

Emir Erişir, Esat Gümüşkaya, Hüseyin Kırcı, Nuray Misir

## ALKALINE SULPHITE ANTHRAQUINONE PULPING OF CAUCASIAN SPRUCE (*PICEA ORIENTALIS* L.) CHIPS WITH ADDED SODIUM BOROHYDRIDE AND ETHANOL

*The study determined and compared the yield, viscosity, and chemical and physical properties of the pulps obtained as a result of Alkaline Sulfite–Anthraquinone (AS-AQ) pulping of Caucasian spruce wood with and without the addition of sodium borohydride (ASAB process) and ethanol (ASAE). It was found that the addition of ethanol to the AS-AQ pulping had a favourable influence on the screened yield and kappa number of the pulps. The addition of  $\text{NaBH}_4$  to the AS-AQ pulping in general also had a favourable influence on these pulps' indices, provided that the amount added was not higher than 1–2% and the time of pulping was 180 mins. The higher yield of the ASAE pulps resulted from the higher retention of both cellulose and hemicelluloses, while the higher yield of ASAB pulps resulted from the higher retention of hemicelluloses and lignin. Regarding the AS-AQ pulping conditions, a distinct negative effect of modification on the viscosity of the pulps was observed in the case of the  $\text{NaBH}_4$  additions to this pulping process. The viscosity reduction was, however, lower with extended pulping time. The static strength properties (tensile index and burst index) of the ASAB and ASAE pulps were in general lower than the AS-AQ pulps. In the case of the tear index, the tendency was similar. The addition of ethanol and especially  $\text{NaBH}_4$  to the AS-AQ pulping had a distinctly unfavourable influence on the whiteness and brightness of the pulps.*

**Keywords:** spruce wood, alkaline-sulfite-anthraquinone pulping, additives, sodium borohydride, ethanol, pulp evaluation

### Introduction

In recent years, the issue of research and development based on eco-friendly technologies has been one of the most widespread subjects in the pulp and paper industry as well as other subject areas. For a long time, the Kraft (Sulphate) pulping

---

Emir Erişir ([eerisir@ktu.edu.tr](mailto:eerisir@ktu.edu.tr)), Esat Gümüşkaya ([gkaya@ktu.edu.tr](mailto:gkaya@ktu.edu.tr)), Hüseyin Kırcı ([kirci@ktu.edu.tr](mailto:kirci@ktu.edu.tr)), Department of Pulp and Paper Technology, Karadeniz Technical University, Trabzon, Turkey; Nuray Misir ([nuray@ktu.edu.tr](mailto:nuray@ktu.edu.tr)), Department of Forest Engineering, Karadeniz Technical University, Trabzon, Turkey

process has been the most widely-used process in the world for the production of pulp from wood. Despite there being several advantages in the process, problems such as low pulp yield and high consumption of bleaching chemicals to reach lower kappa numbers, plus the additional issue of bad odour, still remain.

In the late sixties and early seventies, a more eco-friendly pulping process "Alkaline Sulfitte (AS)" was developed as an alternative to the Kraft process [Ingruber, Allard 1970; Ingruber et al. 1971; Virkola et al. 1981; Patt et al. 1998; Sixta et al. 2006]. AS pulping is a cooking process in which the cooking liquor is mainly made up of NaOH and Na<sub>2</sub>SO<sub>3</sub> with a cold cooking pH of 10.0–13.5. Investigations of AS pulping have indicated that it is possible to obtain Kraft-like pulp properties in terms of the pulping yield, unbleached brightness and especially bleached pulp strength and also reduce the odour problems associated with the Kraft process [Hauki, Reilama 1982; Ingruber et al. 1982; Gullichsen, Fagelholm 1999]. However, the AS pulping process had some disadvantages such as lowered rates of delignification at a high chemical charge and decreased pulping yield in the same kappa number range compared to that of the Kraft pulping process. To reach the delignification rate of the Kraft pulping process, the proportion of sodium hydroxide in the AS cooking liquor was increased, but the yield of the AS pulping process diminished as a result of carbohydrate degradation in stronger alkaline pulping conditions [Sixta et al. 2006].

In all types of alkaline pulping conditions, two dominant reaction types occur upon cellulose chains [Fengel, Wegener 1989]: The Alkaline Hydrolysis and Peeling-off Reactions. Generally, the degree of polymerization (DP) of polysaccharide is affected mostly by the alkaline hydrolysis. The peeling-off reactions begin from so-called Reducing End Groups (REG), which are at the end of cellulose chains and have reactive aldehyde carbonyl groups [Lai 2001; Sixta et al. 2006; Henriksson, Lennholm 2009]. The new REGs on cellulose chains are also created as a result of the cleavage of glycosidic bonds during alkaline hydrolysis reactions. Therefore, the REGs of cellulose chains must be stabilized against undesirable alkaline reactions. Stabilization of REGs can be recognized in different ways: oxidation, reduction or derivatization [Testova et al. 2014].

During the eighties, the addition of anthraquinone (AQ) and related compounds to the alkaline pulping process opened up new possibilities for developing novel processes. Many studies have revealed that with the addition of AQ, the efficiency and selectivity of delignification by oxidation improve. Compared to the Kraft process, the AQ in AS-AQ pulping under alkaline conditions behaved selectively, providing both a higher yield and viscosity at a given kappa number [Virkola et al. 1981; Kettunen et al. 1982].

In order to improve pulp properties, the AS-AQ pulping was modified by adding methanol (ASAM) or ethanol (ASAE) to replace 50% of the water in the cooking liquor [Patt, Kordsachia 1986; Kirci et al. 1994]. The pulps produced by the ASAM and ASAE processes showed better strength properties, higher

yield and improved bleachability compared to the Kraft process [Kordsachia, Reipschläger 1990; Sixta et al. 2006; Hedjazi et al. 2009].

Using the ASAM process as opposed to the Kraft process, a lower kappa number can be achieved without degradation in the cellulose chains [Patt et al. 1998]. However, methanol and ethanol are highly volatile and flammable solvents. Therefore, the recovery of chemicals used during cooking is problematic. Methanol is also known to be highly toxic for humans [Oliet et al. 2002; Patt et al. 2003; Sixta et al. 2006].

In the late fifties, several groups used sodium borohydride to increase the rate of delignification and total pulp yield in the Kraft pulping process. Courchene obtained a good review for these earlier studies on the effects of sodium borohydride [Courchene 1998]. Later, some researchers [Tutuş 2005; Akgul, Temiz 2006; Istek, Özkan 2008; Istek, Gonteki 2009; Tutuş et al. 2010; Testova et al. 2013] investigated the influence of sodium borohydride (BH) on the Kraft pulping process using different raw materials and cooking conditions. They concluded that sodium borohydride stabilizes the reduction REGs of the polysaccharides regarding the peeling-off reaction in alkaline pulping conditions, and caused an increase in the pulping yield. On the other hand, the effects of sodium borohydride in the AS-AQ pulping process of spruce wood have not previously been investigated. The aim of this study is to determine the effects of adding sodium borohydride to the AS-AQ pulping (ASAB) of spruce chips by characterizing the pulp and paper sheet properties as well as to improve the knowledge of the effects of boron additives on alkaline pulping methods.

## Materials and methods

Caucasian spruce wood samples (*Picea orientalis* L.) used as the raw material were collected in the Eastern Black Sea region of Turkey. For the pulping experiments, the spruce wood was debarked and homogeneously chipped by hand into chips of 20.0 × 20.0 × 3.0 mm. After determining the moisture content of the air dried chips, 800.0 g of spruce chips (grams oven-dry basis) were weighed separately in a polyethylene bag.

The sampling, preparing and measuring of the chemical composition of the wood were carried out according to TAPPI Test Methods: Sampling and Preparing Wood for Analysis [TAPPI T257 cm-12:2012], Solvent Extractives of Wood and Pulp [TAPPI T204 cm-07:2007], Water Solubility of Wood and Pulp [TAPPI T207 cm-08:2008], One Percent Sodium Hydroxide Solubility of Wood and Pulp [TAPPI T212 om-12:2012], Alpha, Beta and Gamma-Cellulose in Pulp [TAPPI T203 cm-09:2009] and Acid-Insoluble Lignin in Wood and Pulp [TAPPI T222 om-11:2011]. Wise's Chloride method was used to determine the holocellulose content of the wood and Kürschner-Hoffner's approach was used for to determine the cellulose content [Browning 1967].

The spruce chips were digested by the Alkaline Sulfite Anthraquinone (AS-AQ) method. Ethanol (instead of half (50%) of the water in the cooking liquor) and  $\text{NaBH}_4$  (1, 2, 3%; calculated as Oven-Dried wood) were added to improve the pulp yield and delignification ratio. The liquor-to-wood ratio for all the cooks (L/g) was 4/1. The Active Alkali charge, AQ charge and cooking temperature were consistent at 25%, 0.2% (calculated as Oven-Dried wood) and 180°C, respectively. The pulping processes were carried out in a batch-type digester rotating at 4 rpm with an automatic temperature control. The pulping conditions of the spruce wood are presented in table 1.

**Table 1. Pulping conditions of spruce wood chips**

| Methods | Trials | Time [min] | Et OH [%] | $\text{NaBH}_4$ [%] |
|---------|--------|------------|-----------|---------------------|
| AS-AQ   | A1     | 150        | -         | -                   |
|         | A2     | 180        | -         | -                   |
| ASAE    | E1     | 150        | 50        | -                   |
|         | E2     | 180        | 50        | -                   |
| ASAB    | B1     | 150        | -         | 1                   |
|         | B2     | 150        | -         | 2                   |
|         | B3     | 150        | -         | 3                   |
|         | B4     | 180        | -         | 1                   |
|         | B5     | 180        | -         | 2                   |
|         | B6     | 180        | -         | 3                   |

The chips were impregnated for 60 min at 115°C in pulping conditions before the main cooking process began. The cooking trials were carried out in a batch type digester rotating at 4 rpm with automatic temperature control. 800 g of wood chips (calculated as Oven-Dried wood) were used for each cooking trial. The cooking time, ethanol and  $\text{NaBH}_4$  addition ratios were selected as variables for each process.

The pulp yield and reject ratios were determined according to the TAPPI T210 cm-03 standard method [2003]. The kappa number [TAPPI T236 om-06:2006] and viscosity [SCAN cm 15:88:1988] of the pulp were determined by conducting duplicate experiments. The holocellulose content of the pulps was determined using the standards mentioned above. The Alpha-Cellulose content of the pulps was determined according to TAPPI T429 cm-10 [2010].

The pulps were beaten to  $50 \pm 2^\circ\text{SR}$  by a Valley type hollander [TAPPI T200 sp-10:2010]. The freeness levels of the pulp were determined according to SCAN-C 19:65 standard methods [1964]. The paper sheets were produced by a Rapid-Kothen Sheet Forming Machine. The tensile, burst and tear indexes of the paper sheets were determined according to the TAPPI T494 om-01 [2006], T403 om-10 [2010] and T414 om-12 [2012] standards, respectively. The optical

[ISO 2470-1:2009; ISO/DIS 11476] and color [ISO/CD 5631:2009] properties of the pulps were measured using an Elrepho-3300 diffuse reflectance spectrophotometer. The statistical analyses were recorded by Statgraph plus 5.0 software.

## Results and discussion

Table 2 shows the main components of the spruce woody cell walls (carbohydrates, lignin and wood extractives) determined using the previously discussed standard methods, and the results of previous studies for comparison.

**Table 2. Chemical content and solubility of spruce wood**

| Chemical Content               | Determined | Serin et al. 2003 | Hafizoğlu, Usta 2005 | Ucar 2005 |
|--------------------------------|------------|-------------------|----------------------|-----------|
| Holocellulose [%]              | 72.62      | 73.56             | n/a                  | 80.4      |
| Alphacellulose [%]             | 46.20      | 43.08             | 43.55                | 50.5      |
| Holocellulose – Alphacellulose | 26.42      | 30.48             | n/a                  | 29.9      |
| Cellulose [%]                  | 54.97      | 55.97             | 53.80                | n/a       |
| Lignin [%]                     | 26.21      | 26.93             | 27.50                | 26.1      |
| Alcohol-benzene solubility [%] | 4.16       | 1.11              | 1.90                 | 1.5       |
| % 1 NaOH solubility [%]        | 12.19      | 10.58             | 11.85                | 10.5      |
| Hot water solubility [%]       | 2.98       | 1.83              | 2.30                 | 2.6       |
| Cold water solubility [%]      | 2.63       | 0.99              | 0.90                 | n/a       |

The main components of the wood (cellulose, hemicellulose and lignin) indicated a good correlation with previous studies but the solubility of the wood was slightly higher than that of Serin et al. [2003], Hafizoğlu, Usta [2005] and Ucar [2005]. The differences between the chemical compositions of the spruce wood samples could have originated from the age and ecological factors of the trees in their plantation areas.

All the cooks were performed at 180°C and the cooking time was a variable of 150 and 180 min. The active alkali charge was 25.0% on the basis of wood chips (calculated as Oven-Dried wood), calculated as NaOH. The Na<sub>2</sub>SO<sub>3</sub>/NaOH ratio was constant at 80/20, calculated as NaOH. The results of the AS-AQ, ASAE and ASAB cooks are listed in table 3. The chemical contents of the pulps (holocellulose and  $\alpha$ -cellulose) obtained from the AS-AQ, ASAE and ASAB processes were also determined and are given in table 3.

It is clearly seen in table 3 that all of the results of the ASAB pulping trials resulted in a higher screening yield than that of the AS-AQ cooking trials in similar cooking conditions. Generally, some wood carbohydrates (hemicelluloses and small cellulose chains) are degraded and dissolved in the alkaline pulping liquor. The positive effect of sodium borohydride in the alkaline pulping conditions can

be accounted by selectively reducing the effect on the carbonyl groups of cellulose chains to alcohols [Istek, Özkan 2008; Istek, Gonteki 2009; Tutuş et al. 2010; Testova et al. 2014].

**Table 3. Some the pulp properties of AS-AQ, ASAE and ASAB cooking trials**

| Methods |    | pH of Cooking Liqour |       | Cooking yield [%] |          |       | Kappa No | Holocel. [%] | Alphacel. [%] |
|---------|----|----------------------|-------|-------------------|----------|-------|----------|--------------|---------------|
|         |    | white                | black | rej.              | screened | total |          |              |               |
| ASAQ    | A1 | n/a                  | 10.00 | 4.57              | 47.11    | 51.68 | 42.1     | 90.54        | 86.52         |
|         | A2 | 13.19                | 9.72  | 4.49              | 46.35    | 50.84 | 41.9     | 89.90        | 85.86         |
| ASAE    | E1 | 13.47                | 9.98  | 3.12              | 49.25    | 52.37 | 32.3     | 92.18        | 87.56         |
|         | E2 | 13.43                | 9.89  | 3.09              | 49.16    | 52.25 | 30.9     | 92.60        | 87.33         |
| ASAB    | B1 | 13.17                | 10.42 | 4.32              | 49.78    | 54.10 | 37.9     | 91.78        | 84.45         |
|         | B2 | 13.13                | 10.36 | 4.69              | 51.62    | 56.31 | 48.8     | 89.96        | 84.06         |
|         | B3 | 13.14                | 10.28 | 5.49              | 48.73    | 54.22 | 48.6     | 88.96        | 85.64         |
|         | B4 | 13.22                | 10.33 | 1.95              | 49.64    | 51.59 | 35.1     | 92.21        | 84.82         |
|         | B5 | 13.18                | 10.36 | 2.73              | 51.27    | 54.00 | 42.3     | 92.33        | 84.16         |
|         | B6 | 13.12                | 10.21 | 3.09              | 49.73    | 52.82 | 44.9     | 92.72        | 84.44         |

Besides this, it can be seen from the data in table 3 that the amount of reject in the B1 pulping (the addition of 1%  $\text{NaBH}_4$  to the AS-AQ method) was lower than in the A1 method (the AS-AQ pulping without additives), but it rose proportionally with the amount of  $\text{NaBH}_4$  used. The same trend can also be observed in the case of the kappa number of ASAB pulps; with the addition of 1% of  $\text{NaBH}_4$  (calculated as Oven-Dried wood) to the pulping liqour, the kappa number of the B1 pulp was lower by 7 units than that of the A1 pulp. However, in the case of process with 3%  $\text{NaBH}_4$  added (B3), it was higher by 2 units than the A1 pulp.

Thus, the reason for the reject increase in the ASAB process as a result of the higher amounts of  $\text{NaBH}_4$  addition is the decrease in the delignification effectiveness of the wood at higher amounts of boron additive, which negatively affect the transformation ability of the wood into pulp, composed of separate fibers.

Some data concerning the influence of  $\text{NaBH}_4$  on yield, kappa number and the amounts of reject of Kraft pulps can be found in literature. For example, Akgül et al. [2007] reported that using  $\text{NaBH}_4$  in Kraft pulping led to a small decrease in the kappa number compared to the controlled Kraft cooking using *Brutia pine* (*Pinus brutia* ten.) wood as a raw material. They also confirmed that a significant yield increase was observed when using  $\text{NaBH}_4$  in Kraft pulping. Çöpür and Tozluoğlu [2008] reported that adding AQ and  $\text{NaBH}_4$  to the Kraft pulping of *Brutia pine* (*Pinus brutia* ten.) wood resulted in an increase in the pulp yield and a reduction in both kappa number and rejects.

The lowering effectiveness of the delignification in the case of the ASAQ pulping with higher amounts of  $\text{NaBH}_4$  could also be the result of decreased hemicellulose degradation, known to be covalently connected with lignin which binds fibres together in the wood matrix and is also located in the fibre wall. Another cause could possibly be the reaction of  $\text{NaBH}_4$  with  $\text{NaOH}$  and  $\text{Na}_2\text{SO}_3$  at higher amounts of the former. However, the pH measurements of the black liquor did not confirm this. The pH values of the black liquors in all the ASAB trials in table 3 were significantly higher than those of the other pulping methods.

In table 3, the results of the ASAE pulping experiments of the Caucasian spruce wood are compared to those of the AS-AQ and ASAB pulps produced. The presence of ethanol in the AS-AQ pulping accelerated delignification significantly. From the kappa number measurements of the ASAE pulps, the amount of residual lignin resulted in approximately 10 units lower than that of the AS-AQ pulps. The use of ethanol also positively affected the yield of the pulps and reject content in the AS-AQ pulping process, which were higher by approximately 2.5% and lower by approximately 1.43%, respectively, than that of the AS-AQ process.

The issue of influence on the use of  $\text{NaBH}_4$  and EtOH in the pulping yield of the ASAB and ASAE pulps was also studied in terms of the contents of cellulose, hemicelluloses and lignin in the pulps. This was done on the basis of the  $\alpha$ -cellulose, hemicellulose and lignin contents in the pulps (the hemicellulose constituents of the pulps were determined by the difference between the holo- and  $\alpha$ -cellulose contents). The results of the calculations are presented in figs. 1–3.

Figs. 1–3 show that the reason for the higher yield in the ASAE process was due to a higher retention of both the  $\alpha$ -cellulose (higher by approximately 1.0–1.5% in fig. 1) and hemicelluloses (higher by approximately 0.6–1.2% in fig. 2), but not the lignin (lower content of lignin in fig. 3). With regards to the ASAB process, the cause of the higher yield of pulps was different. The higher pulping yield during the ASAB process essentially originated from a higher retention of hemicelluloses and lignin in some experiments (the  $\alpha$ -cellulose content in the ASAB pulps was lower than in the ASAQ pulps). According to Courchene, Istek and Ozkan, a decrease in  $\alpha$ -cellulose content in ASAB pulps can result from higher hemicellulose content [Courchene 1998; Istek, Özkan 2008].

Table 3 represents the relationships between the pulp viscosity and pulping conditions of the AS-AQ without and with the addition of ethanol or sodium borohydride. The data would seem to suggest that the viscosity of the pulps showed a decrease with the addition of sodium borohydride to the AS-AQ liquor, as compared to the viscosity of the AS-AQ pulps. The drop in pulp viscosity was slightly lower with extended pulping time. The effect could be explained by the increasing retention of hemicellulose and lignin in the ASAB pulps with lower DP and  $\alpha$ -cellulose content.

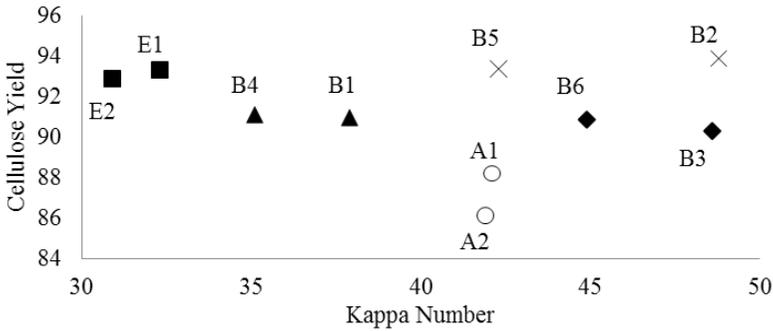


Fig. 1. The Cellulose Yield of AS-AQ, ASAE and ASAB pulps

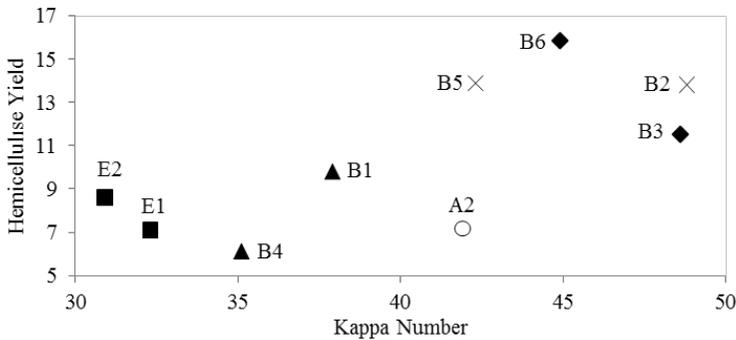


Fig. 2. The Hemicellulose Yields of AS-AQ, ASAE and ASAB pulps

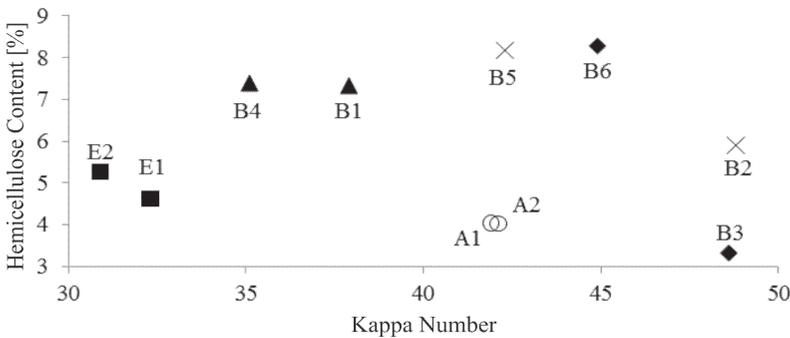
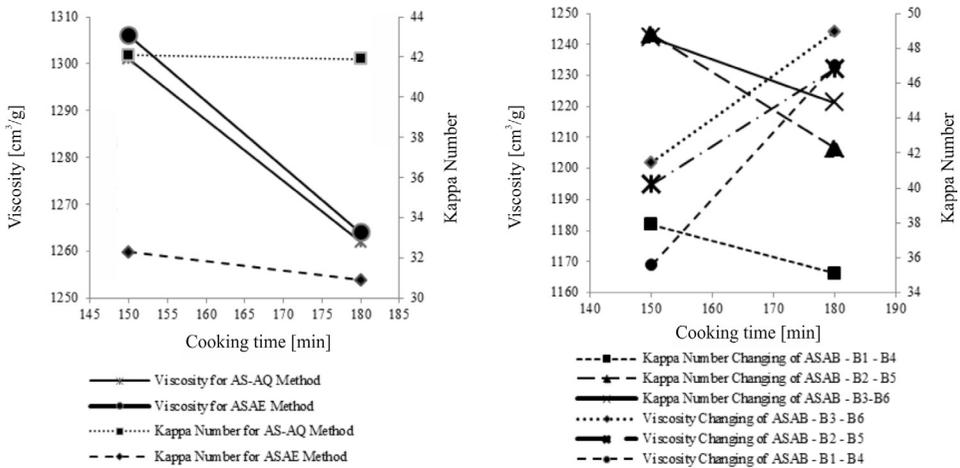


Fig. 3. Hemicellulose contents of AS-AQ, ASAE and ASAB pulps

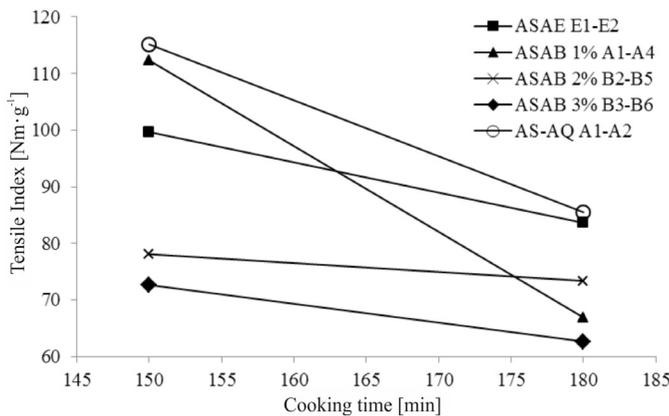
Concerning the effect of the cooking time on the pulp viscosity, lower viscosity values were obtained in the cooking trials with extended times of 180 mins with regards to the AS-AQ and ASAE pulping experiments. However, in the case of the ASAB pulping trials, the viscosity values of the pulps were affected differently by the cooking times. For instance, with a lengthened cooking time, an increase in the pulp viscosities could be noticed. This tendency was irrespective of the amount

of  $\text{NaBH}_4$  added and can be explained by the lower content of lignin in the B4-B6 pulps than in the B1-B3 ones. The effects of the sodium borohydride on the pulp viscosity displayed a good correlation with that documented in the literature. For example Çöpür, Tozluoğlu [2008]; Tutuş et al. [2010] and Gülsoy, Eroğlu [2011] found that using sodium borohydride in Kraft pulping considerably decreased the viscosity values of Kraft-Borohydride pulps. They also reported that when the amount of sodium borohydride in Kraft pulping was increased, the pulp viscosity rose by a small proportion [Akgül, Temiz 2006; Çöpür, Tozluoğlu 2008].

The effect of using  $\text{NaBH}_4$  and EtOH in the ASAQ pulping was also evaluated in terms of the strength and optical properties of the resulting pulps. These results are presented in figs. 4–6 and in table 4.



**Fig. 4.** Effects of cooking time on viscosity and kappa number in AS-AQ, ASAE and ASAB pulping; AS-AQ and ASAE pulping trials on left, ASAB pulping trials on right



**Fig. 5.** Comparison of tensile strength of pulps in 50°SR

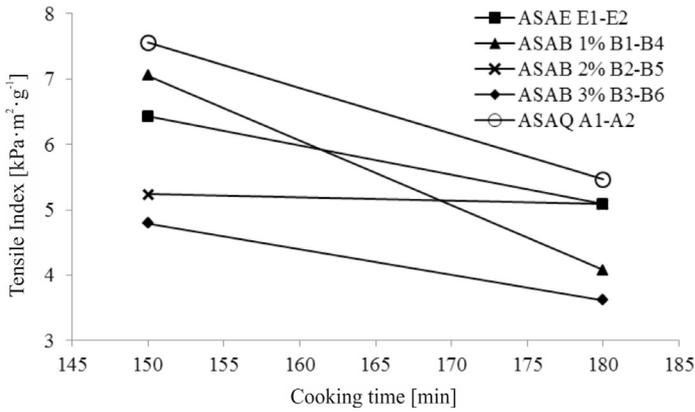


Fig. 6. Comparison of tear strength of pulps in 50°SR

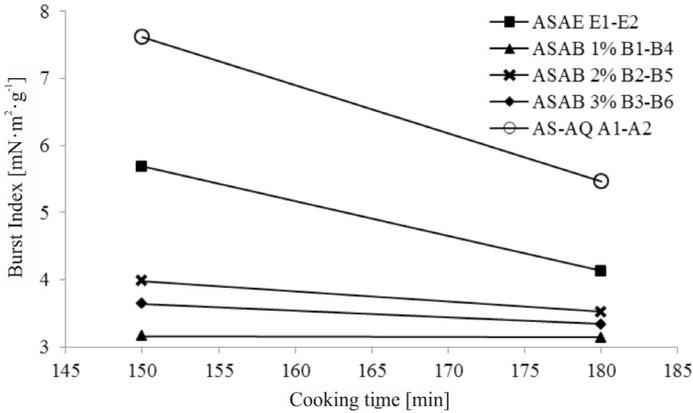


Fig. 7. Comparison of burst strength of pulps in 50°SR

Figs. 4 and 5 show that the static strength properties (tensile index and burst index) of the ASAB and ASAE pulps were in general lower than those of the AS-AQ pulps by relatively 34.2 and 13.7%, respectively. As for the tear index (dynamic strength property), the tendency was similar (fig. 6). The tear strength of the ASAB and ASAE pulps greatly decreased compared to that of the AS-AQ pulps, by relatively 23.3 and 10.9%, respectively. Taking into account these results, on the whole the ASAE pulps had better static and dynamic strength properties than the ASAB pulps.

According to Gülsoy and Eroğlu [2011]; Akgül et al. 2007, the lower strength properties of the paper sheets (tensile, burst and tear) obtained from the Kraft-NaBH<sub>4</sub> process than those of Kraft pulps can be explained by the higher pulp yield which results from the increased retention of hemicelluloses, which decrease the fiber content per unit weight of oven dried pulp and the cellulose/hemicellulose ratio in the pulp.

**Table 4. The Optical and Colour properties of papersheets (50 SR°) of AS-AQ, ASAE and ASAB pulps**

| Methods | Trials | Whiteness [% ISO] | Brightness [% ISO] | Opacity [% ISO] | <i>L</i> * | <i>a</i> * | <i>b</i> * |
|---------|--------|-------------------|--------------------|-----------------|------------|------------|------------|
| AS-AQ   | A1     | 50.7              | 35.97              | 93.86           | 76.49      | 4.32       | 18.26      |
|         | A2     | 50.5              | 36.01              | 91.64           | 76.37      | 4.09       | 17.99      |
| ASAE    | E1     | 48.3              | 35.08              | 93.95           | 75.01      | 4.40       | 16.89      |
|         | E2     | 46.98             | 33.77              | 93.2            | 74.18      | 4.69       | 17.24      |
| ASAB    | B1     | 44.41             | 29.23              | 94.7            | 72.5       | 5.02       | 20.85      |
|         | B2     | 42.83             | 27.63              | 96.25           | 71.44      | 5.13       | 21.50      |
|         | B3     | 41.97             | 26.84              | 95.92           | 70.85      | 5.56       | 21.74      |
|         | B4     | 46.04             | 30.36              | 94.82           | 73.57      | 4.66       | 21.01      |
|         | B5     | 43.28             | 28.08              | 96.69           | 71.68      | 5.19       | 21.29      |
|         | B6     | 42.65             | 27.32              | 97.06           | 71.31      | 5.30       | 21.79      |

Table 4 shows the optical properties of the ASAQ, ASAB and ASAE pulps.

The data from table 4 show that additions of ethanol and especially  $\text{NaBH}_4$  to the ASAQ pulping had an unfavorable influence on the whiteness and brightness of the pulps. The whiteness and brightness of the ASAE and ASAB pulps was lower by relatively 17.8% and 5.1%, respectively, than the indices of the ASAQ pulps. Thus, the addition of EtOH to the ASAQ pulping affected the optical properties of the pulps negatively but as not much as addition of  $\text{NaBH}_4$ . The fact that these properties of the ASAE and ASAB pulps were lower than in the case of the ASAQ pulps, even when the kappa number of the former pulps was lower, suggests that additions of EtOH and  $\text{NaBH}_4$  may favour the creation of chromophores in pulps. In a previously published study, it was shown that adding  $\text{NaBH}_4$  to Kraft cooking of brutia pine chips,  $\text{NaBH}_4$  showed a beneficial effect on the brightness of the paper sheets [Çöpür, Tozluoğlu 2008].

The optical property of the pulps, which was also determined, was opacity. The data from table 4 shows that the addition of EtOH and  $\text{NaBH}_4$  to the ASAQ pulping improved the opacity, but this was a consequence of the lower brightness values of the ASAE and ASAB pulps.

## Conclusions

The AS-AQ, ASAE and ASAB pulping processes of spruce (*Picea orientalis* L.) wood were carried out in a laboratory. The physical and chemical properties of the pulps were compared. The results were as follows:

1. The addition of ethanol to the ASAQ pulping in general had a favourable influence on the screened yield and kappa number of the pulps.

2. The addition of  $\text{NaBH}_4$  to the ASAQ pulping also had a similar influence on the screened yield and kappa number of the pulps on the condition that the amount added was not higher than 1–2% and the time of pulping was 180 min.
3. The higher yield of ASAE pulps ed from the higher retention of both cellulose and hemicelluloses, while the higher yield of ASAB pulps resulted from the higher retention of hemicelluloses and lignin.
4. A distinct negative effect regarding the modification of the ASAQ pulping conditions on the viscosity of the pulps was observed in the case of additions of  $\text{NaBH}_4$  to this pulping process. The decrease in viscosity with reference to these pulps was lower with extended pulping times.
5. The static strength properties (tensile index and burst index) of the ASAB and ASAE pulps were in general lower than the AS-AQ pulps. In the case of the tear index, the tendency was similar.
6. The addition of ethanol and especially  $\text{NaBH}_4$  to the ASAQ pulping had an unfavourable influence on the whiteness and brightness of the pulps.

## References

- Akgül M., Temiz S.** [2006]: Determination of Kraft- $\text{NaBH}_4$  pulping condition of Uludag Fir (*Abies bornmuelleriana* Mattf.). Pakistan Journal of Biology and Science 9 [13]: 2493–2497
- Akgül M., Çöpür Y., Temiz S.** [2007]: A comparison of Kraft and Kraft-Sodium borohydrate brutia pine pulps. Building and Environment 42 [7]: 2586–2590
- Browning B.L.** [1967]: Methods of Wood Chemistry. Vol. II. John Wiley and Sons Inc. New York.
- Courchene C.E.** [1998]: The tried, the true, and the new – getting more pulp from chips -modifications to the Kraft process for increased yield. Proceedings of 1998 Breaking the Pulp Yield Barrier Symposium. Available from: <http://www.tappi.org/Bookstore/Technical-Papers/Conference-Papers/1998/YIE98/Tried-the-True-and-the-New-Getting-More-Pulp-from-Chips-1998-Breaking-the-Pulp-Yield-Barrier-Sy.aspx>
- Çöpür Y., Tozluoğlu A.** [2008]: A comparison of Kraft, PS, Kraft-AQ and Kraft- $\text{NaBH}_4$  pulps of Brutia pine. Bioresource Technology 99 [5]: 909–913
- Fengel D., Wegener G.** [1989]: Reactions in Alkaline Medium. In: Wood, Chemistry, Ultrastructure, Reactions. Walter de Gruyter and Co., Berlin: 296–319
- Gullichsen J., Fagelholm C.J.** [1999]: Chemical Pulping. In: Papermaking Science and Technology – Book B. Tappi Press, Finland.
- Gülsoy S.K., Eroğlu H.** [2011]: Influence of sodium borohydride on Kraft pulping of European black pine as a digester additive. Industrial & Engineering Chemistry Research 50 [4]: 2441–2444
- Hafizoğlu H., Usta M.** [2005]. Chemical composition of coniferous wood species occurring in Turkey, Holz als Roh- und Werkstoff 63 [1]: 83–85
- Hauki T., Reilama I.** [1982]: The chemical cycle and recovery of chemicals. NS-AQ pulping. Proceedings of International Sulfite Pulping Conference, Toronto, Ontario: 41–46
- Hedjazi S., Kordsachia O., Patt R., Latibari A.J., Tschirrer U.** [2009]: Alkaline sulfite-antraquinone (AS/AQ) pulping of wheat straw and totally chlorine free (TCF) bleaching of pulps. Industrial Crops and Products 29 [1]: 27–36

- Hendriks A.T.W.M., Zeeman G.** [2009]: Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresource Technology* 100 [1]: 10–18
- Henricksson G., Lennholm H.** [2009]: Cellulose and Carbohydrate Chemistry. In: Ek M., Gellerstedt G. and Henriksson G. (ed.), *Wood Chemistry and Biotechnology*, Vol. 1. The Series of Pulp and Paper Chemistry and Technology. Walter de Gruyter GmbH & Co. KG, 10785 Berlin. 71–101
- Ingruber O.V., Allard G. A.** [1970]: Alkaline Sulphite Pulping. Canada Patent 847218.
- Ingruber O.V., Hill V., Allard G. A.** [1971]: Controlled Alkaline Sulphite Pulping. United States Patent US 3 630 832 A.
- Ingruber O.V., Stradal M., Histed J.A.** [1982]: Alkaline Sulphite-Anthraquinone Pulping of Eastern Canadian Woods. *Pulp and Paper Canada* 12: 79–88
- Istek A., Özkan İ.** [2008]: Effect of sodium borohydride on *Populus tremula* L. Kraft pulping. *Turkish Journal of Agriculture and Forestry* 32: 131–136
- Istek A., Gonteki E.** [2009]: Utilization of sodium borohydride (NaBH<sub>4</sub>) in Kraft pulping process. *Journal of Environmental Biology* 30 [6]: 5–6
- Kettunen J., Reilama I., Ruhanen M.** [1982]: A case-study – converting a Kraft mill into a NS-AQ mill. In: Goyal G. C. (ed.), *Anthraquinone Pulping: A TAPPI press Anthology of Published Papers*. Atlanta-1997: 401–405
- Kirci H., Bostanci S., Yalinkilic M.K.** [1994]: A new modified pulping process alternative to sulfate method alkali-sulfite-anthraquinone-ethanol (ASAE). *Wood Science and Technology* 28 [2]: 89–99
- Kordsachia O., Reipschläger B.R.** [1990]: ASAM pulping of birch wood and chlorine free pulp bleaching. *Paperi Puu* 72 [1]: 44–50
- Lai Y.Z.** [2001]: Chemical Degradation. In: Hon D. N. S. and Shiraishi N. (ed.), *Wood and Cellulosic Chemistry*. Marcel Dekker, Inc: 453–512
- Oliet M., Garcia J., Rodriguez F., Gilarranz M.A.** [2002]: Solvent effects in autocatalyzed alcohol-water pulping comparative study between ethanol and methanol as delignifying agents. *The Chemical Engineering Journal* 87 [2]: 157–162
- Patt R., Kordsachia O.** [1986]: Production of pulps using alkaline sulfite solutions with an addition of anthraquinone and methanol. *Das Papier* 40 [10]: 1–8
- Patt R., Kordsachia O., Schubert H., L.** [1998]: The ASAM process. In: Young R. A. and Akhtar M. (ed.), *Environmentally Friendly Technologies for the Pulp and Paper Industry*. Wiley, John and Sons, Incorporated: 101–131
- Patt R., Kordsachia O., Rose B.** [2003]: Modified Alkaline Sulfite pulping. *Wochenblatt Für Papierfabrikation* 131: 892–897
- Serin Z., Gümüskaya E., Ondaral S.** [2003]: A Review of the Chemical Composition of Different Softwoods, Hardwoods and Annual Plants. *Proceedings of Forest for Food and Water, IFSS Symposium*. İstanbul: 348–361
- Sixta H., Potthast A., Krottschek A.W.** [2006]: Sulfite Chemical Pulping. In: Sixta H. (ed.), *Handbook of Pulping*. Wiley-VCH Verlag GmbH & Co. Weinheim: 109–475
- Teleman A.** [2009]: Hemicelluloses and Pectins. In: Ek M., Gellerstedt G. and Henriksson G. (ed.), *Wood Chemistry and Biotechnology*, Volume 1. The Series of Pulp and Paper Chemistry and Technology. Walter de Gruyter GmbH & Co. KG, 10785 Berlin: 101–121
- Testova L., Nieminen K., Penttilä P. A., Serimaa R., Potthast A., Sixta H.** [2014]: Cellulose degradation in alkaline media upon acidic pretreatment and stabilisation, *Carbohydrate Polymers* 100: 185–194
- Tutuş A.** [2005]: The utilization of the boron compounds in pulping and bleaching. *Proceedings of I. National Boron Symposium*. Ankara: 399–404

- Tutuş A., Ateş S., Deniz İ.** [2010]: Pulp and paper production from spruce wood with Kraft and modified Kraft methods. *African Journal of Biotechnology* 9 [11]: 1648–1654
- Ucar M.B.** [2005]: A Comparative Study on the Chemical Composition of Oriental Spruce Woods *Picea orientalis* from Planted and Natural Forests. *Chemistry of Natural Compounds* 41 [5]: 494–498
- Virkola N.E., Pusa R., Kettunen J.** [1981]: Neutral sulfite AQ pulping as an alternative to kraft pulping. In: Goyal G.C. (ed.), *Anthraquinone Pulping: A TAPPI press Anthology of Published Papers*. Atlanta-1997: 401–405

### List of standards

- ISO 2470-1:2009** Paper, board and pulps - Measurement of diffuse blue reflectance factor – Part 1: Indoor daylight conditions (ISO brightness)
- ISO/CD 5631:2009** Paper and board - Determination of colour by diffuse reflectance – Part 1: Indoor daylight conditions (C/2 degrees).
- ISO/DIS 11476** Paper and board – Determination of CIE whiteness, C/2° (indoor illumination conditions)
- SCAN cm 15:88:1988** Viscosity of Cellulose in Cupperethylenediamine Solution (CED)
- SCAN-C 19:65:1964** Drainability of pulp by the Schopper Riegler Method
- TAPPI T200 sp-10:2010** Laboratory Beating of Pulp (Valley Beater Method)
- TAPPI T203 cm-09:2009** Alpha, Beta and Gamma-Cellulose in Pulp
- TAPPI T204 cm-07:2007** Solvent Extractives of Wood and Pulp
- TAPPI T207 cm-08:2008** Water Solubility of Wood and Pulp
- TAPPI T210 cm-03:2003** Sampling and Testing Wood Pulp Shipments for Moisture
- TAPPI T212 om-12:2012** One Percent Sodium Hydroxide Solubility of Wood and Pulp
- TAPPI T222 om-11:2011** Acid-Insoluble Lignin in Wood and Pulp
- TAPPI T236 om-06:2006** The kappa number of Pulp
- TAPPI T257 cm-12:2012** Sampling and Preparing Wood for Analysis
- TAPPI T403 om-10:2010** Bursting Strength of Paper
- TAPPI T414 om-12:2012** Internal Tearing Resistance of Paper (Elmandorf Type Method)
- TAPPI T429 cm-10:2010** Alpha-Cellulose in Pulp
- TAPPI T494 om-01:2006** Tensile Properties of Paper and Paperboard (Using Constant Rate of Elongation Apparatus)

### Acknowledgements

The authors would like to thank The Scientific and Technological Research Council of Turkey (TUBITAK) for financial support (Project no: 108O875).