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EFFECTS OF SODIUM BOROHYDRIDE ON BIOKRAFT PULPING OF EUROPEAN BLACK PINE (PINUS NIGRA ARN.)

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Abstract:

In this study, the influences of sodium borohydride ($NaBH_4$) on properties of kraft pulp and paper obtained from European black pine (Pinus nigra Arn.) chips treated with Ceriporiopsis subvermispora for periods varying from 20 to 100 days were investigated. Biokraft-$NaBH_4$ cookings were done under the fixed cooking conditions by adding $NaBH_4$ at the amounts of 0.5%, 1%, 1.5%, and 2% (oven dried wood) to the cooking liquor. For comparison, $NaBH_4$ free biokraft cooking was carried out. The results revealed that addition of $NaBH_4$ to cooking liquor during biokraft pulping not only increases the pulp screened yield but also decreases kappa number of pulp. In addition, brightness of biokraft-$NaBH_4$ papers was higher than those of biokraft papers. However, tear index, burst index, and tensile index of biokraft-$NaBH_4$ pulps were found lower than biokraft pulps.

Key words: Biokraft pulping, sodium borohydride, pulp yield, Ceriporiopsis subvermispora, European black pine.

1. Introduction

For many years, the most researchers have aimed to increase pulp yield by reducing carbohydrate losses. In chemical pulping, pulp yield depends on holocellulose content of wood. The degradation mechanism of polysaccharides caused by alkaline solution was known well, pulp yield variations that occur during cooking could be understood (Courchene, 1998). Cooking chemicals broke carbohydrate chains with degradation reactions such as peeling and alkaline hydrolysis. Decreasing in pulp yield can be prevented by changing the structure of carbohydrate reducing end. The carbonyl groups in the reducing end were transformed into hydroxyl or carboxyl group by adding reducing or oxidizing additives to cooking liquor. Thus, reducing end of polysaccharides becomes stabile and polysaccharides aren't affected by degradation reactions mentioned above. Pulp yield can then be increased by up to 3-5 % (on oven dried wood) depending on the charge of the additives Earlier studies have indicated that pulp yield is increased by adding $NaBH_4$ (Hartler, 1959, Pettersson and Rydholm, 1961, Tutuş, 2005, Akgül and Temiz, 2006, Akgül et al, 2007, Çöpür and Tozluoğlu, 2008, İstek and Özkan, 2008, İstek and Gönteki, 2009, Gülsoy, 2009, Tutuş et al. 2010a,b).

Biopulping is defined as the treatment of wood chips with lignin-degrading fungi prior to conventional pulping methods. The biological delignification of wood by white-rot fungi was perhaps first earnestly considered by Lawson and Still (1957) at the West Virginia Pulp and Paper Company Research Laboratory (now Westvaco Corporation) (Akhtar et al., 1998). Since 1957, many researchers have studied on using white rotted wood and nonwood in pulping processes. Although using chips pretreated with white rot fungi in mechanical pulping had been intensively studied, its using in chemical pulping methods such as kraft, soda, sulfite, and organosolv had attracted less attention (Mendonça et al., 2002). In earlier studies, biokraft pulping from wood and nonwood species is studied by various authors (Oriaran et al. 1990, Ahmed et al. 1998, Bajpai et al. 2001, Mendonça et al. 2002, Mohiuddin et al. 2005, İmamoğlu and Atik, 2007, Çöpür and Tozluoğlu 2007, Ateş et al. 2008, Yadav et al. 2010). The studies related to the influence of digester additives on biokraft pulping had a limited number. Çöpür and Tozluoğlu (2007) studied effects of several additives such as $NaBH_4$, AQ on biokraft pulping. Recently, Ateş et al. (2008) investigated effects of AQ on biokraft

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pulping. The aim of this study is to investigate the effects of $NaBH_4$ on biokraft pulping of European black pine chips treated with Ceriporiopsis subvermispora.

2. Material and Methods

European black pine (Pinus nigra Arn.) spreads over more than 3.5 million hectares from western North Africa through southern Europe to Asia Minor (Isajev et al. 2004). Ceriporiopsis subvermispora FP-90031-sp was obtained from the Center for Forest Mycology Research at the USDA Forest Products Laboratory, Madison, Wisconsin. Freshly cut European black pine (Pinus nigra Arn.) obtained from Bartın province of Turkey, and it was debarked and chipped into approximately 3.5-1.5-0.5 cm size wood chips. Chips were kept frozen until used. Inoculum preparation, chip sterilization and inoculation were carried out as previously described by Bajpai et al. (2001). Wood chips were incubated at 27°C and 75% relative humidity. Samples of wood chips were removed for pulping at 20, 40, 60, 80 and 100 days intervals.

Biokraft and biokraft-$NaBH_4$ cookings conditions were: 18% active alkali as Na_2O, 35% sulfidity, 4:1 liquor/wood ratio, 170 °C cooking temperature, 90 min to cooking temperature and 60 min at to cooking temperature. $NaBH_4$ added cookings were made by adding 0.5%, 1%, 1.5%, and 2% $NaBH_4$ (oven dried wood) into cooking liquor. 600 g of oven dried wood chips for each experiment were cooked in 15 L electrically heated laboratory cylindrical type rotary digester. At the end of pulping, pressure was reduced to atmospheric pressure. After digestion, pulps were washed free of black liquor and disintegrated in a laboratory type pulp mixer with 2 L capacity. Disintegrated pulps were screened using Somerville type pulp screen with 0.15 mm slotted plate (TAPPI T 275). And then pulps were beaten to 50 °SR in a Valley Beater according to TAPPI T 200. Kappa number (TAPPI T 236), screened yield (TAPPI T 210), viscosity (SCAN-CM 15-62), and freeness of pulps (ISO 5267-1) were determined according to relevant standard methods. Then, 75 g/m^2 handsheets were made by Rapid-Kothen Sheet Former (ISO 5269-2). The handsheets were conditioned (TAPPI T 402). Tensile index (TAPPI T 494), burst index (TAPPI T 403), tear index (TAPPI T 414), opacity (TAPPI T 519), brightness (TAPPI T 525) of handsheets were determined in accordance with relevant standard methods.

3. Results and Discussion

The kappa number of pulp gives information regarding efficiency of cooking, residual lignin content in pulp, and delignification degree of pulp. The kappa numbers of biokraft-$NaBH_4$ pulps were decreased by adding $NaBH_4$ (Table 1). The lowest kappa number was determined as 37.16 in 1.5% $NaBH_4$ added cooking of 80 days incubated chips.

The pulp viscosity is related to DP of polysaccharides (especially cellulose). Therefore, the degradation of polysaccharides during cooking leads to decrease in pulp viscosity. Pulp viscosity of biokraft-$NaBH_4$ pulp was lower than that of biokraft pulp (Table 1). The lowest viscosity was determined in 2% $NaBH_4$ added cooking of 60 days incubated chips. The cause of decreasing in pulp viscosity can be attributed to higher hemicellulose retention in biokraft-$NaBH_4$ pulps.

Table 1. Pulp properties of biokraft and biokraft-$NaBH_4$ pulps.

Incubation Time (day)	$NaBH_4$ Ratio (%)	Kappa Number	Viscosity (cm^3/g)	Screened Yield (%)	Reject Ratio (%)	Total Yield (%)
20	-	43.94±0.19	971.29±0.49	46.34	1.62	47.96
20	0.5	42.37±0.23	970.44±1.15	48.91	1.65	50.56
20	1.0	43.32±0.13	939.98±4.28	50.06	0.98	51.04
20	1.5	44.32±0.15	944.41±27.41	51.78	1.23	53.01
20	2.0	43.83±0.56	968.77±14.73	52.52	1.42	53.94
40	-	46.62±0.27	1071.15±21.58	46.86	1.94	48.80
40	0.5	39.72±0.06	1043.05±27.67	48.86	0.99	49.85
40	1.0	39.28±0.17	1000.62±18.02	49.93	0.87	50.80
40	1.5	40.52±0.86	1050.16±12.46	50.86	0.99	51.85
40	2.0	41.37±0.35	1084.95±18.02	52.89	0.75	53.64
60	-	43.84±0.34	1097.77±19.91	46.20	1.43	47.63
60	0.5	41.96±0.10	1021.73±16.08	49.60	0.80	50.40
60	1.0	41.86±0.20	1023.10±9.55	52.01	0.65	52.66
60	1.5	37.42±0.23	962.95±11.66	52.67	0.67	53.34

60	2.0	39.44±0.32	936.72±12.18	54.84	0.60	55.44
80	-	47.89±0.26	1037.71±19.51	47.29	1.59	48.88
80	0.5	40.51±0.01	1000.84±16.55	47.82	1.08	48.90
80	1.0	41.73±0.06	1059.69±16.08	50.00	0.59	50.59
80	1.5	37.16±0.26	962.92±1.04	52.38	0.36	52.74
80	2.0	39.16±0.09	994.64±2.68	53.38	0.41	53.79
100	-	43.01±0.14	1092.25±12.78	45.79	1.21	47.00
100	0.5	38.30±0.44	976.64±8.80	48.58	0.59	49.17
100	1.0	37.35±0.12	976.53±26.39	50.94	0.67	51.61
100	1.5	43.70±0.17	1018.94±7.85	53.88	0.57	54.45
100	2.0	38.91±0.29	1073.81±24.98	53.81	0.57	54.38

The pulp yield of biokraft-$NaBH_4$ pulps was determined to be higher than that of biokraft pulp (Table 1), which corresponds well with earlier investigation related to biokraft-$NaBH_4$ pulping (Çöpür and Tozluoğlu, 2007). The cause of pulp yield increase can be ascribed to prevention of degradation reactions by $NaBH_4$ during cooking. 2% $NaBH_4$ added cooking of 60 days incubated chips had the highest screened yield, screened pulp yield was increased by 8.64% (from 46.20% to 54.84%). In a 500 tons/day pulp mill, this may result in 93.51 tons/day of additional pulp production. The yield increase provides economical benefits to the pulp mill. Addition of digester additives also allows more efficient utilization of wood resources. There is significant correlation (R^2=63%) between pulp yield and kappa number of biokraft and biokraft-$NaBH_4$ pulps (60 days incubated), as seen in Fig.1.

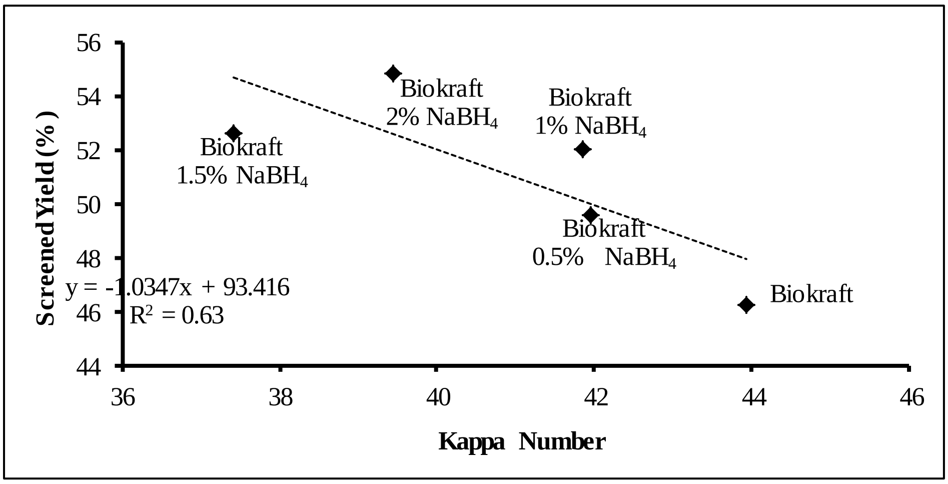

Figure 1. Screened yield vs. kappa number with $NaBH_4$ ratio as parameter.

Reject ratio of pulps gives information about pulping efficiency and penetration of cooking liquor to chips. The reject ratios of biokraft-$NaBH_4$ pulps were decreased by adding $NaBH_4$ (Table 1). The lowest reject ratio was determined as 0.36% in 1.5% $NaBH_4$ added cooking of 80 days incubated chips. In an earlier study reported that reject ratio of biokraft-$NaBH_4$ pulps was lower than that of biokraft pulp (Çöpür and Tozluoğlu, 2007).

Tear index, burst index, and tensile index of handsheets obtained from biokraft-$NaBH_4$ pulps beaten up to 50 °SR were slightly lower than those of biokraft pulps (Table 2). The strength losses were consistent with increases in $NaBH_4$ adding. Similar strength losses were reported in a previous study (Çöpür and Tozluoğlu, 2007). Strength losses of pulp can be ascribed to increasing in pulp yield. Increasing in pulp yield leads to decrease in fiber amount per unit weight of oven-dried pulp and to decrease in cellulose/hemicellulose ratio of pulp. A high positive correlation (R^2=97%) was found between tear and tensile index of biokraft and biokraft-$NaBH_4$ pulps (20 days incubated), as seen in Fig.2. This result shows that tear index and tensile index decrease in parallel with the addition of $NaBH_4$ to biokraft pulps.

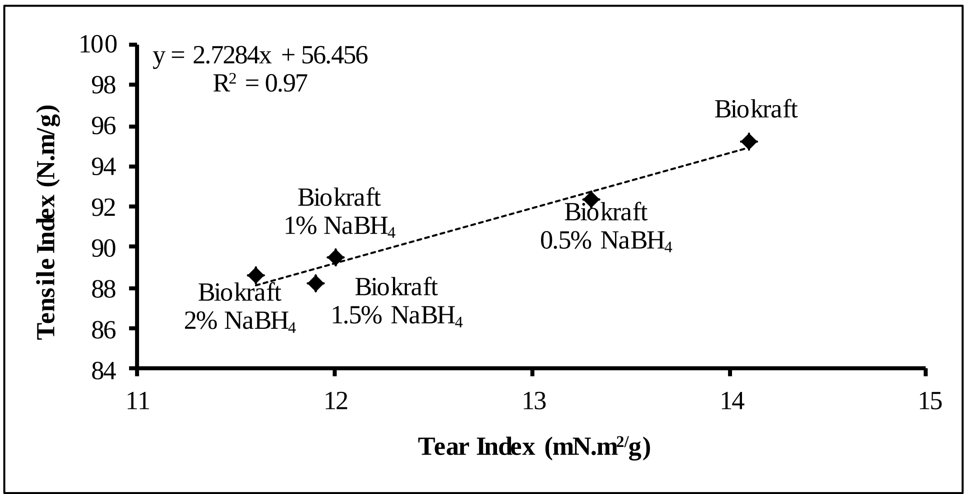

Figure 2. Effect of $NaBH_4$ ratio on tear index vs. tensile index of biokraft pulps.

Table 2. Some mechanical and optical properties of biokraft and biokraft-$NaBH_4$ handsheets.

Incubation Time (day)	NaBH4 Ratio (%)	Tear Index (mN.m^2/g)	Burst Index (kPa.m^2/g)	Tensile Index (N.m/g)	Opacity (%)	Brightness (%)
20	-	14.0±0.8	6.6±0.7	95.6±7.3	99.27	15.42
20	0.5	13.3±0.6	6.2±0.6	92.4±4.8	99.09	16.25
20	1	12.0±0.5	6.3±0.5	89.5±3.7	98.29	17.06
20	1.5	11.9±0.7	6.1±0.6	88.2±4.8	98.71	17.42
20	2	11.6±0.6	6.0±0.5	88.6±4.8	98.82	17.18
40	-	10.6±0.4	5.7±0.3	87.9±4.7	98.87	15.43
40	0.5	10.8±0.5	5.6±0.3	86.8±4.3	98.63	16.69
40	1	10.1±0.6	5.5±0.3	87.5±2.8	98.40	17.23
40	1.5	10.7±0.3	5.4±0.3	86.0±2.8	98.54	17.30
40	2	10.2±0.6	5.5±0.4	87.2±3.5	98.53	18.16
60	-	10.7±0.2	5.4±0.3	83.8±1.9	98.57	15.85
60	0.5	10.2±0.3	5.4±0.3	86.0±5.1	98.85	16.41
60	1	9.9±0.4	5.5±0.3	83.2±2.1	98.41	17.32
60	1.5	9.6±0.6	5.1±0.3	88.0±4.7	98.25	17.75
60	2	9.8±0.6	5.3±0.4	88.3±4.0	98.09	18.02
80	-	9.5±0.1	4.7±0.1	82.7±5.1	98.92	15.43
80	0.5	9.2±0.2	4.9±0.4	83.9±3.8	98.88	16.37
80	1	9.3±0.2	4.9±0.2	82.4±3.7	98.70	16.93
80	1.5	9.2±0.6	4.7±0.2	84.9±4.0	98.27	18.77
80	2	8.7±0.5	5.0±0.3	83.9±3.5	98.17	18.86
100	-	8.8±0.2	5.3±0.2	82.4±3.7	99.05	15.89
100	0.5	8.2±0.4	5.2±0.2	97.1±5.3	98.44	17.17
100	1	8.4±0.5	5.2±0.3	95.2±4.6	98.23	18.44
100	1.5	8.6±0.3	5.4±0.3	96.2±2.9	98.50	18.15
100	2	8.4±0.3	5.1±0.4	89.7±5.3	98.40	18.49

The brightness of biokraft-$NaBH_4$ pulps was found higher than those of biokraft pulps (Table 2). Brightness of biokraft-$NaBH_4$ pulps was increased in direct proportion to the increase of adding $NaBH_4$ ratio. The highest brightness was determined in 2% $NaBH_4$ added cooking of 80 days incubated chips. These results were similar to an earlier study (Çöpür and Tozluoğlu, 2007). A strong correlation (R^2=73%) between brightness (50 °SR) and kappa number of biokraft and biokraft-NaBH4 pulps (80 days incubated) was observed (Fig.3). This result indicates that kappa number can be used to estimate the brightness of biokraft and biokraft-$NaBH_4$ pulps. The opacity of handsheets obtained from biokraft-$NaBH_4$ pulps was similar to biokraft pulps.

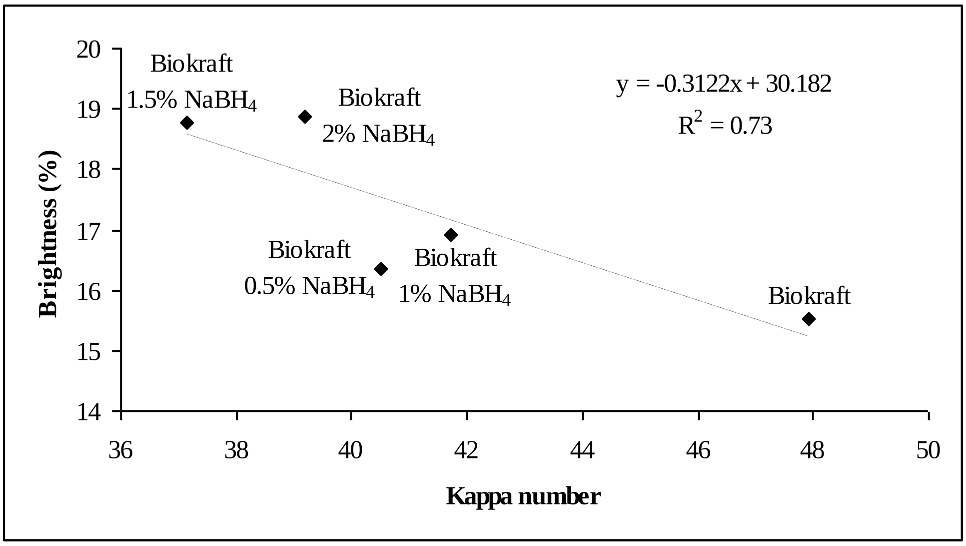

Figure 3. The relationship between brightness and kappa number of biokraft and biokraft-$NaBH_4$ pulps.

4. Conclusions

The results of this study indicated that using $NaBH_4$ in biokraft pulping provides various benefits. The most important advantage of using $NaBH_4$ in biokraft pulping is significant increases in the pulp yield. Another advantage of $NaBH_4$ added biokraft cookings is higher pulp brightness. However, $NaBH_4$ is an expensive additive. In addition, $NaBH_4$ decreased the paper strength. If paper strength is not a necessity, $NaBH_4$ can be used as digester additive during biokraft pulping.

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