Determination of Kraft-NaBH₄ Pulping Condition of Uludag Fir (Abies Bornmuelleriana Mattf.)

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Abstract: The aim of this study is to evaluate the effects of NaBH₄ on pulp and paper properties on conventional kraft pulping. The chemical composition of the Uludag fir wood was determined and this wood was utilized as raw material in pulping experiments. Two sets of pulping experiments were conducted in this study. In the first set, six conventional kraft cookings were made to determine the optimum conventional kraft cooking conditions by altering the cooking time and active alkali taking into account the kappa number and the pulping yield. The obtained results indicated that the optimum kraft cooking condition was accomplished when kraft cook was made using 18% active alkali for a cooking period of 90 min at 170°C. Cooking at these conditions gave 46.3% screened yield, 28.5 kappa number and 1102 cm² g⁻¹ viscosity for Uludag fir. A second set of cookings was made taking into account the optimum kraft cooking condition and 1, 2 and 3% NaBH₄ was added to the cooking digester based on oven dry wood. The results showed a significant decrease in pulping rejects and increase in pulping yield when NaBH₄ was added to the cooking digester. This finding indicated higher pulping selectivity of NaBH₄ added kraft method. In addition, higher pulp viscosity and brightness were observed in the NaBH₄ added kraft method. On the other hand, the strength properties obtained in Kraft-NaBH₄ was a slightly reduced compared to the conventional kraft method.

Key words: Kraft pulping, delignification, yield, kappa number, mechanical properties, sodium borohidrate, Uludag fir

INTRODUCTION

Today paper industry experiences various difficulties such as raw material deficiency, low pulp yield, energy losses and pollution. The most significant ones are low pulp yield and raw material deficiency. Due to this, recent studies concentrate on increasing the yield of available raw material. Studies mentioned that 1-4% increase in pulp yield was obtained on kraft cooking experiments using various boron compounds. Despite this, yield increase should not impact on the advantages of kraft pulping negatively. Maximizing the pulping yield results in a reduction in wood cost and thus causes large economic benefits. The future paper mills will be the minimum impact mills that have reduction in raw material consumption by maximizing the yield.

The relative rate of removal of miscellaneous wood components during pulping determines the yield at any given degree of delignification, as determined relationship between yield and kappa number. Pulping yield is dependent on the modifications of the chemical reactions during pulping, process modifications and composition of the raw material. Increase in the yield of kraft pulps can be primarily accomplished by greater hemicellulose retention, because cellulose losses are a relatively small fraction of the total yield loss. It is not susceptible to control by prevention of endwise depolymerization since the significant fraction of the hemicellulose losses is due to physical dissolution. Thus, all chemical reactions that occur during pulping have an effect on pulp yield including endwise depolymerization and stopping reactions; depolymerization by alkaline hydrolysis of glycosidic bonds and hydrolysis of acetyl groups. While having an effect on pulp properties, process modifications can maintain an increase in the yield of kraft pulp depending on restraining or avoiding the peeling reaction, accelerating delignification, removing barriers to efficient mass transfer, or a combination of these.

Experiments are being prepared to design more selective cooking processes to produce pulps with a higher pulp yield and viscosity for a given kappa number. The achievements in selectivity results in further decrease in kappa number (Kocurek, 1989; Hakanen et al., 1997; Jameel et al., 1995; Ateş and Kiraz, 2001). Additives such as polysulphide and antiruenone (AQ) are among the opportunities.

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Tutuş (2005) investigated sodium borohydride added to sulphate cooking of wheat straw and found out that 0.5, 1 and 1.5% addition of sodium borohydride increased the screened yield importantly. 0.5 addition of sodium borohydride resulted in a yield of 39.45%. Moreover, 1.5% addition of sodium borohydride increased the yield to 41.85. 1.5% NaBH₄ addition to sulphate cooking increased the yield by 2.95 points. In addition, 1% NaBH₄ addition to pulp cooking increased the total yield by 3.83% points. In accordance with those results, sodium borohydride acts as a catalyst and protects the reducing end groups from peeling reaction and increases the screened yield of pulp.

Borohydride is a powerful reducing agent that converts the carbonyl group in the reducing end units of carbohydrate chains to hydroxyl groups. Since a carbonyl group must be present in the end unit for initiation of the peeling reaction, the conversion of carbonyls to hydroxyls by borohydride prevents peeling. The major effect of borohydride is to prevent the acceleration of glucomannan removal that otherwise occurs at 100°C. This entails that the acceleration is due to peeling (Hafizoglu, 1982). Similarly, the earlier removal of glucomannan which was unaffected by borohydride, was due to physical dissolution of a soluble fraction. The rate and extent of glucomannan removal are relatively unaffected by alkali concentration. The absence of any beneficial effect of borohydride shows that dissolution, not peeling, is the dominant mechanism. At the higher temperatures, the adverse effect of borohydride may be attributed to higher alkali concentration in borohydride cooks. Xylan removal, unlike glucomannan removal, is accelerated by increased alkali concentration (Courchene, 1998). Recent studies focused on increasing the yield of available raw material using boron compounds as additives (Bujonovic et al., 2003; Bujonovic et al., 2004). Sodium borohydride could be utilized as an additive to improve the yield of hemicelluloses in kraft cook. Therefore, the objective of this study was to examine the effect of sodium borohydride addition on pulp and paper properties.

**MATERIALS AND METHODS**

Having natural potential in Turkey and mostly utilized in Turkish sulphate mills, Uludağ Fir (Abies borrmiuelleriana Mattf.), is an important wood species. Çaycuma OYKA Sulphate Mill, Turkey supplied the Uludağ Fir woodchips for the pulping experiments in this study. Form is obtained from the West Blacksea region of Turkey by The Çaycuma OYKA Sulphate mill. Wood chips were collected from the chips yard of Çaycuma OYKA Sulphate Mill according to the Tappi Standard RC 84. The chips had the moisture content of 15% (oven dry basis) (Tappi T 258 om-89).

Samples were taken and prepared according to Tappi T 257 om-85 for chemical tests. Holocellulose, cellulose and α-cellulose contents were determined according to the chlorite (Wise and Karl, 1962) and Tappi (Tappi T 203 om-71) methods, respectively. The following tests were implemented to determine the lignin (Tappi T 222 om-98) and ash (Tappi T 211 om-93) contents. The solubility properties were also determined based on alcohol-benzene (Tappi T 204 om-97), cold and hot-water (Tappi T 207 om-93) and 1% NaOH (Tappi T 212 om-98) methods.

For each experiment, 600 g of chips (o.d.) were cooked in a 15L rotating digester. 170°C was the maximum cooking temperature. The maximum cooking temperature was reached at 90 min. In order to determine the optimum cooking conditions, total of six kraft cooks were conducted by kraft method. Parameters for these experiments are given in Table 1. From those preliminary experiments the 5th kraft cook resulted in the optimum cooking conditions regarding pulping yield and kappa number. Therefore, kraft-sodium borohydride cooks were accomplished based on the optimum kraft pulping conditions. Kraft-sodium borohydride cooks were conducted only altering the NaBH₄ concentrations in cooks. 1, 2 and 3% (o.d. wood) NaBH₄ added to the digester along with the wood chips based on oven dry chip weight. Having used a laboratory flat screen with a slot width of 0.006" (0.15 mm), the pulps were disintegrated, washed with hot tap water (40°C) and then screened.

<table>
<thead>
<tr>
<th>Method</th>
<th>NaBH₄ (%)</th>
<th>Cooking time</th>
<th>Total yield, % o.d. wood</th>
<th>Rejects, % o.d. wood</th>
<th>Kappa No</th>
<th>Viscosity (cP g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>1</td>
<td>16</td>
<td>-</td>
<td>60</td>
<td>46.34</td>
<td>49.14</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>16</td>
<td>-</td>
<td>90</td>
<td>48.02</td>
<td>44.31</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>16</td>
<td>-</td>
<td>120</td>
<td>52.30</td>
<td>41.11</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>16</td>
<td>-</td>
<td>120</td>
<td>56.59</td>
<td>41.11</td>
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<tr>
<td></td>
<td>3</td>
<td>16</td>
<td>-</td>
<td>120</td>
<td>58.82</td>
<td>41.11</td>
</tr>
<tr>
<td>Kraft-NaBH₄</td>
<td>1</td>
<td>18</td>
<td>1</td>
<td>90</td>
<td>45.95</td>
<td>31.67</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>18</td>
<td>2</td>
<td>90</td>
<td>46.53</td>
<td>28.51</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>18</td>
<td>3</td>
<td>90</td>
<td>46.90</td>
<td>28.51</td>
</tr>
</tbody>
</table>

* Active alkali as % Na₂O/weight of o.d. wood; ** o.d. wood weight
The yield contents of the pulps and rejects were determined according to Tappi (T 210) in the laboratory environment by gravimetric measurements. The screened yield was determined from duplicate analyses. Adding the yield of rejects to the screened yield gave total pulp yield. Double experiments also displayed the kappa number (Tappi T230) and viscosity (SCAN cm 15:88) of the pulp samples.

Pulps were beated with Valley type beater (Tappi T 200) to 50°SR freeness level. The freeness level of the pulps was determined according to Tappi T 227. The handsheets for physical and mechanical tests were produced in a Rapid Köhben machine in accordance with relevant Tappi (T 205) method. Some mechanical tests were made according to the Tappi T 220.

**RESULTS AND DISCUSSION**

The chemical composition of Uludag fir used in these pulping experiments and of Butia pine and Oriental spruce are shown in Table 2. Results have mentioned that holocellulose, cellulose, lignin and ash contents of Uludag fir wood are similar to those of other softwood species, origins in Turkey. On the other hand, 1% NaOH solubility values of Uludag fir was somehow higher compared to the Butia pine and Oriental spruce. The pH values measured from black liquor indicated that the pH of the black liquors ranges from 11.8 (P3) and 13.57 (B3). This finding shows that the active alkali was not totally consumed in any of the cooks.

Pulp properties of total yield, rejects, kappa number and viscosity values for kraft and kraft-NaBH₄ pulps have shown in Table 1. The optimum pulping conditions taking into account the pulping yield, cooking rejects and kappa number found to be kraft cook P5. Kraft cook P5 gave pulp with 43.45% (o.d. wood) of yield, 0.83% (o.d. wood) rejects and 32.2 of kappa number. Hence, kraft-NaBH₄ pulps were cooked at that optimum pulping conditions which are 18% active alkali and 25% sulfidity for 90 min (the temperature to reach max temp was 90 min). Kraft-NaBH₄ pulping was achieved while adding 1, 2 and 3% NaBH₄ to the cooking liquor. Increasing cooking time (at maximum temperature) from 60 to 120 min and active alkali from 16 to 18% lowered the kappa number and pulp yield of the produced pulps. Results indicated a linear correlation (Fig. 1) between kappa number and pulp yield as also observed earlier (Kleppe, 1981; Çöpür et al., 2003; Çöpür, 2006) for kraft pulps.

Experiments were implemented to determine and compare the effect of NaBH₄ on pulp properties. The pulp properties of kraft-NaBH₄ showed that adding NaBH₄ to cooking liquor resulted in pulps that have higher screened pulp yield (Fig. 1). The yield increase in NaBH₄ added cooks is explained with higher carbohydrate retention and reduction in rejects. The optimum yield increase was observed when adding 2% NaBH₄ to the cooking liquor and kraft-NaBH₄, pulp gave 2.9% (o.d. wood) higher
Fig. 4: Effect of AA and NaBH₄ in pulp tear index

Fig. 5: Effect of AA and NaBH₄ in pulp breaking length

Fig. 6: Effect of AA and NaBH₄ in pulp burst index

screened yield when compared to the reference kraft cook (P5). Khaustova et al. (1971) Gahir and Khrisov (1973) Diaconescu and Petrovan (1976) also reported similar results for pulping yield. In addition to yield increase, the added NaBH₄ in kraft-NaBH₄ can significantly decrease the level of rejects in pulping of Uludag fir as shown in Table 1. The rejects observed in kraft P5 was 0.83% (o.d. wood) but the reject was much lower in Kraft-NaBH₄ method varying from 0.26 to 0.14% (o.d. wood), which depends on the level of NaBH₄ in the cook. Higher amount of NaBH₄ in the cook decreased the reject obtained in pulping.

The results also pointed out that the addition of NaBH₄ to the white liquor impacts the kappa number and based on addition level, kappa number of the pulps were observed to be lower compared to the kraft pulp (P5). However, studies with sodium metaborate in the literature (Bujonovic et al., 2003, 2004) showed no change in kappa number for any sodium metaborate levels in kraft cook. Consequently, Kraft-NaBH₄ method resulted in an increase in the screened pulp yield while lowering the rejects and lignin content of the pulps. Hence, yield increase in Kraft-NaBH₄ method could be explained with the carbohydrates preserving mechanism of the NaBH₄.

Figure 2 shows Pulps viscosity measured for kraft and kraft-NaBH₄ pulps. A simultaneous decrease in viscosity and kappa number was observed for kraft pulps that also observed earlier (Çamir et al., 2005; McDonough, 1998). A sharp decrease in viscosity of the kraft pulps was explained with alkaline pulping for extended times that increases the fraction of amorphous regions and correlates consistently to a lower viscosity. Lower alkali charge in kraft pulping resulted in slightly higher viscosity for pulps even they were cooked to the same cooking time. This could be underlined with higher chain breakage on polysaccharides due to the alkali cleavage of the glycosidic bonds for pulps with lower kappa number. Results pointed out that NaBH₄ preserved the degree of polymerization of the cellulose chains and resulted in a higher viscosity. Opposite to observations on kraft pulps, kraft NaBH₄ better preserved the carbohydrate chains and improved the viscosity of the pulps through to the lower kappa number. Increase in NaBH₄ up to 2% had the much beneficial effect on pulps kappa number (Fig. 1) and viscosity (Fig. 2).

Figure 3 shows the brightness of kraft and kraft-NaBH₄ pulps. The brightness of the pulps increased through higher cooking time for pulps cooked applying 18% AA but a small decrease was observed for pulps cooked under 16% AA. 2 and 3% addition levels significantly improve the pulps brightness according to the results of studies with NaBH₄.

The strength properties of the pulps were assessed at 50 °SR freeness level. There was a 11% relative difference in tear index between pulps produced with and without NaBH₄ treatment (Fig. 4). The pulps with NaBH₄ had lower tearing resistance. 3% NaBH₄ addition gave the lowest pulp tear strength. The reason for the lower tear strength could be explained by the higher pulp yield of Kraft NaBH₄ pulps, which results in fewer load-bearing fibers for a given weight sample of the pulp (Page, 1985). Breaking length (Fig. 5) and burst index (Fig. 6) of the papers produced using 16 and 18% AA decreased through to the lower kappa numbers. When NaBH₄ was added in pulping experiments, the same trend with higher magnitude was also observed.
CONCLUSIONS

The pulping studies showed that with the use of NaBH₄, in kraft-NaBH₄, a small decrease (12%) in the kappa number was measured compared to the control kraft cook (P5). If lower kappa numbers were desired with NaBH₄, higher alkali and cooking time will be necessary. A significant yield increase was observed when using NaBH₄ in kraft-NaBH₄ pulping. 1% NaBH₄ in kraft-NaBH₄ pulping resulted in a 1.67% higher pulp yield. Higher NaBH₄ in cooks improved the pulping yield more and up to 3.3% higher yield was observed when adding 3% NaBH₄. Considerable achievements on pulp viscosity and brightness were measured when adding NaBH₄ in kraft-NaBH₄ pulping. On the other hand, tear and burst strength and breaking length of the kraft-NaBH₄ pulps was lower compared to the control kraft cook (P5). This could be improved while optimizing the cooking conditions based on cooking variables.

REFERENCES

Kleppe, P.J., 1981. A mill trial with the addition of a small amount of AQ to kraft and polysulphide pulping. Paperi ja Puu., 63: 204