bioresources.com

A LARCH BIOREFINERY: INFLUENCE OF WASHING AND PS CHARGE ON PRE-EXTRACTION PSAQ PULPING

Hanna S. Hörhammer,[a],* and Adriaan R. van Heiningen [a,b]

This study deals with a biorefinery concept based on larch wood. Wood chips of Siberian larch (*Larix sibirica* Lebed.) were treated with water before pulping at the optimal pre-extraction (PE) condition of 150 °C and 90 minutes. Through PE, about 12.4% of the wood mass is dissolved, mainly from the arabinogalactan hemicellulose component. Fermentation of the hemicellulose-rich larch extract with *Bacillus coagulans* resulted in consumption of all C6 and C5 sugars and produced lactic acid in high yield. PE before pulping resulted in lower (4 to 5%) pulp yield than for control kraft pulps. However, the pulp yield loss may be reduced by addition of polysulfide (PS) and anthraquinone (AQ). The present study focuses on the effect of the degree of washing of the extracted chips and that of the PS charge in PSAQ pulping on the final properties of the pulp. Three different levels of washing and three different PS charges were tested. The characteristics of the extract, wash water, pulp, and black liquor samples were determined. The amount of sugars in the combined stream of collected extract and wash water obtained by mild washing was 10.2% on o.d. wood.

*Contact information: a: Department of Forest Products Technology, Aalto University, P. O. Box 16300, 00076 Aalto, Finland; b: Department of Chemical and Biological Engineering, University of Maine, 5737 Jenness Hall, Orono, ME 04469-5737, USA; *Corresponding author: hanna.horhammer@aalto.fi*

INTRODUCTION

The traditional pulp and paper industry faces big challenges in the current market. In particular, mills in the temperate northern part of the globe must find new ways to remain competitive. Recently, the focus has turned to the possibility of producing other products in addition to or even replacing paper and board (van Heiningen 2006). In one of these biorefinery concepts, the hemicelluloses are extracted before kraft pulping, and then they are utilized as feedstock for biofuels or biochemicals production, while the extracted wood chips are pulped into kraft fibers (Frederick *et al.* 2008; Yoon *et al.* 2008; Al-Dajani *et al.* 2009; Helmerius *et al.* 2010; Kämppi *et al.* 2010; Vila *et al.* 2011; Yoon *et al.* 2011). The hemicelluloses have been used for the production of liquid fuels such as ethanol (Walton *et al.* 2010; Liu *et al.* 2010), butanol (Survase *et al.* 2011), jet and diesel fuel (Xing *et al.* 2010), and gasoline (Li *et al.* 2011). Chemical conversion of hemicelluloses into commodity chemicals such as furfural, formic, and acetic acid has been reported by Xing *et al.* (2011), and their fermentation into lactic acid by Walton *et al.* (2010) and Hörhammer *et al.* (2011).

bioresources.com

Water hydrolysis of wood was studied in the 1940s (Overbeck and Muller 1942). During extraction, the acetyl groups of the hemicellulose are released as acetic acid, leading to a decrease in pH of the extract. The increased acidity leads to cleavage of glycosidic bonds and thus reduced molecular weight of the hemicelluloses so that they become soluble (Chen *et al.* 2010). Hot-water extraction is therefore autocatalytic and is called autohydrolysis (Amidon and Liu 2009). Unfortunately, as a result of the acidic conditions, high temperature pre-extraction with water leads to a significant pulp yield and paper strength loss after subsequent kraft pulping. For bleachable grade kraft pulp made from loblolly pine, a yield loss of 6% is obtained at about 8% (both on original wood) sugars in the extract (Yoon *et al.* 2008; Yoon and van Heiningen 2008), similar to 7% yield loss at about 7% extract sugars for Scots pine (Kautto *et al.* 2010). For a bleachable grade hardwood kraft pulp, the yield loss for silver birch after a mild water hydrolysis is about 4% at 4% sugars in the water extract (Helmerius *et al.* 2010), 10% yield loss for *Eucalyptus globulus* at a similar percentage of sugar extraction (Mendes *et al.* 2009), and about 11% pulp yield loss after collecting the same level of sugars in the water extract for aspen (Al-Dajani *et al.* 2009).

Since the net revenue obtained from the extracted sugars (for example by fermentation to ethanol) is generally smaller than that of paper grade pulp, it is essential that the pulp yield loss be small compared to the amount of sugars in the extract. This motivated Yoon *et al.* (2010) to use a reductive treatment before kraft pulping to stabilize the residual hemicelluloses in hot water extracted loblolly pine wood chips. The hemicelluloses remaining after hot water extraction are more prone to peeling during kraft pulping because of their decreased molecular weight and thus increased content of reducing ends. Sodium borohydride at 1% charge on wood dissolved in mild alkaline sodium sulfide was used to convert the reducing ends to stable alditols, thereby eliminating the 7% pulp yield loss during subsequent kraft-AQ pulping. In a subsequent study, Yoon *et al.* (2011) stabilized the end groups of hemicellulose after hot water treatment by oxidation using polysulfide. A 15 to 20% polysulfide charge minimized the kraft-AQ pulp yield loss to 2%, while combining oxidative and reductive treatments of 15% polysulfide, 0.5% $NaBH_4$, and 0.1% AQ completely eliminated the 7% pulp yield loss caused by water extraction of 10% sugars obtained at a wood yield of 86%. This shows that stabilization of the degraded hemicelluloses after hot water treated wood is possible, albeit at an impractically high polysulfide charge and using prohibitively expensive sodium borohydride. Finally, it is also shown by Yoon *et al.* (2010, 2011) that the pulp properties are the same as that of regular kraft pulp if the yield loss is minimal.

In the present study, we investigate hot water extraction of larch wood chips at a high percentage of hemicellulose removal while minimizing kraft pulp yield loss. Larch wood was chosen as feedstock because its main hemicellulose component, arabino-galactan, is easily dissolved in water (Sjöström 1993; Cote *et al.* 1966). Also, to further increase the economic viability, the extracted and hydrolyzed hemicellulose was converted into higher-value lactic acid. Because larch kraft pulps have lower yield, brightness, and strength properties (except for tear strength) than pine and spruce kraft pulps (Nevalainen and Hosia 1969b; Hakkila *et al.* 1972; Einspahr *et al.* 1983; Uprichard and Gray 1973) this species is rarely used for pulp production, despite the presence of very large resources of Siberian larch (*Larix sibirica* Lebed.) in Northwestern Russia

(Nevalainen and Hosia 1969a; Venäläinen 2001). However, with significant extra revenue coming from hemicellulose-derived lactic acid, and without adverse effect on kraft pulp yield and quality, the larch-based biorefinery has significant potential. Lactic acid is the building block for poly(lactic acid) (PLA). In today's world of green chemistry and concern for the environment, PLA is of high interest because it is made of renewable sugar resources, and it is biodegradable (Gruber *et al.* 2006; Wolf *et al.* 2005). Currently, 140,000 MT/year of PLA is produced by NatureWorks LLC in Blair, NE, USA using fermentation of glucose derived from starch.

Polysulfide (PS) and anthraquinone (AQ) are well-known pulping additives to increase pulp yield. PS and AQ oxidize the reducing end groups of polysaccharides to aldonic acid groups, thus stabilizing the polysaccharides against peeling reactions (Teder 1969; Dimmel *et al.* 2003). AQ additionally accelerates the delignification rate of pulping (Dimmel *et al.* 2003). In softwood, the yield is enhanced by higher retention of glucomannans due to PS and better preservation of cellulose due to AQ (Pekkala 1986). A synergism exists when PS and AQ are used together in alkaline pulping (Dimmel *et al.* 2003; Pekkala 1986; Luthe and Berry 2005; Jiang 1995; Berthold *et al.* 1999; Sturgeoff and Bernhard 1998; Li *et al.* 1998). In PSAQ, pulping glucomannan is the main hemicellulose that contributes to the yield increase (Pekkala 1986; Luthe and Berry 2005; Jiang 1995).

Earlier experiments by our research group have provided proof of concept for a biorefinery based on Siberian larch (*Larix sibirica* Lebed.) using pre-extraction PSAQ pulping. It was shown that after extensive washing of the extracted chips, a 4% PS charge minimized the yield loss caused by pre-extraction (Kämppi *et al.* 2010). Later, the optimal conditions for the pre-extraction for this PE-PSAQ process were determined to be 150 °C for 90 minutes (Hörhammer *et al.* 2011). Also, fermentation of the larch extract into lactic acid has been investigated with good results (Hörhammer *et al.* 2011). A preliminary economic analysis of this larch-based biorefinery shown in Fig. 1 was performed by Hörhammer *et al.* (2009).
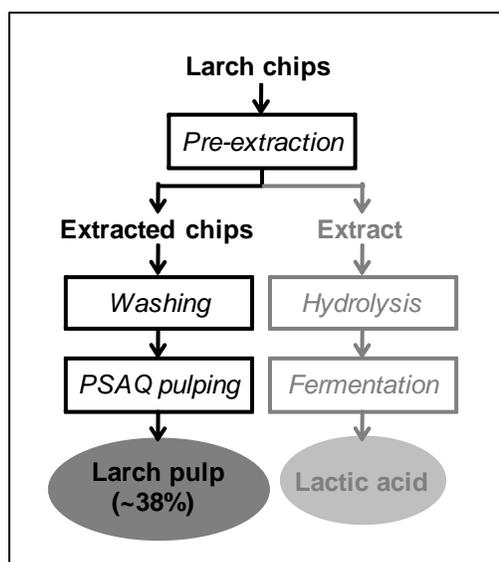
Fig. 1. Process scheme of a larch biorefinery based on the PE-PSAQ process and fermentation

About 3/5 of the dissolved hemicellulose sugars are obtained by draining the extract after hot water treatment at L/W of 3.5 L/kg. However, the residual dissolved sugars in the wet wood are likely to consume a significant amount of alkali during pulping, and therefore washing is needed between the pre-extraction and pulping step. The aim of the present research was to study the effect of the degree of washing of the extracted chips and that of the PS charge on the PE-PSAQ pulp yield and properties. Three different levels of washing (no, mild, and extensive), and three different PS charges (0.5, 1.0, and 2.0%) were tested. These PS charges are more practically viable than the 4% used in our earlier studies. The characteristics of the extract, wash water, pulp, and black liquor samples were also determined. The dry matter, ash content, and heating value of the black liquor were determined in order to quantify the effect of the extraction on its combustion properties.

EXPERIMENTAL

Wood chips of Siberian larch were processed in this study. The chips were pre-extracted with water followed by PSAQ pulping. Variables were the degree of washing between the extraction and pulping step, and the PS charge during PSAQ pulping. Also, reference conventional kraft cooks were performed. The detailed process conditions for the different trials are presented in Table 1.

Wood Chips

Siberian larch (*Larix sibirica* Lebed.) mill chips from the Baikal region in Russia were used. The basic density of the chips was 466 kg/m^3 (SCAN-CM 43:95). Chips were defrosted and screened to remove oversize chips and fines (SCAN-CM 40:01). The thickness of the accepted chips was 7 to 8 mm. The screened chips were re-frozen and stored. Shortly before actual processing, they were again defrosted. 300 g o.d. chips were used for each trial.

Pre-Extraction (PE)

The laboratory water pre-extraction trials were conducted in a hot air-bath cooking system containing six rotating autoclaves (2.5 L each). For the PE, the autoclaves were charged with 300 g o.d. larch wood chips and water at a liquor-to-wood ratio (L/W) of 3.5 L/kg (o.d.). The PE was performed at 150 °C for 90 min (heat-up time of 60 min not included). These conditions were earlier determined to be the optimal conditions for this type of a larch biorefinery (Hörhammer *et al.* 2011). After water extraction the extract was drained.

Washing of Pre-extracted Chips

Three different levels of washing were tested; no, mild, and extensive washing. In the case of no washing, the extracted, drained, and centrifuged chips go straight to PSAQ pulping. In the mild washing procedure, fresh water was added to the drained chips to again obtain a L/W ratio of 3.5 L/kg (o.d.) and then kept at 80 °C for 60 min (heat-up time of 30 min not included). Extensive washing includes 2 times 10 min washing in 5 L

water at 23 °C followed by immersing in 25 L water overnight. The extracted chips were washed with fresh water. The wash water was removed from the extracted and washed chips by centrifugation and kept separate from the extract for analysis. The unwashed extracted chips were also centrifuged before pulping.

Pulping

The pulping trials were performed in the same digester as the PE trials. For the pulping, the autoclaves were charged with cooking liquor and the extracted wood chips. The PSAQ pulping was conducted under the following conditions: L/W 3.5 L/kg (o.d.), effective alkali (as NaOH) 20%, AQ 0.1%, sulfidity 38%, cooking temperature 167 °C, and H-factor 1250 h. Three different PS charges were tested: 0.5%, 1.0%, and 2.0%. For the kraft cook, a higher alkali charge (23%) and H-factor (1650-1850 h) were used in order to reach a kappa number of around 25.

Table 1. Process Conditions for Pulping of *Larix sibirica*

Pulp	Kraft 1	Kraft 2	PE-PSAQ								
Wash of extracted chips	-	-	No	No	No	Mild	Mild	Mild	Ext	Ext	Ext
PS charge	-	-	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
Washing											
L/W	-	-	-	-	-	3.5	3.5	3.5	∞	∞	∞
Washing temperature, °C	-	-	-	-	-	80	80	80	23	23	23
Washing time	-	-	-	-	-	1 h	1 h	1 h	1 d	1 d	1 d
Cooking											
L/W	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Cooking temperature, °C	167	167	167	167	167	167	167	167	167	167	167
Heat-up time, min	60	60	60	60	60	60	60	60	60	60	60
H-factor, h	1650	1850	1250	1250	1250	1250	1250	1250	1250	1250	1250
Effective alkali charge, %	23	23	20	20	20	20	20	20	20	20	20
Polysulfide charge, %	-	-	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
Anthraquinone charge, %	-	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
White liquor											
EA, g NaOH/L	125.6	125.6	125.1	125.1	125.1	125.5	125.5	125.5	127.0	127.0	125.1
Sulfidity, %	37.6	37.6	38.1	38.1	38.1	38.0	38.0	38.0	38.0	38.0	38.1
Polysulfide liquor											
EA, g NaOH/L	-	-	124.2	123.1	120.3	123.0	122.0	119.2	124.3	122.6	120.3
Sulfidity, %	-	-	38.6	39.8	42.1	38.1	39.5	42.0	38.6	39.9	42.1
NaOH addition, g	-	-	0.4	1.3	3 .5	1.0	2.0	4.1	1.1	2.3	3.5

Analyses

The cooking liquors, *i.e*. white liquor and PS liquor, were analyzed according to SCAN-N 2:88 using an automatic titrator (Mettler Toledo DL53, Switzerland) shortly before the cook. The pulps were thoroughly washed, screened, and homogenized before analyses. Kappa number (SCAN-C 1:00), viscosity (SCAN-CM 15:99), and residual alkali (SCAN-N 33:94) were determined. The sugar content in the extract was analyzed according to NREL TP-510-42623 by HPAEC (Dionex ICS-3000). The monomeric sugars were analyzed from unhydrolyzed extracts, while the total sugars were determined

from hydrolyzed extracts. After the NREL hydrolysis, the insoluble lignin was gravimetrically determined and the soluble lignin analyzed with UV at 205 nm with an extinction coefficient of 110 L/g cm. The pH of the liquors was measured with a pH electrode, and the density was determined by weighing a certain volume of the sample at 23 °C. The dry solids content of the extract and wash water samples was determined by drying a sample at 105 °C overnight. The dry solids content of the black liquor samples was determined according to SCAN-N 22:96. The heating value of three black liquor samples was determined by Nab Labs Oy (Rauma, Finland) according to DIN 51900. The ash content in black liquor was determined by burning the sample in a muffle furnace at 700 °C (KCL 59:83). The analyses were performed in at least duplicates. More analyses were performed if the variation was large.

RESULTS AND DISCUSSION

Material Balances during Pre-treatment and Washing

300 g o.d. wood chips containing 200 mL water was charged to the pre-extraction stage together with 850 mL fresh water. After the pre-extraction, about 630 mL of extract was drained from the chips, while about 420 mL extract remained in the extracted chips. In other words, about 3/5 of the extract was drained. 12.4% (dry solids) wood was dissolved during pre-extraction, and 7.4% (dry solids) wood was collected from the wood chips by drainage.

Table 2 describes the inputs and outputs of pre-extraction and of the three different washing cases – no, mild, and extensive washing. The not-washed extracted chips were centrifuged before pulping. In the mild wash case, 630 mL fresh water was added to the washing. For extensive washing, the volume of fresh water used for washing was significantly larger (35 L). The extracted and washed chips were drained and centrifuged. In the case of mild washing, about 720 mL of wash water containing about 4% dissolved wood (dry solids) was removed. The chips contained about 330 mL water when they entered the pulping stage. Depending on the type of washing, different amounts of dissolved solids were charged with the pre-extracted wood to pulping. More dissolved solids were removed with more washing. Therefore, less washing of pre-extracted chips results in larger amounts of dissolved solids entering pulping. The dissolved solids consume chemicals during pulping and should therefore be removed before the cooking stage.

Based on the data in Table 2, amounts of wood removed and washing characteristics can be calculated. 7.4% on wood was removed by pre-extraction, 8.5% on wood by PE-centrifugation, and 11.4% on wood by PE-mild wash-centrifugation. The percentage collected dissolved wood compared to that dissolved during PE was also determined. The washing is described by a dilution factor and washing efficiency. The dilution factor describes the volume of fresh water (L) added per amount of wood charged to washing (0.3 o.d. kg). The dilution factor for the no wash was 0, for the mild wash 2, and for the extensive wash 117, respectively. The washing efficiency is described by comparing the percentage of dissolved wood solids in the removed wash waters to the

bioresources.com

maximum removable amount for each washing case. For extensive washing, the washing efficiency is 100% and for mild washing, it is 69%.

Table 2. Material Flows for the Three Different Types of Washing of Pre-Extracted Chips of Siberian Larch

	PE (150 C/ 90 min) L/W 3.5		No wash		Mild wash L/W 3.5		Extensive wash L/W ∞	
	Wood %	Liquid mL	Wood %	Liquid mL	Wood %	Liquid mL	Wood %	Liquid mL
IN to PE or wash								
Wood	100	200		420		420		420
Additional water		850		0		630		35000
Before drainage								
Liquid phase	12.4	1050		420	5.8	1050	max	35420
OUT								
Drainage	7.4	630			3.5	630		35000
Centrifugation			1.1	90	0.5	90		90
Drainage+Centrif.					4.0	720	max	35090
PE+Wash, % on wood			7.4+1.1 = 8.5		7.4+4.0 = 11.4			
Removed/Dissolved, %	7.4/12.4*100 = 60		8.5/12.4*100= 69		11.4/12.4*100 = 92			
Dilution factor, L/kg			0/0.3 = 0		0.63/0.3 = 2		35/0.3 = 117	
Washing efficiency, %					4.0/5.8*100= 69		max/max*100 = 100	

Drainage leaves about 420 mL of liquid in wood. Centrifugation leaves about 330 mL of liquid in wood.
PE+Wash=Removed wood by PE+Removed wood from wash
Removed/Dissolved=Wood totally removed by PE and washing/Wood dissolved in PE
Dilution factor=Volume of wash water/Amount of original wood
Washing efficiency=Removed wood during current washing/Amount possible to remove*100

Cooking Results

The basic cooking results from the trials conducted within this study are presented in Table 3. The kappa numbers of the pulps were about 26, except for the unwashed PE-PSAQ pulps, which have kappa numbers around 30. A higher EA charge (23% compared to 20%) was used for the kraft cook in order to reach the kappa number around 26.

Table 3. Results from Pulping with Siberian Larch

Pulp	Kraft 1	Kraft 2	PE-PSAQ								
Wash of extracted chips	-	-	No	No	No	Mild	Mild	Mild	Ext	Ext	Ext
PS charge	-	-	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
Pulp:											
Yield, %	40.4	40.2	36.9	37.3	38.3	37.2	36.8	38.4	37.2	37.2	38.1
Reject, %	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1
Kappa number	26.1	24.2	29.8	31.0	30.9	26.3	25.5	25.9	25.0	25.4	25.5
Viscosity, mL/g	941	882	1128	1129	1173	1023	1024	1005	1039	1029	1053
Black liquor:											
pH	13.3	13.1	13.2	13.2	13.1	13.4	13.4	13.3	13.3	13.3	13.2
ResEA, g NaOH/L	11.9	10.8	7.0	7.7	6.3	8.8	9.6	6.8	9.8	10.2	6.7

The yield for the latter control kraft cook of about 40% was 2 to 3% higher than those of the PE-PSAQ treatment. The viscosity was higher for the PE-PSAQ pulps. The residual alkali was higher than 6 g NaOH/L in all black liquor samples, which means that there was enough alkali in all cooks.

Influence of Washing and PS Charge

Total pulp yields obtained for the PE-PSAQ cooks are presented as a function of kappa number in Fig. 2. Washing reduced the kappa number from 30 to 26. The mild wash was sufficient to obtain this effect. PS charges of 0.5% and 1.0% give yields of about 37%, whereas the yield increased to above 38% with a PS charge of 2%. If the unwashed PE-PSAQ pulps had been cooked to kappa number 26, more alkali would have been consumed and the yield would have been lower.
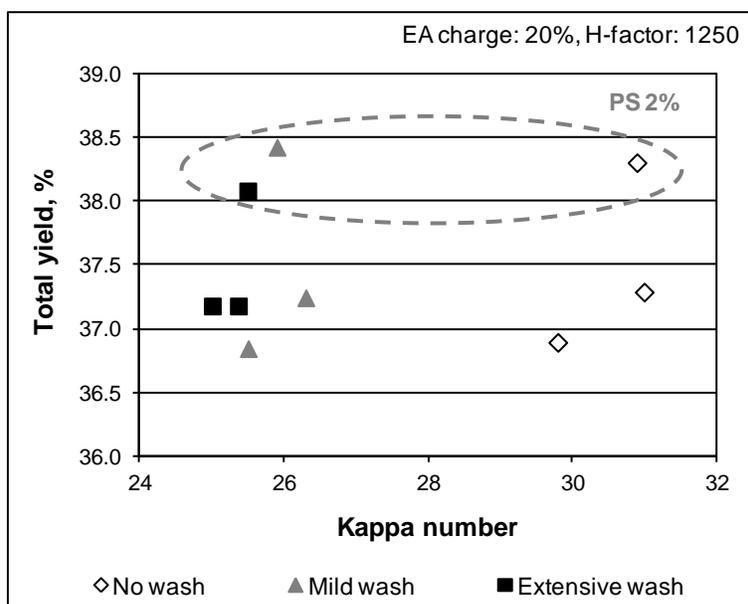

Fig. 2. Total pulp yield versus kappa number

In Fig. 3 the viscosity is plotted against PS charge. No washing of extracted chips resulted in about 100 mL/g higher viscosity, but these pulps also had a higher kappa number. There was no significant difference between the final viscosity and kappa numbers of the pulps produced after a mild or extensive wash. The PS charge had no influence on the viscosity.

More alkali was consumed with no washing and when the PS charge was 2.0%. When the extracted chips were not washed, the dissolved sugars remained within the extracted wood and the pH of the wood for pulping was about 4. The dissolved sugars remaining in the pre-extracted chips and the acidity consumed a significant amount of the cooking chemicals, while PS decomposed to elemental sulfur. Washing of extracted chips removes the dissolved sugars and acetyl groups/acetic acid from the chips, resulting in decreased consumption of cooking chemicals. Based on these results, the optimal and most practical conditions would be a process including pre-extraction at 150 °C for 90 minutes, followed by a mild wash and PSAQ pulping at a PS charge of 2%.
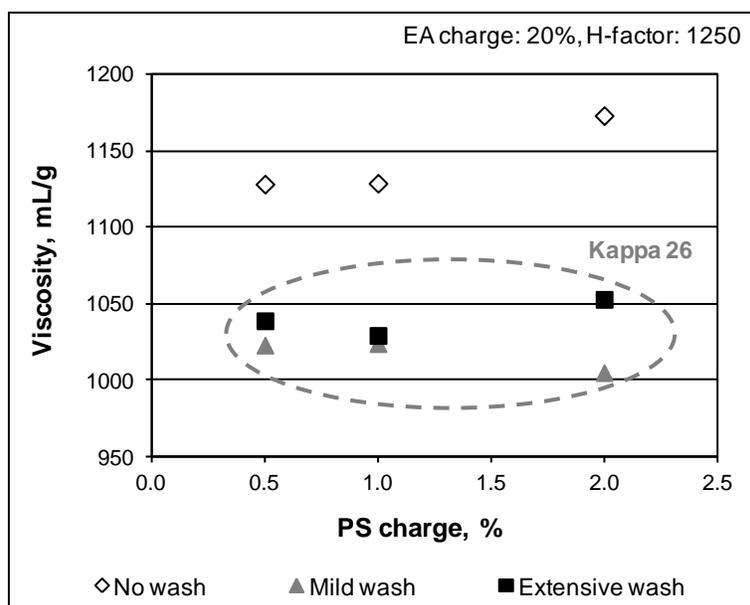
bioresources.com

Fig. 3. Viscosity of pulp versus PS-charge

Composition of Larch Extract, Wash Water, Pulps, and Black Liquor

The characteristics and compositions of the larch extract and of the wash water obtained from the mild wash of the pre-extracted chips are presented in Table 4. The sugars are reported as anhydrosugars, *i.e.* as originally present in larch. The liquid volume collected after PE at 150 °C for 90 min is 630 mL with a density of 1.025 kg/L. 7.4% on wood dissolved wood (dry solids) is removed by drainage. The total sugars in the collected extract represents 6.7% based on the original oven dry wood, mainly arabinogalactan.

Table 4. Characteristics of Larch Extract, Wash Water, and the Combined Stream

	Extract (150 C/ 90 min)				Wash water (Mild wash)				Combined stream (Ext+Ww)
Total volume, mL	1050				1050				
Collected volume, mL	630	*Drainage*			720	*Drain.+Centrif.*			1350
pH	4.0				4.1				~4,1
Density, g/cm3	1.025				1.002				1.013
	Conc. g/L	Amount g	Collected % on wood	Total % on wood	Conc. g/L	Amount g	Collected % on wood	Total % on wood	Collected % on wood
Dry solids	35.5	22.3	7.4	12.4	16.6	12.0	4.0	5.8	11.4
Carbohydrates	31.0	19.5	6.7	11.2	13.9	10.0	3.4	5.0	10.2
Ara	5.7	3.6	1.2	2.0	2.5	1.8	0.6	0.9	1.8
Gal	19.9	12.6	4.3	7.2	8.3	6.0	2.1	3.0	6.4
Glu	1.0	0.6	0.2	0.4	0.5	0.4	0.1	0.2	0.3
Xyl	1.7	1.1	0.4	0.6	1.0	0.7	0.2	0.4	0.6
Man	2.7	1.7	0.6	1.0	1.6	1.2	0.4	0.6	1.0
Monomeric sugars	3.9	2.5	0.8	1.4	2.8	2.0	0.5	0.8	1.4
Oligomeric sugars	27.1	17.1	5.9	9.8	11.1	8.0	2.9	4.2	8.8
Lignin	2.1	1.3	0.4	0.7	0.6	0.4	0.1	0.2	0.6

Assuming that the amount of remaining water has the same total dissolved sugar concentration leads to a total dissolved sugar amount of 11.2% (collected 6.7%) on wood and a total solids content on wood of 12.4% (collected 7.4%). Mild washing removes an additional 3.4% of carbohydrates, giving a total carbohydrate removal of 10.2% in the combined extract and wash water. Comparison of the latter number with the calculated total dissolved amount of sugar of 11.2% suggests that after washing, about 9% (= (11.2-10.2)/11.2*100) of the dissolved sugars remain in the wood chips. This percentage is higher for lignin (about 14%) most likely because of slower diffusion of the dissolved lignin. Finally it can be seen that the amount of sugars plus lignin in the extract and wash water are somewhat lower than the dry solids contents, *i.e.* 7.1% (= 6.7 + 0.4) and 3.5% (= 3.4 + 0.1), compared to 7.4% and 4.0%, respectively.

The carbohydrate compositions of the different pulps based on original wood are presented in Fig. 4. The PE-PSAQ pulps subjected after PE to a mild or an extensive washing are here compared to the control kraft pulp, because they had essentially the same kappa number as the control (kappa 26). The no-wash pulps had kappa numbers around 30, and are therefore more difficult to compare. It can be seen that these PSAQ pulps had about 2 to 3% on wood less glucan, 0 to 1% on wood less mannan, and about 1% on wood less xylan than the control kraft pulp. The amount of galactan was very small, and no arabinan could be detected in all cases, including the control kraft pulp. This shows that it is advantageous to remove as much of the arabinogalactan during pre-extraction, because it will dissolve anyway during kraft cooking in the black liquor. The lower glucan content in the final pre-extracted kraft pulp is not due to removal of glucose during pre-extraction. This means that the extra cellulose loss during cooking is mostly responsible for the pulp yield loss of the PE-PSAQ pulps.
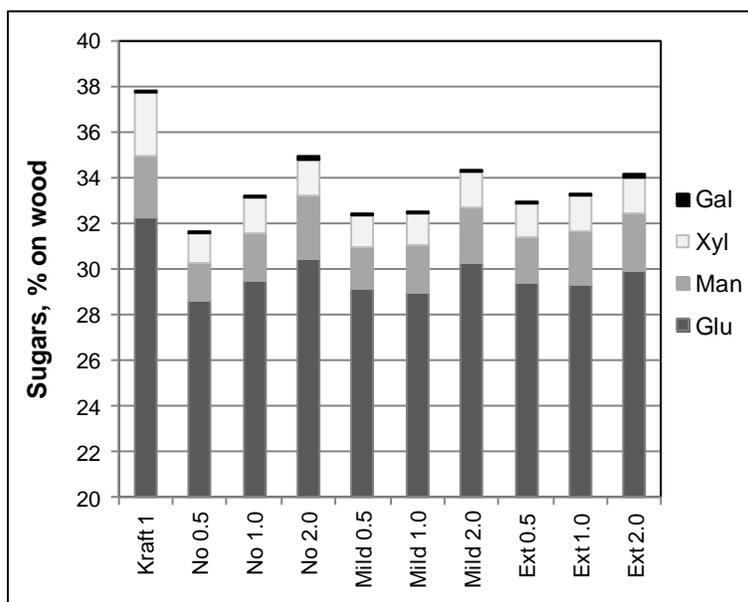

Fig. 4. Carbohydrates in kraft pulp and PSAQ pulps

Among the PE-PSAQ pulps, it can be seen that a higher PS charge preserved glucan and mannan, which was also claimed in the literature (Pekkala 1986; Luthe and Berry 2005; Jiang 1995; van Heiningen *et al.* 2004). The xylan and galactan contents were similar in all PE-PSAQ pulps. The decrease in glucan content in the PE-PSAQ pulps compared to the kraft pulp was most likely due to hydrolytic cleavage of cellulose during PE treatment. This leads to a lower DP of cellulose and new reducing ends, which contribute to additional peeling during subsequent PSAQ cooking. No significant amount of cellulose was dissolved as glucan during PE treatment because the DP was too high for dissolution. More cellulose will be retained by increasing the AQ charge (van Heiningen *et al.* 2004) or by adding sodium borohydride, as was done by Yoon *et al.* (2010). The lignin and extractives contents for both kraft pulp and PE-PSAQ pulps were about 1.3% on wood and 0.1% on wood, respectively.

The characteristics of the kraft control and two PE-PSAQ black liquors obtained after the mild washing step are presented in Table 5. The dry solids contents of the two PE-PSAQ black liquors were lower than the control because of the 3% lower alkali charge. The similar or higher heating values of the PE-PSAQ black liquors compared to the control implies that the amount of dissolved organics was similarly decreased as the inorganics.

The slightly higher heating value for the Mild 0.5 sample was due to the slightly higher wood dissolution, resulting in a lower pulp yield than for the Mild 2.0 sample. Because of the very similar organics to inorganics ratio, it is unlikely that the burning properties of black liquor will be affected when converting from conventional kraft to the PE-PSAQ process for larch wood.

Table 5. Heating Values for Three Black Liquor Samples

Pulp	Kraft 1	PE-PSAQ	
Wash of extracted chips	-	Mild	Mild
PS charge	-	0.5	2.0
Density, g/cm^3	1.153	1.117	1.117
Dry matter, % on liquor	21.6	18.7	18.7
Ash, % on liquor	0.45	0.46	0.46
Heating value (Hu,p (wf)), MJ/kg	13.9	14.4	13.9

Comparisons with Other Processes

The pre-extraction PSAQ process with a mild wash and a PS charge of 2% (PE-Mild-PS(2%)AQ process) was compared to kraft, pre-extraction kraft, and pre-extraction PSAQ at 4% PS charge, the latter two performed with extensive washing of the extracted chips (PE-Ext-Kraft and PE-Ext-PS(4%)AQ).

In Fig. 5, the total pulp yield of these four processes are shown as function of the kappa number. The PE-Ext-Kraft and PE-Ext-PS(4%)AQ were performed earlier within the same project (Kämppi *et al.* 2010), whereby the pre-extraction was performed at 160 °C for 60 min rather than 150 °C for 90 min, resulting in the dissolution of about 15% and 11.2% sugars, respectively.
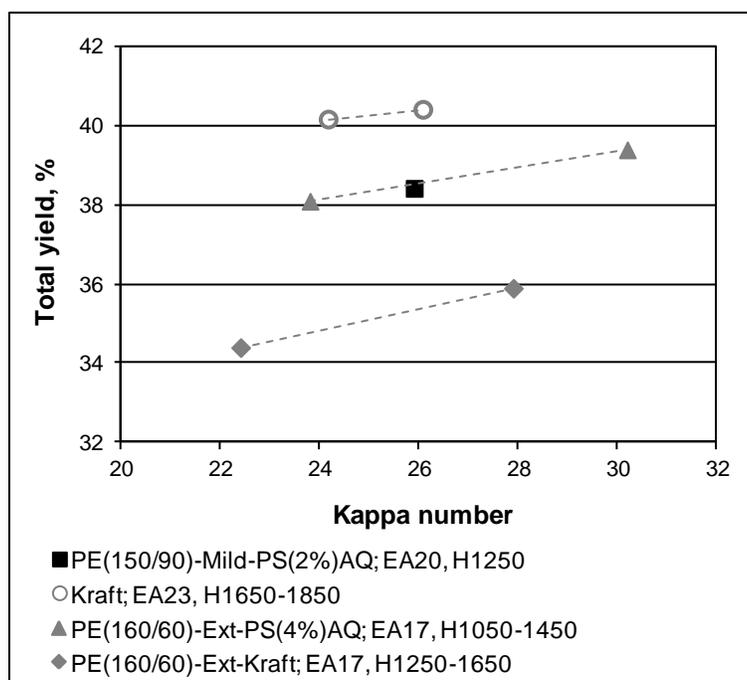
Fig. 5. Total pulp yield versus kappa number. The PE-Mild-PS(2%)AQ pulp is compared with other pulps

From Fig. 5 it can be seen that removing carbohydrates through PE at a level of 15% on wood reduced the pulp yield by about 5% at kappa number 26 (circles *vs.* diamonds). This loss was significant, but still smaller than the 7% yield loss obtained for Scots pine at about 7% PE sugars (Kautto *et al.* 2010), showing that without stabilization of the carbohydrates, the PE sugar yield minus pulp yield loss is 10% (15% minus 5%) for larch compared to essentially zero for Scots pine. The latter has also been found for loblolly pine and hardwoods, as was reviewed earlier. The obvious explanation is that for larch, a large amount of arabinogalactan can be extracted before it is almost fully removed during kraft pulping, while for other softwoods as well as for hardwoods the removal of glucomannan and xylan in significant amounts also leads to significant additional peeling of these hemicelluloses during pulping and thus a large yield loss.

By using 2% PS and 0.1% AQ, the yield loss was reduced to 2% at a PE sugar yield of 11.2%. In comparison, Yoon *et al.* (2011) also obtained 2% pulp yield loss for loblolly pine at 10% PE sugars, but at an order of magnitude higher PS charge of 15 to 20% with also 0.1% AQ. The explanation for the higher efficiency in yield retention of PS in the present experiments is that milder extraction conditions are used with larch as feedstock (because of the higher solubility of arabinogalactan) leading to fewer new reducing ends in the residual hemicelluloses, as well as cellulose and thus requiring less oxidative stabilization by PS and AQ. Most of the 2% pulp weight loss was due to cellulose loss (see Fig. 4).

It is interesting to note that Yoon *et al.* (2010) were able to fully recover all cellulose and pulp yield by treatment of loblolly pine PE pulp with 1% $NaBH_4$ before kraft-AQ pulping. This suggests that a reductive treatment is most effective to stabilize cellulose. Unfortunately, a more economical reductive treatment is still lacking.

The PE-Mild-PS(2%)AQ process can be judged to be better than the PE-Ext-PS(4%)AQ of Kämppi *et al.* (2010), because the former also achieves a 2% lower pulp yield but with half the PS charge and only about 4% less PE sugars (11.2% *vs*. 15%, 6.7% and 9% as received). By combining the extract and the wash water streams in the PE-Mild-PS(2%)AQ process, the collected sugar yield would be 10.2%. Other beneficial aspects of the PE-Mild-PSAQ process compared to the kraft process are lower alkali charge (20% vs. 23%) and 600 h lower H-factor (1250 vs. 1850 h). Drawbacks besides the 2% pulp yield loss are additional operating cost (*e.g.* PS and AQ) and capital cost (PE vessel and extract processing equipment).

CONCLUSIONS

This study investigates the influence of washing of the pre-extracted chips and the PS charge on the pre-extraction PSAQ pulping process. The characteristics of extract, wash water, pulp, and black liquor samples were also determined. Based on the results from this study, the following conclusions can be made:

1. A mild wash between pre-extraction (PE) treatment and PSAQ pulping is sufficient to achieve efficient delignification during pulping, and it increases the amount of recovered sugars.

2. The amounts of carbohydrates dissolved during PE are 11.2%, of which 3/5 were removed by drainage (6.7%). Mild washing removed additional 4.3% of carbohydrates. The combined stream would contain 10.2% (on original wood) of sugars for production of value added products such as lactic acid.

3. A PS charge of 2% is required to reduce the pulp yield loss from 5% to 2%. Increased PS charge increases mainly the glucan and mannan yield in the pulp.

4. It is unlikely that the burning properties of black liquor are affected when converting from conventional kraft to the PE-PSAQ process for larch wood.

ACKNOWLEDGMENTS

REFERENCES CITED

Al-Dajani, W. W., Tschirner, U. W., and Jensen, T. (2009). "Pre-extraction of hemicelluloses and subsequent kraft pulping, Part II: Acid- and autohydrolysis," *Tappi J.* 7(9), 30-37.

Amidon, T. E., and Liu, S. (2009). "Water-based woody biorefinery," *Biotechnology Advances* 27(5), 542-550.

bioresources.com

Berthold, F., Lindfors, E.-L., Olm, L., Tormund, D., and Lindström, M. (1999). "Influence of alkalinity on the yield increasing effect of simultaneous addition of polysulfide and anthraquinone, studied on softwood and carbohydrate model systems," Proceedings, 10th International Symposium on Wood and Pulping Chemistry, Yokohama, Japan, June 7-10, 1999, Japan TAPPI 2, 264-267.

Chen, X., Lawoko, M., and van Heiningen, A. (2010). "Kinetics and mechanism of autohydrolysis of hardwoods," *Bioresource Technol.* 101(20), 7812-7819.

Cote, W. A. Jr., Day, A. C., Simson, B. W., and Timell, T. E. (1966). "Studies on larch arabinogalactan. I. The distribution of arabinogalactan in larch wood," *Holzforschung* 20(6), 178-192.

Dimmel, D., Anderson, S., and Izsak, P. (2003). "A study aimed at understanding the AQ/polysulfide synergistic effect in alkaline pulping," *J. Wood Chem. Tech.* 23(2), 141-159.

Einspahr, D. W., McDonough, T. J., and Joachimides, T. (1983). "Kraft pulping characteristics of European, Japanese and European × Japanese larch hybrids," *Tappi J.* 66(8), 72-76.

Frederick, W. J., Lien, S. J., Courchene, C. E., DeMartini, N. A., Ragauskas, A. J., and Iisa, K. (2008). "Co-production of ethanol and cellulose fiber from Southern Pine: A technical and economic assessment," *Biomass and Bioenergy* 32(12), 1293-1302.

Gruber, P. R., Henton, D. E., and Starr, J. (2006). "Polylactic acid from renewable resources," *Biorefineries - Industrial Processes and Products* 2, 381-407.

Hakkila, P., Nikki, M., and Palenius, I. (1972). "Suitability of larch as pulpwood for Finland," *Paperi Puu* 54(2), 41-58.

Helmerius, J., Vinblad von Walter, J., Rova, U., Berglund, K. A., and Hodge, D. B. (2010). "Impact of hemicellulose pre-extraction for bioconversion on birch Kraft pulp properties," *Bioresource Technol.* 101(15), 5996-6005.

Hörhammer, H., Walton, S., and van Heiningen, A. (2009). "Producing lactic acid from larch in a kraft mill," Proceedings, The 7th Biennial Johan Gullichsen Colloquium, Espoo, Finland, November 19, 2009. Finnish Paper Engineers' Association, 67-76.

Hörhammer, H., Walton, S., and van Heiningen, A. (2011). "A larch based biorefinery: Pre-extraction and extract fermentation to lactic acid," *Holzforschung* 65(4), 491-496.

Jiang, J. E. (1995). "Extended delignification of southern pine with anthraquinone and polysulfide," *Tappi J.* 78(2), 126-132.

Kautto, J., Henricson, K., Sixta, H., Trogen, M., and Alén, R. (2010). "Effects of integrating a bioethanol production process to a kraft pulp mill," *Nord. Pulp Paper Res. J.* 25(2), 233-242.

Kämppi, R., Hörhammer, H., Leponiemi, A., and van Heiningen A. (2010). "Pre-extraction and PSAQ pulping of Siberian larch," *Nord. Pulp Paper Res. J.* 25(2), 243-248.

Li, N., Tompsett, G. A., Zhang, T., Shi, J., Wyman, C. E., and Huber, G. W. (2011). "Renewable gasoline from aqueous phase hydrodeoxygenation of aqueous sugar solutions prepared by hydrolysis of maple wood," *Green Chemistry* 13, 91-101.

Li, Z., Ma, H., Kubes, G.J., and Li, J. (1998). "Synergistic effect of kraft pulping with polysulphide and anthraquinone on pulp- yield improvement," *J. Pulp Paper Sci.* 24(8), 237-241.

Liu, T., Lin, L., Sun, Z., Hu, R., and Liu, S. (2010). "Bioethanol fermentation by recombinant *E. coli* FBR5 and its robust mutant FBHW using hot-water wood extract hydrolyzate as substrate," *Biotechnology Advances* 28, 602-608.

Luthe, C., and Berry, R. (2005). "Polysulphide pulping of western softwoods: Yield benefits and effects on pulp properties," *Pulp Paper Can.* 106(3), 27-33.

Mendes, C., Carvalho, M., Baptista, C., Rocha, J., Soares, B., and Sousa, G. (2009). "Valorization of hardwood hemicelluloses in the kraft pulping process by using an integrated biorefinery concept," *Food and Bioproducts Processing* 87, 197-207.

Nevalainen, K., and Hosia, M. (1969a). "The suitability of larch as fibre raw material. Part I: Larch and its properties," *Paperi Puu* 51(5), 433-438.

Nevalainen, K., and Hosia, M. (1969b). "The suitability of larch as fibre raw material. Part II: Larch as fibre raw material," *Paperi Puu* 51(6), 503-510.

Overbeck, W., and Muller, H. F. (1942). "Hydrolysis of different wood species with water under pressure and the resulting changes of the wood constituents, the lignin in particular," *Berichte der Deutschen chemischen Gesellschaft* (A and B Series) 75(7), 909-920.

Pekkala, O. (1986). "Prolonged kraft cooking modified by anthraquinone and polysulphide," *Paperi Puu* 68(5), 385-400.

Sjöström, E. (1993). *Wood chemistry. Fundamentals and Applications*, 2nd edition, Academic Press, San Diego, 293.

Sturgeoff, L., and Bernhard, S. (1998). "Synergy of anthraquinone/polysulfide pulping: the effect of sulfidity," Proceedings, TAPPI Pulping Conference, Montreal, Canada, October 25-29, 1998. TAPPI Press, 3-8.

Survase, S. A., Jurgens, G., van Heiningen, A., and Granström, T. (2011). "Continuous production of isopropanol and butanol using *Clostridium beijerinckii* DSM 6423," *Appl. Microbiol. Biotechnol.* 91, 1305-1313.

Teder, A. (1969). "Some aspects of the chemistry of polysulfide pulping," *Svensk Papperstidning* 72(9), 294-303.

Uprichard, J. M., and Gray, J. T. (1973). "Papermaking properties of kraft pulps from New Zealand grown softwoods," *Appita* 27(3), 185-191.

Van Heiningen, A., Tunc, M.S., Gao, Y., and Da Silva Perez, D. (2004). "Relationship between alkaline pulp yield and the mass fraction and degree of polymerization of cellulose in the pulp," *J. Pulp Paper Sci.* 30(8), 211-217.

Van Heiningen, A. (2006). "Converting a kraft mill into an integrated forest biorefinery," *Pulp Paper Can.* 107(6), 38-43.

Vila, C., Romero, J., Francisco, J. L., Garrote, G., and Parajó, J. C. (2011). "Extracting value from *Eucalyptus* wood before kraft pulping: Effects of hemicelluloses solubilization on pulp properties," *Bioresource Technol.* 102, 5251-5254.

Venäläinen, M., Harju, A., Nikkanen, T., Paajanen, T., Velling, P., and Viitanen, H. (2001). "Genetic variation in the decay resistance of Siberian larch (*Larix sibirica* Ledeb.) wood," *Holzforschung* 55(1), 1-6.

Walton, S. L., Bischoff, K. M., van Heiningen, A., and van Walsum, G. P. (2010). "Production of lactic acid from hemicellulose extracts by *Bacillus coagulans* MXL-9," *J. Ind. Microbiol. Biotechnol.* 37(8), 823-830.

Wolf, O., Crank, M., and Marscheider-Weidemann, F. (2005). "Techno-economic feasibility of large-scale production of bio-based polymers in Europe," *Technical Report EUR 22103 EN*, European Communities, 50-65.

Xing, R., Subrahmanyam, A. V., Olcay, H., Qi, W., van Walsum, G. P., Pendse, H., and Huber, G. W. (2010). "Production of jet and diesel fuel range alkanes from waste hemicellulose-derived aqueous solutions," *Green Chemistry* 12, 1933-1946.

Xing, R., Qi, W., and Huber, G. W. (2011). "Production of furfural and carboxylic acids from waste aqueous hemicellulose solutions from the pulp and paper and cellulosic ethanol industries," *Energy Environ. Sci.* 4, 2193-2205.

Yoon, S.-H., MacEwan, K., and van Heiningen, A. (2008). "Hot-water pre-extraction from loblolly pine (*Pinus Taeda*) in an integrated forest products biorefinery," *Tappi J.* 7(6), 27-32.

Yoon, S.-H., and van Heiningen, A. (2008). "Kraft pulping and papermaking properties of hot-water pre-extracted loblolly pine in an integrated forest products biorefinery," *Tappi J.* 7(7), 22-27.

Yoon, S.-H., Cullinan, H., and Krishnagopalan, G. A. (2010). "Reductive modification of alkaline pulping of southern pine, integrated with hydrothermal pre-extraction of hemicelluloses," *Ind. Eng. Chem. Res.* 49, 5969-5976.

Yoon, S.-H., Cullinan, H., and Krishnagopalan, G. A. (2011). "Polysulfide-borohydride modification of southern pine alkaline pulping integrated with hydrothermal pre-extraction of hemicelluloses," *Tappi J.* 10(7), 9-16.