

Biomimetic TCF Bleaching of Pulp by Simple Inorganic Complexes of Cupric/Cobalt Acetate

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ABSTRACT: Oxygen delignified kraft pulp from eucalyptus (*E. urophylla* × *E. grandis*) was catalytically pretreated in aerobic condition using ammonium persulfate in presence of catalysts like cupric acetate and/or cobalt acetate in acetic acid-water solution, i. e. $S_2O_8^{2-}-Cu^{2+}$, $S_2O_8^{2-}-Co^{2+}$ and $S_2O_8^{2-}-(Cu^{2+}+Co^{2+})$. Final bleached pulp after pretreatment with the three catalytic systems showed higher delignification (23.45%, 21.85% and 19.63% respectively), better optical properties (82.93, 82.18 and 81.92% ISO brightness respectively) and pulp viscosity (787, 791 and 762 mL/g respectively; mL/g: intrinsic viscosity unit of pulp) than the control pulp (14.12% delignification, 77.33% ISO brightness and 746 mL/g viscosity). $S_2O_8^{2-}-Cu^{2+}$ and $S_2O_8^{2-}-Co^{2+}$ showed similar reduction in hydrogen peroxide consumption (61.91%, 62.48%), and $S_2O_8^{2-}-(Cu^{2+}+Co^{2+})$ showed a greater reduction in hydrogen peroxide consumption than the two treatments (83.05%). Some improvements in tensile and tear strength of the resulting pulp were observed. The new sequence also yields composite effluents with larger percentage of lignin aromatic compounds compared to the control.

KEY WORDS: Cupric/cobalt acetate, Ammonium persulfate, TCF bleaching, Eucalyptus pulp, Aromatic compounds.

INTRODUCTION

The pulp and paper industry always has to search for alternatives to chlorine based bleaching practices for environmental issues and stringent pollutants discharge standard. Peroxide is always technologically attractive candidate for the replacement of chlorine and chlorine dioxide [1]. However, due to the limited reactive ability of residual lignin, peroxide is unable to fully replace the chlorine containing bleaching agents. Many efforts aimed to improve the reactivity of hydrogen peroxide have been made to improve delignification and bleaching efficiency [2,3]. Harsher reaction conditions were commonly employed

to increase the reactive efficiency of peroxide. For examples, high temperature is usually necessary to obtain high reactive ability of bleaching agents. However, under alkaline conditions, high temperature accelerates the decomposition of hydrogen peroxide, which not only reduces the amount of peroxide available for bleaching [4], but also increases the amount of radicals formed, which have a detrimental effect on carbohydrates [5]. Under acidic conditions, high temperatures could result in severe cellulose degradation due to the acid hydrolysis of cellulose [6, 7]. A variety of research has been carried

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out to catalyse and activate peroxide delignification of chemical pulps [8]. Pulp pretreatment aimed to activate the lignin prior to an alkaline peroxide stage offers another possibility for improving the overall selectivity of peroxide delignification. These pretreatment agents include nitrogen dioxide, ozone, peroxide, peracetic acid and even enzymes [9-11]. These pretreatment methods resulted in improved delignification and selectivity in the subsequent alkaline peroxide bleaching process. The increased reactivity of the kraft residual lignin toward alkaline hydrogen peroxide was responsible for the higher brightness gains observed [12].

It is evident, furthermore, that there are several disadvantages in using enzymes in the biobleaching of pulp, being sensitive to environmental condition, difficulty to obtain and expensive [13]. The potential of biomimetic delignification systems offers new possibility for improving the reactivity of residual lignin toward hydrogen peroxide [14]. For example, *Crestini & Tagliatesta* [15] described the use of several synthetic porphyrins (porphyrins: heterocyclic macrocycles composed of four modified pyrrole subunits interconnected at their α -carbon atoms via methine bridges) as lignin peroxidase models in the oxidative degradation of pulps, lignin and lignin model compounds. A number of simple inorganic complexes (peroxydisulfate plus Cu, Co, Ag, Fe and Mn) which mimic the reaction pathways for ligninase were used as catalysts to form aryl cation radicals. These results showed that these simple complexes facilitate the oxidative degradation of phenols such as lignin model compounds [16-19]. However, to the best of our knowledge these simple systems have not been tested for their ability to mimic ligninases in the bleaching of kraft pulp. For these reasons, based on the model compounds reaction studies [17], several pretreatment systems (ammonium persulfate plus cupric/cobalt acetate) were used to bleach the oxygen delignified eucalyptus kraft pulp for the improvement of the peroxide delignification. The results may be beneficial to explore the green chemical pathways of pulp bleaching process.

EXPERIMENTAL SECTION

Materials

Laboratory oxygen delignified eucalyptus (*E. urophylla* \times *E. grandis*) kraft pulp with 45.3% ISO brightness,

11.26 kappa number and 967 mL/g viscosity was used. The yield of laboratory unbleached kraft pulp was 47% with a kappa number of 17.58, 35.2% ISO brightness and an 1127 mL/g viscosity (both stored at 4 °C). Before bleaching, the pulp was thoroughly washed with tapwater and distilled water to remove all residual black liquor.

The chemicals used in this work were of analytical grade purity and used without further purification, unless otherwise noted (Sinopharm Chemical Reagent Co, Ltd., China). The glassware and plasticware were thoroughly washed with distilled water and then rinsed with deionized water.

Bleaching

The new total chlorine free (TCF) bleaching sequence was used for the oxygen delignified eucalyptus kraft pulp. Three catalytic pretreatments (Cat-stage) were performed in a flask with three necks while atmospheric oxygen was bubbled into the flask in order to assess their effects on TCF bleaching. The reaction was maintained at constant condition, namely: stirring at 70 °C for 2 h; 5% pulp consistency; 0.01% $\text{Cu}(\text{CH}_3\text{COO})_2$ ($\text{S}_2\text{O}_8^{2-}\text{-Cu}^{2+}$), 0.01% $\text{Co}(\text{CH}_3\text{COO})_2$ ($\text{S}_2\text{O}_8^{2-}\text{-Co}^{2+}$), 0.005% $\text{Cu}(\text{CH}_3\text{COO})_2$ + 0.005% $\text{Co}(\text{CH}_3\text{COO})_2$ [$\text{S}_2\text{O}_8^{2-}\text{-(Cu}^{2+}\text{+Co}^{2+})$], 2:1 (M/M) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ /metal acetate and use of 20% acetic acid. For comparison, the control tests were additionally performed by using 5% pulp consistency at 70 °C and 2 h.

After treatment with catalysis, the pulp was efficiently washed with distilled water prior to alkaline extraction. Subsequent extraction and bleaching were done on catalytically pretreated pulp in parallel at 10% consistency (adjusted with distilled water).

Following the treatment with catalysis, an amount of catalytically pretreated pulp of 10 g was extracted with 1.5% NaOH and 0.5% H_2O_2 (an EP-stage) at 70 °C for 1 h, after which the pulp was thoroughly washed with distilled water. In order to reduce degradation of cellulose, the charge of 0.1% MgSO_4 and 0.05% DTPA (diethylenetriaminepentaacetic acid) was always added in EP stage.

An alkaline peroxide bleaching treatment (a P-stage) was conducted by using 2% H_2O_2 , 1.5% NaOH, 1.0% Na_2SiO_3 , 0.1% DTPA and 0.1% MgSO_4 at 80 °C for 2.5 h. Residual hydrogen peroxide was analysed in the bleaching effluent by standard titration.

Table 1: Kappa number and viscosity after each bleaching stage of pulp pretreated at different catalytic stage.

Parameter	Catalytic pretreatment			
	S ₂ O ₈ ²⁻ -Cu ²⁺	S ₂ O ₈ ²⁻ -Co ²⁺	S ₂ O ₈ ²⁻ -(Cu ²⁺ +Co ²⁺)	Control
Kappa number after Cat stage	10.94	10.55	10.82	11.05
Reduction (% ^a) in kappa number after Cat stage	2.84	6.31	3.91	1.87
Kappa number after Ep stage	9.82	9.97	10.15	10.26
Reduction (% ^a) in kappa number after Ep stage	12.79	11.44	9.86	8.88
Kappa number after P stage	8.62	8.80	9.05	9.67
Reduction (% ^a) in kappa number after P stage	23.45	21.85	19.63	14.12
Viscosity (mL.g ⁻¹) after Cat stage	826	779	771	730
Viscosity (mL.g ⁻¹) after Ep stage	799	778	751	728
Viscosity (mL.g ⁻¹) after P stage	787	791	762	746

a) % Means "relative to the value of oxygen delignified kraft pulp".

All calculations were based on the oven dry pulp weight.

Methods

Pulp viscosity was measured in cupric-ethylenediamine (CED) solution according to SCAN-CM 15:88 standard. Kappa number, a measure of residual lignin in the pulp, was determined according to TAPPI T 236 om-99 with a standard deviation less than 2%. To analyse pulp qualities, the resulting pulp was refined to the degree of 45±1°SR at medium consistency in a laboratory disc refiner (PFI mill) using 0.1 mm disc gap and formed into handsheets. Drainage properties were determined according to ISO 5267 (Schopper-Riegler °SR). Handsheet formation for physical test was performed according to TAPPI T205 sp-02 [20]. Physical properties of pulp hand-sheets were examined according to TAPPI T220 sp-01 standard [21]. The brightness of the pulp was measured according to TAPPI T525 om-06 with standard deviation less than 3% [22].

All parameters were determined as many times as recommended in their corresponding standard method, being the resulting experimental errors within the accepted ranges.

Composite effluents for analyses were generated by the procedures as follows, which were described by *Cates et al.* [23]. Oxygen delignified eucalyptus kraft pulp was stirred in a 2.5% pulp consistency with deionized water for 5 min.

The suspension was filtered, and the effluent was discarded. The pulp deionized was bleached with Cat(EP)P sequence. After each bleaching stage, the pulp suspension was diluted with deionized water to a 2.5% pulp consistency and stirred for 5 min, and then filtered. The filtrate was collected and adjusted to pH 2.5 with sulfuric acid. Residual peroxide in filtrate was eliminated with an equivalent amount of sodium sulfite. Residual suspended particulates were removed by passing the filtrates through a 40-µm sintered filter. Composite effluents were generated from by mixing equal portions of filtrates from individual stages for each bleaching sequence. Composite effluents were subjected to molecular size separation in two fractions by ultrafiltration with an ultrafiltration cell (FD-JH-JS Ultrafiltrater, China) using a 1000-Dalton (1kDa) membrane. All samples were diluted to one fifth with deionized water and their UV were measured at 280 nm with a spectrophotometer (UV-2201 Spectrophotometer, Japan). Absorption at 280 nm was used as a parameter for indicating concentrations of lignin and aromatic lignin degradation products [24]. All measurements were replicated.

RESULTS AND DISCUSSION

The delignification efficiencies using the three catalytic pretreatments were compared and the results were listed in Table 1. The catalytic agent of S₂O₈²⁻-Cu²⁺ showed maximum delignification whereas S₂O₈²⁻-(Cu²⁺+Co²⁺)

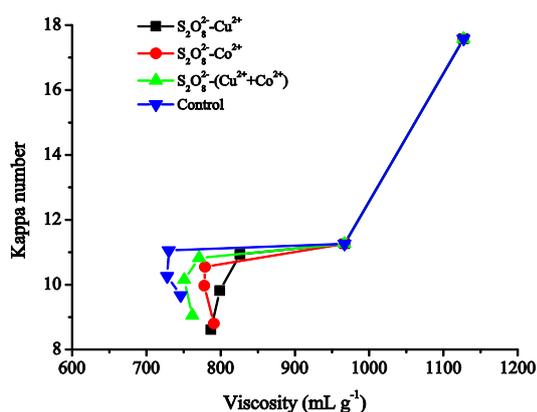


Fig. 1: Kappa number vs. viscosity after different stages of bleaching sequences. mL/g: intrinsic viscosity unit of pulp.

showed minimum delignification achieved in terms of kappa number reduction related to oxygen delignified kraft pulp (Table 1).

In the whole sequence, the delignification achieved in terms of kappa number reduction ranged from 23.45%-19.63% (Cat(EP)P) to 14.12% (Control) related to oxygen delignified kraft pulp. These differences of five or more points (9.33-5.51) compared with the control were higher than those caused in the Cat- (4.44-0.97) and Cat(EP) (3.91-0.98) stage. This can be explained if we consider that the pretreatment with catalysis not only delignified but also modified the residual lignin into a form which was easier to remove in the subsequent P stage.

Table 1 represented the viscosity of the cellulose pulps, an indirect method which reflects the length of the polysaccharides chains. The introduction of the catalysis not only did not cause viscosity decrease, but also increased the pulp viscosity. The higher viscosity of the carbohydrate after each stage resulted from the extraction of the short chains of polysaccharides, mainly hemicelluloses, possibly since the Cat-stage facilitated the release of hemicellulose preferentially over cellulose. The pulps pretreated with the three Cat-stages showed lower content in pentosan (7.64%, 7.38% and 7.41% respectively) than the control (7.96%) as determined according to TAPPI T 223 cm-01. Pentosan content in hardwood pulp indicates the retention or loss of hemicellulose in general during pulping and bleaching processes. In comparison with enzymatic pretreatment,

results obtained by Oudia et al. have demonstrated that high biodelignification can be similarly achieved without decreasing pulp viscosity [25].

Fig. 1 graphically represented the relation between kappa number and viscosity for the Cat(EP)P bleaching of oxygen delignified eucalyptus kraft pulp. The Cat-stage reduced the kappa number of pulp while its viscosity was maintained at a higher level, depending on the catalytic system used at the Cat-stages: S₂O₈²⁻-Cu²⁺ experiments showed always the highest viscosity, S₂O₈²⁻-(Cu²⁺+Co²⁺) showed always the lowest one at the same kappa number level.

In the Cat(EP)P bleaching, the considerable reduction in hydrogen peroxide consumption and the gain in brightness of P-bleached pulp were also observed in comparison with the control sample (Table 2). Cat-pretreated sample using catalytic condition of S₂O₈²⁻-(Cu²⁺+Co²⁺) had the highest value of H₂O₂ consumption reduction, which is interesting since its brightness value had a higher level. This reflected the activation of catalytic pretreatment on residual lignin although the gain in brightness at Cat-stage was small as compared to the control (Table 2). Based on these results obtained, it could be inferred that lignin oxidation by the catalytic system facilitates the action of hydrogen peroxide on pulp, consequently reducing the required amount of this chemical and increasing the brightness of TCF-bleached pulp.

All these results lead to conclude that the catalytic pretreatment has a similar effect on the pulp bleaching with that of ligninolytic enzyme pretreatment proposed by other authors. *Eugenio et al.* [26] stated that the pretreatment of eucalyptus kraft pulp with laccase of *Streptomyces ipomoea* CECT 3341 not only improved the delignification and brightness, but also significantly contributed to the reduction of required chemical amounts in comparison with the control when L(EP) was used as a bleaching sequence. The viscosity of L-pretreated pulp was only slightly reduced in any case.

Absorbance of TCF composite effluent relative to lignin aromatic compounds was measured at 280 nm as shown in Table 3 for elucidating the lignin degradation in pulp bleaching. The total absorbance at 280 nm of the composite effluents from (S₂O₈²⁻-Cu²⁺)(EP)P, (S₂O₈²⁻-Co²⁺)(EP)P and [S₂O₈²⁻-(Cu²⁺+Co²⁺)](EP)P was 6%, 60% and 106% up on that of the control respectively.

Table 2: Brightness after each bleaching stage of pulp pretreated at different catalytic stage.

Parameter	Catalytic pretreatment			
	S ₂ O ₈ ²⁻ -Cu ²⁺	S ₂ O ₈ ²⁻ -Co ²⁺	S ₂ O ₈ ²⁻ -(Cu ²⁺ +Co ²⁺)	Control
Brightness (% ISO) after Cat stage	48.20	48.97	48.64	48.17
Brightness (% ISO) after Ep stage	62.31	61.63	60.46	60.44
Brightness (% ISO) after P stage	82.93	82.18	81.92	77.33
H ₂ O ₂ consumption (%)	36.27	35.73	16.17	95.23
Reduction ^b in H ₂ O ₂ consumption (%)	61.91	62.48	83.05	-

b) % Means "relative to the value of control".

Table 3: Change in absorbance at 280 nm of aromatic compounds in composite effluents.

Sequence	ControlEpP	(S ₂ O ₈ ²⁻ -Cu ²⁺)EpP	(S ₂ O ₈ ²⁻ -Co ²⁺)EpP	[S ₂ O ₈ ²⁻ -(Cu ²⁺ +Co ²⁺)]EpP
Total Abs	0.96	1.02	1.53	1.98
Abs (<1000 Da)	0.73	1.14	1.51	1.02
Abs (>1000 Da)	0.32	0.45	0.40	0.92

The [S₂O₈²⁻-(Cu²⁺+Co²⁺)](EP)P sequence had particularly large total absorbance although there was less overall kappa number reduction (33.4%) in these stages compared to the (S₂O₈²⁻-Cu²⁺)(EP)P (39.08%) and (S₂O₈²⁻-Co²⁺)(EP)P (39.60%). Aromatic compound loadings in composite effluents, therefore, depend not only on the pulp kappa number, but also may depend on the acetate salts used to catalyse the residual lignin. However these findings may explain the superior removal of lignin observed in Cat(EP)P bleaching when compared to the control.

On the other hand, the compounds in composite effluent from TCF bleaching stages were separated into two fractions with molecular weights lower and higher than 1 kDa for analyses of their UV measurement at 280 nm. The composite effluents had lower concentrations of high-molecular-weight aromatic compounds (>1000 Da) (Table 3), therefore, lignin of high-molecular-weight in pulp was considered to be more recalcitrant compared to that of low-molecular-weight, lignin reactions occurred primarily in the low-molecular weight fraction for all bleachings. Similarly *Moldes & Vidal* [27] found in the L(EP) bleaching of eucalyptus kraft pulp that the compounds in the high-molecular-weight fraction were minor components of the effluent from the L stage, the effluent from the EP-stage was rather different, the high-molecular-weight fraction prevailed.

After complete catalytic bleaching sequence, the different resulting TCF pulps obtained were also refined

to the degree of 45±1°SR and the physico-mechanical properties were analysed. The effect of catalytic systems on pulp properties differs depending on the catalytic agents used.

The resistance properties obtained in this work showed the different behavior of TCF pulps depending on the parameter measured: tear index was lower (10%-18% lower than control experiment) when cupric acetate and cobalt acetate were applied at Cat-stage. This parameter showed an interesting improvement on this value at the same refining conditions (7% higher than control experiment) when the combination of the two acetate salts (Cu²⁺+Co²⁺) was used, indicating more flexible fibers. More flexible fibers create more crossing-linking or hydrogen bonding potential between polysaccharide chains, increasing the paper strength [28]. Tensile index showed a 2%-20% improvement on this parameter indicating a increasing fiber-fiber union capability compared to control experiment (Table 4). Tensile values obtained from different pulps confirmed that Cu²⁺ or Co²⁺ pretreated pulp showed higher strength than the pulp pretreated in presence of (Cu²⁺+Co²⁺) at same values of beating degree. Only slight differences on tensile strength were also observed between Cu²⁺ and Co²⁺ pretreatments (Table 4), as they presented similar viscosity of pulp (Table 2). Burst index showed almost the same result as tensile index due to more bonding between the fibers.

Table 4: Physical property after P stage of pulp pretreated at different catalytic stage.

Cat pretreatment	Tensile index (N·m/g)	Tear index (mN·m ² /g)	Burst index (kPa·m ² /g)
Kraft pulp	88.42	8.43	5.32
O-delignified pulp	85.32	7.06	5.04
S ₂ O ₈ ²⁻ -Cu ²⁺	84.34	6.84	5.07
S ₂ O ₈ ²⁻ -Co ²⁺	83.04	6.21	5.59
S ₂ O ₈ ²⁻ -(Cu ²⁺ +Co ²⁺)	71.63	8.13	5.06
Control	70.39	7.58	4.51

The introduction of simple inorganic complexes in Cat-stage showed similar improvements in physical properties of pulp to those from metal salen complexes although the delignification was improved in lower extent. Metal salen complexes improved tensile index of Cat(EP)PP [29] and CatDQP [30] bleached eucalyptus pulp.

CONCLUSIONS

A new TCF bleaching sequence with catalytic pretreatment stage (Cat(EP)P) was successfully applied with eucalyptus kraft pulp. The catalytic pretreatment had different effect on pulp properties. Cupric acetate, cobalt acetate and their combination as catalysts in ammonium persulfate-acetate salt system performed high delignification and brightness values. Regarding physico-mechanical properties of pulp, some improvements in tensile and tear strength were observed after the application of the new TCF bleaching sequence. The highest delignification, brightness and tensile index values were obtained when cupric acetate was used as catalyst in Cat(EP)P bleaching of eucalyptus kraft pulp. Bleaching of eucalyptus pulp with the new TCF sequence also yields composite effluent with higher concentration of lignin aromatic compounds than the control.

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