Integration of xylan extraction prior to kraft and sodaAQ pulping from South African grown *Eucalyptus grandis,* giant bamboo and sugarcane bagasse to produce paper pulps, value added biopolymers and fermentable sugars.

by

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Declaration

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Vena Phumla Faith **March 2013**

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Abstract

The extraction of hemicelluloses prior to pulping that would have been dissolved in black liquor during pulping process, is an attractive alternative for pulp and paper mills as they, in addition to their core products, can increase their revenue by producing biofuels, biopolymers, paper additives and other chemicals. However, the amount of hemicelluloses extracted will be limited by the requirement to maintain pulp yield and pulp quality in comparison to existing pulping processes.

In the present study, mild alkaline (NaOH) and dilute sulphuric acid conditions were used to extract hemicelluloses from *Eucalyptus grandis*, giant bamboo (*Bambusa balcooa*) and sugarcane (*Saccharum officinarum*) bagasse (SCB) prior to kraft or sodaAQ pulping processes. The effects of catalyst concentration, temperature and reaction time on hemicelluloses pre-extraction were studied, using a statistical experimental design to investigate conditions under which hemicelluloses could be extracted prior to alkaline pulping with minimal interference on cellulose (glucan) content. Subsequently, selected pre-extracted materials were subjected to kraft or sodaAQ pulping to evaluate the effect of the hemicelluloses pre-extraction on cooking chemicals, pulp yield and properties. This study also included evaluation of hot water hemicelluloses pre-extraction of SCB as it was part of a dilute sulphuric acid experimental design. The pulp yield, cooking chemicals and handsheet strength properties were compared with those obtained from kraft or sodaAQ pulping of non extracted raw materials.

The results showed that alkaline pre-extraction options investigated preserves the pulp yield with minimal effect on handsheet strength properties depending on the choice of the subsequent pulping method while a fraction of xylan was extracted in polymeric form. In addition, less active alkali was required to delignify the xylan extracted materials.

The integration of hemicelluloses pre-extraction by alkaline methods into a kraft pulping process was preferred for giant bamboo and *E. grandis* since it maintained pulp yields at desired industrial levels of 50%, and pulps within a bleachable kappa number range.

Another advantage observed was the reduction in total cooking active alkali required to delignify alkaline extracted giant bamboo or *E. grandis* by 8or 3 percentage points respectively. However, the compromise to maintain the pulp yield was obtained when only 13.6% or 12.4% polymeric xylan was solubilised from giant bamboo or *E. grandis* respectively. Slight improvement in burst index of the handsheet was observed for extracted giant bamboo. On the other hand, pulp viscosity was increased by 13% due to the removal of low molecular weight hemicelluloses, while the breaking strength of the handsheet was also increased by 8.9% for pulps produced from extracted *E. grandis*.

In the case of sugarcane bagasse, hemicelluloses pre-extraction by alkaline methods integrated well with the sodaAQ pulping process. It enabled a xylan recovery of 69.1%, while providing pulp with higher screened pulp yield (45.0%), with an advantageous decrease in kappa number (15.5). The handsheet tear index was superior without reduction in viscosity compared to pulp produced from non extracted SCB.

On the contrary, results obtained from optimised dilute sulphuric acid pre-extraction of all the tested feedstocks were found to negatively impact subsequent kraft or sodaAQ pulping processes resulting in lower pulp yields and poorer strengths properties. Nonetheless, the differences were better when sodaAQ pulping was used compared to kraft pulping. SodaAQ protects the carbohydrates against the peeling reaction under alkaline medium.

Conversely, pre-extraction of SCB with hot water resulted in low concentration of xylo-oligomers (5.7%), while the subsequent sodaAQ pulping resulted in no pulp yield reduction. The tear index and optical brightness of the handsheet papers produced from hot water extracted SCB were slightly improved while the breaking length, tensile and burst indexes were similar to those of pulps produced from non extracted SCB fibres.

Of equal importance were the observed higher tear and burst indexes of handsheets produced from giant bamboo compared to *E. grandis* for both extracted and non extracted materials prepared under similar pulping processes. The advantage of bamboo was due to the larger fibre length and different morphological properties to those of hardwoods.

However, the pulps produced from giant bamboo showed higher kappa numbers than those pulps produced from *E. grandis* due to the high condensation behaviour of bamboo lignins under alkaline conditions. Higher kappa numbers explained the higher demand for subsequent bleaching chemicals.

In conclusion, the pulp mill biorefinery concept through hemicelluloses pre-extraction with NaOH can be achieved with modified kraft pulping or the sodaAQ pulping processes, but it depends on the type of raw material, extraction method and quality and performance requirements of a particular paper. The low pulping chemicals demand, comparable pulp yields and the improvement in some physico-chemical properties of the pulps from pre-extracted materials were observed. Furthermore, owing to xylan pre-extraction a larger amount of (extracted) material could be loaded into the digester as when non-extracted materials were used.

Opsomming

Ekstraksie van hemiselluloses wat tydens verpulping in die swartloog opgelos word, bied ‘n aantreklike alternatief aan pulp- en papiermeulens om, addisioneel tot hul hoofprodukte, hul inkomste deur die vervaardiging van biobrandstowwe, biopolimere, papierbymiddels en ander chemikalië, daardeur te kan verhoog. Die hoeveelheid hemiselluloses wat ge-ekstraheer kan word, sal egter beperk word deur die vereiste dat pulpopbrengs en –kwaliteit tydens bestaande verpulpingsprosesse gehandhaaf moet word.

In hierdie ondersoek is matige alkaliese (NaOH) en verdunde swawelsuurtoestande gebruik om hemiselluloses vóór kraft- of natriumantrakinoonverpulping uit *Eucalyptus grandis*, reuse bamboes (*Bambusa balcooa*) en suikerriet (*Saccharum officinarum*) bagasse, mee te ekstraheer.

Die invloed van katalisatorkonsentrasie, temperatuur en reaksietyd is mbv ‘n statistiese, eksperimentele ontwerp ondersoek om die toestande te bepaal waaronder hemiselluloses, met minimale effek op die sellulose (glukaan) –inhoud, vóór alkaliese verpulping ge-ekstraheer kan word. Die pre-ge-ekstraheerde materiale, met hoë glukaan- en voldoende hemiselluloses-inhoud, is vervolgens aan kraft- en natriumantrakinoonverpulping onderwerp om die invloed van pre-ekstraksie van hemiselluloses op die verpulpingsreagense, pulpopbrengs en -eienskappe vas te stel. Hierdie studie het ook die evualering van warmwater hemisellulosespre-ekstraksie van suikerrietbagasse, wat deel is van ‘n verdunde swawelsuur eksperimentele uitleg, ingesluit. Pulpopbrengs, die hoeveelheid verpulpingsreagense en handveleienskappe van dieselfde materiale wat nie vooraf ge-ekstraheer is nie, is vergelyk.

Die resultate toon dat alkaliese pre-ekstraksie metodes wat ondersoek is die pulpopbrengs met minimale effek op handvel sterkte-eienskappe afhangende van die keuse van daaropvolgende pulpmetode kon handhaaf terwyl ‘n fraksie van xilaan in polimeriese vorm ge-ekstraheer is. Addisioneel, is minder aktiewe alkali benodig om die xilaan ge-ekstraheerde materiale te delignifiseer.

Die integrasie van hemisellulosespre-ekstraksie dmv alkaliese metodes tydens ‘n kraft verpulpingsproses is vir reuse bamboes en *E. grandis* verkies omdat pulpopbrengste op ideale industriële vlakke van 50% gehandhaaf en is en pulp in ‘n bleikbare kappa nommergebied interval kon lewer. ‘n Verdere voordeel wat waargeneem is was die vermindering in die totale gekookte aktiewe alkali benodig vir reuse bamboes of *E. grandis* met 8 of 3 persentasiepunte onderskeidelik. Die kompromie om die pulpopbrengs te handhaaf is verkry toe slegs 13.6% of 12.4% polimeriese xilaan opgelos is vanuit reuse bamboes of *E. grandis* onderskeidelik. ‘n Effense verbetering in bars-indeks van die handvelle is waargeneem vir ge-ekstraheerde reuse bamboes. Pulpviskositeit het met 13% gestyg agv die verwydering van die lae molekulêre massa hemiselluloses, terwyl breeksterkte van handvelle ook met 8.9% toegeneem het vir pulp verkry uit pre-gekstraheerde *E. grandis*.

NaOH pre-ekstraksie van 69.1% xilaan (droë massa) uit suikerriet bagasse (SCB) het ‘n hoër natriumantrakinoon, gesifte pulpopbrengs gelewer (45.0%) met ‘n verbeterde afname in kappa-getal (15.5) en uitstekende skeursterkte sonder verlaging in viskositeit, soos vergelyk met nie-ge-ekstraheerde suikkerrietbagasse.

Daarteenoor het die resultate verkry met die geoptimeerde verdunde swawelsuur pre-ekstraksie van al die getoetste rumateriale getoon om‘n negatiewe effek te gehad het op die daaropvolgende kraft- of natriumantrakinoonverpulping dws het laer pulpopbrengste en swakker sterkte-eienskappe opgelewer. Die verskille was nietemin kleiner toe natriumantrakinoonverpulping ipv kraftverpulping gebruik is. Antrakinoon beskerm die koolhidrate teen die afskilreaksie in alkaliese medium.

Daarteenoor het pre-ekstraksie van suikerrierbagasse met warm water tot 'n lae hoeveelheid (5.7%) xilaanoligomere gelei, terwyl die daaropvolgende natriumantrakinoonverpulping geen verlaging in pulpopbrengs veroorsaak het nie. Skeursterkte en optiese helderheid van handvelle wat uit warm water ge-ekstraheerde suikerrietbagasse vervaardig is, het ietwat verbeter terwyl breek-, trek- en barssterkte dieselfde was as van suikerrietbagasse pulp wat nie ge-ekstraheer is nie. Net so belangrik was die waargenome hoër skeur- en barsindekse van handvelle vervaardig van reuse bamboes in vergelyking met *E. grandis* van beide ge-ekstraheerde en nie ge-ekstraheerde materiale voorberei onder dieselfde verpulpings toestande. Bamboes se sterker eienskappe was as gevolg van die hoër vesellengte en ander morfologiese eienskappe as diévan loofhout. Pulp wat vervaardig is van reuse bamboes het ‘n hoër kappanommer getoon as pulp van *E. grandis* as gevolg van die hoë kondensasiegedrag van bamboeslignien onder alkaliese toestande. Hoër kappanommers kon die gepaardgaande hoër aanvraag vir bleikchemikalieë verklaar.

Ten slotte, die pulpmeul bio-raffinaderykonsep nl. deur hemisellulosesekstraksie met NaOH gekombineer met óf ‘n gemodifiseerde kraft verpulping óf ‘n gemodifiseerde natriumantrakinoon verpulping, is wel uitvoerbaar. Dit word egter sterk beïnvloed deur die tipe ru-materiaal en die ekstraksie-metode gebruik, asook deur die kwaliteits- en gebruiksvereistes van verskillende tipes papier. ‘n Lae aanvraag vir verpulpingschemikalieë, vergelykbare pulpopbrengste en die verbetering in fisies-chemiese eienskappe van pulp vanaf pre-ge-ekstraheerde materiale is waargeneem. Verder kon, as gevolg van xilaan ekstraksie, meer ge-ekstraheerde materiaal in die verteerder gelaai word as wanneer nie-ge-ekstraheerde materiaal gebruik is.

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Finally, I humbly bow before the Almighty God for showering his blessings upon me and giving me the strength, courage, endurance, wisdom and chance to reach this important milestone in my academic life.

Jeremiah 1: 4 The Lord said to me; “I chose you before I gave you life and before you were born.
Jeremiah 29:11-12 I alone, know the plans I have for you, plans to bring you prosperity and not disaster, plans to bring about the future you hope for. Then you call to me. You will come and pray to me, and I will answer you.

This work is dedicated to the following people that I treasured: mother Nomathemba (Nhonho) Vena, brother Ayanda (Stulo), sisters Gcobisa and Phelela, cousin Malibongwe and nephews Asanda and Zingce.

If we knew what it was we were doing,
It would not be called research, would it?
Albert Einstein

List of Publications

This dissertation is based on the following papers, which in the text are referred to by their roman figure and appended at the end of the dissertation.

Paper I

Dilute acid extraction of hemicelluloses from *Eucalyptus grandis* and its effect on kraft and sodaAQ pulp fibres and handsheets properties**.**

Vena P.F.; Brienzo, M., García-Aparício, M.P., Görgens J.F. and Rypstra, T.

Submitted for publication to Tappi Journal.

Under Review

Paper II

Effect of alkaline hemicelluloses pre-extraction on kraft pulp fibres from *Eucalyptus grandis***.**

Vena P.F.; García-Aparício, M.P., Brienzo, M., Görgens J.F. and Rypstra, T.

Accepted for publication in the Journal of Wood Chemistry and Technology, 21 January 2013

Paper III

Impact of hemicelluloses pre-extraction on pulp properties of sugarcane bagasse.

Vena P.F.; García-Aparício, M.P., Brienzo, M., Görgens J.F. and Rypstra, T.

Accepted for publication in the Journal of Cellulose Chemistry and Technology, 25 October 2012.

Paper IV

Hemicelluloses extraction from giant bamboo prior to kraft or sodaAQ pulping and its effect on pulp physical properties.

Vena P.F.; Brienzo, M., García-Aparício, M.P., Görgens J.F. and Rypstra, T.

Submitted for publication to Holzforschung.

Decision: Revision

Paper V

Hemicelluloses extraction from bamboo prior to Kraft and sodaAQ pulping to produce paper pulps, value added biopolymers and bio-ethanol.

Vena P.F.; Görgens J.F. and Rypstra, T.

Cellulose Chemistry and Technology 2010, 44 (4-6), 153-163.

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Author's contribution to the appended papers I-V:

Vena P.F., participated in the conception and design of the study, performed all the experimental work and wrote the manuscripts. All the co-authors commented on the manuscripts, read and approved.

Contents

Keywords and General definition

AQ	-anthraquinone (pulping catalyst/accelerator)
Active alkali	-active ingredients in the pulping process i.e., NaOH + Na_2S (both as Na_2O)
Delignification	-removal of lignin from plant material by dissolution
Kappa number	-amount of residual lignin in pulp after digestion
Pulp	- plant material separated into fibrous form
Sulfidity/Sulphidity	-ratio of Na_2S to the active alkali expressed as percentage [Na_2S]/ [NaOH + Na_2S] x 100%
Beating	-mechanical treatment of pulp fibres to develop their paper technical properties, such as ability to bond each other
Brightness (%ISO)	-colour of pulp, measured against whiteness of MgO at 457 nm wavelength
Freeness (°SR)	-measure of the rate of wetness/drainage of pulp
Breaking length (km)	-measure the length of the paper strip that will break under its own weight
Tear index (mN m^2/g)	-force required to tear paper
Burst strength (kPa m^2/g)	-puncture resistance of paper

CHAPTER 1: Introduction to hemicelluloses pre-extraction incorporation in a pulp mill biorefinery

1.1 Background and motivation

World demand for paper and paperboard is anticipated to grow from 300 million tonnes to over 490 million tonnes by the year 2020, which is expected to raise the cost of pulp wood (Agnihotri et al., 2010). The increasing demand coupled with environmental concerns, have increased interest in alternative feedstocks and processes for more efficient, integrated use of the raw material according to the "zero waste" context (Ohara, 2003; Kamm and Kamm, 2004). In this context, the implementation of the bio-refinery concept in the existing chemical pulp mills is regarded as a strategy for the sustainable co-production of paper, fuels, power and high value chemicals from diverse and heterogenous lignocellulosic materials (Carvalheiro et al., 2008).

Another intrinsic aspect of a biorefinery facility is the flexibility in terms of raw material. In this dissertation three different raw materials were selected: a hardwood (*Eucalyptus grandis*), an herbaceous grass (sugarcane bagasse) and a woody grass (giant bamboo). *Eucalyptus grandis* (*E. grandis*) was selected since this is one of the main sources of fibre used for pulp production in South Africa. The total capacity of approximately 1 350 000 tons of chemical pulp per annum is generated mainly from Eucalyptus in South Africa's pulp mills (Chamberlain et al., 2005). Sugarcane bagasse (SCB) represents an alternative and cheap fibre option to the South African pulp industry. The South African sugar industry generates approximately 6 million tonnes of sugarcane bagasse annually, from which around 70 000 tons of unbleached and 60 000 tons of bleached bagasse pulp grades are produced per annum (Mashoko et al., 2008; Naledi, 2004).

Another feedstock that can be considered in South Africa is giant bamboo (*Bambusa balcooa*). Bamboo is certainly a much newer feedstock, although its suitability for pulping has increased interest in its use as an alternative lignocellulosic feedsctock. Several commercial plantations are under investigation, but no scientific data on production yields for local context (Biomass Corporation SA (Pty) Ltd).

1.2 Research aim

The objective of the pulping process is to remove lignin and retain the polysaccharides, in particular the cellulose fibres for pulp and paper production (Fengel and Wegener 2003). The chemical pulps are mainly produced from alkaline treatments processes namely kraft pulping and soda pulping. The kraft pulping process is the preferred methodology for woody biomass, and employs a mixture of sodium hydroxide (NaOH) and sodium sulphide (Na_2S) for cooking. In the case of soda pulping, the application is limited to nonwoody biomass i.e. agricultural by-products, and uses mainly NaOH, although it can incorporate other chemicals such as anthraquinone (AQ) in the sodaAQ variant (López et al., 2005; Khristova et al., 2006; Gonzàlez-Garcìa et al., 2010).

Figure 1 illustrates the steps of a typical kraft pulp mill process and the modified process incorporating a hemicelluloses pre-extraction step. In a conventional kraft pulping process, the wood chips are primarily subjected to a solution of NaOH and Na_2S known as white liquor. During this step, the mjority of hemicelluloses, along with most of the lignin, are dissolved in the delignification stage and used for energy recovery (Lisboa et al., 2005; Santiago et al., 2008). Another fraction of hemicelluloses remains with the fibre, which is necessary to provide certain properties in the final product (Fardim and Duran, 2004; Silva et al., 2011). Given the low heating value of hemicelluloses (13.6 MJ/kg) compared with that of lignin (27.0 MJ/kg), its underutilisation in the present pulping processes is evident (van Heiningen, 2006; Yoon et al., 2011).

The extraction of hemicelluloses before the pulping process and further conversion to value added products under the biorefinery concept have significant potential to provide additional income for pulp and paper mills, while continuing to meet the growing demand for pulp and paper (Ragauskas et al., 2006; van Heiningen, 2006). The extracted hemicelluloses could constitute a feedstock for several products such as bioethanol, biopolymers and chemicals (Gabrielii et al., 2000; Ragauskas et al., 2006; Ren et al., 2007a; Mendes et al., 2009). Most interestingly, the extracted hemicelluloses can be used as strength additive either in its extracted form or derivatised for paper pulp production to create desired properties of the paper that is to be produced (Ren et al., 2007b, Postma et al., 2012). Moreover, the implementation of hemicelluloses pre-extraction could lead not only to the reduction of chemicals and cooking times, but also to the increment production capacity since the extracted wood chips have a lower mass compared to non extraction (Huang et al., 2010).

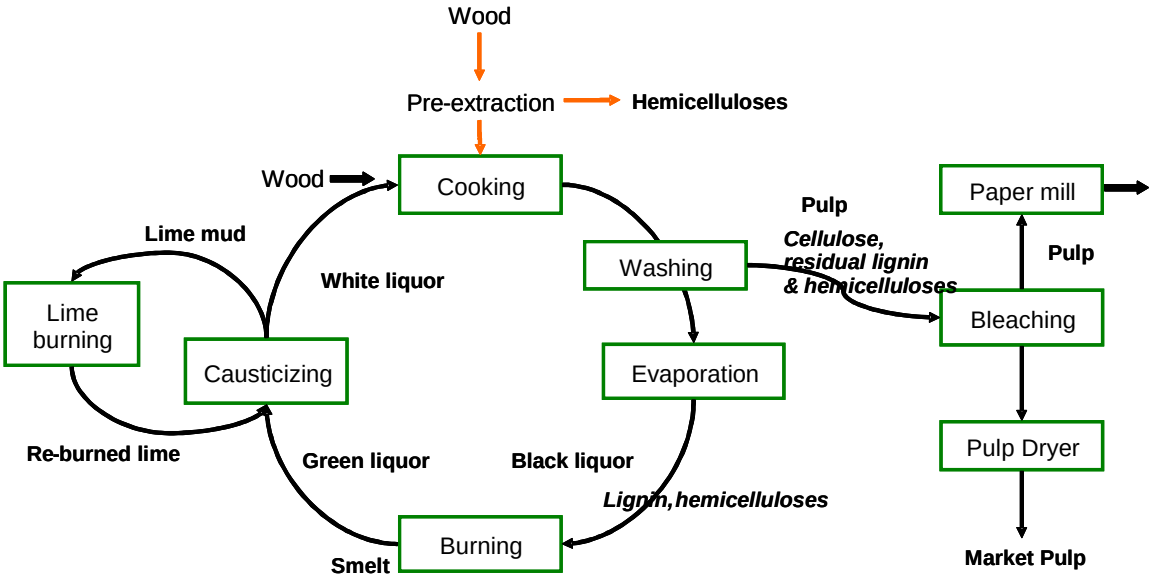

Figure 1. Conventional kraft pulping process (black arrows) and modified process (orange arrows) including hemicelluloses pre-extraction (redrawn from Gullichsen et al., 2000).

Extraction of hemicelluloses prior to pulping can be carried out by a variety of treatments including steam pretreatment (San Martin et al., 1995), dilute acid extraction (Parajo et al., 1994; Al-Dajani et al., 2009), hot water extraction (Casebier et al., 1969, Kubikova et al., 1996, Yoon and van Heiningen 2008; Kämppi et al., 2010) and alkaline extraction (Brienzo et al., 2009; Sixta and Schild 2009; Liu et al., 2010). Among these treatments, dilute acid and alkali treatments were selected in the present study (papers **I-V**) partly because dilute acid is a cheap and effective way of hemicelluloses removal (Koukios and Valkanas, 1982). Furthermore alkaline methods can be integrated into pulping without major changes in pH (Al-Dajani and Tschirner, 2008; Yoon et al., 2008). The limitations of alkaline methods in comparison to dilute acid include the conversion of some alkali to large amount of salts during the extraction process and that becomes a challenge for alkaline treatments (Hu and Ragauskas 2012). This phenomenon increase the capital cost of recycling alkali (Mosier et al., 2005). The integration of hemicelluloses pre-extraction and pulping in a combined approach, however, require an optimisation of hemicelluloses pre-extraction conditions and subsequent adaptation of pulping requirements. The pre-extraction should be optimised for selective extraction of hemicelluloses with minimal degradation of the cellulose component of the papermaking fibre, thereby avoiding a reduction in the pulp yield and quality from the combined pre-extraction-pulping process. At the same time, the fibres should contain sufficient hemicelluloses for the production of high quality pulps. The optimal process conditions for combined hemicelluloses-and-pulp production will depend on composition and structural properties of the raw materials selected for this study.

1.3 General aim of the study.

Based on the above background and considerations, the general aim of the present study was to investigate the process conditions that would maximise hemicelluloses extraction from South African grown *E. grandis*, SCB and giant bamboo prior to pulping, without negatively affecting the subsequent pulp yield and paper properties significantly.

1.4 Objectives identified for the study.

The following objectives were identified and addressed, in order to accomplish the general aim:

Objective 1

To analyse the composition (extractives, carbohydrates, lignin, and ash) of *E. grandis*, depithed SCB and giant bamboo obtained from local sources (papers **I-V**).

The study has provided information on the composition of different lignocelluloses materials that are associated with pulp and paper manufacturing in South Africa such as *E. grandis* and SCB. Similar work was done on giant bamboo, a potential fibre source available in South Africa. The chemical composition in terms of carbohydrates, lignin and inorganic substances was determined (Table 2 in section 2.3). This was necessary to establish their response to hemicelluloses pre-extraction and subsequent pulping technologies.

Objective 2

To investigate by experimental design the effects of reaction conditions (catalyst concentration, temperature and reaction time) of dilute acid and mild alkaline pre-extractions on hemicelluloses yield and cellulose recovery in the fibre residue obtained from *E. grandis* chips (4-8mm thickness), depithed SCB and giant bamboo chips of 4-8mm thickness comprised of nodes and internodes.

The strategy to accomplish this objective was to selectively extract hemicelluloses by varying reaction conditions using experimental designs. The solid residue obtained after each pre-extraction condition was characterised for its chemical composition. In this way, it was possible to establish the reaction conditions that could solubilise optimum hemicelluloses whilst high cellulose (glucan) and enough hemicelluloses were retained in the solid residue. The experimental optimisation was repeated for all three feedstocks considered in this study, and the results are presented on the appended papers (**I-V**).

Objective 3

Based on the outcomes of Objective 2, to select those fibre residues for further micro and macro-pulping, kraft or sodaAQ, in order to determine the effects of hemicelluloses pre-extraction on pulp properties and paper quality.

To address this objective, we first screened selected conditions obtained from previous experiments, for their ability to improve alkaline pulping by means of quantitative analysis of pulping trials of extracted materials on a micro scale. Pulping conditions that improved pulp properties were selected and performed on the pilot scale and the pulp yield and properties were compared to the pulps produced from sodaAQ/kraft pulping of non-extracted materials. The experimental optimisation was repeated for all three feedstocks considered in this study, and the results are distributed on the appended papers (**I-V**).

Objective 4

To compare the integration of hemicelluloses pre-extraction prior to pulping in 3 different sources of lignocellulosic materials: *E. grandis* (hardwood), SCB (herbaceous) and giant bamboo (woody grass).

In the evaluation of the results obtained after macro pulping it was essential to make a comparison among the studied materials to determine the feasibility of this kind of technical integration when using different lignocellulosic materials.

This comparison between raw materials, and the impact of raw material properties on optimised process conditions, is covered in Chapter 2 (section 2.7) as well as in General Conclusions (Chapter 3).

1.5 Statement of novelty

To the author's knowledge, there is no information in the public domain on hemicelluloses pre-extraction from giant bamboo followed by an alkaline pulping with strong elements of the biorefinery approach. The study reported in this dissertation is a first investigation with dilute acid hydrolysis and mild alkaline extraction of bamboo for the production of fermentable sugars and xylan polymers with the aim of adding value to hemicelluloses that would have been wasted in pulping black liquors.

Secondly, pulp and paper characteristics of giant bamboo were compared with those obtained from *E. grandis* and depithed SCB mainly used as fibre source in the South African pulp industry. Since South Africa is ranked the 18th largest producer of pulp and 24th largest producer of paper and board, a large amount of hemicelluloses or their sugars are currently only burnt to generate steam and energy for the recovery boilers. Extraction of hemicelluloses from *E. grandis* or SCB prior to pulping is presently not done in the South African pulp industry. The present study investigated dilute acid or mild alkaline methods to extract xylan from *E. grandis* (Papers **I** and **II**) SCB (Paper **III**) and giant bamboo (Paper IV and V) prior to established kraft or sodaAQ pulping processes used by South african pulp industry.

The work done in this study on hemicelluloses extraction from these lignocellulosic materials showed the prospects of hemicelluloses utilisation with improved profitability options for the industry.

CHAPTER 2: Literature review and findings of the present study

2.1 Introduction

2.1.1 Importance and overview of the pulping processes

The importance of paper products in modern life is obvious to everyone. No manufactured product plays a more vital role in every aspect of human activity. Paper provides the means for recording, storage and dissemination of information. The largest utilisation of paper is for printing, writing, wrapping, packaging and sanitary purposes (Baecker, 1995; Saika et al., 1997; Ververis et al., 2004).

Paper and other related products are manufactured from a fibrous cellulosic mass called pulp obtained after cellulose-bearing raw material has been broken down into individual fibres. The task can be accomplished mechanically, chemically or by combinations of these treatments. Existing commercial processes are generally categorised as chemical, semi-chemical, chemi-mechanical or mechanical (Biermann, 1996; Fengel and Wegener, 2003; Sridach, 2010). These processes differ mainly by the nature of the process employed and the yield of pulp obtained. Typically, chemical processes produce a pulp yield in the range 35 to 65%, semi-chemical 70 to 85%, chemi-mechanical 85 to 95% and mechanical processes 93 to 97% (Biermann, 1996; Henriksson and Gatenholm 2002). These yield differences show that the chemical process effectively separates the cellulose from lignin present, whereas the mechanical process converts all the components present. The choice of the process will depend on the nature of the material to be pulped and the grade of paper or board product desired (Fengel and Wegener 2003). Chemical processes are often used commercially to produce fibre for strength and high quality printing products such as kraft paper or fine paper (Muneri, 1997). Mechanical and chemi-mechanical processes produce pulp for lower grade products such as newsprint and paper board (Kayserberg, 1989).

2.1.2 Lignocellulose materials and pulping methods

Wood is largely the conventional raw material for pulp and paper production worldwide, and accounts for 90% of total fibre input (Little et al., 2003). Globally approximately 300 million tons of paper is produced per year and the demand for paper or paper products is expected to continue to increase (Jun and Tschirner, 2010). Pulps produced from Eucalyptus are dominating the world hardwood pulp markets (Patt et al., 2006). Economical and technical reasons for the utilisation of eucalypts come from its fast growth rate under suitable conditions, with good tree form and excellent wood quality for pulp production (Little et al., 2003; Patt et al., 2006; Moussaouiti et al., 2012). In South Africa, eucalyptus hybrid clones are grown over short rotations ranging from six to nine years in order to meet the increasing demand for pulpwood (Little et al., 2003).

With the future of the wood-based fibre supply being debated worldwide, increasing interest is being shown to use various alternate fibrous resources for papermaking. Scarcity and depleting forest resources combined with increased paper demand are the driving forces to use nonwood materials such as cereals straw, sugarcane bagasse, bamboo, esparto grass, abaca (manila hemp), sisal and kenaf (De Lopez et al., 1996; Madakadze et al., 1999; Jun and Tschirner, 2010; Ribas Batalha et al., 2012). Wastepaper and waste paperboard are already available fibre sources and will become even more important in the future due to improved techniques of secondary fibre pulping (Fengel and Wegener, 2003).

Sugarcane bagasse (SCB) is the second most commonly used nonwood fibre plant material for pulp and paper production in many parts of the world including India, Brazil, China, South Africa and others due to its availability (Liu et al., 2006). The annual production of bagasse throughout the world exceeds 54 million tons on dry basis (Rowell et al., 1991; Samariha and Khakifirooz, 2011). Bamboo is also the preferred nonwood material used for the production of paper after SCB, specifically in Asian countries where the giant grass plants are indigenous covering an area of over 180 000 km^2 (Scurlock et al., 2000). Unlike wood,

bamboo grows rapidly and can be felled after 3 years and it provides pulps comparable to or resembles in quality that of hardwood pulps (Vû et al., 2004; He et al., 2007).

The main chemical pulping processes for lignocelluloses are the alkaline kraft and soda pulping processes (Haygreen and Bowyer, 1982). Generally, softwoods (spruce, hemlock and pine) and hardwoods (acacia, beech, birch, and eucalyptus) are used for the production of kraft paper pulps (Bierman, 1996; Pinto et al., 2005; Jahan et al., 2008) whilst nonwood material (sugarcane bagasse, reeds, straws, kenaf, bamboo, etc.) has been explored for soda pulping (De-Lopez et al., 1996; Kamthai, 2007; Agnihotri et al., 2010; Mossello et al., 2010). However, kraft pulping process is the best process for bamboo due to its structural resemblance to woods (Vû et al., 2004).

In South Africa, *E. grandis* is the major wood species used for pulp production, and accounts for 59% of all the produced chemical pulps. *Pinus patula* also contributes to the production of the pulps. SCB on the other hand has received a considerable amount of attention in South Africa as the major nonwood resource. The volume and types of pulp outputs from South Africa's pulp mills are listed in Table 1 (Chamberlain et al., 2005).

Table 1. Pulp production by grade from South Africa's pulp mills. (adapted from Chamberlain et al., 2005).

Pulp grade	Production (1000 t)	Percentage	Application
Chemical	1,350	59%	Printing and writing; Cartonboard or corrugated paper
Mechanical	277	12%	Newsprint, Magazine grade paper
Semichemical	155	7%	Linerboard, fluting, Low-cost printing paper, Grease-proof paper, Bond papers,
Dissolving	490	22%	Sold exclusively on international market
Total	2,272	100%	

In principle, fibres are produced by degrading or dissolving, under chemical pulping processes, the lignin that binds the individual cellulosic fibres (Santos et al., 2011). Lignin is thus extracted by subjecting the raw material to extreme pH values, high temperature and pressure, while leaving the cellulose fibres intact (Pinto et al., 2005; Lourenco et al., 2012). The majority of hemicelluloses in lignocellulose are solubilised and extracted together with lignin during pulping processes commonly used in industry, where after lignin and hemicelluloses are co-processed in the "black liquor" stream (Lisboa et al., 2005). In practice, separation of the cellulose, hemicelluloses and lignin is never completely realised, yet satisfactory compromises are reached in these processes. The pulp produced is very strong depending on the type of cellulosic sources and coooking conditions used (Sridach, 2010) and can be bleached to a high brightness (Macloed et al., 1995; Rahmati et al., 2007). The unbleached pulp is mainly used for cartonboard or corrugated paper, whilst bleached pulp is used for writing and printing papers (Muneri, 1997). However, the disadavantages of kraft pulping processes are pollution constraints and the lower pulp yield (Holmberg and Gustavsson, 2007; Kamthai, 2007).

Mechanical pulping methods on the other hand use mechanical force, heat and/or pressure, and sometimes mild chemical treatments to physically disrupt wood structure into pulp (Li et al., 2006). The most important industrial mechanical pulp processes are Stone groundwood (SGW) and Thermomechanical pulp (TMP) (Kayseber, 1989). Unlike chemical pulping methods, inexpensive sawdust, edgings, chipped slabs and short fibred hardwoods are utilised as raw materials. The advantages of these pulping processes are relatively low pollutant generation, high yield (above 90%) and pulps that give good print quality (Holmberg and Gustavsson, 2007). This pulp is suitable for grades of paper that do not require high strength properties, and short utility papers such as newsprint and magazine grades. The disadvantages of mechanical pulps are the high amounts of energy required and the paper turns yellow with exposure to air and light due to the presence of lignin in the pulp (Biermann, 1996).

However, chemical pre-treatments have been introduced to overcome some of the above problems associated with mechanical pulping in chemi-thermomechanical pulping (CTMP) processes (Henriksson and Gatenholm, 2002; Ren et al., 2010). This process typically pre-treats the raw material with 1 to 4% of sodium sulfite. The advantages obtained included an increase in strength properties and increase in brightness; however the chemical costs makes this process expensive (Wright et al., 1995).

Semichemical pulping processes use a combination of chemical and mechanical treatments (Hocking, 2005). They generally require some mechanical agitation to disintegrate the wood chips after chemical treatment. The principal semichemical process is the neutral sulfite, semichemical (NSSC) process. The principal process involves up to 15% sodium sulfite liquor and 4-5% sodium carbonate impregnation of the raw material prior mechanical defibration (Manskinen et al., 2011). The main advantages of the NSSC process are low requirements with regard to wood quality and species, high pulp yields (above 60%), low consumption of chemicals at a given residual lignin content, low capital investment and profitable small production units as compared to full chemical pulping (Biermann, 1996). Such pulps are used to produce linerboard, fluting, low-cost printing paper and several other paper grades, depending on the special pulp properties obtained by varied pulping conditions (Samriha and Khakifirooz, 2011). However, the strength values (except burst strength) and the freeness are lower than those of comparable full chemical pulps (Fengel and Wegener 2003).

Dissolving pulp is a low-yield bleached pulp ranging from 30 to 35% characterized by high alpha cellulose (>90%) content. These pulps contain low hemicelluloses (1 to 10%) and lignin (<0.05%) contents compared to other types of paper pulps (Behin et al., 2008; Ribas Batalha et al., 2012). The pulp is produced by acid prehydrolysis of hemicelluloses from lignocellulosic material followed by kraft pulping of the extracted material (cellulignin) to solubilise lignin (Kouskios and Valkanas, 1982; Ibrahim et al., 1996; Li et al., 2010). The pulp is then subjected to cold alkali extraction integrated with bleaching process to improve cellulose purity.

These pulps are used as raw material for the production of cellophane, viscose rayon, and celluloses derivatives such as cellulose esters (acetates and nitrates). The production of dissolving pulp is disadvantaged by high costs due to low pulp yield and restrictions due to the environmental problems caused by bleaching with hazardous chlorine and chlorine based compounds (Behin et al., 2008; Ribas Batalha et al., 2012). However totally chlorine-free bleaching techniques have been developed for dissolving pulps.

2.2 Hemicelluloses applications

Hemicelluloses extraction prior to pulping to develop new biofuels (Ren et al., 2007a) and biopolymer based materials (Ebringerová and Heinze, 2000) has become an interesting topic in recent years as part of the biorefinery approach. Hemicelluloses are one of the main polymeric constituent in wood and herbaceous plants biosynthesised in large quantities. Approximately 20-35% of the dry mass of hardwood (eucalyptus) (Mendes et al., 2009), agricultural residues (sugarcane bagasse) (Sun et al., 2004) and grasses (bamboo) (Scurlock et al. 2000) are hemicelluloses (Biermann, 1996). An estimated annual production of hemicelluloses on the earth from plants is in the range of 60 billion tons (dry basis; Grondahl et al., 2004). Thus, hemicelluloses represent an ernomous renewable resource that remains almost completely unused or under-utilised in combustion processes during pulping production for papermaking (Ragauskas et al., 2006; van Heiningen, 2006).

Xylans, the principal hemicelluloses in hardwoods and nonwood materials, can be used as pure poly-and oligomers or unpurified extracts containing bound proteins, phenolic substances or other polysaccharides (Hromádková et al., 2006; Kohnke et al., 2008; Ebringerová and Heinze, 2000). This influences with end uses as well as the production cost.

Xylans are known to interact specifically with the surfaces of celluloses fibre during alkaline kraft pulping process, to improve some properties in the pulp (Bhaduri et al., 1995; Ban et al., 2011). Historically, hemicelluloses such as galactomannans, glucomannan and recently xyloglucans from annual plants (locust bean gum, guar gums, ramie straw) have been exploited as natural beater additives and dry strength aids (Lima et al., 2005; Ren et al., 2009). Hence, pulp strength properties that are important for packaging grades, such as tensile, bursting strength and folding endurance, can be improved by hemicelluloses addition (Ahrenstedt et al., 2008; Schwikal et al., 2011). This is the strong incentive to favour extraction of hemicelluloses from *E. grandis*, SCB and giant bamboo prior to pulping under alkaline conditions (papers **II, III and IV**) and their re-introduction on pulp fibres as additives to raise the content of hemicelluloses, which is a preferred approach instead of the adjustment of pulping conditions (Westbye et al., 2006; Silva et al., 2011). Besides, higher xylan content on the surfaces of pulp fibres might increase the strength independently of the surface charge (Bhardwaj et al., 2004; Ren et al., 2009). However, addition of pre-extracted hemicelluloses back to the pulp fibre was beyond the scope of this study, which focussed on integrated pre-extraction-pulping process development.

An alternative path for increasing the suitability of hemicelluloses as sizing additives and adhesives in papermaking, is by functionalising the hydroxyl groups of the xylose units in hemicelluloses. For example, quaternized xylan-rich SCB hemicelluloses have been reported to strengthen properties of sheets formed from old corrugated container pulp (Ren et al., 2007b). Quaternization involves modification of hemicelluloses hydroxyl group through addition of 2.3-epoxypropyltrimethylammonium chloride (ETA), thus enhancing their solubility and yielding a cationic or ampholytic polymers (Schwikal et al., 2011).

The development of second generation biofuels such as bioethanol, which can be manufactured from fermentation of monomeric sugars present in the hemicelluloses extracted prior to pulping, is another application area of interest (Mao et al., 2010; Chandel et al., 2011).

In the case of ethanol production from hardwoods, agricultural residues and grasses, the hemicelluloses contain pentose sugars (five carbon; xylose, arabinose) and six carbon sugars (glucose, mannose) (Taherzadeh and Karimi, 2007a; Amidon and Liu, 2009). The production of ethanol from lignocellulosic biomass involves the hydrolysis of the polysaccharides into monomeric sugars syrup and the fermenting of the sugars to ethanol by micro organisms prior to distilling and dehydrating ethanol (Mosier et al., 2005). A comprehensive literature is available on the hydrolysis of polysaccharides either enzymatically or chemically by e.g. dilute sulfuric acid or hot water (Pessoa Jr et al., 1996; Laser et al., 2002; Rabinovich et al., 2002; Sun and Cheng 2002; Jorgensen et al., 2003). Once the monosaccharides are released from the lignocellulose matrix, the pentose sugars can be cofermented by newly developed metabolically engineered strains such as *Zymomonas mobilis* or recombinant *Escherichia coli* (McMillan et al., 1999; Wyman, 1999; Taherzadeh and Karimi, 2007b).

The potential of relatively pure xylans, which may be used in various industrial and non-industrial applications, can be extended by appropriate modifications of the molecular structure. For example, xylans obtained from hardwood have been tested as hydrogels, the crosslinked networks of hydrophilic polymers that are capable of retaining considerable amounts of water without disintegration (Gatenholm and Gabrielli, 1998). Hydrogels may play an important role as matrices for controlled release of pharmaceutical proteins and for encapsulation of living cells. Xylans also have shown a promising potential to become very attractive alternative renewable materials for packaging coatings and barrier films (Grondahl et al., 2004). In addition, furfural is an interesting product of xylan degradation that can subsequently be converted into a large variety of furan compounds, which can be used as starting materials for adhesive and additives to plastics manufacturing (Benko et al., 2007).

2.3 Lignocellulose biomass composition

Current lignocellulosic materials for papermaking can be classified in five categories: hardwoods (aspen, poplar, eucalyptus), softwood (pine, spruce), agricultural byproducts (sugarcane bagasse, wheat straw), herbaceous biomass (switchgrass, miscanthus) and woody grasses (giant bamboo, kenaf) (Belayachi and Delmas, 1995; Biermann, 1996).

The main macromolecular components of all lignocellulosic biomass are cellulose, hemicellulose and lignin. Other components found in lesser proportion are pectins, extractives and inorganic matter. The chemical composition and structural properties of the lignocellulosic material determine its response to processing conditions (Patt et al., 2006; Jun and Tschirner, 2010). The proportions and chemical composition of these components differ depending on the type of feedstock.

Table 2 summarises the composition of the raw materials used in the present study, together with other lignocelluloses that are used for pulp and paper production.

Table 2. Chemical composition of wood and nonwood found in the literature and those obtained in the present study used for pulp and paper production (% oven dry mass).

Raw material	Total extractives	Ash	Glucan	Xylan	Arabinan	Galactan	Mannan	Klason lignin	Acetyl group	Reference
Softwoods										
Loblolly Pine	3.5	na	42.4	6.3	1.1	1.8	9.1	28	1	Wei et al., 2011
Spruce	n.a	na	49.9	5.3	1.7	2.3	12.3	28.7	n.a	Söderstrom et al., 2004
Hardwoods										
**E. grandis*	3.3±0.4	1.7	47.2±4.2	14.9±1.1	0.5	n.a	n.a	26.8±1.7	n.a	Paper I
**E. grandis*	4.2±1.0	1.2	52.6±2.0	15.3±0.3	0.5	n.a	n.a	20.9±2.0	n.a	Paper II
E. grandis	3.3	na	44.7	15.3	n.a	n.a	n.a	25.8	n.a	Emmel et al., 2003.
E. grandis	3.5	na	44.9	11.4	n.a	n.a	n.a	26.2	n.a	Yu et al., 2010
E. grandis	n.a	na	46.7±0.3	11.5±0.3	0.5	1.2	1	29.2±0.3	2.8	Alves et al., 2010
Herbaceous										
*SCB	4.1±0.5	2.6	46.3±2.5	25.9±2.1	2.4±1.0	n.a	n.a	18.2±2.1	2.6	Paper III
SCB	6	4	36	22	2	1	n.a	19	n.a	Diedericks et al., 2011
SCB	1.7	2.7	52.4	25.8	n.a	n.a	n.a	21.7	n.a	Rezayati-Charani and Mohammadi-Rovshandeh, 2005
SCB	9.1	1.4	44.9	22.2	1.1	n.a	n.a	19.1	2.6	Canilha et al., 2011
Woody grasses										
*Giant bamboo	7.1±0.2	2.4	54.6±2.0	21.6±1.5	1.1±0.6	n.a	n.a	25.2±3.2	n.a	Paper IV-V
Bambusa vulgaris	n.a	na	50.4±0.3	19.6	1.1	0.4	0.3	23.4±0.3	2.4	Alves et al., 2010
Moso bamboo	13	1.4	41.3	22	1.1	0.3	0.6	22.8	n.a	Li et al., 2012

SCB = sugarcane bagasse. n.a. = not available

*Mean and standard deviation of four measurements

Generally, giant bamboo and SCB contain more glucan and xylan (holocellulose) than *E. grandis* or the two softwoods pine and spruce, which are the species used currently for commercial production of pulp and paper (Martin et al., 1995; Little et al., 2003). The combination of high glucan and xylan content in the raw material suggests that reasonable yields of pulp could be obtained from bamboo material (Scurlock et al., 2000; Lei et al., 2010). Moreover, the xylan represents a valuable feedstock for the production of high valued products in a pulp mill biorefinery, whilst enough xylan can be retained in extracted solid materials for improving pulp quality under suitable process conditions (Ragauskas et al., 2006; van Heiningen, 2006).

The amount of lignin was on lower side in SCB whereas the lignin content of giant bamboo was comparable to the ranges reported for *E. grandis* and pine. This could imply that SCB in general would be more easily delignified, requiring milder and shorter processing conditions than the giant bamboo and wood sources (Madakadze at al., 1999; Ververis et al., 2004; del Rio et al., 2007; Dutt and Tyagi, 2011). However, various factors including the three dimensional structure of lignin and its interaction with cellulose and hemicelluloses in lignin carbohydrate complexes (LCCs), and the degree of polymerisation of lignin, might also account for the changes in extraction and delignification rate (Steward et al., 2006).

Relative to other materials giant bamboo has a higher extractives content and therefore could demand extensive preparation processes (Ribas Batalha et al., 2012).

2.4 Cellulose

In pulping, the most important lignocellulosic material component to retain and protect is cellulose, which is a strength bearing, linear, high molecular mass polysaccharide (Sun et al., 1999; Palm and Zacchi, 2004). Cellulose or β-(1→4) glucan is a linear polymer of glucose or cellobiose units with about 10 800 or 10 300 glucose residues i.e. degree of polymerisation (DP) for grasses and hardwoods respectively (Biermann, 1996; Fengel and Wegener, 2003). The chains are packed in a parallel alignment by means of hydrogen and Van der Waals bonds in so-called elementary fibrils, originally considered to be 3 to 4 nm wide and containing about 36 chains – although larger crystalline fibrils up to 16 nm have also been discovered (Ha et al., 1998). These elementary fibrils are then packed in microfibrils, where the elementary fibrils are connected to each other by hemicelluloses, an amorphous polymer of different sugars, as well as other polymers such as pectin substances and held together by lignin (Delmer and Amor 1995). The microfibrils are often associated in the form of macrofibrils (Fig 2) (Karimi et al., 2006).

Cellulose fibrils consist of crystalline regions that vary from 80-70% for grasses and 96-89% for native cellulose (cotton) and the remainder being composed of disorganised (amorphous) region (Fengel and Wegener, 2003). The depolymerisation of cellulose under dilute acid hydrolysis primarily occurs in the amorphous region to a certain level called the levelling-off or limiting DP (LODP). This phenomenon is also influenced by the length of the cellulose crystallites (Hakansson et al., 2005).

In papers **I, III** and **V**, the decrease in cellulose (glucan) content of the lignocellulosic raw material, after dilute sulphuric acid extraction of hemicelluloses (primarily xylan) from *E. grandis*, SCB and giant bamboo was less than 10%. This indicated low cellulose degradation during extraction, although some acid hydrolysis of cellulose may result in reduction in cellulose DP, contributing to the pulp fibre strength losses (Koukios and Valkanas, 1982; Yoon and van Heiningen, 2008; Mendes et al., 2009).

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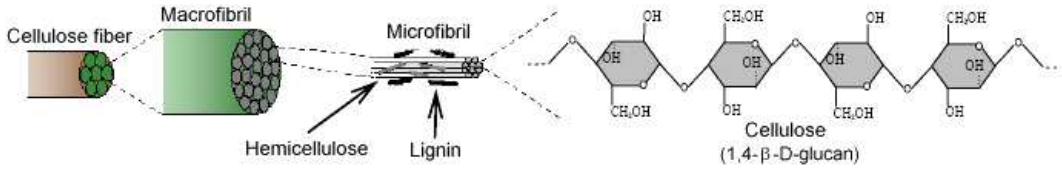


Figure 2. Structure of cellulose (adapted from Karimi et al., 2008).

2.5 Hemicelluloses

Unlike cellulose, hemicelluloses are heterogeneous polymers of five-carbon sugars or pentoses (β-D-xylose, α-L-arabinopyranose, α-L-arabinofuranose) and six-carbon sugars or hexoses (β-D-glucose, β-D-mannose, α-D-galactose), as well as of some hexuronic acids (β-D-glucuronic, β-D-galacturonic, α-D-4-O-Methylglucuronic) and deoxy-hexoses (α-L-rhamnose and α-L-fucose) (Jeffries, 1994; Ebringerova and Heinze, 2000). They are characterised by being soluble in acids, hot water and most frequently in aqueous alkali (Gabrielli et al., 2000; Glasser et al., 2000; Hoije et al., 2005; Nabarlatz et al., 2007).

The hemicelluloses content and structure differ between softwoods, (e.g. pine) hardwoods (eucalyptus), woody grasses (giant bamboo) and grasses (sugarcane bagasse). The DP of hardwood xylan (150-200) is higher than that of softwood xylan (70-130) and 65-90 for nonwood xylan (Sjöholm et al., 2000; Saha, 2003).

The major hemicelluloses in softwoods are acetylated galactoglucomannans and arabino-4-O-methyl-D-glucurono-β-D-xylan (arabinoglucuronoxylan) (Holmbom, 2003; Willför et al., 2005; Peng et al., 2012). The L-arabinofuranose units are linked by α-(1→3) bond to the xylan backbone. The ratio of arabinofuranoside groups to xylose residues is approximately 1:8 and acetyl groups are rarely attached to softwood xylan (Biermann, 1996). Hardwood and nonwood hemicellulose is mainly *O*-acetyl-4-*O*-methyl-D-glucorono-β-D-xylan (glucuronoxylan) (Fig 3). Hardwood glucuronoxylan is highly acetylated at the C-2 and C-3 positions with the amount of about 8-17% of total xylan and in the case of nonwood is 6-7% of total xylan (Biermann 1996; Vû et al., 2004).

To the partially acetylated xylan backbone of hardwoods every tenth xylose units in the main chain is linked to a side group of 4-O-methylglucuronic acid (10 Xyl: 1 Me-GluA) whereas in nonwood the average ratio is 26:1 (Xyl: Me-GluA). In contrast from hardwood xylans, on average, every 13th xylose contained an L-arabinofuranose unit linked by an α-(1→3) bond like that of softwood xylans (Fig 4) (Brillouet et al., 1982; Sun et al., 1996; Sun et al., 2004; Wen et al., 2011). Due to the furanosidic structure of the arabinose side chains, they are easily hydrolysed by acids. In general, highly branched xylans are more hydrophilic and bind less tightly to cellulose, whereas molecules with infrequent side chains are less hydrophilic and bind more tightly to cellulose (Amidon and Liu 2009). The reducing ends of hardwood xylans contain trace amounts of rhamnose and galacturonic acid in the following sequence: β-D-Xylp-1→4-β-D-Xylp-1→3-α-L-Rhap-1→2-α-D-GalpU-1→4-β-D-Xyl (Evtuguin et al., 2003). This structure has been reported to be responsible for the alkali resistance of the xylan molecule, as the galacturonic acid makes it stable after the removal of the reducing xylose unit (Peng et al., 2012). In addition, small amounts of glucomannans are also reported to be present in hardwood hemicelluloses at about 2-5%, having a glucose to mannose ratio that varies between 1:2 and 1:1, depending on wood species (Sjöström et al., 2000).

In the plant cell wall hemicelluloses act as filler between cellulose and lignin to increase the stability of the cellulose-hemicelluloses-lignin matrix (Hocking, 2005). Hemicelluloses play a major role in papermaking pulps as they assist to increase bonding strength of the fibres and improvement of the pulp tensile and burst strength (Bhaduri et al., 1995; Mosello et al., 2010).

In the present study, the extractability of xylan by either dilute sulphuric acid or mild alkaline conditions from SCB was easier compared to *E. grandis* and giant bamboo (papers **I-V**). Among the extraction conditions tested, the best compromise between xylan extraction yields and minimal effect on fibre quality was the use of 0.3% H_2SO_4 at 120°C where original dry mass 23.8% xylan from SCB fibres (paper **III**) and only 11.3% xylan from giant bamboo chips were recovered under such conditions (paper **V**). Extraction of xylan from *E. grandis* with 0.3% H_2SO_4 at 140°C resulted in 21.4% xylan recovery (paper **I**).

This was in good accordance with the chemical composition of the different raw materials, in particular their lignin content. The solubilisation of the xylan components of giant bamboo was difficult, probably due to the condensation of the bamboo lignin under acidic conditions which may have decreased the xylan release since xylan is linked to lignin (Vû et al., 2004). Another explanation could be high extractives content which likely hindered the chip impregnation. Previously, using a hot water extraction method, only 9.9% of the xylan could be removed from bamboo relative to 29.9% recovered from eucalyptus (Ribas Batalha et al., 2012).

Alternatively, mild alkaline xylan pre-extraction from SCB effectively solubilised 69.1% of xylan based on original dry material under 1.5M NaOH; 65°C; 3h (paper **III**). In comparison, only 13.6% or 12.4% xylan was extracted from giant bamboo or *E. grandis* based on original material under 1M NaOH, 90°C, 4h or 2M NaOH, 40°C, 4h respectively (papers **II** and **IV**). Compact structure, besides the lignin content of *E. grandis* and giant bamboo materials, might have hindered the penetration of alkaline extraction liquor into the chips, thus decreasing the xylan removal rate. These results correspond with earlier findings in which alkaline pre-extraction solubilised 57% xylan in barley straw (De Lopez et al., 1996) compared to 24.8 - 29.8% xylan that could be recovered from aspen hardwood chips prior to chemical pulping processes without reducing pulp yield (Al-Dajani and Tschirner, 2008).

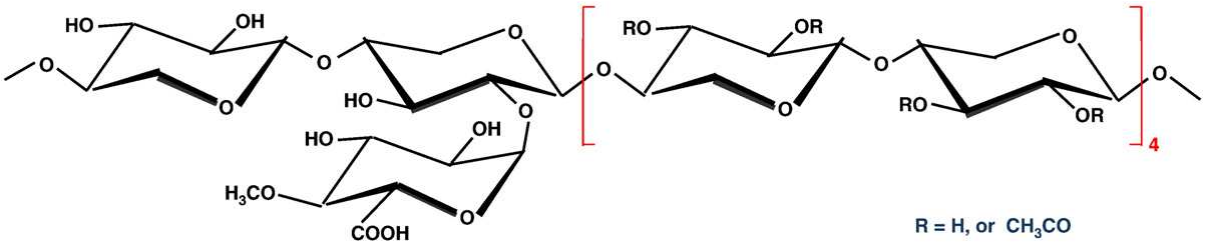


Figure 3. Stereochemical structure of a common hardwood hemicelluloses: glucuronoxylan. (redrawn from Amidon and Liu 2009).

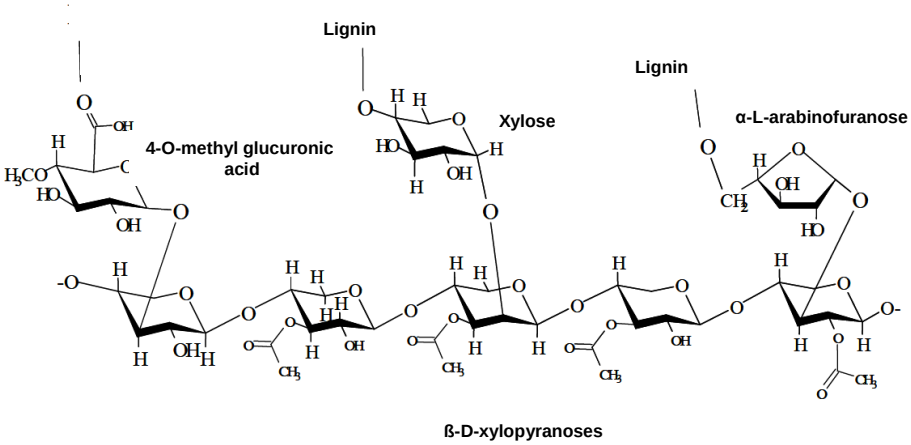
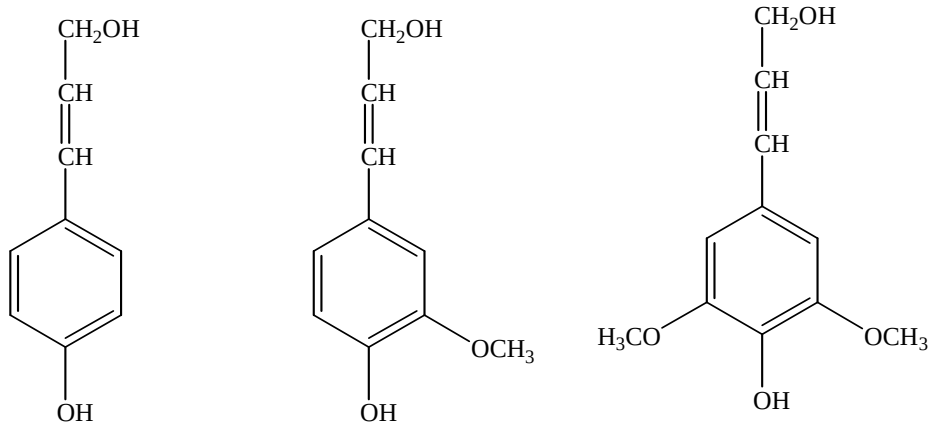


Figure 4. Chemical structure of arabino-*O*-acetyl-4-*O*-methyl-D-glucorono-β-D-xylan from nonwood. (redrawn from Subramaniyan and Prema 2002).

2.6 Lignin

Accessibility of plant cell wall polysaccharides to chemical treatments is limited by many physical and chemical properties/factors, including the presence of lignin in fibres (Steward et al., 2006). Lignin is an aromatic polymer composed of three building blocks: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Fig 5) consists of p-hydroxyphenyl (H), guaiacyl (G; 4-hydroxy-3-methoxyphenyl) and syringyl (S; 4-hydroxy-3,5-dimethoxyphenyl) units respectively (Govender et al., 2009; Li et al., 2010). The substituents are connected by both ether and carbon-carbon linkages.



p-coumaryl alcohol coniferyl alcohol sinapyl alcohol

Figure 5. The aromatic alcohols that are precursors in the synthesis of lignin (redrawn from Govender et al., 2009).

The amount of lignin in softwoods is generally higher than in other types of lignocellulose, and it is characterised by higher amounts of G units (one methoxy group) (Guerra et al., 2008), while the hardwood lignin has H,G and S units (two methoxy groups) (Hu and Ragauskas, 2012), and the herbaceous contain all the three precursors (G, H, S) with higher amount of H units than wood (Madakadze et al., 1999; Rencoret et al., 2007; Agnihotri et al., 2010). It is reported that a favourable G:H:S ratio make SCB lignin to be solubilised more easily by alkali, in comparison to *E. grandis* and giant bamboo.

The data in Table 3 obtained from the present study shows that higher alkalinity was required to delignify non-extracted giant bamboo to achieve pulp with comparable kappa number as *E. grandis*. On the other hand, milder sodaAQ pulping was used to delignify SCB. The higher alkaline requirement for delignification of giant bamboo may be due to the higher extractives content or higher degree of condensation of bamboo lignins (Salmela et al., 2008). The difference in H:S:G ratio of 1:2:2.1 and 0.1:2:1 for bamboo and eucalyptus respectively, has been reported which indicates a higher degree of condensation in bamboo lignin compared to that of eucalyptus (Ribas Batalha et al., 2012). These reactions are undesirable because they could lead to restriction of dissolution of lignin since a higher molecular mass is achieved (Gellerstedt et al., 2004).

Table 3. Kraft and sodaAQ pulp properties from non-extracted *Eucalyptus grandis*; giant bamboo and sugarcane bagasse

	E. grandis[1] Kraft pulping	giant bamboo[2]	sugarcane bagasse[3] sodaAQ pulping
Active alkali (NaOH) %	17	18.7	14
Sulfidity (%)	22	25	-
Anthraquinone (%)	-	-	0.1
kappa number	20.0	22.7	22.8
Pulp yield (%)	45.7	41.2	40.1
Viscosity (cP)	7.2	10.0	7.2

[1]Data from paper **I**
[2]Data from paper **IV**
[3]Data from paper **III**

2.7 Other components

Extractives and inorganic constituents of lignocelluloses can cause production problems related to pitch formation during pulp and paper production (Lopez et al., 2012).The cell wall extractives consists of rosin waxes, fatty acids, phenols, terpenes, steroids, etc., whereas the inorganic content or ash (SiO_2, Ca, K, Mg, Fe, Co and Mn) content is influenced by the amount of silica present in plants (De Lopez et al., 1996; Scurlock et al., 2000; Cheng et al., 2010; Ribas Batalha et al., 2012).

Nonwood material normally has higher extractives and silica content than wood (Hurter, 1988; Kaur et al., 2010). Extractives are released from fibres during pulping and agglomerate to the so-called colloidal pitch (Hassler, 1988; Jahan et al., 2012). The consequences are poor dewatering of pulps due to blockage of the paper machine wire and leave stains in the resulting paper sheets (Covey et al., 2006; Marques et al., 2007). On the other hand, dissolved silica in the pulping liquor (black liquor) led to difficulties in the recovery of cooking sodium and energy by creating scaling problems, plugging boilers and increasing viscosity, which hinders both evaporation and combustion of the black liquor (Chaudhur, 1993; Deniz et al., 2001; Dutt and Tyagi, 2011).

These challenges make chemical recovery of black liquor produced from nonwood material difficult, less efficient, and costly as compared to recovery of black liquor from wood.

Silica can be removed by precipitation from black liquor by partial acidification with carbon dioxide from flue gasses or by addition of calcium oxide (Covey et al., 2006). Moreover, the problem of silica can be reduced through alkaline hemicelluloses pre-extraction processes (De Lopez et al., 1996; Cheng et al., 2010).

2.8 Morphology of the fibre and its influence on pulp and paper properties

In considering wood or nonwood as a source of fibre for the production of pulp and paper, two factors must be taken into account: the yield of fibre per given volume or weight of raw material (more so in the chemical processes), and the quality of the resulting fibre. The former depends on the characteristics of the feedstock prior to pulping and the process employed in its conversion into pulp, while the latter is mainly a result of morphological features of the individual fibres and their modification brought about by the methods of conversion (Vaughn et al., 2003). The fibre variables responsible for determining the physical characteristics and quality of pulp and paper are classified under fibre morphological aspects. These variables are fibre length, cell wall thickness, fibre coarseness, fibre strength, and interfibre bonding (Haygreen and Bowyer, 1996; Sridach, 2010). Table 4 summarizes the morphological characteristics of hardwood (*E. grandis)*; grasses (SCB); woody grass (bamboo) and softwood (pine) reported in the literature (Sykere, 1994; Agnihotri et al., 2010; Dutt and Tyagi, 2011).

SCB fibres are of 1.1-1.5mm length and 20-21.4 micron diameter which is similar to hardwoods such as *E. grandis* (0.9-1.1 mm and 19.2-20.1 micron respectively). However, the quality of the pulp obtained from SCB (nonwood) is inferior to that of *E. grandis* (hardwood) as reported by other authors (Table 5, papers **I** and **II**, Belayachi and Delmas 1995).

The average length and cell wall thickness of fibres in bamboo species are comparable to that of softwood fibres indicating for the production of pulps of similar quality (Ogunsile and Uwajeh, 2009). Hence, the large scale delignification of bamboo is conventionally based on techniques similar to those generally applied to wood (Salmela et al., 2008).

Fibre length generally influences the tearing strength of paper; the greater the fibre length, the higher will be the tearing resistance of paper, as observed with giant bamboo in Table 5 (Muneri, 1997; Fardim and Duran, 2004). Paper made from fibres that are too short will have insufficient common bonding area between fibres, and as a result there will be points of weakness for stress transfer within the sheet, and the paper will be low in strength (Haygreen and Bowyer, 1982).

Fibre diameter and wall thickness influences the fibre flexibility (Dutt and Tyagi, 2011). Thick walled fibres adversely affect the bursting strength, breaking strength, and folding endurance of paper. The paper manufactured from thick walled fibres will be bulky with coarse surface texture, and containing a large amount of void volume. Thin walled cells on the other hand, collapse readily to form dense, well-bonded paper, low in tear but high in other strength properties (Deniz et al., 2004; Agnihotri et al., 2010).

Fibre lumen width affects the beating of pulp. The smaller the fibre lumen width, the poorer will be the beating of pulp because of the penetration of liquids into empty spaces of the fibres (Mosello et al., 2010). Indeed, *E. grandis* pulps required longer time to beat followed by giant bamboo whereas the SCB pulp required the shortest beating time (Table 6).

SCB and bamboo have a higher Runkel ratio, compared to *E. grandis*, which was anticipated to negatively affect the breaking length (Patt et al., 2006; Moussaouiti et al., 2012). This assumption was confirmed by the low breaking length observed with SCB and giant bamboo relative to *E. grandis* (Table 5).

Bamboo has the highest cell wall thickness to lumen diameter (L/D) ratio compared to SCB and Eucalyptus (Table 4). The greater the L/D ratio, the greater the fibre flexibility and the better the chance of forming well-bonded papers (Haygreen and Bowyer, 1996).

Table 4. Morphological characteristics of Eucalyptus, Sugarcane bagasse, Bamboo and Pine found in the literature

Species	Fibre length (L), mm	Fibre width (D), μm	Lumen diameter (d), μm	Cell wall thickness (w), μ	Runkel ratio (2w/d)	Slenderness ratio (L/D)	Rigidity coefficient (2w/D)
Bhadrachalam *E. grandis* (Dutt and Tyagi 2011)	1.1	19.2	3.2	12.2	0.5	55.2	0.3
Saharanpur *E. grandis* (Dutt and Tyagi 2011)	0.9	20.1	2.8	14.3	0.4	52.3	0.3
E. tereticornis (Agnihotri et al., 2010)	0.7	14.2	3.4	5.4	3.2	49.3	0.8
E. robusta (Agnihotri et al., 2010)	1.1	19.0	12.1	3.4	0.6	56.3	0.4
Indian Sugarcane bagasse (Agnihotri et al., 2010)	1.5	21.4	6.3	7.7	2.5	70.6	0.7
Mexican Sugarcane bagasse (Agnihotri et al., 2010)	1.1	20.0	2.0	4.0	0.7	56.5	0.4
India *Bambusa vulgaris* (Skyere 1994)	2.0	15.1	4.0	5.5	2.8	134.0	-
Phillipine *Bambusa vulgaris* (Skyere 1994)	2.3	17.0	4.0	7.0	3.5	137.0	-
Ghana *Bambusa vulgaris* (Skyere 1994)	2.7	14.6	9.7	5.0	1.0	182.0	-
Pinus kesiya (Dutt and Tyagi 2011)	2.3	40.7	34.8	5.9	0.3	56.5	0.03

Table 5. Handsheets paper strength properties derived from non-extracted sugarcane bagasse, *Eucalyptus grandis* and giant bamboo

Properties	SCB[1]	*E. grandis*[2]	giant bamboo[3]
Kraft pulping			
Beating time (min)	23	80	40
Drainage rate(^{0}SR)	45	40	44
Tear index (kPa.g/m^2)	3.6	8.4	14.4
Burst index (mN.g/m^2)	5	5.3	7.1
Breaking length (km)	3.8	5.9	5.3
sodaAQ pulping			
Beating time (min)	20	55	40
Drainage rate(^{0}SR)	45	40	47
Tear index (kPa.g/m^2)	3.8	4.1	15.9
Burst index mN.g/m^2	4.7	4.7	5.5
Breaking length (km)	4.9	5.7	3.4

[1]Data from paper **III**
[2]Data from paper **I**
[3]Data from paper **IV**

2.9 Pulping processes

2.9.1 Chemical pulping process

All pulping processes have continuously developed to improve economic performance and to meet new requirements of improved product quality and cleaner environmental practises. Of the two alkaline pulping processes i.e. kraft and soda, the kraft process is the dominating alkaline pulping process worldwide accounting for more than 90% of the chemical pulps (Sixta and Schild, 2009; Sridach 2010). This is mainly based on the higher yields and superior pulp properties with kraft pulping (*kraft* means strength or power in German) compared to soda pulping (Macloed et al., 1995; Tutus et al., 2010). At the same time, the kraft process accommodates a variety of wood species and can tolerate high amounts of extractives as well as bark residues (Biermann, 1996).

Conversely the acidic sulfite pulping process cannot be applied satisfactorily to wood species containing much resin such as pine and other acid resistant materials (Sixta and Austria, 1998). Kraft pulping offers shorter cooking times than sulfite chemical pulping due to shorter heat up time and typically higher final cooking temperatures (170°C vs 140°C) (Hocking, 2005). The heating up time is reduced to protect degradation of carbohydrates at high temperatures (Biermann, 1996). Kraft pulping processes are advantaged by well established processing of the cooking spent liquor (black liquor), including the recycling of the pulping chemicals and waste water, generation of process heat, as well as production of some secondary products such as lignin derivatives, tall oil and turpentine from pine species (Fengel and Wegener, 2003; South Africa NEDLAC, 2004; Chirat et al., 2012). However, there are also some disadvantages such as odour problems, darker pulps and low beating abilities.

Although the soda process has been mainly replaced by the kraft process it is still an important process for the production of nonwood fibre pulps (Sadawarte, 1995; Resalati et al., 2012). In soda pulping the cooking liquor is composed mainly of sodium hydroxide. The application of pulping additives such as anthraquinone (AQ) has increased the extent of delignification, so that it is comparable to that of the kraft method (Macloed, 1983; Khristova et al., 2006). To explain the mechanism of AQ in the soda pulping, a cyclic mechanism has been proposed (Fig 6) in which AQ is reduced by polysaccharides to anthrahydroquinone (AHQ^{2-}) which is soluble in alkali medium, and the reduced AHQ^{2-} species is oxidised back to AQ by lignin (Francis et al.,2007; Venica et al., 2008; Kaur et al., 2010). The AQ can take part again in the redox cyle. The added AQ therefore acts as a catalyst in promoting the splitting of the β-aryl ether linkages of the lignin structure, and the stabilisation of carbohydrate against end peeling by the oxidation of the reducing end group to a carboxyl (Khristova et al., 2006; Kamppi et al., 2010).

More hemicelluloses are retained compared to cellulose, due to more end-groups per unit mass, when using sodaAQ than the traditional kraft process (Dimmel et al., 2003; Bose et al., 2009). Hence, AQ addition works efficiently when a high content of hemicelluloses are required from soda pulping process.

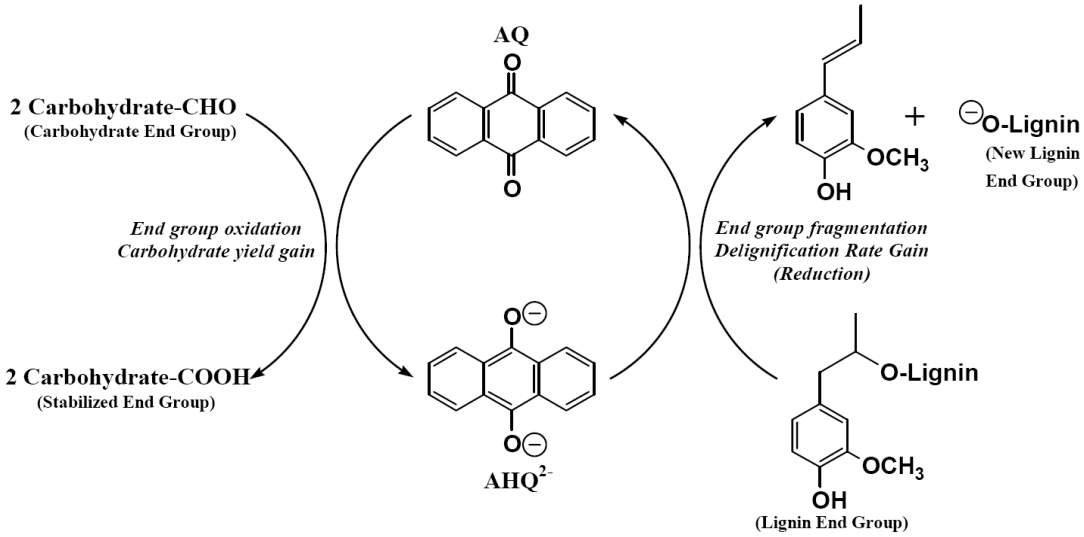


Figure 6. Schematic reaction cycle of anthraquinone as cooking additives. (adapted from Francis et al., 2007)

Kraft pulping processes utilise an aqueous solution of sodium hydroxide (NaOH) and sodium sulphide (Na_2S), also called white liquor, to remove lignin from wood chips at a high alkaline pH of 12 to 14 (Yoon et al., 2001). The liquor to wood ratio is 3/1 to 5/1 w/v. The wood chips are charged to the digester together with white liquor, heated to a cooking temperature of about 165 to 170ºC and are allowed to cook between 1.5 to 2 hours (Pinto et al., 2005; Tutus et al., 2010). Industrial white liquor also contains sodium carbonate resulting from recovery cycle. The digester systems are continuous or batch, though in many current kraft pulp mills still use the older batch system which is characterised by higher flexibility and lower maintenance costs (Rao and Corbin, 1993; Biermann, 2006).

Ideally for a uniform cooked pulp, each fibre should receive the same chemical treatment for the same length of time at the same temperature. For this to occur the chemical reagents are transported into the lignin rich middle lamella of the wood by bulk penetration under the influence of pressure and by diffusion of ions from the cooking liquor into water which is already present in the wood chips (Obst, 1985; Dang and Nguyen, 2007; Kaur et al., 2010).

The objective of chemical pulping is delignification (removal of lignin) and leave cellulose and hemicelluloses in non degraded form. During this treatment, the hydroxyl (-OH) and hydrosulfide (-HS) anions of cooking liquor react with the lignin, causing the polymer to degrade to smaller fragments which then dissolve (Santiago and Neto, 2007). The delignification proceeds in three different phases: the initial phase, the bulk and the final or residual phase (Chakar and Ragauskas, 2004; Santiago et al., 2008). The initial delignification takes place below temperature of 140°C and is controlled by diffusion, while the main bulk delignification runs at temperatures above 140°C - 170°C until about 90% of the lignin is dissolved (Lindgren and Lindström, 1996; Lourenco et al., 2012). The degradation of the lignin macromolecule proceeds through the cleavage of the β-alkyl-aryl-ether bonds and carbon-carbon linkages holding the phenyl propane units together (Gierer, 1985). This type of cleavage resulted into the liberation of lignin fragments, thus increased their dissolution, as illustrated in Figure 7. On the other hand, condensation reactions of lignins might occur that lead to the formation of alkali stable linkages. These reactions retard lignin dissolution and are therefore undesirable. In the last stage of lignin removal, ascribed to cleavage of carbon-carbon linkages, the rate of delignification significantly decreases and marks the end of the cook (Gierer, 1980).

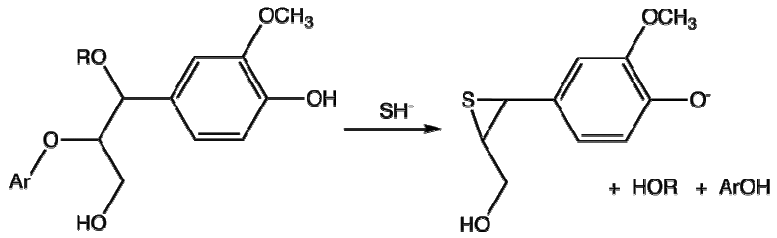


Figure 7. Net reaction in depolymerization of lignin by SH^- (Ar = aryl, R = alkyl groups) (redrawn from Chakar and Ragauskas, 2004).

At the end of the cooking process, the black liquor is separated from the pulp fibres in the subsequent washing and sent to the kraft chemical recovery system (Xu et al., 2006). The kraft pulping process normally has pulp yields of 45-50% (w/w), with the residual lignin of about 4-5% (by weight) (Chakar and Ragauskas, 2004).

The selectivity in the kraft pulping process is poor, and a part of the polysaccharides is removed and dissolved in the cooking liquor due to high alkali concentrations, which contributes to a decrease in the pulp yield. Hemicelluloses are degraded to larger extent (>50%) than cellulose (<20%) during kraft pulping, due to their lower degree of polymerisation and amorphous state (Henriksson and Gatenholm, 2001; Lounge Jr et al., 2010). Polysaccharide degradation processes occur by stepwise end-initiated depolymerisation, called primary peeling reaction, and random alkaline hydrolysis of glycosidic bonds, followed by secondary peeling reaction (Santiago et al., 2007). The peeling reaction starts at about 100°C and proceeds at the reducing end until the competing stopping reaction has formed a stable acid end group (Fengel and Wegener, 2003).

Glucomannan is sensitive to peeling and degrades to low molecular mass products whereas xylan may be dissolved into the cooking spent liquor (black liquor) without being extensively degraded (Danielsson et al., 2006; Berggren et al., 2003). Some of the dissolved xylan can re-adsorb on the surface of cellulosic fibre (Henriksson and Gatenholm, 2001; Magaton et al., 2011).

The decrease in solubility of xylan is due to the deacetylation and formation of hexenuronic acid (HexA), resulting from the elimination of methanol from the 4-O-methylglucuronic acid groups (MeGlUA) – which are side groups linked to the xylan backbone (Genco et al., 1990; Pedroso and Carvalho, 2003). The rate of the alkaline hydrolysis becomes severe at temperatures above 150°C, i.e. at the bulk stage and the degradation is more pronounced for hemicelluloses than for cellulose, but it still maintains its crystallinity due to the readsorbed hemicelluloses (Virtanen et al., 2006).

The residual lignin content of the pulp is measured as kappa number and the kappa number for typical bleachable hardwood pulp is about 20-30 (Muneri, 1997; Fardim and Duran, 2004). Kappa number is a good indicator of chemical demand for bleaching to remove the residual lignin on pulp fibres.

The re-adsorption of xylan on the cellulose fibres observed during pulping can retard the bleaching process, since the adsorbed polymer acts as a physical barrier to the penetration of chemicals used to remove the residual lignin. In addition, the presence of HexA reacting with bleaching chemicals increases their consumption, and also increases the difficulty of reaching a high degree of brightness (Kautto et al., 2010). Furthermore, HexA is strongly associated with paper yellowing that increases the brightness reversion with age (Pedroso and Carvalho, 2003; Kaur et al., 2010). The hemicelluloses content of pulp in particular affects not only the yield, but also the strength and other papermaking properties. As such, a decrease in xylan content leads to a decrease in packaging related strengths properties such as tensile strength and tear index (Schwikal et al., 2011, Mosello et al., 2012).

An important characteristic of the kraft process is that the spent delignification liquor (black liquor), consisting of soluble lignin and lower molecular lignin degradation products, cellulose, hemicelluloses fractions and inorganic chemicals separated from the pulp fibres in the washing stage, is concentrated and burnt to generate steam and inorganic smelt (Biermann, 1996; Fengel and Wegener 2003). The smelt composed of sodium sulphide and sodium carbonate is dissolved in water to form green liquor, which is reacted with calcium hydroxide to regenerate the sodium hydroxide for white liquor.

Degraded hemicelluloses and cellulose in the black liquor have a heating value of 13.5 MJ/kg, which is about half that of lignin (27 MJ/kg) (van Heiningen, 2006). The net heating values of the carbohydrates are decreased due to the consumption of alkali to neutralise the acetyl groups released from xylan (Yoon and van Heiningen 2008; Helmerius et al., 2010). The recoverable heating value of the degraded polysaccharides in black liquor is also reduced by the amount of energy required to convert hydroxides to oxides during combustion (Amidon and Liu, 2009).

Therefore, the separation of hemicelluloses before pulping could increase the overall efficiency of the process by decreasing the pulping chemical consumption and energy of kraft pulp mill (Yoon and van Heiningen 2008; Marinova et al., 2009). These hemicelluloses represent a good prospect for an integrated kraft pulp mill based biorefinery for the production of higher value added chemicals and materials in addition to the present fibre products (Ragauskas et al., 2006). However, it is important to analyse the effects of the hemicelluloses extraction step on the pulping process into which it is integrated with the aim of maximising hemicelluloses yield without negatively affecting pulp yield or quality, as was done in the present study (papers **I-V**).

2.10 Pulp mill biorefinery with hemicellulose pre-extraction integrated with pulping

A biorefinery is a concept for the collection of processing technologies used to convert the components of various biomass feedstocks into various materials, chemicals and energy, much likewise to petroleum refineries (Ragauskas et al., 2006; Carvalheiro et al., 2008). Kraft pulping serves as the most suitable basis for explaining the lignocellulosic material biorefinery concept into practise (van Heiningen, 2006; Huang et al., 2010). It accommodates a variety of feedstocks, recovers and reuses all pulping chemicals and the fibres show excellent paper making properties (Fengel et al., 2003).

One biorefinery concept involves pre-extraction of hemicelluloses fraction, which is normally wasted in the black liquor of kraft pulp mills prior to pulping while continuing to maintain the quality standards for pulp and paper products (Ragauskas et al., 2006; van Heiningen, 2006; Luo et al., 2012). This approach to a biorefinery has been nvestigated in the present study, taking into consideration the unique properties of local feedstocks.

There are various potential effective extraction methods to solubilise hemicelluloses from lignocellulosic biomass including alkaline, hot water and dilute acid (Mosier et al., 2005; Carvalheiro et al., 2008). Hemicelluloses maintain more oligomeric or polymeric sugars in extracted liquor during alkaline extraction (Al-Dajani and Tschirner, 2008; Yoon et al., 2008; Sixta and Schild 2009), while acidic extraction conditions break down hemicelluloses into a mixture of monomeric and oligomeric sugars (Parajo et al., 1994; Springer et al., 1985; Mendes et al., 2009; Canilha et al., 2011). Research work on the dilute acid hydrolysis of various lignocellulose materials have defined optimal process conditions as temperature range of 120-210ºC, sulphuric acid concentration typically 0.25-8 wt% and reaction time from 10 minutes to 33 hours (Lavarack et al., 2002; Garrote et al., 2001; Hu and Ragauskas, 2012). Hot water treatments convert the hemicelluloses fraction into a mixture of sugar oligomers and monomeric sugars (Garrote et al., 2001; Leschinsky et al., 2008; Al-Dajani et al., 2009; Lei et al., 2010).

2.10.1 Mild alkali extraction of hemicelluloses (xylans)

Alkaline (NaOH in this case) extraction techniques are delignification processes with significant solubilisation of hemicelluloses as well. The mechanism of alkaline hydrolysis is saponification of intermolecular ester bonds crosslinking hemicelluloses and lignin (Sun et al., 1995; Liu et al., 2011).

Alkaline pre-extraction is well suited for combination with kraft pulping, since there will be no change in pH, can be carried out at lower temperatures and pressure than pulping and maintain subsequent pulp yield (Al-Dajani and Tschirner, 2008; Helmerius et al., 2010; Jun et al., 2012).

It has been reported that the alkaline extraction would be more suitable for hemicelluloses extraction from hardwoods than softwoods (Helmerius et al., 2010, Walton et al., 2010). This is based on the fact that, during kraft pulping process, the hemicellulosic fraction is degraded through the alkaline peeling reaction and most of glucomannans (the softwood hemicellulose) are degraded whilst xylan (hardwood hemicellulose) is more stable and solubilised as oligomers (Fardim and Duran, 2004; Patt et al., 2006; Schild et al., 2010). Accordingly, nonwood materials have been shown to exhibit similar hemicellulosic components as hardwoods which make them suitable for the alkaline pre-extraction approach of hemicelluloses (Biermann, 1996; Peng et al., 2012). However, in order to maintain the pulp yield and minimise the loss of pulp strength, the presence of hemicelluloses is necessary in the fibre matrix (Yoon and van Heiningen, 2008; Mossello et al., 2010). Therefore, the optimised conditions are always the compromise between hemicelluloses extraction and the quality of the pulp obtained from the solid residues of hemicelluloses extraction.

The present study presents the notion to integrate the alkaline pre-extraction of hemicelluloses from *E. grandis*, giant bamboo and SCB prior to pulping and subsequent kraft or sodaAQ pulping of the extracted materials. The detailed examination of the comparative studies between *E. grandis*, SCB and giant bamboo can be found in the appended papers **II, III** and **IV** respectively. A summary of the most promising findings is presented in Table 6 below.

Table 6. Extraction conditions, xylan recovery yield, and pulping conditions for non-extracted and alkaline extracted giant bamboo *Eucalyptus grandis* and sugarcane bagasse

	Raw materials					
Pulping process	**giant bamboo**		***E. grandis***		**sugarcane bagasse**	
	Kraft pulping				sodaAQ pulping	
	Extraction condition					
	Non-extracted	1M NaOH, 90°C, 240 min	Non-extracted	2M NaOH, 40°C, 240 min	non-extracted	1.5M NaOH, 65°C, 180 min
Xylan yield						
g/100g OD (% theoretical xylan)		3.0 (13.6)		2.1 (12.4)		18.0 (69.1)
cooking conditions						
Active alkali (%)	18.7	-	18.7	-	14.0	-
Sulfidity (%)	25	35.7	25	35.7	-	-
AQ (%)	-	-	-	-	0.1	0.1
*Time at 170°C (min)	30	30	45	30	30	25
NaOH in chips/residue (g)	169.6	59.3	165.4	99.2	130.4	141.1
NaOH from Na_2S (g)	30.9	21.3	28.1	32.9	-	-
Total NaOH in cook (%)	19.4	10.7	19.4	15.5	-	-
NaSH charge (g)	43.2	29.8	42.2	49.6	-	-
*Pulp properties						
Pulp yield (%)	41.2±2.0	50.4±1.5	53.1±3.0	51.1±2.0	40.1±2.0	45.0±1.3
Rejects (%)	8.7±1.3	5.0±0.5	1.7±0.4	0.6±0.5	15.7±1.0	3.3±2.2
kappa number	22.7±0.9	29.9±1.1	20.0±2.5	20.8±1.8	22.8±0.9	15.5±1.1
Viscosity (cP)	10.2±2.0	10.2±1.2	8.1±0.5	9.4±0.7	7.2±1.7	7.1±1.0
Residual alkali (g/L)	7.0±1.4	6.3±2.0	7.5±1.5	6.2±2.0	6.0±2.0	9.0±0.8
**Handsheets strength properties						
Beating time (minutes)	40	40	80	60	20	22
Drainage rate (˚SR)	44	41	40	39	45	38
Tensile index (Nm/g)	51.6±3.1	44.1±2.5	40.1±1.3	43.1±1.1	49.0±1.0	43.8±0.1
Tear index (kPa.m^2/g)	14.4±0.5	13.7±3.5	9.9±2.0	9.8±1.5	3.8±0.2	8.8±0.8
Burst index (mN.m^2/g)	7.1±0.4	7.3±0.2	5.3±0.4	5.2±0.1	4.7±1.2	4.3±0.1
Breaking length (km)	5.3±0.6	4.5±0.6	4.1±0.5	4.4±0.5	5.0±0.4	4.5±0.3
Brightness (ISO)	41.4±1.2	31.6±0.6	43.3±1.0	50.4±1.2	39.3±0.3	55.8±0.9

*Cooking time of extracted materials was reduced to avoid degradation of carbohydrates due to high concentration of NaSH in the cook

** Mean values and standard deviation of three measurements

***Mean values and standard deviation of ten measurements

The optimised alkaline extraction of xylan from the studied *E. grandis* followed by modified kraft process of the extracted material showed no effect in screened pulp yield and pulp quality (Table 6). Interestingly, alkaline pre-extraction of xylan from giant bamboo improved the kraft pulp yield by 9.2% while retaining the pulp viscosity. However, the high pulp yield was probably due to the high residual lignin content in pulps produced from extracted giant bamboo chips measured as kappa number.

Approximately 12.4% or 13.6% of xylan could be extracted from *E. grandis* or giant bamboo respectively, whilst the screened pulp yields were maintained at desired pulp mill levels of 50% and the kappa numbers were within the bleachable range as those of pulps produced from non-extracted materials (papers **II** and **IV**). This could be explained by the low total NaOH concentration of 16% or 11% used during delignification of pre-extracted *E. grandis* or giant bamboo chips respectively compared to 19% used for non-extracted chips (Table 6), which might have limited the alkaline hydrolysis of carbohydrates and their peeling reaction (Södahl et al., 2004; Jun et al., 2012). The lower NaOH concentration required for hemicellulose-extracted residues was in agreement with the earlier work on the effect of alkaline pre-extraction on pulping conditions (Yoon et al., 2011), showing potential for pre-extraction to reduce the pulping chemicals consumption. The kraft pulping of alkaline extracted *E. grandis* or giant bamboo was unique in that no NaOH charge was added to the kraft cook except for the NaOH carried by the chips from the pre-extraction stage and NaOH generated from sodium sulphide. This explains the lower total NaOH charge used for delignification of extracted giant bamboo compared to extracted *E. grandis*. In addition, the dissolution of xylan and other components from the material in the pre-extraction stage might have contributed to less alkali demand for delignification of extracted materials. Nonetheless, compared with alkaline extracted *E. grandis*, the high pulp yield for alkaline extracted giant bamboo was achieved at greater kappa number (29.9 vs 20.8) and high viscosity. High kappa number explains high demand of subsequent bleaching chemicals (Ribas Batalha et al., 2012). On the other hand, pulps with high viscosity might improve the fibre strength properties (Gurnagul et al., 1992).

The modified kraft pulping process of *E. grandis* or giant bamboo, with pre-extraction of hemicelluloses, was better in terms of pulp quality than previously reported for aspen hardwood chips (Al-Dajani and Tschirner, 2008). The reported modified kraft pulping method of alkaline extracted aspen chips resulted in no pulp yield loss, although a reduction in viscosity was observed (Al-Dajani and Tschirner, 2008).

The discrepancy could be due to the amount of xylan pre-extracted from the aspen chips, which was twice as high (24.8% vs 12.4% and 13.6%) than that extracted in the present study. This is in agreement with previous results by other authors, according to which the quoted kraft pulping process of *E. grandis* from which 42% xylan was extracted caused a reduction in pulp yield (Lounge Jr et al., 2010). Limiting the yield of hemicelluloses from alkaline extraction can therefore avoid a reduction in both pulp yield and tensile or breaking strength handsheet property from subsequent kraft pulping.

Handsheet strength testing of kraft pulps obtained from alkaline-extracted *E. grandis* residues showed an improvement in breaking length, tensile index and optical brightness by 6.8%, 7.0% and 14.1% respectively to those of pulps produced from non-extracted raw materials at 40±5˚SR (Table 6 and paper **II**). On the other hand all the pulps exhibited similar tear and burst indexes. Breaking length, tensile and burst indexes correlates strongly with interfibre bonding, while tear index depends strongly on fibre length (Fardim and Duran, 2004). The percentage yield of xylan retained in the pulp after kraft pulping of the extracted *E. grand*is chips (Paper **II**, Table 5) appeared to have been sufficient for the maintenance of tensile index or breaking strength property of the resultant pulp. The overall analysis of the results suggest that fibres produced from alkaline extracted *E. grandis* residues under the selected kraft pulping conditions were well bonded to one another and thus presented good conformability without fibre shortening (Liu et al., 2012). Alkaline hemicelluloses pre-extraction from southern mixed hardwoods prior to kraft pulping showed no effect on tensile strength but increased the tear index compared to kraft pulps produced from non-extracted wood chips (Yoon et al., 2011).

For giant bamboo, alkaline xylan pre-extraction showed a slight improvement in burst index by 3% while tensile index and breaking length were reduced by 14.5% and 15% respectively compared to pulps produced from non-extracted bamboo (Table 6 and paper **IV**). The reduction in strength properties might be due to xylan deficiency in pulp samples produced from alkaline pre-extracted bamboo (Helmerius et al., 2010). The alkaline pre-extraction of aspen hardwood chips also showed reduction of about 10% in tensile index due to alkaline extraction; although no other strength properties were reported (Al-Dajani and Tschirner, 2008). On the other hand, the tear index of hand sheets prepared from alkaline-extracted giant bamboo pulps declined by 5% at 40°SR and optical brightness was reduced relative to non extraction

Generally, giant bamboo had higher handsheet tear and burst indexes compared to *E. grandis* (Table 6). The observed increase was 31.4% and 28.0% for handsheet tear and burst indexes, respectively, for kraft pulps from alkaline extracted giant bamboo residues, relative to similar raw materials from *E. grandis*. The observed improvement in pulp strength for bamboo may be explained by the longer fibre length and very thick cell wall of bamboo compared to hardwoods (Vû et al., 2004). Nevertheless, alkaline extraction of *E. grandis* resulted in brighter pulps compared to those of giant bamboo. The darker pulps produced from giant bamboo may be due to higher degree of condensation of bamboo lignins compared to that of eucalyptus (Ribas Batalha et al., 2012).

Alkaline-extraction of 69.1% xylan from SCB combined with sodaAQ pulping showed a remarkable decrease in kappa number of the resulting pulp, with no yield loss, in comparison to pulps from non-extracted SCB (Table 6 and paper **III**). In addition, the handsheet tear index and optical brightness of the pulp obtained from xylan pre-extracted SCB residues were improved. The burst index, tensile index and breaking length of the pulp obtained from xylan pre-extracted SCB residues were comparable to those of pulps produced from non-extracted SCB. These results are in agreement with those reported for similar work done on other herbaceous plants such as barley straw (De-Lopez et al., 1996).

2.10.2 Dilute acid extraction of hemicelluloses (xylans)

Much is reported in the literature about the introduction of dilute acid extraction (prehydrolysis) of hemicelluloses from hardwood prior to kraft pulping for the production of dissolving pulps (Koukios and Valkanas, 1982; Vila et al., 2011, Saeed et al., 2012). However, the acid hydrolysis of hemicelluloses during dissolving pulp production may be too harsh for maximum hemicelluloses recovery (Behin et al., 2008). The mechanism of acid prehydrolysis involves cleavage of α-aryl ether bonds in lignin and hydrolysis of the non-crystalline part of cellulose, which resulted in a structure with reduced DP but with higher crystallinity (Pessoa et al., 1997; Fengel and Wegener, 2003). However, reduction in DP of cellulose can compromise the pulp yield and paper strength properties (Al-Dajani et al., 2009; Mendes at al., 2009). Within this as background, optimum conditions for dilute sulphuric acid extraction of hemicelluloses from *E. grandis*, SCB and giant bamboo that would lead to desired pulp properties have been investigated. Complete details can be found in papers **I**, **III** and **IV** respectively. An overview of the main findings is summarised in Table 7 below.

Table 7. Pulp properties and handsheets paper strength properties obtained after kraft or sodaAQ pulping of non-extracted and acid extracted *Eucalyptus grandis*, sugarcane bagasse and giant bamboo

Raw material	***E. grandis***		**sugarcane bagasse**		**giant bamboo**		***E. grandis***	
Pulping process	Kraft pulping				sodaAQ pulping			
Extraction condition	non-extracted	0.3% H_2SO_4, 140°C, 30min	non-extracted	0.3% H_2SO_4, 140°C, 30min	Non-extracted	0.3% H_2SO_4, 140°C, 30min	non-extracted	0.3% H_2SO_4, 140°C, 30min
Xylan yield								
% theoretical (xylose + oligomer)	-	21.4	-	23.8	-	11.3	-	21.4
cooking conditions								
Active alkali (%)	17	17	12	12	16	16	17	17
Sulfidity (%)	22	22	20	20	-	-	-	-
AQ (%)	-	-	-	-	0.1	0.1	0.15	0.15
Time at 170°C (min)	90	90	30	30	30	30	120	120
Pulp properties								
Pulp yield (%)	45.7±1.0	40.9±2.0	41.3±1.1	39.5±1.2	43.1±1.2	40.6±2.0	43.9±0.5	42.3±1.5
Rejects (%)	1.7±0.5	5.2±0.3	5.9±1.0	3.7±0.5	17.2±1.0	17.5±1.2	4.4±1.1	4.1±0.8
kappa number	20±2.5	26.8±1.5	7.0±2.2	6.0±1.2	22.9±0.5	27.8±0.2	22.8±1.0	20.9±1.2
Viscosity (cP)	7.2±1.2	5.2±1.1	3.5±1.4	2.5±1.3	7.0±2.5	10.0±1.0	6.3±1.2	6.7±2.1
Handsheet strength properties								
Beating time (min)	80	55	23	25	35	20	55	55
Drainage (°SR)	40	45	45	46	39	36	40	43
Tensile index (Nm/g)	51.9±1.9	44.3±2.2	51.2±1.4	29.4±2.5	33.2±4.0	45.4±4.2	45.9±1.5	41.9±2.0
Tear index (kPa.m^2/g)	8.4±1.3	4.2±1.5	3.0±1.7	2.6±1.3	15.9±0.8	14.7±0.1	4.1±1.8	4.0±1.5
Burst index (mN.m^2/g)	5.3±1.1	4.2±1.5	5.2±0.5	3.4±0.4	5.5±0.6	5.5±0.8	4.7±1.0	3.9±0.9
Breaking length (km)	5.9±0.5	4.5±0.5	4.6±1.1	2.6±2.1	3.4±0.5	4.6±0.4	4.7±0.8	4.3±1.2
Brightness (ISO)	48.4±2.0	37.8±2.4	52.2±1.1	54.9±1.3	38.8±0.5	31.6±1.3	38.0±1.9	42.2±1.8

In the present study, no suitable conditions were found for the combined acid extraction of hemicelluloses with subsequent kraft or sodaAQ pulping process that resulted in a similar pulp yield and properties as when pulping non-extracted chips. Generally, extraction of hemicelluloses using dilute sulphuric acid disadvantaged the subsequent pulping process in terms of pulp yield, quality and handsheet paper strength properties for all the tested feedstocks (Table 7, papers **I**, **III** and **IV**). However the differences were lower when sodaAQ was applied in acid pre-extracted materials compared to kraft pulping. Reduction in kraft pulp properties due to acid pre-hydrolysis confirmed reported results by other authors (Yoon and van Heiningen, 2008; Aldajani et al., 2009; Mendes et al., 2009; Testova, 2006). The poor response can be explained by the decrease in molecular mass of xylan under acidic conditions and thus the increased content of reducing end groups and with the xylan becoming easily soluble in the subsequent alkali medium (Mussatto et al., 2006). Consequently, the cellulose chains became more susceptible to the peeling reaction because the xylan layer on the cellulose fibrils was partially removed, hence the reduction in pulp yield and quality (Helmerius et al., 2010; Duarte et al., 2011). The increase of carbohydrates reaction due to acid extraction, explains the extra requirement of cooking alkali (NaOH), resulting in a decrease of the residual active alkali (Mendes et al., 2009; papers **II**, **III** and **IV**). The residual active alkali measured in black liquors obtained from acid extracted *E. grandis* and giant bamboo was 1.5-3.3 g/L, which was below the recommended 6-8 g/L (Lounge Jr et al., 2010). This strongly suggests that more cooking chemicals would be required to pulp acid extracted materials.

Alternatively, dilute acid xylan extraction from giant bamboo or *E. grandis* chips resulted in sodaAQ pulps with higher pulp viscosities, especially so for giant bamboo compared to kraft pulps. AQ in sodaAQ pulping process oxidises the reducing end groups of carbohydrates that might have been generated during the pre-extraction stage and stabilises their peeling reaction (Bose et al., 2009). The retention of carbohydrates could possibly improve the strength properties of pulps produced from acid pre-extracted giant bamboo compared to pulps produced from non-extracted giant bamboo.

As expected, sodaAQ pulping of acid extracted giant bamboo residues resulted in similar handsheet burst index and improved tensile index and breaking length by approximately 26% compared to sodaAQ pulping of non-extracted giant bamboo. It has been reported in the literature that strength properties such as tensile and breaking length is more dependent on cellulose characteristics than xylan content (Silva et al., 2011). The handsheet brightness was reduced due to acid pre-extraction implying high demand of bleaching chemicals (Mendes et al., 2009)

Generally, sodaAQ pulps produced from giant bamboo gave handsheets with higher tear and burst indexes compared to *E. grandis*. On the other hand, sodaAQ pulping of acid extracted giant bamboo resulted in improved tensile strength, tear and burst indexes and similar breaking length compared to sodaAQ pulps produced from acid extracted *E. grandis* residues. High pulp viscosity and longer fibre length observed for giant bamboo increased the fibre strength properties compared to *E. grandis* (Table 4). However, acid extraction of giant bamboo decreased the optical brightness of pulps than those produced from *E. grandis*. Pulps produced from giant bamboo had higher residual lignin content compared to that of *E. grandis*.

Dilute acid extraction prior to pulping has been suggested for the production of dissolving pulps (Koukios and Valkanas, 1982). Although dilute acid extractions in general lead to a reduction in pulp yields, it has been found to increase the alpha cellulose content (Vila et al., 2011; Ribas Batalha et al., 2012).

2.10.3 Hot water extraction of hemicelluloses (xylans)

Hot water pre-extraction of hemicelluloses from lignocellulosic material is of interest because it is cheap and environmentally friendly, corrosion problems are limited and results in simpler downstream processes, i.e. no sludges are generated compared to dilute acid and alkaline methods (Walton et al., 2010). However, the implementation of hot water pre-extraction processes is hindered by low hemicelluloses (sugar) solubilisation under the too mild conditions (Lei et al., 2010; Vila et al., 2011). The mechanism of hydrolysis and subsequent dissolution of lignocellulosic material is promoted by acetic acid formed from hydrolysis of acetyl groups and uronic acid substitutions removed by hydronium ions coming from water auto-ionisation, both lowering the pH of the extract to the range of 3-4 (Garrote and Parajo, 2002). Considering hardwoods and nonwoods as feedstocks, acetylated glucuronoxylan is the major hemicelluloses; the application of hot water extraction to these feedstock would generate a separate value added stream mainly consisting of xylo-oligosaccharides (Jahan and Rahman, 2012; Yoon et al., 2008; Alfaro et al., 2010). The hot water hydrolysis is selective to hemicelluloses whereas cellulose is retained in solid residue and shows improved susceptibility to further treatments due to the structural changes of the lignocellulosic matrix (Garrote and Parajo, 2002; Lei et al., 2010). In the present study, hot water extraction of SCB was studied since the dilute acid extraction significantly compromised the pulp properties (paper **III**). Table 8 shows the effect of hot water xylan pre-extraction of SCB on pulp yield, quality and handsheet strength properties.

Table 8. Pulp properties and handsheets paper strength properties obtained after sodaAQ pulping of non-extracted and hot water extracted sugarcane bagasse

Extraction conditions	non-extracted	Hot water, 120°C, 30min
cooking conditions		
Active alkali (%)	14.0	14.0
AQ (%)	0.1	0.1
Time at 170°C (min)	30	30
Pulp properties		
Pulp yield (%)	40.1±2.0	41.3±1.5
Rejects (%)	15.7±1.0	14.7±0.5
kappa number	22.8±0.9	20.9±0.5
Viscosity (cP)	7.2±1.7	5.5±2.0
Handsheet strength properties		
Beating time (minutes)	20	20
Drainage rate (˚SR)	45	40
Tensile index (Nm/g)	49.0±1.0	48.8±1.5
Tear index (kPa.m^2/g)	3.8±0.2	4.7±0.5
Burst index (mN.m^2/g)	4.7±1.2	5.0±1.4
Breaking length (km)	5.0±0.4	5.0±0.3
Brightness (ISO)	39.3±0.3	41.5±1.6

Pre-extraction of hemicelluloses from SCB with hot water resulted in low concentration of xylo-oligomers (5.7%). Subsequent sodaAQ pulping of extracted material showed similar screened pulp yield with a slight reduction of a kappa number compared to the pulps produced from non-extracted SCB. However, a decrease in pulp viscosity due to hot water pre-extraction was observed, indicating carbohydrate depolymerisation. This finding could be attributed to the formation of low molecular mass carbohydrates with high reducing end groups under hot water acidic conditions that becomes more susceptible to the peeling reaction under the subsequent alkaline medium (Aldajani et al., 2009).

The tear index and optical brightness of the handsheet papers produced from hot water extracted SCB were slightly improved while the breaking length, tensile and burst indexes were similar to those of pulps produced from non-extracted SCB fibres despite the reduction in viscosity (Table 8). The chemical composition of the pulps produced from hot water pre-extracted SCB showed a higher hemicelluloses content (72.5% glucan and 24.4% xylan) compared to pulps produced from non-extracted SCB (83.5% glucan and 6.8% xylan).

Fibre weakening during sodaAQ pulping of hot water pre-extracted SCB residues indicated by the viscosity reduction was probably compensated by the improved bonding ability due to enough hemicelluloses retains in the pulp fibres. Similar benefits on pulp properties have been proved for SCB by integration of hot pre-extraction of hemicelluloses with sodaAQ pulping (Lei et al., 2010).

CHAPTER 3: Conclusions and Suggestions for future work

The present study expands the current research area based on pulp mill biorefinery, aiming at extraction of hemicelluloses from South African grown *E. grandis*, sugarcane bagasse (SCB) and giant bamboo prior to alkaline pulping with the opportunity to produce value added products in addition to pulp and paper products. Pulp produced from southern eucalyptus and SCB is increasing its share of the global pulp market. Therefore, it is important that hemicellulose extraction and pulping should not impact on pulp yield or quality. Hemicelluloses extraction technologies including mild alkaline or dilute sulphuric acid combined with subsequent kraft or sodaAQ pulping of the extracted material were investigated in the present study. Pre-extraction of SCB with hot water was part of the dilute sulphuric acid experimental design and was used to evaluate the effect of xylan pre-extraction at lower levels. Extracting the hemicelluloses turns out to be fairly easy but a method to perform this extraction without negatively affecting the pulp yield or quality was the main challenge. The integrated hemicelluloses extraction and pulping approach produced significant conclusions and explains the ideas for the direction of future work that are discussed in this section.

3.1 Conclusions from the present study

Based on the experimental data obtained in the present study, the following conclusions can be drawn:

Of the xylan pre-extraction processes investigated i.e. dilute acid and mild alkaline, the latter demonstrated favourable results. It was possible to solubilise high molecular mass xylan of 53,400 g/mol from *E. grandis* (paper **II**), 32,793 g/mol from SCB (paper **III**) or 42,500 g/mol from giant bamboo (paper **IV**) prior to modified kraft or sodaAQ pulping whilst subsequent kraft or sodaAQ pulping of the extracted materials retained or improved final pulp yields and pulp viscosities at comparable kappa number.

Futhermore, the demand of the pulping chemicals could be reduced although a decrease of <20% in some handsheet strength properties was observed.

Among the three different lignocellulosic materials studied, SCB required milder processing conditions compared to *E. grandis* and giant bamboo. As expected, attractive xylan yield of 69.1% was easily recovered from herbaceous SCB under moderate alkaline conditions while *E. grandis* and giant bamboo had lower xylan solubility with only 12.4% and 13.6% recovered respectively. The combination of high xylan content together with lower lignin content in the non-extracted SCB explains the reasonable yields of xylan extracted from SCB prior to pulping and low processing chemical demand when the SCB was well depithed.

Nonetheless, although prepared under different pulping process, pulp fibres produced from SCB are generally of lower quality in terms of handsheet strength properties compared to *E. grandis* while giant bamboo was better or comparable to those of *E. grandis*. Alkali xylan extraction combined with mild sodaAQ pulping was the preferred option for SCB. This can be contrasted with the alkaline extraction process which integrated well with kraft pulping for both *E. grandis* and giant bamboo. The difference of chemical composition and morphological properties among the three feedstocks studied was evident in both xylan solubilisation and subsequent pulping performance.

The overall screened yield of kraft pulps produced from alkaline pre-extracted *E. grandis* or giant bamboo was maintained at desirable industrial levels of 50% and bleachable kappa number range without reduction in viscosity. These conditions improved tensile index and breaking length for pulps produced from extracted *E. grandis* and a slight increase in burst index was observed for pulps produced from extracted giant bamboo. On the other hand, although the pulping process used for sugarcane bagasse was sodaAQ, alkaline extraction improved the pulp yield (45%) with no reduction in pulp viscosity.

These conditions provided brighter pulps with superior tear index whilst breaking length and burst index was retained in the same level as those of pulps produced from non-extracted SCB.

Another important feature of alkaline pre-extraction of SCB was that, the higher pulp yields were produced at lower kappa number unlike high kappa number observed from giant bamboo and *E. grandis* pulps. In fact, pulps produced from giant bamboo presented higher kappa number compared to pulps produced from *E. grandis* treated under similar pulping conditions. This could be ascribed to higher extractives content observed for giant bamboo and more condensed lignin structures as documented in other works (Ribas Batalha et al., 2012). Therefore, a larger demand of bleaching chemicals to remove residual lignin can be expected for bamboo pulps.

Handsheet strength properties produced from beaten non-extracted or extracted giant bamboo pulps presented high tensile and breaking length as *E. grandis* pulps similarly treated, that are currently used commercially as fibre source in SA pulp industry. Particularly, the tear and burst indexes of giant bamboo pulps were much higher than in *E. grandis* pulps. Morphological properties of bamboo such as longer fibre length and thicker cell walls than that of hardwoods, positively influenced the tear and burst indexes of bamboo pulps.

Contrary to mild alkaline, dilute sulphuric acid pre-extraction of xylan did not favour the subsequent modified kraft pulping of the pre-extracted *E. grandis*, SCB or giant bamboo. The screened pulp yield and the overall handsheet paper strength properties were compromised. This could be attributed to the formation of low molecular mass carbohydrates with high reducing end groups under acidic condition that becomes more hydrolysed in the subsequent high alkaline conditions of the kraft pulping process.

When selecting the best pulping process for integration of dilute sulphuric acid hemicelluloses pre-extraction and pulping process, sodaAQ pulping is recommended depending on the amount of pre-extracted xylan. Moderate alkali charge, comparable pulp yield and handsheets strength properties observed for giant bamboo in which 11.3% xylose was extracted under dilute acid conditions made sodaAQ pulping more attractive compared to kraft pulping. AQ has an effect on stabilisation of carbohydrates against peeling reaction in pulping process.

Combination of hot water pre-extraction of SCB together with sodaAQ pulping may be the more attractive method as pulp yield was increased and the tear and burst indexes were improved. However, the hot water method was disadvantaged by liquid fractions containing lower xylan concentrations compared to acid pre-extractions.

Pre-extraction step of SCB can serve the purpose to decrease the scaling problems influenced by the silica present in most non-wood materials during pulping process, thereby improving the efficiency in chemical recovery of black liquor. The silica will solubilise from the fibres during the initial xylan extraction stage, although some purification of the solubilised xylan may be required.

The dissolution of xylan and other components into the extraction media decreased the mass of the extracted material and can increase the pulping capacity without additional investment in pulping digester. Moreover, xylan can be removed before pulping without degradation in molecular mass under alkaine conditions and the extracted xylan represents a valuable product.

With regards to the investigation of the suitability of giant bamboo as a potential source of fibre for South African pulp and paper industry, the present study showed that giant bamboo can produce pulp of sufficient quality for papermaking, especially so for the alkaline extracted giant bamboo. By utilisation of giant bamboo as a raw material for pulp and paper products, future prospects both for giant bamboo and pulp and papermaking industry will emerge. The pulp produced for giant bamboo revealed characteristics suitable for the production of paperboards.

3.2 Suggestions for future work

The recommendations for the future work within the pulp mill biorefinery concept are towards the improvement and optimisation of the alkaline xylan recovery approach and conditions of the subsequent pulping with the aim to make the recovery of value added xylan and the pulping process more effective and competitive.

3.2.1 Mild alkaline extraction of xylan

- The simplicity of the alkaline pre-extraction method is an encouraging element towards the development of industrial processes for an integrated xylan extraction and alkaline pulping approach for *E grandis,* giant bamboo and SCB. The operations used to recover xylan were selected because they are already used in line with kraft pulping process, and the ease of scale up to production scale has been documented (Huang et al., 2010). The selected operations are mixing, filtering/separation of solids from liquid fraction, concentration/evaporation, and separation of xylan; all of which are conducted at low temperatures. The process of xylan pre-extraction has been taken from laboratory scale to large scale with less difficulty in achieving the set operation conditions and replicating the yield and quality of the extracts especially so for *E. grandis* and giant bamboo. Future work on the implementation of the xylan extraction technique at industrial scale, the main issue to address might be mainly related to the large volume of water and would require additional recycling for reuse.

- The extraction process needs to be improved to maximise the xylan recovery yield. In the present study, the xylan recover yield for *E. grandis* (paper **II**) obtained was lower (12.4% vs 24.8%) than reported by other workers for aspen hardwood chips (Al-Dajani and Tschirner, 2008). The difference in xylan yield may be related to differences in separation membranes used for isolation of xylan from alkaline extraction liquors. A cellulose tube dialysis (12kDa cut-off) membrane was used in the present study to isolate xylan from the aqueous alkaline media (due to the limitation of laboratory facilities), which might have resulted in the loss of xylan fractions in the system compared to ultrafiltration membranes used in the referenced study. Nonetheless, nanofiltration membranes are said to be more suitable than ultrafiltration for isolation of xylan from alkaline extraction liquors (Schlesinger et al., 2006).
- The existence of silica is still a very significant problem when working with nonwood materials, that might affect the xylan recovery yield and quality. Therefore desilication prior to pre-extraction is recommended.
- The further fate of the alkaline extracted xylan needs to be identified. The use of the extracted xylan could be studied in paper and corrugated board applications were colour is less important as the FTIR and chemical composition results of the extracted xylans revealed the xylan-lignin association (paper **II**, **III** and **IV**). Furthermore, the characterisation of the extract quantitatively would be necessary to get the material balances add up to 100%. Other components of the raw material dissolved in the liquor extract and became unaccounted in the material balance calculations.
- Structural changes primarly in cellulose and lignin obtained after xylan extractions together with pulp fibres should be reviewed. Analysis of these fractions with quantitative and qualitative analytical techniques such as GC/MS, HPLC/MS, SEC, FTIR, etc., might give a key feature needed to develop more efficient xylan pre-extraction and pulping integration approach.

- Recycling and reuse of NaOH used for xylan extraction should be explored.

  For an alkaline pre-extraction approach to be commercially attractive and economically feasible, all the chemicals from the extraction stage should be recovered and reused. A literature reference found after the experiments were completed, suggest that the most realistic way is to use alkaline solutions such as green liquor (Na_2CO_3 + Na_2S) or white liquor (NaOH + Na_2S), already present in the pulp mill (Jun et al., 2012). However, there are some limitations reported with the green liquor such as, that hemicelluloses recovery yields are low, pressurised vessels will be required due to high extraction temperatures, and xylans are recovered in the form of low molecular mass oligomers. Such challenges can be improved by utilisation of white liquors since extractions are performed under atmospheric conditions. It would be interesting to explore these bases for South African grown *E. grandis* and giant bamboo. The application of the proposed bases on SCB will be constrained by their high alkaline strength which will damage the SCB fibres.

3.2.2 Pulping processes

- The integration of xylan extraction with chemi-thermomechanical pulping process should be considered. The research developments in biorefinery based xylan extraction has so far focused on chemical pulping processes (kraft and sodaAQ) and few attempts have been applied to mechanical pulping processes. Mechanical pulps account for 12% of the total pulp production in South Africa (Table 1). The chemical pre-treatment stage in chemi-thermomechanical pulping process could be easily rendered to serve as the pre-extraction stage without major capital investment. However, due to the advantages of mechanical or chemi-thermomechanical pulping such as low cost due to high pulp yield, the severe conditions used in the chemical delignification can be avoided.

Therefore, intensive research on pre-extraction to balance the potential xylan extraction yield and production of high yield pulps is necessary.

- No characterisation of black liquor was performed in the present study. Hemicelluloses pre-extraction prior to pulping might change the properties of black liquor produced after pulping of the extracted materials. Therefore it will be interesting to investigate the effect of the changes in black liquor in terms of viscosity, organic loading, heating values and the chemical composition (by use of Ultraviolet spectroscopy, HPLC/MS and GC/MS) as a means to close to mass balance over the process.

3.3 References

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Paper I

Dilute sulphuric acid extraction of hemicelluloses from *Eucalyptus grandis* and its effect on kraft and sodaAQ pulp and handsheet paper properties

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Abstract

The extraction of hemicelluloses prior to pulping is an attractive process to be incorporated in the pulp and paper mills to generate a valuable by-product in addition to core products. Pulp produced from eucalyptus grown in the Southern hemisphere is increasing its share of the global kraft pulp market. Therefore, it is important that hemicelluloses extraction and pulping should not impact on pulp yield or quality. Hemicelluloses from *Eucalyptus grandis* wood chips were extracted with dilute sulphuric acid prior to kraft or sodaAQ pulping. H_2SO_4 concentration, temperature and extraction time were varied to improve xylan yield with minimal effects on the cellulose content of extracted wood chips.

Wood chips with 21.3%, 39.5% and 60.2% of their xylan (determined as xylose + oligomer) extracted were subjected to kraft or sodaAQ pulping to evaluate the impact on cooking chemicals, pulp yield and properties.

Kraft or sodaAQ pulping of extracted wood chips with 39.5% and 60.2% xylan extraction at varied cooking conditions decreased pulp yield and properties. Modified sodaAQ pulping of the wood chips from which 21.3% of xylan was extracted using a low alkali charge maintained pulp yield, viscosity and kappa number as non extraction. Due to extraction, the handsheet's burst index was reduced whilst less difference in tensile index, tear index and breaking length between pulps produced from extracted and non extracted materials were observed. Extraction can more likely preserve fibre strength properties if initial xylan solubilisation yield can be reduced.

Application: This study provided information about the amount of polysaccharides (particularly xylan) to be extracted and best pulping process to be used for integration of dilute acid hemicelluloses pre-extraction on hardwood and pulping process within the context of pulp mill biorefinery.

1. Introduction

During commercial chemical pulping processes, significant amounts of hemicelluloses and small amounts of cellulose are removed from wood together with lignin [1]. The extracted hemicellulosic products are very complex, hindering their separation and further purification from the pulping black liquor [2]. Instead, the black liquor is generally burned in the chemical recovery unit along with lignin to produce steam for mill operations [1]. However, hemicelluloses provide less than 20% of 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 utilised efficiently in the combustion process. Moreover, hemicelluloses can be used as raw material for production of furans, xylitol, bioethanol or as strength additives for paper-making [4, 5]. Which represents a significantly higher value application than thermal energy production. In this context, the extraction of hemicelluloses prior to pulping could provide value-added products in a pulp mill biorefinery approach [4]. Moreover, as extraction reduces the mass of wood material, it enables the loading of more material in the digester thereby improving productivity [6]. 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 [7, 8].

Extraction of hemicelluloses from hardwoods (aspen, birch, *E. globulus*, and sugar maple) with dilute acids prior to kraft or sodaAQ pulping has been performed on laboratory [9, 10]; semi-large and industrial scale [8, 11]. The application of dilute acid extraction prior to 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 [10].

The combination of acid extraction and subsequent sodaAQ pulping of the extracted wood chips afforded higher pulp yields than when the kraft pulping process was used [9]. Other acidic extraction methods such as hot water also imply reduction on pulp yields but with comparable pulp viscosity [12, 7].

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 [8, 7, 12]. Thus, careful selection of 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 [13]. The objective of this study was to investigate the yield of dilute acid hemicelluloses extraction under various extraction conditions from *E. grandis* grown in South Africa prior to alkaline pulping. Kraft or soda anthraquinone (sodaAQ) pulping was performed on the extracted cellulignin 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 xylan yield, but also by the hemicelluloses and the nature of holocellulose retained in the wood chips for the subsequent pulping process. Pulping of selected extracted wood chips was performed at micro-scale under different conditions and large scales. The effect of hemicelluloses extraction on pulp yield and pulp quality measured as handsheet paper properties was determined.

2. Materials and methods

2.1. 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 (H_2SO_4) were purchased from Merck, and BUSPERSE 2262 anthraquinone (AQ) was obtained from Buckman Laboratories, Hammarsdale, South Africa.

2.2. Wood chemical analysis

The fraction of air dried *E. grandis* chips was sub-sampled and ground in a Retsch mill to 40 mesh size and used for chemical analysis. Oven dry mass (ODM) was obtained by heating at 105±2°C until a constant mass was achieved. Ash content, ethanol/cyclohexane solubility, hot water solubility and acid insoluble lignin were determined according to TAPPI standard methods, T211 om-85, T264 om-88 and T222 om-88 respectively [14]. Four replicates were used.

The sugars (glucan, xylan and arabinan) and acetic acid in *E. grandis* were determined after hydrolysis with 72% H_2SO_4, according to National Renewable Energy Laboratory (NREL) Analytical Procedure (LAP 013) [15]. The high pressure liquid chromatograph (HPLC) system used for quantification comprised of 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 was analysed with a UV detector. The column was operated at 65°C with a mobile phase of 5mM H_2SO_4 and a flow rate of 0.6 mL min^{-1}.

2.3. Hemicelluloses extraction of E. grandis wood chips

2.3.1. Experimental design

The experiments on dilute acid extraction were carried out according to a 2^3 full factorial experimental design created and evaluated in Statistica 7.1 (Statsoft Inc., Tulsa, USA) and Design Expert version 8 [16]. Dilute H_2SO_4 extraction variables were: acid concentration (0.3 - 0.7% v/v), temperature (120 - 140°C) and extraction time (20 - 30 min). Three assays were carried out at the center point to estimate the random error required for the analysis of variance (ANOVA). Xylan content of the liquid and glucan content of the solid fraction were taken as the responses of the factorial designs. The statistical significance of the regression coefficient was determined by the coefficient of determination, R^2.

2.3.2. Dilute acid extraction

Air dried samples containing 100 g oven dry wood chips (4 - 8 mm thickness) and H_2SO_4 solutions were mixed according to a 2^3 full factorial design and introduced into micro reactors (bombs). The solid to liquor ratio was 1:4 g/mL. Filled bombs were placed in a digester of 15 dm^3 capacity enclosed by heating jackets. Selected reaction temperatures (120 - 140ºC) were monitored with thermocouples at different extraction times (25 – 30 minutes).

2.4. Liquid fraction characterisation from dilute acid extraction

After extraction, the bombs were cooled in a water bath at room temperature. 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 its sugars (xylose, glucose and arabinose), acetic acid and sugar degradation products (furfural and hydroxymethylfurfural) using the HPLC procedure described in NREL method [17]. The fractions of the xylan-rich hydrolysates were further subjected to a post hydrolysis treatment using a dilute acid treatment at 121ºC for 10 min to convert all the remaining oligosaccharides to monosaccharides as described in the NREL method [15]. Acid soluble lignin (ASL) was quantified by Ultra Violet (UV) spectroscopy method, determining the absorbance of hydrolysate at 205 nm wavelength, using the 1 cm light path cuvette. A 4% solution of H_2SO_4 was used as reference blank.

The concentration of ASL was determined employing equation:

$$\text{ASL, estimated (g/L)} = \{ [A]/ [b \times a] \} \times df \quad (1)$$

Where A = absorbance at 205 nm, df = dilution factor; b = cell path length, 1 cm; a = absorptivity, equal to 110 L/g cm

2.5. Characterisation of solid fraction obtained after dilute acid extraction

The wood chips obtained after dilute H_2SO_4 extraction was rinsed with distilled water until neutral, 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 [14]. The extraction mass balance (EMB) can be calculated with the following equation [18]:

$$\text{Extraction mass balance} = \frac{\sum C_{Li} + \sum C_{Si}}{\sum C_{Ri}} \quad (2)$$

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.

2.6. Scanning electron microscope

The portion of the *E. grandis* residue from dilute sulphuric acid pre-extractions was mounted onto metal stubs with double-coated carbon adhesive tape. The samples were sputtered with gold in a high vacuum S150A sputter coater. Finally, the samples were examined using a LEO1430VP scanning electron microscope (SEM).

2.7. Micro-scale pulping after hemicelluloses extraction

The acid extracted *E. grandis* wood chips were thoroughly washed with water to remove the acid and air dried. Washed *E. grandis* wood chips from extraction runs 3, 4 and 8 (Table 2) were submitted to kraft (Table 4) or sodaAQ (Table 5) micro pulping.

The experiments were carried out according to the central composite design created and evaluated by Statistica 7.1 (Statsoft Inc., Tulsa, USA).

The pulping conditions used in this study were selected to achieve a kappa number range of 20 - 27. Pulp kappa number (parameter related with remaining lignin levels in pulp) was determined by standard TAPPI method T236 cm-85.

Kraft pulping cooking conditions were: active alkali (NaOH): 15.3 - 18.7%, sulfidity: 21 - 26%, and pulping time: 20 - 70 min. The cooking conditions for sodaAQ pulping were: active alkali (NaOH): 15.3 - 18.7%, anthraquinone: 0.07 - 0.2%, and pulping time: 50 - 100 min. Non-extracted *E. grandis* chips were also submitted to kraft or sodaAQ pulping under similar cooking conditions for comparison. The cooking conditions were selected in agreement with previous work done on kraft or sodaAQ pulping of hardwoods [13, 19, 20].

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 micro reactors (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 (nondisintegrated 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 (nondisintegrated fibre bundles) and then spin dried to a consistency of approximately 30%. Screened pulp yield was calculated as a percentage of ODM of the raw material using the formula:

$$\text{Pulp yield (\%)} = \frac{\text{Oven dry mass of pulp}}{\text{Initial oven dry mass } \textit{E. grandis}} \times 100 \qquad (3)$$

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

2.8. Large scale pulping after hemicelluloses extraction

Wood chips yielding the best results in micro pulping were repeated on a large scale in a 15 dm^3 batch type digester. The cooking time was chosen to reach the targeted kappa number range of 20 - 27. Solid residue run 3 (0.3% v/v H_2SO_4, at 140°C for 20 min) was submitted to kraft or sodaAQ pulping processes. Non-extracted wood chips were pulped for comparison.

Kraft pulps of non-extracted and H_2SO_4 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 SodaAQ pulps, 1000 g dry mass non-extracted or 882.9 g dry mass extracted material were exposed in a solution of 17% active alkali (NaOH) and 0.15% anthraquinone (AQ) for 120 minutes at 170°C. All active alkali and sulfidity masses were expressed as equivalent mass of Na_2O. At the end of the cooking process, the fibres were treated as explained in section 2.5.

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

Screened 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 instead of capillary viscometer. Pulp viscosity was determined by dissolving pulp sample into a cupricethylenediamine solution prepared according to TAPPI methods T230 om-89 [17]. 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.

2.9. Testing of physical strength properties of the handsheet

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 [14]. Burst index, breaking length and tear index was measured by TAPPI standards no, 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). The standard deviation was below 5% showing good reproducibility.

3. Results and discussion

3.1. Non-extracted Eucalyptus grandis wood chips composition

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 [21, 22]. *E. grandis*, like other hardwoods, have a high proportion of xylan compared to arabinan indicating that substantial amount of xylose will be generated during the acid extraction process [23, 24].

3.2. Dilute acid extraction of E. grandis wood chips

3.2.1 Yield of sugars in the liquid fraction

As illustrated in Table 2, the composition of the liquid fraction after different dilute H_2SO_4 extraction of the *E. grandis* wood chips conditions 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).

The dilute H_2SO_4 extraction resulted in a xylo-oligomeric rich liquid fraction up to 12.8% of the total xylan content. Increasing the temperature, acid concentration, extraction time and their interactions increased the solubilisation of xylan (Fig 1). 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; Table 2). Under these conditions, the concentration of furfural and HMF was <2g/L and acetic acid was <10g/L which was below the inhibition limit for micro-organisms renders the liquid fraction suitable to be used for the production of biofuels such as bioethanol [10, 25]. Also, acid soluble lignin (ASL) up to 2.7% raw material was present in the liquid fraction showing minor solubilisation of lignin fraction.

Previous reports of yields recovered xylose from hemicelluloses dilute H_2SO_4 extraction of *E. grandis* residues closely agree with those found in the present study [26].

3.2.2 Statistical analysis after dilute acid extraction of E. grandis wood chips

Statistical analysis was performed to evaluate the effect of process variables on xylan solubilisation and subsequent recovery in the liquid fraction. A first order model was developed to describe the relationship between xylan recovery (y_1) in the liquid fraction with H_2SO_4 concentration (x_1), temperature (x_2) and extraction time (x_3). The model's suitability of fit and its statistical significance after eliminating the insignificant terms is shown in Table 3. Xylan recovery model is described by the following equation:

$$y_1 = 21.7 + 5.3x_1 + 18.1x_2 + 6.2x_3 + 4.7x_1x_2 + 4.1x_2x_3 \quad (4)$$

The equation further confirmed that an increase in temperature was the factor that influenced the recovery of the solubilised xylose the most, followed by acid concentration, and then extraction time. The response surface described by the above model equation where xylan recovery is plotted as a function of H_2SO_4 concentration and temperature at a fixed extraction time of 25 minutes is shown in Figure 2. The response surface showed that an increase in H_2SO_4 concentration and temperature would increase the recovery of xylose product in the liquid fraction after solubilisation, expressed as percentage of xylan present in the raw material.

However, these same conditions might produce undesired sugar degradation product such as furfural (Table 2), which limit the acceptable increases in control parameters of the extraction process [10, 26].

3.3. Chemical composition of extracted E. grandis wood chips

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). To favor the subsequent pulping processes, the amount of glucan retained in the solid residue should be as high as possible. Enough xylan should be retained in the extracted wood chips as is required in pulping to improve pulp quality [8, 27].

Dilute H_2SO_4 extraction can selectively solubilise xylan resulting in glucan rich solid residues. However, most hardwoods contain about 5 - 10% easily hydrolysable cellulose which are dissolved under dilute concentrations below 1% v/v and at moderate temperatures [1]. Compared with glucan content in the original *E. grandis* (i.e., 47.2%), the glucan range after dilute acid extraction varied from yield 42.6% to 46.4% dry mass original material. 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 [10, 27].

Dilute H_2SO_4 extraction resulted in higher acid insoluble (Klason) lignin content than the starting material, sometimes above 100% (Table 2; run 4 and run 8). This could be due to the repolymerisation of sugar degradation products (such as Furfural) and/or polymerisation with lignin to form a lignin-like material called pseudo-lignins [28]. In addition, pseudo-lignins can be generated from carbohydrates without a contribution from lignin during dilute acid extraction especially under severe extraction conditions [29]. Scanning electron micrograph of dilute acid pre-extracted *E. grandis* residue showed the presence of spherical droplets on the outer surface of the extracted material that might be attributed to pseudo-lignin (Fig 3) [22]. Fibres covered by hydrophobic lignin could retard the penetration of chemicals and lignin solubilisation during pulping of the extracted wood chips [11].

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 of the respective 14.9% xylan present in the non-extracted *E. grandis* wood chips. The quantity of xylan removed from wood chips under dilute acidic conditions prior to pulping might reduce the interfibre bonding of the pulp, hence a decrease in tensile and burst indexes of paper handsheets may be observed [7, 10, 12].

3.4. Evaluation of pulp properties at micro-scale

In order to evaluate the efficiency of xylan pre-extraction together with subsequent pulping in an integration approach, micro pulping experiments of selected extracted *E. grandis* were performed, with non-extracted *E. grandis* chips used as control. The 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. *E. grandis* chips obtained from dilute H_2SO_4 pre-extraction condition runs 3, 4, and 8 were used. These dilute H_2SO_4 conditions were selected to incorporate the range of xylan (determined as xylose + oligomer) removed from the feedstock, at 21.3, 39.5 and 60.2% for runs 3, 4, and 8, respectively (Table 2).

In Table 4 and 5, the comparative values of screened pulp yield, rejects and kappa number of the pulps obtained from extracted *E. grandis* wood chips of runs 3, 4, and 8, and non-extracted wood chips after kraft and sodaAQ micro-scale pulping respectively are shown.

Generally, extracted wood chips with 39.5% (run 4) and 60.2% (run 8) xylan extraction produced dark and low yield pulps with high rejection levels (Table 4 and 5). This finding could be attributed the higher xylan removal of the initial extraction together with the decrease in molecular mass of xylan under acidic conditions. Thus, the increased content of reducing end groups and the xylan becomes easily soluble in the subsequent alkali medium. Consequently, cellulose became more susceptible to the peeling reaction because the xylan layer on the cellulose fibrils was partially removed, hence the decrease in pulp yield [10, 11]. The hydrophobic nature of lignin might have affected the ability of pulping liquor to penetrate and diffuse through the cell wall structure of the plant material, hence high rejection levels [23]. In a previous study, H_2SO_4 extraction of hemicelluloses from aspen hardwood chips prior to kraft pulping produced dark and brittle wood chips undesirable for subsequent pulp production [11].

The wood chips from run 3, from which 21.3% of xylan was extracted, showed less difference in pulp yield compared to non extraction.

An interesting result in Table 4, show that extracted wood chips from run 2 required 1% point lower alkali charge and 15 minutes shorter cooking time compared to the non-extracted wood chips (run 11) to reach a similar pulp yield (52.8% vs 52.3%). However, the benefit is lowered relative to non extraction by higher kappa number (34.4 vs 28.8) as enhanced delignification could reduce the pulp yield [19]. Regards to sodaAQ pulping process, of the pulping conditions shown in Table 5, the optimum one was run 13 for acid extraction provided the pulp yield (50.5%), which was comparable to pulps from non-extracted material of run 14 (50.2%). Dilute acid extraction allowed a reduction of 50 minutes in cooking time with aqueous solution of 17% active alkali and 0.15% AQ. A similar trend of reduction in cooking time was observed when sugar maple chips were given an acid pretreatment and then delignified by sodaAQ [9]. However, in the present study, it was necessary to delignify to higher kappa number (36.7 vs 30.7) to maintain optimum pulp yields for acid extracted wood chips.

The wood chips from run 3, from which 21.3% of xylan was extracted, was therefore preferred to wood chips from which 39.5% and 60.2% xylan was extracted for further pulp quality and handsheet paper strength evaluation.

3.4.1 Statistical analysis after kraft and sodaAQ pulping of acid extracted E. grandis wood chips

The models (Eqn 5 and 6) used to evaluate the data obtained after kraft (Table 4) or sodaAQ pulping (Table 5) of acid extracted wood chips (run 3) were refined according to the analysis of variance (ANOVA). As shown in Table 6 the models fitted the experimental data well after elimination of insignificant terms. The experimental variables i.e. active alkali (x_1), sulfidity (x_2) and pulping time (x_3) after kraft pulping had significant influence only on kraft pulp yield of extracted wood chips and can be explained by the following second order equation:

$$\text{Pulp yield (\%)} = 38.8 - 3.1x_1 - 2.7x_2 + 5.0x_1^2 + 5.3x_2^2 + 3.6x_3^2 \qquad (5)$$

The equation revealed that active alkali (NaOH) and sulfidity are the most influencing variables on pulp yield during kraft pulping. By using the equation it may be recommended that longer pulping time at lower active alkali and sulfidity could be used to improve the pulp properties such as kappa number. This recommendation is in accordance with the literature [12, 28, 30].

On the other hand, no statistical significance was found for the second order model between pulp yield or kappa number and the process variables performed with sodaAQ pulping process. The results were considered to be described better by the first order model. The statistical significance of active alkali (NaOH) concentration, pulping time and the interaction between these variables was shown only on the kappa number of the pulp produced from acid extracted wood chips. Nonetheless, kappa number is one of the most important pulp property used to measure the efficiency of pulping processes [31].

First order regression equation 6 describes the kappa number of the H_2SO_4 extracted wood chips as a function of active alkali concentration (x_1) and pulping time (x_2)

$$\text{Kappa number} = 37.9 - 1.6x_1 + 0.7x_2 - 1.1x_1x_2 \qquad (6)$$

The negative sign of the active alkali concentration coefficient and the positive sign of the pulping time coefficient in Eqn 6 suggest low kappa number at lower dosages of alkali charge and longer pulping times. However, excessive delignification might negatively affect the fibre quality resulting in low pulp yield and paper strength properties [24].

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

Kraft or sodaAQ pulping of *E. grandis* chips from which 21.3% xylan was extracted was repeated on a large scale to confirm the micro pulping results. Non-extracted wood chips were also pulped. Based on micro pulping results, the pulping time was extended for all cooks to establish the desired bleachable kappa number range (20 - 27). Previously, increase in cooking time reduced kappa number but also resulted in additional pulp yield loss [10, 19]. The cooking conditions and yields are presented in Table 7.

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 extraction (1000 g). In addition, the total NaOH used for kraft or sodaAQ cooking of acid extracted *E. grandis* wood chips was reduced (171.8 g vs 194.1g) and (150.1 g vs 170 g) respectively.

3.5.1 Pulping performance

No suitable conditions were found in this study for the combined acid extraction and subsequent kraft pulping process that resulted in similar pulp yield and properties when pulping non-extracted wood chips. Dilute acid extraction caused reduction in screened pulp yield and residual active alkali of the kraft process at higher kappa number relative to non extraction. A decrease in kraft pulp yield due to acid pre-extraction was confirmed for birch wood [12]. Pulp viscosity was reduced by acid pre-extraction possibly due to high cellulose degradation [10, 11, 32] and this might results in handsheet strength loss, which can limit pulps applications [19]. Dilute acid pre-extraction also decreased the xylan content of the pulps emphasing the hypothesis of handsheet strength loss [7, 10, 12].

Unlike the kraft process, the combined process of dilute H_2SO_4 xylan extraction and modified sodaAQ pulping preserved the pulp yield and quality. 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 [20, 32].

3.6. Effect of dilute acid xylose extraction on handsheet properties

Regarding handsheet strength properties, the main effect of reduced viscosity and xylan content was observed in burst, tensile, tear indexes and breaking length of kraft pulps produced from dilute acid extracted materials (Table 7).

The handsheet burst, tensile, tear indexes and breaking length were decreased by 20.8%, 14.6%, 41.7% and 23.7% respectively at maximum degree of beating. Several authors suggest that the main effects of acid pre-extraction on pulp strength properties were the consequence of reduction in interfibre bonding [8, 19]. 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 pulps produced from non-extracted wood chips.

On the other hand, the differences in handsheet strength properties were lower when sodaAQ was applied in acid extracted wood chips. Acid extraction prior to sodaAQ pulping reduced the handsheet's burst index by 17.0% whereas a minimal loss of 8.7%, 2.4%, and 8.5 % were observed for tensile index, tear index and breaking length respectively at maximum degree of beating. Smaller decrease in xylan content retained in pulps produced from acid pre-extracted material was observed compared to pulps produced from non extracted material, hence, less difference in tensile index, tear index and breaking length. Nevertheless, the pre-extraction promoted an increase in optical brightness.

The low strength properties observed from kraft or sodaAQ pulps produced from acid extracted wood chips enabled to be used for printing and writing papers where strength is of lower importance [33, 34].

Among the two pulping methods tested in combination with dilute H_2SO_4 xylan extraction, sodaAQ confirmed its good potential in terms of moderate cooking conditions, comparable pulp yields and strength properties compared to kraft pulping.

Conclusions

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. About 60.2% xylan present in *E. grandis* wood chips can be extracted under suitable conditions. From 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 without reduction in viscosity after modified sodaAQ pulping process. The strength properties of the resulting pulps can be acceptable for paper production depending on the extent of xylan extracted. A potential increase of digester load by 12% was observed. Dilute H_2SO_4 extraction prior to kraft pulping was detrimental to pulp yield and quality.

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Tables

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

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

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.

Table 2 The composition of liquid and solid fraction after sulphuric acid extraction of *E. grandis* under process variables defined by a 2^3 full factorial design.

Pre-extraction conditions				Liquid fraction								**d**Solid fraction			**e**EMB		
Run	H_2SO_4 % x_1	Temp °C x_2	Time min x_3	*[a]Xyl (%)	[b]Xyl % theoretical	Xylo-oligomer %	[c]Xylan recovery yield %	*Glc %	*ASL %	Acetic acid g/L	Furfural + HMF g/L	Glc %	Xyl %	*AIL %	Glc (%)	Xyl (%)	Lignin (%)
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**
9-11	0.5	130	25	5.0 ± 0.2	33.6 ± 1.7	11.6 ± 1.5	45.2 ± 1.4	5.0 ± 1.0	1.7 ± 0.1	3.4 ± 0.1	0.02	42.6 ± 0.2	7.2 ± 0.5	23.9 ± 1.3	91.2	93.2	94.8

aXylose based on g/100g raw material

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

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

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

eExtraction 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 were 3.2% and 11.4% respectively, and the raw *E. grandis* has 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

Table 3 Analysis of variance for the regression model of xylan solubilisation after dilute sulphuric acid extraction of *E. grandis* chips.

Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob > F
Model	3472.1	6	578.7	457.7	0.0002
X_1	223.9	1	223.9	177.1	0.0009
X_2	2627.0	1	2627.0	2077.9	<0.0001
X_3	309.7	1	309.7	244.9	0.0006
X_1X_2	176.0	1	176.0	139.2	0.0013
X_1X_3	0.07	1	0.07	0.06	0.8255
X_2X_3	135.4	1	135.4	107.1	0.0019
Curvature	1197.6	1	1197.6	947.3	<0.0001
Lack of Fit	0.1	1	0.1	0.06	0.8354
Pure Error	3.7	2	1.6		
Cor Total	4673.5	10			
Residual	3.8	3	1.3		
R^2	0.998				

Table 4 Kraft micro-scale pulping results according to the central composite design 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 (%)**			
Run	**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**
1	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
2	**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
3	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
4	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
5	18	22	60	46.3	34.6	28.7	45.8	33.3	32.3	33.3	29.3	0.04	0.06	0.45	0.06
6	18	22	30	45.6	32.2	29.8	47.9	34.9	32.7	33.8	29.7	0.71	0.19	0.24	0.20
7	18	25	60	41.9	35.1	29.7	50.3	34.3	32.0	33.3	29.5	0.19	0.23	0.26	0.04
8	18	25	30	43.3	31.9	29.4	39.3	33.8	32.9	33.4	30.6	0.29	0.20	0.23	0.17
9	15.32	23.5	45	46.6	30.7	30.3	47.7	33.7	33.2	34.6	30.4	0.04	0.29	0.24	0.08
10	18.68	23.5	45	43.5	34.1	32.4	58.3	33.6	33.2	33.9	27.8	0.08	0.16	0.10	0.10
11	**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**
12	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
13	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
14	17	23.5	20	43.2	30.9	43.6	43.7	35.3	33.9	34.2	30.7	0.00	0.61	0.85	0.00
15-19	17	23.5	45	38.9±0.9	33.4±3.3	33.7±1.8	46.0±0.2	33.9±0.1	33.1±0.3	32.6±0.5	29.4±0.6	0.1±0	0.1±0	0.1±0.1	0.1±0.1

Table 5 SodaAQ micro-scale pulping results according to the central composite design 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 (%)**		
Run	**AA (%)**	**AQ (%)**	**Time (min)**	**run 3**	**run 4**	**non-extraction**	**run 3**	**run 4**	**non-extraction**	**run 3**	**run 4**	**non-extraction**
1	16	0.10	60	45.6	29.2	46.8	37.8	40.1	31.9	10.6	11.89	0.44
2	16	0.10	90	37.3	31.1	48.8	39.6	40.1	31.4	13.1	12.04	0.74
3	16	0.2	60	42.0	29.7	44.2	37.8	40.0	32.3	6.7	12.08	0.62
4	16	0.2	90	37.9	31.3	48.7	39.6	40.1	31.9	8.5	10.14	0.75
5	18	0.10	60	41.5	35.7	52.0	36.9	36.6	31.9	2.9	5.57	1.98
6	18	0.10	90	47.3	37.2	47.4	36.8	35.1	30.9	6.4	10.00	0.19
7	18	0.2	60	45.3	36.4	46.3	37.8	38.2	31.1	5.4	6.01	0.30
8	18	0.2	90	41.7	34.8	49.1	36.9	37.1	30.4	4.7	2.79	0.21
9	15.32	0.15	75	36.6	30.2	45.7	38.9	40.0	32.2	14.9	15.00	1.30
10	18.68	0.15	75	43.1	35.4	49.5	35.5	36.2	30.9	4.1	6.05	0.48
11	17	0.07	75	42.6	34.0	52.4	37.4	40.0	31.5	6.8	10.66	0.50
12	17	0.23	75	40.3	34.1	49.4	38.9	39.9	31.9	5.4	2.08	1.49
13	**17**	**0.15**	**50**	**50.5**	35.9	49.9	**36.7**	39.8	33.0	**4.2**	11.06	1.24
14	**17**	**0.15**	**100**	36.7	35.7	**50.2**	39.7	39.7	**30.7**	7.5	7.30	**0.54**
15-19	17	0.15	75	41.2±1.5	33.3±0.6	48.9±1.2	37.6±0.4	39.9±0.1	31.9±0.4	7.4±2.9	9.8±0.2	0.3±0

Table 6 Analysis of variance (ANOVA) of the regression models of the pulp yield obtained after kraft pulping and kappa number obtained after sodaAQ pulping of dilute acid extracted *E. grandis* wood chips.

Kraft pulping						SodaAQ pulping					
Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob > F	Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob > F
Model	163.92	6	27.32	5.59	0.0088	Model	8.97	6	1.49	10.46	0.0403
x_1	32.42	1	32.42	0.024	0.0243	X_1	0.84	1	0.84	5.9	0.0933
x_2	25.46	1	25.46	5.21	0.0457	X_2	0.11	1	0.11	0.79	0.4386
x_3	17.7	1	17.77	3.63	0.0858	X_3	5.27	1	5.27	36.9	0.009
x_1^2	69.86	1	69.86	14.28	0.0036	X_1X_2	0.094	1	0.094	0.66	0.4773
x_2^2	79.64	1	79.64	16.28	0.0024	X_1X_3	2.53	1	2.53	17.74	0.0245
x_3^2	36.44	1	36.44	7.45	0.0212	X_2X_3	0.11	1	0.11	0.79	0.4386
						Curvature	0.22	1	0.22	1.57	0.2984
Residual	48.91	10	4.89			Residual	0.43	3	0.14		
Lack of Fit	47.28	8	5.91	7.24	0.127	Lack of Fit	0.094	1	0.094	0.56	0.5324
Pure Error	1.63	2	0.82			Pure Error	0.33	2	0.17		
Cor Total	212.83	16				Cor Total	9.62	10			
R^2	0.87					R^2	0.96				

Table 7 Kraft and sodaAQ large 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 H_2SO_4 at 140°C for 20 min)

	Pulping Process			
	Kraft		SodaAQ	
Cooking parameters	non-extracted	0.3% v/v H_2SO_4, 140˚C, 20 min	Non-extracted	0.3% v/v H_2SO_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_2S (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
Handsheet properties				
Drainage rate (°SR)	44	45	40	43
Burst index ($kPa.m^2/g$)	5.3±1.1	4.2±1.5	4.7±1.0	3.9±0.8
Tensile index (Nm/g)	51.9±1.9	44.3±2.2	45.9±1.5	41.9±2.0
Breaking length (km)	5.9±0.5	4.5±0.5	4.7±0.8	4.3±1.2
Tear index ($mN.m^2/g$)	8.4±1.3	4.9±1.5	4.1±1.8	4.0±1.5
Brightness (% ISO)	48.4±2.0	37.8±2.4	38.0±1.9	42.2±1.8

Figure captions

Fig 1. Standardized Pareto chart to estimate the effects of concentration, temperature and extraction time on xylan solubilisation in the liquid fraction after dilute sulphuric acid extraction.

Fig 2. Estimated response surface described by the model equation (1) for xylan yield obtained after sulphuric acid extraction showing the influence of temperature and sulphuric acid concentration for an extraction time of 25 minutes.

Fig 3. Scanning electron microscope micrograph showing pseudo-lignin deposits on wood chip surface after dilute sulphuric acid extraction of *E. grandis*.

Fig 1

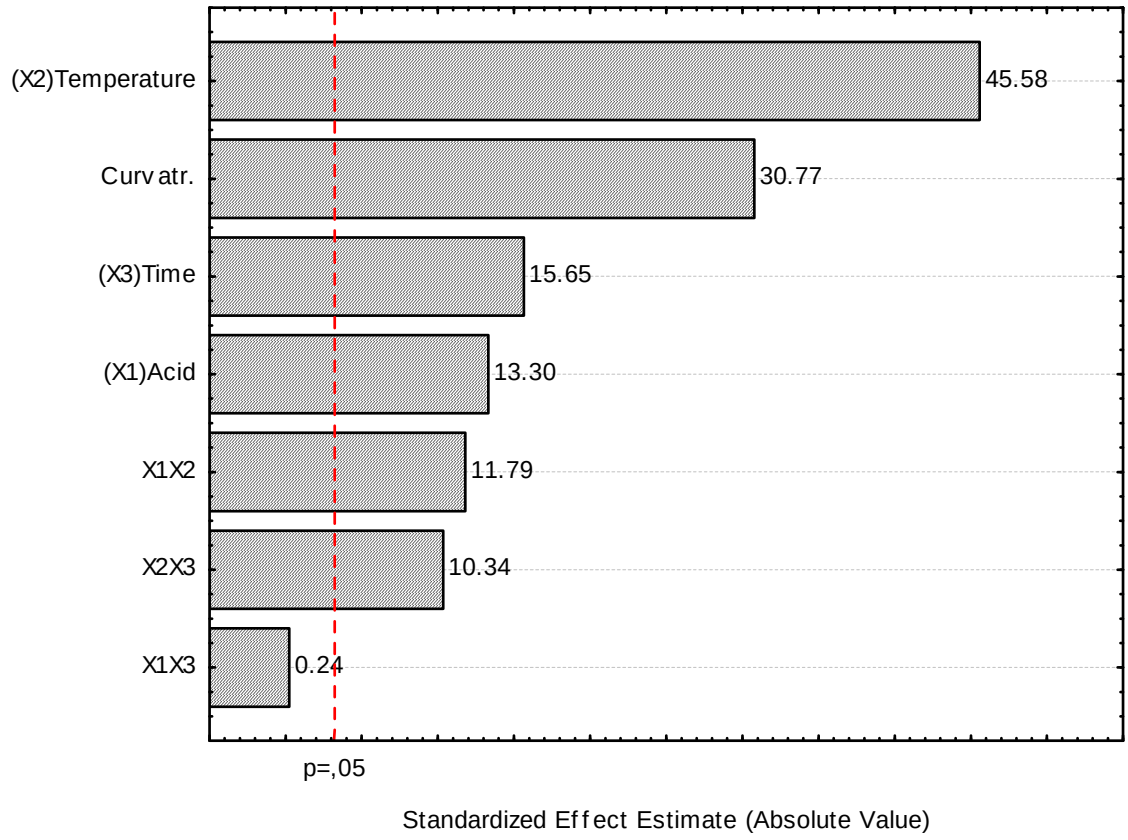


Fig 2

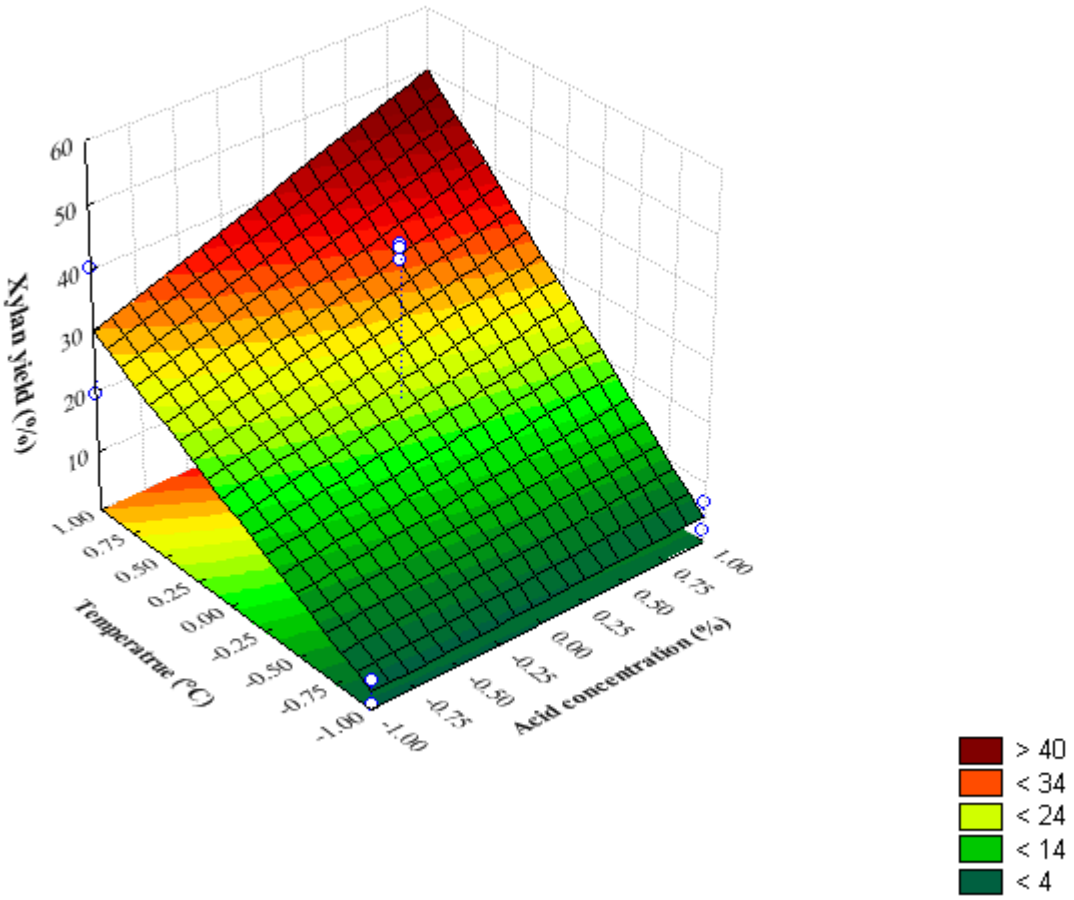
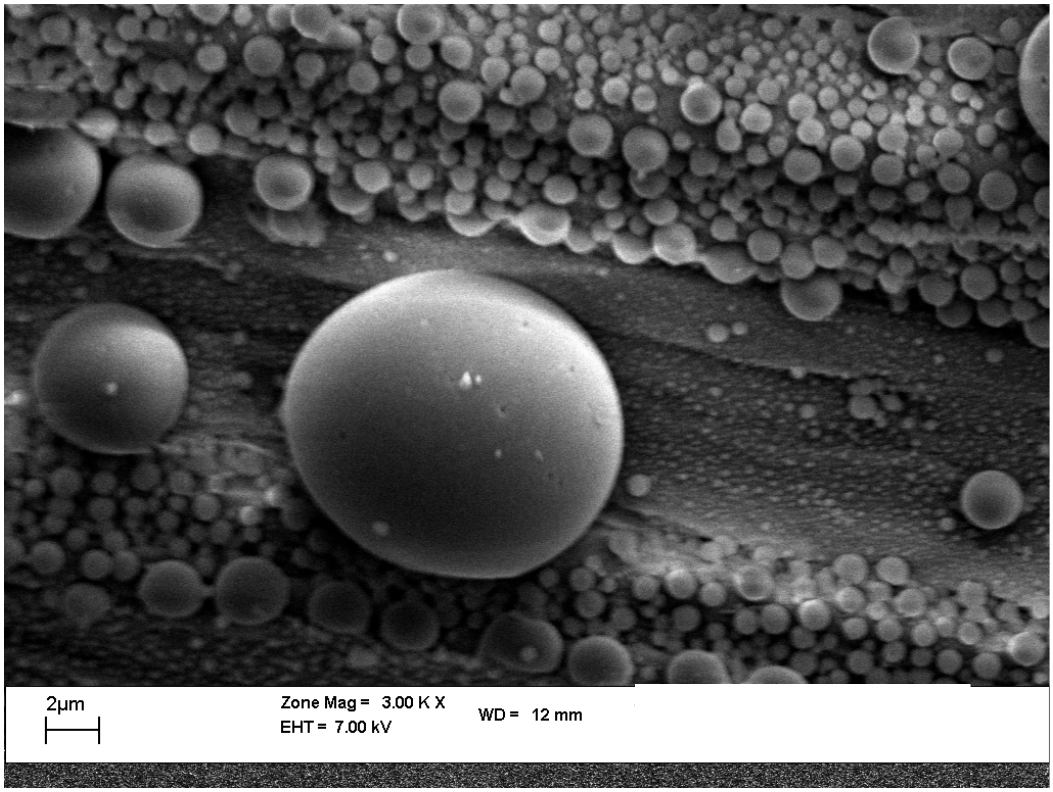


Fig 3



Paper II

Effect of alkaline hemicelluloses extraction on kraft pulp fibres from *Eucalyptus grandis*

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Abstract

The alkaline extraction of hemicelluloses from hardwoods prior to pulping, for further conversion to value added products, seems to be a promising pathway for current paper mills to increase profit and improve sustainability. However, the amount of hemicellulose extracted will be limited by the requirement to maintain pulp quality and pulp yield in comparison to existing pulping processes. The effects of NaOH concentration, temperature and time on hemicellulose extraction of *Eucalyptus grandis* were studied, using a statistical experimental design. Extracted wood chips were subjected to kraft pulping to evaluate the effect of the extraction on cooking chemicals, pulp quality and handsheet paper strengths.

The selective xylan recovery (12.4% dry mass) from *E grandis* combined with low cooking active alkali charge and less cooking time advantaged the xylan extraction and subsequent modified kraft pulping process under the studied conditions. Pulp viscosity, breaking strength and tensile index of handsheets were slightly improved.

Keywords: biorefinery, xylan extraction, *Eucalyptus grandis*, kraft pulping, pulp quality, handsheet paper strength

1. Introduction

The transition of the current pulp mills into the so called integrated forest biorefinery (IFBR) entails the incorporation of a hemicellulose extraction step for an efficient use of the raw material.[1-2] During kraft pulping hemicelluloses are degraded into low value hydroxyl acids and end up in the black liquor with degraded lignin and thus cannot be utilized directly in its polymeric form.[1]

High molar mass hemicelluloses may be used in novel industrial applications such as biopolymers and barrier films, and could also, after hydrolysis, serve as a source of sugars for fermentation to biofuels or specialty chemicals.[3-4] Hemicelluloses can be alternatively applied as wet end additive in papermaking.[5] Hardwood xylan obtained by alkaline extraction, for instance, has been shown effective to improve fiber bonding and surface sizing in paper making.[6]

Eucalyptus grandis is one of the main sources of hardwood in the Southern hemisphere and most widely used in both wood and paper industries in South Africa, Brazil and other southern or tropical countries.[7] The regions with the largest hardwood areas in South Africa are the provinces of KwaZulu-Natal and Mpumalanga South where 541 000 ha was planted with *Eucalyptus* species in 2003. *E. grandis* occupied an area of 311 000 ha, 58% of the total hardwood area.[8] Economical and technical reasons for the utilisation of eucalypts come from its low production cost due to high forest productivity and high pulping yield.[9] The high pulp yield obtained from *E. grandis* is explained by a high content of syringyl lignin, which is easier to pulp. Moreover, eucalyptus xylan is highly rich in methyl glucuronic acid (MeGlcA), which contributes to a high yield for eucalyptus paper pulps.[10]

Eucalyptus wood contains about 13% 4-*O*-methylglucuronoxylans, which represents 18% of its carbohydrate fraction and 71% of its hemicellulose content.[11] Hemicellulose dissolved from *E. grandis* during kraft pulping may reach 62% of their original amount and around 10% of the cellulose is lost as well, this shows a significant impact on process yield.[12]

Hemicelluloses can be extracted from hardwoods via various methods such as dilute acid, hot water and alkaline extraction.[4,13-15]

However, minimal interference with the subsequent pulping process is required since the production of high quality papermaking fibres at high yield will remain the main concern for pulp and paper mills.[2] Hemicelluloses extraction will affect the mill production in different ways, for example, the severe conditions in hot water and dilute acid extraction can have a negative impact on the fibres. The cellulosic fibres can possibly be damaged, resulting in a reduction in the degree of polymerization (DP) of cellulose, pulp yield loss and/or lower strength properties of paper.[4,7] In contrast, under alkaline conditions extraction of hemicelluloses has been proven technically viable to a sufficient extent.[13-15] Hemicelluloses showed high solubility under alkaline conditions and no pH adjustment or water washing is required for subsequent alkaline pulping. Moreover, alkali extractions generally require temperatures below 90°C, to minimize carbohydrate modification reactions. Alkaline extraction of hemicelluloses from aspen hardwood chips prior to kraft pulping using 1 - 2 M NaOH at 50 - 90°C afforded about 20 - 25% of hemicelluloses while the pulp yield was maintained, although the reduction in pulp viscosity was observed.[13]

The world production of pulps for paper manufacturing from eucalyptus has attained 10 million tons/year, which is near one-third of the total hardwood pulp produced.[16] The international *eucalyptus* quantities processed provide an excellent starting point to consider the biorefinery approach, i.e. to adapt the existing chemical pulp mills to produce new value added products while continuing to meet the growing demand for pulp and paper. Previous studies have demonstrated the feasibility of alkaline pre-extraction on hardwoods.[13-15] In this context, this study firstly investigates the alkaline yield of hemicelluloses extraction under various reaction conditions from *E. grandis* grown in South Africa, prior to alkaline pulping with minimal interference on cellulose content. In following the biorefinery approach, the second objective was to pulp the extracted wood chips showed minimal degradation of cellulose content in the residual cellulignin using kraft pulping method to determine the effect of hemicelluloses extraction on pulp and paper quality.

The chemical charge during kraft pulping was as well controlled to optimize the pulp yield. The best extraction method was regarded as the one in which a maximum amount of hemicelluloses was recovered while simultaneously the yield and quality of the pulp was maintained at industrially acceptable levels (50% screened pulp yield with a kappa number of 22 or less).[17-18]

2. Materials and methods

2.1. Materials

E. grandis chips were supplied by Mondi Business Paper in KwaZulu-Natal, South Africa. The wood 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. Pullulan standards purchased from Polymer Standard Service (PSS) in Germany were used to estimate molecular weight of the isolated xylan fractions

2.2. Chemical composition of E. grandis wood chips

Ground particles of 40 mesh size were used for the determination of *E. grandis* chemical composition. Moisture content was determined by drying a representative sample using an oven at 105 ± 2°C until a constant mass was achieved. Ash content, ethanol/cyclohexane and hot water soluble extractives were determined according to TAPPI standard methods, T211 om-85 and T264 om-85 respectively (Table 1).[19]

Before analysis of the monosaccharide content in the extractive free *E. grandis*, a two step hydrolysis with 72% and 4% sulfuric acid, respectively, was performed to convert oligomeric into monomeric sugars by the standard procedure recommended by NREL.[19] At the end of the acid hydrolysis, the amount of acid insoluble lignin was determined gravimetrically by filtering the hydrolysate through the Gooche crucible. The extracted wood chips collected were washed with deionised water until the filtrate had a neutral pH. The amount of acid insoluble lignin collected was determined after drying the extracted wood chips to constant mass at 105ºC for 4 - 5 h.

Then the hydrolysate was filtered through 0.22 μm membranes and the acid soluble lignin was determined by a UV at 205 nm. Subsequently, the hydrolysate was analysed for sugars by a Thermo separation product HPLC. The HPLC system comprised of 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, equipped with a Cation-H cartridge (Biorad, Johannesburg, RSA). Sugars were measured with an RI detector. The column was operated at 65°C with a mobile phase of 5 mM sulfuric acid and a flow rate of 0.6 mL min^{-1}.

2.3. Xylan extraction of E grandis wood chips

The mild alkaline extraction of xylan from *E. grandis* was performed as described elsewhere with some modifications.[13] The liquor-to-wood ratio was fixed at 4:1 L/Kg. The 100 g dry mass (DM) chips were mixed with NaOH (1 - 2 M) solution in Schott bottles and placed in a shaking, hot water bath and kept at the desired temperature (40 - 90°C) and time (120 - 240 min). At the end of the desired extraction time, the bottles were cooled in room temperature water. The extracted wood chips were collected by filtration on a 100 mesh screen, thoroughly washed with distilled water until the pH was neutral and air dried.

A 2^3 full factorial experimental design created and evaluated in Statistica 7.1 (Statsoft Inc., Tulsa, USA) and Design Expert version 8 [21] was applied to determine the suitable combination of the extraction variables for the xylan extraction. Three assays were carried out at the center point to estimate the random error required for the analysis of variance (ANOVA). The statistical significance of the regression coefficient was determined by the multiple coefficient of determination, R^2.

2.4. Compositional analysis of the solid and liquid fractions obtained after xylan extraction of E. grandis wood chips

The wood chips obtained after each extraction was milled to characterize for xylan, lignin, and glucan content of the extracted wood chips using the same methods as for raw wood analysis except for the extractives content determination.

The xylan rich filtrates containing a complex mixture of solubilised materials (oligosaccharides, lignin products, extracting chemicals, etc) were concentrated in a rotary evaporator at 40°C to approximately one-third of the original volume. Filtrates were then purified by dialysis against de-ionised water for 3 days using a dialysis cellulose acetate membrane with a 12 kDa molecular weight cut off. An economical viable separation process could be developed.[22] The samples were conditioned in liquid nitrogen and freeze dried. The oven dry mass of the recovered xylan precipitates was determined.

The hemicellulose recovery yield was estimated according to the following relations:[23]

$$\%\text{Hemicellulose precipitate} = \frac{\text{Oven dry mass of hemicellulose precipitate}}{\text{Oven dry mass non-extracted } \textit{E. grandis}} \times 100 \quad (1)$$

$$\%\text{Hemicellulose recovery} = \frac{\%\text{hemicellulose precipitate}}{\%\text{Hemicellulose of } \textit{E grandis}} \times 100 \quad (2)$$

The lignin fractions associated with the hemicelluloses were determined as described elsewhere.[24]

2.5 Size exclusion chromatography

The weight average molecular weight of the alkaline extracted xylan was determined using size exclusion chromatography (SEC). The isolated hemicellulose was dissolved in deionised water to obtain a final concentration of 1 g L^{-1}. The solution was stirred continuously at room temperature for 2 hours and filtered through 0.2 µm membranes. The SEC system consisted of three SUPREMA aqueous columns (PSS, Germany), connected in series with the pore sizes 30 Å, 3000 Å, 3000 Å respectively. Detection was conducted using a Dionex UltiMate 3000 HPLC system with a Varian 380-LC detector which is an Evaporative Light Scattering (ELS) detector. Solution of deionised water containing 0.05% sodium azide (NaN_3) was used as eluent and the flow rate was maintained at 1 mL min^{-1}. The column's temperature was kept at 25°C. The detector output was analysed with the Chromeleon® Version 6.80 software package.

2.6. Spectroscopy analysis of xylan

The FT-IR spectra were recorded in reflectance mode using the Smart Performer from Thermo equipped with ZnSe lenses. Prior to analysis, a sample of freeze dried xylan was conditioned in phosphorus pentoxide, and a small portion of the dried xylan was placed on the ZnSe horizontal ATR, and 16 scans with a resolution of 4 cm^{-1} were accumulated over the range of 4000 - 650 cm^{-1}. The operating and data manipulating software was the basic OMNIC package.

2.7. Micro pulping after xylan extraction of E. grandis wood chips

E. grandis wood chips from alkaline extraction run 6 (Table 2) were directly subjected to kraft pulping without washing. Under these conditions the combination of high yield xylan (12.4%) recovered in the liquid fraction accompanied with high glucan content in the extracted wood chips was observed. Sodium sulfide concentration ranging from 31.4% to 40% was added in the extraction cooks. Sodium hydroxide was generated from the added sodium sulfide.

Non-extracted *E. grandis* chips were also submitted to kraft pulping and the cooking conditions were selected according to the optimum conditions for kraft pulping South African eucalyptus species: 18.7% active alkali, 25% sulfidity, and pulping time was fixed at 30 min.[24] The maximum cooking temperature was kept constant at 170°C and the liqour-to-wood ratio was 4:1 L/Kg for all pulping experiments.

Pulping experiments were carried out in micro reactors (bombs) on dry wood chips containing 100 g oven dry material. Temperature and pulping time were monitored during the process. Pulping 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 (nondisintegrated wood retained by this screen) from the fibres; the accepted pulp was collected on a bottom 100 mesh screen.

The pulp was then screened through a 0.15 mm screen to remove shives (nondisintegrated fibre bundles) and then spin dried to a consistency of approximately 30%. Screened pulp yield was calculated as a percentage of the initial oven dry mass of the material used using the formula:

$$\text{Pulp yield (\%)} = \frac{\text{Oven dry mass of pulp}}{\text{Initial oven dry mass of wood chips}} \times 100 \quad (3)$$

The rejects and the shives collected were placed in an oven to dry at 105°C over night to establish the oven dry mass and weighed. The reject and shive content together were expressed as a percentage of original DM of *E. grandis*.

Pulp kappa number (parameter related with residual lignin content in pulp) was determined by standard TAPPI method T236 cm-85.

2.8. Large scale pulping after hemicelluloses extraction

Wood chips yielding the best results in micro pulping were also pulped on a large scale in a 15 dm^3 batch type digester. After the extraction of hemicelluloses from 1000 g DM chips, the extracted chips were directly subjected to pulping without washing. The cooking conditions were: 35.7% sodium sulfide, 16% Active Alkali at 170°C for 30 min. Non-extracted wood chips were also pulped by exposing 1000 g DM chips to 18.7% Active alkali and 25% sulfidity for 45 min at 170°C with the same liquor-to-wood ratio. At the end of the cooking process, the fibres were treated as explained above. The carbohydrate content of pulp fibres were determined by using NREL method as for raw wood analysis (section 2.2).

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

2.9. Pulp evaluation and handsheet formation

Pulp tests were performed according to the TAPPI standard methods [19] except for the viscosity. Total pulp yield and rejects were determined as a percentage of the original DM of the raw material. Pulp kappa number was determined by standard TAPPI method T236 cm-85. Pulp viscosity, parameter related with the degree of polymerization of pulp polysaccharides, was determined by dissolving pulp sample into cupricethylenediamine (CED) solution prepared according to TAPPI methods T230 om-89 but using a Brookefield viscometer instead of a capillary viscometer. The pulp solution was transferred to a Brookefield RVTD 382 viscometer and agitated at 100 rpm using a spindle number 21.

The temperature in the sample holder was maintained at 25ºC ± 1 with the aid of Haake thermostatic circulator (model D8-G). The pulp viscosity was measured in centipoises (cP).

The development of handsheets 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 degrees Schopper Riegler (˚SR) was measured according to TAPPI T227 om-99. Handsheets of about 60g/m^2 were formed according to TAPPI T205 om-88 using British Standard handsheet making equipment.

2.10. Testing of physical properties of the handsheets

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 standard methods: Burst index, breaking length, and tear index were measured by TAPPI Standard no, 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).

3. Results and discussion

3.1. Raw material composition

The chemical composition determined for *E. grandis* wood chips is listed in Table 1: 4.2% extractives, 1.2% ash, 21.1% total lignin, 52.7% glucan and 15.8% hemicelluloses. The lignin content was lower than 28.9-29.6% reported for *E. grandis* in the literature probably due to the variation in growth conditions.[26-27] Low lignin content in practice showed the potential of the material to undergo easier delignification which makes the studied material attractive for pulp mill biorefinery.[10] Xylan content (15.3%) was generally higher than other values reported in literature (12.4%).[10] Xylan made the largest portion of hemicelluloses and was therefore considered throughout in this study.

3.2. Effect of xylan extraction on E. grandis wood chips

E. grandis chips were extracted under alkaline solutions to recover xylan prior to subsequent kraft pulping. The alkaline extraction conditions were varied to provide adequate conditions that could solubilise high xylan, but at the same time preserving cellulose (glucan) and enough xylan in the solid residue for paper pulp production. The extraction conditions, xylan recovery and the chemical composition of the washed extracted wood chips are listed in Table 2. All the results are based on original oven dry raw material.

Mild alkaline conditions allowed solubilisation of wood components mainly xylan. The maximum recovery yield was 16% dry mass obtained under the severe condition (2M NaOH, 90 C, 240 min). Increase in NaOH concentration, temperature and reaction time increased the xylan solubilisation from *E. grandis* and subsequent recovery. Separation and purification of xylan by using cellulose acetate membrane might have resulted in part of xylan being lost in the system. Ultrafiltration or nanofiltration separation and purification systems can improve the hemicellulose recovery.[13,22]

Analysis of extracted wood chips showed that extraction of *E. grandis* with mild alkaline conditions released part of cellulose and removes lignin depending on the severity of the extraction conditions (Table 2). The reduction of 4.6 to 7.2% for glucan and 6.2 to 24.2% for lignin content under the studied conditions was observed.

This could be ascribed to the disruption of the bonds between lignin and carbohydrates.[22] Among the alkaline extraction conditions studied, the best compromise between xylan solubilisation and less degradation of cellulose from *E. grandis* wood chips was obtained at run 6 in Table 2. The recovered xylan was 12.4% dry mass and the glucan content retained in the extracted wood chips was 94.7% (49.9% vs 52.7% of the non-extracted *E grandis*), whilst the xylan and lignin content were 80.4% (12.3% vs 15.3%) and 75.8% (16.0% vs 21.1%) dry mass, respectively, which was suitable to be used for subsequent kraft pulp production.

The statistical linear regression model (Eqn 4) of the data obtained for xylan solubilisation in the liquid fraction was tested for adequacy by analysis of variance (ANOVA.) The suitability of fit and statistical significance is presented in Table 3 after eliminating the terms found statistically insignificant. The mathematical model that describes the xylan solubilisation (y_1) is described by the following equation:

$$y_1 = 8.3 + 6.2x_1 + 2.6x_2 + 4.3x_3 \qquad (4)$$

The equation showed that NaOH concentration (x_1) was the factor that had the strongest influence on xylan solubilisation than extraction time (x_3), while temperature (x_2) showed the little effect, which agreed with the observations of other authors.[11]

Further analysis of the experimental data through response surface plots revealed that an optimum xylan solubilisation can be obtained by increasing alkali charge and extraction time when the temperature was fixed at 65°C (Fig 1). However, the factors were limited to the selected values, to avoid excessively high extraction yields of xylan from wood chips prior to pulping, which might promote the degradation of cellulose through alkaline peeling, which leads to subsequent losses of kraft pulp viscosity and pulp strength.[12, 13]

3.2.1. Characterization of mild alkaline extracted xylan

Mild alkaline conditions could solubilise xylan from *E. grandis* in oligomer or polymeric form through the cleavage of ester bonds between polysaccharides and lignin.[22] The extracted xylan and their derivatives could be used as paper additives to improve the properties of pulp fibres in papermaking process.[5]

In this regard, the average molecular weight of xylan sample obtained under the alkaline extraction conditions run 6 (2 M NaOH; 40°C for 240 min) was estimated by size exclusion chromatography (SEC). These conditions were of interest since they resulted in high glucan content retained in the extracted wood chips and subsequently used for kraft pulping evaluation. The average molecular weight of the xylan sample obtained by SEC was approximately 53, 400 g mol^{-1}, which was in the range of xylan extracted in similar manner from other feedstocks.[22,28]

FT-IR spectroscopic analysis was used to determine the structural changes in the extracted xylan. Figure 2 shows the spectra of xylan obtained by conditions of run 6 compared with that of commercial birch wood xylan. The IR spectra of the two xylans were similar in the regions 1100 - 600 cm^{-1} and 3500 - 2500 cm^{-1}. They contained an identical set of transmission bands differing only in intensity, indicating a similar structure of these xylans.

The greatest difference was observed in the region 1800 - 1300 cm^{-1}. A polymeric chain consisting of pure xylopyranose units should not have noticeable absorption at 1800 - 1500 cm^{-1}.[29] Therefore, the absorption in this region was due to vibrations of a different type of substituent in the main chain and (or) the xylan side chains. Furthermore, the FT-IR spectra of *E. grandis* xylan exhibited a band at 1574 cm^{-1} that was due mainly to stretching vibrations of C=C and C–H groups and skeletal vibrations of phenol rings confirming the presence of lignin residues.[30] Xylan containing phenolic groups can be used for the production of packaging films.[22]

3.3. Properties of pulp and handsheets obtained from extracted E. grandis wood chips

Wood chips from alkaline extraction run 6 (12.4% xylan extracted; 2 M NaOH at 40°C for 240 min) were directly subjected to kraft micro pulping under different sodium sulfide conditions to assess the effect of xylan extraction on cooking chemicals, pulp yield and properties. After the extraction step the wood chips absorbed NaOH which retained with the wood chips, and that was taken into consideration during the cooking process. Additional NaOH was generated from the sodium sulfide added to the cooking system.

The cooking conditions and properties of the pulps obtained from extracted and non-extracted *E. grandis* wood chips are summarized in Table 4. The total NaOH charge present in the system during cooking of the extracted wood chips was approximately 4.7 – 6.7% less compared to non extraction due to removal of xylan and other wood components. Modified kraft cooking of extracted wood chips under 35.7% sulfidity maintained the pulp yield at similar kappa number as non-extraction.

Based on the aforementioned preliminary micro pulping experiments, kraft cooks under 35.7% sulfidity for wood chips from which 12.4% xylan extracted were conducted on a large scale in a same manner as in micro pulping. The effect of scale up was evaluated in terms of pulping chemicals requirements, pulp yield and handsheet strength properties. The cooking conditions, pulp composition and handsheets strength properties are presented in Table 5 and Figure 3, respectively.

The results showed that because of xylan extraction the wood chips mass was reduced from 1000 g to 961.0 g and that could increase the digester capacity.[31] Consequently a reduction in the total loading of NaOH charge (134.7 g vs 194.1 g) needed for delignification was possible. Furthermore, because of high concentration of sodium sulfide added in the liquor when cooking extracted wood chips, high concentration of sodium hydrosulfide (NaSH), which tends to make lignin more soluble, was generated. Therefore, the cooking time of extracted wood chips was reduced by 15 minutes to avoid severe degradation action which might have a negative effect on pulp yield. If the NaOH present in the liquid fraction after the extraction step can be recovered and reused for either extraction or pulping could make this process even more economical.[31-32]

There were no significant changes in the overall pulp properties (pulp yield, rejects, kappa number and viscosity) when 12.4% xylan was extracted from *E. grandis* wood chips prior to pulping. Screened pulp yield recorded for both non-extracted and alkaline extracted wood chips was comparable (53.8±3.0 vs 51.1±1.0 respectively) at similar kappa number value of 20 (Table 5). These values were considered appropriate within pulp yield specification of Mondi kraft pulp mill, Richards Bay in South Africa.[17]

It was apparent that the comparable overall pulp yield depends on the extent of xylan extraction from wood chips prior to pulping together with the utilisation of low alkali charge and cooking time.[13,32,33] The residual active alkali measured from pulping black liquors of alkaline extracted wood chips was within the required limit (6 - 8 g L^{-1} (Na_2O) which otherwise might have resulted in lignin readsorption on the pulp fibres.[12]

A rejection level of wood chips was below 1% for pulps produced from extracted wood chips. It can be speculated that good pulping response due to alkaline extraction was related to alteration and swelling of fibres under alkaline conditions during extraction step.[15] This resulted in softening of the chips and ease of fibre separation during subsequent pulping. Moreover, the extraction with alkali prior to delignification favored a more uniform cook, thereby shortening the cooking time.

An additional advantage observed in this study was that alkaline extraction of *E. grandis* chips improved pulp viscosity by 13% compared to pulps produced from non-extracted wood chips, thus giving less evidence of severe cellulose degradation by extraction. Viscosity is related to degree of polymerization of cellulose, therefore it is an indirect measure of chemical damage of cellulosic fibre in laboratory cooking 9reduction in chain length).[19] The viscosity was measured with Brookefield viscometer, normally used to determined viscosity of coating for paperboard production. Although this viscometer provides lower viscosity values compared to capillary viscometer, its consideration is valuable in terms of comparison between the extracted and non-extracted pulps evaluated in this study. An increase of cellulose degradation observed for extracted wood chips could be explained by the removal of the low molecular mass hemicelluloses since the viscosity averages the DP of the cellulose and hemicelluloses.[32] Additionally, low levels of alkali used to pulp extracted wood chips might have preserved the degradation of the fibres. Additionally, alkaline xylan extractions might have caused rearrangement in the cell wall structure leading to the formation of xylan-cellulose co-aggregates which were resistant to degradation.[34] At the same time transformation of eucalyptus xylan side chains (methylglucuronic acid) to hexenuronic acid under alkaline medium is well documented.[13]

This transformation renders xylan more stable towards alkaline degradation, consequently reducing the accessibility of cellulose microfibrils linked to the stable xylan and hence limiting its degradation.

The carbohydrate composition of the pulp showed a reduction in glucan and xylan content retained in the pulp fibres produced from alkaline extracted wood chips by only 9.8 and 3.5 percentage unit, respectively, compared to pulps produced from non-extracted wood chips (Table 5). The percentage yield of individual polysaccharide retained in the pulp after kraft pulping might influence the strength properties of the pulp fibres.[5] For instance, lower fibre strength is often obtained by either lower cellulose content or higher fibre damage.[35] The correlation between fibre strength and cellulose content was found up to 70 - 80% cellulose content.[36] In addition, several studies reported the importance of preserving xylan during pulping because xylan-to-cellulose interaction improves tensile index or breaking strength property of the resultant pulp.[13, 37]

In the present study, the retention of 73.9% glucan and 19.5% xylan content of the pulp produced from alkali extracted material appeared to have been sufficient for the maintenance of the strength properties of the pulp at the beating degree of 40 °SR. In fact, the tensile index (Fig 3A) and breaking strength (Fig 3B) of handsheet produced from pulps obtained from alkaline extracted wood chips was increased by only 7% and 9.0% respectively. Similar benefit on tensile strength property by extraction of aspen chips with kraft white liquor prior to kraft pulping had been reported.[38] This finding could be attributed to the observed increase in viscosity since cellulose degradation governs the strength of the fibre to a certain degree.[35] Simultaneously, tear index (Fig 3 C) due to alkaline extraction was maximum at 20 ˚SR and improved by 6.3% and it declined slightly by 0.2% at 40 ˚SR and burst indexes (Fig 3D) were very similar in both scenarios. A decrease in tear index in pulp is common after the tear strength has passed the maximum due to reduction in fibre length, fibre strength and fibre-fibre bonding.[37] The burst indexes (Fig 3D) were reduced in both scenarios.

The comparison of these results with those from Al-Dajani *et al.* (2008) showed a disagreement in tensile strength although the method of extraction and pulping conditions were similar.[13] The authors reported ~10% decrease in tensile index due to alkaline extraction and regrettable no another strength properties were tested. This could be attributed to the extent of xylan extraction which was approximately double the amount of xylan extracted in the present study. Another aspect that might have resulted in this reduction in the referenced results was the reduction in viscosity due to alkaline extraction. In various pulp applications, either tensile index or tear is the important strength property. [18]

The reverse development of tear and tensile strength of the pulps is shown in Figure 3E. A constant decrease in tear index after it reaches a certain critical value with the steady growth in tensile index is the expected result.[9] Tear index is certainly affected by fibre length as previously mentioned, which may have been reduced because of fibre cutting. Lower refining requirements would decrease fibre cutting and result in higher tear properties. Conversely, tensile strength correlates strongly with inter-fibre bonding capacity and suggest mild alkali pre-extraction has no negative effect on the fibre bonding.[39-40] High tensile and tear index observed for handsheets produced from alkaline extracted wood chips are favorable for the manufacture of wrapping and packaging paper.[9,18] The improvement in optical brightness (Fig 3F) of handsheets due to alkaline extraction was observed. Lighter pulps would require less bleaching chemical and this could reduce the economic demands in the IFBR process of the alkaline extracted *E grandis* wood chips.[15]

The overall analysis of the results showed that the mass removal of hemicelluloses should be limited during extraction and pulping processes since their presence is desirable in pulps, because within a certain optimum range they are able to contribute towards pulp yield and hand sheets strength properties. [13, 39-40]

4. Conclusions

This study provided strong evidence that it is technically feasible to extract approximately 12.4% xylan under mild alkali conditions from *E. grandis*, with a minimum effect on final kraft pulp yield and physical properties, as measured by handsheet testing. The alkaline extraction of 12.4% xylan prior to pulping in combination with low alkali concentration and less cooking time used for cooking extracted wood chips retained the pulp yield with similar kappa number as non extraction. The breaking length/tensile index and optical brightness of the handsheets measured were improved, at the same time both tear and burst index were not affected. The improvement in physico-chemical properties of the pulps depends on the extent of xylan extraction from wood chips, thus limiting the amount that could be extracted without negatively impacts on pulp yield and properties.

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Table(s)

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

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

	Component	% ODM*	Analytical method
Extractives	Ethanol/Cyclohexane soluble extractives	3.0 ± 1.0	TAPPI T264 om-88
	Water soluble extractives	1.2 ± 0.5	
Carbohydrates	Glucan	52.7 ± 2.0	LAP 013
	Xylan	15.3 ± 0.3	
	Arabinan	0.5	
	Ash content	1.2 ± 0.2	TAPPI T222 om-85
	Acid insoluble lignin	16.7± 2.0	LAP 013
	Acid soluble lignin	4.4± 1.5	

(*) Mean values and standard deviation of four measurements.

Table 2. The yield of xylan and composition of wood chips after alkali extraction of *E. grandis* under process variables defined by a 2^3 full factorial design.

Pre-extraction conditions				Xylan pre-extraction efficiency				[b]Solid fraction after extraction			[c]EMB (%)		
Run	NaOH M	Temperature (˚C)	Time (min)	Xylan precipitate yield %	[a]Xylan recovery yield %	Lignin (% xylan)	Lignin % dry raw *E. grandis*	Glucan %	Xylan %	Acid insoluble lignin (%)	Glucan	Xylan	Lignin
1	1	40	120	0.6	3.9	4.9	1	51.1	13.9	18.6	94.6	94.8	92.9
2	1	40	240	1.0	6.7	8	1.7	50.2	13.5	18.3	94.8	94.8	94.8
3	1	90	120	0.5	3.5	6.1	1.3	50.3	13.8	17.8	99.7	93.5	90.5
4	**1**	**90**	**240**	**1.9**	**12.4**	**16.1**	**3.4**	**49.9**	**12.3**	**16.0**	**93.7**	**92.8**	**91.9**
5	2	40	120	0.7	4.8	2.4	0.5	50.4	13.4	19.8	94.4	92.2	96.2
6	2	40	240	1.6	10.3	14.8	3.1	49.7	12.5	16.6	93.3	92.2	93.4
7	2	90	120	1.3	8.5	6.9	1.5	49.9	12.9	18.4	93.3	92.8	94.3
8	2	90	240	2.5	16.0	14.1	3	48.9	11.9	17.1	94.4	94.1	95.3
9-11	1.5	65	180	1.0±0.04	6.5±0.3	9.0±0.8	1.9±0.1	50.3±0.3	13.6±0.5	18.6	93.4	94.5	97.2

[a]Analysis data are based on the oven dry xylan of non-extracted *E. grandis*
[b]Analysis data are based on the oven dry non-extracted *E grandis*
[C]Extraction mass balance (EMB) was calculated for each component in the *E. grandis* as e.g. xylan in the liquid and solid fraction after Run 4 were 1.9% and 12.3% respectively, and the raw *E grandis* has 15.3% xylan before the extraction. The total extraction mass balance = [(1.9+12.3)/15.3]*100 = 92.8%

Table 3. Analysis of variance for the regression model of xylan solubilisation after alkaline extraction of *E. grandis*.

Source	Sum of squares	DF	Mean square	F-value	Prob>F
Model	126.41	6	21.07	12.22	0.0325
Residual	5.17	3	1.72		
Lack of fit	1.98	1	1.98	1.24	0.3811
Pure error	3.19	2	1.68		
Cor Total	144.53	10			
R^2	0,964				

Table 4. Kraft micro-pulping results of 12.4% xylan extracted (2M NaOH, 40°C, 240 min) *E. grandis* wood chips.

Parameters	Non-extracted	Xylan extracted (2M NaOH,40˚C, 240 min)		
Cooking conditions				
Active alkali (%)	18.7			
NaOH in wood chips	16.5	9.9	10.0	10.7
Sulfidity (%)	25	31.4	35.7	40
NaOH from Na_2S (g)	3.0	2.9	3.9	4.1
Total NaOH in cook (g)	19.5	12.8	13.9	14.8
Maximum Temp (°C)	170			
Time at 170°C (min)	45	30		
Pulp properties*				
Screened pulp yield (%)	53.7±1.8	46.0±1.0	51.0±2.4	45.4±3.2
Rejects (%)	1.8±0.1	2.5±0.4	1.0±0.6	0.8±0.7
Kappa number	21.3±0.5	23.3±0.2	20.4±0.8	14.6±0.4

*Mean values and standard deviation of four measurements.

Table 5. Large scale cooking conditions and properties of the pulps obtained from non-extracted and 12.4% xylan extracted *E. grandis* wood chips

Parameters	Non-extracted	Xylan extracted 2M NaOH, 40˚C, 240 min
Pulping conditions		
Active alkali (%)	18.7	
Sulfidity (%)	25	35.7
Maximum Temp (°C)	170	
Time at 170 °C (min)	45	30
Chips/residue (OD, g)	1000	961.0
NaOH in chips/ residue (g)	165.4	99.2
NaOH from Na_2S (g)	30.2	35.5
NaOH total in cook (g)	195.6	134.7
NaSH charge (g)	42.2	49.6
Pulp evaluation*		
Screened pulp yield (%)	53.8±3.0	51.1±2.0
Screening rejects (%)	1.7±0.4	0.6±0.5
Kappa number	20.0±2.5	20.8±1.8
Viscosity (cP)**	8.1±0.5	9.4±0.7
Carbohydrate composition of pulp according to LAP 013		
Glucan (%)	83.7	73.9
Xylan (%)	22.3	19.5
Black liquor characteristics		
Residual alkali (g L^{-1})	7.5±1.5	6.2±2.0

*Mean values and standard deviation of four measurements.
**Viscosity determined in a Brookefield viscometer with spindle 21 with Pulp CED solution.

Figures

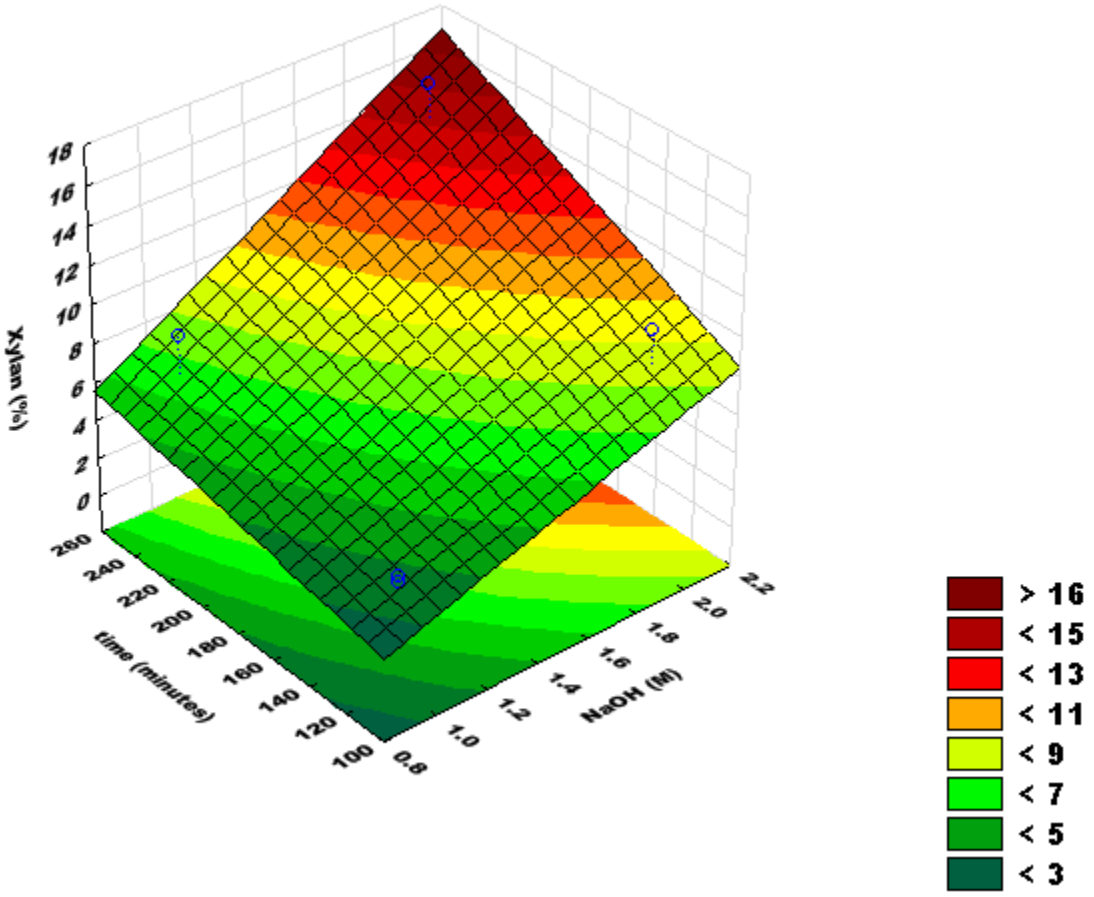

Figure 1. Response surface for xylan yield obtained after alkaline extraction of *E. grandis* wood chips showing the influence of NaOH concentration and extraction time at a fixed temperature of 65°C.
105x85mm (96 x 96 DPI)

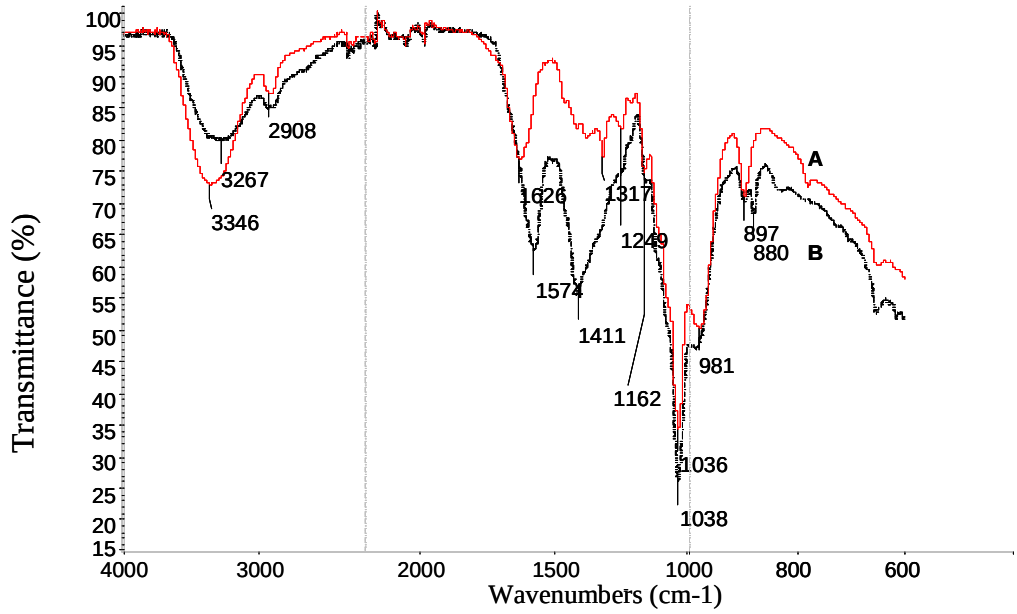

Figure 2. FT-IR spectra of commercial birch wood xylan (A) and xylan fraction extracted from *E. grandis* wood chips (B) with 2M NaOH at 40°C for 240 minutes.
162X115mm (96 x 96 DPI)

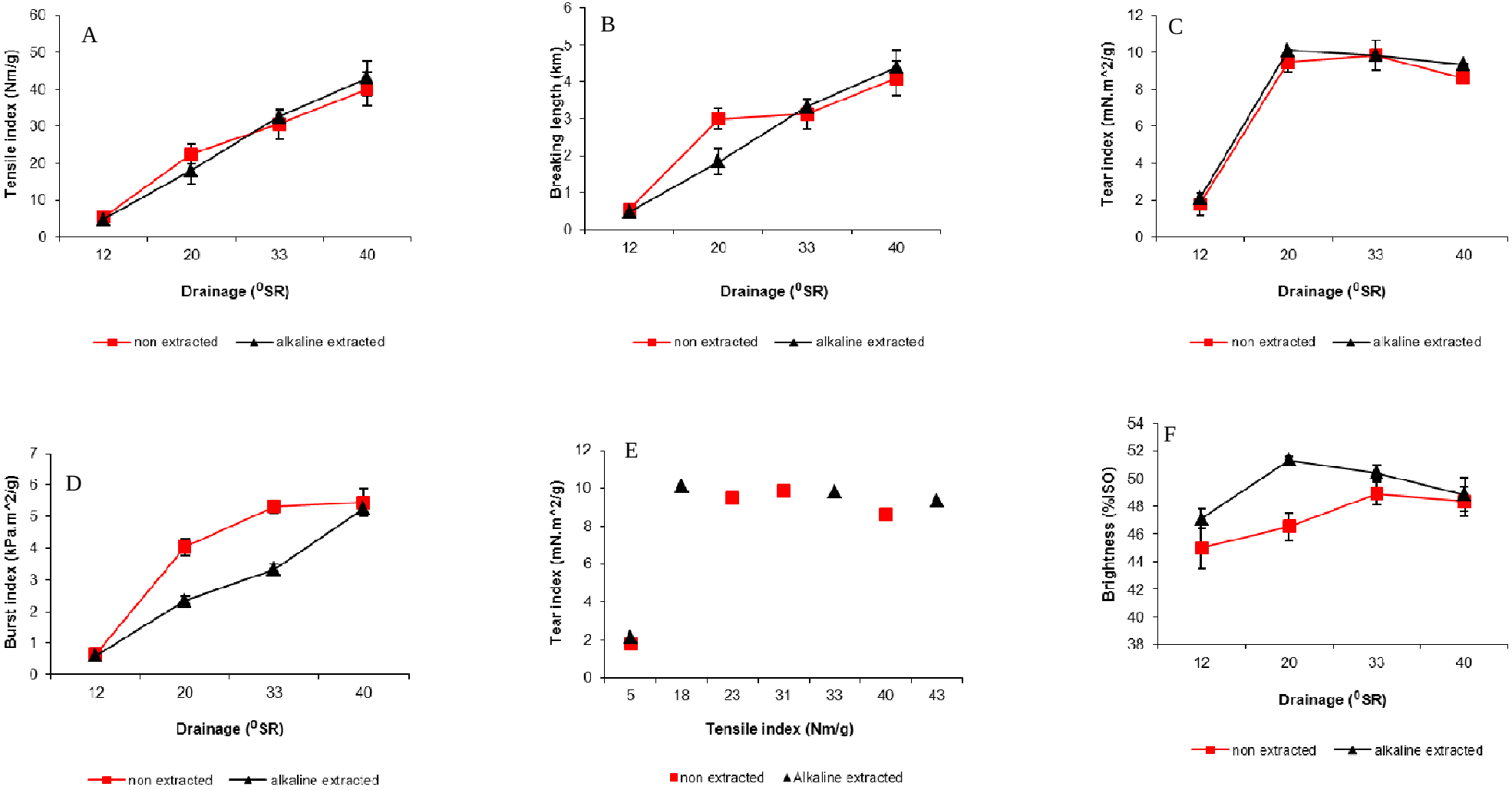

Figure 3. (A) handsheet tensile index; (B) breaking length; (C) tear index; (D) burst index; (E) tear-tensile relationship and (F) optical brightness as a function of drainage in °SR of *E. grandis* after kraft pulping in large scale.
209x111mm (96 x 96 DPI)

Paper III

Impact of hemicelluloses pre-extraction on pulp properties of sugarcane bagasse

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Abstract

The extraction of hemicelluloses that otherwise would be wasted in the black liquor, can be integrated with chemical pulping processes in a biorefinery approach that will generate a sugar rich feedstock for production of fuels and chemicals. Extractions of hemicelluloses from sugarcane bagasse with dilute sulphuric acid or mild alkaline conditions were performed using a central composite experimental design. Selected solid residues obtained after dilute acid, hot water (zero acid) or mild alkaline pre-extractions were subjected to soda or sodaAQ pulping, while kraft pulping of the dilute acid pre-extracted solid residue was also performed. The integration of hemicellulose pre-extraction by alkaline methods into a sodaAQ-based pulping process was preferred for sugarcane bagasse as feedstock, since it enabled xylan recovery of 69.1%, while providing pulps with superior tear strength and brighter pulps.

Keywords: biorefinery, xylan extraction, sugarcane bagasse, chemical pulping, pulp quality, handsheet strengths

1. Introduction

Sugarcane bagasse (SCB) is the second most commonly used non wood fibre plant material for pulp and paper production in numerous parts of the world including South Africa, Central Asia, the Middle East and North America.[1] The South African sugar industry produces approximately 6 million tonnes of sugarcane bagasse annually, from which about 70 000 tons of unbleached and 60 000 tons of bleached bagasse pulp grades are produced per annum.[2,3] Besides its availability, SCB is characterised by high cellulose (40 - 50%) and hemicellulose content (xylan: 28 - 30%), but lower lignin content (19 - 21%) compared with other wood feedstocks such as *Eucalyptus* or pine, generally used for pulp and paper production.[4,5] Because of lower lignin content, SCB is more easily delignified, requiring milder and shorter cooking conditions than wood sources. Another interesting feature of nonwood which is different from wood is the silica, a component of ash. While SCB is quite low in silica compared with other nonwood fibres, at 0.5% it is at least twenty times higher than in eucalyptus and its removal is crucial during pulping processes.[6]

Among the pulping processes, soda pulping (using NaOH only) is the preferred method for sulphur-free, chemical pulping of SCB in South Africa.[7] The addition of pulping additives such as anthraquinone (AQ) in bagasse soda pulping improves pulp yield and delignification rates, while reducing carbohydrate degradation.[8] However, SCB consists of pith which constitutes 30-35% by weight of SCB. This material does not produce papermaking fibre but consume more chemicals in the pulping process and has high ash content than the fibrous parts of SCB rendering poor drainage of pulp and inhibits chemical recovery.[9] Hence, effective depithing is an essential requirement to avoid wastage of chemicals and to minimise the ash/silica content.[10]

A pulp mill generates substantial amounts of organic by-products in the form of black liquor, generated by the degradation of lignin and hemicelluloses.[11] The black liquor streams are today mainly used as fuel source at the pulp mill to produce electricity and steam whilst cooking chemicals are regenerated.[12]

Compared with wood, chemical recovery in SCB and other nonwood soda pulping black liquor stream is the major problem due to high cost, high viscosity, low settling rate and silica inclusion in black liquor thus causing the sludge non-reusable after re-burning.[13] Silica can be removed by precipitation from black liquor by reduction of pH with carbon dioxide from flue gasses or by addition of calcium oxide.[6] The viable option to minimise capital costs for soda recovery is by using fluidised bed type furnace for combustion of black liquors as demonstrated at Sappi Stanger mill in South Africa.[6] However the calorific value of the black liquor solids from soda pulping of nonwood is still inferior than that of kraft pulping of wood.[13]

Considering that hemicelluloses degraded in the black liquor have a low heating value (13.6 MJ kg^{-1}) compared to lignin (27.0 MJ kg^{-1}), it could instead be processed to value added chemical products within a pulp mill biorefinery.[11,14] Non-degraded (polymeric) hemicelluloses have valuable properties such as potential paper additives, biopolymers and speciality chemicals, while it can be used in monomeric form for bioethanol production.[15,16] In addition, the extraction of hemicelluloses can favour the cooking liquor impregnation during subsequent pulping, thereby reducing the cooking time and lowering the required alkali charge.[17] Another advantage of the application of pre-extraction is the reduction of ash/silica content in the pre-extracted residues, circumventing the associated problems with chemical recovery.[18]

Various pre-treatment methods to extract hemicellulosic components from sugarcane bagasse have been reported. These include dilute acid pre-treatment, hot water extraction, ionic liquids, alkaline extraction and alkaline/peroxide treatment.[17,19-20] Dilute acid hydrolysis mostly generates oligomeric and monomeric hemicelluloses-derived sugars, mainly xylose, that can be the platform for the production of chemicals such as ethanol, furfural and xylitol.[4,15,21] On the other hand, alkaline treatment originates high molecular weight hemicelluloses-derived polymers in particular xylan, that might be used for the production of biopolymers.[5,16] Moreover, extracted xylan can undergo modification and used as papermaking additive.[16]

However, in developing an appropriate hemicelluloses pre-extraction process, not only the yield and the composition of extracted hemicelluloses should be considered, but also the properties of pulp produced from the hemicelluloses pre-extracted, fibrous residue (cellulignin).[14] This is due to the fact that certain physical properties of pulp require the presence of hemicelluloses in the fibre matrix.[22] Previously, handsheet paper strength properties such as burst index and tensile index were reduced when hot water or alkaline extraction was applied on SCB or rice straw prior to sodaAQ pulping.[17,22] In this context, the present work compares different extraction treatments prior to pulping of SCB. The effect of reaction conditions of dilute sulphuric acid or mild alkaline treatments on hemicelluloses pre-extraction from SCB originated from South Africa was investigated by central composite design. Additionally, hot water treatment was applied for comparison. Those conditions under which significant hemicelluloses could be extracted, while ensuring minimal interference on cellulose content in the residual cellulignin, were selected for further soda, sodaAQ or kraft pulping. The impact of hemicelluloses pre-extraction on pulp properties and paper quality using soda or sodaAQ pulping methods was evaluated.

2. Material and methods.

2.1. Materials

Sugarcane bagasse (Saccharum *officinarum*) was provided by TSB sugar, located in Mpumalanga, South Africa. The sugarcane bagasse (SCB) was air dried, depithed and conditioned at 23°C and 55% relative humidity before use. Sodium hydroxide (NaOH) and sulphuric acid were purchased from Merck and BUSPERSE 2262 Anthraquinone (AQ) was donated by Buckman Laboratories, Hammarsdale, South Africa. Pullulan standards purchased from Polymer Standards Service (PSS) in Germany were used to estimate the molecular weight of the isolated xylan fractions.

2.2. Hemicelluloses pre-extraction of sugarcane bagasse

Dilute sulphuric acid and mild alkali pre-extraction were carried out according to the central composite experimental design created and evaluated in Statistica 7.1 (Statsoft Inc., Tulsa, USA) and Design Expert version 8.[23] The experimental range and the process parameters' codification are given in Table 1. The sequences of dilute sulphuric acid and mild alkaline experiments are illustrated in Table 2 and Table 3, respectively. Three assays were carried out at the center points to estimate the random error required for the analysis of variance (ANOVA). Xylan content in the liquid was considered as the response of the experimental design. The statistical significance of the regression coefficient was determined by the coefficient of determination, R^2.

2.2.1. Dilute acid and hot water pre-extraction

Samples of 40 g ODM, depithed SCB and sulphuric acid solutions (0.1 - 0.6%) were mixed in the desired portions and introduced into micro reactors (bombs) according to the central composite design (Table 2). The solid to liquor ratio was 1:6 g mL^{-1}. Filled bombs were placed in a digester of 15 dm^3 capacity enclosed by heating jackets. Selected reaction temperatures (86 - 154°C) were monitored with thermocouples at different reaction times (6 - 74 min). Pre-extraction with hot water (run 9, Table 2) was part of the dilute sulphuric central composite experimental design and was similarly performed at 120°C for 40 min to evaluate the effect of xylan pre-extraction at lower levels.

2.2.2. Alkaline pre-extraction

The mild alkaline extraction of hemicelluloses was performed as described elsewhere, without using the chlorination step.[24] A similar treatment procedure was followed as in dilute sulphuric acid extractions. 40 g ODM SCB were mixed with the NaOH solution (0.7 - 2.34 M) in 500 mL Schott bottles and placed in a shaking hot water bath at 23 - 90°C. Similarly, conditions at 107°C were performed in micro bombs placed in hot water pressurised digester. At the end of the treatments, the fibres were squeezed by hand to recover the hemicellulose.

2.3. Liquid fraction characterization

2.3.1. Liquid fraction from dilute acid and hot water pre-extraction

At the end of the dilute sulphuric acid and hot water pre-extraction, the bombs were cooled in room temperature water. The liquid and the solid fraction were separated by filtration on a 100 mesh screen. The xylan-rich hydrolyzate was collected and a sample was filtered through 0.2 μm membranes and analysed for its content of sugars and by-products.

To identify the presence of oligosaccharides, the fractions of the xylan-rich hydrolyzates were subjected to a dilute acid treatment at 121°C for 10 min to convert all oligosaccharides to monosaccharides, according to the NREL method.[25] It was assumed that the difference in monomeric sugars between the samples was in oligomeric form.

The sugars (glucose, xylose and arabinose), acetic acid and by-products (hydroxymethylfurfural and furfural) present in the liquid fraction were analysed by high pressure liquid chromatograph (HPLC) as described elsewhere.[26]

2.3.2. Liquid fraction from mild alkali pre-extraction

The xylan-rich filtrates containing a complex mixture of solubilised materials (oligosaccharides, lignins, extracting chemicals, etc.) were concentrated in a rotary evaporator at 40°C to approximately one third of the original volume. Filtrates were then purified by dialysis against de-ionized water for 3 days using a dialysis cellulose membrane with a 12kDa molecular weight cut off. This membrane cut off had been chosen, since it was shown feasible for the separation and purification of hemicelluloses in the laboratory scale.[24] The samples were conditioned in liquid nitrogen and freeze-dried. The ODM of the recovered hemicellulose precipitates was determined.

The hemicellulose recovery yield was estimated according to the following relations.[27]

$$\%\text{Hemicellulose precipitate} = \frac{\text{Oven dry mass of hemicellulose precipitate}}{\text{Oven dry mass non-extracted SCB}} \times 100 \quad (1)$$

$$\%\text{Hemicellulose recovery} = \frac{\%\text{Hemicellulose precipitate}}{\%\text{Hemicellulose of SCB}} \times 100 \quad (2)$$

The lignin fractions associated with the hemicelluloses were determined as described elsewhere.[19]

2.3.2.1. Size exclusion chromatography

The molecular mass of the extracted hemicellulose was determined using size exclusion chromatography (SEC). The isolated hemicellulose was dissolved in deionised water to obtain a final concentration of 1 g L^{-1}. The solution was stirred continuously at room temperature for 2 hours and filtered through 0.2 µm membranes. The SEC system consisted of three SUPREMA aqueous columns (PSS, Germany), connected in series with the pore sizes 30 Å, 3000Å and 3000Å, respectively. Detection was conducted using a Dionex UltiMate 3000 HPLC system with a Varian 380-LC detector, which is an Evaporative Light Scattering (ELS) detector. Solution of deionised water containing 0.05% sodium azide (NaN_3) was used as eluent and the flow rate was kept at 1 mL/min. Column temperatures were kept at 25°C. The detector output was analysed with the Chromeleon® Version 6.80 software package.

2.3.2.2. Spectroscopy analysis of hemicelluloses

The FT-IR spectra were recorded in reflectance mode using the Smart Performer from Thermo equipped with ZnSe lenses. Prior to analysis, a sample of freeze dried xylan was further dried in phosphorus pentoxide, and a small portion of the dried hemicellulose was placed on the ZnSe horizontal ATR, and 16 scans with a resolution of 4 cm^{-1} were accumulated over the range of 4000 - 650 cm^{-1}. The operating and data manipulating software was the basic OMNIC package.

2.4. Characterization of raw material and solid fractions

2.4.1. Chemical composition

The depithed SCB was ground into powder in a Retsch mill and a fraction of 40 mesh size was accepted for chemical analysis. Oven-dry mass (ODM) of the powder 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 SCB was determined.[28] All the experiments were carried out in four replicates and the experimental results were represented as the mean ± standard deviation of four identical conditions.

The solid fractions obtained after dilute sulphuric acid or mild alkaline pre-extraction were rinsed with distilled water and air dried. Dried samples were milled prior to polysaccharides and residual lignin content determination, using the same standard methods as those used for the raw materials except for the extractives determination.[28, 29]

The polysaccharides in extractive free SCB and solid residues were calculated based on glucose, xylose, and arabinose after a two step hydrolysis with 72% H_2SO_4 and 4% H_2SO_4 respectively, according to National Renewable Energy Laboratory (NREL) Analytical Procedure.[29] The concentrations of these compounds were determined by high pressure liquid chromatograph.[26]The equation for the extraction mass balance was as follows.[30]

$$\text{Extraction mass balance} = \frac{\sum C_{Li} + \sum C_{Si}}{\sum C_{Ri}} \qquad (3)$$

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

2.4.2. Scanning electron microscope

The portion of the SCB fibres from dilute sulphuric acid and alkaline pre-extractions were mounted onto metal stubs with double-coated carbon adhesive tape. The samples were sputtered with gold in a high vacuum S150A sputter coater. Finally, the samples were examined using a LEO1430VP scanning electron microscope (SEM). Similar analysis was performed on non-extracted sugarcane bagasse for comparison.

2.5. Micro pulping after hemicelluloses pre-extraction

Non-extracted SCB and solid residues from hot water (run 9: water, 120°C and 40 min) and dilute sulphuric acid (run 15: 0.3% v/v H_2SO, 120°C and 40min) pre-extractions were submitted to soda or sodaAQ micro pulping. Prior to pulping, the dilute sulphuric acid pre-extracted solid residues were thoroughly washed with water to neutralize and air dried. The experiments were carried out according to the central composite design created and evaluated by Statistica 7.1 (Statsoft Inc., Tulsa, USA). The range of cooking conditions for soda pulping were: Active alkali (NaOH): 20 - 22% and reaction time: 25 - 37 min. SodaAQ pulping conditions ranges were: Active alkali (AA): 14 - 16%, anthraquinone (AQ): 0.05 - 0.1%, and reaction time: 30 - 70 min. The conditions were selected in agreement with previous reports on the pulping of SCB.[8, 17, 31]

Likewise, after the completion of the alkaline pre-extraction step, alkaline extracted residue run 15 (1.5 M NaOH, 65°C, 180 min) was directly subjected to pulping without washing. Only 0.1% AQ was added in the cooks.

The maximum cooking temperature was kept constant at 170°C and the SCB-to-liquid ratio was fixed at 1:7 g mL^{-1} for all pulping experiments. Pulping was carried out in micro bombs that could accommodate 40g oven dry SCB. 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, washed through a 10 mesh screen to separate the rejects from the fibres, and the accepted pulp was collected on a 100 mesh screen. The pulp was then screened through a 0.15 mm screen, to remove shives and then spin dried to a consistency of approximately 30%.

Screened pulp yield was calculated as a percentage of the ODM of the pulps obtained in relation to the initial ODM of the raw material.

$$\text{Pulp yield (\%)} = \frac{\text{Oven dry mass of pulp}}{\text{Initial oven dry mass SCB}} \times 100 \qquad (4)$$

The rejects and the shives collected were placed in an oven to dry at 105°C overnight to establish the oven dry mass and weighed. The reject and shive content were together expressed as a percentage of original dry mass of SCB. Pulp kappa number was determined by standard TAPPI method T236 cm-85.

2.6. Large scale pulping

The best results obtained from micro pulping were repeated on a large scale. Solid residue from run 9 (hot water, 120°C and 40 min) and run 15 (1.5 M NaOH, 65°C and 180 min) were submitted to sodaAQ pulping process. Pulping of 500 g ODM pre-extracted was carried out in a 15 dm^3 batch type digester. SodaAQ pulping conditions for hot water were 14% AA and 0.1% AQ for 30 min at 170°C. In the case of mild alkaline pre-extracted residues, no additional NaOH and only 0.1% AQ was added to the SCB fibres. Alternatively, 500 g dry mass of the dilute acid pre-extracted run 15 (0.3% v/v H_2SO_4, 120°C and 40 min) was subjected to kraft pulping under the following conditions: 12% AA and 20% sulfidity.[32] All SCB fibres were digested for 30 min at 170°C and the products of pulping treated as per section 2.5.

All active alkali and sulfidity masses are expressed as equivalent mass of Na_2O.

2.6.1 Characterization of pulping black liquors

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

2.7. Pulp evaluation and handsheet formation

Pulp tests were performed according to TAPPI standard methods.[28] Total pulp yield and rejects were determined as a percentage of the ODM of the raw material. Pulp kappa number was determined by standard TAPPI method T236. Pulp viscosity was determined by dissolving pulp sample into a cupricethylenediamine 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 handsheets 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-92. Handsheets were formed according to TAPPI T205 om-88 using British Standard handsheet making equipment.

2.8. Testing of physical properties of the handsheets

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. Burst index (hydrostatic pressure required to rupture the test specimen), breaking length (maximum load or weight that a strip of paper will support before pulling apart), and tear index were measured by TAPPI Standard no T403 om-91, T404 om-87 and T414 om-84 respectively. The brightness was measured in ISO units using a reflectance photometer (Zeiss Elrepho 65843, Germany).

3. Results and discussion.

3.1. Raw material composition

The chemical composition of sugarcane bagasse (SCB) is listed in Table 4. SCB contained 1.7% ethanol/cyclohexane soluble extractives, 2.4% water soluble extractives and 2.6% ash content. The ash content was within the range (0.7 - 2.6%) reported in the literature for depithed SCB but higher than in wood (0.2 - 1.5%), probably due to the high silica contents of SCB and contamination with soil.[5, 6, 8]

Nevertheless, SCB had higher proportion of hemicelluloses (28.0 %), mainly as xylan (25.9%) than wood.[33] The Klason lignin content averaged 18.2% was lower than 26.8% reported for wood based materials.[33]

SCB constitutes an alternative to the well-established wood sources of fibre. Its high holocellulose content together with lower lignin makes this feedstock a good candidate for the integration of increased hemicellulose pre-extraction prior to pulping and the production of high pulp yields when the material is well depithed.

3.2 Effect of xylan pre-extraction on sugarcane bagasse

3.2.1. Liquid fractions

The effectiveness of dilute sulphuric acid and mild alkaline (NaOH) treatments for xylan extraction from SCB prior to pulping was investigated. The experimental results presented in Table 2 and Table 3 include data on the recovery of the reaction products such as sugars, oligomers, sugar degradation products furfural and hydroxymethylfurfural (HMF), acetic acid and acid soluble lignin (ASL) obtained after dilute sulphuric acid and mild alkaline pre-extraction, respectively. The major component considered in the analysis of the liquid fraction was the xylan yield, measured as the combined monomeric and oligomeric xylose content. The sugar degradation products, acetic acid and ASL were considered as by-products in the dilute sulphuric acid pre-extraction process that may inhibit possible subsequent biological conversion.[34] ASL was also considered as an impurity for mild alkaline pre-extracted xylan.[19]

The results show that dilute sulphuric acid conditions can selectively solubilize xylan from SCB, originating liquid fractions rich with xylo-oligomers with up to 17.8% of the total xylose content (Central point, Table 2). The importance of adding an acid catalyst to improve xylan solubilisation from SCB structure was confirmed by the low xylose yields (11.9% DM) obtained when hot water extraction was performed at 120°C for 40 min. Xylan yields in the liquid fractions increased with the increase in reaction time, temperature and acid concentration. The maximum recovery of xylose of 73.1% (57.7% monomeric and 15.4% oligomeric) was obtained when pre-extraction of xylan was performed under 0.3% v/v H_2SO_4 at 120°C for 74 min. At the same time, the concentration of sugar degradation compounds and acetic acid derived from acetyl groups were below the reported levels of inhibition for subsequent fermentation processes, i.e. 0.5 to 2 g L^{-1} for both HMF and furfural and 4 to 10 g L^{-1} for acetic acid.[34] Under these conditions, less than 3% of the cellulose and lignin content of SCB was solubilised, indicating little or no degradation of these polymers.

Alternatively, xylan can be quantitatively recovered from SCB with mild alkaline conditions (Table 3). Increase in NaOH concentration had a dominant influence on high xylan solubilisation and subsequent recovery in the liquid fraction. The maximum xylan recovery yield was 81.1% obtained using the highest NaOH concentration of 2.3 M at moderate temperature of 65°C. Alkaline pre-extraction conditions also solubilised a noticeable amount of lignin (4.1 – 24.3%) associated with the recovered xylan.

Statistical significance of the experimental data was determined by ANOVA. The influence of process parameters could be described by quadratic models (Equations 4 and 5) whose suitability of fit and statistical significance after eliminating the insignificant terms are presented in Table 5. The mathematical model that describes the xylan solubilisation (y_1) during dilute sulphuric acid pre-extraction under the conditions studied can be represented by the equation:

$$y_1 = 4.9 + 4.2x_1 + 4.5x_2 + 3.9x_3 + 2.4x_1x_3 + 1.8x_1x_2 \qquad (4)$$

According to the equation (1), both acid concentration (x_1) and temperature (x_2) are the factors that influenced the xylan solubilisation the most followed by reaction time (x_3). On the other hand, equation 2 represents the yield of xylan after alkaline pre-extraction (y_2) as a function of NaOH concentration (x_1) and temperature (x_2). The negative sign indicates that an increase in temperature would eventually compromise the xylan yields as previously reported.[27]

$y_2 = 19.1 + 5.2x_1 + 3.9x_2 – 3.7x^2_2$ (5)

By fixing the reaction time at 40 min for dilute acid and 180 min for mild alkaline pre-extractions the above model equations allowed the generation of the response surface plots shown in Figure 1. Although the model for dilute acid pre-extraction can only be used to predict the xylan yield within the studied range, an increase in temperature beyond the tested range (Figure 1A) would promote degradation of xylan. This fact is supported by the formation of furfural at 154°C and corroborated in other studies (Table 2, run 12).[4] In the case of mild alkaline pre-extraction (Figure 1B), the optimal xylan yield can be obtained when the NaOH concentration and temperature were fixed at star points (2.3 M and 65°C). In addition, the graph in Figure 1B indicates a decline in xylan yield when raising temperatures to values higher than 65°C.

3.2.2. Characterization of mild alkaline pre-extracted xylan

Alkaline conditions could generate oligomer or polymeric xylan fractions from SCB whose derivatives can be used to strengthen properties of sheets formed from old corrugated container pulp.[16] This is based on the hydrolysis of the ester linkage between plant polysaccharides and lignin, which enhances the solubility of the hemicelluloses, without reducing their molecular mass.[5]

On this basis, the average molecular mass of a xylan sample obtained under the alkaline pre-extraction conditions run 15 (1.5 M NaOH; 65°C for 180 min) was estimated by the size exclusion chromatography (SEC). The xylan pre-extraction carried out under these conditions resulted in a cellulose rich solid residue that was selected for subsequent soda or sodaAQ pulping evaluation and optimisation.

The average molecular mass of the xylan sample obtained by SEC was approximately 32,793 g mol^{-1}, which was within the range of the structural characterization carried out by Sun et al 2004.[5] The high molecular weight xylan can be used in paper and corrugated board applications.[7]

Further analysis of the xylan component obtained by conditions of run 15 was performed by FT-IR spectroscopy to determine the changes of the structure during alkaline pre-extraction. The FTIR spectra of xylan obtained was similar to that of commercial oat spelt xylan (Figure 2). However, in the pre-extracted xylan the intensity of 3288, 2918 and 1403 cm^{-1} bands were much lower than that of oat spelt xylan (3346, 2921 and 1412 cm^{-1}), suggesting lower concentration of O-H, C-H and CH_2 linkages, respectively. It was also noted that the band at 1034 cm^{-1}, which was ascribed to C–O, C–C and C–OH linkages, appeared in both xylan samples. A sharp band at 897 cm^{-1} indicated the presence of β-glucosidic linkage (C–O–C) between the sugar units in the hemicellulose.[5] Obviously the appearance of bands (1243, 1558 and 1574 cm^{-1}) corresponding to lignin were observed in alkaline pre-extracted xylan sample.[5,35] The presence of lignin could limit the application of the xylan in various paper products as the lignin reduces the brightness of the xylan.[36] The alkali soluble lignin can be minimised through delignification of the material prior to xylan extraction; however some of these processes might be detrimental to the cellulosic fibre.[19] Therefore this option was not considered in the present study.

3.2.2. Solid fraction

Xylan pre-extraction processes can change the amount and structure of other polymers. Ideally the amount of cellulose (glucan) retained in the solid residue should be high and reduced lignin content would be beneficial to retain potential as feedstock to the subsequent pulping processes. Moreover, some of the hemicelluloses are required in the cellulignin residues, as some are necessary to contribute to the quality of pulps obtained from these residues.[37] The composition of the solid residues from dilute acid and mild alkaline pre-extractions, expressed as percentages (%) of original raw material (dry weight), is listed in Table 2 and Table 3, respectively.

Additionally, the effect of pre-extraction methodology on the SCB structure was evaluated by SEM (Fig 3).

Dilute acid pre-extraction of xylan showed no impact on glucan and lignin content retained in the solid residue compared to the raw material (Table 2). However, the dilute acid treatment disrupted the fibres of SCB after pre-extraction of xylan as can be observed in Figure 3B. Compared with glucan content in the original SCB (i.e., 46.3%), the glucan range after dilute acid extraction varied from 41.4 to 45.0%, the acid insoluble lignin ranged from 17.9 to 20.5% raw material, relative to 18.2% acid insoluble lignin content present in non-extracted SCB. On the other hand, hot water pre-extraction (zero acid) generated solid residue with 43.8% glucan and the acid insoluble lignin content was 18.3%.

In comparison, mild alkaline pre-extractions led to solid residues formed mainly by high glucan content (43.2 to 46.2%) and low acid insoluble lignin (13.2 to 17.3%) as shown in Table 3. Considering lignin as a barrier during processing of cellulosic fibres, pre-extraction with alkaline would favour pulping processes. This was also supported by the interruption of fibres shown by SEM micrographs (Fig 3C) due to mild alkaline xylan pre-extraction.

The amount of hemicellulose retained in the solid residue depended on the solubilisation yield during the pre-extraction step. The hemicellulose content of solid residues from dilute sulphuric acid pre-extraction varied from 6.7 to 23.8% ODM (Table 2), whilst lower values (3.4 to 14.5% ODM, Table 3) were obtained for solid residues from mild alkaline pre-extractions.

3.3. Properties of the pulps

3.3.1 Pulp evaluation on micro scale

In order to assess the efficiency of the xylan pre-extraction together with subsequent pulping in an integration approach, pre-screening micro pulping experiments of selected pre-extracted solid residues were carried out, with non-extracted SCB used as control. The screening criteria were used to identify pulping conditions for SCB residues after xylan extraction that could provide similar or higher pulp yield, low kappa number and low reject levels, compared to pulps produced from similar pulping processes with non-extracted SCB.

Solid residues with maximum glucan content and some of the hemicelluloses and lignin were selected for soda or sodaAQ micro pulping. Solid residue obtained from dilute sulphuric acid pre-extraction run 15 (0.3% v/v H_2SO_4, 120°C for 40 min) was used, containing 45.0% glucan; 14.6% xylan and 18.4% lignin content. Hot water pre-extraction resulted in a solid residue with 43.8% glucan; 23.3% xylan and 18.3% lignin that was also investigated. On the other hand, mild alkaline pre-extracted from run 15 (1.5 M NaOH, 65°C, for 180 min) was preferred, with solid residues containing 43.2% glucan; 6.2% xylan and 13.2% lignin.

The effect of pulping conditions on pulp yield, kappa number and percentage rejects for non-extracted SCB and dilute acid or hot water xylan pre-extracted solid residues are shown in Table 6. The results presented in Table 6 were obtained under extreme and intermediate conditions of soda or sodaAQ pulping. Likewise, the pulping results obtained after alkaline pre-extraction are shown in Table 7.

Among the pulping processes used, sodaAQ process gave the most favourable results regardless of the xylan pre-extraction process. AQ primarily has an effect on degradation of lignin and stabilization of carbohydrates in pulping process.[22] As a result, pulp yield was higher, while the rejects and kappa numbers were reduced when AQ was added (0.08 - 0.1%). Moreover, the NaOH concentration required was lower (14 - 16%) relative to soda only pulping where high concentrations of NaOH were used (20 - 22%).

Dilute acid pre-extraction disadvantaged the subsequent soda or sodaAQ pulping process. Low screened pulp yields (below 40%) and high percentage rejects, from 9 - 13%, were obtained. The high kappa number observed (35-39) revealed that, contrary to expected, dilute sulphuric acid reduced the delignification efficiency of the pre-extracted residues. This finding could be due to pseudolignin formation during dilute acid treatment that is known to be difficult to oxidize and solubilize during pulping.[20, 38] Therefore, more alkali would be required to improve delignification of acid pre-extracted solid residue. On the contrary, sodaAQ pulping of hot water pre-extracted SCB under the best conditions (14%NaOH, 0.1% AQ for 30 min) improved the screened pulp yield up to 53.6% at lower kappa number (28.9) and reject level (0.5).

As expected, sodaAQ pulping of alkaline pre-extracted SCB significantly improved the solubilisation of lignin during the cooking process, resulting in reduced kappa number (15.8) at lower residence time (25 minutes). This process, however, should be optimised to prevent carbohydrates degradation according to requirements of the final product

3.3.2. Pulp evaluation on large scale

SodaAQ pulping of mild alkaline and hot water pre-extracted solid residues was repeated on the large scale in order to confirm the micro pulping results. Kraft pulping was applied on large scale for dilute acid pre-extracted residues since it is more efficient in delignification of high lignified wood chips.[12] The cooking conditions and yields are presented in Table 8.

The extraction of 69.1% of xylan under mild alkaline conditions improved screened pulp yield by 10.8% at lower kappa number (15.5), and less rejects levels compared to pulping of non-extracted SCB. High pulping efficiency of alkaline pre-extracted solid residues observed in this study might be ascribed to the opening of the cell wall structure due to initial removal of lignin and xylan (Fig 4).[17] Consequently, high concentration of alkali measured as residual active alkali (RAA) was recorded in pulping black liquors of alkaline pre-extracted SCB implying lower alkali consumption during cooking probably due to the removal of ash content (2.6% vs 0.6%) and extractives. Lower chemical consumption can be expected from the pulps with low kappa number during subsequent bleaching operations. Moreover, carbohydrate degradation measured in terms of viscosity was not observed during pulping, indicating better delignification and selectivity of the sodaAQ pulping used.[8] Similar benefits on pulp properties have been proved in other herbaceous materials such as cereal straw by integration of alkali pre-extraction of hemicelluloses with sodaAQ pulping.[27]

Alternatively, the combined process of hot water pre-extraction together with sodaAQ pulping of the solid residue showed similar screened pulp yield with comparable kappa number. However, a significant decrease in pulp viscosity by 24% was observed, indicating carbohydrate degradation. This could be prevented by applying lower cooking temperatures.[17]

The chemical composition of the sodaAQ pulps showed a reduction in xylan content due to pre-extraction which might affect the handsheet strength properties.[22] Several studies emphasised the importance of xylan for the strength properties of pulp fibres.[39, 40]

Compared with soda or sodaAQ pulping (Table 6), kraft pulping generated pulps with considerably reduced kappa number (6) and rejects levels (3.7%), resulting in low screened pulp yield (39.5%), which compared well with values obtained for kraft pulps of delignified SCB with *Panus tigrinus* strain.[32] Although kraft pulp process was the best option to delignify dilute acid pre-extracted materials, milder pulping conditions may be recommended in order to prevent peeling reactions thereby increasing cellulose retention.[12]

3.3.2. Hand sheets strength properties

The importance of preserving hemicelluloses on pulp fibres to create more hydrogen bonding potential between fibres and therefore enhancing the strength properties has been reported.[43] Thus, pre-extraction of xylan was expected to impact the bonding strength properties of the hand sheets produced from these pulps. The burst index, tear index, breaking length and ISO brightness properties of hand sheets produced from sodaAQ (Fig 4) or kraft (Fig 5) pulping of xylan pre-extracted SCB were compared with those produced from non-extracted SCB. The tensile-tear relationship of the sodaAQ pulps is given in Figure 6. All the pulps were beaten to enhance the fibre-fibre bonding, thereby improving hand sheets strength properties. Strength properties were found to increase with increase beating up to 40°SR for sodaAQ pulps, whereas 45°SR was optimum for kraft pulps.

Interestingly, alkaline conditions for hemicellulose extraction provided brighter sodaAQ pulps with superior tear index by 56%. The burst index and breaking length were similar to those of pulps produced from non-extracted SCB. While burst and breaking length correlate strongly with fibre bonding, tear index also depends strongly on fibre length.[31] These results suggest that fibres were well bonded to one another and thus presented good conformability without fibre shortening. In several occasions, for evaluating tear strength, it is more essential to compare tear strength at a certain tensile level (Fig 6).

Although higher tear index was observed for pulps produced from extracted SCB there was a reduction in tensile index relative to pulps produced from non-extracted SCB. This may be due to xylan insufficiency in pulp samples produced from alkaline pre-extracted SCB as shown in Table 8.[41] The overall improvements in pulp yield and handsheets strength properties associated with alkaline pre-extraction of SCB together with the recovered xylan complement the proposed pulp mill biorefinery concept.[11]

In line with this study, the strength properties of the sodaAQ pulps produced from alkaline pre-extracted cereal straw remained at a very good level.[27] The high strength values of pulps could be advantageous for pulps used for packaging papers but of secondary importance when used in printing and writing papers.[31]

Regarding the physical strength properties of the sodaAQ pulps produced from hot water extracted residue, they were generally improved despite the reduction in viscosity. Tear and burst index was insignificantly increased by 6% and 5% respectively. The breaking length and tensile index was similar, whilst the optical brightness was reduced by 4%. Fibre weakening during sodaAQ pulping of hot water pre-extracted residue showed by the viscosity reduction was to some extent compensated by the improved bonding ability of fibres due to the preservation of hemicelluloses. Thus the bonding strength properties (tear and burst index) of pulps produced from hot water extracted pulps were still higher than those of pulps produced from non-extracted SCB. The strength values obtained in this study resembled those found when hot water pre-extracted SCB was previously subjected to sodaAQ pulping.[17]

The overall strength properties of Kraft pulps from acid pre-extracted residues were significantly reduced (Fig 5). Compared to non-extracted SCB pulp, there was a significant reduction in both tear and breaking length but the optical brightness of the pulps was similar. This could be attributed to the non selectivity and more complete removal of lignin under the selected kraft pulping conditions, leading to severe degradation of carbohydrates and therefore to inferior strength properties of fibres.[42] These results showed that kraft pulping of acid pre-extracted residue had to be optimised to maintain strength properties at higher levels.

4. Conclusions

Sugarcane bagasse has proven to be a feasible raw material for production of xylan rich liquid fractions by suitable dilute acid or alkaline pre-extraction conditions prior to chemical pulping processes that could be used as a substrate for further industrial practises. Although from the perspective of pulp production in the biorefinery concept, it has been shown that dilute acid pre-extractions promoted a high xylose yield compared to hot water, it did not favour the subsequent soda/AQ or kraft pulping processes. Pre-extraction with hot water did not affect adversely the subsequent sodaAQ pulping, resulting in an increase in pulp yield and lower kappa number although the viscosity was compromised. The tear and burst index of these pulps were improved with a slight reduction in breaking length and optical brightness.

Regarding the mild alkali pre-extraction, it yielded significant amount of xylan (69.1%) prior to sodaAQ pulping without deterioration of the quality of the final pulp. In fact, higher pulp yields were produced at lower kappa number without reduction in viscosity. These conditions provided brighter pulps with superior tear index whilst breaking length and burst index was retained in the same level as those of pulps produced from non-extracted SCB. Alkali extraction combined with sodaAQ pulping was therefore the preferred option for SCB.

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Tables

Table 1. Variables and corresponding coded levels used in the central composite designs for diluted acid and mild alkali pre-extractions.

Pre-extraction method	Variables	Coded Levels				
		-1.68	-1	0	1	1.68
Diluted acid	Acid concentration (%, v/v)	0	0.1	0.3	0.5	0.6
	Temperature (ºC)	86	100	120	140	154
	Reaction time (min)	6	20	40	60	74
Mild alkali	Alkali concentration (M)	0.7	1	1.5	2	2.34
	Temperature (ºC)	23	40	65	90	107
	Reaction time (min)	79	120	180	240	281

Table 2. Composition of liquid fraction and solid residue resulting from dilute sulfuric acid pre-extraction of hemicelluloses from sugarcane bagasse

Pre-extraction conditions				Liquid fraction							[c]Solid fraction			[d]EMB	
Run	H_2SO_4 %	Temp °C	Time min	Xyl %	[a]Xyl % theoretical	Xylo-oligomers %	[b]Xyl recovery yield %	Glc %	Acetic acid g/L	Furfural + HMF g/L	Glucan %	Xylan %	AIL %	Glc (%)	Xylan (%)
1	0.1	100	20	1.1	4.4	0.6	5.0	0.7	0.1	-	44.8	23.5	17.8	98.2	95.0
2	0.1	100	60	1.8	7.0	3.4	10.4	0.7	0.2	-	44.2	22.2	18.7	97.2	92.8
3	0.1	140	20	1.6	6.3	2.0	8.3	0.8	0.1	-	42.1	22.7	17.9	92.6	94.0
4	0.1	140	60	4.9	18.9	10.3	29.2	1.2	0.4	0.05	43.2	19.7	19.0	96.4	91.1
5	0.5	100	20	0.8	3.1	3.5	6.6	1.1	0.1	-	43.4	23.1	17.9	96.2	92.3
6	0.5	100	60	6.6	25.5	5.3	30.8	0.4	0.2	-	43.4	17.6	20.5	97.6	93.4
7	0.5	140	20	5.2	20.0	4.6	24.6	0.5	0.2	-	44.5	19.0	18.2	98.0	93.4
8	0.5	140	60	13.1	50.5	0	41.1	2.0	0.2	0.28	44.9	12.2	18.5	99	97.6
Star point acid concentration															
9	**0**	**120**	**40**	**1.5**	**5.7**	**6.2**	**11.9**	**0.6**	**0.6**	**-**	**43.8**	**23.3**	**18.3**	**95.3**	**95.7**
10	0.6	120	40	7.3	28.1	12.7	40.8	0.5	0.1	-	43.5	15.3	19.2	96.6	94.9
Star point temperature															
11	0.3	86	40	0.3	1.3	6.5	7.8	0.3	0.3	-	44.2	23.8	18.3	93.6	93.3
12	0.3	154	40	10.2	39.3	0	36.1	1.7	0.1	0.3	43.0	14.5	19.3	98.2	95.3
Star point reaction time															
13	0.3	120	6	1.2	4.6	3.6	8.2	0.4	0.7	-	43.8	22.7	17.4	95.5	92.3
14	0.3	120	74	14.9	57.7	15.4	73.1	1.8	0.1	-	41.4	6.7	18.6	93.5	96.3
Central points															
15-19	**0.3**	**120**	**40**	**6.2±2.0**	**23.8±3.4**	**17.8±1.1**	**41.7**	**1.2**	**0.4**	**0.16**	**45.0±0.9**	**14.6±1.0**	**18.4±0.9**	**99.7**	**98.1**

[a]Analysis data are based on the oven dry xylan of non-extracted SCB
[b]Obtained by addition of Xylose (% theoretical) and Xylo-oligomer (%)
[c]Analysis data are based on the oven dry non-extracted SCB

[d]Extraction mass balance (EMB) was calculated for each component in the SCB as e.g. xylan in the liquid and solid fraction after Run 9 were 1.5% and 23.3% respectively, and the raw SCB has 25.9% xylan before the extraction. The total extraction mass balance = [(1.5+23.3)/25.9]*100 = 93.3%.
*Xyl – Xylan; Glc – Glucan; AIL – Acid insoluble lignin

Table 3. Results of the experiments according to a central composite design obtained after mild alkali pre-extraction of hemicelluloses from sugarcane bagasse in terms of xylan recovery and the composition of the solid fraction.

Pre-extraction conditions				Xylan pre-extraction efficiency				[b]Solid fraction after extraction			[c]EMB (%)		
Run	NaOH (M)	Temp (˚C)	Time min	Xylan precipitate yield %	[a]Xylan recovery yield %	Lignin (% xylan)	Lignin % dry raw SCB	Glucan %	Xylan %	Acid insoluble lignin (%)	Glucan	Xylan	Acid soluble lignin
1	1	40	120	11.5	44.4	7.9	1.4	43.8	12.5	16.6	94.6	92.7	98.9
2	1	40	240	11.5	44.4	9.4	1.7	43.9	12.4	16.3	94.8	92.3	98.9
3	1	90	120	12.2	46.9	8.9	1.6	46.2	12.3	16.3	99.7	94.2	98.4
4	1	90	240	12.4	47.9	9.9	1.8	43.4	12.0	16.2	93.7	94.0	98.9
5	2	40	120	13.3	51.4	7.5	1.4	43.7	10.9	16.6	94.4	93.3	98.9
6	2	40	240	15.9	61.4	16.2	2.9	43.2	7.6	15.0	93.3	90.6	98.4
7	2	90	120	17.8	68.7	22.9	4.2	43.2	6.8	13.5	93.3	94.9	97.3
8	2	90	240	21.0	81.1	24.3	4.4	43.7	2.7	13.1	94.4	91.4	96.2
Star point NaOH concentration													
9	0.66	65	180	10.0	38.6	4.1	0.8	43.3	14.5	17.2	93.5	94.6	98.9
10	2.34	65	180	20.8	80.3	21.7	4.0	43.5	3.4	13.7	94.0	93.3	97.3
Star point temperature													
11	1.5	23	180	12.1	46.7	3.5	0.6	43.2	11.7	17.3	93.3	92.0	98.4
12	1.5	107	180	18.9	73.0	17.4	3.2	43.3	5.7	14.5	93.5	95.1	97.3
Star point reaction time													
13	1.5	65	92	17.9	69.1	15.8	2.9	43.8	5.7	14.8	94.6	90.9	97.3
14	1.5	65	308	18.7	72.2	20.0	3.6	43.6	6.4	14.2	94.2	97.1	97.8
Central point													
15-19	1.5	65	180	17.9±1.1	69.1	18.1±3.1	4.0	43.2±1.2	6.2± 0.1	13.2 ±0.5	93.2	92.5	94.5

[a]Analysis data are based on the oven dry xylan of non-extracted SCB

[b]Analysis data are based on the oven dry non-extracted SCB
[C]Extraction mass balance (EMB) is calculated as explained in Table 2

Table 4. Chemical composition of non-extracted sugarcane bagasse.

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

Component	SCB	Analytical methods
Ethanol/cyclohexane soluble extractives	1.7 ± 0.5	TAPPI T264 om-88
Water soluble extractives	2.4 ± 1.0	
Glucan	46.3 ± 2.5	LAP 013
Xylan	25.9 ± 2.1	
Arabinan	2.1 ± 1.0	
Acetyl group	2.6 ± 0.7	
Acid insoluble lignin	18.2 ± 2.1	TAPPI T222 om-88
Ash	2.6 ± 1.2	TAPPI T211 om-85

Table 5. Analysis of variance from the regression representing xylan yield after dilute sulfuric acid (y_1) and mild alkaline (y_2) pre-extraction of sugarcane bagasse

Source	Sum of squares		Degree of freedom		Mean square		F-value		Prob>F	
	y_1	y_2	y_1	y_2	Y_1	y_2	y_1	y_2	y_1	y_2
Model	202.59	333.03	9	6	22.51	55.5	30.43	3.26	<0.00001	0.0482
Residual	5.18	170.33	7	10	0.74	17.03				
Lack of fit	5	166.93	5	8	1	20.87	11.11	12.25	0.0847	0.0776
Pure error	18	3.41	2	2	0.09	1.7				
Total error	207.77	503.36	16	16						
R^2	0.97	0.82								

Table 6. Soda and soda-AQ micro pulping conditions, pulp yield and properties for non-extracted, 5.7% (hot water, 120°C and 40 min) and 23.6% (0.3% v/v H_2SO_4, 120°C, and 40 min) xylo-oligomer extracted sugarcane bagasse residues.

Soda												
	Cooking onditions			non extraction			Hot water extraction (120°C, 40 min)			Acid extraction (0.3% v/v H_2SO_4, 120°C, 40 min)		
Run	Active alkali (% DM)	AQ (% DM)	Time at 170°C (min)	Screened pulp yield (%)	Rejects (%)	Kappa Number	Screened pulp yield (%)	Rejects (%)	Kappa number	Screened pulp yield (%)	Rejects (%)	Kappa number
1	20	-	25	34.2	7.6	34.8	39.7	6.4	32.3	35.9	11.0	38.4
2	20	-	35	32.4	6.0	34.0	35.1	7.8	33.2	35.4	12.7	38.3
3	22	-	25	33.2	9.0	34.3	38.3	6.2	32.1	35.4	12.2	38.3
4	22	-	35	33.2	9.3	34.6	39.4	5.8	32.7	36.8	10.9	36.9
5	21	-	30	34.5	9.9	33.7	37.0	4.4	32.7	37.4	9.4	38.2
6	21	-	37	34.2	9.7	33.5	35.4	8.0	32.0	36.7	10.9	38.1
Soda-anthraquinone												
Run												
1	14	0.05	30	43.0	6.0	31.9	41.3	5.3	29.4	39.0	9.7	35.2
2	14	0.1	30	46.2	4.9	31.5	53.6	0.5	28.9	39.9	9.0	35.0
3	16	0.05	30	39.4	7.1	31.6	41.8	6.2	28.7	38.8	10.2	34.3
4	16	0.10	30	36.4	9.3	31.9	49.9	3.8	28.8	39.4	9.9	34.0
5	15	0.08	70	31.9	9.9	31.3	36.5	11.5	27.8	39.9	8.9	33.8
6	15	0.08	45	40.0	8.7	31.9	43.0	5.8	28.6	38.3	13.1	33.2

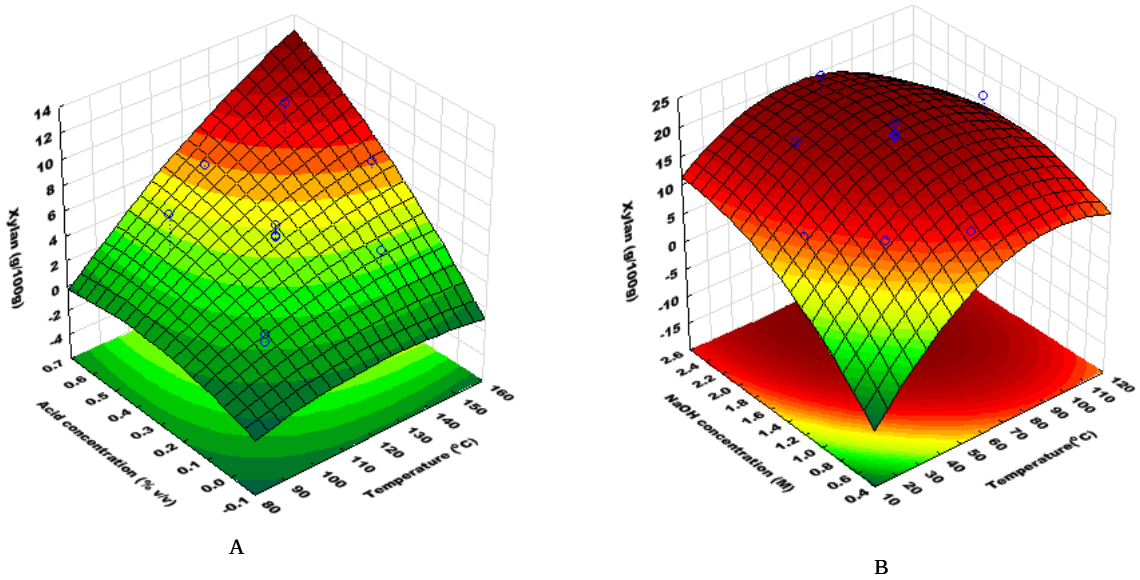
Table 7. Soda-AQ micro pulping conditions, pulp yield and properties for non-extracted and 69.1% (1.5M NaOH, 65°C, and 180 min) xylan extracted sugarcane bagasse residues.

				Non-extraction			1.5M NaOH, 65°C and 180 min		
Replicates	NaOH in residue (g)	AQ (% DM)	Time at 170°C (min)	Screened pulp yield (%)	Rejects (%)	Kappa number	Screened pulp yield (%)	Rejects (%)	Kappa number
4	8.3±0.6	0.1	25	-	-	-	40.3±1.6	2.0±0.1	15.8±0.3
4	7	0.1	30	46.2±0.5	9.1±1.5	34.5±2.0	-	-	-

Table 8. Pulping conditions and pulp evaluation of non-extracted and pre-extracted sugarcane bagasse at large scale.

Pulping process	Soda-AQ			Kraft	
	Non extraction	Hot water, 120°C, 40 min	1.5M NaOH, 65˚C, 240 min	Non Extraction	0.3 v/v H_2SO4, 120°C, 40min
Pulping conditions					
Active alkali as Na_2O (%)	14.0	14.0		12.0	12.0
Anthraquinone (%)	0.1	0.1	0.1		
Sulfidity as Na_2O (%)				20.0	20.0
Liquor-to-bagasse ratio	7:1	7:1	7:1	7:1	7:1
Time at 170˚C (min)	30	30	30	30	30
Pulp yield					
Screened yield (%)	40.1	41.3	45.0	41.3	39.5
Rejects (%)	15.7	14.7	3.3	5.9	3.7
Pulp evaluation					
Viscosity (cP)	7.2	5.5	7.1	3.5	2.5
Kappa number	22.8	20.9	15.5	7.0	6.0
Black liquor analysis					
Residual active alkali (g/L)	2.0	2.5	9.0		

Figures



A B

Figure 1. (A) Estimated response surface for xylan yield obtained after sulphuric acid hydrolysis showing the influence of temperature and acid concentration for a residence time of 40 minutes. (B) Estimated response surface for xylan yield obtained after NaOH extraction showing the influence of temperature and NaOH concentration for a residence time of 180 minutes.

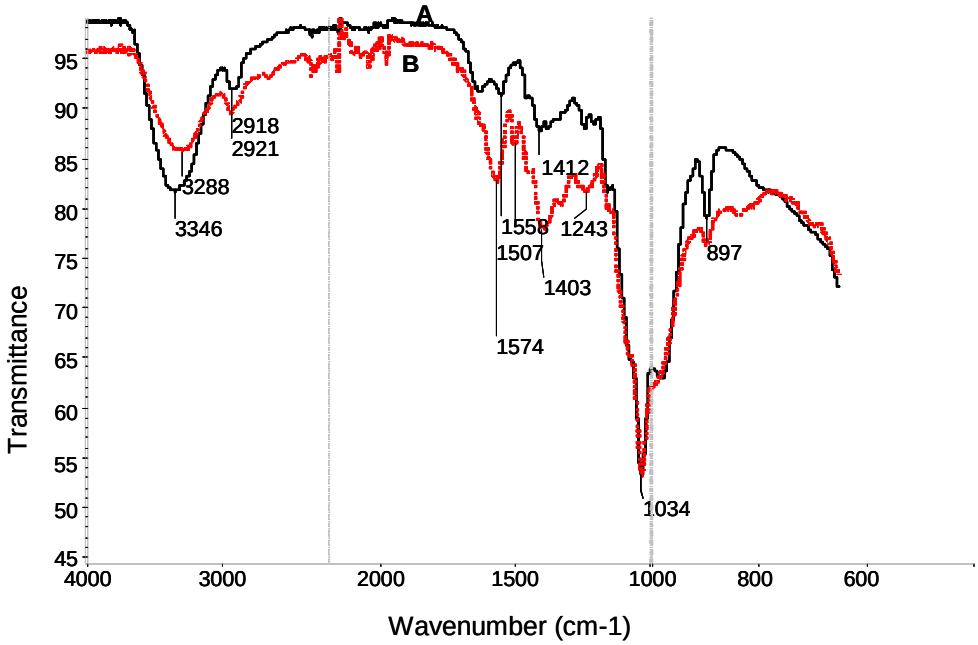


Figure 2. FT-IR spectra of (A) commercial oat spelt xylan and (B) xylan fraction (dialysed with 12 kDa molecular weight cut off cellulose acetate membrane) extracted from sugarcane bagasse with 1.5 NaOH at 65°C for 180 minutes.

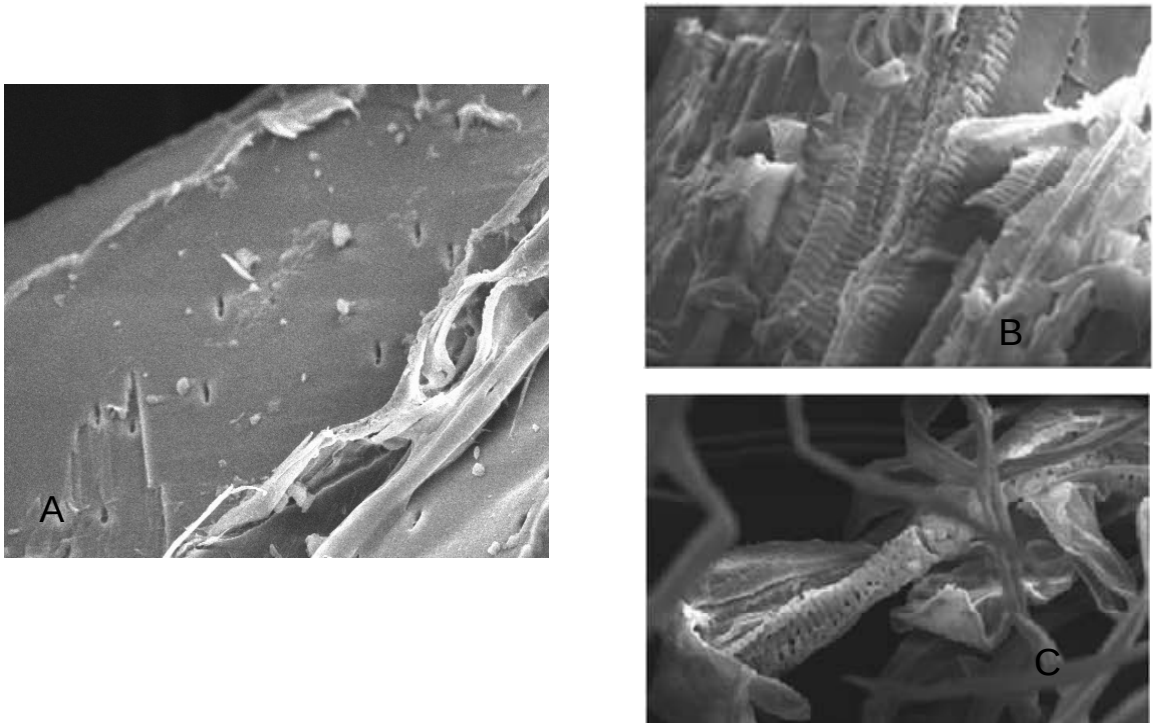


Figure 3. Scanning electron microscope micrographs of non-extracted (A), dilute sulphuric acid (B) and alkaline (C) pre-extracted sugarcane bagasse residues.

Scale: Mag = 500x ; EHT = 7.0 kV; width = 15 mm

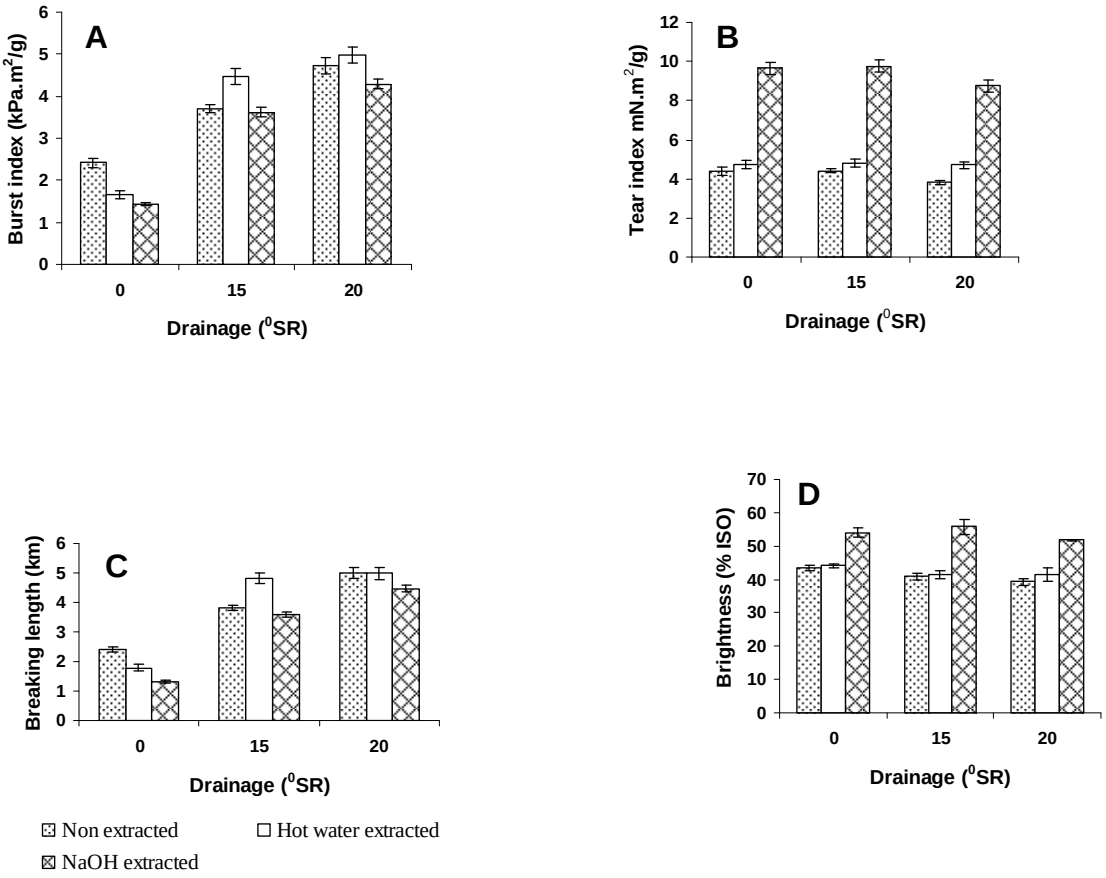


Figure 4. Handsheet properties as a function of drainage in °SR of sugarcane bagasse after sodaAQ pulping in large scale.

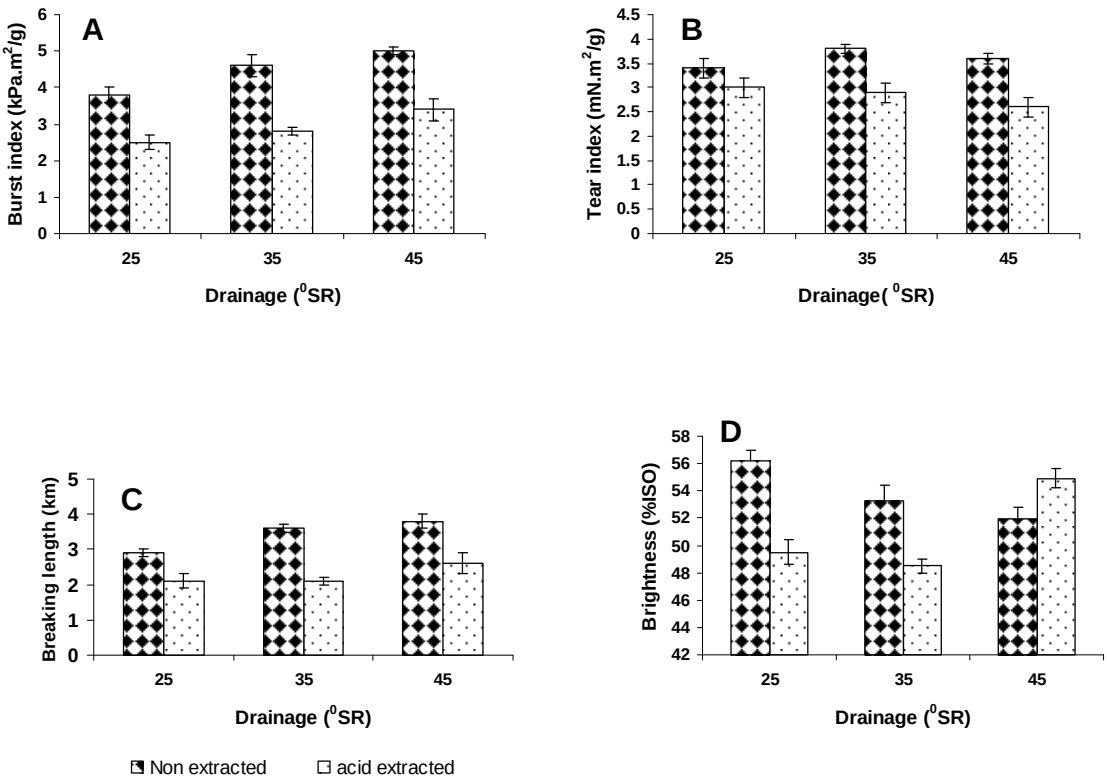


Figure 5. Handsheet properties as a function of drainage in °SR of sugarcane bagasse after kraft pulping in large scale.

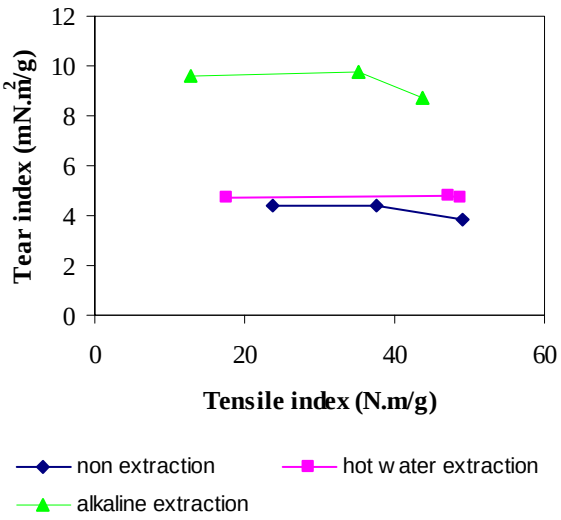


Figure 6. Tensile-tear relationship of non-extracted, hot water and alkaline extracted sugarcane bagasse after soda-AQ pulping in large scale.

Paper IV

Hemicelluloses extraction from giant bamboo prior to kraft or soda-AQ pulping and its effect on pulp physical properties

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Abstract

Hemicelluloses that would have been dissolved in black liquor during pulping were pre-extracted from giant bamboo chips with sodium hydroxide prior to kraft and soda-AQ pulping. The effects of sodium hydroxide concentration, temperature and time on hemicelluloses extraction were studied using a statistical experimental design and further compared with acid pre-extraction followed by soda-AQ pulping. Results showed that sodium hydroxide concentration exerted the strongest influence, solubilising up to 20.4% dry mass of the available xylan with 2.0M NaOH at 90°C for 240 minutes. However, the extraction of 13.6% dry mass xylan with 1M NaOH at 90°C for 240 min provided kraft pulps with reduced reject levels, higher screened pulp yields (50.4%) without reduction in viscosity and slight improvement in burst index of the hand sheets. In the case of dilute acid pre-extraction prior to soda-AQ pulping, the amount of pre-extracted xylan to maintain the pulp yield was limited to 11.3% with an increment of the viscosity compared to non-extracted bamboo.

Among the two xylan pre-extraction and subsequent pulping integration processes, alkaline pre-extraction prior to kraft pulping resulted in slightly higher pulp quality for giant bamboo. Furthermore, the pulping capacity of the original pulp mill could be increased by 16%.

Keywords: alkali and acid pre-extraction, biorefinery, giant bamboo, handsheet strengths, hemicelluloses, kraft pulping, pulp quality, , soda-AQ pulping.

1. Introduction

Hemicelluloses, solubilised during kraft pulping of suitable lignocellulosic biomass, such as bamboo, are presently underutilised. In current pulp production processes they are incinerated in the recovery furnace together with the dissolved lignin (Ragauskas et al. 2006). The recovery and purification of the modified and degraded carbohydrates from the pulping effluents, to a sufficient extent for use as commodity chemicals, are challenging (Walton et al. 2010). Recovery of hemicelluloses prior to pulping and further conversion to value added products under the biorefinery concept offers an interesting economic opportunity for the paper mill (van Heiningen 2006). The pre-extraction of hemicelluloses implies less alkali is requirements for cooking to a certain kappa level, increment in the rate of delignification and possible reduction of the bleaching chemicals consumption. At the same time pulp production capacity is enhanced by improving the overall alkaline pulping, for both kraft and soda-AQ processes (De Lopez et al. 1996; Al-Dajani and Tschirner 2008; Sixta and Schild 2009). Such integration of hemicelluloses pre-extraction with alkaline pulping lead to improvement in both pulp properties and production capacity without loss in yield, as already demonstrated in recovery furnace limited Kraft pulp mill (Al-Dajani and Tschirner 2008; Huang et al. 2010).

Bamboo, a naturally fast growing and potentially low cost lignocellulosic material, is most frequently used for the production of paper and as a reinforcing fiber (He et al. 2008). Especially in Asia where 50% of pulp production is harvested from wild forests (Scurlock et al. 2000). When preparing chemical pulps from bamboo, Kraft pulping is generally preferred to soda pulping since it provides satisfactory delignification as well as high yield and viscosity (Vu et al. 2004). This can be attributed to the fact that fiber dimensions and main chemical constituents of bamboo typically bear a close resemblance to those of woody materials. The glucan content of bamboo (40-52.6%) is comparable to the reported cellulose content of softwoods (40-52%) and hardwoods (38-56%) (Vena et al. 2010).

The main hemicelluloses present in bamboo is an *O*-acetyl-4-*O*-methylglucuronoxylan which accounts for approximately 25% of the cell wall material.

The acetyl group content represents 6-7% of the total xylan, compared to the 8-17% acetyl group content in hardwood xylan. Bamboo lignins have a higher content of phenolic hydroxyl groups than wood lignins, resulting in a higher reactivity to pulping (Salmela et al. 2008). However, bamboo kraft lignin shows a higher degree of condensation compared to wood pulps, thereby being more resistant to bleaching like that of wood pulps (Salmela et al. 2008). For this reason, the large-scale delignification of bamboo is conventionally based on techniques similar to those generally applied to wood pulping.

Pre-extraction of hemicelluloses from lignocellulosic material prior to pulping can be implemented with alkali, acid or hot water (De Lopez et al. 1996; Mendes et al. 2009; Rodriguez-Lopez et al. 2012; Vena et al. 2010). For hardwoods, alkaline pre-extraction prior to kraft pulping has been shown as one of the most promising fractionation technologies as it allows the recovery of high molecular mass xylan without reducing the pulp properties and yield (Al-Dajani and Tschirner 2008; Al-Dajani and Tschirner 2010; Sixta and Schild 2009). The xylan polymers isolated can be used for the production of various chemicals including biopolymers (Sixta and Schild 2009). In contrast, dilute acid pretreatments provides extract with higher yield hemicelluloses of lower degree of polymerization, more suitable for other applications, i.e., bioethanol production by hydrolysis and fermentation. The combination of dilute acid pre-extraction with soda-AQ pulping has been proven to improve pulp yield when compared to kraft pulping (Vena et al. 2010).

Although many literature reports address the pre-extraction of hemicelluloses from different lignocellulosic materials prior to kraft pulping, few have evaluated the potential of bamboo.

Therefore, taking into account the large fraction of hemicelluloses present in bamboo, a comparative study of an integrated xylan pre-extraction and Kraft pulping process for South African grown giant bamboo is of great importance in exploring and promoting the integral utilisation of this biomass. In this context, the objective of the present study was to evaluate the effects of alkali and acid pre-extractions on pulp and paper properties.

Firstly, the reaction conditions under which hemicelluloses could be extracted with mild alkaline conditions from giant bamboo with minimal interference on the cellulose (glucan) content were investigated. In following the biorefinery approach, the selected solid residue was pulped using kraft pulping method to determine the effect of hemicelluloses pre-extraction on pulp and paper quality. Subsequently, a follow-up study of the previous work on the effects of hemicelluloses extraction with selected dilute sulphuric acid on soda-AQ pulps was also undertaken.

2. Materials and methods

2.1. Materials

The bamboo used in the study, *Bambusa balcooa,* was collected in the Western Cape province of South Africa. Giant bamboo stems were chipped using a Wigger pilot chipper. The chips were screened and a 4-8 mm chip size fraction comprised of nodes and internodes was selected for further experiments. The material was conditioned at 23°C and 55% relative humidity before use. Sodium hydroxide and sulfuric acid were purchased from Merck, and Busperse 2262 anthraquinone (AQ) was donated by Buckman Laboratories, Hammarsdale, South Africa.

Pullulan standards purchased from Polymer Standards Service (PSS) in Germany were used to estimate the molecular weight of the isolated xylan fractions.

2.2 Hemicellulose pre-extraction of giant bamboo

Mild alkaline (NaOH) pre-extraction was carried out according to a central composite design (CCD) created and evaluated in Statistica 7.1 (Statsoft Inc., Tulsa, USA) and Design Expert version 8. Process conditions are illustrated in Table 1. Three assays were carried out at the center point to estimate the random error required for the analysis of variance (ANOVA). Xylan content of the liquid was taken as the response of the experimental design. The statistical significance of the regression coefficient was determined by the coefficient of determination, R^2.

The conditions applied for dilute acid extraction were 0.3% v/v H_2SO_4, 5/5/1 (mL g^{-1}) pre-extraction liquor ratio to feed stock ratio at 120°C for 30 min and were selected from a previous work (Vena et al. 2010).

Alternatively, the alkaline extraction of xylan from bamboo was performed as described elsewhere (Al-Dajani and Tschirner 2008). The pre-extraction liquor ratio to feed stock ratio was 4:1 mL g^{-1}. Samples of 100 g oven dry mass bamboo chips (4-8 mm thickness) and NaOH solution (0.7-2.34M) were mixed in the desired portions and introduced into Schott bottles. The bottles were placed in a shaking hot water bath at 23-90°C and kept at the desired time.

Similarly, conditions at 107°C were performed in micro bombs placed in hot water pressurised digester. At the end of the desired extraction time, the bottles and bombs were cooled in room temperature water.

2.3. Characterisation of extraction liquors

At the end of the alkaline pre-extraction, the liquid and the solid fraction were separated by filtration on a 100 mesh screen. The hemicelluloses rich filtrates containing a complex mixture of solubilised materials (poly- and oligosaccharides, lignins, extracting chemicals, etc.) were concentrated in a rotary evaporator at 40°C to approximately 1/3 of the original volume. Filtrates were then purified by dialysis against de-ionised water for 3 days using a dialysis cellulose membrane with a 12 kDa molecular weight cut off. The samples were conditioned in liquid nitrogen and freeze dried. The oven dry mass of the extracted xylan was determined.

The hemicelluloses recovery yield was estimated according to the following relations (De Lopez et al. 1996).

$$\%\text{Hemicellulose precipitate} = \frac{\text{Oven dry mass of hemicellulose precipitate}}{\text{Oven dry mass non-extracted bamboo}} \times 100 \quad (1)$$

$$\%\text{Hemicellulose recovery} = \frac{\%\text{Hemicellulose precipitate}}{\%\text{Hemicellulose of bamboo}} \times 100 \quad (2)$$

The lignin fractions associated with the hemicelluloses were determined as described elsewhere (Brienzo et al. 2009).

2.3.1 Size exclusion chromatography

The molecular mass of the alkaline extracted xylan was determined using size exclusion chromatography (SEC). The isolated xylan was dissolved in deionised water to obtain a final concentration of 1 g L^{-1}. The solution was stirred continuously at room temperature for 2 hours and filtered through 0.2 µm membranes.

The SEC system consisted of three SUPREMA aqueous columns (PSS, Germany), connected in series with the pore sizes 30 Å, 3000 Å, 3000 Å respectively. Detection was conducted using a Dionex UltiMate 3000 HPLC system with a Varian 380-LC evaporative light scattering (ELS) detector. Solution of deionised water containing 0.05% sodium azide (NaN_3) was used as eluent and the flow rate was maintained at 1 $mL \cdot min^{-1}$. The column's temperature was kept at 25°C. The detector output was analysed with the Chromeleon® Version 6.80 software package.

2.3.2. IR-spectroscopy analysis of hemicelluloses

The FT-IR spectra were recorded in reflectance mode using the Smart Performer from Thermo equipped with ZnSe lenses. Prior to analysis, a sample of freeze dried xylan was further dried in phosphorus pentoxide, and a small portion of the dried hemicelluloses was placed on the ZnSe horizontal ATR, and 16 scans with a resolution of 4 cm^{-1} were accumulated over the range of 4000 - 650 cm^{-1}. The operating and data manipulating software was the basic OMNIC package.

2.4. Characterisation of raw material and solid fractions

2.4.1 Chemical composition

The fraction of the bamboo chips was sub-sampled and ground in a Retsch mill and a fraction of 40 mesh size was accepted for chemical analysis. Oven dry mass (ODM) of the powder 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 bamboo was determined. All the experiments were carried out in four replicates and the experimental results were represented as the mean ± standard deviation of four identical conditions.

The solid fractions obtained after alkaline pre-extraction were rinsed with distilled water and air dried. Dried samples were milled prior to polysaccharides and residual lignin content determination, using the same standard methods as those used for the raw materials except for the extractives determination.

The polysaccharides in extractive free giant bamboo and solid residues were calculated based on glucose, xylose, and arabinose after a two step hydrolysis with 72% H_2SO_4 and 4% H_2SO_4 respectively, according to National Renewable Energy Laboratory (NREL) Analytical Procedure (Sluiter et al. 2008). The concentrations of these compounds were determined by high pressure liquid chromatograph as described elsewhere (García-Aparicio et al. 2011).

The equation for the extraction mass balance was as follows (Won et al. 2012):

$$\text{Extraction mass balance} = \frac{\sum C_{Li} + \sum C_{Si}}{\sum C_{Ri}} \quad (3)$$

Where C_i is the mass of each sugar component (glucose or xylose) as determined through HPLC chromatography, the subscripts L, S, and R refer to the extracted liquid, extracted solids and raw giant bamboo, respectively.

2.4.2 Fiber length

Bamboo chips were macerated as described elsewhere (Kigkr 1971; Vena et al. 2010). Fiber length of 100 fibers was measured with a digitiser.

2.5 Pulping

Non-extracted giant bamboo and solid residue from alkaline pre-extraction (run 4: 1M NaOH at 90°C for 240 min) were submitted to the kraft pulping process. After the completion of alkaline pre-extraction step of the hemicelluloses from 1000 g dry mass bamboo chips, the extracted bamboo chips were directly subjected to pulping without washing. Only 35.7% sodium sulphide was added in the cooks (Al-Dajani and Tschirner 2008). Non-extracted bamboo was also pulped by exposing 1000 g dry mass chips to 18.6% sodium hydroxide and 25% sulphidity.

Soda-AQ pulps were prepared from dilute acid pre-extracted bamboo chips with 11.3% xylan extracted. Bamboo chips of 1000 g dry mass were subjected to 0.3% v/v H_2SO_4, 5.5:1 (mL g^{-1}) pre-extraction liquor to feed stock ratio at 120°C, for 30 min. Prior to pulping, the acid pre-extracted solid residues were thoroughly washed with water to neutralise the acid and air dried. Soda-AQ pulping conditions were: Active alkali – 16%, anthraquinone – 0.1%, and reaction time – 30 min. Soda-AQ pulps from non-extracted bamboo chips were also prepared under similar conditions.

The conditions were selected in agreement with previous work done on soda-AQ pulping of giant bamboo (Vena et al. 2010). All active alkali and sulphidity masses are expressed as equivalent mass of Na_2O.

Pulping was carried out in a 15 dm^3 batch type digester. All the bamboo chips were digested for 30 min at maximum cooking temperature of 170°C. Heating time to maximum temperature was 120 min. The cooking time was measured from the moment that the system reached the maximum temperature. At the end of the cook, fibers were separated from the black liquor, washed through a 10 mesh screen to separate rejects (uncooked material) from the fibers, and 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 fiber bundles) and then spin dried to a consistency of approximately 30%. Screened pulp yield was calculated as a percentage of the ODM of the pulps obtained in relation to the initial ODM of the raw material.

$$\text{Pulp yield (\%)} = \frac{\text{Oven dry mass of pulp}}{\text{Initial oven dry mass bamboo}} \times 100 \qquad (4)$$

The rejects and the shives collected were placed in an oven to dry at 105°C overnight to establish the oven dry mass and weighed. The reject and shive content were together expressed as a percentage of original dry mass of giant bamboo. Pulp kappa number (parameter related with residual lignin content in pulp) was determined by standard Tappi method T236 cm-85.

Pulp viscosity was determined by dissolving pulp sample into a cupricethylenediamine 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 temperature in the sample holder was maintained at 25ºC ± 1 with the aid of Haake thermostatic circulator (model D8-G). The pulp viscosity was measured in centipoises (cP).

2.6 Handsheets

2.6.1 Formation

The development of handsheets 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-92. Handsheets were formed according to TAPPI T205 om-88 using British Standard handsheet making equipment.

2.6.2 Testing of physical 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. Burst index (hydrostatic pressure required to rupture the test specimen), breaking length (maximum load or weight that a strip of paper will support before pulling apart), and tear index were measured by Tappi standard no T403 om-91, T404 om-87 and T414 om-84 respectively. The brightness was measured in ISO units using a reflectance photometer (Zeiss Elrepho 65843, Germany).

3. Results and discussion

3.1. Raw material composition and fiber length

The average values of four replicates of the chemical components and fiber length measured for giant bamboo are given in Table 2. Giant bamboo showed the following composition (%ODM): 4.1% of ethanol/cyclohexane soluble extractives, 3.0% of water soluble extractives, 2.4% of ash, 54.6% of glucan, 21.6% of xylan, 1.1% of arabinan and 25.2% of Klason lignin. Xylan contributed the most to the hemicelluloses content and was therefore considered throughout this study. The average fiber length was 2.9 mm.

The chemical composition and specific properties of giant bamboo will determine not only the response to hemicelluloses pre-extraction and subsequent pulping technologies but also the quality of the final product. The chemical composition is in agreement with reported values in literature for bamboo and comparable to that of wood (Vu et al. 2004; García-Aparicio et al. 2011). The extractives content and fiber length were in the range of softwoods whereas the lignin and hemicelluloses contents were similar to hardwoods (Scurlock et al. 2000).

3.2. Alkaline pre-extraction

3.2.1 Xylan recovery and statistical analysis

Table 3 summarises the yields of xylan recovered and the chemical composition of the solid residues generated under different alkaline pre-extractions conditions. The xylan recovery ranged from 1.2 to 4.4 g/100 g ODM (oven dry raw material), corresponding to 5.6 to 20.4% of the xylan content in untreated bamboo. The highest xylan yield of 20.4% was obtained with 2M NaOH at 90°C for 240 min (Run 8).

The determined values of xylan yield were used to evaluate the effects of the experimental variables, i.e., NaOH concentration, reaction time and temperature on xylan solubilisation. The effects and their significance of temperature, NaOH concentration and time on xylan yield can be visualised in the standardized Pareto chart (Fig 1). NaOH concentration exerted the strongest effect on xylan yield, followed by time and temperature at 95% of confidence level. Given that the curvature was also significant, a full central composite design with star points was used to evaluate whether a second order model could fit to the experimental data of the xylan recovery. The square of the correlation coefficient (R^2) of 0.95 was obtained when considering only the significant variables, meaning that 95% of the experimental data for the xylan yield was attributed to the process variables studied. The lack of fit, which describes the variation of the data around the fitted models, was not significant implying good agreement between the predicted and experimental values at 95% of confidence level (Table 4). According to these results a second order model was accepted to describe the xylan recovery from bamboo under mild alkaline conditions. The mathematical model that describes the variation of the xylan solubilisation during alkaline pre-extraction under the studied conditions can be represented by the equation:

$$\text{Xylan (\%)} = 11.3 + 1.18X_1^2 - 0.77X_2^2 + 1.63X32 + 1.17X_1 + 1.58X_2 + 3.24X_3 \qquad (5)$$

In the equation (5) X_1, X_2, X_3 are the coded values of the operational variables temperature (°C), reaction time (min) and NaOH concentration (M), respectively.

Figure 2 illustrates the response surface for Equation 5 where the xylan yield is plotted as function of temperature and reaction time considering NaOH concentration at higher level. The highest xylan yields were obtained after pre-extraction with 2.34M NaOH at 65°C reaching the value of 3.4 g of xylan per 100 g ODM which is about 15% of the theoretical xylan. Although higher concentrations of NaOH and temperature would have provided higher xylan yield (Figure 2), these factors were limited to the selected values to prevent cellulose degradation through alkaline peeling, which in turn would have lead to reduction in pulp yield and pulp strength (Al-Dajani and Tschirner 2008).

Similar xylan yields have been obtained for alkali pre-extraction of hardwoods such as aspen wood chips (Al-Dajani and Tschirner 2008) and Eucalyptus grandis chips (Vena et al. 2013). However, other pre-extraction methods such as dilute acid have been proven to provide up to 83.4% of xylan yield form giant bamboo (Vena et al. 2010). The lower total xylan yield recovered under alkaline condition was expected since the solubilisation of xylan occurred without reduction in molecular mass (Helmerius et al. 2010).

The pre-extraction conditions from run 4 (1M NaOH at 90°C for 240 min) were selected for subsequent kraft pulping evaluation and optimisation, since they resulted in significant yield of xylan while preserving most of glucan content in residue for pulping.

3.2.2. Characterization of xylan

Alkaline hemicelluloses pre-extraction is based on the hydrolysis of the ester linkage between plant polysaccharides and lignin, which increases the solubility of the hemicelluloses, without reducing their molecular mass (van Heiningen 2006). As a result, it generates oligomer or polymeric xylan fraction from giant bamboo that could be modified and used to improve the cellulosic fibers. The pre-extracted xylan was therefore characterised to evaluate its potential application. The molecular mass of the xylan pre-extracted under Run 4 was estimated by size exclusion chromatography (SEC). The average molecular mass of the xylan sample obtained by SEC was 42,500 g mol^{-1}, which is within the range of the sequential extraction of bamboo performed by Shi et al. (2011).

The FT-IR spectra of xylan component attained by condition of run 4 are illustrated in Figure 3B. The isolated xylan showed the same basic structure to that of commercial birchwood xylan (Fig 3). The FT-IR spectra presented a sharp band at 897 cm^{-1} indicating the presence of β-glucosidic linkage (C–O–C) between the sugar units in the hemicelluloses (Shi et al. 2011). The bands 1120 cm^{-1} and 1037 cm^{-1} were typical of xylans. The bands between 1223 cm^{-1}, 1329 cm^{-1} and 1421 cm^{-1} are attributed to the stretching and bending vibrations of C–H, C–C and C–OH linkages (Wen et al. 2011; Sun et al. 2012).

The alkaline extraction removed not only the xylan but also the lignin due to the cleavage of ester bonds that join the lignin and/or hemicelluloses compounds causing their solubilisation in the liquid fraction as shown by lignin bands between 1461 cm^{-1} and 1595 cm^{-1} in the FT-IR spectra (Fig 3) (Wang et al. 2008). The band at 3353 is attributed to the stretching of the OH groups (Brienzo et al. 2009, Luo et al. 2012).

Extraction of hemicelluloses combined with high dissolution of lignin and swelling of cellulose could improve the delignification rate for subsequent pulping (Sixta and Schild, 2009; Lyytikäinen et al. 2011). However, the presence of lignin limit possible applications of the extracted xylan to products such as corrugated board where colour is of less importance.

3.2.3. Pre-extracted solid residues

Chemical analysis of pre-extracted bamboo residues was performed to determine the total recoveries of glucan, xylan and lignin during the pre-extraction process (Table 3). The amount of glucan retained in the solid residue should be as high as possible to maintain a high pulp yield in the subsequent pulping processes. Likewise, certain amount of hemicelluloses is required in the extracted material to improve several physical properties of pulps (Silva et al. 2011).

Alkali extraction conditions studied resulted in solid residues with high glucan content (46.9 to 52.8%) and low acid insoluble lignin (10.7 to 18.5%) relative to glucan content (52.6%) and acid insoluble lignin (25.2%) present in the ODM non-extracted material. The xylan content of solid residues from alkaline extracted material varied from 13.2 to 19.1% ODM. Alkaline pre-extracted material could favour the subsequent pulping process due to reduction on the lignin content (Al-Dajani and Tschirner 2008; Lyytikäinen et al. 2011).

Following the pulp mill biorefinery integration approach, the solid residue from Run 4 (1M NaOH at 90°C for 240 min, 13.6% of xylan extracted) was selected for kraft pulping based on the larger glucan content (52.8% ODM) together with acceptable residual xylan for maintenance of pulp quality (17.0% ODM), both required to obtain high pulp yields.

3.3. Evaluation of pulp properties obtained from pre-extracted giant bamboo

Bamboo chips from alkaline extraction run 4 (13.6% xylan extracted) were directly subjected to kraft pulping to assess the effect of xylan extraction on cooking chemicals, pulp yield and properties. Additionally, the solid residue from which 11.3% xylan was acid pre-extracted (0.3% v/v H_2SO_4, 5.5/1 pre-extraction liquor to feedstock ratio at 120°C, for 30 min) was subjected to soda-AQ pulping. The former pulping combination was selected on the basis of a previous work, where it was demonstrated its beneficial effect on pulp yield compared to subsequent kraft pulping (Vena et al. 2010).

The cooking conditions, xylan yield, sugar composition and pulp properties of non-extracted and pre-extracted pulps are presented in Table 5. It is worth to note that xylan pre-extraction could reduce considerably the amount of chemicals required for subsequent pulping. For example, the total NaOH for cooking was reduced from 200.5 to 80.6 g for non-extracted and alkali pre-extracted bamboo, respectively. The results showed that less active alkali could be required in pulping to delignify the xylan extracted residues of bamboo (Table 5). Moreover, because of xylan extraction the wood chips mass was reduced from 1000 g to 840.0 g and 880.0 g after alkaline pre-extraction and acid pre-extraction, respectively. Therefore, more extracted bamboo chips could be loaded into the digester relative to the non-extracted bamboo.This could lead to an increase by 16% in the case of kraft pulping or 12% for soda-AQ pulping of the original pulp mill without additional investment in pulping digesters (Huang et al. 2010).

More importantly, alkali pre-extraction of xylan improved the kraft pulp yield by 9.2% units while retaining pulp viscosity compared to non-extracted giant bamboo. This showed a more efficient fiber separation as one of the objective of alkaline pre-extraction is to improve pulping performance and swelling of the fibers (Ragauskas et al. 2006). This outcome was confirmed by the reduction in reject levels implying ease of fiber separation. However, to maintain the high pulp yield, it was necessary to delignify the extracted bamboo to higher kappa number (29.9 vs 22.7) which is an economic disadvantage for bleaching (Kautto et al. 2010).

Alternatively, the combined process of xylan pre-extraction with dilute sulphuric acid and soda-AQ pulping provided similar pulp yield at slightly higher kappa number compared to non-extracted bamboo. However, slight increase in viscosity (10 cP vs 7 cP) was observed for pulps from acid-extracted bamboo. This was unexpected, since it is known that under acidic conditions the degree of polymerisation (DP) of cellulose and hemicelluloses has a tendency to decrease, resulting in accelerated peeling reaction and yield loss under subsequent alkali pulping conditions (Mendes et al. 2009). Nevertheless, the decrease in the degree of branching of xylan during acid pre-extraction could have promoted a higher frequency of hydrogen bonds between xylan and the accessible fraction of cellulose, leading to the lower degradation of carbohydrates (Bose et al. 2009). Moreover, AQ addition oxidises the reducing ends of carbohydrates favouring carbohydrate retention (Bose et al. 2009). The retention of the DP of cellulose could possibly improve the strength properties of pulps prepared from acid pre-extracted bamboo relative to pulps produced from non-extracted bamboo (Silva et al. 2011).

3.3. Handsheet properties

The burst index, tear index, breaking length and ISO brightness properties of handsheets produced from kraft and soda-AQ pulps from giant bamboo are shown in Table 5. All the pulps were beaten to enhance the fiber-fiber bonding thereby improving handsheet strength properties. Strength properties were found to be increased with increasing beating level up to 40°SR, except for tear index that was at a maximum at 25°SR. A decrease in tear index in pulp is common after the tear strength has passed the maximum due to reduction in fiber length, fiber strength and fiber-fiber bonding (Fardim and Duran 2004).

The xylan deficiency in pulp samples produced from alkaline pre-extracted bamboo could lead to reduction in strength properties after kraft pulping. Compared to pulps produced from non-extracted bamboo, pulps produced from alkaline pre-extracted bamboo showed a slight improvement in burst index by 3% whilst tensile index and breaking length were reduced by 14.5% and 15% respectively.

On the other hand, the tear index of hand sheets prepared from alkaline extracted pulps was improved by 9% at 25°SR (data not shown) and declined by 5% at 40°SR. The handsheet brightness due to alkaline pre-extraction was reduced as indicated by high kappa number of the pulp.

The alkaline pre-extraction of aspen hardwood chips also showed reduction of about 10% in tensile index due to alkaline extraction; although no other strength properties were reported (Al-Dajani and Tschirner, 2008).

Interestingly, strength properties of soda-AQ pulps from which xylan was pre-extracted under acidic conditions were not significantly reduced at the maximum degree of beating. Extraction of xylan could therefore be optimised to guarantee reasonable strength properties at adequate refining energy. At a beating degree of 40°SR, the breaking length and tensile index of handsheet prepared from acid pre-extracted bamboo was at a maximum, and increased by 21.9% and 26.7% respectively compared with that of the handsheets from non-extracted bamboo. In addition, handsheets prepared from both non-extracted and acid pre-extracted bamboo exhibited the same burst index at maximum beating degree. Retention of the hemicelluloses and lower degradation of cellulose apparently contributed to the retention of strengths (Fardim and Duran 2004). On the other hand a reduction by 7.9% of the tear index was observed for handsheet produced from acid pre-extracted bamboo due to reduction in fiber length, fiber strength and fiber-fiber bonding. The decrease in strength properties observed for handsheets produced from non-extracted bamboo could be related to the reduction in viscosity of the pulp as it governs the strength properties to a certain degree (Gurnagul et al. 1992)

These results are consistent with those reported on similar work done in the literature, which showed that the nature of the cellulosic fibers obtained after xylan extraction is governed by the amount of hemicelluloses extracted and the choice of the subsequent pulping method (Al-Dajani and Tschirner 2008; Elmore and Falls 1984). Although some strength properties were slightly reduced, these results represent the key elements to realisation of a lignocellulose-based biorefinery.

According to the results, the extracted residue can be pulped with lower active alkali while maintaining the same production rate even with higher pulp yields specifically for alkaline xylan pre-extraction combined with kraft pulping which means lower production cost. Moreover, xylan can be removed before pulping without excessive degradation of cellulose and the extracted xylan represents a valuable product (van Heiningen 2006). If the NaOH present in the liquid fraction after the pre-extraction can be recovered and reused for either pre-extraction or pulping could make the process even more economical (Huang et al. 2010).

5. Conclusions

The fast growth and low cost of giant bamboo coupled with high glucan and hemicelluloses content make bamboo an interesting raw material for the co-production of paper and value-added products in a biorefinery pulp mill. This study confirms the feasibility of integration of hemicellulose extraction with subsequent pulping of lignocellulosic materials, depending on the extraction technology and quality and performance requirement of a particular paper. Among the two xylan pre-extraction studied for giant bamboo, the results showed that alkaline pre-extraction prior to kraft pulping was slightly of higher quality compared to acid pre-extraction. The extraction of 13.6% dry mass xylan with mild alkali conditions favoured the subsequent kraft pulping leading to a reduction in rejects levels, improvement in pulp yields and a kappa number of pulp within the acceptable bleachable range. Moreover, there was no reduction in the pulp viscosity compared to the non-extracted bamboo. These conditions resulted in hand sheets with a slight reduction in breaking length, tensile and tear index and similar burst index at maximum beating degree. Furthermore, the combination of alkaline pre-extraction with kraft pulping could increase the pulping capacity by 16% without additional investment in pulping digesters.

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Tables

Table 1. Sequence of experiments according to a central composite design for alkaline pre-extraction of hemicelluloses of giant bamboo.

Run	Temperature (°C) (X_1)	Reaction time (min) (X_2)	NaOH concentration (M) (X_3)
1	40	120	1
2	40	240	1
3	90	120	1
5	90	240	1
5	40	120	2
6	40	240	2
7	90	120	2
8	90	240	2
9	65	180	0.7
10	65	180	2.3
11	23	180	1.5
12	107	180	1.5
13	65	79	1.5
14	65	281	1.5
15	65	180	1.5
16	65	180	1.5
17	65	180	1.5
18	65	180	1.5
19	65	180	1.5

Table 2. Chemical composition and fiber length determined for giant bamboo (*Bambusa balcooa*). Components are expressed as percentage of the original oven dry material (% ODM).

Component		% ODM*	Analytical method
Extractives	Ethanol/cyclohexane soluble extractives	4.1 ± 0.1	TAPPI T264 om-88
	Water soluble extractives	3.0 ± 0.2	
Carbohydrates	Glucan	54.6 ± 2.0	
	Xylan	21.6 ± 1.5	LAP 013
	Arabinan	1.1 ± 0.6	
	Acid insoluble lignin	25.2 ± 3.2	TAPPI T222 om-88
	Ash	2.4 ± 0.01	TAPPI T211 om-88
	Average fiber length (mm)		
Fiber characteristics	Min	Max	Average
Fiber length	2.1	4.0	2.9±1.3

(*) Mean values and standard deviation of four measurements.

Table 3. Composition of xylan and solid fraction after alkali extraction of giant bamboo under process variables defined by CCD.

Run	Pre-extraction conditions		Xylan pre-extraction efficiency					[b]Solid fraction after extraction			[c]EMB (%)		
	NaOH (M)	Temperature (˚C)	Time min	Xylan precipitate yield %	[a]Xylan recovery yield %	Lignin associated with pre-extracted xylan (%)	Lignin in pre-extracted xylan (% lignin in non-extracted bamboo	Glucan %	Xylan %	Acid insoluble lignin (%)	Glucan	Xylan	Acid soluble lignin
1	1	40	120	1.5	6.9	15.4	5.7	50.4	19.1	18.5	92.4	94.9	95.9
2	1	40	240	2.2	10.4	20.8	9.0	50.3	17.8	15.2	92.2	92.5	96.2
3	1	90	120	2.3	10.8	21.0	5.9	52.1	18.4	18.3	95.5	95.7	96.1
4	**1**	**90**	**240**	**3.0**	**13.6**	**21.2**	**3.1**	**52.8**	**17.0**	**21.1**	**96.8**	**92.1**	**96.0**
5	2	40	120	3.5	16.0	14.3	12.2	46.0	16.8	12.0	84.4	93.4	96.1
6	2	40	240	3.6	16.5	23.1	9.3	45.7	15.8	14.9	83.8	89.4	95.9
7	2	90	120	3.8	17.7	30.8	12.4	51.7	15.1	12.1	94.8	87.6	97.4
8	2	90	240	4.4	20.4	28.6	13.5	48.0	15.7	10.7	88.0	92.9	96.0
Star point NaOH concentration													
9	0.66	65	180	2.5	11.7	33.3	7.6	49.5	18.6	15.8	90.8	97.6	92.9
10	2.34	65	180	3.4	15.7	25.0	13.6	45.8	15.8	10.8	83.9	88.8	96.9
Star point temperature													
11	1.5	23	180	1.2	5.6	8.3	9.7	45.3	17.0	14.5	83.1	84.2	96.2
12	1.5	107	180	2.3	10.7	23.1	10.1	51.0	17.3	14.0	93.5	90.8	95.6
Star point reaction time													
13	1.5	65	92	2.2	10.3	16.7	9.4	46.9	17.9	14.9	85.9	92.9	96.6
14	1.5	65	308	4.3	19.7	25.0	12.2	49.7	13.2	12.0	91.0	80.6	96.1
Central point													
15-19	1.5	65	180	2.1±0.5	9.7	22.3±0.1	5.8	47.8±1.0	16.5± 0.5	17.9 ±0.2	87.6	85.9	94.0

[a]Analysis data are based on the oven dry xylan of non-extracted giant bamboo

[b]Analysis data are based on the oven dry non-extracted giant bamboo
[c]Extraction mass balance (EMB) was calculated for each component in the giant bamboo as e.g. xylan in the liquid and solid fraction after Run 4 were 3.0% and 17.0% respectively, and the raw giant bamboo has 21.6% xylan before the extraction. The total extraction mass balance = [(3.0+17.0)/21.6]*100 = 92.1%.

Table 4. Analysis of variance of the linear (L) and quadratic (Q) models describing the xylan yield during alkaline pre-extraction of giant bamboo.

Factor	Sum of squares	Degrees of freedom	Mean square	*P*
Model	258.45	6	43.08	0.0001
Temperature (L)	18.67	1	18.67	0.0046
Time (L)	34.19	1	34.19	0.0006
NaOH (L)	143.60	1	143.60	0.0001
Temperature (Q)	15.73	1	15.73	0.0076
Time (Q)	6.76	1	6.76	0.0541
NaOH (Q)	29.86	1	29.86	0.0010
Lack of fit	14.01	8	14.01	0.0509
Error	0.18	2	0.092	
Total	272.65	16		

Table 5. Extraction conditions, xylan recovery yield, pulping conditions and pulp properties for non-extracted and extracted giant bamboo.

Pulping process	Kraft pulping		sodaAQ pulping	
	Extraction condition			
	non-extracted	Alkali extraction (1M NaOH, 90°C, 240 min)	non-extracted	Acid extraction (0.3% v/v H_2SO_4, 120°C, 30 min)
Xylan yield				
g/100g OD (% theoretical xylan)	-	3.0 (13.6)	-	2.5 (11.1)
cooking conditions				
Active alkali (%)	18.7	-	16	16
Sulfidity (%)	25	35.7	-	-
AQ (%)	-	-	0.1	0.1
Cooking Temp (°C)	170	170	170	170
Time to 170°C (min)	120	120	120	120
Time at 170°C (min)	30	30	30	30
Chips/residue (g)	1000	840	1000	880
NaOH in chips/residue (g)	169.6	59.3	164.4	144.7
NaOH from Na_2S (g)	30.9	21.3	-	-
Total NaOH in cook (g)	200.5	80.6	-	-
NaSH charge (g)	43.2	29.8	-	-
Carbohydrates content in pulps (LAP 013)				
Glucan (%)	75.4	84.1	73.3	77.6
Xylan (%)	21.1	14.3	24.6	13.6
Pulp properties				
Pulp yield (%)	41.2±2.0	50.4±1.5	43.1±1.2	40.6±2.0
Rejects (%)	8.7±1.3	5.0±0.5	17.2±1.0	17.5±1.2
kappa number	22.7±0.9	29.9±1.1	22.9±0.5	27.8±0.2
Viscosity (cP)	10.2±2.0	10.2±1.2	7.0±2.5	10±1.0
Handsheet strength properties				
Drainage rate (°SR)	40	40	40	40
Tensile index (Nm g^{-1})	51.6±3.1	44.1±2.5	33.2±4.0	45.4±4.2
Tear index (kPa.m^2 g^{-1})	14.4±0.5	13.7±3.5	15.9±0.8	14.7±0.1
Burst index (mN.m^2 g^{-1})	7.1±0.4	7.3±0.2	5.5±0.6	5.5±0.8
Breaking length (km)	5.3±0.6	4.5±0.6	3.4±0.5	4.3±0.5
Brightness (ISO)	41.4±1.2	31.6±0.6	38.8±0.	31.6±1.3

Figures

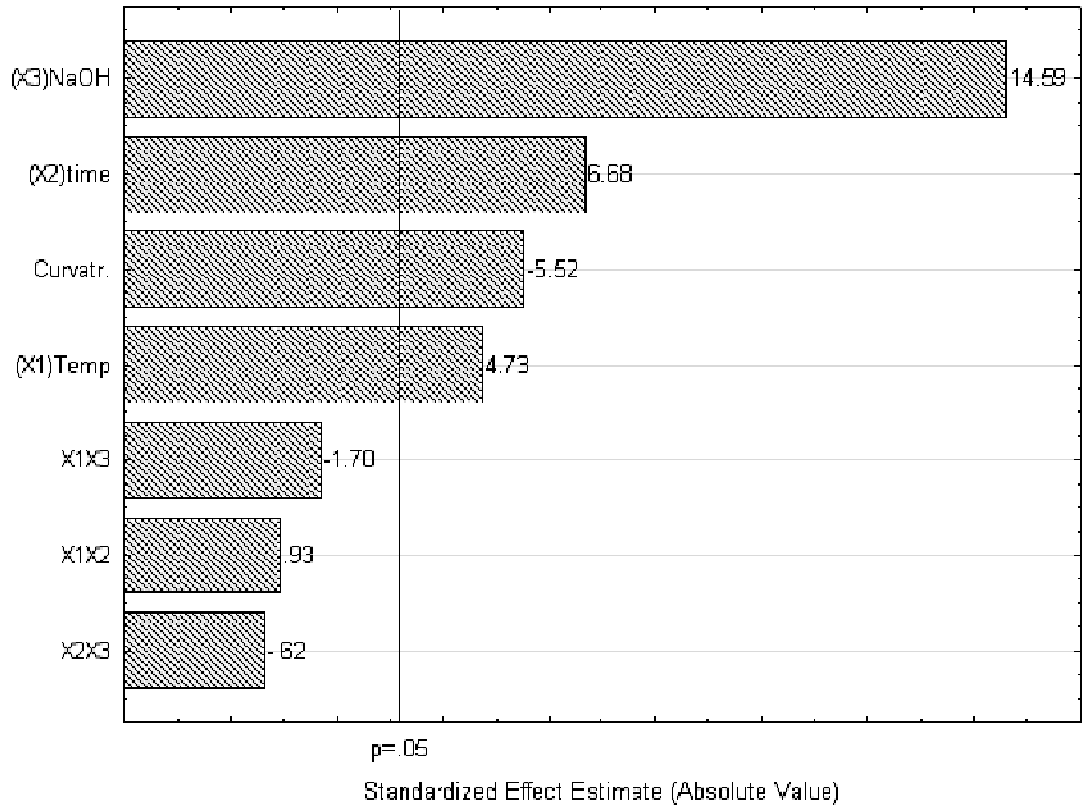

Fig. 1. Standardized Pareto chart representing the of NaOH concentration, reaction time and temperature on xylan yield after alkaline pre-extraction of giant bamboo.

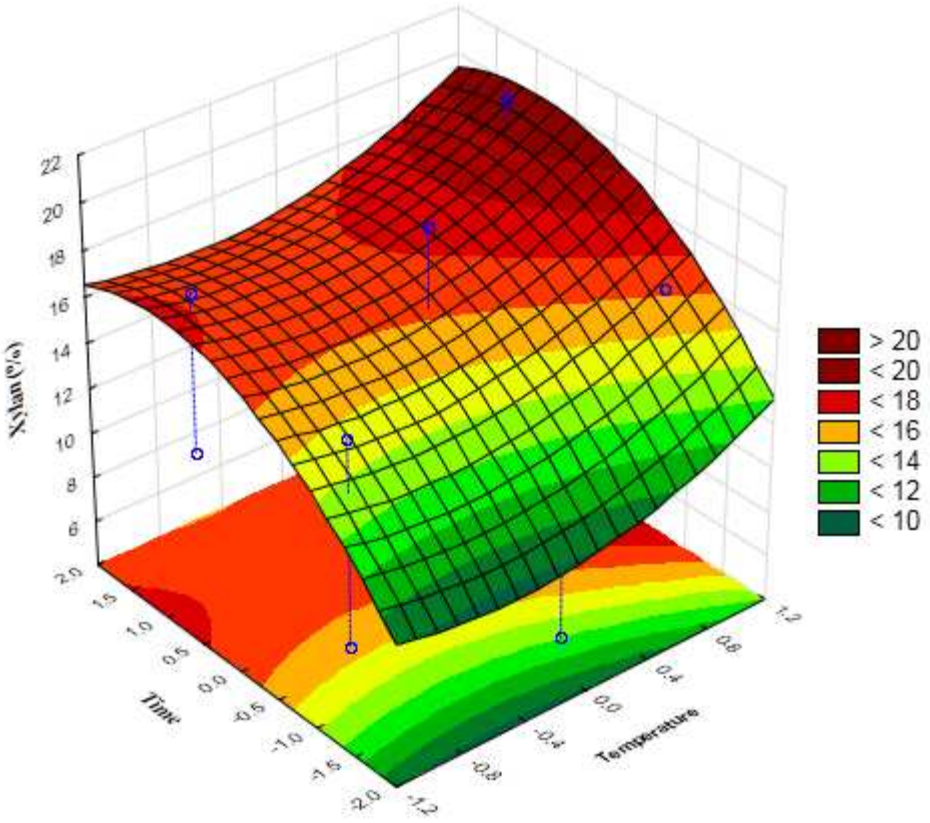

Fig. 2. Response surface for xylan yield obtained after alkaline pre-extraction showing the influence of temperature (°C) and time (minutes) considering NaOH concentration at higher level.

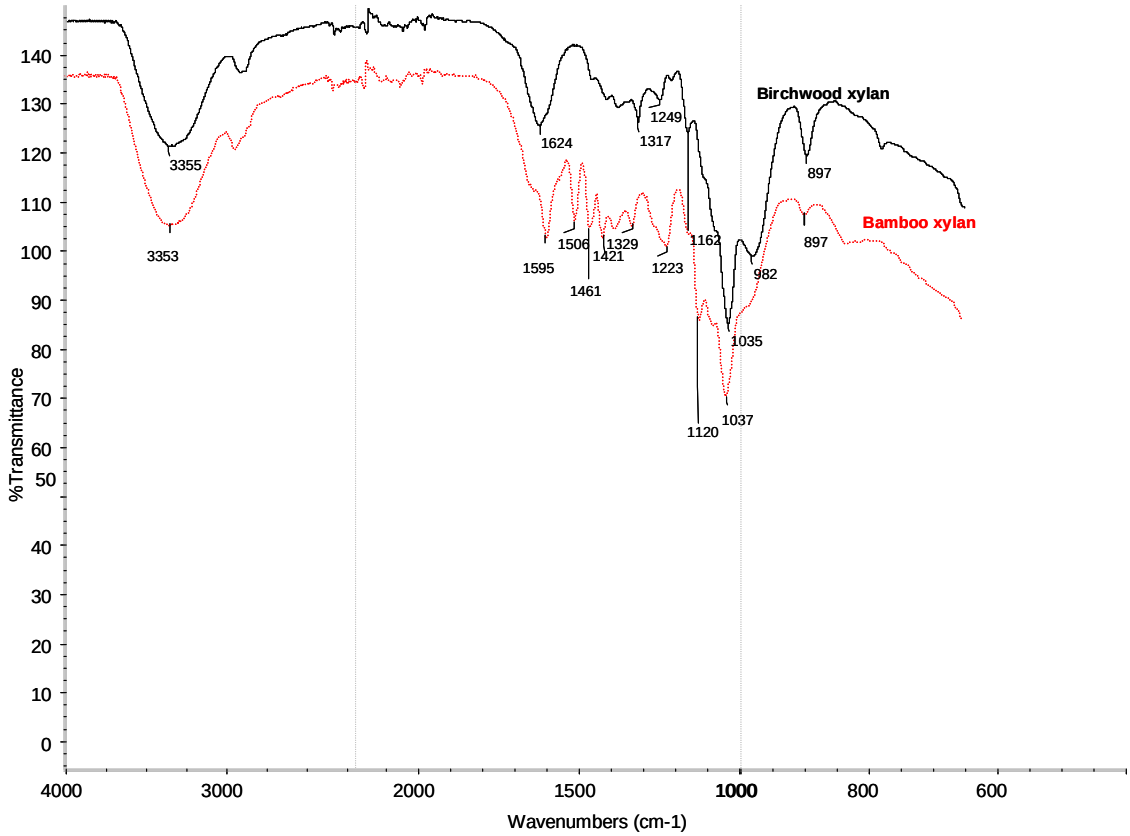

Fig. 3. FT-IR spectra of commercial birchwood xylan and xylan fraction extracted from giant bamboo with 1M NaOH at 90°C for 240 minutes.

Paper V

HEMICELLULOSE EXTRACTION FROM BAMBOO PRIOR TO KRAFT AND SODA AQ PULPING TO PORDUCE PAPER PULPS, VALUE-ADDED BIOPOLYMERS AND BIO-ETHANOL

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Hemicelluloses were pre-extracted from giant bamboo with dilute H_2SO_4 prior to Kraft and sodaAQ pulping. The reaction conditions were selected to convert most of the hemicelluloses into soluble monomeric sugars, leaving almost unaltered the cellulose and lignin in the residual solid phase. A Central Composite Design was used to study four pre-extraction variables: H_2SO_4 concentration (0.1–0.5% v/v), solid/acid solution ratio (1/3.5–1/5.5 g/mL), temperature (80–140 ˚C) and time (10–50 min). Temperature had a dominant influence on the hydrolysis process. A maximum xylose yield of 83.4% (based on oven dry raw material mass) was obtained at a 0.4% v/v H_2SO_4 concentration, a solid/solution ratio of 1/4 (g/mL), at 140 °C and pre-extraction time of 40 min. The bamboo from which 2.4% hemicellulose was pre-extracted, was subsequently pulped by both kraft and soda AQ pulping methods. Soda AQ pulping gave the best response in terms of pulp yield, viscosity and kappa number, compared to the non-extracted bamboo, pulped under similar conditions.

Keywords: bio-refinery, hemicellulose extraction, giant bamboo, dilute acid hydrolysis, kraft pulping, sodaAQ pulping, pulp yield, kappa number, pulp viscosity

INTRODUCTION

Hemicelluloses, solubilized during kraft pulping of a suitable biomass, such as bamboo, are presently under-utilized in pulp production, where they are incinerated in the recovery furnace together with the dissolved lignin.[1,2] However, within the bio-refinery concept, the extraction of hemicelluloses from suitable biomass prior to pulping, followed by fermentation of the monomeric sugars with genetically engineered yeast to produce bio-ethanol, could contribute to address the growing biofuel need. At the same time, the pulp production is enhanced by improving the overall alkaline pulping process, for both kraft and sodaAQ processes. Cooking times can be reduced and cooking liquor impregnation enhanced. Such integration of hemicellulose pre-extraction with alkaline pulping can yield to improved pulp properties and improved production capacity, as has been demonstrated for recovery furnace-limited Kraft pulp mills.[1,3]

As heteropolymers of neutral and modified pentoses and hexoses, hemicelluloses can constitute about 25–35% of the plant cell walls.[4] Pre-extraction of hemicelluloses with dilute acid and further production of ethanol from the extracted sugars has been extensively studied.[5,6] Hemicelluloses can be also extracted from the biomass, using water and/or alkaline solutions, if oligomers and polymers of hemicelluloses are desired.[1,7,8]

Bamboo, a naturally growing and a low cost lignocellulosic material,[9] is most frequently used for the production of paper, textiles, food and reinforcing fiber, as well as in constructions.[10,11] Bamboo fiber morphology and its chemical constituents are comparable to those of wood.[12] The glucan content of giant bamboo (40–48%) is comparable to the reported[13] cellulose content of softwoods (40-52%) and hardwoods (38–56%. The main hemicellulose present in bamboo is a 4-O-methyl-D-glucuronoarabinoxylan linked by a β–(1→4) bond, which accounts for approximately 25% of the cell wall components.[13,14]

The acetyl group content is 6–7% of the total xylan, compared to the 8–17% acetyl group content of hardwood and non-acetylated softwoods. Bamboo lignins have a higher content of phenolic hydroxyl groups than wood lignins, resulting in a higher reactivity to pulping. However, during kraft pulping, bamboo kraft lignin shows a higher degree of condensation, thus it is more resistant to bleaching than that of wood pulps.[15]

Based on its high hemicelluloses content, bamboo can be considered as a very attractive raw material for combined ethanol and paper production. To obtain xylose-rich solutions from bamboo, treatments of the raw material that hydrolyze the sugars from the hemicellulosic fraction, but do not significantly affect cellulose and lignin, should be selected. Several treatments that can perform such fractionation have been reported, the most frequently studied one being hydrolysis with dilute acids.[5,6,16] It consists[17] of the hydrolysis of the hemicellulosic fraction with diluted acid concentrations, ranging between 0.1 and 1% v/v, performed at moderate temperatures, between 100–150 ˚C. Under such moderate operational conditions, the acid medium hydrolyzes the hemicelluloses, with limited degradation of the cellulose fraction.[6,18]

The liquid phase (hydrolysate) will be constituted of monomeric sugars, such as xylose, glucose, arabinose, as well as decomposition products of the hemicelluloses, such as oligomers and acetic acid, generated by the hydrolysis of the acetyl groups and/or decomposition products of monosaccharides, such as furfural, a product of the dehydration of pentoses, and hydroxymethylfurfural, a product of dehydration of hexoses.[5,16] Hence, if ethanol is produced, neutralization of the liquid fraction prior to fermentation will be required.

In this study, the reaction conditions under which hemicelluloses could be extracted with dilute sulphuric acid from hemicelluloses-rich, South African grown giant bamboo (*Bambusa balcooa*) prior to alkaline pulping, were investigated. The reaction conditions of this acid catalyzed hydrolysis were selected to convert most of the hemicelluloses fraction into soluble monomeric sugars and leave the cellulose and lignin fractions mostly unaltered in the residual solid phase. The effects of acid concentration, temperature and reaction time were assessed using a central composite experimental design. Yield of the recovered sugars (*e.g.* glucose, xylose and arabinose) and of other by-products, such as hydroxymethylfurfural, furfural and acetic acid, present in the hydrolysate, were determined by HPLC. The solid residue was pulped by kraft and soda anthraquinone (sodaAQ) pulping methods. Pulp yields, kappa number and viscosities of the pulps produced from pre-extracted and non-extracted bamboo were determined, to develop a combined process for the production of hemicellulose hydrolysate and pulp from giant bamboo.

EXPERIMENTAL

Raw material

The bamboo used in the study, *Bambusa balcooa*, was collected in the Western Cape region of South Africa. Giant bamboo stems were chipped using a Wigger pilot chipper. Chips were screened and the chip size fraction between 4–8 mm was selected for further investigation. The material was conditioned at 23 °C and 55% relative humidity before use.

The composition of the raw material was determined[19] by both standard methods of the Technical Association of the Pulp and Paper industry (TAPPI) (T264 om-88, T 211 om-85, T222 om-88; T 223 cm-84) and by the standard Laboratory Analytical Procedures for biomass analysis provided by the National Renewable Energy Laboratory (NREL; Colorado, USA, http://www.nrel.gov/biomass/analytical_procedures.html).

Determination of bamboo fiber length

Maceration was achieved by dissolving 10 g chromic acid in 190 mL of distilled water, and 15 mL nitric acid was added, to form a Jeffrey's solution.[20] The chips were placed in a test tube, covered with the solution and kept in an oven at 40 °C for 48–72 hr. The solution was changed daily. The fibers were washed with distilled water, separated with a glass rod, stored in a safranin green solution for 5 min, after which the solution was drained. The fibers were then subjected to a 70% ethanol solution for 2 min, and finally immersed in xylene for 5 min. The fibers were mounted on microscope slides using Entellan, and measured with a digitizer.

Experimental design and dilute acid pre-extraction of Giant Bamboo

Experiments on dilute acid pre-extraction were carried out[21] according to a Central Composite Design (CCD), created and evaluated in STATISTICA 7.1 (Statsoft Inc., Tulsa, USA). Acid concentration, solid/solution ratio, temperature and reaction time were systematically varied (Table 1) from 0.1–0.5% v/v; 1/3.5–1/5.5 g/mL; 80–140 °C and 10–50 min at maximum temperature, respectively. The conditions were selected in agreement with previous works done on dilute acid pre-treatments of non wood materials.[5,6,18]

The bamboo chips and acid solution were mixed in the desired portions and introduced into the micro bombs. The filled bombs were placed in a digester of 15 dm^3 capacity enclosed by heating jackets. The reaction temperatures selected were monitored with thermocouples. At the end of the acid treatment, the bombs were cooled in water. The hemicelluloses-rich hydrolysate was collected for further chemical analysis for sugars and by-products and the solid residues were recovered by filtration, washed with water and air dried. The percentage of solid recovery, based on oven dry mass of the (original) raw material, was determined. A fraction of the extracted residue was sub-sampled and prepared for chemical analysis using the same standard methods as those used for the raw materials. The solid residue was then stored in the conditioning room prior to further pulping experiments.

Pulping processes

Run No.22 from dilute acid treatment was selected for kraft and sodaAQ pulping experiments. These conditions were selected because maximum glucose was observed in the solid residue after dilute acid treatment, as illustrated in Figure 1B. The studied pulping conditions applied in this work are comparable to those used by other researchers,[11,12] with slightly less reaction time at maximum cooking temperature. Maximum cooking temperature was kept constant at 170 °C and the solid-to-liquid ratio was fixed at 1/5.5 (g/mL) for all pulping experiments.

The cooking liquor used in kraft pulping was prepared from commercial sodium hydroxide (Merck) and sodium sulphide (Merck). Sodium hydroxide and BUSPERSE 2262 Anthraquinone (Buckman laboratories, Hammarsdale, South Africa) were used for soda AQ pulping. Pulping experiments were carried out (as shown in Table 2) in micro bombs that could accommodate 80 g oven dry chips. Temperature and reaction time were monitored during the process. The cooking time was measured from the moment that the system reached the maximum temperature. In the end of cooking, the fibers were separated from the black liquor and washed through a 10 mesh screen, to separate the rejects from the fibers, and the accepted pulp was collected on a 100 mesh screen. The pulp was then screened in a Packer slotted laboratory screen. Total pulp yield and rejects were determined as a percentage of the original dry mass (DM) of the raw material. Pulp kappa number and viscosity were determined by standard TAPPI methods (T236 and T230, respectively). Pulp viscosities, determined as centipoise (cP), were converted to the degree of polymerization (DP) of the polysaccharides, according to the formula:[22]

$$DP^{0.905} = 0.75[954 \log (X)-325]$$

where X is viscosity in centipoises.

Chemical analysis

The hydrolysate fraction obtained after dilute acid pre-extraction was filtered through 0.45 µm membranes and analyzed for its content in monomeric sugars, soluble oligomers and by-products. Oligosaccharide concentration was determined as the difference in monomers sugar concentration, before and after acid hydrolysis of oligosaccharides to monomeric sugars. The sugars (glucose, xylose and arabinose) and by-products (acetic acid, hydroxymethylfurfural and furfural) present in the liquid fraction were analyzed with an Aminex HPX-87H Ion Exclusion Column equipped with a Cation-H cartridge (Biorad, Johannesburg, RSA). Sugars were measured with a RI detector (Waters 2141, Microsep, Johannesburg, RSA), whereas the by-products were analyzed with an UV detector at 220–280 nm (Waters 2487, Microsep, Johannesburg, RSA).

The column was operated at 65 °C with a mobile phase of 5mM sulphuric acid and a flow rate of 0.6 mL/min. Likewise, after completion of mild acid hydrolysis (4% [v/v] H_2SO_4, 121 ºC, 60 min) of the solid fraction obtained after each pre-extraction glucose, xylose and arabinose concentrations were measured by HPLC, as described above.

RESULTS AND DISCUSSION

Raw material composition and fiber length

The chemical composition and fiber lengths of South African grown giant bamboo are shown in Table 3. A cellulose content of 44.4% and a pentosan component of 24.7% consisting of about 90% dry mass original material xylose and traces of arabinose were observed. The lignin content (22%) and average fiber length (2.9 mm) values agreed with those reported in the literature.[11,12,23]

Dilute acid pre-extraction

Yield of sugars in the liquid fraction

The composition of the hydrolysate fraction after dilute acid treatment of bamboo is illustrated in Figure 1A. To evaluate the efficiency of dilute acid as a fractionation method for hemicelluloses solubilisation, without cellulose and lignin degradation, the effect of acid concentration, temperature, reaction time and solid loading on the hydrolysis of the xylan and glucan from bamboo was determined by a statistically-experimental design. The effects and their significance are given in the standardized Pareto chart (Fig 2A). Both temperature and acid concentration influenced the xylose yield in the liquid fraction, but temperature showed the strongest effect. Solids loading and the reaction time had no significant effect on xylan hydrolysis within the selected pre-extraction conditions.

Spearman's rho statistical tests were also used to assess the effect of different pre-extraction conditions.[24] A significant correlation between xylan hydrolysis and temperature was noticed, as the *p* value was less than 0.01.

In the present study, the highest xylose amount recovered in the liquid fraction ranged between 18.4 and 19.1 g/100 g of xylose in the raw material, achieved in Runs 20 (temperature 160 °C, 0.3% acid concentration) and 14 (temperature 140 °C, 0.4% acid concentration), respectively (Fig. 1A). This represents approximately 80–83.4% of the xylose present in the original dry raw material. This effect has been reported[25] on the other lignocellulosic material, where 79.6% of the total xylose of *Eucalyptus grandis* residues were obtained utilizing 0.65% of sulphuric acid concentration at 157 °C. Treatment of hardwoods with 0.8% sulphuric acid at 190 °C produced[26] 87% xylose.

Glucose concentration in the liquid hydrolysate fraction was of 0.8–4.1 g/100 g original material, when bamboo was treated at temperatures between 140–160 °C, and the soluble lignin content was equivalent to 0.18% of the lignin present in the raw material, solubilized under the above-described conditions (Fig. 3). These results indicated minor degradation on cellulose and lignin. The highest concentration of HMF (1.36 g/100 g DM), furfural (0.41 g/100 g DM) and acetic acid (1.34 g/100 g DM) were obtained at a temperature of 160 °C and 0.3% acid concentration). A similar behavior during degradation of the cell wall components at high temperatures was previously reported.[6,27] Literature data on the inhibiting effect of these compounds show that the acetic acid[18] can be an inhibitor of microbial growth from 4 to 10 g/L, about (0.5–2 g/L) being reported[28] for both HMF and furfural. The concentrations of inhibitors in the hydrolysate are therefore acceptable for the fermentation of the xylose, glucose and arabinose components.

Composition of the solid residue after dilute acid treatment

In the experiments, the total glucose in the solid fraction was 83.0–99.2 % dry mass of raw material (Fig. 1B). These results demonstrate that degradation of the cellulose fraction in the raw material was limited during dilute acid hydrolysis. However, temperatures between 140 and 160 °C and an acid concentration above 0.3% resulted in the formation of HMF (Fig. 4), indicating degradation of the glucose portion. As shown in Figure 2B, temperature had a dominant influence on the glucose retained in the solid residue. The xylose retained in the solid fraction constituted between (0 and 94%) of the original dry material (Fig. 1B). At high temperature (160 °C), no xylose was detected in the solid fraction, and the formation of furfural was observed in the liquid fraction (Fig. 4). As indicated by statistical analysis, temperature is the main limiting factor of acid hydrolysis for maximum xylose removal.

After dilute acid fractionation, the acid insoluble lignin in the solid fraction varied from 64.5-110.1% dry original material (Fig. 3). The high lignin content in the solid fraction might have resulted from the tendency of lignin to be depolymerized and then repolymerized in a different morphology during hemicellulose hydrolysis.[29] When dilute acid extraction is performed in batch systems, both lignin dissolution and precipitation is promoted.[30] Large fractions of lignin react to soluble products, which further react[30] to form insoluble compounds, if left in the reactor. Moreover, coating of cellulosic fibers with these lignin-like material would restrict the substrate area availability for subsequent treatments.[3] Dilute acid pre-extraction of bamboo support the idea of a possible optimization for removing sufficient hemicelluloses by dilute acid treatment, while not adversely affecting the celluloses and lignin fraction, which will therefore be favorable when temperature of 120 °C, acid concentration of ≤ 0.3% at shorter reaction time are used.

Pulping of hemicellulose extracted bamboo

After hemicellulose pre-extraction of bamboo with dilute acid, a solid residue from Run 22 was selected for pulping. These conditions were preferred as a maximum glucose content was observed in the solid residue after dilute acid pre-extraction. The extracted solid residue was subjected to Kraft pulping under different cooking conditions (14–16% effective alkali, 15–35% sulfidity and keeping for 30–70 min at maximum temperature). Soda AQ pulping conditions: 14–16% active alkali, 0.05–0.1% anthraquinone, keeping at maximum temperature for 30–70 min.

Temperature and solid loading were kept constant at 170 °C and 5.5 mL/g, respectively, in all pulping experiments. The pulp properties of bamboo produced after kraft and sodaAQ pulping were determined. The non-extracted bamboo was also pulped under similar conditions and used for comparison purposes.

Kraft pulping

Tables 4A and 4B list the comparative values of pulp yield, viscosity, kappa number and degree of polymerization of the pulps obtained from both pre-extracted and non–extracted bamboo chips. The pulping yields recorded for non-extracted bamboo were 45.5–55.1%, compared to 40.7–50.3%, recorded for the pre-extracted bamboo. Under similar pulping conditions, the kraft pulp yields obtained from bamboo are comparable to those given in literature,[11,12] of 48.1–54.3% and 42.7–48.9%, respectively. Comparing the best pulping yields (Run 5 in Tables 4A and 4B), non-extracted bamboo produced 9% higher pulp yields than those of pre-extracted pulps. The yield loss during pulping, due to hemicelluloses pre-extractions with dilute acid and hot water was previously reported.[32] Kraft pulp yields of 51.1% and kappa number of 17.1 for acid pre-extracted mixed hardwoods, compared to 53.2% pulp yield and kappa number of 16.7 from non-extracted yields were reported.[33]

The kappa number was lower for pre-extracted pulps (4.4–12.8), compared to the non-extracted ones (6.5–13.8). The results showed that an increase in active alkali from 14-16%, combined with an increase in sulfidity from 15–35% resulted in a decrease in kappa number for both pre-extracted and non-extracted pulps (Run 4 in Tables 4A and 4B). Reduction in kappa number is explained by the higher delignification rate induced by the presence of sodium hydrogen sulfide in the pulping liquor, resulting[29] in lignin dissolution. A high sulfidity (35–45%) in lower effective alkali (14–16%) resulted[11] in pulps with lower kappa numbers (11–15).

In this work, cellulose degradation during pulping was measured in terms of viscosity, values of 4.3–8.5 cP and 4.4–16 cP being obtained from pre-extracted and non-extracted pulps, respectively. The viscosity values here measured are comparable to the results obtained[34] when *Panus tigrinus* delignification strains were used prior to kraft pulping of sugarcane bagasse (2.3–6.8 cP). According to literature data, [35] in modern kraft pulp mills, viscosity ranges from 30 cP after kraft pulping of wood. Variation in pulp viscosity is associated with the hemicellulose content of pulps.[36] Pulp with high hemicelluloses content is reported[22] to undergo low cellulose degradation, resulting in high viscosity pulps. Decrease in the DP of cellulose beyond ~1600 post pulping and beyond ~700, respectively, after bleaching could reduce[3] the paper sheet strength properties. According to the present study, hemicelluloses pre-extractions with dilute acid might have influenced the reduction of viscosity. Treatment with hydrochloric acid during vapour phase was reported to cause cellulose degradation.[37]

Soda anthraquinone (AQ) pulping

A comparison of pre-extracted and non-extracted Bamboo chips by sodaAQ pulping is presented in Tables 5A and 5B. Dilute acid pre-extraction resulted in higher pulp yields (41.36–55.02%), compared to the values registered in the untreated material (40.36–48.85%), which could be explained by the decrease in the branching degree on xylan during dilute acid pre-extraction. A higher frequency of hydrogen bounds between xylan chains, and between xylan and the accessible fraction of cellulose could be promoted, leading to a lower degradation of carbohydrates.[2] Composition of the raw material and process modifications prior to pulping may affect the pulp yield.[38] A study was conducted on dilute acid and alkaline pre-extraction of hemicellulose from Aspen, alfafa stems, switch grass and hybrid poplar and subsequently subjected the solid residue on kraft and SodaAQ pulping.[32] The best preliminary results obtained gave a pulp yield of around 43%, obtained with poplar and switchgrass.

It was explained that overall composition or the raw material could also affect pulp yield. Acid pre-extraction prior to sodaAQ of hardwood showed pulp yields of 52.7%, and a kappa number of 15.9, compared to 53% pulp yield and kappa number of 16.6 for non-extracted pulps.[39]

The kappa numbers observed from pre-extracted pulps are lower (31.0–33.4), compared to those from the non-extracted ones (35.6–38.8). Although anthraquinone has been reported to have a maximum effect on lignin degradation, in the present study bamboo delignification was difficult to attain, as it can be inferred by the kappa number values obtained (over 30). Nonetheless, the addition of AQ to adjust pulping conditions could also result in a lower kappa number reduction, and higher pulping yield.[12] Literature reports that the condensation reactions of lignin occur at higher rate during soda AQ pulping,[40] which could be a disadvantage of sodaAQ pulps, because most of the condensed lignin structures are less reactive to conventional bleaching chemicals, compared to the uncondensed ones.[40]

Out of the six pulping conditions shown in Table 5, the optimum one, based on viscosity, was in Run 5. Pre-extracted pulp showed a pulp yield of 41.36, kappa number -33.35 and pulp viscosity of 13.8 cP, compared to a pulp yield of 41.44, kappa number - 35.6 and pulp viscosity of 17.33 cP. The advantage of pulps with high viscosity and low kappa number is that, if a lower kappa number is required, subsequent delignification through bleaching could be carried out with less bleaching chemicals, while retaining appropriate pulp strength values.[41]

Comparative kraft and sodaAQ pulping behavior of pre-extracted bamboo

Generally, soda-AQ pulping of pre-extracted bamboo has a positive effect on pulp yield (41.36–55.02%) compared to Kraft pulping with (40.7–50.3%) pulp yields. Kraft pulps are well-known for their low pulp yields, compared to soda-AQ pulps.[2,12]

A high delignification efficiency was shown for pre-extracted Kraft pulps compared to pre-extracted soda-AQ pulps. Kappa number values of 4.4–12.8 were observed for pre-extracted Kraft pulps compared to 31.0–33.4 for pre-extracted soda pulps. However, although the kappa number is an important quality index of pulp and also a key parameter for pulping, a higher kappa number reduction in kraft pulps also caused higher reduction in pulp viscosity (4.3–8.5 cP), compared to sodaAQ pulps with highest viscosity (11.3–14.33 cP). This called for an economic balance between the environmental benefits and pulp degradation. Compared with the raw material, dilute acid pre-extracted residues with a constant kappa number, pulped by soda-AQ, will maximize product yield and pulp quality, while minimizing consumption of energy and chemicals (Fig. 5B).

Conclusions

- About 80–83% of the xylose present in bamboo can be hydrolyzed with 0.3% (v/v) acid concentration at 160 °C, and 0.4% (v/v) at 140 °C, respectively. However, these conditions showed a slight degradation to cellulose and hemicelluloses, as indicated by the presence of 0.41g/100g DM furfural and 1.36 g/100 g DM HMF at 160 °C. The amount of acetic acid in the hydrolysate was 1.34 g/100 g DM.
- Kraft pulping of pre-extracted solid residue resulted in a 9% yield reduction, compared to non-extracted bamboo, at best cooking results (Run 5, Table 4). Lower kappa number and very low viscosity were observed for pre-extracted pulps.
- Increase in pulp yield by 7.4% was obtained from pre-extracted sodaAQ pulps compared to the non-extracted sodaAQ pulps generated under similar pulping conditions (Run 4, Table 5). Lower kappa numbers and high viscosity were observed.
- When selecting the best pulping process for integration of dilute hemicelluloses pre-extraction and pulping process, sodaAQ pulping is recommended. Although still busy with screening of experiments for optimum conditions, the present trial showed excellent promise for integrating hemicelluloses pre-extraction with dilute acid and utilisation of the solid residue for pulp production.

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Table 1

Sequence of experiments according to the Central Composite Design for dilute acid pre-extraction of hemicelluloses from bamboo

Run	Acid concentration (v/v %)	Solid/Acid solution (g/ml)	Temperature (°C)	Residence time (min)
1	0.2	1/4	100	20
2	0.2	1/4	100	40
3	0.2	1/5	100	20
4	0.2	1/5	100	40
5	0.2	1/4	140	20
6	0.2	1/4	140	40
7	0.2	1/5	140	20
8	0.2	1/5	140	40
9	0.4	1/4	100	20
10	0.4	1/4	100	40
11	0.4	1/5	100	20
12	0.4	1/5	100	40
13	0.4	1/4	140	20
14	0.4	1/4	140	40
15	0.4	1/5	140	20
16	0.4	1/5	140	40
17	0.1	1/4.5	120	30
18	0.5	1/4.5	120	30
19	0.3	1/4.5	80	30
20	0.3	1/4.5	160	30
21	0.3	1/3.5	120	30
22	0.3	1/5.5	120	30
23	0.3	1/4.5	120	10
24	0.3	1/4.5	120	50
25	0.3	1/4.5	120	30

Table 2

Sequence of experiments for Kraft and sodaAQ pulping of hemicellulose pre-extracted bamboo

Run	1	2	3	4	5	6
Active alkali (%DM)	14	14	16	16	15	15
Sulfidity (% DM)	15	35	15	35	25	25
Anthraquinone (% DM)	0.05	0.05	0.05	0.05	0.117	0.075
Time at 170°C (min)	30	30	30	30	70	45

Table 3

Chemical composition expressed in percentage of oven dry mass original material and fiber length of giant bamboo before pre-extraction

Component		% Content (based on oven dry mass)
Ethanol/cyclohexane soluble extractives		4.1 ± 0.1
Water soluble extractives		3.0 ± 0.2
Ash		2.4± 0.01
Cellulose		44.4± 0.4
Pentosan		24.7 ± 1.7
Monosaccharides	Glucose	30.5 ± 2.0
	Xylose	22.9± 0.4
	Arabinose	0.20 ± 0.01
Klason lignin (acid insoluble)		22.0 ± 0.9

Mean values and standard deviation of four measurements

Fiber characteristics	Min	Max	Average (mm)
Fiber length	2.1	4.0	2.9 ± 1.3

Table 4

Comparison of Kraft pulping results from non-extracted and 2.4% hemicelluloses pre-extracted giant bamboo (0.3% v/v, 1/5.5 solid/acid solution ratio, 120 °C for 30 min)

Table 4A

	Kraft pulping conditions			**Pulp characteristics of the pre-extracted material**				
Run	Effective alkali (% DM)	Sulfidity (% DM)	Time at 170°C (min)	Screened pulp yield (%)	Rejects (%)	Kappa number	Viscosity (cP)	Pulp DP
1	14	15	30	43.3	10.5	7.3	8.5±0.9	794
2	14	35	30	40.7	7.3	8.8	7.3±1.1	696
3	16	15	30	41.7	9.4	5.6	7.7±0.3	731
4	16	35	30	41.9	7.4	4.4	8.5±0.9	794
5	15	25	70	50.3	14.7	12.8	4.8±0.3	434
6	15	25	45	46.7	13.1	11	4.3±2.5	367

Table 4B

	Kraft pulping conditions			**Pulp characteristics of non-extracted raw material**				
Run	Effective alkali (% DM)	Sulfidity (% DM)	Time at 170°C (min)	Screened pulp yield (%)	Rejects (%)	Kappa number	Viscosity (cP)	Pulp DP
1	14	15	30	47.0	9.4	12.9	14.5±1	1147
2	14	35	30	47.5	7.0	10.9	8.2±0.3	771
3	16	15	30	48.2	5.5	10.1	6.3±0.4	603
4	16	35	30	45.5	4.4	6.5	8.8±0.4	817
5	15	25	70	55.1	15.3	13.8	16.0±5.6	1213
6	15	25	45	49.9	14.5	12.2	4.4±2.7	381

Table 5

Comparison of sodaAQ pulping results from non-extracted and 2.4% hemicelluloses pre-extracted bamboo (0.3% v/v, 1/5.5 solid/acid solution ratio, 120 °C for 30 min)

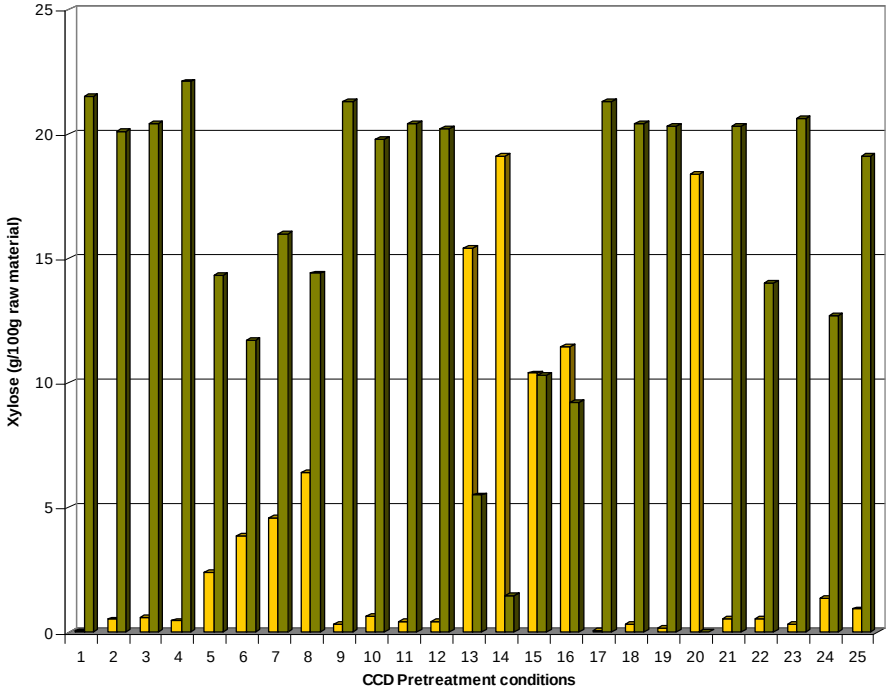
Table 5A

SodaAQ pulping conditions				**Pulp characteristics of pre-extracted material**				
Run	Active alkali (% DM)	Anthraquinone (% DM)	Time at 170°C (min)	Screened pulp yield (%)	Rejects (%)	Kappa number	Viscosity (cP)	Pulp DP
1	14	0.05	30	55.02	5.16	31.64	11.33±1.0	982
2	14	0.1	30	49.73	11.81	32.49	12.33±0.3	1038
3	16	0.05	30	46.61	12.71	32.49	12.17±0.3	1030
4	16	0.1	30	52.23	13.22	33.23	14.33±0.6	1139
5	15	0.075	70	41.36	12.48	33.35	13.83±0.3	1115
6	15	0.075	45	51.2	7.54	31.0	12.5±0.9	1048

Table 5B

SodaAQ pulping conditions				**Pulp characteristics of non-extracted material**				
Run	Active alkali (% DM)	Anthraquinone (% DM)	Time at 170°C (min)	Screened pulp yield (%)	Rejects (%)	Kappa number	Viscosity (cP)	Pulp DP
1	14	0.05	30	43.82	17.22	38.7	20.5±0.9	1381
2	14	0.1	30	48.56	17.82	38.8	15.33 ±1.1	1184
3	16	0.05	30	40.36	10.81	37.6	12.17 ±0.3	1030
4	16	0.1	30	44.84	17.28	35.8	12.33 ±0. 9	1038
5	15	0.075	70	41.44	13.47	35.6	17.33 ±0.3	1267
6	15	0.075	45	42.95	15.5	38.0	14.17 ±2.5	1131

A



B

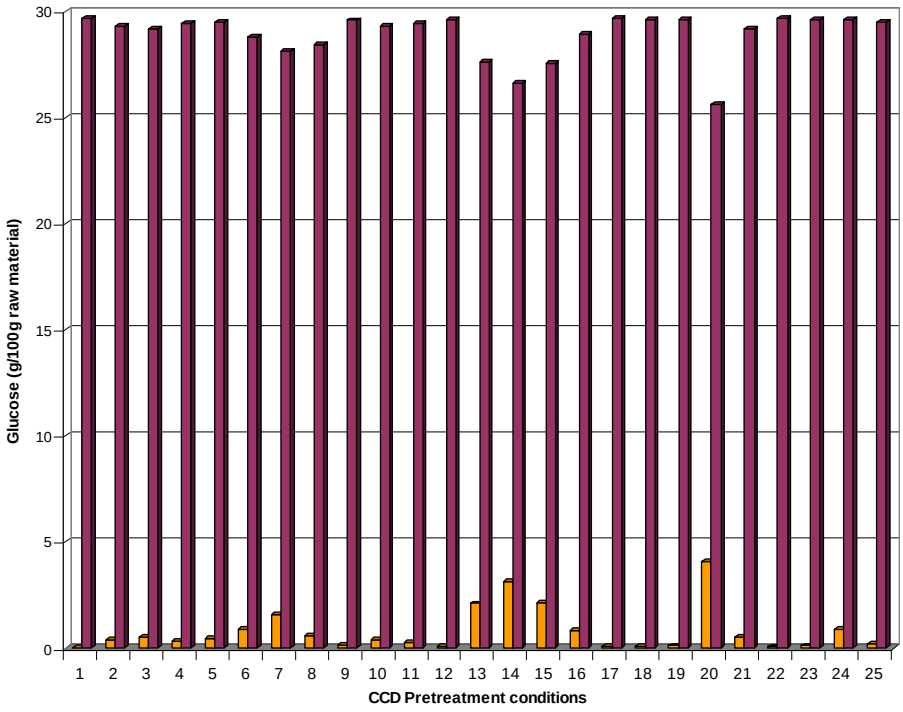


Figure 1. Total xylose yield (A), expressed as g/ 100 g of raw material, and total glucose yield (B), expressed as g/100g of raw material

(A) liquid (■) and solid (■) fractions under different pre-treatment conditions
(B) liquid (■) and solid (■) fractions under different pre-treatment conditions

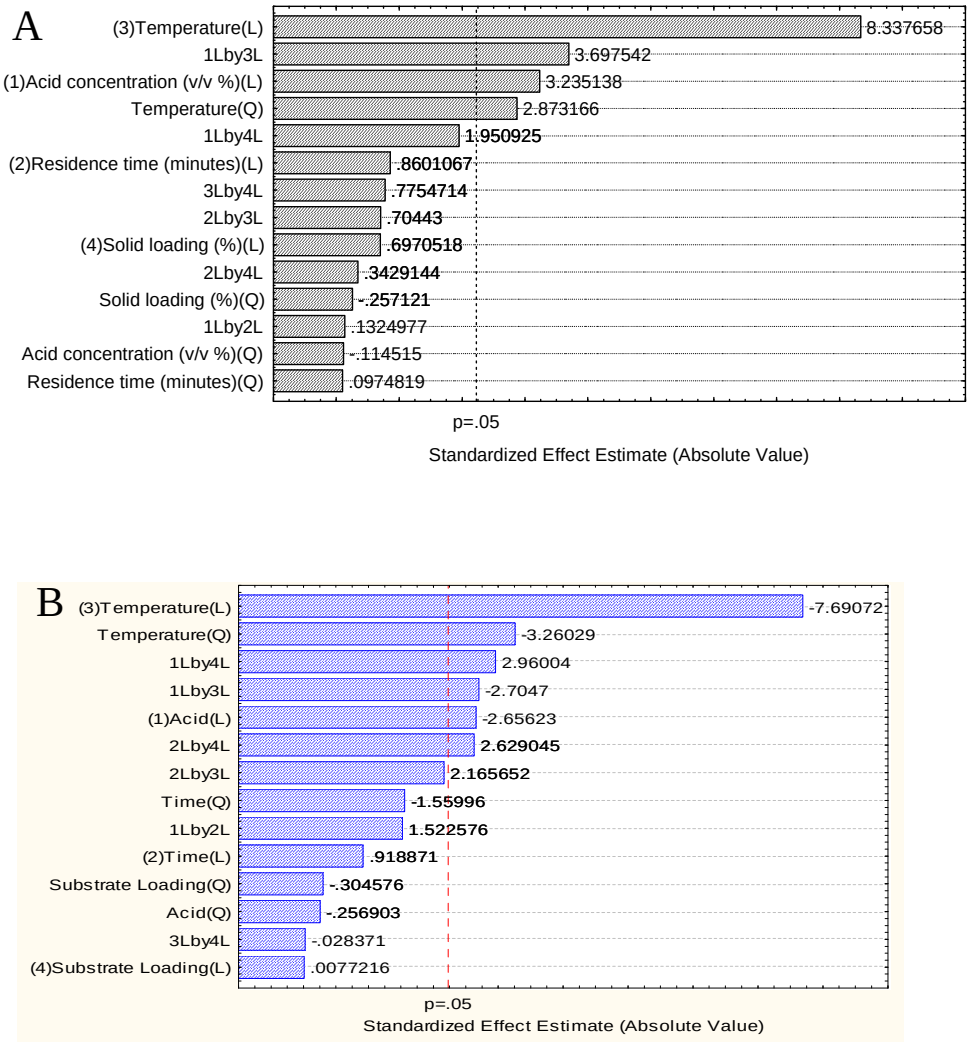


Figure 2. Standardized Pareto charts for (A) xylose solubilised in the liquid fraction and for (B) glucose retained in the solid residue

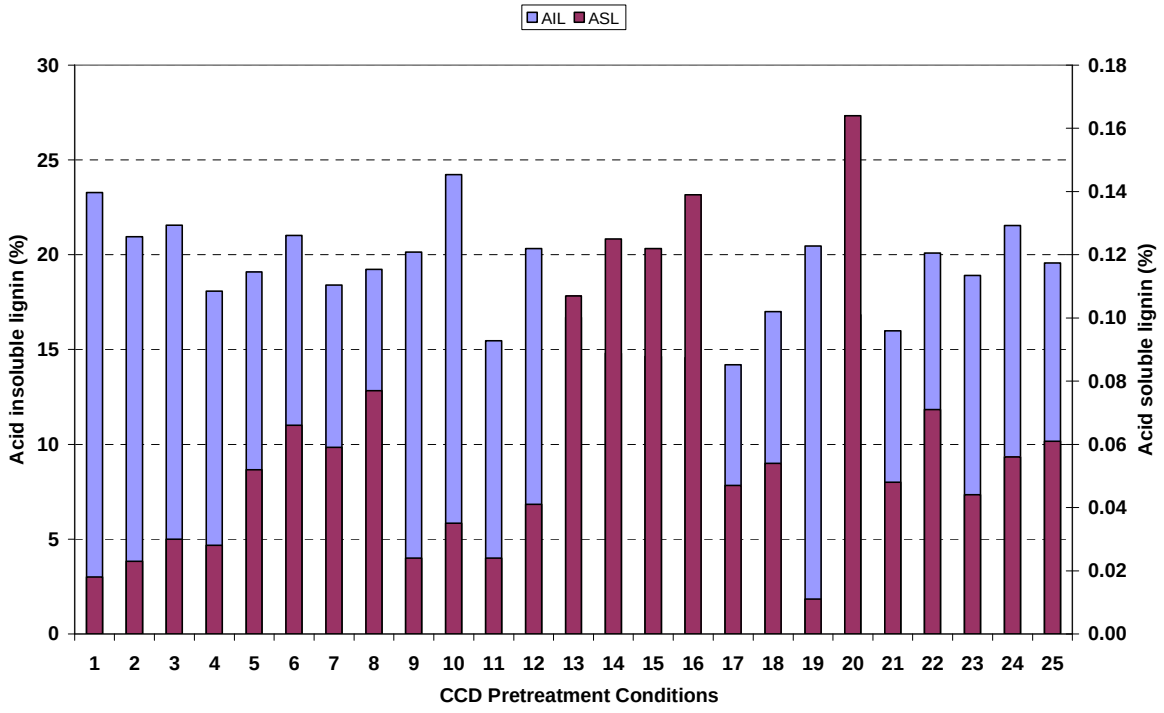


Figure 3. Acid insoluble lignin (%) in the solid fraction and acid soluble lignin (%) in the liquid fraction from each pre-treatment conditions of the CCD

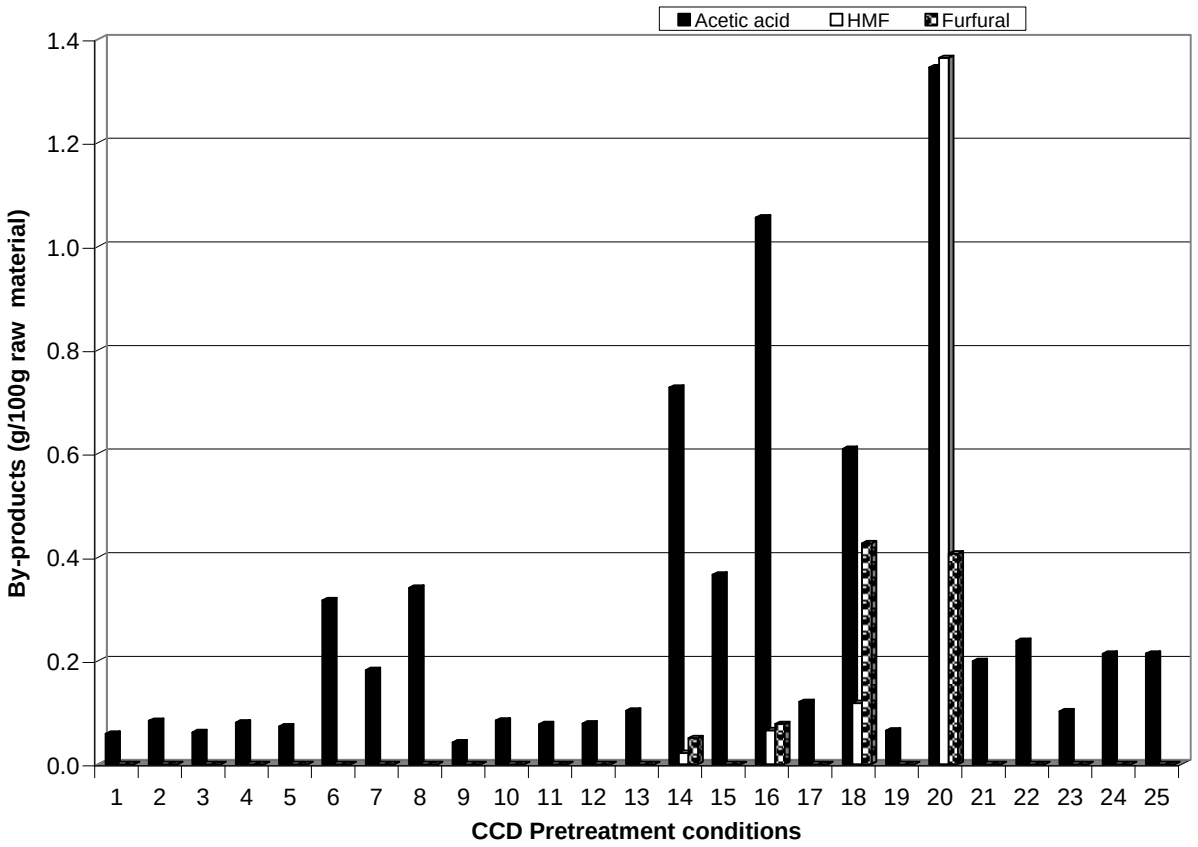


Figure 4. Degradation products in the liquid fraction

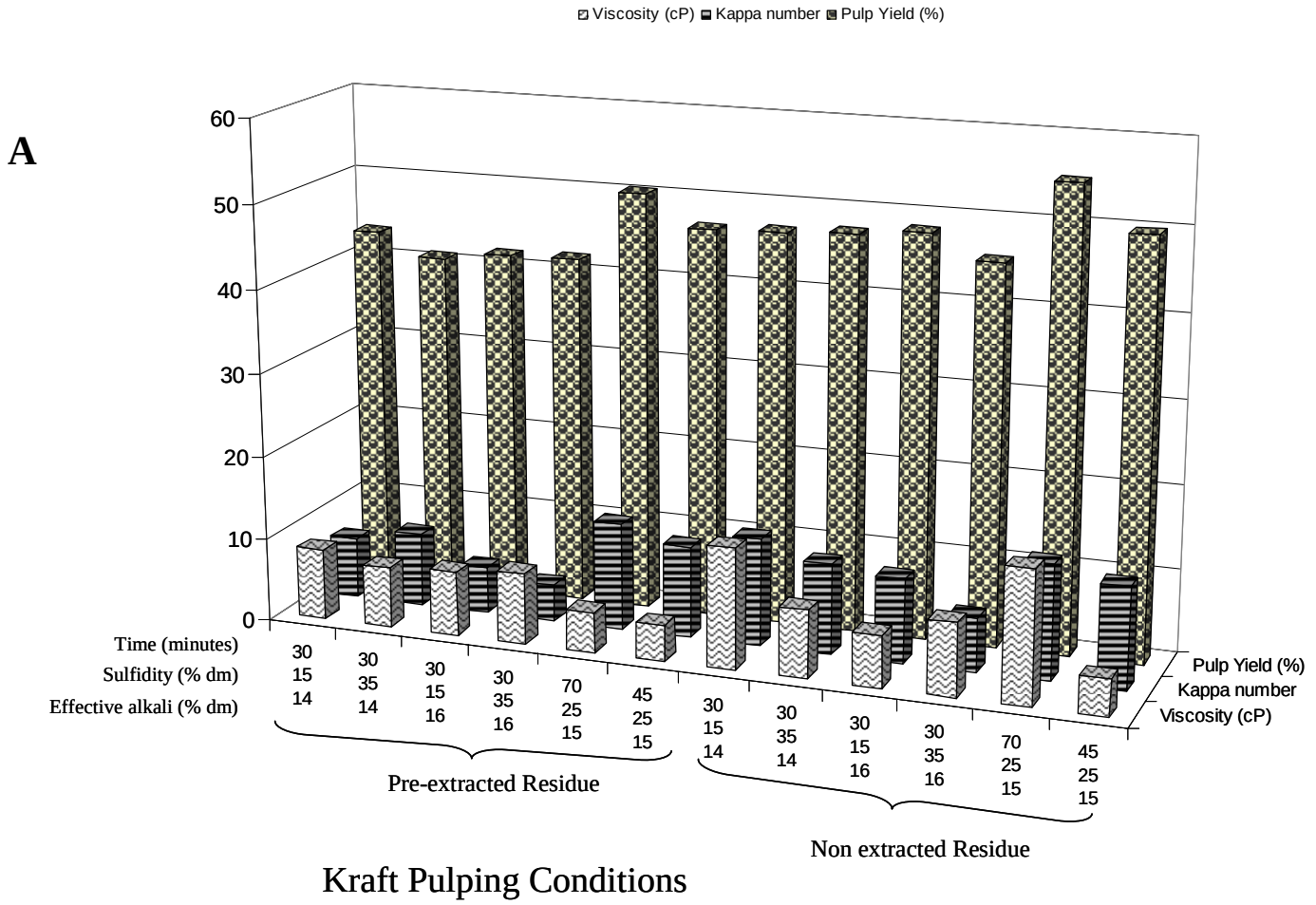


Figure 5A. Pulp properties of pre-extracted and non-extracted bamboo after Kraft pulping process.

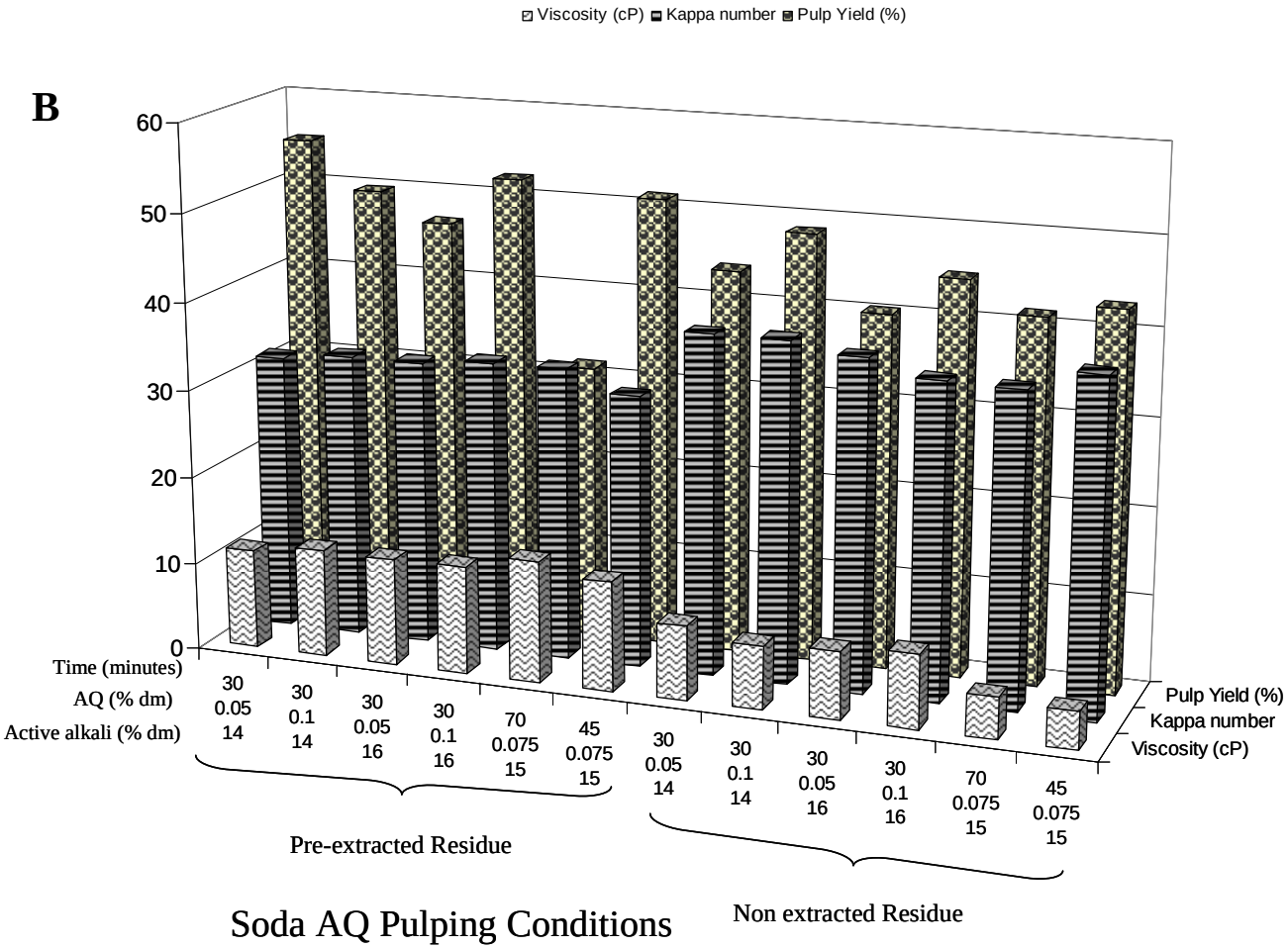


Figure 5B. Pulp properties of pre-extracted and non-extracted bamboo after sodaAQ pulping process