EFFECT OF HOT-WATER AND MILD ALKALINE EXTRACTION ON SODA-AQ PULPING OF WHEAT STRAW

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Up to now numerous wood treatments have been conducted mostly in the form of pre-hydrolysis of wood, focusing on hemicelluloses pre-extraction for co-production of pulp and chemicals. Our objective in this research was to investigate the effect of hot-water and green liquor pre-extraction of wheat straw on cooking process and papermaking properties of soda-AQ pulp. Wheat straw chips were treated with pure water and green liquor at 140 and 150 °C, respectively, to obtain 10 and 15% pre-extraction weight losses in both extraction methods. Cooking pre-extracted straw required less H-factor to get the target kappa number of about 20 and less PFI mill refining revolutions. The strength indices of hot-water pre-extracted pulps at both levels of pre-extracted weight losses, and of green liquor pre-extracted pulp only at 10%, were comparable to those of control pulp, except for tear index.

Keywords: Wheat straw; Pre-extraction; Green liquor; Soda-AQ pulping

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INTRODUCTION

Rapid increase in energy demand is resulting in limited availability of conventional energy sources, *e.g*. fossil fuels. This issue has an impact on the economy of energy intensive industries like pulp and paper mills and on the environment (Van Walsum 2009). During chemical pulping, nearly 50% of hemicelluloses are partly dissolved in the black liquor along with lignin. Hemicelluloses degradation products, mainly a complex mixture of sugar acids, are difficult to separate and purify from the resulting black liquor, which is normally burned in a recovery boiler to produce electricity and thermal energy (Vanessa *et al.* 2011). The hemicelluloses, however, have a low heating value and are not used cost-effectively through conventional pulping processes. The objective of integrated forest products biorefinery (IFBR) is to adopt existing chemical pulp mills to produce new biomaterials while continuing to meet growing demand for pulp and paper products. The integrated forest biorefinery provides a future pathway to long term growth and profitability for pulp and paper industry. A significant amount of hemicelluloses are extracted from the residual wood chips prior to pulping in IFBR (Yoon *et al.* 2008a). The extraction of hemicelluloses from wood chips prior to pulping can increase pulp yield and production rate and produce higher value chemicals and polymers.

In addition, in many countries the wood supplies availability will not continue to meet the rising demand for very long (Deniz *et al.* 2004). Moreover the emergence of bio-fuels will lead to an increased demand for wood and thus it seems likely that both wood consumption and wood prices will increase as a consequence (Jahan *et al.* 2009). So, concerns about long term fiber supply and more stringent environmental restrictions have increased the interest in non-wood raw materials for paper manufacture (Goel *et al.* 2000). The open structure and low lignin content of cereal straw makes its chemical processing relatively easy in particular non-sulfur processes.

Up to now different extraction methods prior to pulping including autohydrolysis (hot-water extraction), alkaline, near neutral, and acidic extractions in different raw materials have been investigated in order to determine the optimized extraction conditions.

Smith *et al.* (2008) and Yoon *et al.* (2008) reported that the pH of the extracting solution provides detailed information about the reaction conditions. Yoon *et al.* (2008) and Al-dajani *et al.* (2009) concluded that the hot-water (autohydrolysis) should be terminated before the pH of the hydrolysate drops below 3.5. Lei et al. (2010) in the hot-water pre-extraction of baggase found that the strength properties of pulps were still acceptable when the mass removal was about 10 to 15%. Yoon *et al.* (2008b) investigated the possible practical implementation of the near neutral pre-extraction process on hardwoods at various elevated temperatures with sodium hydroxide, sodium carbonate and green liquor. They found that the pulp yield was only 1% lower than that of control pulp, and no significant difference in paper strength was found in handsheet tests.

In this study the effect of hot-water and green liquor pre-extraction of wheat straw on cooking process and papermaking properties of soda-AQ pulp has been investigated.

EXPERIMENTAL

Preparing the Raw Material

Wheat straw was cut into 2 to 3 cm length pieces and quickly washed with tap water for elimination of non-fibrous impurities and at last dried for hot-water and green liquor pre-extraction studies.

Hot-water and Green Liquor Pre-extraction

The green liquor was prepared from Mazandaran wood and paper industries (MWPI) and its composition is shown in table 1.

Table 1. Chemical Composition of Green Liquor Used in Pre-extraction Process

Density	1.2 g/cm³
Sodium oxide	143 g/lit
Sodium sulfide	110 g/lit
Suspended solid	0.05 g/lit
pH	14

The pre-extraction and cooking experiments were conducted in a digester with 6 cylindrical 2.5 liter bombs rotating in hot glycerin oil. In each pre-extraction and cooking process, 100 grams (oven dried basis) of wheat straw chips were subjected to pure water and green liquor extraction and/or cooking, at liquor to wood ratio of 6 to 1.

The chips were first impregnated with the pre-extraction liquors for 30 minutes at room temperature, and then subjected to pre-extraction at 130, 140, and 150 °C for hot-water and at 140 °C for green liquor pre-extraction. 3 % total alkali, based on OD straw, was used for green liquor pre-extraction. After pre-extraction, the liquor has been separated from the chips for pH measurement, and then washed with tap water on a 200 mesh screen and air dried for weight loss determination.

Pulping

The soda-AQ pulping of control and pre-extracted straw chips, were done at different cooking times (20 to 90 minutes), temperatures (150 to 160 °C), alkali charges (14 to 18 % as NaOH), and 0.1% AQ in order to achieve the target kappa number of about 20. After cooking, the black liquor was drained for pH measurement and the pulp was washed with tap water on a 200 mesh screen. The screened yield was determined gravimetrically and kappa number was determined according to T236 om-85.

Refining and Handsheet Properties

The pre-extracted and control pulp samples were refined with a PFI mill to a freeness level of about 33 °SR according to the TAPPI T 248-sp standard. Handsheets with a basis weight of 60 g/m² were made using a laboratory handsheet former, then pressed and dried according to TAPPI T205 sp-95. Burst, tear and tensile strength were measured according to the related TAPPI standards. The data were analyzed using SAS statistical software. The results of handsheet properties were analyzed with factorial experiment in completely randomized design. Duncan test with 99% confidence level used for comparing and grouping the mean values.

RESULTS AND DISCUSSION

Pre-extraction

As can be seen in Tables 2 and 3, the higher the H-factor of the pre-extraction process, the higher was the weight loss but at lower pH of extracted liquor. The straw weight loss during pre-extraction was varied with pre-extraction conditions from 8 % at the mildest condition (pure water, 130 °C, and 50 min) to 17% at the most severe condition (pure water, 150 °C, and 90 min). The target weight losses of 10 and 15% in hot water pre-extraction were obtained at higher H-factors compared to green liquor pre-extraction. Hot water pre-extraction at 150 °C for 30 and 60 min (run NO 9 and 10) and green liquor pre-extraction at 140 °C for 60 and 90 min (run NO 13 and 14) were needed for 10 and 15 % weight losses, respectively. The final pH of hot-water pre-extracted liquor was lower than green liquor (4.1 to 4.5 versus 5.5 to 6.1), although the initial pH of green liquor solution was 13 versus about 7 for pure water. The pH drop during green liquor and water extraction is caused by forming acetic acid through hydrolysis of acetyl groups in the hemicelluloses and the pre-extraction process is autocatalytic (Yoon *et al.* 2008b; Amidon 2008; Testova 2006; Tunc *et al.* 2010).

Table 2. The Effects of Hot-water Pre-extraction Conditions on Straw Weight Loss and Final pH

Run	T_{max} (°C)	Time at maximum temperature (min)	H – factor (hr)	Weight loss (%)	Final pH
1	130	50	29	8.05	unavailable
2	130	60	34	8.4	unavailable
3	130	70	39	8.44	unavailable
4	130	80	43	9.013	4.5
5	140	50	75	11.2	unavailable
6	140	60	87	10.43	4.52
7	140	70	99	11.6	unavailable
8	140	80	112	12.2	unavailable
9	150	30	113	9.98	4.4
10	150	60	196	14.86	4.21
11	150	90	279	17.08	4.09

Table 3. The Effects of Green Liquor Pre-extraction Conditions on Straw Weight Loss and Final pH

Run	T_{max} (°C)	Time at maximum temperature (min)	H – factor (hr)	Weight loss (%)	Final pH
12	140	30	49	7	6.07
13	140	60	87	9.5	5.61
14	140	90	124	14.76	5.45

Soda-AQ Pulping

The pre-extracted straw samples required less H-factor than the control un-extracted sample (lower maximum temperature at lower cooking times) to reach a target pulp kappa number of about 20 (Tables 4, 5, and 6). This might be due to the increased accessibility of the cell wall and cleavage of lignin carbohydrate covalent bonds during pre-extraction (Yoon *et al.* 2008). This result is in agreement with the earlier studies on the effect of pre-extraction on pulping conditions (Yoon *et al.* 2008a,b; Testova 2006). The cooking yield (digester yield) of pre-extracted chips was much higher than that of control one. However, the total pulp yield (based on the original straw) of pre-extracted samples were lower than the control sample at similar kappa number of about 20, but the yield loss was more sever in case of samples pre-extracted at 15% weight loss. Moreover, the total pulp yield in case of 15% weight loss in pre-extraction, was much lower in green liquor than hot water pre-extraction.

Table 4. The Effects of Pulping Conditions on H-factor, Pulp Yield and Kappa Number of Control Straw

Temperature (°C)	Alkalinity (%)	Time (min)	H-factor (hr)	Yield (%)	Kappa number
160	16	30	287	53.0	22
160	16	60	477	51.0	20
160	16	90	677	50.0	17
160	18	30	287	50.2	18
160	18	60	477	49.0	16
160	18	90	677	47.7	15

Table 5. The Effects of Pulping Conditions on H-factor, Pulp Yield and Kappa Number of Hot-water Pre-extracted Chips

Pre-extraction Wt. loss (%)	Cooking temp (°C)	Alkalinity (%)	Time at maximum temp (min)	Pre-extraction H-factor	Total H-factor	Kappa number	Digester Yield (%)	Total yield (%)
10	150	16	30	114	227	22	55.8	50.2
10	150	16	50	156	269	20	55.3	49.8
10	150	16	70	208	321	18.2	53.6	48.2
15	150	16	30	114	315	22	55.7	47.3
15	150	16	45	155	356	19.5	54.7	46.4
15	150	16	60	197	398	19	52.4	44.5
15	160	14	60	490	692	26	54.4	46.2
15	160	16	40	357	559	19	52.2	44.4
15	160	16	60	490	692	16.5	50.7	43.2
15	160	18	60	490	692	15	50	42.5

Table 6. The Effects of Pulping Conditions on H-factor, Pulp Yield and Kappa Number of Green Liquor Pre-extracted Chips

Pre-extraction Wt. loss (%)	Cooking temp (°C)	Alkalinity (%)	Time at maximum temp (min)	Pre-extraction H-factor	Total H-factor	Kappa number	Digester yield (%)	Total yield (%)
10	150	16	30	114	164	22	55.3	49.8
10	150	16	50	156	206	20	55.3	49.8
15	150	16	20	105	230	21.2	53.8	45.7
15	150	16	40	131	226	20	52.7	44.8
15	150	16	60	182	307	17	51.3	43.6

Refining Response

The control and pre-extracted pulp samples were refined to similar freeness level of 33 to 34 °SR. The pulp samples from both hot-water and green liquor pre-extraction at 10% weight loss, needed higher PFI revolutions than control pulp (see figure 1). This is likely due to the lower content of hemicelluloses in the pre-extracted samples in which the fibers have lower swellability and flexibility (Helmerius *et al.* 2010; Yoon and Heiningen, 2008). However, in case of 15 % weight loss, the pre-extracted pulps required lower PFI revolutions than the control pulp because much more hemicelluloses has been lost and the fibers became more brittle and the freeness dropped more rapidly through sever fiber cutting and higher fine formation.

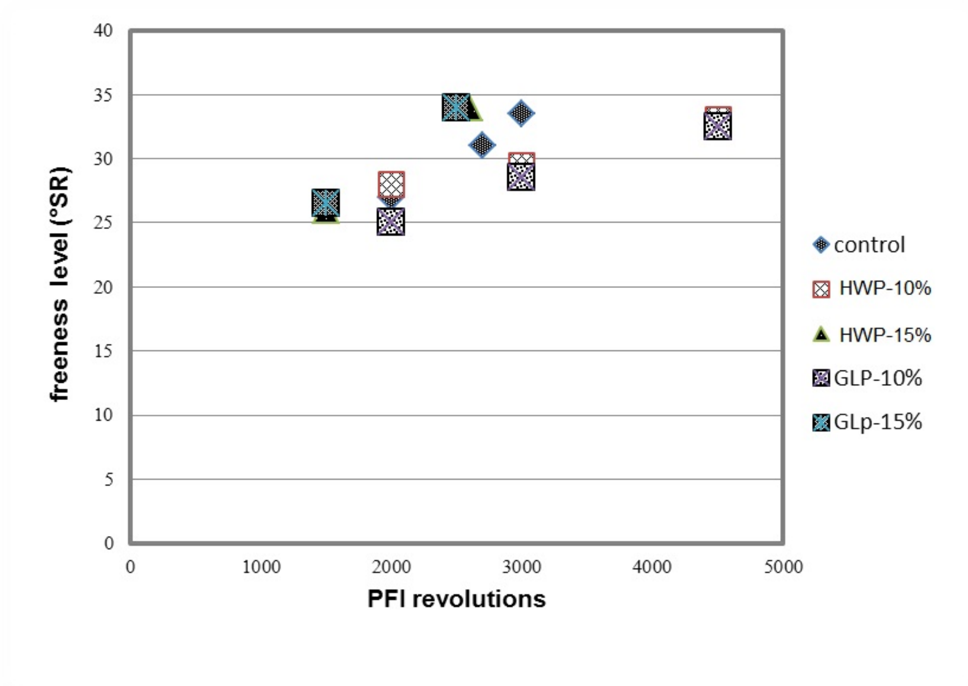

Fig. 1. The refining response of the pre-extracted pulp samples versus control pulp. (HWP-10% and HWP-15% stand for pulps pre-extracted with hot water at 10 and 15% weight losses, respectively. GLP-10% and GLP-15% stand for pulps pre-extracted with green liquor at 10 and 15% weight losses, respectively, and control stand for pulp without any pre-extraction)

Strength Properties

The tensile and burst strengths in the pre-extracted samples at 10% weight loss were similar to the control one. However, these strengths in hot-water pre-extracted pulps were slightly higher than green liquor pre-extracted pulp sample. In both cases, these bonding related strengths were lower in 15% weight loss than 10%, especially in case of green liquor, which may be due to lower inter-fiber bonding ability because of sever dissolution of hemicelluloses during pre-extraction stage and lower refining revolutions.

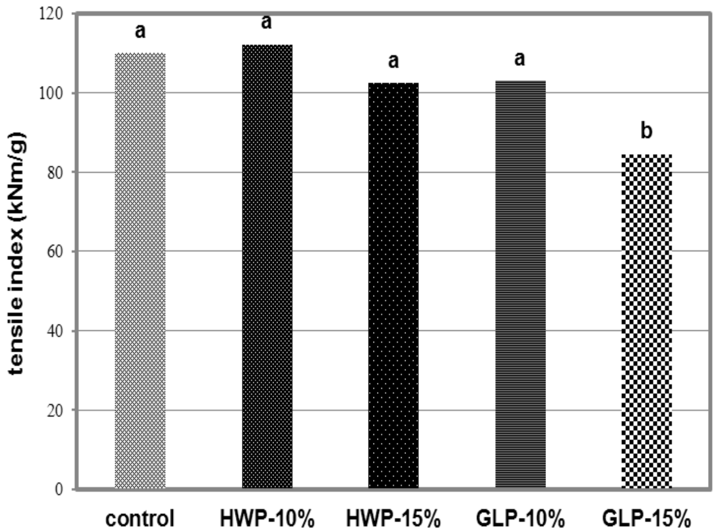

Fig. 2. The effects of different pre-extractions on the tensile index in comparison with control pulp

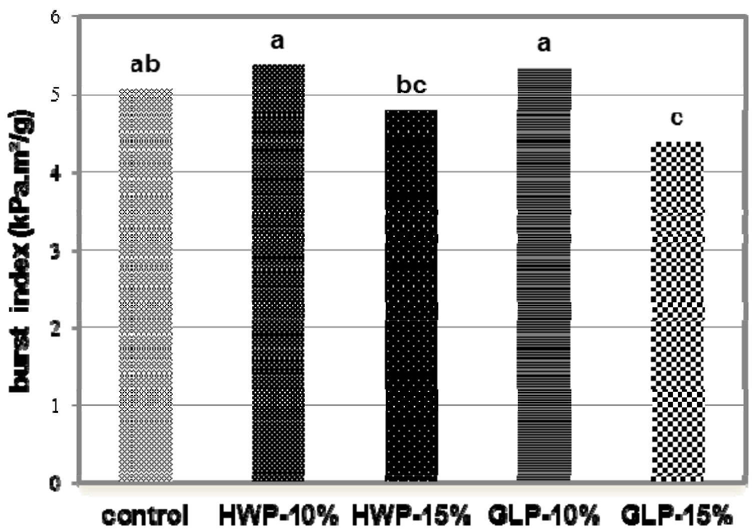

Fig. 3. The effects of different pre-extractions on the burst index in comparison with control pulp

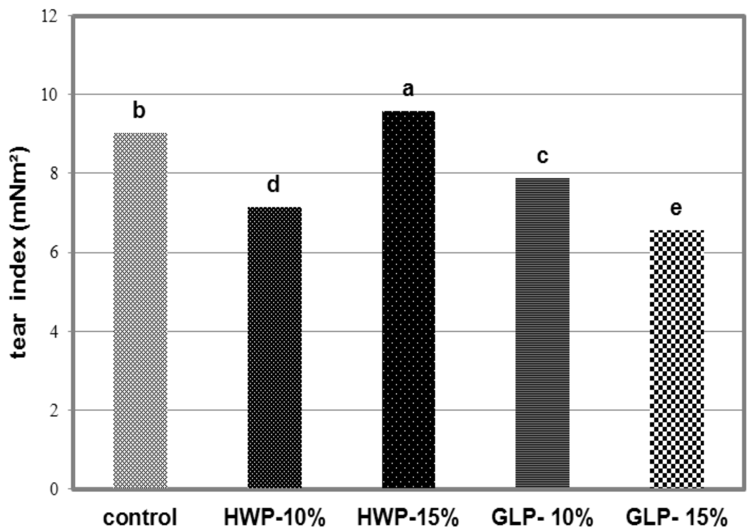

Fig. 4. The effects of different pre-extractions on the tear index in comparison with control pulp

The tear strength mainly depends on fiber length, fiber strength, and degree of inter-fiber bonding (Testova 2006). As is shown in Fig. 4, the tear strength of the control pulp was higher than the pre-extracted samples, except hot-water pre-extracted pulp at 15 % weight loss. The pulp from hot-water pre-extraction at 15% weight loss had higher tear strength than the control and the other pre-extracted samples which may be due to the lowest refining revolutions and relatively lower tensile and burst strengths. The lowest tear strength belonged to green liquor pre-extracted pulp at 15% weight loss, which had also the lowest burst and tensile strengths which may be due to higher dissolution of hemicelluloses and higher brittle and low strength fibers.

CONCLUSIONS

1- The target weight losses of 10 and 15% in hot water pre-extraction were obtained at higher H-factors compared to green liquor pre-extraction.

2- The final pH of hot-water pre-extracted liquor was lower than green liquor. The pre-extracted straw samples, required less H-factor than the control un-extracted sample, to reach a target pulp kappa number of about 20. The total pulp yield in case of 15% weight loss in pre-extraction was much lower in green liquor than hot water pre-extraction.

3- The pulp samples from both hot-water and green liquor pre-extraction at 10% weight loss, due to the lower content of hemicelluloses, needed higher PFI revolutions than control pulp. However, in case of 15% weight loss, the pre-extracted pulps required lower PFI revolutions than control pulp because much more hemicelluloses has been lost and the fibers became more brittle.

4- The tensile and burst strengths in the pre-extracted samples at 10% weight loss were similar to the control one, and these strengths in hot-water pre-extracted pulps were slightly higher than green liquor pre-extracted pulp sample. In both cases, these bonding related strengths were lower in 15% weight loss than 10%; this was true especially in the case of green liquor because of severe dissolution of hemicelluloses during pre-extraction stage and lower refining revolutions. The tear strength of the control pulp was higher than the pre-extracted samples, except hot-water pre-extracted pulp at 15 % weight loss.

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