The Effect of Chlorine Dioxide Charges in Chlorine Dioxide-Alkaline Extraction-Chlorine Dioxide (DED) Sequence on Optical Properties of Kraft Pulp of *Eucalyptus camaldulensis*

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Abstract: Hardwoods are important raw material for making pulp and paper products. *Eucalyptus camaldulensis* is a fast-growing hardwood species with a wide distribution in Iran and can be introduced as appropriate material to compensate the wood shortages of the natural forest. Kraft pulping was performed under different cooking conditions and, based on the relations of pulp yield and kappa number, bleachable kraft pulp at screened yield of 43.3% and kappa number of 31.3 was selected for DED (Chlorine Dioxide-Alkaline Extraction-Chlorine Dioxide) bleaching and its bleachability was studied at different kappa factor in D1 stage. The results indicated that the bleachable kraft pulp from this species has high kappa number at acceptable screened yield and to complete the delignification in the bleaching process, higher kappa factor may be needed in DED bleaching sequence. The main reduction in final kappa number and yield loss were observed at kappa factor level of 0.2 but by further increase in kappa factor up to 0.4, more development were observed in optical properties but at lower opacity.

Key words: Kraft, Kappa factor, *Eucalyptus camaldulensis*, DED bleaching.

1. Introduction

Shortage of cellulosic raw material is a big challenge for the wood and paper industries in Iran. Fast-growing hardwood species like *Eucalyptus* can be introduced as important non-forest raw material for pulp and papermaking. Rahmati [1] investigated the effect of using different active alkali on kraft pulp properties of *E. camaldulensis*. Kraft pulps were made at 18, 20, 22 and 24 percent active alkali under constant cooking condition and the effect on yield, kappa number, rejects and residual alkali in black liquor have been determined. The results indicated that at higher level of alkali concentration, lower kappa and rejects could be obtained but at lower pulp yield and higher residual alkali concentration.

The production of semi-bleached kraft pulp from *E. camaldulensis* was studied by Rashidi [2]. Under different cooking conditions (cooking temperature of 160-170 °C, AA of 18-22% and cooking times of 1.5-3.5 hours) several kraft pulps were made and, based on the kappa-yield relations, the selected kraft pulp at kappa number of 30.5 and yield of 40% had the unbleached brightness of 15% which after oxygen delignification has been semi-bleached to 68% brightness by using one stage peroxide bleaching. Barros et al. [3] investigated the effect of final stage peracetic acid bleaching on the brightness development and paper properties of *Eucalyptus* at D(Ep)D/paa, DHT(Ep)D/paa, DHT/Q(Po)paa, and
Z/ED/paa bleaching sequences. Peracetic acid as a final stage bleaching decreased pulp viscosity, kappa number and hexenuronic acid (HexA) content, but had no significant influence on brightness reversion and L, a, b factors. When pH was close to 5 in final stage of D\textsubscript{HT}(E\textsubscript{P})DD and D\textsubscript{HT}(E\textsubscript{P})D/paa bleaching sequences, similar refinability and bonding strength was obtained in bleached pulp. As pH in peracetic acid bleaching increased to 8.5, these properties were improved to some extent. Colodette et al. [4] studied the bleaching of \textit{Eucalyptus} pulp and showed that high hexenuronic acid content and low oxygen selectivity limited the kappa number decrease less than 9-10 in 1 or 2 stages of oxygen delignification. Application of Mo-catalysed acid peroxide after oxygen stage leads to kappa number decrease of 3-4. A three stage sequence (D-(E\textsubscript{P})-D) was good enough to bleach the \textit{Eucalyptus} kraft pulp. A four stage sequence was suitable to produce high brightness pulp with low brightness reversion. Selecting the bleaching technology without elemental chlorine (D\textsubscript{HT} and D\textsubscript{0}) effected only to some extend on chemical usage. The results also showed that a final peroxide bleaching stage improved the pulp brightness stability. Milanez and Colodette [5] studied appropriate bleaching conditions of \textit{Eucalyptus} kraft pulp in three stage bleaching sequence of D\textsubscript{HT}(PO)D. The results showed that increasing the D\textsubscript{HT} temperature up to 85 °C decreased the kappa number significantly but caused pulp to darken so final pulp brightness was not improved. Reducing pH below 3 in D\textsubscript{HT} stage, pulp darkness and viscosity was decreased with significant decrease in kappa number. Increasing the temperature in P\textsubscript{0} stage from 80 to 95 °C didn’t have any effect on process efficiency and selectivity. Isabel et al. [6] investigated the brightness reversion of bleached \textit{E. globulus} kraft pulp by means of industrial elemental chlorine free technology. The results showed that in D\textsubscript{0}ED\textsubscript{1}D\textsubscript{2} sequence, increasing the temperature in D\textsubscript{0} from 55 to 90 °C increased the brightness stability. In addition, increasing chlorine dioxide charge from 2.8 to 3.2% increased significantly the brightness stability. They also found that adding sulfuric acid in D\textsubscript{0} stage (10 kg/ton) decreased the brightness stability.

2. Material and Data

2.1 Chips Preparation

Logs of \textit{Eucalyptus camaldulensis} were randomly selected from the trees cut in the yard of the Gorgan University and the barks were separated manually. Debarked logs were converted to chips with dimension of 5 × 15 × 20 mm by saw and after being air dried, their moisture content were calculated and collected in plastic bag.

2.2 Kraft Pulping

Prior to cooking the pre-weighted chips were impregnated in cooking liquor overnight. For each trail of kraft pulping 100 g chips, based on OD weight, were cooked under constant condition such as L:W = 6:1, sulfidity 25%, AA 26%, 0.15 AQ, cooking temperature 165 °C and variable cooking time up to 4 h. Kraft pulps were fully washed by tap water on 200 mesh screen and pulp yield was determined as following:

\[
Pulp\ yield = \frac{OD\ pulp}{OD\ chips} \times 100 \quad (1)
\]

2.3 DED Bleaching Sequence

D\textsubscript{1}ED\textsubscript{2} bleaching sequence was used at different kappa factor or various chlorine dioxide charges (Eq. (2)). Unbleached kraft pulp with initial kappa number and brightness of 31.3 of 12.8%, respectively, was bleached using kappa factor of 0.2, 0.3, and 0.4 in D\textsubscript{1} stage. The chlorine dioxide charge in D\textsubscript{2} stage was 25% of the amount used in D\textsubscript{1} stage. DED bleaching conditions are shown in Table 1. NaOH charge in E stage was about 60% of chlorine dioxide charge as available chlorine in D\textsubscript{1} stage.

\[
kappa\ factor= \frac{\%\ Chlorine\ dioxide\ as\ available\ chlorine,\ based\ on\ OD\ pulp}{Kappa\ number} \quad (2)
\]
Table 1  DED bleaching conditions at different kappa factors.*

<table>
<thead>
<tr>
<th>Kappa factor</th>
<th>0.4</th>
<th>0.3</th>
<th>0.25</th>
<th>0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2</td>
<td>E</td>
<td>D1</td>
<td>D2</td>
<td>E</td>
</tr>
<tr>
<td>4.7</td>
<td></td>
<td>12.7</td>
<td></td>
<td>12.1</td>
</tr>
<tr>
<td>1.19</td>
<td>-</td>
<td>4.76</td>
<td>-</td>
<td>0.89</td>
</tr>
<tr>
<td>-</td>
<td>0.75</td>
<td>-</td>
<td>-</td>
<td>0.56</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

* Treatment temperature of 70 °C and consistency of 10% were constant in each stage.

2.4 Pulp Properties

Pulp properties were determined using TAPPI standards, as following:

Kappa number: T2360m-99, Pulp refining: T248 sp-oo;

Freeness: T227om-04, Resistant properties: T220 sp-ol;

Brightness: T452om-02, Opacity = T245om-01.

3. Results and Discussion

3.1 Kappa Number

Residual lignin content or kappa number of the pulp bleached by DED sequence is a function of initial kappa number of unbleached pulp and the kappa factor or the amount of chlorine dioxide charges as available chlorine. *Eucalyptus camaldulensis* being a hardwood species has exceptionally high lignin content similar to softwoods (about 30%), and the bleachable kraft pulp from this species has also high kappa number. Thus in order to complete the delignification in the bleaching stages, higher kappa factor may be needed in DED bleaching sequence. The effect of using different kappa factor on final kappa number of DED bleached pulps is shown in Fig. 1.

A dramatic drop was observed in the DED bleached

![Fig. 1  Effect of kappa factor on final kappa number of DED bleached pulp.](image-url)
3.3 Pulp Brightness

The effect of kappa factor in D₁ stage on the final brightness of DED bleached pulp is shown in Fig. 3. By increasing kappa factor or total chlorine dioxide charge, in addition to developing higher delignification which was indicated by kappa number reduction, higher pulp brightening can be performed.

By reducing final kappa number which is an indication of lower residual lignin content in the bleached pulp, the final brightness are increased through reduction of light absorbing chromophoric groups and, as a result, having lower light absorption coefficient and higher scattering coefficient.

3.4 Yellowness

By increasing the chlorine dioxide charge or kappa factor, brightness increased as shown in Fig. 3 but at the same time yellowness was decreased (Fig. 4) and the differences in yellowness were statistically significant for various kappa factors.

3.5 L, a, b Factors

The effect of kappa factor in D₁ stage or total chlorine dioxide charge on L, a and b factors are shown in Figs. 5, 6 and 7, respectively. Factor L is an indication of pulp lightness and increases by increasing brightness. The substance is purely black or white if the value for L is 0 or 100, respectively. The trend of increasing the L factor by increasing the kappa factor (Fig. 5) was pretty much similar to brightness (Fig. 3). The removal of colored chromophoric groups by delignification and brightening the residual lignin are the main reasons for increasing the L factor or brightness through increasing chlorine dioxide charge.

a and b factors indicate the shade of bleached pulp. In case of b factor, positive and negative values indicate bluish or yellowish shade in bleached pulp, respectively. However, for factor a, positive and negative values indicate reddish or greenish shade, respectively. As shown in Fig. 6, by increasing kappa factor of chlorine dioxide charge, factor a has been decreased and changed from positive to negative value that is a change from reddish shade to slightly

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Fig. 2 Effect of kappa factor on the final yield of DED bleached pulp.

Fig. 3 Effect of kappa factor on final brightness of DED bleached pulp.

Fig. 4 Effect of kappa factor on the yellowness of DED bleached pulp.
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3.6 Opacity

Opacity is an indication of relative resistance to light transmittance through paper thickness and increases by increasing light absorption coefficient (K) and light scattering coefficient (S). During bleaching of chemical pulp, residual lignin of unbleached pulp is mainly removed or at least modified to uncolored structure, as a result, K is reduced and S is slightly reduced by fiber-fiber bonding development. The higher the kappa factor in D1 stage or chlorine dioxide charge, the higher would be the chemical reaction which leads to lower K and S, and reduces the opacity (Fig. 8). The differences between opacity obtained at various kappa factors were statistically significant.

4. Conclusion

Although *Eucalyptus camaldulensis* is a hardwood species, but it has exceptionally high lignin content similar to softwoods (about 30%), and the bleachable kraft pulp from this species has also high kappa
number. Thus in order to complete the delignification in the bleaching stages, higher kappa factor may be needed in DED bleaching sequence. A dramatic drop was observed in the DED bleached pulp residual lignin or final kappa number by using a kappa factor of only 0.2 in D₁ stage (a delta kappa number of 26). By further increase in kappa factor up to 0.4, the reduction in the final kappa number was not that great although the differences were statistically significant.

By increasing kappa factor in D₁ stage or increasing total chlorine dioxide charges, higher delignification was developed as indicated by reduced final kappa number and, as a result, higher pulp brightening can be performed at lower yellowness and opacity. The trend of increasing the $L$ factor by increasing the kappa factor was pretty much similar to brightness. The removal of colored chromophoric groups by delignification and brightening the residual lignin are the main reasons for increasing the $L$ factor or brightness through increasing chlorine dioxide charge.

References