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Effect of pre-hydrolysis on the soda-anthraquinone pulping of corn stalks and *Saccharum spontaneum* (kash)

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ABSTRACT

The limited reserves of fossil fuel and trend of global warming increase interest in renewable resources. In this circumstance, significance has been developed on the production of fuels and chemicals from biomass that will replace fossil fuel. Corn stalks and *Saccharum spontaneum* (kash) are agricultural wastes, which are good raw materials for pulp production. However, there are limitations in achieving the desired pulp quality due to the presence of pith. The pith constitutes 20–35% of the dry matter of the raw materials. It must be removed prior to pulping to obtain good quality pulp. Chemically pith is similar to lignocellulosic, but it does not have fibrous structure. So the pith can be used in producing fuels and chemicals.

Pre-hydrolysis prior to soda-AQ pulping of corn stalks and kash was carried out in order to remove pith as well as to extract hemicelluloses for use as fuel and chemicals. The pre-hydrolysis was performed at 150 °C for 1 h. Pre-hydrolysis extracted 50–60 kg sugars, 28–34 kg lignin and 8–22 kg acetic acid per tonne of corn stalks/kash with the sacrifice of pulp yield. Pre-hydrolysed pulp had less fines resulting in lower drainage resistance (^{0}SR) as compared to non-prehydrolysed counterpart. Pulp produced from the pre-hydrolysed corn stalks and kash had higher tear index but lower tensile index than the non-prehydrolysed counterpart. The pre-hydrolysis process requires careful optimization of the pulping process, and allows lower chemical charges. After $D_0E_pD_1$ bleaching, the differences of pulp yield and physical properties were reduced. The pre-hydrolysed pulp showed almost similar bleachability to non pre-hydrolysed pulp.

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1. Introduction

Increasing greenhouse gas emission and the world petroleum supply depletion have increased interest on alternative renewable resources to replace fossil fuel. The use of biofuels will significantly reduce the net carbon dioxide emission once it replaces fossil fuels because fermentation-derived ethanol is already a part of the global carbon cycle. Therefore, much interest is growing on the Integrated Forest Biorefinery. In this concept, in addition to pulp, chemicals and energy will be produced that will make the mill more profitable and reduce greenhouse gas emissions. In this concept, the hemicelluloses (oligomers and monomers) are extracted to produce new biomaterials and biofuels prior to pulping (van Heiningen, 2006; van Heiningen, Zou, Yoon, Jiang, & Goyal, 2006). An ideal implementation of the integrated biorefinery would not change pulp yield (Al-Dajani & Tschirner, 2008). The only change would be that some of the wood components that are not retained in the pulp would be intentionally directed to the highest economic end use.

Bangladesh is a forest deficient country. So it is critical to find out alternative fibrous maw materials. Many studies have been carried out on alternative fibrous raw materials (Jahan, Chowdhury, Russel, Mun, & Quaiyyum, 2006; Jahan & Farouqui, 2001; Jahan, Farouqui, & Islam, 2000; Jahan, Khalidul Islam, Chowdhury, Iqbal Moeiz, & Arman, 2007; Jahan, Moynul Hasan, Islam, & Chowdhury, 2002). Corn stalks, kash, bagasse, etc. are agricultural wastes in Bangladesh that could be used as fibrous maw materials. As early as 1960, there were reports on the preparation of dissolving grade and high α-cellulose pulp using sugarcane bagasse (Andre, 1960; Htut et al., 1977). However, there were limitations in achieving the desired pulp quality due to the presence of pith in bagasse. Approximately 33–35% of the oven-dry weight of sugar cane bagasse is pith, while corn stalks have a pith content of approximately 21% (Atchison, 1987). It was observed that pith content in kash was about 25%. The problems associated with the presence of pith on pulping and on black liquor characteristics were studied by Kulkarni, Mathur, Naithani, and Pant (1986). In the conventional moist/dry depithing process, fibres can suffer a considerable damage. The mechanical depithing process contributes to an environmental disposal problem. In the conventional depithing process, fibres are damaged during hammering and some useful fibre are lost with pith. This removed pith creates heavy disposal problem. Chemically pith is similar to lignocellulosic materials, but it does not have fibrous structure (Morris Wayman, 1973).

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There has always been interest in the efficient removal of this pith from the fibrous portion of corn stalks and kash so that they could be used for making good quality pulp and paper. In our earlier investigation, it was observed that pith could be efficiently removed from bagasse by pre-extraction (Jahan, Saeed, Ni, & He, 2009) and consequently increased percentage of sugars in the pre-extracted liquor. Corn stalks and kash pith contains a high amount of hemicelluloses (Sanjuán, Anzaldo, Vargas, Turrado, & Patt, 2001) that are valuable raw materials for many value-added products.

Alkaline or acidic extraction of high pith containing raw material prior to pulping may reduce pith and contribute sugars in the pre-extracted liquor. Hemicellulosics can be used directly in polymeric form for novel industrial applications such as biopolymers (Ebringerova, Hromadkova, Kacurakova, & Antal, 1994), hydrogels (Gabrielii, Gatenholm, Glasser, Jain, & Kenne, 2000), or thermoplastic xylan derivatives (Jain, Sjostedt, & Glasser, 2000), or, once hydrolysed, they can serve as a source of sugars for fermentation to fuels, such as ethanol (Niu, Molefe, & Frost, 2003). Pre-extraction may serve for both the purposes of pith removal and recovery of the valuable hemicelluloses for value-added products.

In this paper, hot-water pre-prehydrolysis of corn stalks and kash was carried out to remove pith and recover of hemicelluloses. Subsequently, the extracted corn stalks and kash were subjected to soda-anthraquinone (AQ) pulping and the pulp qualities and bleachability were also evaluated.

2. Experimental

2.1. Raw materials

Corn stalks and kash were collected and cut to 2–3 cm in length. After determination of the moisture content of air dried raw materials, an equivalent to 100 g o.d. (oven dried) was weighed separately in a polyethylene bags for subsequent prehydrolysis and cooking experiments.

2.2. Chemical analysis

The chemical compositions of pith and fibre bundles were carried out by following TAPPI Test Methods: the extractive (T204 om88), water solubility (T207 cm99), Klason lignin (T211 om83). The holocellulose was prepared by treating extractive free bagasse meal with $NaClO_2$ solution (Browining, 1967). The pH of the solution was maintained at 4 by adding $CH_3COOH—CH_3COONa$ buffer and α-cellulose was determined by treating holocellulose with 17.5% NaOH (T203 om93).

2.3. Pre-extraction

The pre-extraction was carried out in an electrically heated oil bath containing 4 bombs each of 1.5 l capacity, The bombs were rotated at 1 rpm. Water pre-extraction was carried out at 150 °C for 60 min. The raw material to liquor ratio was 1:6. The time required to reach maximum temperature was 50 min. After completing prehydrolysis, the bombs were cooled by dipping in cold water and the liquor was drained for analysis.

2.4. Lignin analysis

The dissolved lignin in the pre-hydrolysate was measured based on the UV/Vis spectrometric method at wavelength 205 nm (TAPPI UM 250) or 280 nm (Dence & Lin, 1992). At 280 nm furfural and HMF adsorption strongly interfere with the lignin absorption because their specific adsorption coefficient are more than tenfold higher than for lignin. At 205 nm wavelength furfural and HMF adsorption play only a minor role, therefore the lignin concentration was measured at this wavelength.

2.5. Acetic acid

Acetic acid in the pre-hydrolysate (PHL) was dehydrated by anhydrous sodium sulphate. 1 μL was injected into Gas Chromatograph (GC). Pure glacial acetic acid (GAA) was used as reference standard. Analysis of GAA was carried out on Gas Chromatograph model 14B, Shimadzu, Japan loaded with software Class GC-10 (version-20). The GC was equipped with Flame Ionization Detector (FID) and Capillary Column, FAMEWAX, dimension 15 m × 0.25 mm RESTEC. Before injection the column was conditioned at 180 °C for about 2 h for attaining thermal stability before use. The temperature of the column oven, injection port and detector were 180 °C, 240 °C and 250 °C, respectively.

2.6. Solid contents

The total solid content in the PHL was determined by drying at 105 °C to constant weight.

2.7. Pulping

Pulping of pre-extracted and without pre-extracted corn stalks and kash was done by the soda-anthraquinone (AQ) process in the same digester. Active alkali charge was varied from 14, 16 and 18% on o.d. raw materials or pre-extracted raw materials residue. The following parameters were kept constant in the soda process:

- Anthraquinone charge: 0.1% on o.d. raw materials
- Liquor to fibre ratio: 6:1.
- Temperature was 150 °C.
- Cooking time: 60 min at 150 °C.

2.8. Evaluation of pulps

Pre-extracted and non-extracted corn stalks and kash pulps were beaten in a PFI mill in different revolution and handsheets of about 60 g/m^2 were made in a Rapid Kothen Sheet Making Machine. The sheets were tested for tensile (T494 om-96), burst (T403 om-97) and tear strength (T414 om-98) according to TAPPI Standard Test Methods.

3. Results and discussion

3.1. Pre-hydrolysis

Forest products companies may increase revenue by producing biofuels and chemicals in addition to pulp products in an Integrated Forest Biorefinery (IFBR). In such biorefinery, hemicelluloses are extracted prior to pulping and used for the production of hemicellulose based biomaterial, fuel, acetic acid, etc. The water pre-extraction of corn stalks and kash were carried out 150 °C for 1 h. Pre-hydrolysis dissolved 12.2% biomass components from corn stalks and 11.9% from kash on a dry weight basis.

Acetic acid is an important by-products of the hemicelluloses extraction process. The acetic acid liberated from the corn stalks during hemicelluloses extraction was 2.26%, while it was 0.84% for kash on a dry weight basis. The mechanism of hot water extraction depended in part on the cleavage of *O*-acetyl and uronic acid substitutions that resulted in formation of acetic and other organic acids. Generated acetic acid increased the hydrolysis rate of hemicelluloses (Liu, 2008). Acetyl groups are liberated from the hemicelluloses in the form of acetate when pH is above the p*K*a of acetic acid. At low pH, the acetyl groups lead to the formation of

Table 1
Chemical composition of pre-hydrolysis liquor.

Raw materials	Yield (%)	PHL (% on o.d. raw materials)		
		Solid content	Lignin	Acetic acid
Corn stalks	87.8	10.9	2.8	2.26
Kash	88.1	11.2	3.4	0.84

acetic acid. Concentration of acetic acid in the PHL increased with the increase of pre-hydrolysed H-factor (Walton, Hutto, Genco, Walsum, & van Heiningen, 2010).

The lignin in the PHL was found to be 2.8% for corn stalks and 3.4% for kash (Table 1), which was 25.7 and 30.4% of total solid content of PHL. Lignin degraded phenolics are inhibitors to the downstream fermentation process. It should be removed from the PHL before fermentation process. But this lignin can be the starting material for high value-added applications in renewable polymeric materials development (Kadla et al., 2002; Kouisni et al., 2011; Satheesh, Mohanty, Erickson, & Misra, 2009). The value added applications of lignin not only helps to improve the economic possibility of the biorefinery but also serves as a source of renewable materials.

The solid content in the pre-hydrolysed liquor (PHL) was above 10%. The biomass residue after pre-hydrolysis and solid content in the PHL was close to 99% in both raw materials. This 1% loss in the mass balance due to the degradation in unknown products. This harmonizes with the finding of our previous results (Jahan, Rahman, Nuruddin, Haque, & Chowdhury, 2011) and other researchers (Leschinnsky, Sixta, & Patt, 2009; Tunc & van Heiningen, 2008). The remaining parts of solid content apart from lignin and acetic acid was hemicelluloses. For paper pulp, complete removal of hemicelluloses is unnecessary because they play an important role in formation of sheets and facilitate fibre bonding in sheets. In the present investigation, the purpose of pre-hydrolysis was to remove pith and improve pulping efficiency of pith containing non-wood.

3.2. Pulping

Pulping of pre-hydrolysed and non-hydrolysed (as the reference) corn stalks and kash was carried out by the soda-AQ process and results are given in Table 2. Improved delignification was observed for pre-hydrolysed corn stalks and kash verses the non-hydrolysed counterpart. At 16% alkali charge, the kappa numbers for pre-hydrolysed corn stalks and kash were 2.7 and 2.1 points lower than the non-hydrolysed corn stalks and kash. Jahan et al. (2009) also observed faster delignification for hot-water pre-hydrolysed bagasse. Yoon and van Heiningen (2008) observed 40–60% faster delignification rate of extracted loblolly pine than the corresponding control cook. The unbleached pulp yield of the pre-hydrolysed corn stalks and kash was lower than that of the non-hydrolysed raw materials (Fig. 1). At kappa number 20, pulp was reduced by 3% for corn stalks and 4.5% for kash. Similar results were observed for the pre-hydrolysed bagasse pulping (Jahan et al., 2009). Yoon and van Heiningen's (2008) obtained 3–6% less pulp yield when loblolly pine was pre-hydrolysed with hot-water.

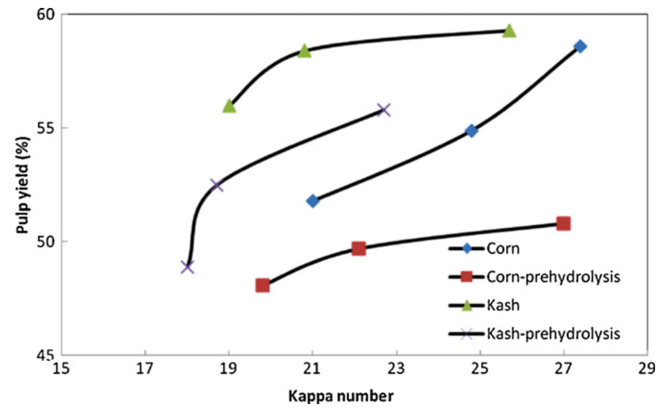

Fig. 1. Effect of pre-extraction on the delignification of corn stalks and kash.

The initial pulp drainage resistance (^{0}SR) is an important parameter for pulp process unit operations, for example, pulp (brownstock) washing efficiency. The initial drainage resistance (measured as Schopper-Riegler beating degree) of pre-hydrolysed pulp was 23–24 ^{0}SR while non-hydrolysed pulp was 31–34 ^{0}SR for corn stalks and 16–17 verses 13–14 for kash. This decrease of drainage resistance certainly improve pulp washing efficiency. High specific area caused the poor drainability of non-hydrolysed pulp due to the high amount of fines in the non-hydrolysed pulp. This was due to high amount of fines in the non-hydrolysed pulp (Jahan et al., 2009). Fig. 2 shows that the non-hydrolysed pulp contained many nonfibrous pith cells while the pre-hydrolysed pulp was relatively clean. Therefore, it is evident that the pre-hydrolysis can effectively dissolve the pith while producing sugars in the PHL.

3.3. Papermaking properties

To evaluate its papermaking properties, the pre-hydrolysed corn stalks and kash pulps were refined in a PFI mill for various revolutions. Fig. 3 shows that the initial drainage resistance SR of the pre-hydrolysed pulps was slightly lower verses the non-hydrolysed pulps, and the development of the SR value of the pre-hydrolysed pulps was also slower due to the loss of fines during pre-extraction stage (Fig. 2). It is shown in Figs. 4 and 5 that the tensile and burst indexes of the pre-hydrolysed pulps were inferior than those of the non-hydrolysed pulp. At 40 ^{0}SR, the tensile index and burst index of the pre-hydrolysed pulps were almost similar. The difference become pronounce at higher ^{0}SR. This may be explained by the loss of hemicelluloses of the pre-hydrolysed pulps. Due to hemicelluloses extraction, the pulp had higher cellulose/hemicelluloses ratios than the non-extracted pulp. Several studies have emphasized the importance of hemicelluloses for the strength properties of pulp fibres. Molin and Teder (2002) showed that fibres with high cellulose/hemicelluloses ratio had lower tensile stiffness and tensile index. Schönberg, Oksanen, Suurnäkki, Kettunen, and Buchert (2001) showed that the tensile index was increased after sorption of xylan to the fibres. The role of xylan in the fibres was further investigated. The chemical sorption of xylan was found to significantly

Table 2
Effects of pre-extraction on the soda-AQ pulping of corn stalks and kash.

	Corn stalk						Kash					
	Without prehydrolysis			Prehydrolysis			Without prehydrolysis			Prehydrolysis		
Alkali charge (%)	14	16	18	14	16	18	14	16	18	14	16	18
Pulp yield (%)	58.6	54.9	51.8	50.8	49.7	48.1	59.3	58.4	56.0	55.8	52.5	48.9
Kappa number	27.4	24.8	21.0	27.0	22.1	19.8	25.7	20.8	19.0	22.7	18.7	18.3
Initial ^{0}SR	31	34	32	24	24	23	16	16	17	14	13	14

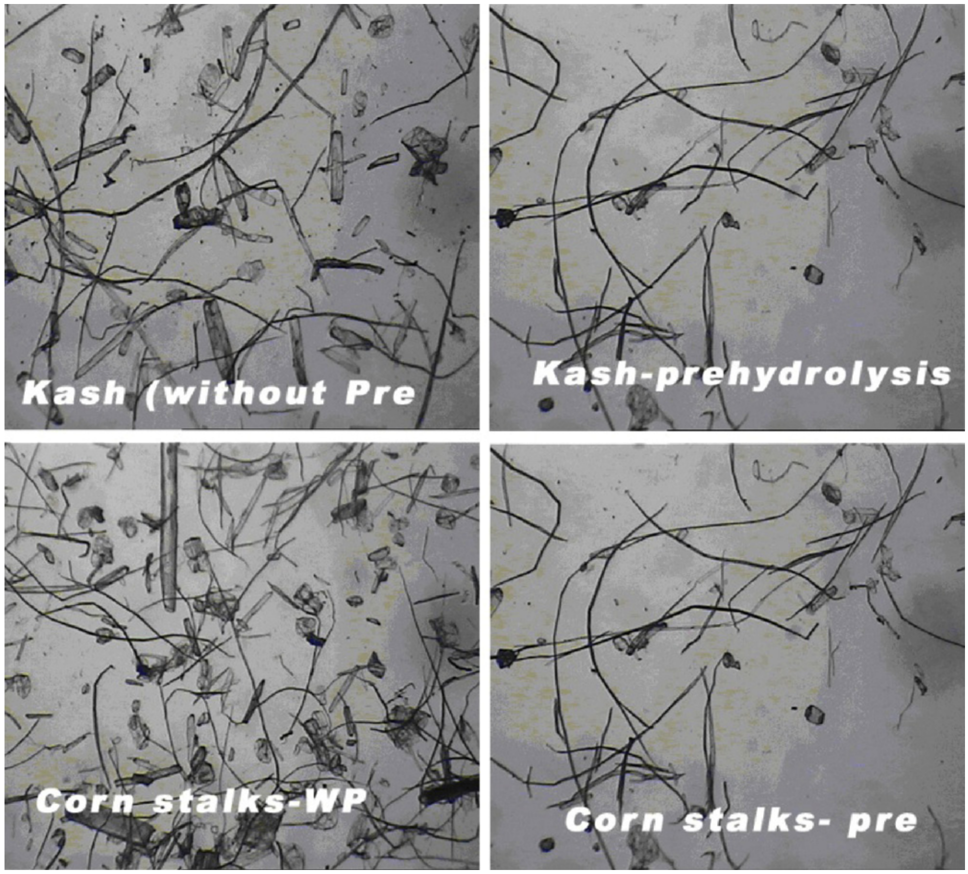

Fig. 2. Effect of pre-extraction on the fines in corn stalks and kash unbleached pulp.

increase the Scott Bond-value, further supporting the significance of xylan on the bonding ability (Schönberg et al., 2001). Addition of 1% (w/w) of hemicelluloses to cellulosic pulp was able to increase the mechanical properties by about 30% (Denis et al., 2003). Al-Dajani and Tschirner (2008) observed that alkaline pre-hydrolysis of aspen prior to pulping reduced the tensile index by 10%. The negative effect of pre-extraction on the tensile strength of kraft pulp loblolly pine was also observed by Yoon and van Heiningen (2008). The tear index of both pre-hydrolysed pulps was higher than the corresponding non pre-hydrolysed pulp (Fig. 6), which indicated that the pre-hydrolysis did not degrade cellulose. The higher tear index of pre-hydrolysed pulps can be explained by lower content of fines. Figs. 6 and 7 represent that the tear index increased in the initial stage of beating followed by decreased with further beating degree. But tensile index increased with beating degree (Fig. 7). This was caused by the removal of the primary wall from the fibres in the initial stage of the beating process, which facilitate inter-fibre bonding. However, excessive beating reduced the fibre length, so decreased the tear index.

3.4. Bleaching

Pre-hydrolysis of hemicelluloses may change bleaching potential of the produced pulps. So unbleached pulps obtained with

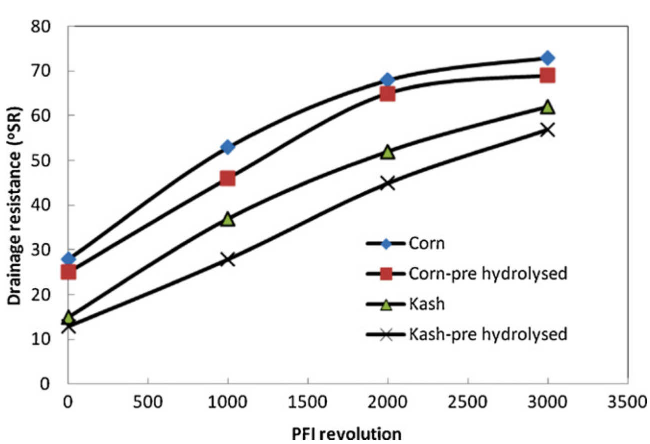

Fig. 3. Effect of pre-hydrolysis on the refining of corn stalks and kash unbleached pulps.

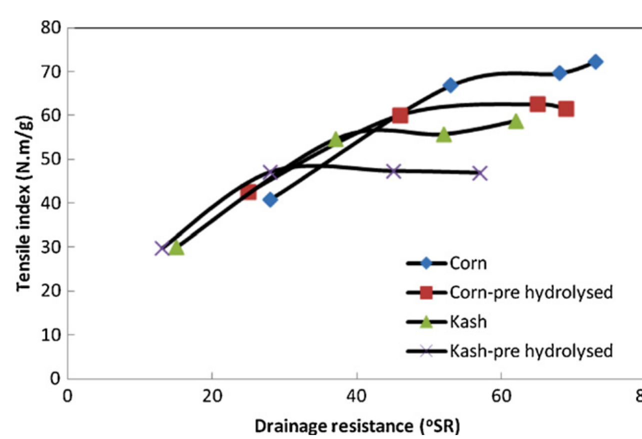

Fig. 4. Effect of pre-hydrolysis on the tensile index development of corn stalks and kash unbleached pulps.

Table 3
Effects of pre-hydrolysis on the bleaching corn stalks and kash.

	Corn stalk		Kash	
	Without pre-hydrolysis	Pre-hydrolysis	Without pre-hydrolysis	Pre-hydrolysis
^{0}SR at 2000 PFI rev	60	57	49	46
Tensile index (N m/g)	56.0	55.9	45.3	35.4
Tear index (mN m^2/g)	7.6	8.0	8.3	11.6
Burst index (kPa m^2/g)	4.7	4.5	4.2	3.5
Brightness (%)	85.4	85.5	84.4	84.8

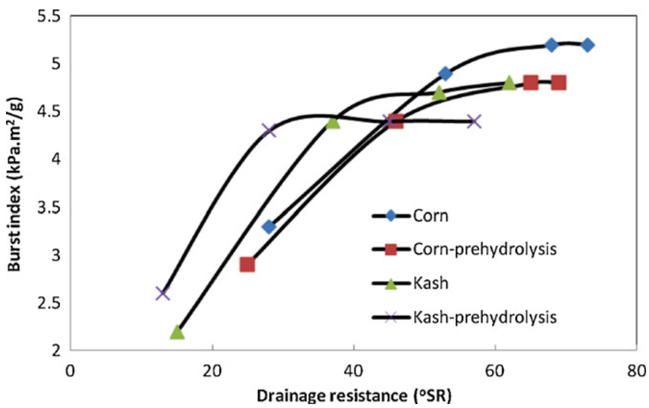

Fig. 5. Effect of pre-hydrolysis on the burst index development of corn stalks and kash unbleached pulps.

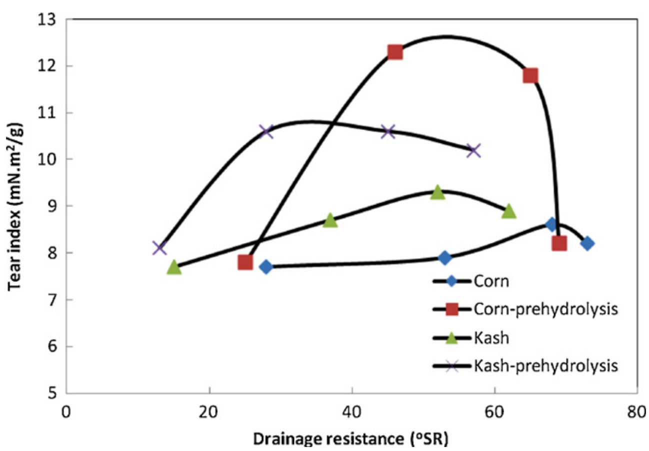

Fig. 6. Effect of pre-hydrolysis on the tear index development of corn stalks and kash unbleached pulps.

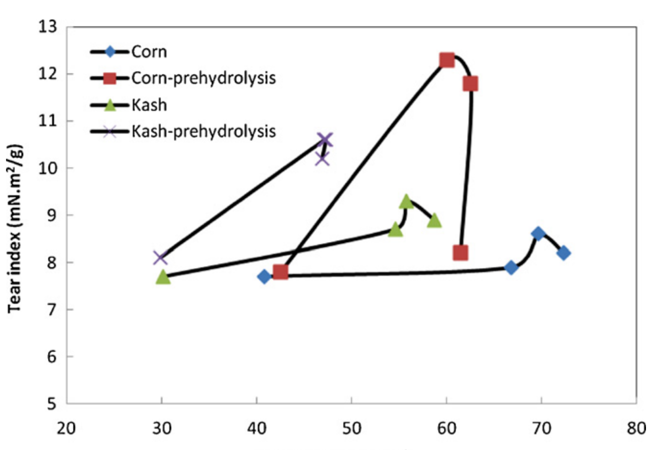

Fig. 7. Tensile-tear relationship of pre-hydrolysed corn stalks and kash unbleached pulps.

and without pre-hydrolysis were subjected to a conventional ECF bleaching ($D_oE_pD_1$) in order to assess the bleachability. The brightness was almost same (84–85%) in all pulps using same bleaching chemicals (Table 3). This indicated that pre-extraction had no impact on pulp bleaching.

For evaluating papermaking properties, bleached pulps were beaten in a PFI mill for 2000 revolution and handsheets were prepared. The ^{0}SR of pre-hydrolysed pulp was 3 points lower than the non pre-hydrolysed pulp due to slightly lower hemicellulose. After bleaching, the tensile index and burst index of pre-hydrolysed corn stalks pulp was almost similar, while these properties of pre-hydrolysed kash pulp were inferior. The tear index of both pre-hydrolysed pulps was higher than the corresponding non pre-hydrolysed pulp.

4. Conclusions

Pre-hydrolysis prior to pulping removed fines, primarily pith, from corn stalks and kash, and consequently increased sugars, lignin and acetic acid in the PHL. Pre-hydrolysed corn stalks and kash showed improved delignification in soda-AQ pulping. The tensile index and burst index of pre-hydrolysed corn stalks and kash unbleached pulps were inferior, while the tear index was superior as compared with the non-hydrolysed counterpart. Pre-hydrolysed pulps showed almost similar bleachability and the gap of strength properties between pre-hydrolysed and non-hydrolysed bleached pulp became narrower. Finally it can be concluded that this new pith removal technique is well suited in an integrated biorefinery concept.

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