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SODIUM CARBONATE PRE-EXTRACTION OF *TREMA ORIENTALIS* IN THE PRODUCTION OF PAPER GRADE PULP

To increase the profitability of the pulp and paper industry, additional value added products from lignocelluloses are needed, and consistent with this goal, a biorefinery concept based on the sodium carbonate pre-extraction of Trema orientalis prior to pulping was proposed. The solid content in the sodium carbonate pre-extracted liquor was much lower than the hot water pre-extraction, which affected the pre-hydrolysis yield and overall pulp yield positively. The alkaline pre-extraction had a beneficial effect on delignification in the subsequent soda-AQ-pulping. In addition, the alkaline pre-extraction improved the pulp bleachability. The papermaking properties of the alkaline pre-extracted soda-AQ pulp were very close to non-extracted pulp after $D_0E_pD_1$ bleaching.

Keywords: *Trema orientalis*; Alkaline pre-extraction; Dissolved biomass; Pulping; Bleaching; Papermaking properties

Introduction

Bangladesh is a populated country with few forests. However, the demand for lignocellulosic materials for pulp production is increasing. In this context an increase in the allocated industrial forestland is almost impossible. Therefore, wood production needs to be increased from the already allocated forestland. *Trema orientalis* has shown a promising fast growing species for pulp production [Jahan et al. 2007, 2008, 2010].

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In recent years, due to global warming, interest has grown in bio-based products [Bozell, Petersen 2010; Stöcker 2008]. As a result, much research is being carried out on hemicellulose pre-extraction prior to pulping [Huaiyu 2009; Yong, Zhang 2011; Jahan et al. 2009]. The pre-extracted liquor contains a considerable amount of sugars, lignin and acetic acid [Saeed et al 2012], which can be a good source of bio-based products [Ahsan et al. 2012; Liu et al. 2014]. A study of hot water pre-hydrolysis prior to kraft pulping of *T. orientalis* [Jahan et al. 2011] revealed that the pulp yield and papermaking properties of the pre-hydrolysed pulp were inferior. The prehydrolysis process prior to pulping needs to be optimized. Autohydrolysis of wood is typically conducted under mild conditions in order to minimize the degradation of the extracted hemicelluloses [Testova et al. 2011; Tunc, van Heiningen 2011]. Mild alkaline pre-extraction produced pulp with better yield and quality, and the extracted hemicelluloses were in oligomeric form [Yoon, van Heiningen, 2008; Jahan, Rahman 2012; Jahan et al. 2013]. Alkaline pre-extraction was the best alternative because xylan extracted in this process had higher molecular mass [Al-Dajani, Ulrike 2008; Al-Dajani, Ulrike 2010]. Many studies have been carried out on near neutral pre-extraction of wood [Schild et al. 2010; Yoon et al. 2011]. Alkali extraction of hemicelluloses from wood chips can be considered well-integrated with an existing alkaline process in alkaline pulping, since it lowers the alkali charge when cooking, although the effectiveness of hemicellulose extraction and recovery is not well-documented for the combining of pulp production with the bioconversion of hemicellulose. Helmerius et al., [2010] studied birch hemicellulose extraction prior to kraft pulping using both hot water and kraft white liquor alkali extractions on the final pulp quality. The study demonstrated that white liquor can be utilized to extract xylan from birch wood chips prior to kraft cooking without decreasing the pulp yield and paper strength properties, while simultaneously impregnating the wood chips with the cooking alkali.

The present study is a continuation of a previous study where molecular weight of extracted hemicelluloses was to be preserved from severe depolymerisation and deacetylation to avoid pulp yield losses. According to previous findings, pH level is a key parameter governing the overall hot-water extraction process and influences the main characteristics of the extracted and residual wood materials [Jahan et al. 2012]. To avoid low pH levels and hydrolytic reactions, extraction with sodium carbonate (Na_2CO_3) solutions – as a common and relatively cheap, weak alkaline buffer – was studied. The objective of this investigation was to extract hemicelluloses from *Trema orientalis*, and determine its effect on soda-AQ pulping. Bleaching and papermaking properties were also evaluated.

Materials and methods

Materials

T. orientalis wood was chipped in a laboratory wood chipper. All the chemicals used in this study were GPR grades and obtained from E-Merck, Germany.

Prehydrolysis

T. orientalis chips were pre-extracted with 4.0% Na_2CO_3 (on the raw material) in a 5 L capacity digester. Pre-extraction was carried out at 170°C for 60 min. The *T. orientalis* to liquor ratio was 1: 4. The time required to reach the maximum temperature was 50 min. After completing pre-extraction, the pressure was released and the digester was cooled by circulating cold water. A sample was then collected from the drained-off liquor for to determine the pH, solid content, lignin and sugars. The percentage of dissolved components was measured gravimetrically.

Pulping

Pulping of the pre-extracted *T. orientalis* was carried out by soda and soda-AQ processes in the same digester as in the pre-extraction. Non-extracted *T. orientalis* chips were pulped by soda and soda-AQ processes for a control experiment. The pulping conditions were as follows:

- Active alkali: 16, 18 and 20% NaOH on the oven-dry (o.d) raw material
- Anthraquinone: 0.1% on the oven-dry (o.d) raw material
- Cooking time: 120 min at a maximum temperature of 170°C. It took 50 min to reach the maximum temperature (170°C) from room temperature.
- Liquor to material ratio: 4:1.

After digestion, the pulp was washed until free from residual chemicals, and screened on a flat vibratory screener (Yasuda, Japan). The screened pulp yield, total pulp yield and screened reject were determined gravimetrically as a percentage of the o.d. raw material. The kappa number of the resulting screened pulp was determined in accordance with Tappi Test Methods (T 236 om-99).

Bleaching

All the pulps were bleached by $D_0E_pD_1$ bleaching sequence. The ClO_2 charge was 2% and the temperature was 70°C for 60 min in the D_0 stage. The pH was adjusted to 2.5 by adding diluted H_2SO_4. In the alkaline extraction stage, the temperature was 70°C for 60 min, and the NaOH and H_2O_2 charge were 2% and 0.5%, respectively. In the final D_1 stage, the ClO_2 charge was 0.5, and the pH was adjusted to 4.5 by adding diluted alkali.

Strength properties

The bleached pulps were beaten in a PFI mill to approx. 40 °SR and handsheets were made to determine the tear index (T414 om-98), tensile index (T404 cm-92), and burst index (T403 om-97). All the properties were determined according to the Tappi Standard Methods given in parentheses.

Results and discussion

Pre-extraction

The amounts of the pre-hydrolysis yield, the solid content and pH values after extraction are presented in table 1. The solid content in the alkaline pre-extracted liquor was much lower than in the hot water pre-extracted liquor (10.9% vs 18.5%) [Jahan et al 2011], which affected the pre-hydrolysis yield. Other studies also showed similar results of lower TDSs in an alkaline pre-extraction [Song et al. 2011]. As shown in table 1, the yield of *T. orientalis* after the alkaline pre-extraction was 89.9, which was 9.7% lower than the hot water pre-hydrolysis [Jahan et al 2011]. In the hot water pre-extraction process, water remained in the liquid state, which generated hydronium ions and catalyzed the reaction. Subsequently, the production of acetic and formic acids from the dissolved hemicellulose lowered the pH of the liquor (pH), which accelerated dissolution of the lignocelluloses. As shown in table 1, in the alkaline pre-extraction, the generated organic acid was neutralized (pH 6.42), which created a mild extraction process. That is why the alkaline pre-extraction dissolved less biomass than the hot water extraction. Walton et al. [Song et al. 2011] showed that hot water extraction released up to 30 g/L sugars from mixed southern hardwood, but resulted in the greatest decrease in pulp yield, dropping from 47% to 35%. Extraction with 2% green liquor increased the pulp yield to 51% while greatly reducing the component sugars to 8 g/L. Song et al. [2011] extracted hemicellulose from Norway spruce and found that at higher concentrations of NaHCO3, the carbohydrate extraction decreased. Hydrolytic depolymerisation of hemicelluloses occurring during extraction with plain water was largely inhibited in the presence of 2.5–5 mM $NaHCO_3$. The hydrolytic deacetylation of the galactoglucomannans was lower at low $NaHCO_3$ concentrations but increased dramatically at higher $NaHCO_3$ concentrations.

As shown in table 1, the wood component dissolution and solid wood residue amounted to more than 100%, which was due to the use of Na_2CO_3 in the pre-extraction process. This was reflected by the ash content in the pre-extracted liquor.

Table 1. Sodium carbonate pre-extraction of *Trema orientalis*

PH	(A) Pre-extraction yield (%)	(B) Solid content in PHL (%)	Ash in PHL	Mass balance (A+B)
6.42	89.9	10.97	5.87	100.87

Pulping

Sulphur-free cooking was one of the focuses of the alkaline pre-extracted pulping. Therefore, in this study, sulphur was replaced by anthraquinone (AQ). The delignification of pre-extracted *T. orientalis* was faster than its non-extracted counterpart. As shown in figure 1, alkaline pre-extraction positively affected delignification during soda-AQ-pulping. The kappa number was lower for the extracted pulps (14.1-22.6) than for the non-extracted ones (17.6-30.6). The results showed that an increase in alkali charge from 16 to 20% resulted in a decrease in the kappa number for both the extracted and non-extracted pulps. Huang et al. [2010] also observed that xylan pre-extracted wood chips required less H-factor and effective alkali to get a similar kappa number to the non-extracted wood chips. Lu et al. [2012] also showed that the lower kappa number of xylan pre-extracted aspen wood chips as apposed to non-extracted wood chips, and the kappa number of the pulps, decreased with increasing pre-extraction time and temperature. This is potentially due to the structure of the pre-extracted wood chips being looser than the raw wood, allowing easier access of the white liquor to the extracted wood chips [Al-Dajani, Ulrike, 2008].

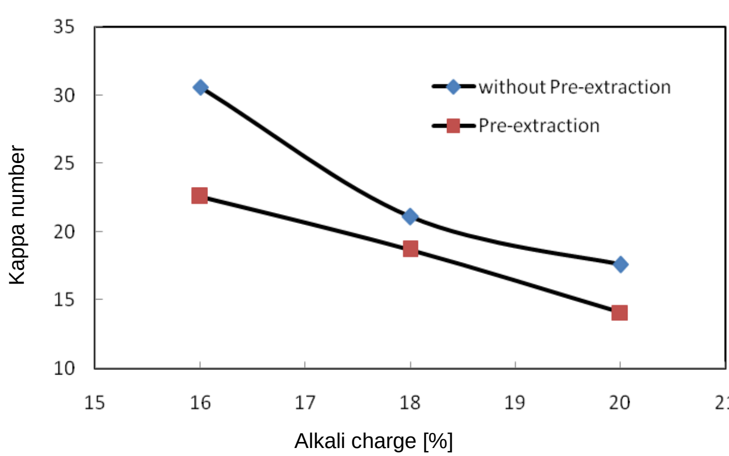

Fig. 1. Effect of pre-extraction on delignification of *T. orientalis*

The screened pulp yield of Na_2CO_3 pre-extracted *T. orientalis* was almost similar at a kappa number of 21-22, where 2% less alkali was required in cooking (table 2). Prehydrolysis increases the porosity of wood chips, partially degrades lignin and cleavages of carbohydrate-lignin bonds, therefore, improving delignification of prehydrolysed biomass [Sixta 2006]. The overall pulp yield (which included pre-extraction and pulping) is shown in parentheses in table 2. Much lower pulp yield was observed. As shown in figure 2, a pulp yield approx. 5% lower was observed in the pre-extracted soda-AQ cooking. The lower pulp yield after xylan removal was well explained by Colodette et al. [2011]. The authors proposed that a) the xylan remaining in the prehydrolysed chips are very sensitive to alkaline cooking because they are severely degraded, b) cellulose chains become more susceptible to alkaline cooking because the xylan layer existing over the cellulose fibrils is partly removed, exposing the cellulose to alkaline attack.

Table 2. Effect of alkali charge on pulping Na_2CO_3 pre-extracted *T. orientalis*

Raw material	Alkali charge (%)	Screened yield (%)	Reject (%)	Total pulp yield (%)	Kappa number
T. orientalis	16 18 20	47.9 49.1 49.0	4.2 1.9 0	52.1 51.0 49.0	30.6 21.1 17.6
Pre-hydrolysed-*T. orientalis*	16 18 20	47.7 48.0 47.3	1.5 0.7 0	49.2 (44.2) 48.7 (43.8) 47.3 (42.5)	22.6 18.7 14.1

(Parenthesis indicates overall yield, prehydrolysis and pulping)

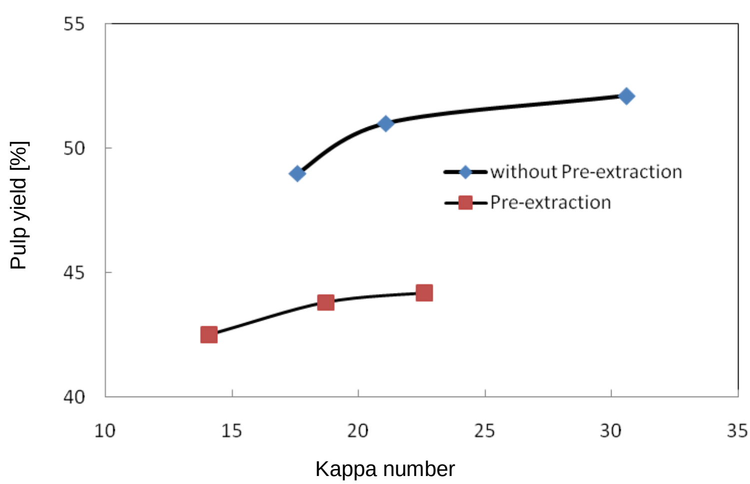

Fig. 2. Pulp yield-kappa number relationship of pre-extracted *T. orientalis*

Papermaking properties and bleaching

Table 3 shows the physical properties of non-extracted and pre-extracted bleached and unbleached pulp from *T. orientalis*. As shown in table 3, the tensile and burst indexes of the non-extracted pulp were higher than that of the extracted pulp at a similar drainage resistance. The harmful effects of pre-extraction on the tensile and burst strength could be explained by the inferior fibre bonding of pulp with low hemicellulose content [Yoon, van Heiningen 2008]. Inferior tensile and burst indexes can be explained by the higher ratios of cellulose/hemicelluloses [Molin, Teder 2002]. Schönberg et al [2001] showed that the tensile index increased after sorption of xylan to the fibres. The chemical sorption of xylan was found to significantly increase the Scott Bond-value, further supporting the significance of xylan to bonding ability [Schönberg et al 2001]. Al-Dajani, Ulrike [2008] observed that alkaline pre-hydrolysis of aspen prior to pulping reduced the tensile index by 10 %. The negative effect of pre-extraction on the tensile strength of kraft pulp loblolly pine was also observed by Yoon, van Heiningen [2008]. This lost tensile index was slightly regained by using AQ in the soda process. As AQ retains carbohydrates during pulping, it increases fibre bonding during sheet formation. Fibre flexibility and strength are the most significant factors when it comes to the tensile strength. The non-extracted and soda-AQ pulp had more flexible fibres, with more bonding giving more energy absorption. The tear index of the pre-extracted unbleached pulp was higher than the non-extracted unbleached pulp (table 3). However, the tear index values of the bleached pulp were almost similar. Helmerius et al. [2010] also showed that non-extracted pulp had lower values of the tearing index than the extracted sample, indicating more flexible fibres.

Table 3. Papermaking properties of soda and soda-AQ pulps from pre-extracted and non-extracted sample

Pulping process		Unbleached				Bleached			
		TI	BI	Ten	Brightness (%)	TI	BI	Ten	Brightness (%)
Non-extracted	Soda	8.6	2.2	42.0	13.5	8.1	2.3	33.6	54.0
	Soda-AQ	8.8	2.7	48.6	13.7	8.4		25.8	77.4
Pre-extracted	Soda	10.2	1.4	32.9	17.1	7.7	1.2	30.9	80.3
	Soda-AQ	10.6	2.1	37.3	19.4	7.8	1.5	25.6	83.8

TI-Tear index, $mN.m^2/g$; BI- Burst index, $kPa.m^2/g$; Ten- Tensile index N.m/g

Pre-extraction of hemicelluloses may change the bleaching potential of the produced pulps, therefore the unbleached pulps obtained with and without pre-extraction were subjected to conventional ECF bleaching ($D_oE_pD_1$) in order to assess bleachability. The brightness of the pulp from the pre-extracted sample was better than the non-extracted sample. The final brightness of the soda-AQ pulp from the pre-extracted sample was 83.8%, which was 6.4% higher than the soda-AQ pulp from the non-extracted sample. This can be explained by the lower initial kappa number of the pre-extracted sample. Similarly, Kautto et al. [2010] showed that prehydrolysis reduced the bleaching chemicals in order to get the target brightness.

Conclusions

Alkaline pre-extraction neutralized the generated acetic acid, consequently reduced the dissolved biomass from *T. orientalis* (10.9%). Alkaline pre-extraction saved 2% alkali to reach a similar degree of delignification with the sacrifice of 1.4% screened pulp yield in the soda-AQ process. Alkaline pre-extraction also improved the bleachability of the *T. orientalis* pulp. The papermaking properties of the pre-extracted pulp were very similar to the non-extracted pulp after bleaching.

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