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[54] **TREATMENT OF LIGNOCELLULOSIC MATERIAL IN AN ALKALINE PULPING LIQUOR CONTAINING ANTHRAQUINONE SULPHONIC ACID FOLLOWED BY OXYGEN DELIGNIFICATION**

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[58] Field of Search **162/65, 89, 76, 72, 82; 8/111, 109; 260/370**

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[57] **ABSTRACT**

Lignocellulosic material is treated with an alkaline pulping liquor containing anthraquinone monosulphonic acid, anthraquinone disulphonic acid or alkali metal salts of said acids followed by treatment with alkali metal hydroxide and oxygen.

14 Claims, No Drawings

TREATMENT OF LIGNOCELLULOSIC MATERIAL IN AN ALKALINE PULPING LIQUOR CONTAINING ANTHRAQUINONE SULPHONIC ACID FOLLOWED BY OXYGEN DELIGNIFICATION

This invention relates to a process for the delignification of lignocellulosic material such as wood, bagasse, straw, etc.

The processing of lignocellulosic material to produce cellulose suitable for the manufacture of paper products involves the removal of lignin and other noncellulosic components such as gums. Reagents that attack lignin without affecting appreciably the cellulose are preferred for this purpose. In the sulphate or kraft process lignocellulosic material is cooked with a mixture of sodium hydroxide and sodium sulphide. In the soda process the cooking is carried out with sodium hydroxide alone. Although these processes are effective in the removal of lignin from lignocellulosic material such as wood, the cellulose component of the material is attacked also to a certain degree, resulting in a lowering of yields and degradation of the product.

In Canadian Pat. No. 895,756 issued on Mar. 21, 1972 to H. E. Worster and M. F. Pudek there is described a two stage soda-oxygen pulping process comprising a first stage sodium hydroxide digestion, followed by defiberization of the product of the sodium hydroxide digestion and a second stage digestion with sodium hydroxide in the presence of excess oxygen. This known process produced pulp in yield comparable to the yield of a conventional kraft process.

It has now been found that lignocellulosic material can be delignified effectively in a two stage process, without intermediate defiberization, comprising a first stage cooking with sulphate or caustic liquor at a temperature higher than used in conventional pulping processes, the cooking being adapted to produce a high yield, followed by a second stage treatment in alkaline medium with oxygen or an oxygen-containing gas under pressure. The cooking periods of the novel process are of the same order as of conventional kraft processes. The novel process provides a pulp in higher yield, of better bleaching response with the production of less pollution than conventional pulping processes.

Thus the main object of this invention is to provide a pulping process that gives an increased yield of cellulosic pulp. A further object is to provide a two stage process that can be carried out as continuous unit operation without an intermediate defiberization step. Additional objects will appear hereinafter.

The process of this invention comprises the steps of

1. treating lignocellulosic material in a closed reaction vessel with a pulping liquor containing alkali metal hydroxide with or without admixture of alkali metal sulphide at a temperature in the range 160°C to 195°C for a period of not greater than 90 minutes and preferably not greater than 60 minutes, the temperature and period of treatment being adapted to provide a pulp yield of 55 to 65 percent by weight.

2. displacing the pulping liquor from the lignocellulosic material with water, or an aqueous solution of alkali metal hydroxide,

3. treating the material in aqueous suspension at a consistency of 2.0 to 30.0 percent by weight for 0.5 to 30 minutes at 20°C to 90°C with 2.0 to 20.0 percent by weight of alkali metal hydroxide, and

4. treating the alkaline material in aqueous medium at a consistency of from 3.0 to 35.0 percent by weight with oxygen or an oxygen-containing gas for 10 to 120 minutes at a temperature of 80°C to 140°C and a partial pressure of oxygen of 30 to 200 pounds per square inch.

When the lignocellulosic material employed is wood, this is first converted into the form of chips. This step will not be required when the lignocellulosic material is of fibrous form.

The process of this invention can be used to delignify either coniferous or deciduous species of wood. By coniferous is meant species such as pine, spruce and balsam fir. By deciduous is meant species such as birch, aspen, eastern cottonwood, maple, beech and oak. When employed with a high density deciduous wood such as birch it is preferable to employ a longer time to reach maximum cooking temperature in the first stage and to add alkali hydroxide in the second stage while the pulp is at low consistency e.g. 2 to 6 percent. It is desirable to remove 40 to 60 percent of the lignin of dense deciduous woods in the first stage.

When the treatment of the first step is carried out with a pulping liquor containing only alkali metal hydroxide, 14 to 24 percent preferably 18 to 22 percent by weight of this, based on the weight of the lignocellulosic material is employed. Normally the liquor will also contain alkali metal carbonate.

When the treatment of the first step is carried out with a pulping liquor containing both alkali metal hydroxide and alkali metal sulphide 8 to 14 percent, preferably 10 to 12 percent by weight alkali metal hydroxide expressed as effective alkali (TAPPI T 1203 OS-61) and 5 to 40 percent, preferably 20 to 30 percent by weight alkali metal sulphide expressed as percent sulphidity (TAPPI T 1203 OS-61), based on lignocellulosic material, is employed. This pulping liquor will normally also contain alkali metal sulphate and alkali metal carbonate.

Effective alkali is the sum of all alkali hydroxide in solution expressed as Na_2O including that formed by hydrolysis of the alkali sulphide, also expressed as Na_2O .

Sulphidity is the total sulphide, expressed as Na_2O , calculated as a percentage of total titratable alkali, including that formed by hydrolysis of the sulphide, also expressed as Na_2O .

Since the first step treatment is carried out in a closed reaction vessel at a temperature in the range 160°C to 195°C in the presence of water, the reaction will take place at supra atmospheric pressure.

It has been found that the yield is increased and delignification is accelerated by the addition to the pulping liquor of 0.02 to 2.0 percent, preferably 0.05 to 1.0 percent, by weight based on the lignocellulosic material, of anthraquinone monosulphonic acid or anthraquinone disulphonic acid, or alkali metal salts of said acids, or mixtures of the aforesaid acids and/or salts. The addition of said anthraquinone compounds is most effective when the first step is carried out with a pulping liquor containing alkali metal hydroxide without addition of alkali metal sulphide.

After the first step treatment with pulping liquor the resulting pulp yield will be 52 to 65 percent, preferably 58 to 62 percent by weight, based upon the lignocellulosic material. The kappa number of the material at the completion of the first step will lie in the range 80-130

for coniferous woods and in the range 40-90 for deciduous woods.

The partially delignified material resulting from the first treatment step is discharged from the pulping vessel and the spent liquor displaced by fresh water or spent liquor from the alkaline oxygen treatment step or "white water" from a later stage of a papermaking process. By "white water" is meant process water that has been used for transfer of slush pulp and has been separated from the pulp for re-use in the process. To the material is then added alkali metal hydroxide. The alkali metal hydroxide may be provided in the form of pulping liquor or "white liquor" such as used in the first stage of the process. This liquor therefore may contain sulphide, sulphate and carbonate in addition to the alkali metal hydroxide. Preferably there is also added 0.1 to 1.0 percent by weight of the pulp of a magnesium salt such as magnesium chloride or magnesium sulphate. The magnesium salt may be added directly as the salt or as a complex formed with the spent liquor from the alkaline oxygen treatment step.

The alkaline lignocellulosic material is then fed without mechanical defiberization into an oxygen treatment vessel. The material is then treated with oxygen or an oxygen-containing gas under pressure.

The product of the oxygen treatment is separated from the spent liquor and washed with water. It will have a residual lignin content of 2 to 6 percent, preferably, 2 to 4 percent of weight of the original lignocellulosic material, corresponding to a yield of 43 to 53 percent by weight.

The alkali metal hydroxide employed as reagent in the process of this invention may be sodium hydroxide or potassium hydroxide. The alkali metal sulphide reagent may be sodium sulphide or potassium sulphide.

The oxygen treated material may be subjected to a bleaching treatment. A conventional bleaching sequence comprising chlorination, alkaline extraction and treatment with chlorine dioxide is sufficient to provide a product having a brightness of approximately 90 units (Elrepho). Alternatively the first bleaching stage may comprise treatment with chlorine dioxide followed sequentially, without intervening washing, by chlorination.

The process of this invention has the advantage that no defiberization is required between the treatment with pulping liquor and the treatment with oxygen. This reduces the amount of equipment required for the process. In distinction to conventional soda pulping which requires cooking periods of several hours the cooking periods of the present invention are of the same order as a conventional kraft process. Employing the process of the present invention wherein the first stage utilizes kraft pulping liquor it is possible to obtain a product in yield which is 6 to 7 percent greater than the yield of a conventional kraft process. When the present process is followed by a conventional bleaching sequence the decrease in yield caused by bleaching is equivalent to the decrease in yield that occurs in bleaching pulp of the same kappa number prepared by the kraft process. In addition, the lessened usage of sulphur-containing reagents results in lessened pollution potential.

The invention is illustrated by the following Examples but its scope is not limited to the embodiments shown therein.

In the Examples the kappa number and viscosity determinations were carried out by the following methods

Kappa Number	TAPPI Method T-236 M-60
Viscosity	TAPPI Method T-230-SU-66

The physical properties of pulps were determined on material processed by a P.F.I. mill to freeness levels of 300 to 500 Canadian Standard Freeness (C.S.F.). Handsheets were prepared in accordance with TAPPI Method (T-200-M-60). The physical properties were determined as follows.

Tensile (breaking length)	TAPPI T-404-M
Burst factor	TAPPI T-403-M
Tear factor	TAPPI T-414-M

EXAMPLE 1

A mixture of spruce and balsam wood chips was subjected to the following treatment sequence.

1. The chips were cooked with kraft liquor containing 12 percent by weight of effective alkali expressed as sodium oxide and 25% sulphidity and 1.0% of anthraquinone- 2-mono-sulphonic acid based on the weight of wood, the ratio of liquor to wood being 4. The maximum temperature of the cook was 180°C and was reached after 60 minutes. The cook was maintained at 180°C for 10 minutes. The yield of the cook was 60.9 percent, the product having a kappa number of 104.
2. The partially delignified wood was washed with water.
3. Without defiberization, the partially delignified wood was impregnated at room temperature with an aqueous solution containing 9.5% sodium hydroxide and magnesium sulphate in an amount containing 0.2% magnesium ion, based on the weight of the partially delignified wood.
4. The alkaline wood was treated in a closed reactor in the presence of water at a consistency of 27 percent, at 115°C for 50 minutes with oxygen under a partial pressure of 80 psi. The delignified product was obtained with a yield of 51.9 percent based on the starting material, and a kappa number of 30 and a viscosity of 13.1 centipoise.
5. The oxygen-treated product of step 4 was subjected to three bleaching steps: chlorination, caustic extraction and chlorine dioxide treatment.

Chlorination: Pulp at 3 percent consistency by weight treated with 6 percent by weight of chlorine for 1 hour at 24°C. Caustic extraction: Pulp at 10 percent consistency by weight treated with 2.9 percent by weight of sodium hydroxide for 2 hours at 65°C. Chlorine dioxide treatment: Pulp at 6 percent consistency by weight treated with 0.6% chlorine dioxide by weight for 3 hours at 70°C.

The pulp was washed with water at the completion of each of the bleaching steps.

The product had a brightness of 88.4 (Elrepho) and a viscosity of 11.8 centipoise. The physical properties of the product are shown in the following Table I.

TABLE I

Freeness C.S.F.	Breaking Length M	Burst Factor	Tear Factor	Bulk cc/gm
500	12,700	103	83	1.33
300	13,300	105	76	1.27

EXAMPLE 2

The same mixture of spruce and balsam wood chips as in Example 1 was subjected to the following treatment sequence.

1. The chips were cooked with soda liquor containing 20 percent by weight of sodium hydroxide based on the weight of wood, the ratio of liquor to wood being 4. Maximum temperature of the cook was 180°C and was reached after 60 minutes. The cook was maintained at 180°C for 60 minutes. The yield was 53.2 percent and the kappa number 106.
2. The partially delignified wood was washed with fresh water.
3. Without defiberization, the partially delignified wood was impregnated at room temperature with an aqueous solution containing 9.0% sodium hydroxide and magnesium sulphate in an amount containing 0.2% magnesium ion, based on the weight of the partially delignified wood.
4. The alkaline wood was treated in a closed reactor in the presence of water at consistency of 27 percent, at 115°C for 50 minutes with oxygen under a partial pressure of 80 psi. The delignified product was obtained with a yield of 46.7 percent based on the starting material, and had a kappa number of 23 and a viscosity of 7.6 centipoise.
5. The oxygen-treated product pulp of step 4 was subjected to three bleaching steps: chlorination, caustic extraction and chlorine dioxide treatment.
Chlorination: Pulp at 3 percent consistency by weight treated with 5.6% chlorine for 1 hour at 24°C. Caustic extraction: Pulp at 10 percent consistency by weight treated with 2.2% sodium hydroxide for 2 hours at 65°C. Chlorine dioxide treatment: Pulp at 6 percent consistency by weight treated with 0.7% chlorine dioxide by weight for 3 hours at 70°C. The pulp was washed with water at the completion of each of the bleaching steps.

The product had a brightness of 88.5 (Elrepho) and a viscosity of 7.3 centipoise. The physical properties of the product are shown in Table II.

TABLE II

Freeness C.S.F.	Breaking Length M	Burst Factor	Tear Factor	Bulk cc/gm
500	11,250	85	90	1.40
300	11,480	89	83	1.31

EXAMPLE 3

The same mixture of spruce and balsam wood chips as in Example 1 was subjected to the following treatment sequence.

1. The chips were cooked with soda liquor containing 20 percent by weight of sodium hydroxide and 0.1 percent by weight of anthraquinone-2-monosulphonic acid based on the weight of the wood, the ratio of liquor to wood being 4. The maximum temperature of the cook was 180°C and was reached after 60 minutes. The cook was maintained at 180°C for 45 minutes. The yield was 52.5 percent and the kappa number 84.
2. The partially delignified wood was washed with fresh water.
3. Without defiberization, the partially delignified wood was impregnated at room temperature with an aqueous solution containing 5.0% sodium hydroxide and magnesium sulphate in an amount containing 0.2% magnesium ion, based on the weight of the partially delignified wood.
4. The alkaline wood was treated in a closed reactor in the presence of water at a consistency of 27 percent, at 115°C for 50 minutes with oxygen under a partial pressure of 80 psi. The delignified product was obtained with a yield of 48.4 percent based on the starting material, and had a kappa number of 28 and a viscosity of 10.8 centipoise.
5. The oxygen-treated product pulp of step 4 was subjected to three bleaching steps: chlorination, caustic extraction and chlorine dioxide treatment.
Chlorination: Pulp at 3 percent consistency by weight treated with 5.6% chlorine for 1 hour at 24°C. Caustic extraction: Pulp at 10 percent consistency by weight treated with 2.7% sodium hydroxide for 2 hours at 65°C. Chlorine dioxide treatment: Pulp at 6 percent consistency by weight treated with 0.7% chlorine dioxide by weight for 3 hours at 70°C. The pulp was washed with water at the completion of each of the bleaching steps.

The product had a brightness of 87.5 (Elrepho) and a viscosity of 10.7 centipoise. The physical properties of the product are shown in Table III.

TABLE III

Freeness C.S.F.	Breaking Length M	Burst Factor	Tear Factor	Bulk cc/gm
500	12,700	84	107	1.37
300	13,300	93	98	1.35

EXAMPLE 4

- A mixture of spruce and balsam wood chips was subjected to the following sequence of treatment.
1. The chips were cooked with kraft liquor containing 12 percent by weight effective alkali expressed as sodium oxide and 25 percent sulphidity based on the weight of wood, the ratio of liquor to wood being 4. The maximum temperature of the cook was 180°C and was reached after 60 minutes. The cook was maintained at 180°C for 15 minutes. The yield of the cook was 60.4 percent, the product having a kappa number of 103.
 2. The partially delignified wood was washed with fresh water.

3. Without refining, the partially delignified wood was impregnated at room temperature with an aqueous solution containing 9.0% sodium hydroxide and magnesium sulphate in an amount containing 0.2% magnesium ion, based on the weight of the partially delignified wood.
4. The alkaline wood was treated in a closed reactor in the presence of water at a consistency of 27 percent, at 110°C for 60 minutes with oxygen under a partial pressure of 80 pounds per square inch. The delignified product was obtained with a yield of 50.5 percent, based on the starting material, and had a kappa number of 25 and a viscosity of 15 centipoise.
5. The oxygen-treated product pulp of step 3 was subjected to three bleaching steps; chlorination caustic extraction and chlorine dioxide treatment. The conditions of the bleaching treatment are as follows.
- Chlorination: Pulp at 3 percent consistency by weight treated with 5 percent by weight of chlorine for 1 hour at 24°C.
- Caustic extraction: Pulp at 10 percent consistency by weight treated with 2.4 percent by weight of sodium hydroxide for 2 hours at 65°C.
- Chlorine dioxide treatment: Pulp at 6 percent consistency by weight treated with 0.7% chlorine dioxide by weight for 3 hours at 70°C.
- The pulp was washed with water at the completion of each of the bleaching steps.
- The product was obtained in 47.25 percent yield based on wood and had a brightness of 88.5 (Elrepho) and a viscosity of 14.9 centipoise.

The strength properties of the product are shown in Table IV.

TABLE IV

Freeness C.S.F.	Breaking Length M	Burst Factor	Tear Factor
500	12,900	101	105
300	14,300	109	98

The chips were cooked with a kraft liquor containing 15.5 percent effective alkali expressed as sodium oxide and 25 percent sulphidity based on wood, the ratio of liquor to wood being 4. The maximum temperature of the cook was 170°C and was reached after 60 minutes. The cook was maintained at 170°C for 120 minutes. The yield of the cook was 45.0 percent, the product pulp having a kappa number of 30.

The material was washed with fresh water and subjected to a five stage bleaching sequence as follows.

Chlorination: Pulp at 3% consistency by weight treated with 6 percent by weight of chlorine for 1 hour at 25°C.

Caustic extraction: Pulp at 10 percent consistency by weight treated with 2.8 percent by weight of sodium hydroxide for 2 hours at 65°C.

Chlorine dioxide treatment: Pulp at 6 percent consistency by weight treated with 1.0% chlorine dioxide by weight for 3 hours at 70°C.

Caustic extraction: Pulp at 10 percent consistency by weight treated with 0.5 percent by weight of sodium hydroxide for 1 ½ hours at 70°C.

Chlorine dioxide treatment: Pulp at 6 percent consistency by weight treated with 0.3% chlorine dioxide by weight for 3 hours at 70°C.

The pulp was washed with water at the completion of each of the bleaching steps.

The product was obtained in 41.2 percent yield based on wood, and had a brightness of 89.0 (Elrepho) and a viscosity of 18.8 centipoise.

The strength properties of the product are shown in Table V.

TABLE V

Freeness C.S.F.	Breaking Length M	Burst Factor	Tear Factor	Bulk cc/gm
500	11,800	105	110	1.15
300	12,600	115	96	1.29

TABLE VI

Yield Comparison Between the Process of this Invention
(Examples 1 to 4)
and a Conventional Kraft Process
(Example 5)
in Delignification of Coniferous Wood

Type of Cook	This Invention				Control
	Soda	Kraft	Soda + AMS	Kraft + AMS	Kraft
Example	2	4	3	1	5
Kappa Number	23	25	28	30	30
Yield % on wood	46.7	50.5	48.4	51.9	45
Increase in yield compared to control % on wood	1.7	5.5	3.4	6.9	
Increase in yield compared to control adjusted to same Kappa Number % on wood	4.2	7.2	4.1	6.9	

AMS = anthraquinone-2-monosulphonic acid

EXAMPLE 5

As comparison to the results obtained in Examples 1, 2, 3 and 4 which employed the process of the invention a mixture of spruce and balsam wood chips were subjected to the following conventional cooking and bleaching steps.

The same wood (spruce and balsam) was used in all 5 examples.

Adjustment of the yield of the control to a yield corresponding to kappa number of Examples 1 to 4 was carried out by interpolation of a plot of kappa number against % yield for the wood species in question.

The plot was based upon the relationship "Percent lignin = 0.15 (Kappa Number) — 0.24" disclosed in "Some Fundamental Aspects of Oxygen Pulping" by R. Marton, 4th Canadian Wood Symposium, Quebec City, July 4-6, 1973. The initial lignin content of the wood was obtained from "Pulpwoods of United States and Canada," I. H. Isenberg, 2nd edition, Institute of Paper Chemistry, Appleton Wisconsin 1951. The slope of the plotted values was 0.332 percent yield per kappa number. The adjusted yield values for the control (Example 5) are shown in Table VII.

TABLE VII

Kappa Number	Yield
23	42.5
25	43.3
28	44.3

TABLE VII

Comparison of Composition of Bleaching Chemicals by the Product of this Invention (Example 1) and of a Conventional Kraft Process (Example 5)		
	Example 1	Example 5 (Control)
Chlorine %	6	6
Sodium hydroxide %	2.9	3.3
Chlorine dioxide %	0.6	1.3

Both products were derived from spruce and balsam wood and prior to bleaching both had kappa numbers of 30. Example 1 was bleached to a brightness of 88.4, Example 5 to a brightness of 89.0.

Compared to the conventional kraft product, the product of this invention required for bleaching the same amount of chlorine but 12 percent less sodium hydroxide and 54 percent less chlorine dioxide.

EXAMPLE 6

A sample of birch wood chips was treated with kraft cooking liquor containing 13.0 percent effective alkali

and 25.0 percent sulphidity at a liquor to wood ratio of 4:1. The maximum temperature of the was 180°C and was reached in 2 hours. The treatment was terminated when 180°C was reached. The yield was 58.1 percent of wood at a kappa number of 42.9.

The product was washed with cold water and split into equal portions A and B. Without defiberization each portion was impregnated with an aqueous solution of 5.6% sodium hydroxide and magnesium sulphate containing 0.2% magnesium ion based on pulp. The impregnation of A was carried out at a pulp consistency of 3 percent followed by pressing to a consistency of 27 percent. The impregnation of B was carried out at a pulp consistency of 27 percent.

Both portions were treated in the same oxygen reactor at the same time at a temperature of 120°C for a period of 40 minutes at a partial pressure of oxygen of 80 psi.

Portion A had a yield of 93.9 percent with 9.8 percent of screen rejects based on pulp weight or a yield of 54.6 percent with 4.9 percent of screen rejects based on wood. The kappa number of the product was 11.1, the viscosity 22.2 cps. Portion B had a yield of 90.3 percent with 16 percent screen rejects based on pulp weight or a yield of 52.5 percent with 7.7 percent screen rejects based on wood. The kappa number was 12.3, the viscosity 16.6 cps.

It can be seen that low consistency impregnation is more effective.

EXAMPLE 7

Nine samples of birch wood chips were delignified in order to evaluate the bleaching response and strength properties of the resulting pulps. Four of the samples were delignified using the process of this invention wherein the first stage employed kraft cooking liquor. Four additional samples were delignified using the process with first stage cooking with soda liquor. One sample serving as control was delignified by a conventional kraft cooking procedure. The details of the delignification procedures are shown in Table IX, the bleaching response in Table X and strength properties in Table XI.

TABLE IX

Sample	Cooking Liquor	First Stage					Second Stage					
		Alkali % on wood	AMS % on wood	Temp. °C	Retention time hours	Kappa Number of pulp	Yield % on wood	NaOH % on pulp	Kappa Number of pulp	Yield % on pulp	Yield % on wood	Viscosity centi-poise
1	Kraft	10.0		180	¼	51	61.2	4.5	15	94.0	57.6	23.8
2	Kraft	10.0	0.5	180	1/6	51	64.6	4.5	17	95.0	61.6	20.4
3	Kraft	10.0		170	1½	53	62.1	4.5	17	90.0	56.6	27.6
4	Kraft	10.0	0.5	170	1	53	61.4	4.5	15	90.0	55.7	21.6
5	Soda	18.0		180	1	49	55.0	4.25	15	90.5	51.4	12.8
6	Soda	16.0	0.1	180	¾	52	56.6	4.5	16	96.7	54.6	15.2
7	Soda	16.0		170	2	55	57.0	4.5	16	89.7	51.0	15.7
8	Soda	18.0	0.1	170	1¼	55	58.7	4.5	16	94.4	55.4	14.5
9	Kraft	13		170	1½	23.8	52.8					36.7
Control												

First Stage

AMS = anthraquinone-2-monosulphonic acid

Alkali charge for kraft cooks — % effective alkali

Alkali sulphide at 25% sulphidity

Alkali charge for soda cooks — % sodium hydroxide

Heating time to maximum temperature — 1 hour

Second Stage

NaOH added to pulp at 27% consistency Oxygen treatment: pulp contained 0.2% magnesium ion. Oxygen pressure 80 psi at 120°C for 60 minutes.

TABLE X

Sample	Cooking Liquor	C % chlorine on pulp	E % NaOH on pulp	Permanganate Number	D % chlorine dioxide on pulp	E % NaOH on pulp	D % chlorine dioxide on pulp	Viscosity Centipoise	Brightness Elrepho
1	Kraft	3.0	1.45	1.6	0.6			19.8	87.0
2	Kraft	3.4	1.65	1.1	0.6			16.5	84.9
3	Kraft	3.4	1.65	1.0	0.6			20.0	85.1
4	Kraft	3.0	1.45	1.3	0.7			15.7	85.4
5	Soda	3.0	1.45	1.4	0.6			10.7	85.0
6	Soda	3.2	1.55	1.6	0.6			12.9	85.4
7	Soda	3.2	1.55	1.4	0.6			12.5	84.6
8	Soda	3.2	1.55	1.2	0.5			11.9	85.2
9	Kraft Control	4.76	2.35	3.4	1.2	0.5	0.3	26.5	88.0

C = chlorination, pulp at 3% consistency at room temperature for 1 hour
E = caustic extraction, pulp at 10% consistency at 65°C for 2 hours
D = chlorine dioxide treatment, pulp at 6% consistency at 70°C for 3 hours

TABLE XI

Sample	Cooking Liquor	Tensile (Breaking Length) KM		Burst Factor		Tear Factor		Viscosity Centipoise
		500 CSF	300 CSF	500 CSF	300 CSF	500 CSF	300 CSF	
1	Kraft	10.8	12.3	73	79	106	95	19.8
2	Kraft	10.6	11.9	66	82	91	81	16.5
3	Kraft	10.1	11.0	72	79	105	94	20.0
4	Kraft	11.0	11.6	70	81	89	81	15.7
5	Soda	9.9	11.0	60	73	98	93	10.7
6	Soda	9.7	11.5	60	75	121	91	12.9
7	Soda	9.9	10.8	65	77	105	93	12.5
8	Soda	10.2	11.0	65	72	99	90	11.9
9	Kraft Control	10.8	11.0	68	71	112	91	26.5

TABLE XII

Yield Comparison Between the Process of this Invention (Example 7, Samples 1, 2, 5 and 8) and a Conventional Kraft Process (Example 7 Sample 9) in Delignification of Deciduous Wood (Birch)					
This Invention					Control
Type of cook	Soda	Kraft	Soda +AMS	Kraft +AMS	Kraft
Sample	5	1	8	2	9
Kappa Number	15	15	16	17	23.8
Yield % on wood	51.4	57.6	55.4	61.6	52.8
Increase in yield compared to control % on wood	-1.4	4.8	2.6	8.8	
Increase in yield compared to control adjusted to same Kappa Number % on wood	2.4	8.6	5.9	11.7	

Adjustment of yield of the control to a yield corresponding to the kappa number of Samples 1, 2, 5 and 8 was carried out as in in Examples 1 to 4. The slope of the plot of percent yield against kappa number was 0.415 percent yield per kappa number. The adjusted yield values for the control (Sample 9) are as follows.

TABLE XIII

Kappa Number	% Yield
15	49.0
16	49.5
17	49.9

EXAMPLE 8

A mixture of spruce and balsam fir wood chips was subjected to the following treatment sequence.

1. The chips were cooked with soda liquor containing 20 percent by weight of sodium hydroxide based on the weight of wood, the ratio of liquor to wood being 4:1. The cook contained 0.1 percent by weight based on wood of anthraquinone-2-monosulphonic acid. The maximum temperature of the cook was 180°C and was reached after 1 hour. The cook was maintained at 180°C for 50 minutes. The kappa number of the product was 82.4.
2. The partially delignified wood was washed with fresh water.
3. Without defiberization, the partially delignified wood was impregnated at room temperature with an aqueous solution containing 5.5 percent by weight of sodium hydroxide and magnesium sulphate in an amount containing 0.2 percent magnesium ion based on the weight of partially delignified wood.

4. The alkaline wood was treated in a closed reactor in the presence of water at a consistency of 27 percent at 115°C for 50 minutes with oxygen under a partial pressure of 80 pounds per square inch. The delignified product was obtained in a yield of 92.3 percent by weight based on the material from step (2) with 2.0 percent screen rejects. The material had a viscosity of 12 centipoise and a kappa number of 35.7.

treated additionally with 0.1 percent by weight of anthraquinone-2-monosulphonic acid (AMS). In all samples the liquor to wood ratio was 4:1. The maximum temperature of the cooks was in all cases 170°C. After digestion the partially delignified product was washed with water. The conditions of the cooks and the characteristics of the product pulp are shown in Table XIV.

TABLE XIV

Sample	Alkali %	Sulphidity %	Time to reach 170°C Hours	Retention time at 170°C Hours	Yield % on wood	Screen Rejects % on wood	Kappa Number	Viscosity cps
1	10.5	25.0	2	23/60	62.5		49.9	
2	12	25.0	1	2	54.2	2.6	20.3	64.4
3	16		2	1½	60.8		51.3	
4	16		2	1	60.9		51.3	
	+0.1% AMS							
5	18		1	2½	55.7	0.8	24.1	26.7

5. The oxygen-treated product pulp of step 4 was subjected to three bleaching steps: chlorination, caustic extraction and chlorine dioxide treatment.

Chlorination: Pulp at 3.0 percent consistency by weight treated with 7.14 percent by weight chlorine for 1 hour at 25°C.

Caustic Extraction: Pulp at 12 percent consistency by weight treated with 3.57% sodium hydroxide for 2 hours at 65°C.

Chlorine dioxide treatment: Pulp at 6 percent consistency by weight treated with 1.0 percent chlorine dioxide by weight for 3 hours at 70°C. The bleached product had a brightness of 85 (Elrepho) and a vis-

The products of Samples 1, 3 and 4 were treated, at a consistency of 3 percent in water, with sodium hydroxide and magnesium sulphate in amount equal to 0.2% magnesium ion. The products were then pressed to a consistency of 27 percent and treated in an oxygen reactor with oxygen under a partial pressure of 80 psi for 50 minutes at 115°C. The oxygen-treated material was then treated for 2 minutes in a Cowles Dissolver with additional water. The product was then washed with water. The results are shown in Table XV which includes data on Samples 2 and 5 for purposes of comparison. Sample 2 is a conventional kraft cook; Sample 5 a conventional soda cook.

TABLE XV

Sample	NAOH %	Yield % on pulp	Yield % on wood	Screen Rejects % on wood	Viscosity cps	Kappa Number	Yield of Sample 2 adjusted for Kappa Number of sample % on wood	Difference in yield % on wood
1	3.5	90.8	56.8	3.97	38.8	14.1	51.9	4.9
2			54.2	2.6	64.4	20.3	54.2	
3	4.0	91.6	55.7	1.1	22.3	16.4	52.8	2.9
4	4.0	94.2	57.4	2.4	27.3	19.3	53.8	3.6
5			55.7	0.8	26.7	24.1	55.6	-0.1

cosity of 10.6 centipoise. The yield was 92.1% based on the weight of the oxygen-treated pulp i.e. the reduction in yield during bleaching was 7.9 percent.

EXAMPLE 9

Five portions of eastern cottonwood chips were subjected to differing delignification treatments. Eastern cottonwood is a low density deciduous wood, in distinction to birch, a high density deciduous wood. In the first step all portions were treated in a 3 liter digester with cooking liquor at a liquor to wood ratio of 4:1. The maximum temperature of the cooks was 170°C. Blow-down was simulated by a 2 minute residence time of the product with added water in a "Cowles Dissolver." Samples 1 and 2 were treated with kraft cooking liquor; Sample 3 to 5 with soda cooking liquor. The percentage of the sodium hydroxide alkali reagent is expressed in Samples 1 and 2 as effective alkali; in Samples 3 to 5 as weight percent sodium hydroxide. Sample 3 was

The yield of Sample 2 (conventional Kraft) was adjusted to a yield corresponding to the kappa numbers of Samples 1, 3 4 and 5 as described for preceding examples.

All 5 samples were next subjected to bleaching sequences. All samples were subjected to the sequence; chlorination, caustic extraction with sodium hydroxide, and treatment with chlorine dioxide. Samples 2 and 5 were subjected to the additional sequence; caustic extraction with sodium hydroxide, and treatment with chlorine dioxide. The material was washed with water after each bleaching step. The results are shown in Table XVI.

The physical properties of the bleached products were measured. These are shown in Table XVII.

TABLE XVI

		1	2	SAMPLE 3	4	5
% Cl ₂		2.8	4.06	3.28	3.86	4.82
°C Temp.	C	25	25	25	25	25
hr Time		1	1	1	1	1
% NaOH		1.4	2	1.6	1.9	2.81
°C Temp.	E	65	65	65	65	65
hr Time		2	2	2	2	2
% ClO ₂		0.5	1	0.5	0.5	1
°C Temp.	D	70	70	70	70	70
hr Time		3	3	3	3	3
% NaOH			0.6			0.5
°C Temp.	E		65			65
hr Time			2			2
% ClO ₂			0.5			0.5
°C Temp.	D		70			70
hr Time			3			2
Brightness		89.5	89.9	87.4	88.5	87.4
Reversion		5.0	2.6	4.1	4.0	3.1
cps Viscosity		24.3	40.9	17.0	21.3	16.5
% Yield on pulp		93.8	94.7	95.2	95.6	95.0
% Yield on wood		53.3	51.3	53.0	54.8	52.9
% Yield less yield of Sample 2		2.0		1.7	3.5	1.6
% Yield less yield of Sample 5		0.4	-1.6	0.1	1.9	

TABLE XVII

Sample	Tensile Breaking Length KM		Burst Factor		Tear Factor		Bulk cc/gm	
	500 CSF	300 CSF	500 CSF	300 CSF	500 CSF	300 CSF	500 CSF	300 CSF
1	8.0	10.0	51	72	99	88	1.34	1.24
2	7.4	9.4	45	61	89	89	1.36	1.27
3	7.5	9.7	49	65	98	84	1.38	1.27
4	8.5	10.1	50	66	101	93	1.38	1.27
5	7.1	8.7	38	60	89	86	1.43	1.27

What we claim is:

1. A process for the delignification of lignocellulosic material which comprises the steps of
 1. treating lignocellulosic material in a closed reaction vessel with pulping liquor containing a reagent selected from the group consisting of an alkali metal hydroxide and a mixture of an alkali metal hydroxide and an alkali metal sulphide, wherein there is added to said pulping liquor 0.02 to 2.0 percent, preferably 0.05% to 1.0% by weight, based on the weight of the lignocellulosic material of a material selected from the group consisting of anthraquinone mono sulphonic acid, anthraquinone disulphonic acid, alkali metal salts of said acids and admixtures of aforesaid acids and salts, at a temperature in the range 160°C to 195°C for a period of not greater than 120 minutes and preferably not greater than 90 minutes, the temperature and period of treatment being adapted to provide a pulp yield of 55 to 65 percent by weight,
 2. displacing the pulping liquor from the lignocellulosic material with water, or an aqueous solution of alkali metal hydroxide,
 3. treating the lignocellulosic material without prior defiberization at a consistency of 2.0 to 30.0 percent by weight in aqueous suspension for 0.5 to 30 minutes at 20°C to 90°C with 2.0 to 20.0 percent by weight of alkali metal hydroxide.
 4. treating the alkaline lignocellulosic material in aqueous medium at a consistency of from 3.0 to

- 35.0 percent by weight with oxygen or an oxygen-containing gas for 10 to 120 minutes at a temperature of 80°C to 140°C and a partial pressure of oxygen of 30 to 200 pounds per square inch, and
5. washing the oxygen treated lignocellulosic material with water.
2. A process as claimed in claim 1 wherein the lignocellulosic material is a coniferous species of wood.
3. A process as claimed in claim 1 wherein the lignocellulosic material is a deciduous species of wood.
4. A process as claimed in claim 1 wherein the pulping liquor employed in the first step contains 14.0 to 24.0 percent, preferably 18.0 to 20.0 percent by weight, based upon the weight of the lignocellulosic material, of alkali metal hydroxide.
5. A process as claimed in claim 1 wherein the pulping liquor employed in the first step contains 8.0 to 14.0 percent, preferably 10.0 to 12.0 percent, by weight of alkali metal hydroxide expressed as effective alkali, and 5.0 to 40.0 percent, preferably 20.0 to 30.0 percent, by weight of alkali metal sulphide expressed as percent sulphidity, the percentages based upon the weight of lignocellulosic material.
6. A process as claimed in claim 1 wherein during the second step the pulping liquor is displaced from the lignocellulosic material by spent liquor from the oxygen treatment of the fourth step of the process.
7. A process as claimed in claim 1 wherein during the second step the pulping liquor is displaced from the lignocellulosic material by white water.

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- 8. A process as claimed in claim 1 wherein during the third step, 0.1 to 1.0 percent by weight of a magnesium salt is added to the lignocellulosic material, the percentage being based upon the weight of the lignocellulosic material.
- 9. A process as claimed in claim 8 wherein the magnesium salt is magnesium chloride or magnesium sulphate.
- 10. A process as claimed in claim 1 wherein the alkali metal hydroxide is sodium hydroxide or potassium hydroxide.
- 11. A process as claimed in claim 1 wherein during the third step the alkali metal hydroxide is provided in

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- the form of white liquor or oxidized white liquor.
- 12. A process as claimed in claim 1 wherein during the third step the lignocellulosic material is at a consistency of 2 to 6 percent by weight.
- 13. A process as claimed in claim 1 wherein the oxygen-treated lignocellulosic material produced thereby is subjected to a bleaching sequence.
- 14. A process as claimed in claim 13 wherein the bleaching sequence comprises the successive steps of chlorination, caustic extraction and treatment with chlorine dioxide.

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