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Abstract: Sodium borohydride ($NaBH_4$) added kraft pulping was performed using European aspen (*Populus tremula* L.) chips and the effects of the $NaBH_4$ addition on the physical and optical properties of pulps and resultant papers were investigated. In order to determine the optimum cooking parameters, 6 different laboratory experiments were carried out, which indicated that 2 cooking conditions were better than the others. The effects of 1%, 2%, and 3% $NaBH_4$ additions on pulps and paper properties were investigated based on these 2 cooking conditions. It was noted that the increasing level of $NaBH_4$ added improved the screened pulp yield and pulp viscosity levels and reduced the Kappa number. There was no statistical significance regarding the strength properties of kraft-$NaBH_4$ pulps compared to control pulps at 50 ± 3 °SR freeness level. However, the brightness of handsheets was increased by $NaBH_4$ additions.

Key Words: *Populus tremula* L., kraft pulping, sodium borohydride, screened yield, paper properties

Titrek Kavak (*Populus tremula* L.) Kraft Hamuru Üretimine Sodyum Borhidrürün Etkisi

Özet: Bu çalışmada, titrek kavak (*Populus tremula* L.) odunlarından sodyum borhidrür ($NaBH_4$) ilaveli kraft yöntemiyle kâğıt hamuru üretilmiş ve $NaBH_4$'ün hamur verimi ve kâğıdın fiziksel ve optik özellikleri üzerine etkisi incelenmiştir. Optimum pişirme parametrelerin belirlemek için 6 adet ön deneme pişirmesi yapılmıştır. Bu pişirmelerden en yüksek verim ve en düşük Kappa numarası elde edilen 2 pişirme şartları kılavuz olarak seçilmiştir. Bu kılavuz pişirme koşullarına %1–2–3 oranında $NaBH_4$ ilave edilerek 6 adet daha pişirme yapılmıştır. İlave edilen $NaBH_4$ oranına bağlı olarak, hamur verimi ve viskozitesinin arttığı, Kappa numarasının azaldığı tespit edilmiştir. Kontrol pişirmelerine kıyasla, $NaBH_4$ ilaveli 50 ± 3 °SR serbestlik derecesinde üretilen kâğıtların sağlamlık özelliklerinde istatistiksel olarak anlamlı bir fark bulunmamıştır. Buna karşın, $NaBH_4$ ilavesiyle elde edilen deneme kâğıtlarının parlaklık değerleri artmıştır.

Anahtar Sözcükler: *Populus tremula* L., kraft hamuru, sodyum borhidrür, elenmiş verim, kağıt özellikleri

Introduction

The paper industry, like most manufacturing industries, is especially sensitive to the costs of raw materials. Efforts have continued 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 (Axegård et al., 1997).

Early 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

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solutions were realized, investigations 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; Tutuş and Eroğlu, 2004). Adding of pulping additives (anthraquinone, polysulfide, or sodium borohydride) to cooking liquor increases pulp yield through greater retention of hemicelluloses. $NaBH_4$ causes reduction of the carbonyl group located on the end group of cellulose to a 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 (Hafızoğlu, 1982; Courchene, 1998). The 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 borohydride is to prevent the acceleration of glucomannan removal that otherwise occurs at 100 °C (Tutuş and Usta, 2004).

The purpose of this study was to determine the best kraft cooking conditions with $NaBH_4$ addition on *Populus tremula* L. The pulp properties, yield, and effects of $NaBH_4$ addition on the resultant paper properties were especially closely monitored and evaluated.

Materials and Methods

Materials

Wood samples of *P. tremula* L. were collected in the Western Black Sea region, Bartin province, at 150-200 m altitude. The area from which the specimens were taken shows the natural characteristics of the vicinity. *P. tremula* is 20-25 m in height, usually has a cylindrical trunk, is intensely branched and largely crowned, and grows naturally almost everywhere (except for the steppe areas) in Europe, North Africa, Middle Caucasus, and also in a very wide area between Siberia and Japan. Except for the steppe areas of Southern and Central Anatolia, it grows in every forest area of Turkey (İstek, 2006).

Methods

Pulping

In order to determine optimum cooking conditions, six different experiments were conducted by kraft pulping methods. Kraft cooking conditions for *P. tremula* woods were: 16% active alkali concentration as sodium oxide (Na_2O) equivalents, 20-23-26% sulfidity, 4:1 liquor/wood ratio, 170 °C cooking temperature, 90 min time to reach maximum cooking temperature and an additional 60-90 min cooking time for a total of 150 to 180 min cooking time (Table 1). After digestion, pulps were washed thoroughly to remove black liquor. The pulp yields and reject ratios were determined as a percentage of oven-dry raw materials according to TAPPI T 210. The total yield of pulps was obtained by the addition of screened yield and reject ratio.

Table 1. Laboratory-cooking conditions and some properties of *P. tremula* kraft pulps.

Cooking No.	Sulfidity (%)	Active Alkali (%)	Cooking Time (min)	Cooking Temperature (ºC)	Liquor/ Wood	Viscosity ($cm^3 g^{-1}$)	Screened Yield (%)	Kappa No.	Reject Ratio (%)
K1	20	16	150	170	4/1	959	55.1	17.9	1.21
K2	23	16	150	170	4/1	1014	54.5	17.6	0.28
K3*	26	16	150	170	4/1	1027	55.7	15.9	0.67
K4	20	16	180	170	4/1	957	53.9	16.3	0.14
K5	23	16	180	170	4/1	870	53.5	15.9	0.19
K6*	26	16	180	170	4/1	991	54.3	15.4	0.26

K: kraft, *: control pulps

Evaluation of Pulps

Freeness of pulps, Kappa numbers, and viscosity of pulps were determined according to ISO 5267-1, TAPPI T 236, and SCAN cm 15:88 respectively. From preliminary experiments, the 3rd cooking gave the highest screened yield, and the 6th cooking gave the lowest Kappa number. $NaBH_4$ (1%, 2%, and 3%) was added to cooking liquor in the 3rd and the 6th cooking experiments. After cooking, the pulps were beaten to 50 ± 3 °SR (Schopper-Riegler) freeness with a Valley beater (TAPPI T 200). Then, handsheets were produced in a Rapid-Kothen Sheet Former (ISO 5269-2). The physical properties of the handsheets were determined in accordance with the TAPPI T 220. The brightness (ISO 2470) and opacity (ISO 2471) were measured using an Elrepho 2000 diffuse reflectance spectrophotometer. Statistical analyses were performed by means of Statgraph Plus 5.0 software.

Results

Cooking conditions and some properties of *P. tremula* kraft pulps are given in Table 1. The highest viscosity and screened yield were 1027 $cm^3 g^{-1}$ and 55.7% respectively (cooking number K3). On the other hand, the lowest Kappa number obtained was 15.4 (cooking number K6). Physical and optical properties of handsheets of the pulps are given in Table 2. Some properties of *P. tremula* control pulps (K3 and K6) and kraft-$NaBH_4$ pulps are given in Table 3.

In this study, total yield, viscosity, and screened yield increased with the addition of more $NaBH_4$ to the cooking liquor. In contrast, Kappa number and reject ratio decreased (Table 3). The highest screened yield increase obtained was 4.3% at the cooking number KB12 with 3% addition of $NaBH_4$. Physical and optical properties of handsheets of control kraft pulps and kraft-$NaBH_4$ pulps are given in Tables 4 and 5, respectively.

In Table 4, the tensile energy absorption (TEA), burst index, tear index, air permeability, and opacity of the handsheets prepared from the pulps obtained from cooking numbers KB7, KB8, and KB9 did not change significantly ($P < 0.05$). In general, $NaBH_4$ addition in cooking liquors caused some decrease in the strength properties of handsheets. Nevertheless, the decreases observed, especially in pulps generated from KB8 and KB9, were negligible. Breaking length and tensile index of handsheets of K3 were determined as 9.86 ± 0.71 km and 96.66 ± 6.94 N.m g^{-1} respectively. These values were slightly lower, 9.13 ± 0.08 km and 89.51 ± 0.81 N.m g^{-1}, for handsheets of the KB9. The brightness of handsheets was increased significantly by the addition of $NaBH_4$.

Table 2. Physical and optical properties of handsheets of *P. tremula* kraft pulps.

Cooking No.	K1	K2	K3*	K4	K5	K6*
TEA (j m^{-2})	91.59 ± 7.63^{ab}	96.16 ± 12.15^{b}	86.77 ± 8.57^{ab}	84.94 ± 14.03^{ab}	85.74 ± 9.61^{ab}	71.55 ± 9.84^{a}
Breaking length (km)	10.27 ± 0.65^{d}	8.58 ± 0.75^{ab}	9.86 ± 0.71^{cd}	9.01 ± 0.38^{bc}	7.98 ± 0.34^{ab}	7.63 ± 0.20^{a}
Burst Index (kPa.$m^2 g^{-1}$)	4.00 ± 0.23^{c}	3.65 ± 0.24^{abc}	3.85 ± 0.40^{bc}	3.43 ± 0.12^{ab}	3.38 ± 0.28^{a}	3.51 ± 0.15^{ab}
Stretch (%)	2.27 ± 0.25^{a}	2.46 ± 0.40^{a}	2.23 ± 0.36^{a}	2.32 ± 0.19^{a}	2.32 ± 0.29^{a}	1.98 ± 0.32^{a}
Tear Index (mN.m^2 g^{-1})	6.31 ± 0.84^{c}	5.98 ± 0.75^{bc}	5.56 ± 1.28^{abc}	4.66 ± 0.84^{ab}	4.85 ± 0.23^{abc}	4.01 ± 0.38^{a}
Cobb (g m^{-2})	124 ± 19.69^{a}	134 ± 5.86^{a}	141 ± 21.37^{a}	132 ± 8.90^{a}	132 ± 4.38^{a}	135 ± 10.15^{a}
Air permeability (ml min^{-1})	619 ± 14.94^{a}	533 ± 9.29^{a}	614 ± 87.06^{a}	626 ± 12.09^{a}	568 ± 8.81^{a}	525 ± 86.75^{a}
Tensile Index (N.m g^{-1})	100.74 ± 6,34^{d}	84.11 ± 7.41^{ab}	96.66 ± 6.94^{cd}	88.37 ± 3.77^{bc}	78.26 ± 3.37^{ab}	74.83 ± 2^{a}
Brightness (% ISO)	21.52 ± 0.13^{b}	23.25 ± 0.42^{d}	22.23 ± 0.27^{c}	20.61 ± 0.04^{a}	21.28 ± 0.19^{ab}	20.91 ± 0.27^{ab}
Opacity (% ISO)	98.10 ± 0.75^{a}	98.98 ± 2.17^{a}	99.63 ± 0.48^{a}	99.62 ± 0.34^{a}	99.14 ± 0.65^{a}	99.52 ± 1.63^{a}

±: Standard deviation; K: kraft; *: control pulps

[a]: Within a line, means bearing the same letter are not significantly different ($P < 0.05$)

Table 3. Some properties of control and $NaBH_4$ added P. tremula kraft pulps.

Cooking No.	$NaBH_4$ Ratio (%)	Screened Yield (%)	Reject Ratio (%)	Total Yield (%)	Viscosity ($cm^3\ g^{-1}$)	Kappa No.
K3	-	55.70	0.67	56.37	1027	15.90
KB7	1	56.30	0.13	56.43	1071	15.58
KB8	2	56.59	0.16	56.75	1094	15.10
KB9	3	57.43	0.31	57.74	1115	14.70
K6	-	54.30	0.26	54.56	991	15.40
KB10	1	55.34	0.05	55.39	992	15.40
KB11	2	56.45	0.09	56.54	1002	12.70
KB12	3	58.00	0.03	58.03	1034	12.40

K: Kraft, KB: Kraft-$NaBH_4$

Table 4. Physical and optical properties of handsheets of control pulp K3 and $NaBH_4$ added kraft pulping (1%, 2%, 3%).

Cooking No.	K3	KB7	KB8	KB9
NaBH4 Ratio (%)	-	1	2	3
TEA ($j\ m^{-2}$)	86.77 ± 8.57^a	79.74 ± 0.08^a	82.62 ± 0.28^a	79.07 ± 2.17^a
Breaking length (km)	9.86 ± 0.71^b	9.63 ± 0.13^{ab}	9.46 ± 0.28^{ab}	9.13 ± 0.08^a
Burst Index ($kPa.m^2\ g^{-1}$)	3.85 ± 0.40^a	3.55 ± 0.15^a	3.42 ± 0.34^a	3.67 ± 0.15^a
Stretch (%)	2.23 ± 0.36^b	1.86 ± 0.10^a	2.21 ± 0.09^b	1.94 ± 0.04^{ab}
Tear Index ($mN.m^2\ g^{-1}$)	5.56 ± 1.28^a	4.68 ± 0.03^a	4.99 ± 0.43^a	4.47 ± 0.28^a
Cobb ($g\ m^{-2}$)	141 ± 21.37^b	149 ± 8.75^b	132 ± 19.65^{ab}	113 ± 6.54^a
Air permeability ($ml\ min^{-1}$)	614 ± 87.06^a	420 ± 11.35^a	587 ± 112.03^a	434 ± 156.42^a
Tensile Index ($N.m\ g^{-1}$)	96.66 ± 6.94^b	94.37 ± 1.29^{ab}	92.68 ± 2.70^{ab}	89.51 ± 0.81^a
Brightness (% ISO)	22.23 ± 0.27^a	23.54 ± 0.16^b	28.16 ± 0.36^d	24.62 ± 0.39^c
Opacity (% ISO)	99.63 ± 0.48^a	98.65 ± 0.22^a	97.76 ± 1.70^a	99.08 ± 1.48^a

±: Standard deviation, [a]: Within a line, means bearing the same letter are not significantly different ($P < 0.05$)

As can be seen in Table 5, when we compared the properties of TEA, stretch, air permeability, and opacity values of the handsheets of K6 with those of KB10, KB11, and KB12 there were no considerable differences. The use of $NaBH_4$ during kraft pulping significantly increased brightness values in all the experiments. It was observed that the brightness of KB10 gave the highest increase, 26.86 ± 0.37% ISO.

Discussion

The highest screened yield increase was observed in KB12, where addition of 3% $NaBH_4$ increased screened yield from 54.3% to 58.0% (Table 3). Addition of $NaBH_4$ in pulping lowered the amount of screening rejects compared to K3 and K6. It was previously reported that 2% $NaBH_4$ addition improved the kraft pulping yield of birch from 52.6% to 59.2% (Pettersson and Rydholm,

Table 5. Physical and optical properties of handsheets of control pulp K6 and $NaBH_4$ added kraft pulping (1%, 2%, 3%).

Cooking No.	K6	KB10	KB11	KB12
$NaBH_4$ Ratio (%)	-	1	2	3
TEA (j m^{-2})	71.55 ± 9.84^a	66.85 ± 0.57^a	70.64 ± 2.46^a	67.56 ± 4.46^a
Breaking length (km)	7.63 ± 0.20^b	8.07 ± 0.09^c	7.33 ± 0.11^a	7.76 ± 0.08^b
Burst Index (kPa.m^2 g^{-1})	3.51 ± 0.15^{bc}	3.60 ± 0.06^c	3.18 ± 0.21^a	3.28 ± 0.15^{ab}
Stretch (%)	1.98 ± 0.32^a	1.85 ± 0.06^a	2.13 ± 0.09^a	1.88 ± 0.08^a
Tear Index (mN.m^2 g^{-1})	4.01 ± 0.38^{ab}	3.61 ± 0.28^a	4.11 ± 0.08^b	3.97 ± 0.12^{ab}
Cobb (g m^{-2})	135 ± 10.15^b	138 ± 4.32^b	116 ± 4.16^a	115 ± 5.13^a
Air permeability (ml min^{-1})	525 ± 86.75^a	520 ± 64.43^a	399 ± 135.21^a	377 ± 88.51^a
Tensile Index (N.m g^{-1})	74.83 ± 2^b	79.14 ± 0.93^c	71.89 ± 1.08^a	76.11 ± 0.75^b
Brightness (% ISO)	20.91 ± 0.27^a	26.87 ± 0.38^c	25.34 ± 0.17^b	25.91 ± 0.03^b
Opacity (% ISO)	99.52 ± 1.63^a	97.82 ± 1.39^a	98.11 ± 1.69^a	98.95 ± 0.83^a

±: Standard deviation, [a]: Within a line, means bearing the same letter are not significantly different ($P < 0.05$)

1961). Similarly, addition of $NaBH_4$ to the cooking liquor increased pulp yield (Khaustova et al., 1971; Diaconescu and Petrovan, 1976). The increase in pulp yield in hardwoods has been attributed to the stabilization of glucomannan and xylan. At the same time, borohydride converts the carbonyl groups located in the reducing end units of carbohydrate chains to hydroxyl groups (Jiang, 1995; Copur, 2007).

Kappa number was noted to be regularly decreasing parallel to the increase in $NaBH_4$ ratio. In cooking number K6, an increase in the $NaBH_4$ rate from 1% to 3% resulted in a decrease in Kappa number from 15.4 to 12.4. This result can be ascribed to the acceleration of delignification by $NaBH_4$. Akgül et al. (2007) obtained similar results indicating that adding $NaBH_4$ during brutia pine kraft pulping decreased the Kappa number from 29.6 to 27.2.

Our results show that the addition of $NaBH_4$ increased pulp viscosity (Table 3). The highest viscosity was 1115 cm^3 g^{-1} in KB9. The viscosity increase could be because the addition of $NaBH_4$ preserved the degree of polymerization of cellulose chains and resulted in higher viscosity (Akgül et al., 2007).

The optical and strength properties of the pulps were evaluated at 50 ± 3 °SR freeness level. As seen in Tables 4 and 5, the TEA, stretch, air permeability, and opacity values of the handsheets of pulps did not change considerably with the addition of $NaBH_4$ to the cooking liquors. Breaking length and tensile index values of handsheets obtained from KB9 were decreased significantly. However, studies with $NaBH_4$ indicated that adding 1%, 2%, and 3% levels significantly improved pulp brightness compared to the control pulps K3 and K6. This result can be ascribed to the bleaching property of $NaBH_4$. These results agree with the results reported by Tutuş (2005) and Akgül et al. (2007), who concluded that the addition of $NaBH_4$ during kraft pulping increased pulp brightness.

Conclusions

In alkaline pulping hemicelluloses are removed by the dissolution at the beginning of cooking. However, xylans in hardwoods are resistant to alkaline; consequently as the pH decreases during cooking xylans precipitate on the fibers; this results in pulp yield increases. The pulp yield increasing and delignification maximizing studies were based on raw material modifications, pulping additives (anthraquinone, polysulfide, boron compounds etc.), and cooking modifications. A pulping additive, sodium borohydride, acts as a catalyst. Thus, it protects the reducing end groups from a peeling reaction and increases the screened yield of pulp. In this study, 1%, 2%, and 3% $NaBH_4$ added kraft pulp was produced from European aspen (*Populus tremula* L.) chips and its effects on the physical and optical properties of pulp and paper were determined.

The benefits of $NaBH_4$ addition into kraft pulping were a significant increase in pulp yield and a reduction in Kappa number and reject ratio. By the addition of $NaBH_4$ to *P. tremula* kraft pulp yield was increased from 54.56% (K6) to 58.03% (KB12). $NaBH_4$ addition causes a reduction of the carbonyl group located on the end group of cellulose to a 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 (Hafızoğlu, 1982; Courchene, 1998; Tutuş and Eroğlu, 2004). However, it is not clear whether $NaBH_4$ has a similar effect on other plant species or for different pulping methods. Therefore, it is necessary to repeat these experiments with different pulping methods and plant species and under different cooking conditions. In the present study, 3% $NaBH_4$ addition decreased the Kappa number from 15.40% (K6) to 12.40% (KB12). However, 3% $NaBH_4$ addition increased viscosities of pulps from 1027 cm^3 g^{-1} (K3) to 1115 cm^3 g^{-1} (KB9). These are significant differences between the control kraft pulps and the kraft-$NaBH_4$ pulps with regard to physical and optical properties.

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