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# THE INFLUENCE OF POTASSIUM BOROHYDRIDE ($KBH_4$) ON KRAFT PULP PROPERTIES OF MARITIME PINE

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## Abstract
In this study, the effects of potassium borohydride ($KBH_4$) on maritime pine (*Pinus pinaster* Ait.) kraft pulp and paper properties were investigated. 0.5%, 1%, 1.5%, and 2% (based on oven-dried wood) $KBH_4$ added kraft cookings were carried out under the fixed cooking conditions. $KBH_4$-free kraft cooking was also done as control cooking. The results revealed that pulp yield, kappa number, and beating time increased with addition of $KBH_4$ to cooking liquor. The screened yield increased 7.69 point (from 46,21% to 53.90%) with 2% $KBH_4$ addition to control cooking. The brightness values of handsheets were increased with $KBH_4$ addition. Strength properties of handsheets significantly decreased with addition of $KBH_4$.

**Keywords:** Kraft, Potassium borohydride, Pulp yield, Paper strength, Maritime pine

# SAHİL ÇAMI KRAFT HAMURU VE KAĞIDININ ÖZELLİKLERİ ÜZERİNE POTASYUM BORHİDRÜRÜN ($KBH_4$) ETKİSİ

## Özet
Bu çalışmada, sahil çamından (*Pinus pinaster* Ait.) elde edilen kraft kağıt hamuru ve kağıtlarının özellikleri üzerine potasyum borhidrürün ($KBH_4$) etkileri araştırılmıştır. %0,5, %1, %1,5, ve %2 (fırın kurusu oduna göre) oranında $KBH_4$ pişirme çözeltisine ilave edilerek sabit pişirme koşulları altında Kraft pişirmeleri yapılmıştır. Ayrıca, $KBH_4$ ilavesiz kraft pişirmesi kontrol pişirmesi olarak yapılmıştır. Pişirme çözeltisine $KBH_4$ ilavesinin kağıt hamurunun verimi ve kappa numarası ile hamurların dövme sürelerini artırdığı sonucuna varılmıştır. Kontrol pişirmesine %2 $KBH_4$ ilave edildiğinde elenmiş verim 7,69 puan (%46,21'den %53,90'a) artmıştır. $KBH_4$ ilavesi ile kağıtların parlaklık değerleri artmıştır. Kağıtların sağlamlık özellikleri $KBH_4$ ilavesi ile önemli ölçüde azalmıştır.

**Anahtar Kelimeler:** Kraft, Potasyum borhidrür, Kağıt hamuru verimi, Kağıt sağlamlığı, Sahil çamı

## 1. Introduction
Kraft pulping was invented in 1879 by Carl F. Dahl. Since then, many studies carried out to improve the pulp yield by preventing carbohydrate losses. The pulp yield is described as weight of pulps obtained from a given weight of wood. The pulp yield in chemical pulping depends on chemical composition of wood (especially cellulose), cooking conditions, wood anatomy, chip dimensions, wood density, using of digester additives etc. During pulping, pulp yield decreases owing to reactions such as alkaline hydrolysis and peeling. The digester additives such as PS, AQ, and $NaBH_4$ minimize the effect of alkaline hydrolysis and peeling on carbohydrate losses. Thus, pulp yield increases at the end of pulping process.

$KBH_4$ is a powerful reducing agent as $NaBH_4$ that converts carbonyl group in the reducing end units of carbohydrate chain to hydroxyl groups. The effects of kraft pulp and paper properties of boron compounds such as $NaBH_4$ and $NaBO_2$ reported by several researchers (Hartler, 1959; Annergren et al. 1963; Meller and Ritman, 1964; Gabir and Khristov, 1973; Diaconescu and Petrovan, 1976; Bujanovic et al. 2003, 2004; Akgül and Temiz, 2006; Tutuş et al 2010a,b). But, there is no published report related to effect of $KBH_4$ on kraft pulp and paper properties. On the other hand, there are some studies (Koch, 1972; Esteves et al. 2005; Baptista et al. 2006; İstek and Gönteki, 2009) related to using of maritime pine in kraft pulping. In this scope, different ratios of $KBH_4$ are used to evaluate the effects on kraft pulp and paper properties of maritime pine in this study.

## 2. Material and Methods
Maritime pine (*Pinus pinaster* Ait.) naturally spreads from the southern European countries such as Italy, Portugal, Spain and France to North Africa (4 million hectares).



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Maritime pine is economically important species for the timber and paper industry (Knapic and Pereira, 2005). The wood samples of maritime pine were obtained from the Bartin province of Turkey. The samples were chipped manually to 2.5 × 1.5 × 0.5 cm. The chips were air-dried and stored at about 90% dry solids content.

In cooking, laboratory cylindrical type rotary digester was used. In each cooking, digester was charged with 650 g (oven dried, o.d.) of chips. The cooking conditions are shown in Table 1. $KBH_4$-added cookings were carried out by adding 0.5%, 1%, 1.5%, and 2% $KBH_4$ (o.d. wood) into the cooking liquor. $KBH_4$-free kraft cooking was also done as control.

Table 1. Kraft cooking conditions using in this study.

| | |
|---|---|
| Active alkali, on o.d. wood (as $Na_2O$) (%) | 18 |
| Sulfidity (%) | 30 |
| Liquor-to-wood ratio (l/kg) | 4 |
| Cooking temperature (°C) | 170 |
| Time to maximum temperature (min) | 90 |
| Time at maximum temperature (min) | 60 |

At the end of each cooking, pulps were washed to remove black liquor and were disintegrated in a laboratory type pulp mixer. Disintegrated pulps were screened on a vibrating flat screen with 0.15 mm wide slots (TAPPI T 275). Screened pulps were beaten to 35 and 50 °SR freeness level in a Valley Beater (TAPPI T 200). Kappa number, screened yield, and freeness level of pulps were determined TAPPI T 236, TAPPI T 210, and ISO 5267-1, respectively. 75 $g/m^2$ handsheets made by Rapid-Kothen Sheet Former (ISO 5269-2) were conditioned according to TAPPI T 402 standard method. Breaking length, burst index, tear index, brightness, and air permeability of the handsheets were determined according to TAPPI T 494, TAPPI T 403, TAPPI T 414, TAPPI T 525, and ISO 5636-3, respectively.

The data of handsheet properties were statistically studied by analysis of variance (ANOVA) and Duncan test at 95% confidence level. In the Table 3, the same letter in a column denotes that the difference in the mean values of properties among the compared groups is not statistically significant ($p$-value > 0.05).

## 3. Results and Discussion

The kappa number of pulp is an indicator of delignification degree during cooking. The kappa number of control, 0.5%, 1%, 1.5%, and 2% $KBH_4$ added pulps was determined as 51.7, 49.5, 58.1, 63.3, and 61.6, respectively (Table 2). The kappa number increased with addition of $KBH_4$. On the contrary, earlier studies showed that $NaBH_4$ adding to cooking liquor caused to increasing delignification (Çöpür and Tozluoğlu, 2008; Gülsoy and Eroğlu, 2009; İstek and Gönteki, 2009).

The total pulp yield of control, 0.5%, 1%, 1.5%, and 2% $KBH_4$ added pulps was determined as 46.73%, 47.17%, 50.61%, 52.00%, and 54.60%, respectively. This result can be attributed to the prevention of degradation reactions by $KBH_4$ during cooking. The positive effect of $NaBH_4$ on pulp yield reported in earlier studies (Gülsoy and Eroğlu, 2011; Gümüşkaya et al. 2011; Erişir et al. 2015). On the other hand, the screened pulp yield values of control, 0.5%, 1%, 1.5%, and 2% $KBH_4$ added pulps were found to be 46.21%, 46.82%, 49.75%, 51.36%, and 53.90%, respectively. The highest screened yield increasing by 16.64% (7.69 point from 46.21% to 53.90%) obtained from 2% $KBH_4$ added pulps. Thus, wood raw material uses more efficient, and profitability of pulp mill increases.

The reject ratio of control, 0.5%, 1%, 1.5%, and 2% $KBH_4$ added pulps were found to be 0.52%, 0.35%, 0.86%, 0.64%, and 0.70%, respectively. Reject ratio of $KBH_4$ added pulps increased with the addition of $KBH_4$ except of 0.5% $KBH_4$ added cooking.

Table 2. The some pulp properties of kraft and kraft-$KBH_4$ pulps of maritime pine.

| Pulp sample | Screened yield (%) | Reject ratio (%) | Total yield (%) | Kappa number |
|---|---|---|---|---|
| Control | 46.21 | 0.52 | 46.73 | 51.70 |
| 0.5% $KBH_4$ | 46.82 | 0.35 | 47.17 | 49.50 |
| 1% $KBH_4$ | 49.75 | 0.86 | 50.61 | 58.10 |
| 1.5% $KBH_4$ | 51.36 | 0.64 | 52.00 | 63.30 |
| 2% $KBH_4$ | 53.90 | 0.70 | 54.60 | 61.60 |

The beating time of pulps to 35 °SR and 50 °SR increased with $KBH_4$ addition. The beating times to 35 °SR and 50 °SR freeness levels of control, 0.5%, 1%, 1.5%, and 2% $KBH_4$ added pulps were 36 min., 40.5 min, 46 min.,

50 min, and 55 min. and 45 min., 50 min., 56.5 min., 59 min., and 64 min., respectively. This result can be ascribed to higher kappa number of $KBH_4$ added pulps than that of kraft pulp. As known, higher lignin content causes longer beating time.

The tear index of beaten and unbeaten kraft-$KBH_4$ pulps was lower than that of control pulp except of 2% $KBH_4$ added pulp (Table 3). Tear index of beaten pulps statistically significantly increased with 2% $KBH_4$ addition to cooking liquor. The burst index of beaten and unbeaten kraft-$KBH_4$ pulps was lower than that of kraft pulp. The losses in burst index occurring with $KBH_4$ addition were statistically significant in all freeness levels of pulp. Also, $KBH_4$ addition caused to breaking length decreases in both unbeaten and beaten pulps. In literature, similar strength losses were reported in $NaBH_4$ added pulps (Akgül et al. 2007; Çöpür and Tozluoğlu, 2008; İstek and Özkan, 2008). Strength losses of pulp can be attributed to higher kappa number of $KBH_4$ added pulps. As known, fibers having higher lignin content have less flexible. The result of this loss in fiber flexibility was weaker interfiber bonding and, consequently, a lower strength in handsheets of $KBH_4$ added pulps. On the other hand, air permeability and brightness of handsheets statistically significantly increased with $KBH_4$ addition. The highest air permeability and brightness values obtained from 2% $KBH_4$ added pulps. The similar air permeability and brightness increases reported in $NaBH_4$ added pulps by Gülsoy and Eroğlu (2011).

Table 3. Some handsheet properties of kraft and kraft-$KBH_4$ pulps of maritime pine.

| Freeness level (°SR) | $KBH_4$ Ratio (%) | Tear Index ($mN.m^2/g$) | Burst Index ($kPa.m^2/g$) | Breaking Length (km) | Air Permeability (ml/min) | Brightness (%) |
|---|---|---|---|---|---|---|
| Unbeaten | - | 15.06b | 3.23c | 4.30d | 2408.05 | 21.04a |
| | 0.5 | 15.00b | 2.73a | 3.98b | 4394.05 | 22.48b |
| | 1 | 14.43a | 2.75a | 3.68a | >5000 | 22.94c |
| | 1.5 | 14.57a | 3.07b | 4.13bc | >5000 | 23.27d |
| | 2 | 15.18b | 2.76a | 4.20cd | >5000 | 23.66e |
| 35 | - | 8.16a | 5.57a | 8.27a | 18.55a | 15.90a |
| | 0.5 | 8.09a | 5.24b | 8.17a | 22.20b | 16.68b |
| | 1 | 8.06a | 5.21b | 8.01a | 26.90c | 17.83c |
| | 1.5 | 8.17a | 4.94c | 7.86a | 29.09d | 18.13d |
| | 2 | 8.53b | 5.20b | 8.24a | 30.12d | 18.75e |
| 50 | - | 8.32bc | 5.58a | 8.46b | 2.33a | 14.69a |
| | 0.5 | 7.55a | 5.25b | 8.46b | 3.44b | 15.69b |
| | 1 | 7.88abc | 5.26b | 8.07ab | 7.00c | 16.65c |
| | 1.5 | 7.77ab | 4.87c | 7.86a | 7.17c | 17.17d |
| | 2 | 8.42c | 5.27b | 8.30b | 11.06d | 17.92e |

## 4. Conclusions

The results showed that using of $KBH_4$ in kraft pulping of maritime pine caused to the significant yield increase. The highest pulp yield increasing was found in 2% $KBH_4$ added pulp by 16.64% (7.69 point from 46.21% to 53.90%). This is an important result with regard to efficient usage of wood raw material. On the other hand, $KBH_4$ addition caused to strength losses. Also, beating time increased with $KBH_4$ addition. $KBH_4$ is an expensive additive such as $NaBH_4$. Future studies should be carried out to evaluate usage of $KBH_4$ as a digester additive in pulping. Maritime pine is economically important species for paper industry. The effect of $KBH_4$ on other important species for paper industry should be investigated.

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