in which some of the sodium sulfide in the white liquor is partially oxidized to produce polysulfide, or by other known polysulfide processes. Alternatively, in stage 36 polysulfide from an external source may merely be introduced into the white liquor, e.g. polysulfide produced by reacting elemental sulfur with sulfide ions in an aqueous solution under proper conditions; or elemental sulfur may be added to the white liquor instead of polysulfide.

The amount of polysulfide produced, or added, in stage 36 is about 0.5%-8% on wood, expressed as elemental sulfur. Typically, about 2% polysulfide is desirable. If 2% polysulfide is used in conjunction with extended modified continuous cooking, a kraft pulp with a kappa of about 12.5, a viscosity of about 33.7 cp, and a yield of about 44.6% can be made. This yield is equal to that of a conventional cook or extended modified continuous cook pulp at a kappa of about 18-20 without polysulfide, and the viscosity is equivalent to that of a conventional cook pulp at kappa 26, or an extended modified continuous cook pulp at kappa 17.

If an amount of elemental sulfur equivalent to about 0.5-8% polysulfide is used, the results are about 60-75% as good as when polysulfide is used.

Utilizing the apparatus schematically illustrated in the drawings, various methods may be practiced according to the invention. According to one method:

- (a) Two (or more) streams of white liquor, 35, 41, are made up, the first stream (35) having relatively high sulfur content, and the second (41) relatively low sulfur content (even approaching zero).
- (b) Cellulosic comminuted fibrous material (e.g. wood chips) are impregnated with the first stream 35 (e.g. in vessel 37).
- (c) The material is cooked under kraft cooking conditions, in a cooking zone (in vessel 12) with cooking chemicals (the sodium hydroxide and sodium sulfide in the white liquor) to produce kraft pulp.
- (d) The second stream, 41, of white liquor is supplied to the cooking zone (e.g. digester 12) as cooking chemicals; and
- (e) the kraft pulp is washed (e.g. in a wash zone in digester 12, and/or in a separate wash vessel).

According to another aspect of the invention, a slurry of wood chips is treated in a plurality of consecutive stages (e.g. impregnation stage, first and second co-current or countercurrent cooking stages) with white liquor using first and second supplies, differing in the sulfur content thereof. The chips are treated with white liquor under cooking conditions (e.g. in digester 12) in at least one stage, to effect kraft cooking thereof. Black liquor is withdrawn (at 14) and sulfur is recovered from the black liquor, as by heating treating it (at 17) according to the process of US Patent 4,929,307, evaporating it (in 19), etc. (see 22 and 23 in FIGURE 1). The recovered sulfur is added to the first supply of white liquor, as in unit 32, to significantly increase the sulfur content thereof, so that the sulfur content of the liquor in line 35 is substantially greater than that in line 24 (which is sulfur depleted, and may be near zero). The relative sulfur contents of the white liquors in lines 35 and 24 are controlled so as to optimize the viscosity/kappa ratio and/or physical strength properties.

The invention allows advantageous production of kraft pulp to be practiced on an industrial scale -- that is, larger production than reasonably possible in a laboratory, with complete chemical recovery.

The invention may be illustrated by various examples.

Tables IA-IE provide the results of laboratory batch cooks using split white liquor streams with variable sulfur content, according to the invention, and conventional cooks for comparison purposes. In these tables, "CK" means conventional kraft cooking, "MCK" means kraft cooking with multiple introductions of white liquor, with more than one co-current cooking stage, "MCC" refers to Kamy, Inc.'s trademarked modified continuous cooking process in which multiple introductions of white liquor are provided, and a countercurrent cook stage, and "EMCC" refers to Kamy, Inc.'s trademarked extended modified continuous cooking process in which a second countercurrent cook is provided.

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Table II illustrates the advantages achieved when polysulfide is used. The liquid to wood ratio for all cooks in Table II is 4/1. "Sulfidity" refers to sodium sulfide content.

The wood utilized in all of TABLES IA-E and II is southern pine from the Mississippi area. However, the results are applicable to a wide variety of wood species.

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TABLE IA

SPLIT WL WITH VARIABLE SULFIDITY (MCK)

| Cook number Type | CONVENTIONAL KRAFT (CK) | | | | SPLIT WL WITH VARIABLE SULFIDITY (MCK) | | | | | | | |
|----------------------|-------------------------|-------------|-------------|-------------|--|--------------|--------------|--------------|--------------|--------------|--------------|--|
| | A2797 CK | A2798 CK | A2800 CK | A2805 CK | A2793 MCK | A2801 MCK | A2794 MCK | A2802 MCK | A2821 MCK | A2807 MCK | A2856 MCK | |
| Total EA, % Na2O | 14.5 | 14.5 | 16.0 | 16.0 | 14.5 | 16.0 | 14.5 | 16.0 | 16.0 | 16.0 | 16.0 | |
| Impregnation | 14.5 | 14.5 | 16.0 | 16.0 | 8.7 | 9.6 | 8.7 | 9.6 | 9.6 | 9.6 | 9.6 | |
| 1st co-current | - | - | - | - | 3.6 | 4.0 | 3.6 | 4.0 | 4.0 | 4.0 | 4.0 | |
| 2nd co-current | - | - | - | - | 2.2 | 2.4 | 2.2 | 2.4 | 2.4 | 2.4 | 2.4 | |
| Overall sulfidity, % | 35.2 | 30.2 | 30.2 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.1 | 30.2 | 30.2 | |
| Impregnation | 35.2 | 30.2 | 30.2 | 30.0 | 30.0 | 30.0 | 20.0 | 20.0 | 36.9 | 36.9 | 43.7 | |
| 1st co-current | - | - | - | - | 30.0 | 30.0 | 60.0 | 61.0 | 20.2 | 20.2 | 10.0 | |
| 2nd co-current | - | - | - | - | 30.0 | 30.0 | 20.0 | 20.0 | 20.2 | 20.2 | 10.0 | |
| Screened yield, % | 47.3 | 47.4 | 48.3 | 45.4 | 48.3 | 48.5 | 47.9 | 46.2 | 46.7 | 46.3 | 46.4 | |
| Kappa number | 29.3 | 34.2 | 26.7 | 23.1 | 39.8 | 28.5 | 39.6 | 28.2 | 26.5 | 25.9 | 25.6 | |
| Viscosity, cp | 42.7 | 42.3 | 31.2 | 30.3 | 49.0 | 35.9 | 43.9 | 37.6 | 37.1 | 42.4 | 37.4 | |
| Viscosity/kappa | 1.46 | 1.24 | 1.17 | 1.31 | 1.23 | 1.26 | 1.11 | 1.33 | 1.40 | 1.64 | 1.46 | |
| Average v/k | - | - | 1.24 | - | 1.25 | - | 1.22 | - | 1.52 | - | 1.50 | |
| Std deviation | - | - | 0.07 | - | 0.02 | - | 0.16 | - | 0.17 | - | 0.05 | |

Note: All CK cooks had a 4.5 L/W ratio, and all MCK cooks had a 3.1 initial and a 4.5 final L/W ratio. White liquor split pattern with all MCK cooks was 60% of total in the impregnation, 25% in the first cooking stage, and 15% in the second cooking stage.

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TABLE IB

SPLIT WL WITH VARIABLE SULFIDITY (MCK)

| Cook number Type | A2843 | A2857 | A2844 | A2836 | A2847 | A2785 | A2803 | A2796 | A2804 | A2806 | A2808 |
|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | MCK | MCK | MCK | MCK | MCK | MCK | MCK | MCK | MCK | MCK | MCK |
| Total EA, % Na2O | 16.0 | 16.0 | 16.0 | 16.0 | 16.0 | 14.5 | 16.0 | 14.5 | 16.0 | 16.0 | 16.0 |
| Impregnation | 9.6 | 9.6 | 9.6 | 9.6 | 9.6 | 8.7 | 9.6 | 8.7 | 9.6 | 9.6 | 9.6 |
| 1st co-current | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 3.6 | 4.0 | 3.6 | 4.0 | 4.0 | 4.0 |
| 2nd co-current | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.2 | 2.4 | 2.2 | 2.4 | 2.4 | 2.4 |
| Overall sulfidity, % | 29.9 | 30.0 | 30.1 | 37.4 | 37.5 | 37.5 | 37.5 | 37.5 | 37.5 | 37.5 | 37.5 |
| Impregnation | 43.2 | 50.0 | 50.1 | 37.5 | 37.5 | 30.0 | 30.0 | 42.5 | 42.5 | 42.5 | 49.2 |
| 1st co-current | 9.9 | 0.0 | 0.0 | 37.5 | 37.5 | 61.0 | 61.0 | 30.0 | 30.0 | 30.0 | 20.0 |
| 2nd co-current | 9.9 | 0.0 | 0.0 | 37.5 | 37.5 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 20.0 |
| Screened yield, % | 46.4 | 46.2 | 46.6 | 46.6 | 46.6 | 48.0 | 46.1 | 47.4 | - | 46.0 | 46.0 |
| Kappa number | 25.5 | 24.1 | 26.5 | 25.5 | 25.2 | 35.6 | 24.9 | 35.0 | 24.5 | 22.5 | 22.1 |
| Viscosity, cp | 39.2 | 39.9 | 40.7 | 37.6 | 40.7 | 49.3 | 38.4 | 55.1 | 34.7 | 37.5 | 34.1 |
| Viscosity/kappa | 1.54 | 1.66 | 1.60 | 1.47 | 1.62 | 1.38 | 1.54 | 1.57 | 1.42 | 1.67 | 1.54 |
| Average v/k | | 1.63 | | 1.54 | | 1.46 | | | 1.55 | | 1.61 |
| Std deviation | | 0.04 | | 0.10 | | 0.11 | | | 0.13 | | 0.09 |

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TABLE IC

| Cook number Type | A2824 MCK | A2845 MCK | A2859 MCK | A2860 MCK | A2846 MCK | A2837 MCK | A2848 MCK | A2871 MCK | A2849 MCK | A2838 MCK | A2850 MCK |
|----------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Total EA, % Na2O | 16.0 | 16.0 | 16.0 | 16.0 | 16.0 | 16.0 | 16.0 | 16.0 | 16.0 | 16.0 | 16.0 |
| Impregnation | 9.6 | 9.6 | 9.6 | 9.6 | 9.6 | 9.6 | 9.6 | 9.6 | 9.6 | 9.6 | 9.6 |
| 1st co-current | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 |
| 2nd co-current | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 |
| Overall eulfidity, % | 37.5 | 37.3 | 37.4 | 37.6 | 37.7 | 45.3 | 45.0 | 45.4 | 45.1 | 44.8 | 45.2 |
| Impregnation | 49.3 | 55.6 | 55.6 | 62.6 | 62.8 | 45.3 | 45.0 | 45.4 | 55.3 | 54.7 | 61.9 |
| 1st co-current | 20.2 | 9.9 | 10.0 | 0.0 | 0.0 | 45.3 | 45.0 | 45.4 | 29.9 | 29.9 | 20.2 |
| 2nd co-current | 20.2 | 9.9 | 10.0 | 0.0 | 0.0 | 45.3 | 45.0 | 45.4 | 29.9 | 29.9 | 20.2 |
| Screened yield, % | 46.1 | 46.3 | 46.3 | 46.1 | 46.2 | 46.5 | 46.3 | 44.9 | 46.1 | 46.2 | 46.2 |
| Kappa number | 22.9 | 23.4 | 23.0 | 22.2 | 22.8 | 23.2 | 22.8 | 23.5 | 21.9 | 22.0 | 21.8 |
| Viscosity, cp | 38.2 | 39.5 | 39.5 | 48.1 | 39.5 | 36.4 | 39.8 | 38.6 | 38.0 | 41.5 | 41.4 |
| Viscosity/kappa | 1.67 | 1.69 | 1.72 | 2.17 | 1.73 | 1.57 | 1.74 | 1.64 | 1.74 | 1.89 | 1.90 |
| Average v/k | 1.70 | 1.70 | 1.70 | 1.95 | 1.65 | 1.65 | 1.65 | 1.81 | 1.81 | 1.81 | 1.94 |
| Std deviation | 0.02 | 0.02 | 0.31 | 0.31 | 0.09 | 0.09 | 0.09 | 0.11 | 0.11 | 0.11 | 0.08 |

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TABLE ID

| Cook number Type | VARIABLE SULFIDITY MCC | | | | | | VARIABLE SULFIDITY EMCC | | | | | |
|-----------------------------|------------------------|--------------|--------------|--------------|--------------|--------------|-------------------------|---------------|---------------|---------------|--|--|
| | A2839 MCK | A2854 MCC | A2852 MCC | A2861 MCC | A2855 MCC | A2853 MCC | A2858 MCC | A2862 EMCC | A2867 EMCC | A2864 EMCC | | |
| Total EA, % Na2O | 16.0 | 19.5 | 20.1 | 20.1 | 20.1 | 20.2 | 19.8 | 23.6 | 23.6 | 23.6 | | |
| Impregnation | 9.6 | 10.1 | 10.1 | 10.1 | 10.1 | 10.1 | 10.1 | 8.5 | 8.5 | 8.5 | | |
| 1st co-current | 4.0 | 3.1 | 3.1 | 3.1 | 3.1 | 3.9 | 3.1 | 3.1 | 3.1 | 3.1 | | |
| 2nd co-current | 2.4 | 6.3 | 6.9 | 6.9 | 6.9 | 6.3 | 6.6 | 11.9 | 11.9 | 11.9 | | |
| Overall sulfidity, % | 45.3 | 30.4 | 30.0 | 30.0 | 37.4 | 37.6 | 37.6 | 29.9 | 30.2 | 30.5 | | |
| Impregnation | 62.1 | 30.4 | 50.0 | 50.0 | 37.5 | 62.7 | 62.6 | 30.0 | 50.4 | 50.9 | | |
| 1st co-current | 20.0 | 30.4 | 0.0 | 0.0 | 37.5 | 0.0 | 0.0 | 30.0 | 0.0 | 0.0 | | |
| 2nd co-current | 20.0 | 30.1 | 0.0 | 0.0 | 37.0 | 0.0 | 0.0 | 29.0 | 0.0 | 0.0 | | |
| Screened yield, % | 46.1 | 45.4 | 44.5 | 44.7 | 44.9 | 43.5 | 44.4 | 44.4 | 43.3 | 43.3 | | |
| Kappa number | 21.8 | 28.3 | 23.1 | 24.0 | 22.3 | 19.1 | 20.4 | 22.1 | 21.5 | 19.6 | | |
| Viscosity, cp | 43.4 | 37.2 | 38.4 | 37.8 | 37.4 | 35.5 | 35.4 | 42.3 | 47.9 | 45.4 | | |
| Viscosity/kappa | 1.99 | 1.31 | 1.66 | 1.57 | 1.67 | 1.86 | 1.74 | 1.91 | 2.23 | 2.32 | | |
| Average v/k | - | - | 1.62 | - | - | 1.80 | - | - | 2.27 | - | | |
| Std deviation | - | - | 0.06 | - | - | 0.09 | - | - | 0.07 | - | | |

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TABLE IE

| Cook number Type | A2863 | | A2868 | | A2866 | | A2872 | | A2877 | | A2878 | |
|-----------------------------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|
| | EMCC | EMCC | EMCC | EMCC | EMCC | EMCC | EMCC | EMCC | EMCC | EMCC | EMCC | EMCC |
| Total EA, % Na2O | 23.6 | 23.6 | 23.6 | 23.6 | 23.6 | 23.6 | 23.6 | 23.6 | 23.6 | 23.6 | 23.6 | 23.6 |
| Impregnation | 8.5 | 8.5 | 8.5 | 8.5 | 8.5 | 8.5 | 8.5 | 8.5 | 8.5 | 8.5 | 8.5 | 8.5 |
| 1st co-current | 3.1 | 3.1 | 3.1 | 3.1 | 3.1 | 3.1 | 3.1 | 3.1 | 3.1 | 3.1 | 3.1 | 3.1 |
| 2nd co-current | 11.9 | 12.0 | 12.0 | 11.9 | 11.9 | 12.0 | 12.0 | 12.0 | 12.0 | 12.0 | 12.0 | 11.9 |
| Overall sulfidity, % | 37.4 | 37.6 | 37.6 | 37.6 | 37.6 | 37.6 | 37.6 | 37.6 | 45.3 | 45.3 | 45.3 | 45.1 |
| Impregnation | 37.6 | 62.6 | 62.6 | 62.7 | 62.7 | 62.7 | 62.7 | 62.7 | 45.4 | 45.4 | 45.4 | 75.2 |
| 1st co-current | 37.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 45.4 | 45.4 | 45.4 | 0.0 |
| 2nd co-current | 36.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 44.6 | 44.6 | 44.6 | 0.0 |
| Screened yield, % | 43.9 | 44.0 | 44.0 | 43.3 | 44.4 | 44.4 | 44.4 | 44.4 | 44.6 | 44.6 | 44.6 | 44.9 |
| Kappa number | 19.8 | 18.8 | 18.8 | 19.9 | 17.7 | 17.7 | 17.7 | 17.7 | 19.0 | 19.0 | 19.0 | 19.0 |
| Viscosity, cp | 44.2 | 46.2 | 46.2 | 46.3 | 43.5 | 43.5 | 43.5 | 43.5 | 42.8 | 42.8 | 42.8 | 48.6 |
| Viscosity/kappa | 2.23 | 2.46 | 2.46 | 2.33 | 2.46 | 2.46 | 2.46 | 2.46 | 2.25 | 2.25 | 2.25 | 2.56 |
| Average v/k | . | . | . | 2.42 | . | . | . | . | . | . | . | . |
| Std deviation | . | . | . | 0.08 | . | . | . | . | . | . | . | . |

TABLE II

| Cook number | A2961 | A2958 | A2962 | A2959 | A2960 | A2963 |
|---|-------|-------|-------|-------|-------|-------|
| Type | EMCC | EMCC | EMCC | MCK | MCK | EMCC |
| 5 Polysulfide, % | 2 | 2 | 3 | 2 | 3 | nil |
| PRESTEAMING: | | | | | | |
| Time, min | 5 | 5 | 5 | 5 | 5 | 5 |
| Temperature, °C | 110 | 110 | 110 | 110 | 110 | 110 |
| 10 IMPREGNATION: | | | | | | |
| Time, min | 30 | 30 | 30 | 30 | 30 | 30 |
| Temperature, °C | 110 | 110 | 110 | 110 | 110 | 110 |
| Pressure, psig | 150 | 150 | 150 | 150 | 150 | 150 |
| Initial EA, % NaOH | 12 | 16 | 13 | - | - | 12 |
| Initial EA, % Na ₂ O | - | - | - | 11.4 | 12.6 | - |
| 15 Sulfidity, % on AA | 62.5 | 73.6 | 62.5 | 62.5 | 62.5 | 62.8 |
| 2nd EA @ 5 min, % NaOH | 2 | 2 | 2 | - | - | 2 |
| Residual EA, g/L Na ₂ O | 13.6 | 22.0 | 14.4 | 15.9 | 15.7 | - |
| Resid. polysulfide, g/L S' | 1.6 | 1.6 | - | 1.9 | 2.6 | - |
| 20 COCURRENT STAGE: | | | | | | |
| Total time, min | 61 | 60 | 60 | 73 | 75 | 60 |
| Max temperature, °C | 164 | 165 | 164 | 170 | 170 | 165 |
| Time at max, min | 45 | 45 | 45 | 45 | 45 | 45 |
| EA, % NaOH | 5 | 5 | 6 | - | - | 5 |
| EA, % Na ₂ O | - | - | - | 4.75 | 5.25 | - |
| 25 Sulfidity, % | 0 | 0 | 0 | 0 | 0 | 0 |
| Residual EA, g/L Na ₂ O | 8.5 | 14.0 | 8.0 | 10.2 | 9.6 | - |
| COCURRENT STAGE II: | | | | | | |
| Time, min. | - | - | - | 135 | 72 | - |
| Temperature, C' | - | - | - | 170 | 170 | - |
| 30 EA, % Na ₂ O | - | - | - | 2.85 | 3.15 | - |
| Sulfidity, % | - | - | - | 0 | 0 | - |
| COUNTERCURRENT STAGE: | | | | | | |
| Time, min | 240 | 240 | 240 | - | - | 240 |
| Temperature, °C | 164 | 160 | 164 | - | - | 165 |
| 35 EA, % NaOH on wood | 15.3 | 15.4 | 15.4 | - | - | 15.4 |
| Sulfidity, % | 0 | 0 | 0 | - | - | 0 |
| EA, g/L as NaOH | 11.9 | 12.0 | 12.0 | - | - | 12.0 |
| Displacement, L/min. | 0.16 | 0.16 | 0.16 | - | - | 0.16 |
| Displaced volume, L | 38.4 | 38.4 | 38.4 | - | - | 38.4 |
| 40 Displacement Residual : | | | | | | |
| @ 60 minutes, EA g/L Na ₂ O | 6.9 | 10.4 | - | - | - | - |
| @ 120 minutes, EA g/L Na ₂ O | 7.6 | 9.1 | - | - | - | - |
| Total Composite, EA g/L Na ₂ O | 7.3 | 9.6 | - | - | - | - |
| 45 END OF COOKING: | | | | | | |
| Residual EA, g/L NaOH | 10.0 | 10.0 | - | 12.4 | 13.4 | - |
| g/L NaO ₂ | 7.7 | 7.8 | - | 9.6 | 10.4 | - |
| H factor | 2733 | 2239 | 2695 | 2947 | 1935 | - |
| 50 UNBLEACHED PULP: | | | | | | |
| Total yield, % | 45.5 | 44.6 | - | 43.5 | 45.6 | - |
| Rejects, % | 0.02 | <0.01 | - | <0.01 | <0.02 | - |
| Screened yield, % | 45.5 | 44.6 | - | 43.5 | 45.6 | - |
| Kappa, unscreened | 17.1 | 12.4 | 15.1 | 11.7 | 12.6 | - |
| Kappa, screened | 16.9 | 12.6 | - | 11.7 | 14.6 | - |
| Kappa, screened (test 2) | 16.8 | 12.4 | - | 11.7 | 14.4 | - |
| 55 Viscosity, 0.5% CBD, cp | 42.4 | 33.7 | - | 23.6 | 32.3 | - |
| Viscosity, (test 2) | 43.7 | 34.5 | - | 22.0 | 32.4 | - |
| V/K, (test 1) | 2.51 | 2.67 | - | 2.02 | 2.21 | - |

As can be seen from the above examples, the method according to the invention optimizes the viscosity/kappa ratio and/or strength properties of kraft pulp produced, and achieves other advantageous results. The utilization of polysulfide or elemental sulfur as part of the sulfide content of the white liquor also significantly increases yield.

5 While the Tables describe the results of kraft cooks, and white liquor, the invention is applicable to other cooking processes and cooking liquors for the production of paper pulp. With sulfite cooking liquor, and when using other lignin reaction enhancing or carbohydrate degradation slowing chemicals, such as anthraquinone or its derivatives or equivalents, or the like, significant increases in viscosity/kappa ratio or pulp strength properties can be obtained by targeting one cooking liquor to a specific stage (or stages) of the cook, while another cooking liquor is used in other portions.

10 In general, a method is provided in which comminuted cellulosic fibrous material is treated with cooking liquor to obtain cellulosic pulp in the following steps: (a) Providing at least first and second cooking liquors, including a first cooking liquor having a first concentration of lignin enhancing or carbohydrate degradation slowing chemical (e.g. in line 35), and a second cooking liquor (e.g. in line 41) having a second concentration of that lignin enhancing or carbohydrate degradation slowing chemical, the second concentration being from zero to much less than the first concentration. (b) Cooking the comminuted cellulosic fibrous material in several cook stages (e.g. in vessels 12, 37). (c) Targeting the first cooking liquor to one or more, but less than all, of the cook stages, to provide cooking liquor for that one or more stages (e.g. to the co-current impregnation stage in vessel 37). And (d) utilizing the second cooking liquor in at least one cook stage in which the first cooking liquor is not utilized (e.g. introducing it at 42, 43 into co-current or countercurrent cook stages).

20 While the invention has been herein shown and described in what is presently conceived to be the most practical embodiment thereof, it will be appreciated by those in the art that many modifications may be made thereof within the scope of the invention, which scope is to be accorded the broadest interpretation of the appended claims so as to encompass all equivalent methods and procedures.

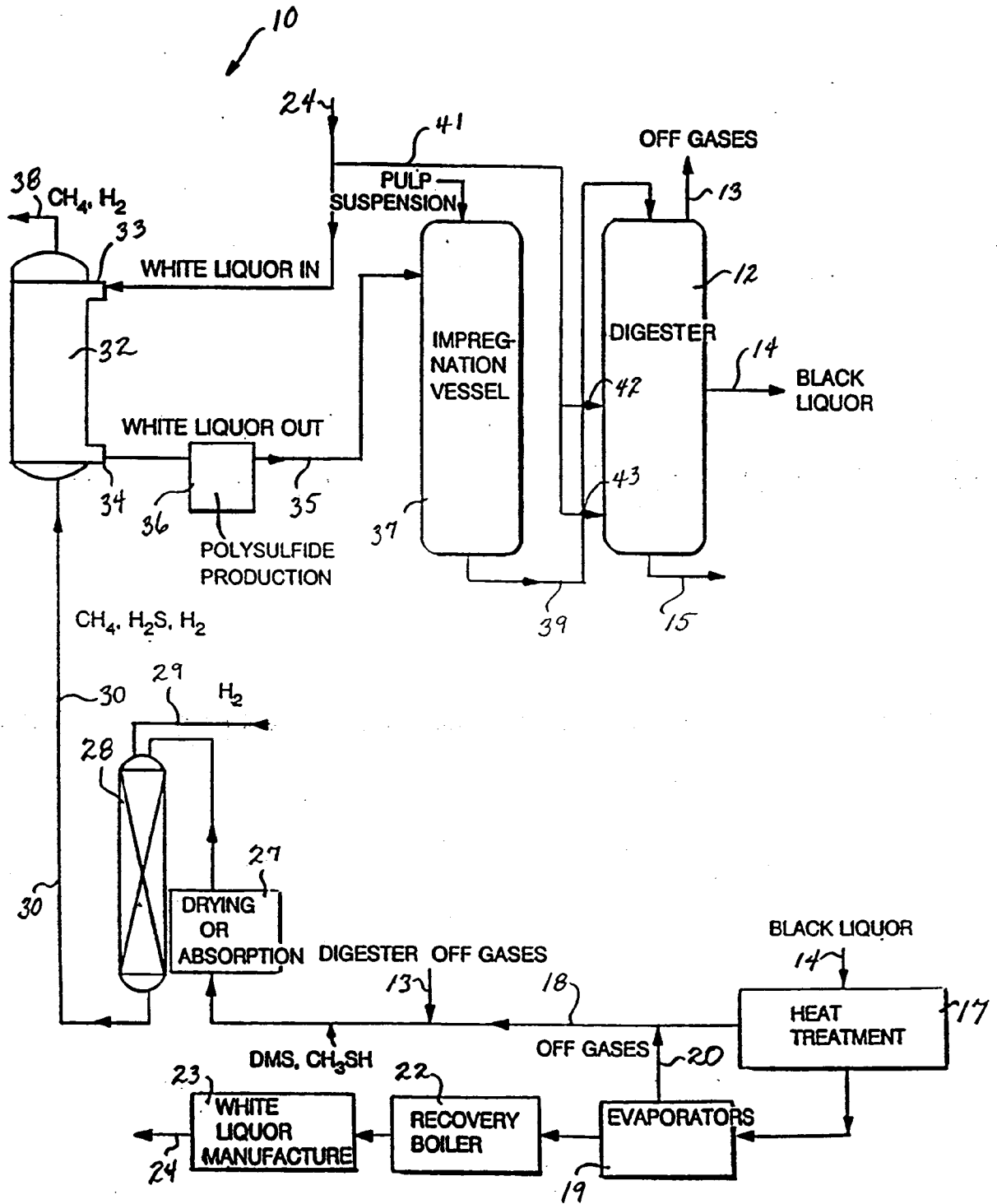
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Claims

- 30 1. A method of producing kraft pulp from cellulosic comminuted fibrous material utilizing white liquor, by impregnating the pulp with white liquor (in 37), then cooking it under kraft cooking conditions (in 12), and then washing it (in 12), characterized by the steps of:
- (a) making at least two streams of white liquor (35, 41), including a second stream (41) having relatively low sulfur content, and a first stream (35) having relatively high sulfur content, substantially higher than the sulfur content of the second stream;
 - 35 (b) impregnating (in 37) the cellulosic comminuted fibrous material with the first stream of white liquor; and
 - (c) cooking (in 12) the cellulosic comminuted fibrous material under kraft cooking conditions, in a cooking zone with cooking chemicals to produce kraft pulp while supplying the second stream of white liquor to the cooking zone as cooking chemicals.
- 40 2. A method as recited in claim 1 further characterized in that steps (a)-(c) are practiced so as to add roughly about 60% of the total cooking chemicals in step (b), and roughly about 40% in step (c).
- 45 3. A method as recited in claim 1 or 2 characterized in that steps (a)-(c), as well as the washing step, are practiced continuously.
4. A method as recited in any of the claims 1 to 3 characterized in that the first white liquor (35) contains sodium sulfide, and wherein steps (a)-(c) are practiced so as to add about 60-90% sodium sulfide from white liquor in step (b), the second stream (41) of white liquor being sodium sulfide depleted.
- 50 5. A method as recited in any of the claims 1 to 4 characterized in that the sulfide of the first stream (35) of white liquor contains about 0.5%-8% polysulfide on wood, expressed as elemental sulfur, or elemental sulfur.
- 55 6. A method of producing kraft pulp by cooking comminuted cellulosic fibrous material with white liquor to produce kraft pulp (in 15) and black liquor (in 14), characterized by the steps of:
- (a) treating a slurry of cellulosic fibrous material in a plurality of consecutive stages with white liquor, including at least first and second stages (37, 12), using a first supply (35) of white liquor to the first

- stage and a second supply (41) to the second stage;
- (b) subjecting the material treated with white liquor to cooking conditions in at least one of the stages (12) to effect kraft cooking thereof, and producing black liquor (in 14);
- (c) recovering sulfur from the black liquor (with 17, 28, etc.); and
- 5 (d) adding the recovered sulfur to the first supply of white liquor (in 32) to significantly increase the sulfur content thereof so that it is greater than the sulfur content of the second supply.
7. A method of producing kraft pulp using white liquor, characterized by the steps of:
- 10 (a) treating cellulosic comminuted fibrous material in a first stage (37) with a first supply (35) of white liquor;
- (b) treating the material in a second stage (12) with a second supply (41) of white liquor; and
- (c) controlling the relative sulfur contents of the first and second supplies of white liquor so as to optimize the viscosity/kappa and/or strength properties of the kraft pulp produced (in 15).
- 15 8. A method for manufacture of cellulosic pulp on an industrial scale utilizing cooking liquor, characterized by the steps of:
- (a) manufacturing two different cooking liquors, one (35) having a high content of sulfurous chemicals and the other (41) having a low content of sulfurous chemicals;
- (b) treating the cellulosic fibrous material in at least two different stages (37, 12) with the two different liquids; and
- 20 (c) recovering the cooking chemicals (17, 19, 22, 23) after treatment of the two different stages, and utilizing the recovered chemicals (in 24) in the practice of step (a).
9. A method of treating comminuted cellulosic fibrous material with cooking liquor to obtain cellulosic pulp, characterized by the steps of:
- 25 (a) providing at least first and second cooking liquors, including a first cooking liquor (35) having a first concentration of lignin enhancing or carbohydrate degradation slowing chemical, and a second cooking liquor (41) having a second concentration of that lignin enhancing or carbohydrate degradation slowing chemical, the second concentration being from zero to much less than the first concentration;
- (b) cooking the comminuted cellulosic fibrous material in several cook stages (in 37, 12);
- 30 (c) targeting the first cooking liquor to one or more, but less than all, of the cook stages (e.g. 37), to provide cooking liquor for that one or more stages; and
- (d) utilizing the second cooking liquor in at least one cook stage (e. g. 12) in which the first cooking liquor is not utilized.
- 35 10. A method as recited in claim 9 further characterized in that the lignin enhancing or carbohydrate degradation slowing chemical is selected from the group consisting essentially of anthraquinone or its derivatives or equivalents, sodium sulfide, and cationic bases.
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FIG. 1





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 89 0125

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|---|---|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
| A | <p>WORLD PATENTS INDEX Week 8038, Derwent Publications Ltd., London, GB; AN 80-66836C & JP-A-55 103 386 (SANYO KOKUSAKO PULP) 8 August 1980 * abstract *</p> <p style="text-align: center;">---</p> | 1,6-10 | D21C3/02 D21C3/26 D21C11/00 |
| A | <p>ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 56, no. 11, May 1986, APPLETON US page 1366; ANDREWS, E.K. ET AL.: 'Extended delignification kraft pulping of softwoods.-Effect of treatments on chips and pulp with sulfide-containing liquors.' * abstract n. 12482 *</p> <p style="text-align: center;">---</p> | 1,6-10 | |
| A | <p>EP-A-0 407 370 (KAMYR AB) * column 1, line 20 - line 42 *</p> <p style="text-align: center;">---</p> | 1,3,6-10 | |
| A | <p>FR-A-1 375 278 (DOMINION TAR & CHEMICAL COMPANY LIMITED) * page 4, line 42 - page 5, line 12 *</p> <p style="text-align: center;">-----</p> | 1,3,4,6 | TECHNICAL FIELDS SEARCHED (Int. Cl.5) D21C |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 14 SEPTEMBER 1992 | Examiner BERNARDO NORIEGA F. |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> | | <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p> | |

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