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Determination of Kraft-$NaBH_4$ Pulping Condition of Uludag Fir (Abies *Bornmuelleriana* Mattf.)

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Abstract: The aim of this study is to evaluate the effects of $NaBH_4$ 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 $cm^3\ g^{-1}$ viscosity for Uludag fir. A second set of cookings was made taking into account the optimum kraft cooking condition and 1, 2 and 3% $NaBH_4$ 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 $NaBH_4$ was added to the cooking digester. This finding indicated higher pulping selectivity of $NaBH_4$ added kraft method. In addition, higher pulp viscosity and brightness were observed in the $NaBH_4$ added kraft method. On the other hand, the strength properties obtained in Kraft-$NaBH_4$ was a slightly reduced compared to the conventional kraft method.

Key words: Kraft pulping, delignification, yield, kappa number, mechanical properties, sodium borohidrate, uludağ fire

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 Kırcı, 2001). Additives such as polysulphide and anthraquinone (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% $NaBH_4$ addition to sulphate cooking increased the yield by 2.95 points. In addition, 1% $NaBH_4$ addition to pulp cooking increased the total yield by 3.83% points. In accordance with those results, sodium borohydride acts as a catalyzer 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 pealing. 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 (Hafızoğlu, 1982). Similarly, the earlier removal of glucomannan which was unaffected by borohydride, was due to physical dissolution of a soluble fraction. The rate and extend 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 borohydrate 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 borohydrite addition on pulp and paper properties.

MATERIALS AND METHODS

Having natural potential in Turkey and mostly utilized in Turkish sulphate mills, Uludağ Fir (*Abies bornmuelleriana* 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. Hollocelulose, 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 cm-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 borohidrate cooks were accomplished based on the optimum kraft pulping conditions. Kraft-sodium borohidrate cooks were conducted only altering the $NaBH_4$ concentrations in cooks. 1, 2 and 3% (o.d. wood) $NaBH_4$ 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 1: Pulping conditions and results of kraft and kraft-$NaBH_4$

Method		A.A (%)*	$NaBH_4$ (%)**	Cooking time	Total yield, % o.d. wood	Rejects, % o.d. wood	Kappa No.	Viscosity (cm^3 g^{-1})
Kraft	P1	16	-	60	46.34	2.50	49.4	1044
	P2	16	-	90	48.02	1.55	44.3	981
	P3	16	-	120	45.30	1.39	42.1	922
	P4	18	-	60	46.31	1.68	41.1	1012
	P5	18	-	90	44.28	0.83	32.2	975
	P6	18	-	120	43.11	0.72	31.5	912
Kraft-$NaBH_4$	B1	18	1	90	45.95	0.26	31.6	1015
	B2	18	2	90	46.53	0.21	28.5	1102
	B3	18	3	90	46.90	0.14	28.8	1115

* Active alkali as % Na_2O/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 T236) and viscosity (SCAN cm 15:88) of the pulp samples.

Pulps were beat 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 Köthen 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-$NaBH_4$ 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-$NaBH_4$ 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-$NaBH_4$ pulping was achieved while adding 1, 2 and 3% $NaBH_4$ 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 $NaBH_4$ on pulp properties. The pulp properties of kraft-$NaBH_4$ showed that adding $NaBH_4$ to cooking liquor resulted in pulps that have higher screened pulp yield (Fig. 1). The yield increase in $NaBH_4$ added cooks is explained with higher carbohydrate retention and reduction in rejects. The optimum yield increase was observed when adding 2% $NaBH_4$ to the cooking liquor and kraft-$NaBH_4$ pulp gave 2.9% (o.d. wood) higher

Table 2: Chemical composition of Uludag fir, Burita pine and Oriental spruce (% of o.d wood)

Component	Uludag fir *	Std	Brutia Pine (Kırcı, 1991)	Oriental spruce (Hafizoğlu,1997)
Holosellullose	67.19	0.21	70.8	71.23
Cellulose	51.78	0.33	54.1	57.83
α-cellulose	43.66	0.30	-	45.2
Lignin	28.14	0.27	27.4	27.8
Ash	0.34	0.26	0.37	0.41
Solubility				
Alcohol-benzene (2/1)	1.60	0.29	5.9	1.22
1% NaOH	11.43	0.20	8.5	5.47
Hot water	2.20	0.26	5.0	1.33
Cold water	1.24	0.22	3.0	0.99

* Mean values are the average of duplicate measurements

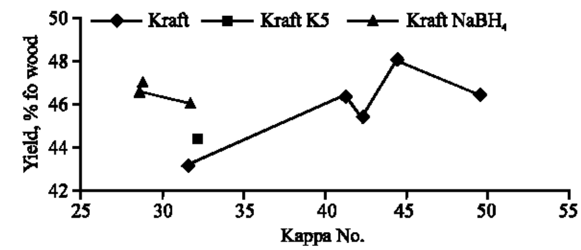

Fig. 1: The total yields of fir vs. kappa number with pulping methods as parameter

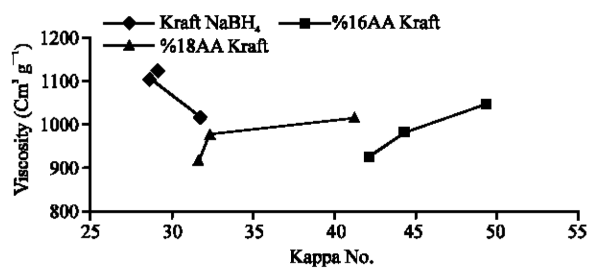

Fig. 2: The viscosity vs. kappa number with pulping method as parameters

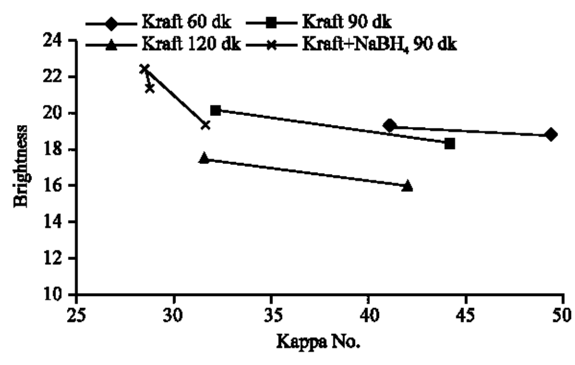

Fig. 3: Brightness of kraft and kraft-$NaBH_4$ pulps

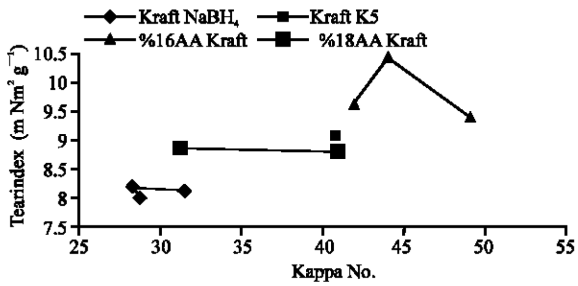

Fig. 4: Effect of AA and $NaBH_4$ in pulp tear index

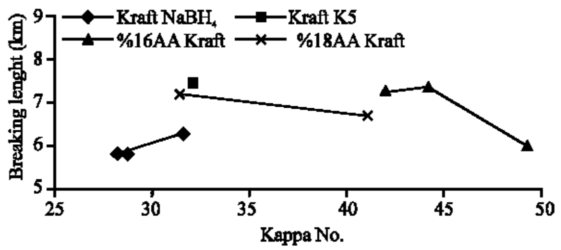

Fig. 5: Effect of AA and $NaBH_4$ in pulp breaking length

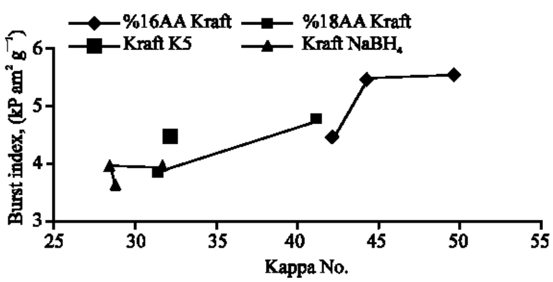

Fig. 6: Effect of AA and $NaBH_4$ in pulp burst index

screened yield when compared to the reference kraft cook (P5). Khaustova *et al.* (1971) Gabir and Khristov (1973) Diaconescu and Petrovan (1976) also reported similar results for pulping yield. In addition to yield increase, the added $NaBH_4$ in kraft-$NaBH_4$ 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-$NaBH_4$ method varying from 0.26 to 0.14% (o.d. wood), which depends on the level of $NaBH_4$ in the cook. Higher amount of $NaBH_4$ in the cook decreased the reject obtained in pulping.

The results also pointed out that the addition of $NaBH_4$ 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-$NaBH_4$ 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-$NaBH_4$ method could be explained with the carbohydrates preserving mechanism of the $NaBH_4$.

Figure 2 shows Pulps viscosity measured for kraft and kraft-$NaBH_4$ pulps. A simultaneous decrease in viscosity and kappa number was observed for kraft pulps that also observed earlier (Çöpür *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 $NaBH_4$ preserved the degree of polymerization of the cellulose chains and resulted in a higher viscosity. Opposite to observations on kraft pulps, kraft $NaBH_4$ better preserved the carbohydrate chains and improved the viscosity of the pulps through to the lower kappa number. Increase in $NaBH_4$ 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-$NaBH_4$ 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 $NaBH_4$.

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 $NaBH_4$ treatment (Fig. 4). The pulps with $NaBH_4$ had lower tearing resistance. 3% $NaBH_4$ addition gave the lowest pulp tear strength. The reason for the lower tear strength could be explained by the higher pulp yield of Kraft $NaBH_4$ 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 $NaBH_4$ was added in pulping experiments, the same trend with higher magnitude was also observed.

CONCLUSIONS

The pulping studies showed that with the use of $NaBH_4$ in kraft-$NaBH_4$, a small decrease (12%) in the kappa number was measured compared to the control kraft cook (P5). If lower kappa numbers were desired with $NaBH_4$, higher alkali and cooking time will be necessary. A significant yield increase was observed when using $NaBH_4$ in kraft- $NaBH_4$ pulping. 1% $NaBH_4$ in kraft-$NaBH_4$ pulping resulted in a 1.67% higher pulp yield. Higher $NaBH_4$ in cooks improved the pulping yield more and up to 3.3% higher yield was observed when adding 3% $NaBH_4$. Considerable achievements on pulp viscosity and brightness were measured when adding $NaBH_4$ in kraft-$NaBH_4$ pulping. On the other hand, tear and burst strength and breaking length of the kraft-$NaBH_4$ pulps was lower compared to the control kraft cook (P5). This could be improved while optimizing the cooking conditions based on cooking variables.

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