THE EFFECT OF ACID PRETREATMENT AND PEROXIDE REINFORCEMENT IN ALKALINE EXTRACTION ON OPTICAL AND STRENGTH PROPERTIES OF *EUCALPYTUS CAMALDULENSIS* KRAFT PULP DURING DED BLEACHING SEQUENCE

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Unbleached kraft pulp from *Eucalyptus camaldulensis* with an initial kappa number of about 31 and brightness of 13% was used to perform bleaching experiments. The results of the first part of this research (using D0ED1 bleaching sequence at different kappa factors of 0.2, 0.3, and 0.4 in D0 stage) showed that the final brightness, even at a kappa factor of 0.4, was relatively low (about 75%). Thus, the effects of acid pretreatment (A stage) and peroxide reinforcement in alkaline extraction (EP *versus* E stage) in D0ED1 bleaching sequence on optical and strength properties of paper were investigated in this study. By applying these treatments, especially peroxide reinforcement, final kappa number, yield, yellowness, opacity, and air resistance were reduced, while brightness and lightness were increased at similar or superior strength properties in comparison with the reference bleaching sequence.

Keywords: Eucalyptus camaldulensis; Kraft pulp; Bleaching; Acid stage; Hydrogen peroxide

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INTRODUCTION

Eucalyptus kraft pulp bleaching technologies have substantially improved in recent decades (Vuorinen *et al.* 2005; Suess *et al.* 1997; Colodette *et al.* 2006; Pikka and Vehmaa 2007; Jiang *et al.* 2002; Medina *et al.* 2008). Between 1985 and 1995, the dominant trend was the introduction of oxygen delignification and the reduction of the use of halogenated compounds, such as AOX, furans, and dioxins (Bist 2007). In the late 90s, the presence of hexenuronic acids (HexA) in unbleached kraft pulps was discovered. HexA are hemicellulose-derived chemicals that consume oxidative chemicals during pulp bleaching. Acid stages carried out at a high temperature are able to change the HexA by hydrolysis or destroy them. Hardwoods, including *Eucalpytus camaldulensis*, contain a large amount of xylan with side groups of 4-o-methylglucuronic acid. During pulping, methanol is eliminated from these groups and 4-deoxy-hex-euronic acid is generated. These HexA are generated during the heating period of the kraft pulping process and slowly degraded in subsequent cooking (Blechschmidt *et al.* 2006). Because hardwood pulping is a fast process, a certain amount of HexA remains after pulping, depending on the pulping conditions. In an analysis of kappa number, Andrew *et al.* (2008) found that the double bond of HexA will react with permanganate, indicating a higher lignin level.

Three to seven kappa units of unbleached hardwood pulps may be attributed to HexA, not lignin. This may affect the bleaching process and the performance of bleaching chemicals. The double bond of HexA will react with electrophilic bleaching chemicals, like chlorine dioxide, and reduce their efficiency.

Hexenuronic acid can be degraded under acidic conditions in a hydrolysis reaction, which requires an elevated temperature and a low pH. However, cellulose is sensitive to acid hydrolysis, and uncontrolled acid treatment may lead to reduced yield, viscosity, and pulp quality (Marechal *et al.* 1993). The main reaction products of acid hydrolysis of HexA are formic acid, furancarboxylic acid, and 5-formyl furancarboxylic acid. These acids are water-soluble and are easily washed off after hydrolysis (Teleman *et al.* 1996).

The oxidation of lignin with chlorine dioxide generates a large amount of low molecular weight lignin fragments, which are water-soluble under alkaline conditions. Hydrogen peroxide is used to reinforce the alkali extraction stage. At alkaline pH, hydrogen peroxide is in equilibrium with the perhydroxyl anion, the active compound in bleaching reactions. The perhydroxyl anion acts as a nucleophile, adds to quinine structures, and eliminates side chains from lignin (Gierer 1982). The resulting oxidized compounds, carboxylic acids, are more hydrophilic and more soluble, better facilitating their extraction (Gierer 1982). The use of hydrogen peroxide during alkali extraction results in a further decrease of the kappa number by up to 2 units and/or an increase of brightness by up to 10 points (Suess and Davies 2006), compared to the alkaline extraction stage without the use of hydrogen peroxide.

An option for bleaching *Eucalyptus* kraft pulp in fewer steps, the combination of acid hydrolysis of HexA with chlorine dioxide delignification (DAhot -P), was studied by Suess and Moodley (2002). They found that with very high charges of chlorine dioxide, it was possible to reach 90% ISO brightness. However, the resulting viscosity was low at a lower yield as a result of the extended treatment at low pH and high temperature. Thanh Nhan (2004) found that it was possible to achieve a final brightness of 89-90% ISO using an ODEpD bleaching sequence in their study on the influence of bleaching sequence and conditions on *Eucalyptus camaldulensis* kraft pulp properties. They reported that at a higher temperature and longer reaction time in D0 stage, more HexA was removed with higher brightness stability, but lower pulp viscosity.

In a previous study, a D0ED1 bleaching sequence was studied at different kappa factors (0.2, 0.3, and 0.4) in D0 stage (Resalati *et al.* 2012). The results showed that the final brightness of the DED bleached eucalypt kraft pulp, even at a kappa factor of 0.4, was relatively low (about 75%). Thus, the effects of acid pretreatment (A stage) and peroxide reinforcement in alkaline extraction (EP *versus* E stage) on optical and strength properties were investigated in this study. In other words, the bleaching sequences ADED, DEPD, and ADEPD were compared to the reference DED bleaching sequence, at a constant kappa factor of 0.4 in D0 stage.

EXPERIMENTAL

The randomly selected trees of *Eucalyptus camaldulensis*, cut in the yard of Gorgan University, were debarked manually and converted into chips with dimensions of 5 × 15 × 20 mm with the use of a saw. After their moisture content was calculated, the air-dried chips were collected in plastic bags. Under cooking conditions 25% sulfidity, 26% active alkali as NaOH, 0.15% AQ, 165 °C cooking temperature, and L:W = 6:1, kraft pulping was done using 100 g OD chips at variable cooking times up to 4 h. The details of the cooking conditions can be found in a previous work (Resalati *et al.* 2012).

Kraft pulps were washed with tap water on a 200 mesh screen and pulp yield was determined gravimetrically. Unbleached kraft pulp with an initial kappa number of about 31 and brightness of 13% was selected to perform the bleaching experiments. Based on sommerville screen analysis, the shives content of the selected pulp was negligible for conducting the bleaching experiment. The bleaching trials were done in plastic bags and the experimental conditions for various stages in bleaching sequences of ADED, DEPD, and ADEPD in comparison with reference DED, at constant kappa factor of 0.4 in D0 stage, are shown in Table 1. Pulp and paper properties were determined using TAPPI standards, such as: kappa number T236 0m-99, air resistance T536 om-96, burst T515 om-92, tensile T525 om-96, tear T414 om-04, brightness T217 os-48, and opacity T245om-96.

Table 1. Experimental Conditions for Various Bleaching Stages

Bleaching conditions		Bleaching stages A	D0	E/ Ep	D1
Kappa factor		-	0.4	-	0.1
Reaction time, min		60	60	60	120
Chlorine dioxide as active chlorine, %		-	12.5	-	3.1
Hydrogen peroxide, %		-	-	0.70	-
Sodium hydroxide, %		-	-	0.75	-
End pH	DED	-	4.4	12.6	4.6
	ADED	2.5	4.3	12.8	4.6
	DEpD	-	4.4	12.6	4.7
	ADEpd	2.5	4.3	12.7	4.7

Pulp consistency: 10%, reaction temperature: 70 °C, all chemical charges based on OD pulp

RESULTS AND DISCUSSION

The kappa number, or residual lignin, in DED bleached pulp depends on the initial kappa number of unbleached pulp and the kappa factor, or chlorine dioxide charge as available chlorine. Although it is a hardwood species, *Eucalyptus camaldulensis* has an exceptionally high lignin content, similar to softwoods (Dutt and Tyagi 2011). The bleachable kraft pulp from this species also has a high kappa number (about 30) at screened pulp yield of about 40%. Thus, in case of not using oxygen delignification, a higher kappa factor may be needed in order to obtain a high brightness in the DED bleaching sequence. Therefore, in case of *Eucalyptus camaldulensis*, the final brightness of DED bleached pulp even at the high kappa factor of 0.4 in D0 stage was 75%, which is relatively low (Resalati *et al.* 2012). Hexenuronic acids (HexA) are generated from xylan chains during kraft pulping, especially in hardwood species rich in xylans, including *E. camaldulensis*, which is relatively stable under alkaline conditions (Marechal 1993). HexA groups not only consume potassium permanganate during kappa number determination and lead to an unreal residual lignin content, but they also consume chlorine dioxide and reduce its efficiency in such a way that the final brightness is lower at a specified kappa factor (Andrew *et al.* 2008).

Bleached Pulp Yield and Kappa Number

The effects of acid pretreatment (A stage) and peroxide reinforcement in alkaline extraction (EP *versus* E stage) on the final bleached pulp yields and kappa number are shown in Figs. 1 and 2.

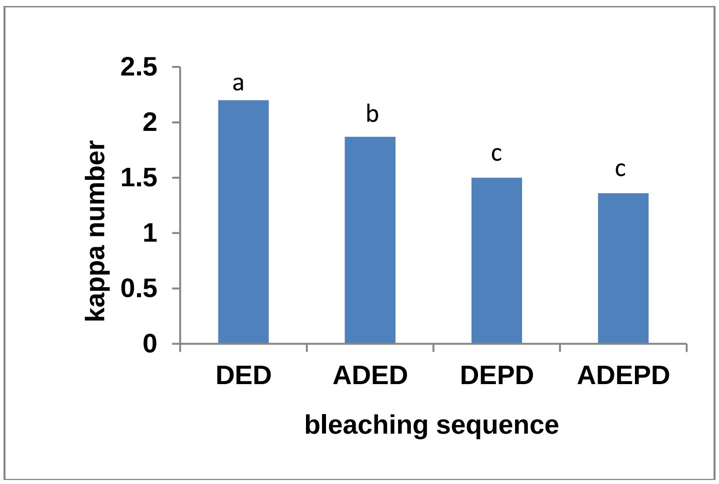

Fig. 1. Effect of acid pretreatment and peroxide reinforcement in alkaline extraction stage on the final kappa number of DED bleached pulp

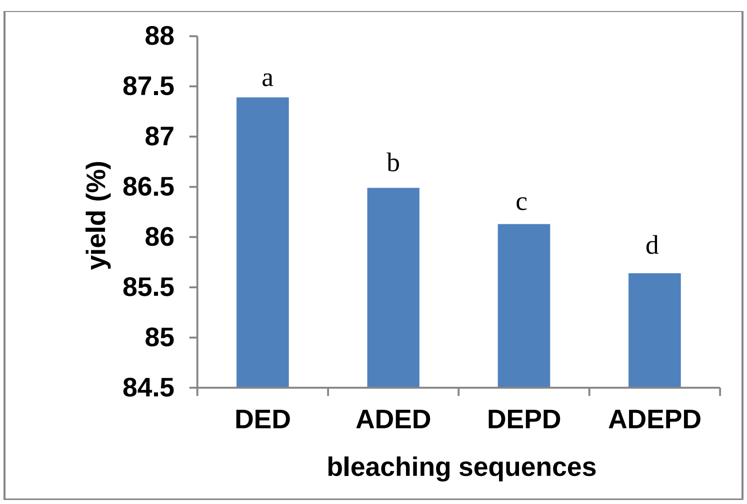

Fig. 2. The effect of acid pretreatment and peroxide reinforcement in alkaline extraction stage on the final pulp yield of DED bleached pulp (based on OD chips)

Both bleached pulp yield and kappa number were reduced by either acid pre-treatment or hydrogen peroxide reinforcement in alkaline extraction, but the rate of reduction in pulp yield was more pronounced than kappa number. The effect of hydrogen peroxide reinforcement on bleached pulp yield and kappa reduction was greater than acid pretreatment. The higher yield loss in the case of hydrogen peroxide reinforcement could be due to increased chemical reaction and oxidations leading to higher alkali-catalyzed dissolution of lignin and hemicelluloses. Compared to the reference DED sequence, the differences in kappa and yield reductions in ADED, DEPD, and ADEPD bleaching sequences were statistically meaningful at 99% confidence level.

Brightness and Yellowness

The effects of acid pretreatment and peroxide reinforcement in alkaline extraction on the bleached pulp brightness and yellowness are shown in Figures 3-4.

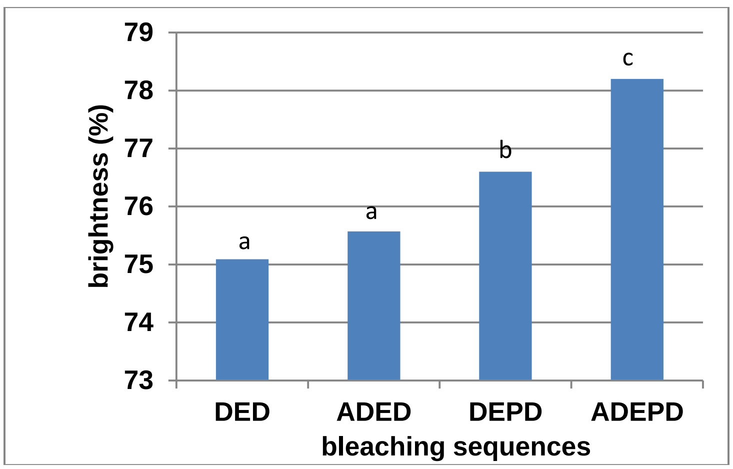

Fig. 3. The effect of acid pretreatment and peroxide reinforcement in alkaline extraction stage on the final pulp brightness of DED bleached pulp

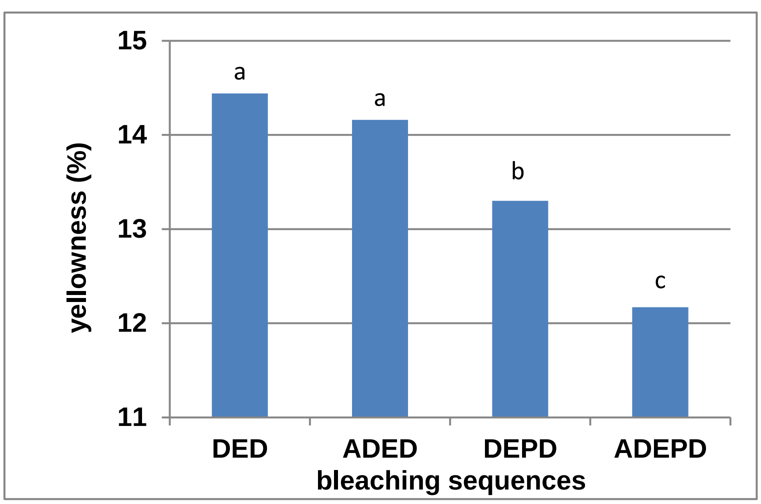

Fig. 4. The effect of acid pretreatment and peroxide reinforcement in alkaline extraction stage on the final pulp yellowness of DED bleached pulp

The brightness was increased and yellowness decreased by both acid pretreatment and hydrogen peroxide reinforcement in E stage, as compared to the reference DED bleaching sequence, and the differences were statistically significant at 99% confidence level. However, the effect of hydrogen peroxide reinforcement on increasing brightness and decreasing yellowness was greater than acid pretreatment. Using peroxide in alkaline extraction not only extended lignin oxidation and its dissolution, but also inhibited alkali yellowing, thus leading to increased brightness with a lower yellowness. However, the highest brightness and lowest yellowness were observed in the case of the ADEpD bleaching sequence, which demonstrated the effect of acid pretreatment on pacifying the HexA groups and increasing the efficiency of chlorine dioxide at a constant kappa factor.

L, *a*, and *b* Factors

The effects of acid pretreatment and peroxide reinforcement in alkaline extraction on *L*, *a*, and *b* factors of the bleached pulps are shown in Figures 5-7.

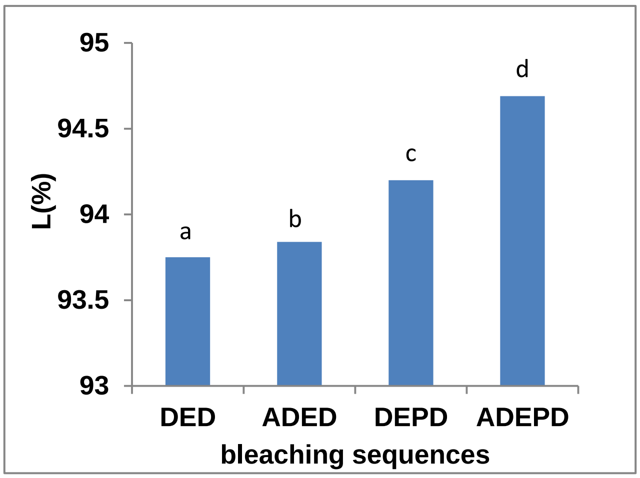

Fig. 5. The effect of acid pretreatment and peroxide reinforcement in alkaline extraction stage on the *L* factor of DED bleached pulp

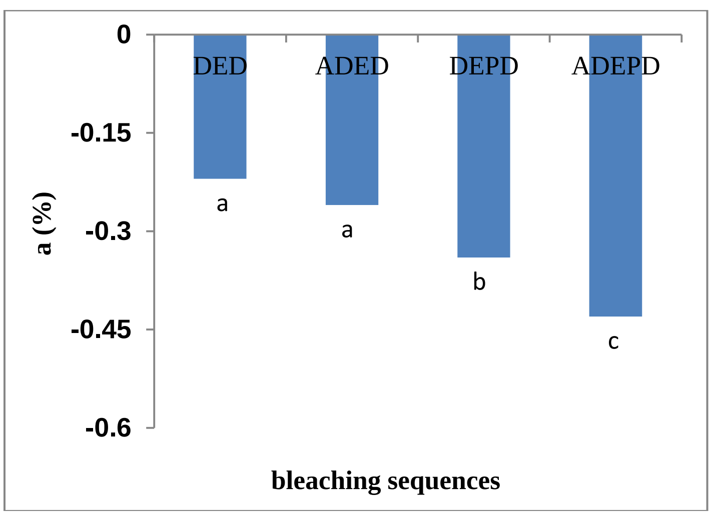

Fig. 6. The effect of acid pretreatment and peroxide reinforcement in alkaline extraction stage on the *a* factor of DED bleached pulp

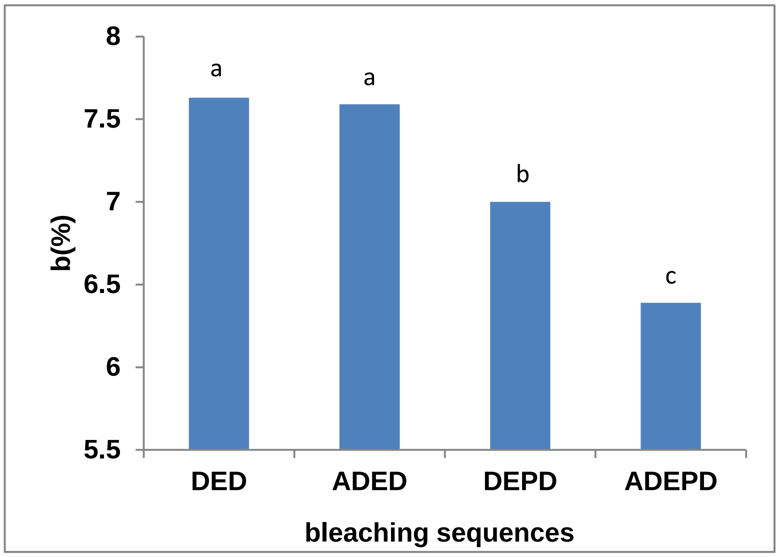

Fig. 7. The effect of acid pretreatment and peroxide reinforcement in alkaline extraction stage on the *b* factor of DED bleached pulp

It is clear that by applying both acid pretreatment and peroxide reinforcement in E stage, the lightness (*L*) was increased, with a decrease in *a* and *b* shades, which led to an increase in whiteness, brightness, and bluish shade and a decrease in yellowish shade. However, a greater increase in L and a more pronounced decrease in *a* and *b* factors than the acid pretreatment occurred in case of peroxide reinforcement. These differences were statistically significant at a 99% confidence level. Moreover, the highest *L* and the lowest *a* and *b* factors were observed in the ADEpD bleaching sequence, showing the combined positive effects of acid pretreatment on relative removal of HexA groups and oxidative reactions of hydrogen peroxide to remove and modify lignin and chromophoric groups, thus increasing the efficiency of chlorine dioxide at a constant kappa factor.

Opacity

The effects of acid pretreatment and peroxide reinforcement in alkaline extraction on opacity and light absorption and scattering coefficients of the bleached pulps using different bleaching sequences are shown in Figures 8 and 9, respectively. The light scattering coefficient (*S*) depends on the free un-bonded surface of fibers or the bulk of paper, while the light absorption coefficient (*K*) directly depends on the concentration of light-absorbing chromophoric groups or types and amounts of residual lignin. The opacity increases when both *S* and *K* are increased. The results showed that by applying both an acid stage and peroxide reinforcement in the E stage, *S* increased, while a decrease was observed for *K* and opacity. The decrease in *K* was due to a reduction in light-absorbing groups, including partial removal of HexA in the A stage, as well as a reduction of kappa and partial oxidation of chromophoric groups in the Ep stage, compared to the reference DED bleaching sequence. The light scattering coefficient increased, due to a reduction in *K*, which was also the main cause for the reduction of opacity, despite the increase in *S*. However, the effect of peroxide reinforcement in the E stage on reduction of *K* and opacity was greater than acid pretreatment.

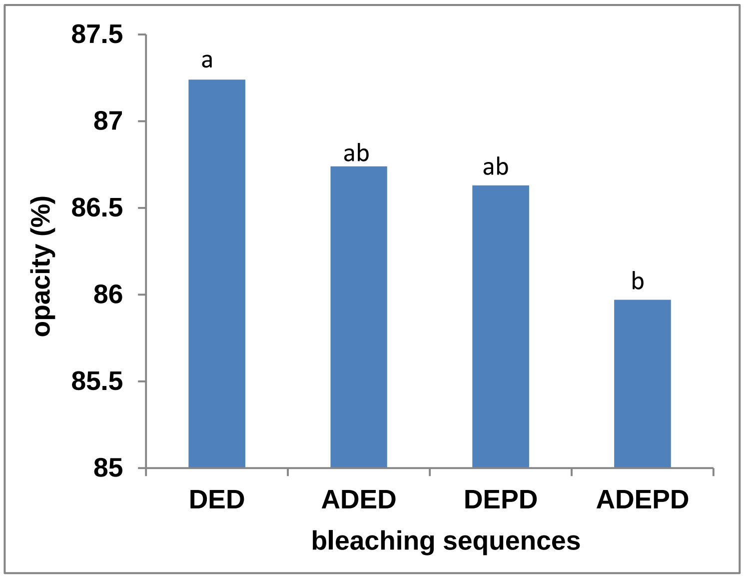

Fig. 8. The effect of acid pretreatment and peroxide reinforcement in alkaline extraction stage in DED bleaching on paper opacity

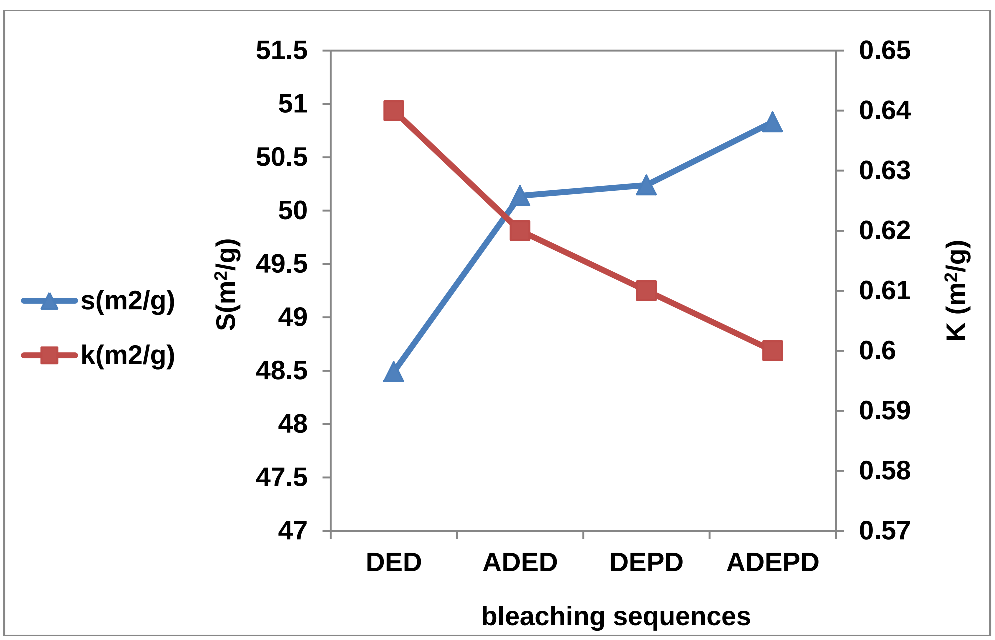

Fig. 9. The effect of acid pretreatment and peroxide reinforcement in alkaline extraction stage in DED bleaching on light scattering and absorption coefficients of paper

Bulk and Air Resistance

The effects of acid pretreatment and peroxide reinforcement in alkaline extraction in DED bleaching sequence on bulk and air resistance of paper are shown in Figs. 10-11.

Bulk, which is defined as volume per unit weight of paper, is an important property of mechanical printing papers that influences the scattering coefficient, opacity, and printability. Air resistance is used to determine the porosity of paper, which is defined as the ratio of pore volume to paper volume. Air resistance increases when density is increased or when bulk is decreased. The results showed that while the bulk of paper was increased by acid pretreatment, it was reduced by peroxide reinforcement in the DED bleaching sequence. The opposite results were observed for air resistance properties. The higher bulk and lower air resistance in the case of acid pretreatment may be due to higher dissolution of hemicelluloses, which could lead to reduced relative bonded area. The generation of carboxylic groups in oxidative reactions of peroxide reinforced alkali extraction (Gierer, 1982) may be a reason to produce lower bulk and higher air resistance due to higher WRV and improved fiber-to-fiber bonding (Lindstrom and Carlsson (1982).

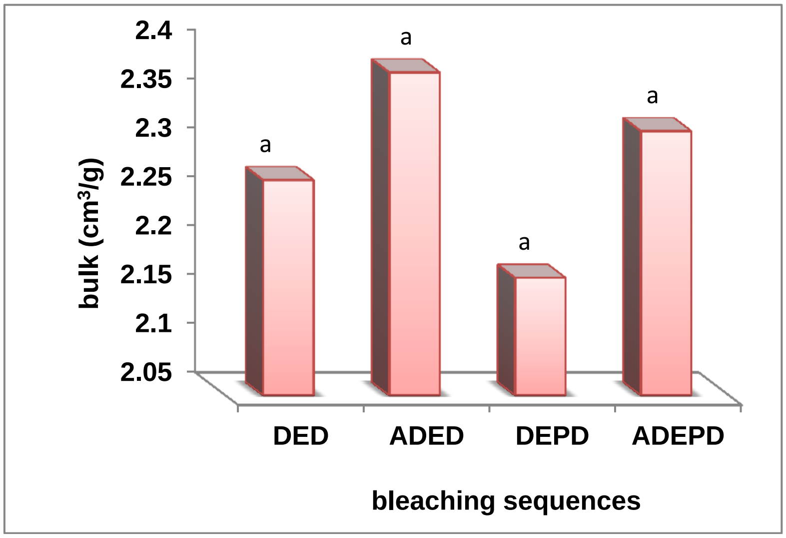

Fig. 10. The effect of acid pretreatment and peroxide reinforcement in alkaline extraction stage in DED bleaching on bulk of paper

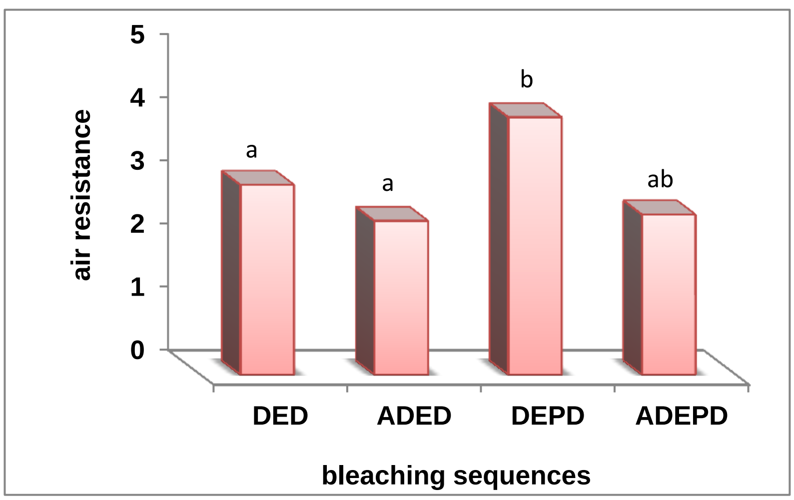

Fig. 11. The effect of acid pretreatment and peroxide reinforcement in alkaline extraction stage in DED bleaching on air resistance of paper

Strength Properties

The effects of acid pretreatment and peroxide reinforcement in alkaline extraction in DED bleaching sequences on tensile, burst, and tear strength of paper are shown in Figs. 12-14. In comparison with the reference DED bleaching sequence, by applying acid pretreatment (ADED or ADEpD bleaching sequence), burst, tensile, and tear strength were reduced. The differences were statistically insignificant for tensile and burst strength, but were significant in case of tear strength. However, in the case of hydrogen peroxide reinforcement in the E stage without any acid pretreatment (DEpD bleaching sequence), the burst, tensile, and tear strength properties of paper increased, compared to pulps bleached using the reference DED sequence. The differences were statistically significant only for tear strength. The higher strength properties obtained from hydrogen peroxide reinforcement in E stage may be due to higher inter-fiber bonding development through the generation of new carboxyl groups, as was indicated by lower bulk, higher air resistance, and lower opacity. The opposite is true for acid pretreatment stage.

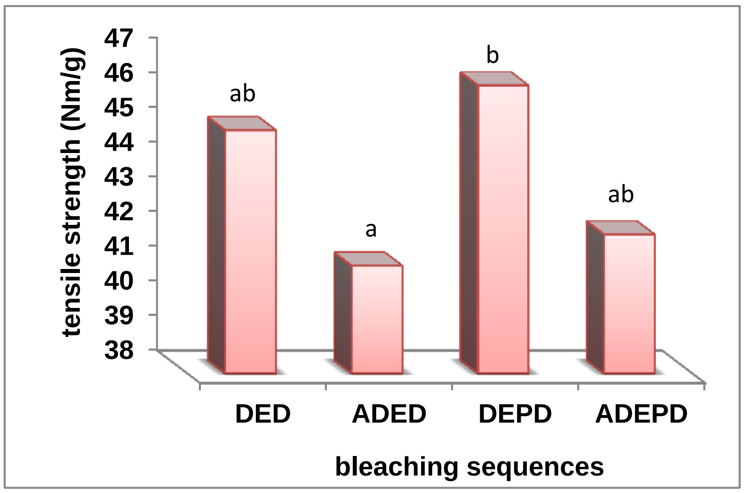

Fig. 12. The effect of acid pretreatment and peroxide reinforcement in alkaline extraction stage in DED bleaching on tensile strength of paper

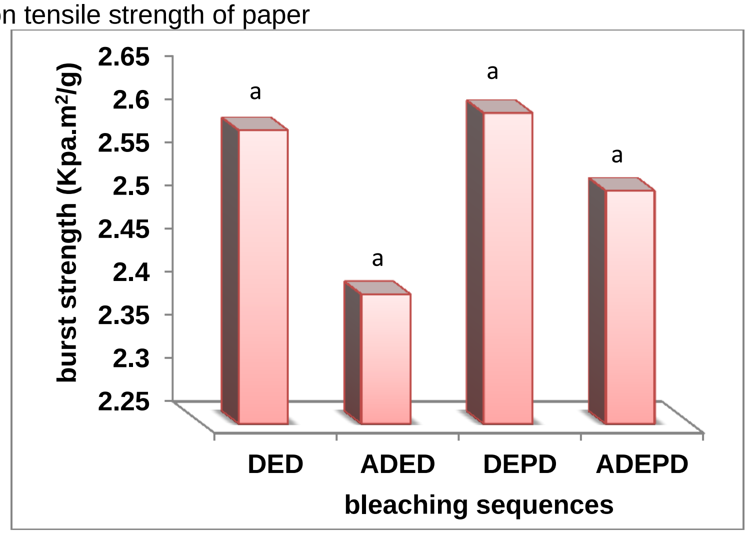

Fig. 13. The effect of acid pretreatment and peroxide reinforcement in alkaline extraction stage in DED bleaching on burst strength of paper

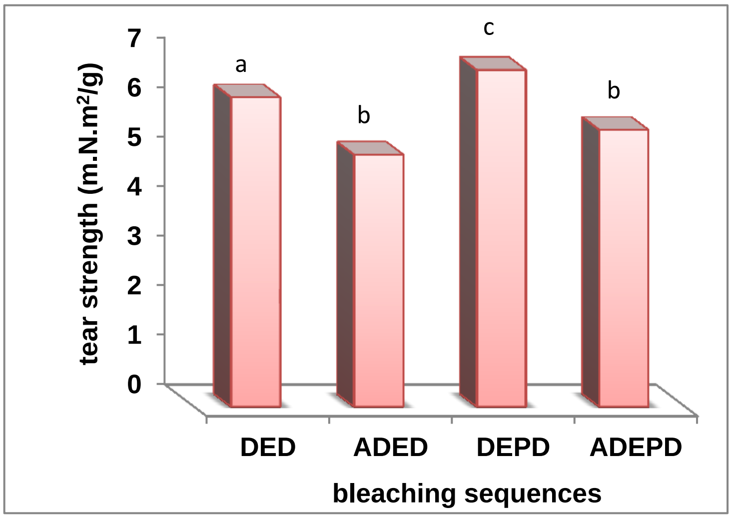

Fig. 14. The effect of acid pretreatment and peroxide reinforcement in alkaline extraction stage in DED bleaching on tear strength of paper

CONCLUSIONS

Eucalyptus camaldulensis, although it is a hardwood species, has an exceptionally high lignin content, similar to softwoods (about 30%). The bleachable kraft pulp from this species also has a high kappa number (about 30) at a screened pulp yield of about 40%. Thus, when oxygen delignification is not used, a higher kappa factor may be necessary to achieve high brightness in the DED bleaching sequence. Thus, the final brightness of DED bleached pulp of *Eucalyptus camaldulensis*, even at the high kappa factor of 0.4 in D0 stage, was relatively low (about 75%). Compared to the reference D0ED1 bleaching sequence, the effects of acid pretreatment (A stage) and peroxide reinforcement in alkaline extraction (EP *versus* E stage) on optical and strength properties of pulp were investigated in the present paper. The major findings are as follows:

1. Both bleached pulp yield and kappa number were reduced by either acid pre-treatment or hydrogen peroxide reinforcement, but the rate of reduction in pulp yield was more pronounced than kappa number. The effect of hydrogen peroxide reinforcement was greater in reduction of bleached pulp yield and kappa number.
2. Brightness was increased and yellowness was decreased by both treatments. However, hydrogen peroxide reinforcement was more effective in increasing brightness and decreasing yellowness.
3. Lightness (*L*) was increased with decrease in *a* and *b* shades by both treatments. This may lead to an increase in whiteness and bluish shade and a decrease in yellowish shade. However, a greater increase in L and a greater decrease in *a* and *b* factors occurred in case of peroxide reinforcement.

4. While the bulk of paper was increased by acid pretreatment, it was reduced by peroxide reinforcement. The opposite results were observed for air resistance properties.
5. The light scattering coefficient (*S*) was increased, while a decrease was observed for the light absorption coefficient (*K*) and opacity
6. By applying acid pretreatment in the A stage (ADED or ADEpD), burst, tensile, and tear strengths were reduced. The differences were statistically insignificant for tensile and burst strengths, but significant in the case of tear strength. However, in the case of hydrogen peroxide reinforcement in E stage without any acid pretreatment (DEpD), the burst, tensile, and tear strength properties improved.

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