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Modification of conventional chlorine dioxide bleaching to hot chlorine dioxide to reduce the fatty and resin acids in bleaching effluent

Abstract: *Environmental constraints and customers' preferences compelled the paper industry for cleaner and greener production. The discharge of wastewater loaded with toxic chlorolignin compounds and fatty acids has been a major concern. Fatty acids present in bleaching effluent are known for causing genetic disorders and sub lethal toxicity in aquatic organisms. Present study emphasized on use of rice straw pulp of kappa number ~15 for elemental chlorine free bleaching. The conventional chlorine dioxide (D_0) bleaching method was modified to hot chlorine dioxide (D_{HT}) with the aim of reducing the amount of fatty acids in bleaching effluent. The 5 bleaching sets having control, D_{HT} sequence with same dose of chemicals and 3 sets of D_{HT} with 10%, 15%, 20% less chlorine dioxide at initial stage were considered. The fatty acids present in the effluent were extracted in dichloromethane and derivatized to methyl esters before analysis by gas chromatography. The amount of fatty acids reduced significantly in D_{HT} based sequences. A reduction of 39% in total fatty acids was observed in D_{HT} sequence having same dose of chlorine dioxide. On reducing the chlorine dioxide by 10%, 15% and 20%, the amount of fatty acids was reduced by 35%, 31% and 29%, respectively.*


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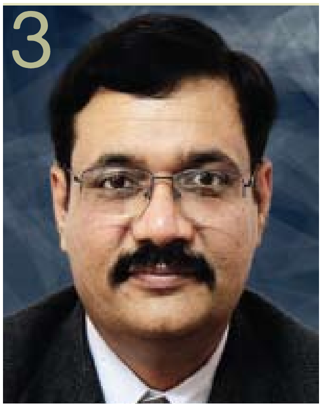
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Key Words: *Rice straw; bleaching; chlorine dioxide; effluent; fatty acids*

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Introduction

The global environmental issues including waste disposal and utilization, global warming, pollution, forest destruction and depletion of natural resources have been enhanced with economic growth. To minimize the impact of industrial development on

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environmental resources, strict policies have been formulated by the governments of the different nations. The pulp and paper industry, which derives its growth from forest based raw materials and use of fresh water resources, is not only imposing the threat to these resources but also facing the shortage of raw materials for sustainable production. The left over lignocellulosic part after harvesting the crops like cereal straws in the agricultural fields have high potential to compete with the hardwoods and softwoods. Rice straw is a potentially available agricultural residue in India that can be used as raw material for papermaking. Rice straw mainly comprises of 33.3% cellulose, 27.3% pentosan, 13.0% lignin and 12.6% ash of which silica is 11.7% (1). Soda-anthraquinone pulping is the most preferred process to convert agro residues to the fibrous pulp as more than half of the raw material can be converted to pulp that results in high pulp yield (2). Addition of catalyst like anthraquinone perks up the delignification rate without much degradation of the cellulosic fibers (3). Bleaching is an integral part of the pulp manufacturing process but associated with discharge of pollutants loaded with toxic components. Bleaching effluents are significantly rich in COD, BOD, colour, total solids, chlorophenolic compounds and fatty resin acids.

Resin and free fatty acids are the lipophilic constituents in woods. These are tricyclic diterpenes of low molecular weight and are the part of wood extractives that protect the wood from insets and microbial attack (4). These resin acids are categorized into abietanes and pimaranes (5). The type of the wood species contributes a lot for the origin of resin and fatty acids within the bleach plant effluent. Pulping process and washing of unbleached pulp also affects the discharge of these acids in the bleach plant effluent (6). Resin acids can undergo a number of chemical modifications including isomerization, dehydrogenation, oxidation and chlorination abiotically during bleached pulp production. These extractives are known for causing genetic disorders and sub lethal toxicity in aquatic organisms (7). These resin fatty acids contribute to approximate 70% of the total toxicity in bleaching effluents (8). Resin acids have high potential for accumulation in fish tissue. Abietic and dehydroabietic acids are found in a large amount and form about 14-35% of the total resin acids (9). Apart from participating in the effluent toxicity, extractives if present in the pulp affect the paper machine runnability, pulp and paper quality (10). This presented the need for routine and rapid monitoring of these compounds and their removal from the bleaching effluents.

Elemental chlorine free (ECF) bleaching using chlorine dioxide is the most preferred stage incorporated during bleaching process by the national and international paper industry as chlorine dioxide is more specific for lignin removal than other oxidizing agents (11). ECF bleaching brightens the pulp without carbohydrates degradation (12). Chlorine dioxide bleaching also results into low biological and chemical oxygen demands, colour, adsorbable organic halides (AOX), chlorophenols, bromophenols and resin fatty acids in the effluent (13). Modification in ClO_2 bleaching at high temperature and low pH (D_{HT}) at first stage offers several advantages in contrast to conventional D_0 bleaching. At high temperature and low pH, the hydrolysis of HexA, which represents the false lignin, take places rapidly (14). Hydrolysis of HexA results into low requirement of oxidizing chemicals during bleaching that further affects the generation of chlorolignin compounds. The consumption of chlorine dioxide may reduce by 40% on modifying the conventional D_0 stage to D_{HT} stage (15).

Studies revealed that the amount of AOX reduced by 40- 50% on modifying the D_0 stage to D_{HT} stage as in D_{HT} stage not only the generation of the these compounds decreased but also the decomposition of the chlorolignin components take place (16,17). The literature available till date on modification of D_0 stage to D_{HT} is concentrated on the brightness reversion, improvement in delignification, removal of HexA and reduction in AOX generation with fewer concerns about the chlorolignin compounds (18,19,20) but no evidences are available regarding the effect of D_{HT} on fatty resin acids generated in bleach plant effluent. The present study focuses on use of agro residue (rice straw) in papermaking. The 15 kappa number pulp was prepared by soda-AQ process which gives the pulp yield of 56%. The pulp was bleached with ECF bleaching following $DE_{OP}D$ sequence and modified sequence $D_{HT}E_{OP}D$ using varied doses of chlorine dioxide at initial stage. The effluent generated in bleaching process was analyzed for the resin fatty acid generation. The results are expressed in terms of reduction in resin fatty acids in D_{HT} based sequence in comparison to the conventional $DE_{OP}D$ sequence bleaching.

Materials and methods

Rice straw processing

The rice straw was obtained from Haryana, India which was washed with hot water and air dried to a dryness of 85%. The total extractives in rice straw were 12.9% as measured by method T 204 om-88. The soda-AQ pulping of the raw material was conducted in autoclave batch digester at 155°C for 20 min. A ramp of 90 min was given to attain the temperature condition. An alkali dose of 12%, 0.05% of anthraquinone and water were added on over dry weight basis of rice straw to maintain a bath ratio of 1:4. After pulping, the black liquor was separated and the pulp was further washed out to remove the residues of the alkali. The pulp was screened and analyzed. The kappa number of the pulp was 15.2. The initial properties of the pulp are given in Table 1

Table 1: Characteristics of unbleached soda-AQ rice straw pulp

Parameters	Unbleached pulp
Kappa number	15.2
Brightness (% ISO)	37.6
Tear index (mNm^2/g)	3.42±0.1
Tensile index (Nm/g)	42.2±1.8
Burst index (kN/g)	2.46±0.05
Double fold	36
Viscosity (cP)	14.4
Drainage (°SR)	36

Bleaching of rice straw pulp

A control set with conventional D_0 stage was executed as $D_0E_{OP}D$ where D represents the chlorine dioxide stage and oxygen reinforced alkali extraction using hydrogen peroxide is denoted by E_{OP}. D_0 stage was modified to D_{HT} and four more sets of pulp were bleached: one at the same dose of chlorine dioxide as in $D_0E_{OP}D$ and other three were at 10%, 15% and 25% lower chlorine dioxide dose at initial stage than conventional process. The dose of the different chemicals (chlorine dioxide, alkali, hydrogen peroxide) and oxygen pressure were selected on the basis of previous studies (1,2). The bleaching conditions for the given study are mentioned in the Table 2.

The pulp was well mixed and experiments were conducted in water bath for D_0, D_{HT} and D stages and in air heated digester for E_{OP} stage. The pulp was filtered after the bleaching process and filtrate was collected as effluent. The brightness of the pulp in $D_0E_{OP}D$ sequence was found to be 82.9% ISO where as in $D_{HT}E_{OP}D$ sequence having same dose of ClO_2 at initial stage as in control, the brightness was found to be 83.6% ISO. For the sequence in which the ClO_2 was reduced by 10% at initial stage, 83.2% ISO brightness was achieved. The comparative brightness to the control set was observed on further reducing the dose of chlorine dioxide to 15 and 20%. The effluent was used to extract the resin fatty acids.

Analysis of fatty and resin acids

Extraction process

The extraction of resin fatty acids in the effluent was done by adopting the method used by Casado

Table 2: Experimental conditions for bleaching

Chlorine dioxide (%)	3.75	3.75	3.37	3.19	3.00	-	0.9
NaOH (%)	-					1.8	-
Peroxide (%)	-					0.5	-
Consistency (%)	5					10	
Initial pH	5.5	2.9				11.0	3.5
End pH	2.9	2.0				10.2	3.0
Temperature (°C)	55	85				75	80
Time (min)	45	120					180

et al (21). 50 mL of the composite effluent of each sequence was diluted to 100 mL. The concentrated hydrochloric acid was added to attain the pH-1.0. The samples were sonicated for 6 h. After sonication, samples were shifted to the separating funnel of 250 mL and 5 mL of dichloromethane (HPLC grade) was added to the samples and contents were shaken for about 2 min. The organic phase was collected in a 50 mL beaker and the process was repeated with another 5 mL of dichloromethane. The extracts after the repeated decantation were mixed and dried over anhydrous sodium sulfate. The organic phase was concentrated to dryness in a rotary vacuum evaporator. Then 3.0 mL of methanol and 1 mg of tridecanoic acid (IS) were added to the extract and transferred to the test tube.

Esterification process

For esterification, 2.0 mL of 14% BF_3 methanolic solution (procured from Sigma Aldrich) was added into the test tubes containing fatty acid extract. The whole contents were placed in a water bath at 70°C for 3 min. To stop the reaction, 2-4 mL of double distilled water was added. After cooling the reaction mixture, 2 mL of dichloromethane was added and the fatty acid methyl esters (FAME) were extracted from the aqueous methanol phase by shaking the test tube for 1 min. The methylene chloride layer containing the fatty acid methyl esters was drawn off and transferred to another test tube. The extraction of leftover FAME in aqueous methanol phase was repeated twice with addition of another 1.0 mL of methylene chloride. The whole content extracted in methylene chloride was mixed properly and dried over anhydrous sodium sulfate. The derivatization process was carried out under the nitrogen stream. The CRM for the FAME was provided by Sigma Aldrich and standard solutions of 0.1, 0.5, 1.0, 1.5 and 2 ppm were prepared. The resin fatty acids abietic, levopimaric, 9,10-dichlorostearic acid, palustric, neoabietic and chlorohydroabietic acids (all obtained from Sigma Aldrich) were derivatized to methyl esters by using the same process as for the effluent. The various FAME present in the sample were detected by matching their retention time (±0.5 min) with those of standards using gas chromatography with FID detector. The programming for analyzing the FAME on GC is given below:

GC conditions for FAME analysis

Column type	- BPx5
Column dimensions	- 30 m x 0.53 mm I.D.
Detector type	- FID
Detector temperature (°C)	- 290
Injector temperature (°C)	- 270
Column temperature (°C)	- Initial 100 for 3 min
	100 – 180 @ 4°C min^{-1}
	180 for 10 min
	180 – 270 @ 15°C min^{-1}
	270 for 10 min
Column pneumatics	- 1.2 mL min^{-1}
Make up nitrogen flow	- 28 mL min^{-1}
Split ratio	- Splitless

1 mL of the standard solution of the fatty acids (FAME mix) and resin fatty acids (derivatized methyl esters) were injected to the GC. The peak area was notified to analyze the extraction efficiency (EE) as per the equation given below:

$$EE\ (\%) = \frac{\text{peak area of the sample}}{\text{peak area of the standard}}$$

Results and discussions

Effect of D_{HT} on saturated and unsaturated fatty acids

For the analysis of resin fatty acids in the bleaching effluent using GC-FID, the effluent after each stage was collected and mixed in their volumetric proportion to prepare the composite effluent. The retention time, response factor and the concentration of fatty acids found in effluent are given in table 3. Lee et al (22) suggested that the acid catalysis in methanol is an effective way for etherification of fatty acid esters. For the fatty acids, the standard containing 37 components of fatty acid methyl esters was run on GC. But in all the samples out of these acids only four were present named palmitic, oleic acid, stearic acid and linoleic acid. The studies on extraction and characterization of cereal straws (rice and wheat) and other non woody species also reported the presence of palmitic, linoleic and oleic acid (23,24,25). Silverio et al (26) on their study on extractives in eucalyptus found that the non hydrolysed and hydrolysed extracts of dichloromethane contain sufficient amount of palmitic, oleic acid and linoleic acid. Freiere et al (27) reported that unsaturated acids like oleic, stearic and linoleic etc. present in hardwood were easily oxidized by the chlorine dioxide bleaching. These fatty acids are removed from the pulp and become the part of the bleaching effluent.

Table 3: Generation of saturated and unsaturated fatty acids in bleaching effluent of different sequences

Compounds	Type	Retention time (min)	Extraction efficiency (%)	% ClO_2	$D_0E_{OP}D$ 3.75	$D_{HT}E_{OP}D$ 3.75	3.37	3.19	3.0
					FAME concentration (g/t)				
Palmitic acid	saturated	30.2	75		2.20	1.36	1.62	1.57	1.61
Stearic acid		30.8	75		1.90	1.09	1.12	1.26	1.31
Oleic acid	unsaturated	35.2	72		1.76	1.04	1.21	1.29	1.37
Linoleic acid		38.3	84		2.40	1.59	1.43	1.58	1.63

In present study, it was found that the highest concentration (8.42 g/t) of the saturated and unsaturated fatty acids was found in the effluent of $DE_{OP}D$ bleaching sequence. Out of 4 fatty acids found in bleaching effluent, the amount of linoleic acid was the highest as 2.40 g/t followed by the palmitic acid. Stearic and oleic acids were also found in noticeable amount in $DE_{OP}D$ sequence. The total amount of these acids were reduced by 39% in $D_{HT}E_{OP}D$ sequence having same amount of chlorine as in control. This may be attributed to the degradation of these long chain fatty acids at high temperature and increased bleaching time. The amount of palmitic acid was reduced by 38% in $D_{HT}E_{OP}D$ sequence and more than 25% in other D_{HT} based sequences having lower amounts of chlorine dioxide in initial stage in comparison to conventional D_0. The % reduction in total fatty acids in sequences with 10%, 15% and 20% less chlorine dioxide than control was found to be 35%, 31% and 29%, respectively. This showed that the chlorine dioxide affected the long chain fatty acids and reduction in chlorine dioxide dose resulted into less reduction of these components. The % reduction in different fatty acids on D_{HT} treatment is shown in figure 1.

Effect of D_{HT} on chloro fatty and resin acids

The resin acids comprise the structure having both hydrophilic carboxyl unit and hydrophobic skeleton (28). Such type of structure makes the resin acids good solublizing agent and responsible for imparting toxicity to the waste water. To estimate the presence and concentration of chloro fatty and resin acids 6 components abietic, levopimaric, 9,10-dichlorostearic, palustric, neoabietic and chlorohydroabietic acids were taken into consideration. The 9,10-dichlorostearic acid, a chloro fatty acid (cFA) was present in significant amount in the $DE_{OP}D$ sequence. Study by Kumar et al (29) also found the presence of such type of chlorofatty acids in the bleaching effluents of mixed hardwood pulp. Out of the total five resin acids studied, the chlorohydroabietic acid was present in the highest amount. In $DE_{OP}D$ sequence 2.58 g/t of the chlorohydroabietic acid was generated. Many studies on pulp and paper effluent reported the presence of chlorohydroabietic acid in the bleaching wastewater (5,7). The abietic acid and neoabietic acid were also found in the different sequences but the levopimaric acid and palustric acid were not present in the bleaching effluents. Belmonte et al (7) found that both abietic and chlorohydroabietic acid constitute about 14% to 30% of the total resin content of the bleaching effluent. Same observations were reported by Conde et al (30) in their study on softwood. The amount of chlorofatty acids and chlororesin acids is given in table 4.

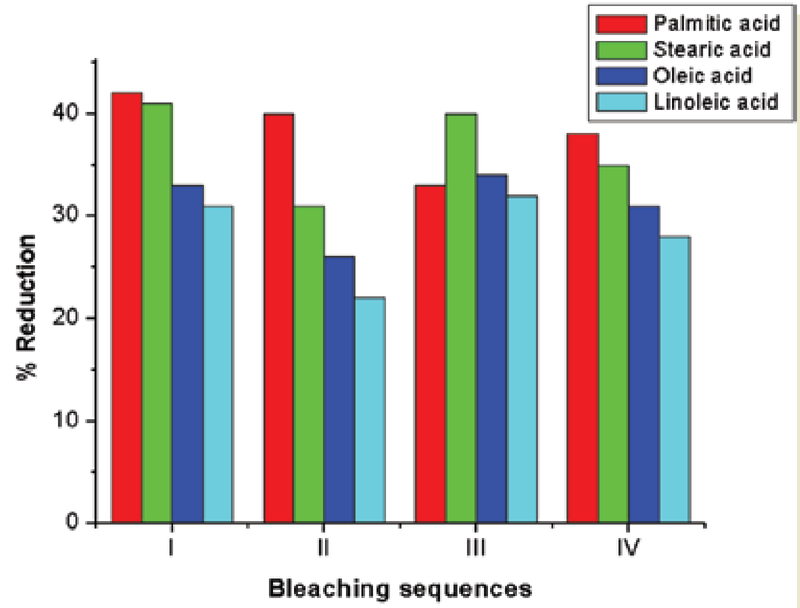

Figure 1: % reduction in saturated and unsaturated fatty acids achieved on modifying the conventional D_0 process to D_{HT} where I- $D_{HT}E_{OP}D$ with same amount of chlorine dioxide as in control II, III, IV - $D_{HT}E_{OP}D$ with 10%, 15% and 20% of less chlorine dioxide in initial stage than control

Table 4: Generation of chloro fatty and resin acids in bleaching effluent of different sequences

Compounds	Retention time (min)	Extraction efficiency (%)	% ClO_2	$D_0E_{OP}D$ 3.75	$D_{HT}E_{OP}D$ 3.75	$D_{HT}E_{OP}D$ 3.37	$D_{HT}E_{OP}D$ 3.19	$D_{HT}E_{OP}D$ 3.0
				FAME concentration (g/t)				
9,10-dichlorostearic acid	34.6	85		0.96	0.85	0.56	0.32	0.25
Chlorohydroabietic acid	35.8	82		2.58	1.96	1.63	1.42	1.14
Abietic acid	54.2	68		0.54	0.34	0.11	0.16	0.14
Neoabietic acid	55.6	64		0.36	0.21	0.20	0.15	0.11

Hubbe et al (31) observed that resin acids are highly stable to chemical degradation and impart high level toxicity to the bleach plant effluent. Modification of conventional D_0 process to D_{HT} imposed significant impact on the fatty and resin acids. The total amount of resin acids was reduced by 29%, 40%, 58%, and 60% in $D_{HT}E_{OP}D$ sequences. The amount of 9,10-dichlorostearic acid was reduced by 32% in $D_{HT}E_{OP}D$ sequence having same dose of the chemicals. The % reduction increased further on decreasing the dose of chlorine dioxide with D_{HT} process and 73% reduction was found on reducing chlorine dioxide dose by 20%. The results are attributed to that most of the chlorine dioxide was consumed in the bleaching process and less residues of chlorine dioxide reacted to the extractives present in the rice straw soda-AQ pulp. The chlorohydroabietic acid that was present in the highest quantity amongst all resin acids in all the sequences was reduced by 24% in $D_{HT}E_{OP}D$ sequence. The % reduction was increased by 37%, 45% and 56% in $D_{HT}E_{OP}D$ sequences with 10%, 15% and 20% less chlorine dioxide than control. This may be attributed to the high temperature during chlorine dioxide bleaching followed by the alkaline extraction. Chlorine dioxide eliminates the ethylenic groups and the reactions of these groups to generate epoxide get ruptured (32). Sithole et al (33) found that alkaline conditions and high temperature are responsible for deresination in the pulp. The study also revealed that enzymatic bleaching followed by D_{EP} sequences reduced the amount of fatty acids and triglycerides to a greater extent. Valto et al (28) also found the presence of such resin acids in paper mill wastewater. The study also revealed that the amount of these resin acids within the pulp depended on the paper manufacturing process performance. The % reduction in different chloro resin acids is given in figure 2.

The amount of abietic acid was reduced to 0.34 g/t in $D_{HT}E_{OP}D$ sequence compared to 0.54 g/t in $D_{HT}E_{OP}D$ sequence. The concentration of abietic acid was lowered down by 48%, 56% and 59% on reducing the dose of chlorine dioxide by 10%, 15% and 20%, respectively. The same trend of reduction was observed for neoabietic acid also. The literature regarding the detailed impacts of D_{HT} during rice straw pulp bleaching on resin fatty acids till date was inadequate to discuss and compare the results of present study.

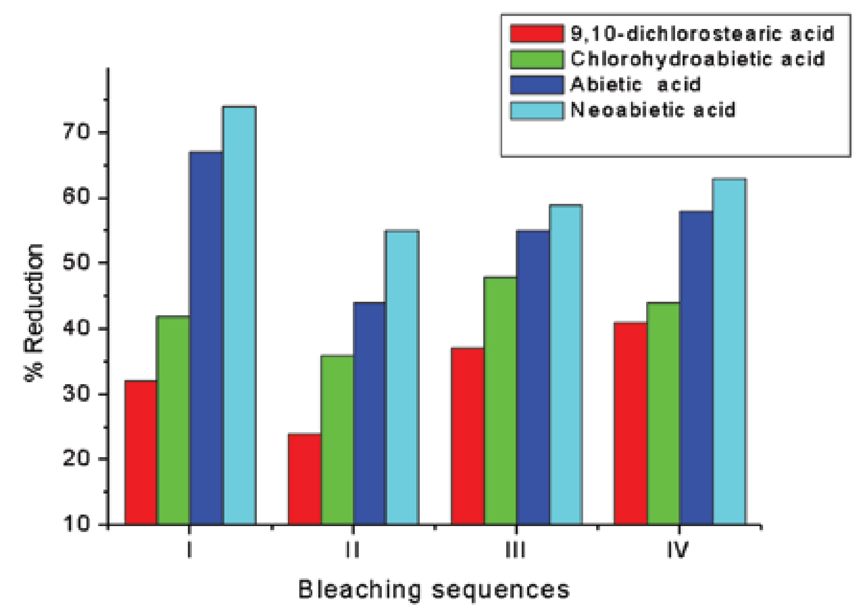

Figure 2: % reduction in chloro fatty and resin acids achieved on modifying the conventional D_0 process to D_{HT} where I- $D_{HT}E_{OP}D$ with same amount of chlorine dioxide as in control II, III, IV - $D_{HT}E_{OP}D$ with 10%, 15% and 20% of less chlorine dioxide in initial stage than control

Conclusions

The present study depicted the use of rice straw in papermaking effective as the soda-AQ pulp produced from it contained required strength characteristics. The amount of the extractives which affect the pulp quality and processing was less in rice straw in comparison to hardwoods and softwoods. In bleaching wastewater, the presence of palmitic acid, oleic acid, stearic acid, linoleic acid, 9,10-dichlorostearic acid, chlorohydroabietic acid, abietic acid and neoabietic acid was observed. The total amount of these fatty and resin acids was the highest i.e. 12.7 g/t in $DE_{OP}D$ sequence. Out of the fatty acids, linoleic acid was found in the highest quantity followed by the palmitic and stearic acid. In resin acids, chlorohydroabietic acid was found in the highest concentration whereas neoabietic was found in traces. The amount of all the components was reduced to 8.24 g/t in $D_{HT}E_{OP}D$ sequence. On decreasing the dose of chlorine dioxide by 10%, 15% and 20% in D_{HT} based sequence, the amount of total fatty and resin acids was reduced to 8.05 g/t, 7.83 g/t and 7.66 g/t. The modification of D_0 to D_{HT} was found to be effective in terms of achieving higher brightness of bleached pulp with significant reduction in toxic fatty and resin acids.

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