

DILUTE SULPHURIC ACID EXTRACTION OF HEMICELLULOSES FROM *EUCALYPTUS GRANDIS* AND ITS EFFECT ON KRAFT AND SODA-AQ PULP AND HANDSHEET PROPERTIES

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The extraction of hemicelluloses prior to pulping is an attractive process to be incorporated in the pulp and paper mills to generate valuable by-products such as xylose and xylo-oligomers in addition to core products. This paper investigates the impact of xylan extraction by dilute acid on cooking conditions, pulp yield and properties during kraft and soda-AQ pulping of *Eucalyptus grandis* wood chips. Modified soda-AQ pulping of the wood chips from which 21.3% of xylan was extracted using a low alkali charge maintained the pulp yield, viscosity and kappa number of non-extracted wood chips. The combination of these processes resulted in chemical reduction while increasing the digester capacity by 12%. Due to extraction, the handsheet properties were reduced, especially the tear index. The degree of hemicellulose pre-extraction and pulping conditions can be optimized based on final paper application.

Keywords: biorefinery, kraft pulping, soda-AQ pulping, dilute acid, hemicelluloses pre-extraction, *Eucalyptus grandis*

INTRODUCTION

Increasing interest in sustainable and renewable energy from lignocellulose sources has fostered the research and development of processes to be incorporated in the current pulping mills for co-production of pulp and other commodities such as biofuels.¹ During commercial chemical pulping processes, a significant amount of hemicelluloses and small amounts of cellulose are removed from wood together with lignin in the black liquor.² The black liquor is generally burned in the chemical recovery unit along with lignin to produce heat and power for mill operations.² However, hemicelluloses provide less than 20% of the total energy for a recovery furnace as the bulk of the energy is derived from the burning of lignin.³ This means that hemicelluloses are not utilized efficiently in the combustion process. Hemicelluloses such as xylan can be used as raw material for the production of xylo-oligosaccharides (XOS), furans, xylitol, bioethanol or as strength additives for paper-making,^{1,4,5} which represents a significantly higher value application than thermal energy production. The extracted hemicellulosic products

are complex, hindering their separation and further purification from the pulping black liquor.⁶ In this context, the extraction of hemicelluloses prior to pulping could provide value-added products in a pulp mill biorefinery approach.^{1,7} Moreover, as extraction reduces the mass of wood material, it enables the loading of more material in the digester thereby improving productivity.^{8,9} Other benefits associated to a pre-extraction step include reduction of non-process elements (NPE) and extractives in the feedstock that cause problems during pulping, reduction of pitch problems and removal of glucuronic acids from the xylan, preventing hexenuronic acid formation during kraft pulping.⁷ All these aspects would result in a decrease of cooking and bleaching requirements, while enhancing the brightness properties.⁷

Dilute acid pretreatment has been proven a good method for the extraction of hemicelluloses with recovery yields of up to 80%.¹⁰ The amount of extracted hemicelluloses, however, must be limited since a required amount of hemicelluloses is necessary in the pulp to maintain pulp yield and paper properties.^{11,12} The extraction of

hemicelluloses from hardwoods (aspen, birch, *E. globulus*, and sugar maple) with dilute acids prior to kraft or soda-AQ pulping has been performed on laboratory,^{7,13} semi-large and industrial scale.^{12,14} The application of dilute acid extraction prior to the kraft pulping process has been shown to decrease the overall pulp yield of the extracted wood chips and other pulp properties such as viscosity and brightness.⁷

The combination of acid extraction and subsequent soda-AQ pulping of the extracted wood chips afforded higher pulp yields than when the kraft pulping process was used.¹³ Other extraction methods, such as hot water, also imply reduction on pulp yields, but with comparable pulp viscosity.^{11,15} The overall assessment of the results obtained from the reference studies shows that the major disadvantages of performing an acid extraction prior to pulping are decreased pulp yield and reduction in strength properties of pulps, due to cellulose depolymerisation (hydrolysis) and decreased residual xylan content.^{11,12,14} Thus, careful selection of the dilute acid extraction conditions is necessary to minimise the negative impact on residual fibres.

Eucalyptus grandis is one of the main timber sources for pulp and paper production in South Africa.^{16,17} The objective of this study was to investigate the yield of dilute acid xylan extraction under various pretreatment conditions from *E. grandis* grown in South Africa prior to alkaline pulping. The pretreatment liquors were evaluated in terms of xylose, XOS and inhibitors content. Kraft or soda anthraquinone (soda-AQ) pulping was performed on the extracted lignocellulose residue to develop a combined process for the production of a hemicelluloses hydrolysate and pulp.

The feasibility of these integrated processes was evaluated not only by the xylose and XOS yield, but also by the xylan and the nature of holocellulose retained in the wood chips for the subsequent pulping process. Pulping of selected extracted wood chips with different residual xylan content was performed on a microscale under different conditions and compared with unextracted wood chips (control). The preferred pulping conditions were adjusted to be applied on a large scale. The effect of xylan extraction on pulp yield and pulp quality measured as handsheet properties was determined.

EXPERIMENTAL

Materials

Eucalyptus grandis chips were supplied by Sappi Manufacturing, Pty (Ltd), South Africa. The *E. grandis* chips were screened and a 4-8 mm chip size fraction was selected for further experiments. The material was conditioned at 23 °C and 55% relative humidity before use. Sodium hydroxide (NaOH) and sulphuric acid (H₂SO₄) were purchased from Merck, and BUSPERSE 2262 anthraquinone (AQ) was obtained from Buckman Laboratories, Hammarsdale, South Africa.

Hemicelluloses extraction of *E. grandis* wood chips

Experimental design

The experiments on dilute acid extraction were carried out according to a 2³ full factorial experimental design created and evaluated in Statistica 7.1 (Statsoft Inc., Tulsa, USA) and Design Expert version 8. Dilute H₂SO₄ extraction variables were: acid concentration (0.3-0.7% v/v), temperature (120-140 °C) and extraction time (20-40 min). The variables and their corresponding coded levels are depicted in Figure 1. Three assays were carried out at the center point to estimate the random error required for the analysis of variance (ANOVA). Xylose and XOS yield of the pretreatment liquor were taken as the responses of the factorial designs. The statistical significance of the regression coefficient was determined by the coefficient of determination, R².

Dilute acid extraction

Air dried samples containing 100 g oven dry wood chips (4-8 mm thickness) and H₂SO₄ solutions were mixed according to a 2³ full factorial design and introduced into microreactors (bombs). The solid to liquor ratio was 1:4 g/mL. The filled bombs were placed in a digester of 15 dm³ capacity enclosed by heating jackets. The selected reaction temperatures were monitored with thermocouples at different extraction times.

After extraction, the bombs were cooled in room temperature water. The liquid and the solid fractions were separated by filtration on a 100 mesh screen. The liquid fraction was filtered through 0.2 µm membranes and analysed for sugars and by-products, as described next. The liquid fractions were further subjected to a post hydrolysis treatment using mild acid hydrolysis to convert all remaining oligosaccharides to monosaccharides, according to the NREL method.¹⁸

Chemical analysis of raw and pretreated solids

The fraction of air dried *E. grandis* chips was subsampled and ground in a Retsch mill to 40 mesh size. Oven dry mass (ODM) was obtained by heating at 105±2 °C until a constant mass was achieved. The ethanol/cyclohexane solubility (TAPPI method T264 om-88), water solubility (T264 om-88), ash (T211 om-

85) and acid insoluble lignin (T222 om-88) of *E. grandis* were determined.¹⁹ Four replicates were used. The amounts of glucan, xylan and arabinan on both extractive-free raw material and pretreated solids were determined by double acid hydrolysis according to the

National Renewable Energy Laboratory (NREL) Analytical Procedure (LAP 013).²⁰ Simple sugars (glucose, xylose and arabinose) in extractive-free *E. grandis* were analysed by HPLC, as described below.

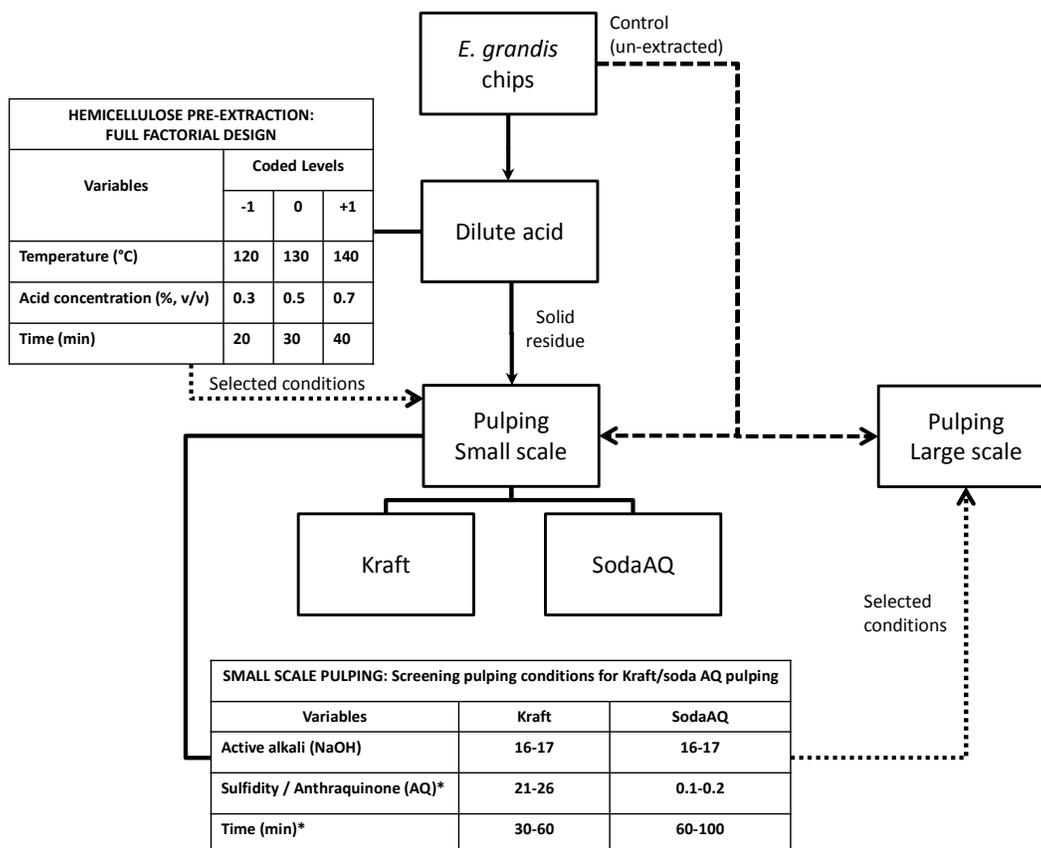


Figure 1: Experimental design followed in this study

The wood chips obtained after dilute H_2SO_4 extraction were rinsed with distilled water until neutral pH was reached, and air dried. The solid fraction was milled to 40 mesh size and the polysaccharides and residual lignin content were determined using the same standard methods as those used for the raw materials, except for the extractives determination.²⁰ The extraction mass balance (EMB) can be calculated with the following equation:²¹

$$\frac{\text{Extraction mass}}{\text{balance}} = \frac{\sum C_L + \sum C_S}{\sum C_R} \quad (1)$$

where C_i is the mass of each sugar (glucose or xylose) component as determined through HPLC, the subscripts L, S, R refer to the extracted liquid, extracted solids and raw *E. grandis*, respectively.

HPLC analysis

The sugars (xylose, glucose and arabinose), acetic acid, and by-products (furfural and hydroxymethyl-

furfural (HMF)) present in the liquid fraction were analysed by HPLC. The high pressure liquid chromatograph (HPLC) system used for quantification comprised a Spectra System P2000 pump, an auto-sampler (AS3000), a UV1000 detector and a Shodex RI-101 refractive index detector. An Aminex HPX-87H Ion Exclusion Column was equipped with a Cation-H cartridge (Biorad, Johannesburg, RSA). Sugars were measured with an RI detector, whereas the acetic acid, furfural and HMF were analysed with a UV detector. The column was operated at 65 °C with a mobile phase of 5 mM H_2SO_4 and a flow rate of 0.6 mL min⁻¹.

Microscale pulping after hemicelluloses extraction

The acid extracted *E. grandis* wood chips were thoroughly washed with water to remove the acid and air dried. *E. grandis* wood chips from extraction runs 3, 4 and 8 were submitted to kraft or soda-AQ micropulping. The cooking conditions were selected in

agreement with previous work done on kraft or soda-AQ pulping of hardwoods^{17,22,23} to achieve a kappa number range of 20-27. Pulp kappa number (parameter related with residual lignin content in pulp) was determined by standard TAPPI method T236 cm-85.¹⁹

The screened cooking conditions for Kraft pulping were: active alkali (NaOH): 16 or 17%, sulfidity: 21-26%, and pulping time: 30-70 min. The range of cooking conditions for soda-AQ pulping were: active alkali (NaOH): 16-17%, anthraquinone: 0.1-0.23%, and pulping time: 50-100 min. Non-extracted *E. grandis* chips were also exposed to kraft or soda-AQ pulping under the same cooking conditions for comparison.

The maximum cooking temperature was kept constant at 170 °C and the solid-to-liquid ratio was fixed at 1:4 g/mL dry mass for all pulping experiments. Pulping experiments were carried out in microreactors (bombs) on dry wood chips containing 100 g oven dry material. Temperature and reaction time were monitored during the process. Cooking time was measured from the moment the system reached the maximum temperature.

At the end of cooking, the fibres were separated from the black liquor and washed through a 10 mesh screen to separate the rejects (uncooked pieces of wood chips) from the fibres. The accepted pulp was collected on a 100 mesh screen. The pulp was then screened through a 0.15 mm screen to remove shives (uncooked fibre bundles) and then spin dried to a consistency of approximately 30%. The pulp was weighed and a representative sample of the known mass was then dried in an oven at 105 °C until a constant mass was reached, to establish the moisture content. The mass of oven dry pulp was then calculated. Screened pulp yield was calculated as a percentage of this value obtained in relation to the initial ODM of the raw material using the formula 2:

$$\text{Pulp Yield (\%)} = \frac{\text{Oven dry mass of pulp}}{\text{Initial oven dry mass } E. grandis} \times 100$$

The rejects and the shives collected were placed in an oven to dry at 105 °C until a constant mass was reached to establish the oven dry mass and weighed. The reject and shive contents together were expressed as a percentage of the original dry mass of *E. grandis*.

Large scale pulping after hemicelluloses extraction

Pre-extracted wood chips yielding the best results in micropulping were also pulped on a larger scale in a 15 dm³ batch type digester. Solid residue from run 3 of dilute acid CCD (0.3% v/v H₂SO₄, at 140 °C for 20 min) was subjected to kraft or soda-AQ pulping processes. Non-extracted wood chips were pulped for comparison. Selected cooking conditions for kraft and soda-AQ were applied, however, the cooking time was extended to reach the targeted kappa number range of 20-27.

Kraft pulps of non-extracted and H₂SO₄ extracted wood chips were generated by exposing 1000 g dry mass non-extracted or 885.2 g dry mass extracted material to 17% active alkali (NaOH) and 22% sulfidity for 90 minutes at 170 °C. For soda-AQ pulps, 1000 g dry mass non-extracted or 882.9 g dry mass extracted material were exposed to a solution of 17% active alkali (NaOH) and 0.15% anthraquinone (AQ) for 120 minutes at 170 °C. At the end of the cooking process, the fibres were treated as explained in the previous section. All active alkali and sulfidity masses were expressed as equivalent mass of Na₂O.

Characterization of pulping black liquors

Pulping black liquors were analysed for residual active alkali (RAA) according to TAPPI standard methods T625 cm-85 (TAPPI 1992).¹⁹

Pulp evaluation and handsheet formation

Pulp tests were performed according to standard methods of the Technical Association of the Pulp and Paper Industry.¹⁹ Total pulp yield, rejects and kappa number were determined as described above. Pulp viscosity (parameter related with the degree of depolymerisation of pulp polysaccharides) was measured with a Brookefield viscometer. Pulp viscosity was determined by dissolving the pulp sample into a cupriethylenediamine solution prepared according to TAPPI methods T230 om-89. The pulp solution was transferred to a Brookefield RVTD 382 viscometer and agitated at 100 rpm using a spindle number 21. The pulp viscosity was measured in centipoises (cP).

The development of handsheet strength, i.e. tear, burst and breaking strength of the pulp fibres, was evaluated by beating, using a Valley beater according to Tappi Standard T200 om-89. The pulp samples were beaten at different intervals and the drainage rate in Schopper Riegler (°SR) was measured according to Tappi T227 om-99. Handsheets were formed according to Tappi T205 om-88 using British Standard handsheet making equipment.

Testing of handsheet physical strength properties

All handsheets were conditioned for 48 hours at 55% relative humidity and 23 °C before being tested. The following strength properties were evaluated of each of ten handsheets according to TAPPI standards.¹⁹ Burst index, breaking length and tear index were measured by TAPPI standards T403 om-91, T404 om-87, and T414 om-88, respectively. The brightness was measured in ISO units using a reflectance photometer (Zeiss Elrepho 65843, Germany).

RESULTS AND DISCUSSION

Dilute acid extraction of *E. grandis* wood chips

The chemical composition of *E. grandis* wood chips is listed in Table 1. *E. grandis* contained a

total of 3.3% extractives, 1.5% ash, 47.2% glucan, 14.9% xylan, 0.5% arabinose and 26.8% Klason lignin. These results compared well with those reported in the literature.^{24,25} *E. grandis*, like other hardwoods, has a high proportion of xylan compared to arabinan, indicating that a substantial amount of xylose will be generated during the acid extraction process.^{26,27} Chips of *E. grandis* were subjected to dilute acid under different conditions according to a full factorial experimental design (Figure 1). Although maximum xylose extraction is preferred for ethanol production, the range of conditions was limited to reduce both cellulose solubilization and inhibitors formation, while ensuring that the solid residues present residual xylan. Thus, the applied conditions could favor the formation of xylo-oligomers (XOS) in the pretreatment liquor, which represent another potential product of interest in the food industry given their prebiotic properties.²⁸

The composition of the liquid and solid fractions after different dilute H₂SO₄ extraction conditions of the *E. grandis* wood chips is shown in Table 2. The liquid fraction consisted of a mixture of sugars, sugar oligomers, xylose and glucose degradation products (furfural and hydroxymethylfurfural, respectively), acetic acid (generated from acetyl groups) and acid soluble lignin (ASL). Temperatures greater than 120 °C were required to solubilize the xylose (21.3-60.2% of the xylan in raw material). The maximum xylan recovery of 60.2% (determined as 47.4% monomeric and 12.8% oligomeric) was obtained under the most severe conditions (run 8: 140 °C, 30 minutes, 0.7% sulphuric acid; Table 2). The central point (runs 9-11: 130 °C, 30 minutes, 0.5% sulphuric acid; Table 2) showed slightly lower XOS yield of 11.6%, suggesting that the optimum for XOS release could be

around the higher level of the parameters evaluated and that these conditions were not severe enough to hydrolyze the extracted XOS into monosaccharides. As expected, run 8 also resulted in the highest levels of inhibitors, such as furans (0.88 g/L) and acetic acid (5.7 g/L) as well as 2.7% solubilization of lignin. These substances reduce the performance of fermentative microorganisms, so generally a detoxification step is applied to render the liquid fraction suitable to be used for the production of biofuels such as bioethanol.^{7,29}

Chemical analysis of extracted *E. grandis* wood chips was performed to examine changes of cellulose (glucan), lignin and xylan content caused by the extraction process (Table 2). Dilute H₂SO₄ extraction can selectively solubilise xylan resulting in glucan rich solid residues. However, most hardwoods contain about 5-10% easily hydrolysable cellulose, which is dissolved under dilute concentrations below 1% (v/v) and at moderate temperatures.² The glucan content in the solid residues after dilute acid extraction varied from 42.6% to 46.4% of the original material (47.2%, oven dry mass). Hydrolysis (depolymerisation) could result in cellulose with a reduced degree of polymerization (DP) and the formation of new reducing end groups, which can possibly increase peeling reactions in the subsequent high alkaline pulping process, resulting in a lower pulp yield.^{7,29}

The xylan retained in the extracted wood chips was obviously influenced by xylan solubilisation during the acid extraction. The xylan content of wood chips from dilute sulphuric acid pre-extraction varied from 5.2% to 14.4% dry mass, which corresponded to 34.9 and 96.6%, respectively, of the xylan present in the non-extracted *E. grandis* wood chips (14.9%, Table 1).

Table 1
Chemical composition of non-extracted *E. grandis* wood chips

Component		% ODM	Analytical methods
Extractives	Ethanol/Cyclohexane soluble extractives	2.2 ± 0.2	TAPPI T264 om-88
	Water soluble extractives	1.1 ± 0.4	
Carbohydrates	Glucan	47.2±4.2	LAP 013
	Xylan	14.9±1.1	
	Arabinan	0.5	
Klason lignin	(Acid insoluble lignin)	26.8± 1.7	TAPPI T222 om-88
Ash content		1.5 ± 0.5	TAPPI T211 om-85

*Mean values and standard deviation of four measurements;

Components are expressed as percentage of the original oven dry material (% ODM)

Table 2
Composition of liquid and solid fractions after sulphuric acid extraction of *E. grandis* under process variables defined by a 2³ full factorial design

Pre-extraction conditions				Liquid fraction								Solid fraction			EMB		
Run	H ₂ SO ₄ %	Temp °C	Time min	Xyl %	^a Xyl % theoretical	Xylo- oligomer %	^b Xylan recovery yield %	Glc %	ASL %	Acetic acid g/L	Furfural + HMF g/L	Glc %	Xyl %	AIL %	Glc %	Xyl %	Lignin %
	x ₁	x ₂	x ₃														
1	0.3	120	20	0.1	0.5	0.6	1.1	0.2	0.4	0.9		46.1	14.4	24.9	98.1	97.8	94.4
2	0.3	120	30	0.1	0.5	1.4	1.9	0.3	0.7	2.1	0.31	45.3	13.7	25.2	96.7	93.8	96.6
3	0.3	140	20	3.2	19.5	1.8	21.3	0.4	1.4	1.3	0.2	43.1	11.4	24.0	92.2	98.0	94.8
4	0.3	140	30	4.5	30.3	9.2	39.5	0.5	1.9	2.9	0.18	43.9	8.4	25.3	94.0	95.9	101.5
5	0.7	120	20	0.2	1.5	3.4	4.9	0.1	0.5	0.8		44.9	12.9	25.4	95.5	91.5	96.6
6	0.7	120	30	0.5	3.4	3.1	6.5	0.2	0.7	0.7	0.03	46.4	13.3	24.6	98.7	95.8	94.4
7	0.7	140	20	5.2	35.2	5.1	40.2	0.4	2.5	4	0.29	43.0	8.4	23.9	91.9	96.6	98.5
8	0.7	140	30	7.1	47.4	12.8	60.2	0.7	2.7	5.7	0.88	43.2	5.2	25.8	93	95.0	106.3
9-	0.5	130	25	5.0	33.6	11.6	45.2	5.0	1.7	3.4	0.02	42.6	7.2	23.9±	91.2	93.2	94.8
11				±	±	±	±	±	±	±		±	±	1.3			
				0.2	1.7	1.5	1.4	1.0	0.1	0.1		0.2	0.5				

^aAnalysis data are based on the oven dry mass of xylan in non-extracted *E. grandis*

^bObtained by addition of Xylose (% theoretical) and Xylo-oligomer (%)

^cAnalysis data are based on the oven dry mass of non-extracted *E. grandis*

^dExtraction mass balance (EMB) was calculated for each component in the *E. grandis* as e.g. xylan in the liquid and solid fraction after Run 3 was 3.2% and 11.4%, respectively, and the raw *E. grandis* had 14.9% xylan before the extraction. The total extraction mass balance = $[(3.2+11.4)/14.9]*100 = 98.0\%$

*Xyl – Xylan; Glc – Glucan; ASL – Acid soluble lignin; AIL – Acid insoluble lignin

The quantity of xylan removed from the wood chips under dilute acidic conditions prior to pulping might reduce the interfibre bonding of the pulp, hence a decrease in the tensile and burst indexes of handsheets may be observed.^{7,11,30}

Dilute H₂SO₄ extraction resulted in enrichment of lignin in the solid residues, sometimes above 100% of the lignin content determined in raw material (Table 2; run 4 and run 8). The generation of pseudolignins could explain the increase in acid insoluble (Klason) lignin content in the solid residue after acid extraction. The formation of polymeric lignin-like structures (pseudolignins) can occur under acid conditions in batch systems for lignocellulose treatment.³¹ It has been further suggested that sugar and/or sugar degradation products (such as furfural) also react with lignin to form pseudolignins. Fibers covered by lignin could retard the penetration of chemicals and lignin solubilisation during pulping of the extracted wood chips.¹⁴

Statistical analysis of xylose and XOS recovery on pretreatment liquor

Statistical analysis was performed to evaluate the influence of process variables (temperature, time and acid concentration) on xylan solubilisation and subsequent recovery in the liquid fraction. A first order model was developed to describe the influence of (A) temperature, (B) H₂SO₄ concentration and (C) extraction time on the recovery of total xylose (y_1) and XOS (y_2) in the liquid fraction. The statistical significance of the model is shown in Table 3. The model and all the parameters evaluated were statistically significant for both xylose and XOS at 95% confidence level ($p < 0.05$). Likewise, there was statistically significant positive interaction between temperature with both acid concentration (p value of 0.0025) and residence time (p value of 0.0017) for xylose recovery, while for XOS only temperature and time interaction were significant (p value of 0.0261). The extent of the impact of the different factors and their interactions on the xylan extraction and XOS, within the studied range, is illustrated in a Pareto chart (Figure 2A and B). As it can be observed, the temperature was the main factor promoting xylan solubilization and recovery from *Eucalyptus* chips, followed by acid concentration, residence time and the interactions of temperature with time and acid

loading. For the XOS recovery, temperature was also the main effect followed by the time, interaction of time and temperature, and acid concentration. The significance of each factor and their interactions are further corroborated by equations, expressed with coded variables that exerted influence on the xylan (3) and XOS (4) recovery:

$$y_1 = 28.9 + 18.35A + 6B + 5.07C + 3.9AB + 4.5AC \quad (3)$$

$$y_2 = 4.67 + 5.1A + 2.85B + 3.9C + 3.65BC \quad (4)$$

The response surfaces described by the above model equations are illustrated in Figure 2. The xylose recovery, as monomer and oligomeric, is plotted as a function of H₂SO₄ concentration and temperature at a fixed extraction time of 25 minutes (Figure 2A). The response surface showed that an increase in H₂SO₄ concentration and temperature would increase further the recovery of xylose product in the liquid fraction after solubilisation, expressed as percentage of xylan present in the raw material. Similarly, the response surface for XOS yield indicates that an increment in temperature and time would increase the XOS content in the pretreatment liquor for the highest acid concentration (0.7%, Figure 2B). However, the same conditions produced undesired sugar degradation products, such as furfural and HMF (Table 2), which limit the values of the control parameters of the extraction process.^{7,10}

Evaluation of pulp properties on microscale

The inclusion of a pre-extraction step should be directed towards the selective removal of the hemicelluloses with minimal detriment of the pulp yield and quality. Enough xylan should be retained in the extracted wood chips, as it is required to improve pulp quality.^{12,32} *E. grandis* chips obtained from dilute H₂SO₄ pre-extraction condition runs 3, 4, and 8 were selected for further pulping. These three dilute H₂SO₄ conditions were selected to evaluate the impact of different degrees of xylan extraction and therefore, different amounts of residual xylan in the solid residue (76.5, 56.4 and 34.9% of the xylan in the raw material for the runs 3, 4 and 8, respectively) on subsequent pulping. Micropulping experiments of non-extracted *E. grandis* chips were performed as control. Screening criteria were used to identify the pulping conditions for *E. grandis* chips obtained after xylan extraction that could

provide similar pulp yield and kappa number, as those of pulps produced from non-extracted

material (Figure 1).

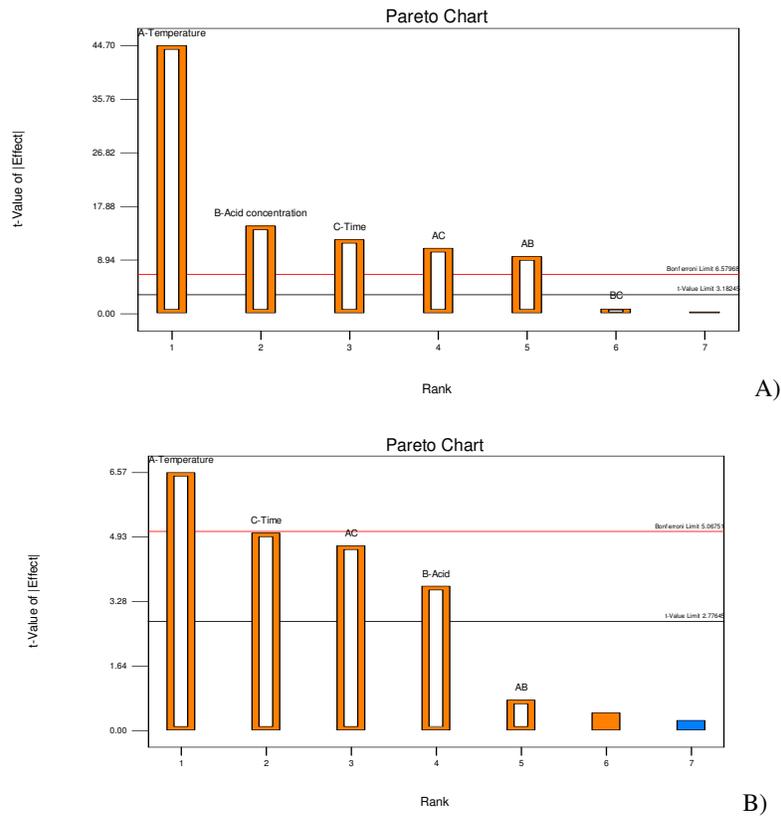


Figure 2: Standardized Pareto chart to estimate the effects of temperature, acid concentration, and extraction time on xylan recovery after dilute acid extraction; (A) xylan recovery considering xylose and xylo-oligosaccharides (XOS); (B) XOS yield

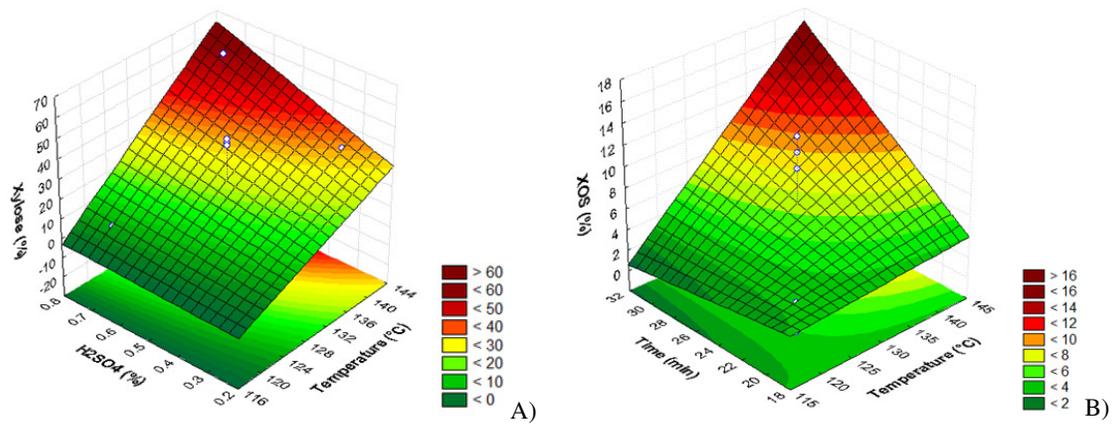


Figure 3: Estimated response surface described by the model equations (3) and (4) for: (A) xylan recovery and (B) xylo-oligosaccharides yield obtained after sulphuric acid extraction. Xylan recovery graph is showing the influence of temperature and sulphuric acid concentration for an extraction time of 25 minutes, while XOS yield is showing the influence of temperature and time at a fixed acid loading of 0.7%

Table 3
Analysis of variance for the regression models of xylose (A) and xylo-oligosaccharides (B) recovery after dilute sulphuric acid extraction of *E. grandis* chips

	Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob > F
A)	Model	3470.56	6	578.43	428.99	0.0002
	A-Temperature	2693.78	1	2693.78	1997.86	< 0.0001
	B-Acid concentration	288.00	1	288.00	213.60	0.0007
	C-Time	206.05	1	206.05	152.81	0.0011
	AB	121.68	1	121.68	90.24	0.0025
	AC	160.20	1	160.20	118.82	0.0017
	BC	0.85	1	0.85	0.63	0.4864
	Curvature	1179.41	1	1179.41	874.72	< 0.0001
	Residual	4.05	3	1.35		
	Lack of Fit	0.13	1	0.13	0.064	0.8242
	Pure Error	3.92	2	1.96		
	Cor Total	4654.01	10			
	R ²	0.998				
B)	Model	126.13	6	21.02	13.29	0.0289
	A-Temperature	52.02	1	52.02	32.88	0.0105
	B-Acid concentration	16.24	1	16.24	10.27	0.0491
	C-Time	30.42	1	30.42	19.23	0.0219
	AB	0.72	1	0.72	0.45	0.5482
	AC	26.64	1	26.64	16.84	0.0261
	BC	0.08	1	0.08	0.05	0.8365
	Curvature	104.63	1	104.63	66.15	0.0038
	Lack of Fit	0.24	1	0.24	0.11	0.7728
	Pure Error	4.74	3	1.58		
	Cor Total	235.50	10			
	Residual	4.74	3			
	R ²	0.9798				

The comparative values of screened pulp yield, rejects and kappa number of the pulps obtained from extracted *E. grandis* wood chips and non-extracted wood chips after kraft and soda-AQ microscale pulping are shown in Table 4 and Table 5, respectively. Compared with the control, the residues with a limited amount of residual xylan (run 4 and run 8) produced dark and lower yield pulps (2.3-19.8% lower pulp yield compared to control) with higher rejection levels, especially in pulps obtained from soda-AQ (3-12.4% higher rejection levels). On the contrary, the solid residues from run 3 (11.4% of xylan) presented less difference in pulp yield compared to non-

extracted wood chips. The decrease in pulp yield could be attributed to insufficient cooking (higher rejects due to uncooked material)³³ and the reduction of xylan content together with the decrease in its molecular mass under acidic conditions. These reductions leave the cellulose more exposed to peeling reactions during the pulping process as demonstrated in Eucalyptus and aspen chips.^{7,34} Furthermore, the presence of (pseudo)lignin in these solid residues (run 4, run 8, Table 2) might have affected the ability of pulping liquor to penetrate and diffuse through the cell wall structure of the plant material, hence increasing rejection levels.²⁵

Table 4
Kraft pulping results for different pulping conditions for run 3 (21.3%); run 4 (39.5%) and run 8 (60.2%) xylan extracted from *E. grandis* chips

Kraft pulping process														
Pulping conditions			Screened pulp yield (%)				Kappa number				Rejects (%)			
AA (%)	Sulfidity (%)	Time (min)	run 3	run 4	run 8	non-extraction	run 3	run 4	run 8	non-extraction	run 3	run 4	run 8	non-extraction
16	22	30	52.8	34.2	32.4	46.5	34.4	33.8	33.7	30.3	0.06	1.14	0.43	0.10
16	22	60	47.0	33.9	28.6	44.9	33.5	33.3	35.3	30.9	0.04	1.32	1.29	0.31
16	25	30	45.3	37.5	28.8	45.1	34.7	32.9	34.9	30.2	1.06	0.92	0.57	0.56
16	25	60	47.9	31.9	27.2	43.6	34.2	33.5	34.0	29.6	0.04	1.42	1.05	0.08
17	20.98	45	47.1	32.5	35.0	52.3	34.2	33.0	33.8	28.8	0.06	0.21	0.46	0.08
17	23.5	45	38.9	33.4	33.7	46.0	33.9	33.1	32.6	29.4	0.1	0.1	0.1	0.1
17	26.02	45	44.0	37.8	43.2	56.3	33.2	32.8	33.1	28.1	0.13	0.15	0.12	0.06
17	23.5	70	43.1	28.2	42.0	44.3	33.3	32.6	33.6	29.6	0.08	0.10	0.07	0.12

Table 5
Soda-AQ pulping results for different pulping conditions for run 3 (21.3%) and run 4 (39.5%) xylan extracted from *E. grandis* chips

SodaAQ pulping process												
Pulping conditions			Screened pulp yield (%)			Kappa number			Rejects (%)			
AA (%)	AQ (%)	Time (min)	run 3	run 4	non-extraction	run 3	run 4	non-extraction	run 3	run 4	non-extraction	
16	0.10	60	45.6	29.2	46.8	37.8	40.1	31.9	10.6	11.89	0.44	
16	0.10	90	37.3	31.1	48.8	39.6	40.1	31.4	13.1	12.04	0.74	
16	0.2	60	42.0	29.7	44.2	37.8	40.0	32.3	6.7	12.08	0.62	
16	0.2	90	37.9	31.3	48.7	39.6	40.1	31.9	8.5	10.14	0.75	
17	0.15	50	50.5	35.9	49.9	36.7	39.8	33.0	4.2	11.06	1.24	
17	0.15	75	41.2	33.3	48.9	37.6	39.9	31.9	7.4	9.8	0.3	
17	0.15	100	36.7	35.7	50.2	39.7	39.7	30.7	7.5	7.30	0.54	
17	0.23	75	40.3	34.1	49.4	38.9	39.9	31.9	5.4	2.08	1.49	

Table 6

Kraft and soda-AQ large scale pulping conditions and pulp characteristics for non-extracted and dilute acid extracted *E. grandis* wood chips (21.3% dry mass xylan extracted with 0.3% v/v H₂SO₄ at 140 °C for 20 min)

Cooking parameters	Pulping process			
	Kraft		SodaAQ	
	Non-extracted	0.3% v/v H ₂ SO ₄ , 140°C, 20 min	Non-extracted	0.3% v/v H ₂ SO ₄ , 140°C, 20 min
Pulping conditions				
Active alkali (%)	17	17	17	17
Sulfidity (%)	22	22	-	-
Anthraquinone (%)	-	-	0.15	0.15
Time at 170 °C (min)	90	90	120	120
Chips/residue (OD, g)	1000	885.2	1000	882.9
NaOH in chips/residue (g)	170	150.4	170	150.1
NaOH from Na ₂ S (g)	24.1	21.4		
NaOH total in cook (g)	194.1	171.8		
NaSH charge (g)	39.6	35		
Pulp characteristics				
Screened pulp yield (%)	45.7±1.0	40.9±2.0	43.9±0.5	42.3±1.5
Rejects (%)	1.7±0.5	5.2±0.3	4.4±1.1	4.1±0.8
Kappa number	20.0±2.5	26.8±1.5	22.8±2.0	20.9±1.3
Viscosity (cP)	7.2±1.2	5.2±1.1	6.3±1.2	6.7±2.1
Carbohydrate composition of pulp according to LAP 013				
Glucan (%)	72.7	72.1	77.7	72.7
Xylan (%)	22.3	18.1	21.8	20.7
Black liquor characteristics				
Residual alkali (g/L)	7.4±2.0	2.9±1.4	3.8±1.5	3.2±1.3

A potential advantage of a hemicellulose pre-extraction step prior to pulping is the improvement of the delignification rate during pulping, which would reduce the cooking time and the amount of chemicals required to reach a target kappa number.^{7,13,35} However, the kappa numbers of the pulps from pre-extracted chips were superior to the control for the pulping conditions evaluated aiming at maintaining the pulp yield. For example, similar pulp yields for pre-extracted (11.4% residual xylan) and non-extracted chips (52.8% vs 52.3%) were obtained under kraft pulping conditions (16% active alkali, 22% sulfidity for 30 minutes for the extracted chips and 17% active alkali, 21% sulfidity for 45 minutes for the un-extracted ones, respectively; Table 4). Although pre-extracted material required lower alkali charge (1% less) and shorter cooking time (15 minutes), these benefits are counteracted by the larger kappa number of the pre-extracted pulp (34.4 vs 28.8 in control) as the need for a stronger delignification would reduce the pulp yield.⁷ Similar to kraft pulping, dilute acid extraction allowed a reduction in cooking time (50 minutes) with an aqueous solution of 17% active alkali and 0.15% AQ to reach a comparable pulp yield to that of the

control (50.5%). A comparable trend of reduction in cooking time was observed when sugar maple chips were given an acid pretreatment and then delignified by soda-AQ.¹³ However, the kappa number of the pulps from pre-extracted residues was also higher than that of the control (36.7 vs 30.7 in control, Table 5), which would imply a delignification step.

Based on these results, the wood chips pre-extracted with dilute acid at 140 °C with acid loading of 0.3% (v/v) for 20 minutes (run 2, Table 2), from which 21.3% of xylan was extracted, was therefore preferred for further large scale pulping and evaluation of pulp quality and handsheet paper strength.

Evaluation of pulp properties from dilute acid extracted wood chips on a large scale

The selected pre-extracted chips were pulped on a large scale to confirm the micropulping results. Non-extracted wood chips were also pulped under the same conditions as the reference. Based on the micropulping results, the pulping time was extended to 90 and 120 minutes for kraft and soda-AQ, respectively, in order to establish the desired bleachable kappa number range (20-

27). The pulping conditions, yields and pulp properties for the control and acid pre-extracted chips are presented in Table 6. Acid extraction can be beneficial due to improvement of the pulping capacity by 12% since the extracted wood chips have a lower mass (882.9-885.2 g) compared to non-extracted ones (1000 g). The combination of dilute acid with kraft or soda-AQ pulping resulted in a reduction of chemicals per cook, although no net reduction per gram of pulped material. As expected, the extension of cooking time resulted not only in a reduction of kappa number, but also in a reduction of pulp yields from both un-extracted and pre-extracted chips.^{7,22}

The combined process of dilute H₂SO₄ xylan extraction and modified soda-AQ pulping gave comparable results to the control. The screened yield, viscosity, reject levels, kappa numbers and residual active alkali were similar to those of non-extracted wood chips, probably due to the protective behavior of AQ on polysaccharides against peeling reactions.^{23,36,37}

On the contrary, dilute acid extraction caused reduction in the screened pulp yield, viscosity and residual active alkali of the kraft process at higher kappa number relative to non-extraction. These findings are consistent with those reported in the literature for the combined process of acid extraction of hardwoods and kraft pulping process.^{7,14} The screened pulp reduction could be explained by the greater rejects (5.2% versus 1.7% in control) due to the reduction in xylan and degradation of carbohydrates during the process, as corroborated by the reduction of the viscosity. The lower values of residual alkali in the black liquor from kraft digestion of pre-extracted chips (2.9 g/L versus 7.4 g/L in the non-extracted) indicated a higher demand of active alkali during the pulping process. The dilute acid pre-extraction soda-AQ pulping of pre-extracted chips led to just a slight reduction in the residual alkali compared with the control (3.2 and 3.8 g/L for the extracted and control, respectively). Nonetheless, the values are still inferior to the recommended dosage of 6-8 g/L and those achieved in the kraft control (7.4 g/L), implying the need of more cooking chemicals to achieve the same level of delignification.

Effect of dilute acid xylose extraction on handsheet properties

The extraction of hemicelluloses from wood chips prior to chemical pulping results in the modification of fibres, which might affect the properties of the handsheets produced from these pulps.^{7,11,34} The burst index, tensile index, tear index, breaking length and ISO brightness of handsheets produced from kraft and soda-AQ pulps are illustrated in Figure 4. All the pulps were beaten to enhance the fibre-fibre bonding, thereby improving handsheet strength properties. The beating degree of about 40 °SR was found to be optimal for all pulps.

The dilute H₂SO₄ extraction resulted in the reduction of the overall handsheet strength and optical properties at the maximum degree of beating for both kraft and soda-AQ pulping (Figure 4). The main handsheet property influenced by the hemicellulose extraction was the tear index for both pulping treatments, with a reduction of 41.7 and 54.5% for Kraft and soda-AQ, respectively. Lower reductions were observed for both pulping methods on other properties, such as burst index (reduction of about 17%) and tensile index (12-15% reduction). The breaking length of the handsheets from pre-extracted chips that underwent soda-AQ treatment seemed to be the least influenced parameter with a reduction of 8% compared to the control. There was a slight gain in the brightness of the handsheets originated from soda-AQ pulps from pre-extracted chips. These results are in line with those of other studies on hardwoods, where the handsheet strength properties of the kraft pulps from dilute acid pre-extracted chips were on average by 50% lower than those of the control.¹² Similar handsheet strength loss from soda-AQ pulping of *E. grandis* chips from which 16% wood solids were extracted in hot water was reported.³⁸

Considering the application of the pulps produced from acid extracted *E. grandis* for papermaking, the deficiency in the tensile and tear indexes will be of greater concern.³⁹ As a comparison, the tensile index attained by kraft and soda-AQ pulping (98.9 and 92.1 Nm/g, respectively) of the acid extracted *E. grandis* chips was lower than the tensile index level reported for commercial unbleached eucalyptus kraft and soda-AQ pulps produced from non-extracted wood chips: 127 and 100.6 Nm/g, respectively.^{39,40}

Likewise, the tear index was reduced drastically due to dilute H_2SO_4 extraction by about half of the tear index reported for commercial kraft (11.0 $mN \cdot m^2/g$) and soda-AQ (8.7 $mN \cdot m^2/g$) eucalyptus pulps produced

without pre-extraction.^{39,40} Nonetheless, the pulps produced from acid extracted wood chips could be used for printing and writing papers where strength is of lower importance.^{39,40}

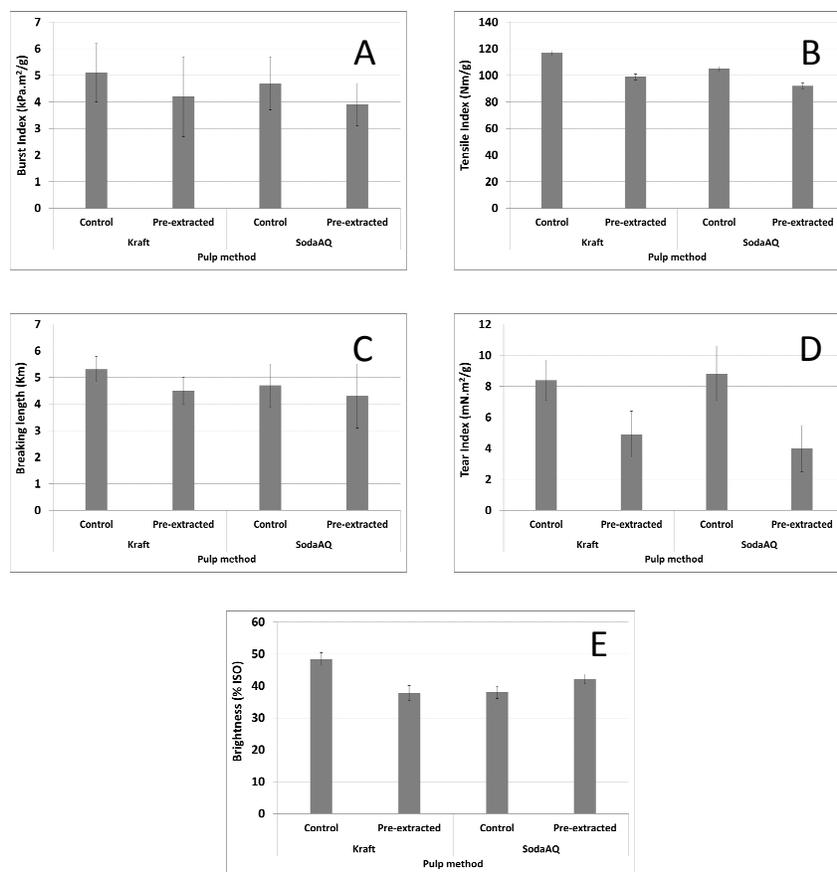


Figure 4: Handsheet properties determined for kraft and soda-AQ pulps from control and pre-extracted *Eucalyptus grandis* chips; (A) burst index, (B) tensile index, (C) breaking length, (D) tear index, (E) brightness

CONCLUSION

Xylan from *E. grandis* wood chips was extracted with dilute H_2SO_4 acid prior to pulping and the extracted wood chips were pulped to evaluate a conceptual approach to a pulp mill biorefinery for co-production of pulp, xylose and xylo-oligomers. Up to 60.2% xylan present in *E. grandis* wood chips could be extracted under suitable conditions for fermentation into bioethanol and/or production of xylo-oligomers. However, from a pulp mill biorefinery perspective, the xylan extraction from South African grown *E. grandis* wood chips should be limited to less than 20% to maintain the pulp yield at a target kappa number without reduction in viscosity after modified soda-AQ pulping process. Among the two pulping methods tested in combination with dilute H_2SO_4 xylan extraction, soda-AQ

confirmed its good potential in terms of moderate cooking conditions and better pulp yields than kraft pulping, especially when pulp strength is not crucial, with reduction in pollution problems. A potential increase of digester capacity of 12% was observed for the conditions selected. The strength properties of the resulting pulps were reduced, but could be acceptable for paper production depending on the extent of xylan extracted.

Therefore, limited xylan removal by milder extraction conditions can be recommended to preserve the fibre. Furthermore, the significant reduction in tear index showed the importance to regulate the refining/beating conditions for pulps produced from acid extracted wood chips to obtain maximum fibre properties rather than accepting freeness/drainage levels

required for kraft or soda-AQ pulps produced from non-extracted wood chips.

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