### IMPACT OF HEMICELLULOSES PRE-EXTRACTION ON PULP PROPERTIES OF SUGARCANE BAGASSE

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Received August 24, 2012

The extraction of hemicelluloses, which 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 under 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 soda-AQ pulping, and kraft pulping of the dilute acid pre-extracted solid residue was also performed. The integration of hemicelluloses pre-extraction by alkaline methods into a soda-AQ-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 brightness.

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

#### INTRODUCTION

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 South Africa, Central Asia, the Middle East and North America.<sup>1</sup> The South African sugar industry generates approximately 8 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.<sup>2,3</sup> Besides its availability, SCB is characterised by high cellulose (40-50%) and hemicelluloses 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.<sup>4,5</sup> 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 silica is quite low in SCB, 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.<sup>6</sup>

Among the pulping processes, soda pulping (using NaOH only) is the preferred method for sulphur-free, chemical pulping of SCB in South Africa.<sup>7</sup> The addition of pulping additives, such as anthraquinone (AQ), in bagasse soda pulping improves pulp yield and delignification rates, while reducing carbohydrate degradation.<sup>8</sup> However, SCB consists of pith, which constitutes 30-35% by weight of SCB. This material does not produce papermaking fibre, but consumes more chemicals in the pulping process and has a higher 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 produces considerable amounts of organic by-products in the form of black liquor, generated by the degradation of lignin and hemicelluloses.<sup>11</sup>

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.<sup>12</sup> 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 making the sludge non-reusable after re-burning.<sup>13</sup> Silica can be removed by precipitation from black liquor by partial acidification with carbon dioxide from flue gasses or by addition of calcium oxide.<sup>6</sup> 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.<sup>6</sup> However the calorific value of the black liquor solids from soda pulping of nonwood is still inferior to that of kraft pulping of wood.<sup>13</sup>

Considering that hemicelluloses degraded in the black liquor have a low heating value (13.6 MJ kg<sup>-1</sup>), compared to lignin (27.0 MJ kg<sup>-1</sup>), it could instead be processed to valuable chemical products within a pulp mill biorefinery.<sup>11,14</sup> Nondegraded hemicelluloses have valuable properties, such as potential paper additives, biopolymers and speciality chemicals, while it can be used in monomeric form for bioethanol production.<sup>15,16</sup> 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.<sup>1</sup> Another advantage of the application of preextraction is the reduction of ash/silica content in the pre-extracted residues, circumventing the associated problems with chemical recovery.

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.<sup>17,19-20</sup> Dilute acid hydrolysis mostly generates oligomeric and monomeric hemicelluloses-derived sugars, mainly xylose, which can be the platform for the production of chemicals, such as ethanol, furfural and xylitol.<sup>4,15,21</sup> On the other hand, alkaline treatment originates high molecular weight hemicellulosesderived polymers, in particular xylan, which might be used for the production of biopolymers.<sup>5,16</sup> Moreover, extracted xylan can undergo modification and be used as papermaking additive.<sup>16</sup> 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 (lignocellulose).<sup>14</sup> This is due to the fact that certain physical properties of pulp require the presence of hemicelluloses in the fibre matrix.<sup>22</sup> 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 soda-AQ pulping.<sup>17,22</sup> 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 a central composite design. Additionally, hot water treatment was applied for comparison. The conditions, under which significant hemicelluloses could be extracted, while ensuring minimal interference with cellulose content in the residual cellulignin, were selected for further soda, soda-AQ or kraft pulping. The impact of hemicelluloses preextraction on pulp properties and paper quality using soda or soda-AQ pulping methods was evaluated.

### EXPERIMENTAL

#### 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.

#### Hemicelluloses pre-extraction of sugarcane bagasse

Dilute sulphuric acid and mild alkali preextractions 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.<sup>23</sup> The experimental range and the codification of process parameters 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 central 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,  $R^2$ .

#### 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<sup>-1</sup>. Filled bombs were placed in a digester of 15 dm<sup>3</sup> 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.

#### Alkaline pre-extraction

The mild alkaline extraction of hemicelluloses was performed as described elsewhere, without using the chlorination step.<sup>24</sup> 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, a treatment at 107 °C was 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 hemicelluloses.

#### Liquid fraction characterization

#### Liquid fraction from dilute acid and hot water preextraction

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  $\mu$ m 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.<sup>25</sup> 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 chromatography (HPLC), as described elsewhere.<sup>26</sup>

#### 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 12 kDa 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.<sup>24</sup> The samples were conditioned in liquid nitrogen and freeze-dried. The ODM of the recovered hemicelluloses precipitates was determined.

The hemicelluloses recovery yield was estimated according to the following relations:<sup>27</sup> %Hemicelluloses precipitate = 100 x Oven dry mass of hemicelluloses precipitate/Oven dry mass non extracted SCB (1) %Hemicelluloses recovery = 100 x %Hemicelluloses precipitate/Hemicelluloses of SCB (2) The lignin fractions associated with the hemicelluloses ware determined as described

hemicelluloses were determined as described elsewhere.<sup>19</sup>

#### Size exclusion chromatography

The molecular mass of the extracted hemicelluloses was determined using size exclusion chromatography (SEC). The isolated hemicelluloses were dissolved in deionised water to obtain a final concentration of 1 g L<sup>-</sup> <sup>1</sup>. 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 of 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. A solution of deionised water containing 0.05% sodium azide (NaN<sub>3</sub>) 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.

#### Spectroscopy analysis of hemicelluloses

The FT-IR spectra were recorded in reflectance mode using a 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<sup>-1</sup> were accumulated over the range of 4000-650 cm<sup>-1</sup>. The operating and data manipulating software was the basic OMNIC package.

## Characterization of raw material and solid fractions

#### 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  $105\pm2$  °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.<sup>28</sup> All the experiments were carried out in four replicates and the experimental results were represented as the mean  $\pm$  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.<sup>28,29</sup>

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.<sup>29</sup> The concentrations of these compounds were determined by high pressure liquid chromatography.<sup>26</sup> The equation for the extraction mass balance was the following:<sup>30</sup>

Extraction mass balance =  $\sum \underline{C}_{\underline{Li}} + \sum \underline{C}_{\underline{Si}}$  (3)  $\sum C_{Ri}$ 

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 SCB, respectively.

#### Scanning electron microscopy

The portions 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). A similar analysis was performed on non-extracted sugarcane bagasse for comparison.

#### 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<sub>2</sub>SO, 120 °C and 40 min) pre-extractions were submitted to soda or soda-AQ micro-pulping. Prior to pulping, the dilute sulphuric acid pre-extracted solid residues were thoroughly washed with water to neutralize and airdried. The experiments were carried out according to the central composite design created and evaluated by Statistica 7.1 (Statsoft Inc., Tulsa, USA). The ranges of cooking conditions for soda pulping were as follows: active alkali (NaOH): 20-22% and reaction time: 25-37 min. The ranges of soda-AQ pulping conditions 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.<sup>8,17,31</sup>

Likewise, after the completion of the alkaline preextraction step, the alkaline extracted residue from 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 SCBto-liquid ratio was fixed at 1:7 g mL<sup>-1</sup> for all pulping experiments. Pulping was carried out in micro-bombs that could accommodate 40 g 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 (uncooked material) 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 (uncooked fibre bundles) and then spin dried to a consistency of approximately 30%.

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

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

Р	re-extracti	on conditi	ons			Liqu	uid fraction				c	Solid fractic	n	<sup>d</sup> E	MB
Run	$H_2SO_4$ ,	Temp.,	Time,	Xyl,	<sup>a</sup> Xyl, %	Xylo-	<sup>b</sup> Xyl recovery	Glc,	Acetic	Furfural +	Glc,	Xyl,	AIL,	Glc,	Xyl,
Kull	%	°Ċ	min	%	theoretical	oligomers, %	yield, %	%	acid, g/L	HMF, g/L	%	%	%	%	%
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	-9.4	41.1	2.0	0.2	0.28	44.9	12.2	18.5	99	97.6
						Star	point acid concer	ntration							
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
						S	star point tempera	ture							
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	-3.2	36.1	1.7	0.1	0.3	43.0	14.5	19.3	98.2	95.3
						S	tar 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	<b>99.</b> 7	98.1

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

<sup>a</sup>Analysis data are based on oven-dry xylan of non-extracted SCB; <sup>b</sup>Obtained by addition of Xylose (% theoretical) and Xylo-oligomer (%); <sup>c</sup> Analysis data are based on oven-dry nonextracted SCB; <sup>d</sup>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 was 1.5% and 23.3% respectively, and the raw SCB had 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

Р	Pre-extraction conditions		ons	Ху	Xylan pre-extraction efficiency					after	<b>°</b> EMB, %		
Run	NaOH, M	Temp, °C	Time, min	Xyl. precipitate yield, %	<sup>a</sup> Xyl recovery yield, %	Lignin, % xylan	Lignin, % dry raw SCB	Glc, %	Xyl, %	AIL, %	Glc	Xyl	ASL
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 c	oncentration	1						
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 tem	perature							
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 reac	tion 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 p	oint							
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

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

<sup>a</sup>Analysis data are based on oven-dry xylan of non-extracted SCB; <sup>b</sup>Analysis data are based on oven-dry non-extracted SCB; <sup>c</sup> Extraction mass balance (EMB) is calculated as explained in Table 2; \*Xyl – Xylan; Glc – Glucan; AIL – Acid insoluble lignin; ASL – Acid soluble lignin

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.

Pulp yield (%) = 100 x Oven dry mass of pulp/ Initial oven dry mass SCB (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 (parameter related to residual lignin content in pulp) was determined by standard TAPPI method T236 cm-85.

#### Large scale pulping

The best results obtained from micro-pulping were repeated on a large scale. The 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 soda-AQ pulping process. Pulping of 500 g ODM preextracted was carried out in a 15 dm<sup>3</sup> batch type digester. Soda-AQ pulping conditions for hot water were as follows: 14% AA and 0.1% AQ, 30 min at 170 °C. In the case of mild alkaline pre-extracted residues, no additional NaOH and only 0.1% AQ were added to the SCB fibres. Alternatively, 500 g dry mass of the dilute acid pre-extracted from run 15 (0.3% v/v H<sub>2</sub>SO<sub>4</sub>, 120 °C and 40 min) was subjected to kraft pulping under the following conditions: 12% AA and 20% sulfidity.<sup>32</sup> All SCB fibres were digested for 30 min at 170 °C and the products of pulping were treated as per section 2.5.

All active alkali and sulfidity masses are expressed as equivalent mass of Na<sub>2</sub>O.

#### Characterization of pulping black liquors

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

#### Pulp evaluation and handsheet formation

Pulp tests were performed according to TAPPI standard methods.<sup>28</sup> Total pulp yield and rejects were determined as a percentage of the ODM of the raw material. Pulp kappa number (parameter related to residual lignin content in pulp) 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.

#### Testing of physical properties of the handsheets

All handsheets were conditioned for 48 hours at 55% relative humidity and 23 °C before testing. The following strength properties were evaluated for 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 Standards 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).

#### **RESULTS AND DISCUSSION 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 nature of field operations of SCB that resulted in contamination with soil.<sup>5,6,8</sup>

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

SCB constitutes an alternative to the wellestablished wood sources of fibre. Its high holocelluloses content together with lower lignin makes this feedstock a good candidate for the integration of increased hemicelluloses preextraction prior to pulping and the production of high pulp yields when the material is well depithed.

# Effect of xylan pre-extraction on sugarcane bagasse

#### 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 preextraction process that may inhibit possible subsequent biological conversion.<sup>34</sup> ASL was also considered as an impurity for mild alkaline preextracted xylan.<sup>19</sup>

The results show that dilute sulphuric acid conditions can selectively solubilize xylan from SCB, originating liquid fractions rich with xylooligomers 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<sub>2</sub>SO<sub>4</sub> 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 inhibition for subsequent fermentation of 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.<sup>34</sup> Under these conditions, less than 3% of the cellulose and lignin content of SCB was solubilised, indicating little or no degradation of these polymers.

 Table 4

 Chemical composition of non-extracted sugarcane bagasse\*

Component	SCB	Analytical methods
Ethanol/cyclohexane soluble extractives	$1.7 \pm 0.5$	TAPPI T264 om-88
Water soluble extractives	$2.4 \pm 1.0$	TAPP1 1204 011-88
Glucan	$46.3 \pm 2.5$	
Xylan	$25.9 \pm 2.1$	LAP 013
Arabinan	$2.1 \pm 1.0$	LAP 013
Acetyl group	$2.6 \pm 0.7$	
Acid insoluble lignin	$18.2 \pm 2.1$	TAPPI T222 om-88
Ash	$2.6 \pm 1.2$	TAPPI T211 om-85

\*Components are expressed as weight percentage of original oven-dry material (% ODM)

Alternatively, xylan can be quantitatively recovered from SCB with mild alkaline conditions (Table 3). The 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 of 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:

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

According to Equation (1), both acid concentration  $(x_1)$  and temperature  $(x_2)$  are 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.<sup>27</sup>

$$y_2 = 19.1 + 5.2x_1 + 3.9x_2 - 3.7x_2^2$$
(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 the degradation of xylan. This fact is supported by the formation of furfural at 154 °C and corroborated in other studies (Table 2, run 12).<sup>4</sup> In the case of mild alkaline pre-extraction (Figure 1B), the optimal xylan yield could 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.

# 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.<sup>16</sup> This 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.<sup>5</sup>

On this basis, the average molecular mass of a xylan sample obtained under the alkaline preextraction conditions of run 15 (1.5 M NaOH; 65 °C for 180 min) was estimated by the size exclusion chromatography (SEC). The xylan preextraction carried out under these conditions resulted in a cellulose rich solid residue that was selected for subsequent soda or soda-AQ pulping evaluation and optimisation. The average molecular mass of the xylan sample obtained by SEC was approximately 32,793 g mol<sup>-1</sup>, which was within the range of the structural characterization carried out by Sun *et al.*<sup>5</sup> The high molecular weight xylan can be used in paper and corrugated board applications.<sup>7</sup>

Further analysis of the xylan component obtained under the conditions of run 15 was performed by FT-IR spectroscopy to determine the changes of the structure during alkaline preextraction. The FT-IR spectra of the xylan

obtained were similar to those of commercial oat spelt xylan (Figure 3). However, in the preextracted xylan, the intensity of 3288, 2918 and 1403 cm<sup>-1</sup> bands was much lower than that of oat spelt xylan (3346, 2921 and 1412 cm<sup>-1</sup>), suggesting lower concentration of O-H. C-H and CH<sub>2</sub> linkages, respectively. It was also noted that the band at 1034 cm<sup>-1</sup>, which was ascribed to C-O, C-C and C-OH linkages, appeared in both xylan samples. A sharp band at 897 cm<sup>-1</sup> indicated the presence of  $\beta$ -glucosidic linkage (C–O–C) between the sugar units in the hemicelluloses.<sup>5</sup> Obviously the appearance of bands (1243, 1558 and 1574 cm<sup>-1</sup>) corresponding to lignin were observed in alkaline pre-extracted xylan sample.<sup>5,35</sup> The presence of lignin could limit the application of the xylan in various paper products as the lignin reduces the brightness of the xylan.<sup>36</sup> 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.<sup>19</sup> Therefore this option was not considered in the present study.

#### 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 a reduced lignin content would be beneficial to retain the potential as feedstock for the subsequent pulping processes. Moreover, some of the hemicelluloses are required in the lignocellulose residues, as some are necessary to contribute to the quality of pulps obtained from these residues.<sup>37</sup> 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 (Figure 3).

Dilute acid pre-extraction of xylan showed no impact on the 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.

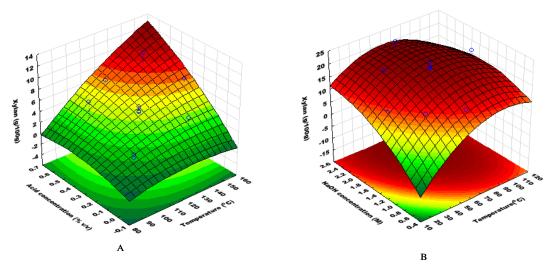


Figure 1: A) Estimated response surface for xylan yield obtained after sulphuric acid hydrolysis showing the influence of temperature and acid concentration for a residence time of 40 min; (B) Estimated response surface for xylan yield obtained after NaOH extraction showing the influence of temperature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

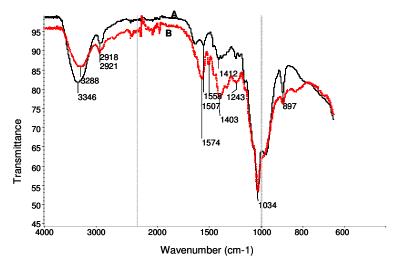
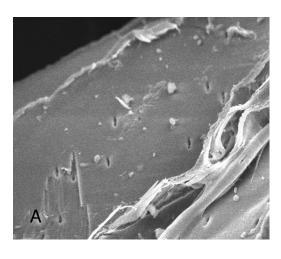


Figure 2: FT-IR spectra of A) commercial oat spelt xylan; and B) xylan fraction extracted from sugarcane bagasse with 1.5 NaOH at 65 °C for 180 min

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 (Figure 3C) due to mild alkaline xylan pre-extraction.

The amount of hemicelluloses retained in the solid residue depended on the solubilisation yield during the pre-extraction step. The hemicelluloses 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.



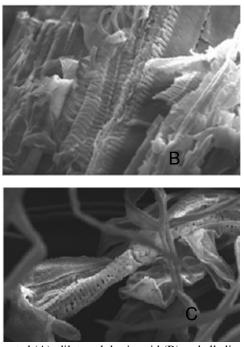


Figure 3: Scanning electron microscope micrographs of non-extracted (A), dilute sulphuric acid (B) and alkaline (C) pre-extracted sugarcane bagasse residues

#### **Properties of the pulps** Pulp evaluation on micro-scale

In order to assess the efficiency of xylan preextraction 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 soda-AQ micro-pulping. Solid residue obtained from dilute sulphuric acid pre-extraction from run 15 (0.3% v/v H<sub>2</sub>SO<sub>4</sub>, 120 °C for 40 min) was used, containing 45.0% glucan, 14.6% xylan and 18.4% lignin contents. Hot water pre-extraction resulted in a solid residue with 43.8% glucan, 23.3% xylan and 18.3% lignin. 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 nonextracted 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 soda-AQ pulping. Likewise, the pulping results obtained after alkaline pre-extraction are shown in Table 7.

Among the pulping processes used, soda-AQ 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 the pulping process.<sup>22</sup> 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 soda-AQ 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 what was 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, which is known to be difficult to oxidize and solubilize during pulping.<sup>20,38</sup> Therefore, more alkali would be required to improve delignification of acid preextracted solid residue. On the contrary, soda-AQ pulping of hot water pre-extracted SCB under the best conditions (14%NaOH, 0.1% AO for 30 min) improved the screened pulp yield up to 53.6% at lower kappa number (28.9) and rejects level (0.5).

As expected, soda-AQ pulping of alkaline preextracted 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 the requirements of the final product.

### Pulp evaluation on a large scale

Soda-AO pulping of mild alkaline and hot water pre-extracted solid residues was repeated on a large scale in order to confirm the micropulping results. Kraft pulping was applied on a large scale for dilute acid pre-extracted residues, since it is more efficient in the delignification of highly lignified wood chips.<sup>12</sup> 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 lower rejects levels, compared to pulping of nonextracted SCB. The 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 (Figure 4).<sup>17</sup> 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 soda-AQ pulping used.<sup>8</sup> Similar benefits on pulp properties have been proved in other herbaceous materials, such as

cereal straw, by integration of alkali preextraction of hemicelluloses with soda-AO pulping.27

Alternatively, the combined process of hot water pre-extraction together with soda-AQ pulping of the solid residue showed a similar screened pulp yield, with a 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.<sup>17</sup>

The chemical composition of the soda-AQ pulps showed a reduction in xylan content due to pre-extraction, which might affect the handsheet strength properties.<sup>22</sup> Several studies emphasized the importance of xylan for the strength properties of pulp fibres.39,40

Compared with soda or soda-AQ 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%), results that were comparable with the values obtained for the kraft pulps of delignified SCB with Panus tigrinus strain.<sup>32</sup> Although the 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.<sup>1</sup>

#### Strength properties of handsheets

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.<sup>43</sup> Thus, pre-extraction of xylan was expected to impact the bonding strength properties of the handsheets produced from these pulps. The burst index, tear index, breaking length and ISO brightness properties of handsheets produced from soda-AQ (Figure 4) or kraft (Figure 5) pulping of xylan pre-extracted SCB were compared with those produced from non-extracted SCB. The tensiletear relationship of the soda-AO pulps is given in Figure 6. All the pulps were beaten to enhance the fibre-fibre bonding, thereby improving the strength properties of the handsheets. Strength properties were found to increase with increased beating, up to 40 °SR for soda-AQ pulps, whereas 45 °SR was optimum for kraft pulps.

Interestingly, alkaline conditions for hemicellulose extraction provided brighter soda-AQ pulps with superior tear index by 56%. The burst index and breaking length were similar to those of the pulps produced from non-extracted SCB. While burst and breaking length correlate strongly with fibre bonding, tear index also depends strongly on fibre length.<sup>31</sup> These results suggest that fibres were well bonded to one another and thus presented good conformability without fibre shortening. On several occasions, for evaluating tear strength, it is more meaningful to compare tear strength at a certain tensile level (Figure 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.<sup>41</sup> The overall improvements in pulp yield and handsheet strength properties associated with alkaline pre-extraction of SCB together with the recovered xylan complement the proposed pulp mill biorefinery concept.<sup>11</sup>

In line with this study, the strength properties of the soda-AQ pulps produced from alkaline preextracted cereal straw remained at a very good level.<sup>27</sup> The high strength values of the pulps could be advantageous for pulps used for packaging papers, but of secondary importance when used in printing and writing papers.<sup>31</sup>

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	Degr freed		Mean	square	F-value		Prob>F		
Model	y <sub>1</sub> 202.59	y <sub>2</sub> 333.03	y <sub>1</sub> 9	y <sub>2</sub> 6	y <sub>1</sub> 22.51	y <sub>2</sub> 55.5	y <sub>1</sub> 30.43	$\begin{array}{c} y_2\\ 3.26\end{array}$	y <sub>1</sub> <0.00001	$y_2 \\ 0.0482$	
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 R <sup>2</sup>	207.77 0.97	503.36 0.82	16	16							

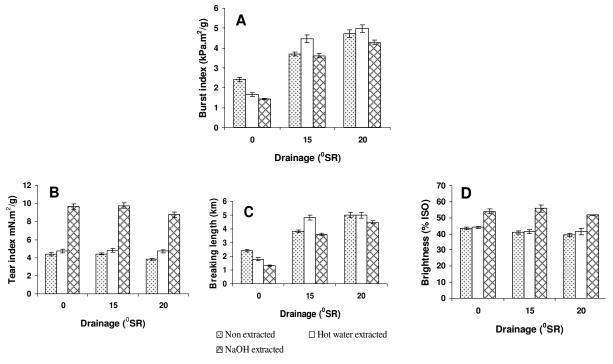


Figure 4: Handsheet properties as a function of drainage of sugarcane bagasse after soda-AQ pulping on a large scale

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						Soda						
	Cooking			Noi	n-extraction		Hot	water extrac	tion		Acid extract	ion
	conditions						(12	20 °C, 40 mi	n )	(0.3% v/	$v H_2 SO_4, 120$	°C, 40 min)
Run	Active alkali,	AQ, %	Time at	Screened	Rejects,	Kappa	Screened	Rejects,	Kappa	Screened	Rejects,	Kappa
	% DM	DM	170 °C,	pulp yield,	%	number	pulp	%	number	pulp	%	number
			min	%			yield, %			yield, %		
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
					Sod	la-anthraqui	inone					
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 6Soda 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<sub>2</sub>SO<sub>4</sub>, 120 °C, and 40 min) xylo-oligomer extracted sugarcane bagasse residues

Table 7

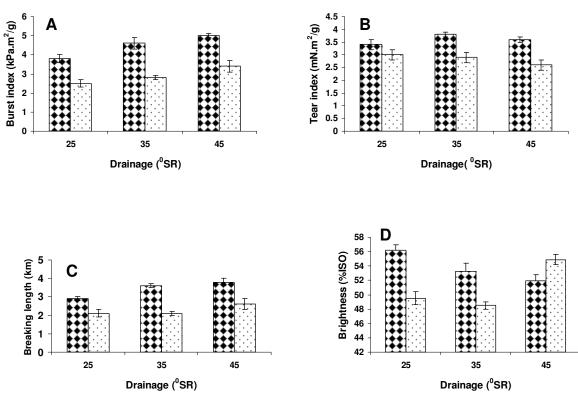
Soda-AQ micro-pulping conditions, pulp yield and properties for non-extracted and 69.1% (1.5M NaOH, 65 °C, and 180 min) xylan extracted sugarcane bagasse residues

				Non-	extraction		1.5M NaOH, 65 °C and 180 min		
Replicates	NaOH in	AQ,	Time at 170 °C,	Screened pulp	Rejects,	Kappa	Screened pulp	Rejects,	Kappa
Replicates	residue, g	% DM	min	yield, %	%	number	yield, %	%	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 on a large scale

Pulping process		Soda-AQ	Kraft			
	Non-	Hot water, 120	1.5M NaOH, 65	Non-	0.3 v/v H <sub>2</sub> SO4,	
	extraction	°C, 40 min	°C, 240 min	extraction	120 °C, 40min	
Pulping conditions						
Active alkali as Na <sub>2</sub> O (%)	14.0	14.0		12.0	12.0	
Anthraquinone (%)	0.1	0.1	0.1			
Sulfidity as Na <sub>2</sub> O (%)				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			



□ Non extracted □ acid extracted

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

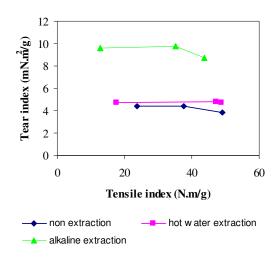


Figure 6: Tensile-tear relationship of non-extracted, hot water and alkaline extracted sugarcane bagasse after soda-AQ pulping in large scale

Regarding the physical strength properties of the soda-AQ 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 were similar, whilst the optical brightness was reduced by 4%. Fibre weakening during soda-AO pulping of hot water pre-extracted residue indicated by the viscosity reduction was to some extent compensated by the improved bonding ability 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 nonextracted SCB. The strength values obtained in this study resembled those found when hot water pre-extracted SCB was previously subjected to soda-AQ pulping.17

The overall strength properties of kraft pulps from acid pre-extracted residues were significantly reduced (Figure 5). Compared to non-extracted SCB pulp, there was a significant reduction in both tear strength and breaking length, but the optical brightness of the pulps was similar. This could be attributed to the nonselectivity 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.<sup>42</sup> These results showed that kraft pulping of acid pre-extracted residue had to be optimised to maintain strength properties at higher levels.

#### CONCLUSION

Sugarcane bagasse has proven to be a feasible raw material for production of xylan-rich liquid fractions by suitable dilute acid or alkaline preextraction conditions prior to chemical pulping processes, which could be used as a substrate for further industrial practices. Although from the perspective of pulp production in the biorefinery concept, it has been shown that dilute acid preextractions 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 soda-AQ pulping, resulting in an increase in pulp yield and lower kappa number, although the viscosity was compromised. The tear and burst indexes 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 soda-AQ 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 at the same level as those of pulps produced from non-extracted SCB. Alkali extraction combined with soda-AQ pulping was therefore the preferred option for SCB.

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