Journal of Environmental Biology **November 2009,** 30(6) 951-953 (2009)

Utilization of sodium borohydride ($NaBH_4$) in kraft pulping process

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(Received: April 24, 2008; Revised received: October 25, 2008; Accepted: November 25, 2008)

Abstract: *Aim of this study is to investigate the effect of adding sodium borohydride ($NaBH_4$) in kraft pulping. First of all, six kraft cooks were carried out for varying active alkali and sulfidity. Then, kraft methods for K1 and K6 cooks were modified by adding 1, 2 and 3 % $NaBH_4$. The results indicated that modifying kraft method (K1) by adding 3% $NaBH_4$ (KB13) resulted in 9.97% (relative percentage) yield increase and 10.1% (relative percentage) kappa reduction. Although the mechanical properties of $NaBH_4$ modified pulps were lower compared to the kraft pulps, $NaBH_4$ modified pulps were much brighter.*

Key words: *Maritime pine, Sodium borohydride, Kraft pulping, Pulp yield, Paper properties*
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Introduction

The paper industry currently faces several difficulties such as raw material deficiency, low pulp yield, energy loss and environmental pollution. Efforts have been continuing to maximize the pulp yield from chemical pulping processes ever since the industry began relying on wood as its primary raw material (Courchene, 1998). The future of the paper industry will be the minimum-impact mill. Minimum-impact means both a reduction in emissions and a reduction in raw material consumption by maximizing the yield of manufacturing processes (Axegard *et al*., 1997).

The paper industry has recently been interested in taking advantage of an environmentally friendly process of utilizing boron compounds in pulping processes. Pulping yield depends on some factors, such as the modification of the chemical reactions and the composition of the raw material during pulping. To counteract the yield losses, several studies and trials were done with the addition of polysulfide, anthraquinone and borohydrate to modified cooks. Studies related to pulp yield increasing focused on modifications to the kraft process with multiple liquor injection and impregnation techniques in order to minimize the alkali degradation of cellulose and hemicellulose. When the chemistry of the kraft process was better understood and the mechanisms for degradation and loss of polysaccharides in alkali solutions were realized, the investigation focused on ways to stabilize the cellulose and hemicelluloses against alkaline attack, leading to higher pulp yields. Stabilization of the polysaccharides against alkali degradation occurs with conversion of carbonyl groups with a reducing or an oxidizing agent, and these reactions prevent a further peeling reaction (Courchene, 1998; Tutus and Eroglu, 2003). Addition of pulping additives (anthraquinone, polysulfide or sodium borohydride) to cooking liquor increases pulp yield through greater retention of hemicelluloses (Tutus and Eroglu, 2004). $NaBH_4$ causes reduction of carbonyl group located on the end group of cellulose to hydroxyl group during the cooking and stops the probable peeling reaction because it is a powerful reducing agent. Thus, a decrease in yield during cooking can be prevented. This reaction can occur in both cellulose and hemicellulose (Courchene, 1998; Hafizoglu, 1982). Peeling reaction initiated in carbonyl groups in the end units is prevented by the conversion of carbonyls to hydroxyls by borohydride. The major effect of borohydrate is to prevent the acceleration of glucomannan removal that otherwise occurs at 100°C (Tutus and Usta, 2004). The aim of this study is to examine the effect of adding $NaBH_4$ into kraft pulping and to compare pulp and paper properties of the resultant pulps.

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Materials and Methods

Material: Freshly cut maritime pine (*Pinus pinaster* Ait), collected in the western Black Sea Region, Bartin-Turkey, was used as raw material. The area from which the specimens were taken shows the natural characteristics of the region.

Manufacture of pulps: The bark and cambium were carefully removed from the wood and the logs were reduced to chips suitable for the subsequent pulping operations. The chips were air-dried and screened to form a uniform chip size through pulping. First, 6 different pilot experiments were conducted by kraft pulping methods. For each experimental point, 700 g of oven-dried pine chips were cooked in a 15 liter rotating digester. Kraft cooking conditions for Maritime pine woods were 20 and 25% active alkali concentration as sodium oxide (Na_2O) equivalents, 25, 30 and 35% sulphidity, 4:1 liquor/wood ratio, 170°C cooking temperature, 90 min sulfidity reaching time to maximum cooking temperature and an additional 90 min cooking time for a total of 180 min cooking time (Table 1). After cooking, pulps were washed thoroughly to remove black liquor, the ratio of pulp yield was determined as a percentage of oven-dried raw materials.

Table - 1: Cooking conditions and some properties of maritime pine kraft and kraft -$NaBH_4$ pulps

Cooking no	Active alkali (%)	Sulfidity (%)	Cooking temp. (°C)	Cooking time (min)	$NaBH_4$ (%)	Screened yield (%)	Reject ratio (%)	Total yield (%)	Kappa No.
K1*	20	25	170	180	-	44.73	0.22	44.95	31.7
K2	20	30	170	180	-	44.24	0.41	44.65	32.3
K3	20	35	170	180	-	43.51	0.30	43.81	30.1
K4	25	25	170	180	-	42.65	0.12	42.77	19.0
K5	25	30	170	180	-	42.94	0.14	43.08	24.7
K6*	25	35	170	180	-	43.55	0.19	43.74	17.6
KB11	20	25	170	180	1	48.46	0.03	48.49	31.4
KB12	20	25	170	180	2	48.43	0.09	48.52	30.1
KB13	20	25	170	180	3	49.19	0.10	49.29	28.8
KB61	25	35	170	180	1	45.74	0.10	45.84	17.4
KB62	25	35	170	180	2	47.75	0.15	47.90	16.2
KB63	25	35	170	180	3	47.60	0.04	47.64	15.4

K = Kraft, KB = Kraft-borohydrate, * = Control pulps

Table - 2: Physical and optical properties of maritime pine kraft-$NaBH_4$ handsheets at 50±3 SR°

Cooking no	TEA (j m^{-2})	Breaking length (km)	Burst index (kPa.m^{2}g^{-1})	Stretch (%)	Tear index (mN m^{2}g^{-1})	Rigthness (%)	Opacity (%)
K1*	107.76±14.12	5.92±0.31	4.46±0.31	2.64±0.23	5.76±0.49	15.18±0.12	85.14±0.74
K2	68.77±14.62	4.82±0.42	4.30±0.43	2.07±0.27	5.68±0.33	15.40±0.52	85.46±0.71
K3	113.13±13.59	5.76±0.42	4.41±0.24	2.83±0.30	5.10±0.51	13.76±0.74	86.80±0.58
K4	66.34±11.50	4.38±0.23	3.14±0.16	2.13±0.25	3.89±0.33	18.94±0.38	81.74±0.36
K5	90.45±16.79	5.12±0.36	3.88±0.48	2.57±0.34	4.74±0.43	17.92±0.87	82.48±1.15
K6*	65.30±15.22	4.43±0.37	3.20±0.29	2.10±0.31	4.66±0.28	18.50±0.52	82.00±1.22
KB11	86.75±17.77	5.58±0.38	3.62±0.83	2.29±0.30	5.45±0.11	17.06±0.15	82.94±0.56
KB12	62.64±7.98	5.00±0.23	3.52±0.27	1.87±0.16	4.10±0.12	20.71±0.95	80.12±0.16
KB13	72.58±5.49	4.53±0.18	2.82±0.11	2.31±0.15	3.63±0.12	22.01±0.32	80.00±0.17
KB61	62.17±10.84	4.48±0.27	2.63±0.19	2.05±0.29	3.51±0.14	21.17±0.98	82.34±0.31
KB62	58.00±9.73	4.26±0.18	2.40±0.14	1.98±0.21	3.14±0.36	23.29±0.69	79.70±0.45
KB63	65.59±9.21	4.36±0.19	2.56±0.24	2.14±0.23	3.42±0.34	24.78±0.25	79.86±0.13

± = Standard deviation, K = Kraft, KB = Kraft borohydrate, * = Control pulp, TEA = Tensile energy absorption

Evaluation of pulps: Freeness of pulps and Kappa numbers were determined according to ISO 5267-1(1999) and TAPPI T 236 (1999), respectively. Obtained pulps were beaten to 50 ± 3°SR (Schopper-Riegler) freeness with Valley beater (TAPPI T 200, 2001). Then, handsheets were produced in a Rapid-Kothen Sheet Former (ISO 5269-2, 2004). The mechanical properties of handsheets were tested in accordance with the TAPPI T 220 (2001). The brightness (ISO 2470, 1999) and opacity (ISO 2471, 1998) were measured using an Elrepho 2000 diffuse reflectance spectrophotometer.

Results and Discussion

The pulp yield increasing and delignification maximizing studies are based on raw material modifications, pulping additives (anthraquinone, polysulfide, boron compounds *etc.*), and cooking modifications. A pulping additive, sodium borohydride, acts as a catalyst. It protects the reducing end groups from a peeling reaction and increases the screened yield of pulp. Cooking conditions and influence of different cooking parameters on Maritime kraft pulps are given in Table 1. In control kraft pulping, the highest screened yield of 44.43% for K1 and the lowest kappa number of 16.7 was obtained in K6 kraft pulping condition. When kraft pulps of K1 and K3 were compared for varying sulfidity levels, increase in sulfidity is expected to increase pulp yield but unexpectedly a decrease on pulp yield and kappa number were observed in this study. The benefits of $NaBH_4$ addition into kraft pulping were a significant increase in pulp yield and reduction in kappa number and reject ratio.

The results indicated that the highest yield increase was observed when K1 kraft pulp was modified with 3% $NaBH_4$. The yield increase observed was 9.97% (relative percentage). This increase in pulping yield is expected and is explained by the stabilization of glucomannan and xylan. In addition, $NaBH_4$ addition causes a reduction of carbonyl groups located on the end group of cellulose to hydroxyl group during the cooking and stops the probable peeling reactions because $NaBH_4$ is a powerful reducing agent; therefore, prevents yield decrease in cooking (Courchene, 1998; Tutus and Eroglu, 2004; Hafizoglu, 1982). However; it is not clear that $NaBH_4$ has the similar effect on other plant species or for different pulping methods. Therefore, it is necessary to repeat these experiments with different pulping methods, plant species and under different cooking conditions. Increase of $NaBH_4$ regularly reduced the kappa number of the pulps. Increasing $NaBH_4$ from 1 to 3% for K1 cook reduced the kappa number from 31.7 to 28.8 (KB13).

Similar findings were observed for cook K6. This finding is explained by the acceleration of delignification as kraft method modified by $NaBH_4$. Earlier studies (Istek and Ozkan, 2008) reported that adding 3% $NaBH_4$ improved the kraft pulp yield of *Populus tremula* from 54.3 to 58.0%, and decreased the kappa number from 15.4 to 12.4. Approximately, 10.1% (relative percentage) reduction in kappa number of maritime pine kraft pulp was observed as a result of 3% $NaBH_4$ addition in this study. Adding 1.5 and 1% $NaBH_4$ to cooking liquor during kraft pulping of wheat straw increased pulp yield by 2.95 and 3.83%, respectively (Tutus, 2005). In another study, using $NaBH_4$ during pulping increased pulp yield and decreased kappa number (Diaconescu and Petrovan, 1976; Khaustova *et al*., 1971).

The mechanical (tensile energy absorption (TEA), stretch, breaking length, burst index and tear index) and optical (ISO brightness and printing opacity) properties of handsheets are given in Table 2. There are significant differences between the control kraft pulps and the kraft-$NaBH_4$ pulps regarding the mechanical and optical properties. Modifying kraft method by $NaBH_4$ resulted in some decrease in the strength properties. The observed loss on mechanical properties may be accounted for on the basis of the decrease in fiber to fiber bonding reduction in fiber length as a result of refining. On the other hand, the decrease on physical properties like breaking length, burst index and tear index as a result of adding $NaBH_4$ could be explained by lower fiber to fiber bonding due to the more hemicelluloses preserved by these methods. The lower mechanical properties of $NaBH_4$ modified pulps could be due to the rigidity of the pulps having higher amount of hemicellulose compared to the kraft pulp (Akgul *et al.,* 2007).

As expected, ISO brightness of $NaBH_4$ modified pulps was higher compared to the kraft pulps. Modifying kraft method by adding 2% $NaBH_4$ (KB12) resulted in 36.43% increase in the pulp brightness. This result can be attributed also to the bleaching property of $NaBH_4$ (Copur, 2007). On the other hand, a slight decrease on opacity was observed for $NaBH_4$ modified pulps. According to the results of this study, adding of $NaBH_4$ cooking liquor was increased yield and brightness fo paper. But, using of $NaBH_4$ during maritime pine kraft pulp was decreased some strength properties of paper.

Acknowledgment

Our very special thanks go to professor Hudaverdi Eroglu for technical conservations.

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