Dissolving pulp from white press cuttings

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ABSTRACT: Upgrading of white press cuttings into dissolving pulp was carried out by acidification followed by alkaline extraction. Acid treatment decreased ash content of white press cutting pulp from 11.25% to 0.33% at pH 2. The yield after acidification and screening was 87%. Alkaline extraction removed hemicelluloses and increased α-cellulose content to 92% with viscosity value of 4.3 mPa.s. The overall pulp yield after alkaline extraction was 76.6%. Alkaline extracted liquor contains 9.2% total organics, mostly pentose sugars in the oligomeric form. The produced dissolving pulp can be used for rayon production.

Application: Acid treatment removes minerals and fillers, and alkaline extraction removes hemicellulose from white press cutting pulp, which makes it easier to convert white press cuttings into dissolving pulp.

Wood is still the main source for pulp and paper production, although nonwood fibers occupy a small space. Pulp is of two types: one is paper grade pulp, and another is dissolving grade pulp. Dissolving grade pulp is used as a raw material in the manufacture of different cellulose-derived products, including viscose rayon. In contrast to paper grade pulp, dissolving pulp must contain a high content of cellulose (90%–99%), low content of hemicelluloses (2%–4%), and traces of residual lignin, extractives, and minerals [1]. High brightness and uniform molecular weight distribution are also desired.

Hemicelluloses are undesirable impurities in dissolving pulps, affecting the cellulose processability, e.g., the filterability and the xanthanation in the viscose process, as well as properties of the cellulose end products, such as the tensile strength of viscose. Dissolving pulp is conventionally produced by acid sulfite process and prehydrolysis kraft process [2-3]. However, the prehydrolysis kraft process is the dominant pulping process for dissolving pulp production. In the prehydrolysis kraft process, prehydrolysis is carried out prior to pulping to remove hemicelluloses from the lignocelluloses.

The manufacture of dissolving pulp requires higher costs than the commonly used paper pulp. Prices of dissolving pulp are higher as compared to paper grade pulp due to yield losses through the removal of hemicelluloses and cellulose losses during prehydrolysis and subsequent alkaline treatment in a kraft process. In the search for low cost alternatives, other raw materials have been proposed, such as upgraded paper grade pulp from wood and nonwood.

A number of investigators have tried to upgrade paper pulp into dissolving pulp [4-7]. The scientists claimed that nitren, a metal complex of tris(2-aminoethyl)amine and nickel(II)-hydroxide, selectively removes hemicelluloses from paper grade pulps. The cellulose content of a eucalyptus kraft pulp could be improved from 81% to 96% by a two-stage extraction with a 3% nitren solution. Moreover, xylans of high purity could be precipitated by lowering the pH value to 4. Hincket et al. [3] and Evans et al. [8] studied the conversion of bleached radiata pine kraft pulp and radiata pine bisulfate pulps to chemical cellulose. Both research groups reported that cold alkali extraction of the bleached pulp produced dissolving pulp with satisfactory chemical properties for nitration grade cellulose. The feasibility of producing dissolving pulp from commercial dried bleached hardwood kraft pulp and bleached nonwood soda-anthraquinone (AQ) pulp by enzymatic and chemical treatment was also studied by Ibarra et al. [9]. Eucalypt and sisal pulps showed high improvement in reactivity, reaching levels near or even higher than that of the eucalypt dissolving pulp (65%–70%), and a low hemicellulose content (2%–4%), when both were submitted to a sequence of treatments consisting of an initial xylanase treatment followed by cold alkaline extraction, along with a final endoglucanase treatment. Köpcke et al. [10] also converted paper grade kraft pulp into dissolving grade pulps by enzymatic treatment followed by alkali extraction. This resulted in low residual hemicellulose pulp with improved cellulose reactivity. Borrega and Sixta [11] purified paper grade pulp into dissolving pulp by hot water extraction (HWE). HWE extracted 50%–80% xylan and up to 50% lignin from unbleached birch kraft pulp. Xylan content further decreased with the increase of extraction temperature, but cellulose yield then decreased.

Reports on the conversion of recycle paper into dissolving pulp are scarce. Due to increasing environmental awareness, recovered paper may offer an alternative resource. In the context of Bangladesh, raw materials are very limited. For this reason, other alternatives are being studied. Among them is the conversion of white waste paper into dissolving pulps by selective removal of mineral fillers and hemicelluloses, which

will be explored in this paper. Mineral fillers removal is an essential part in converting waste paper into cellulose pulp. The mineral fillers content varies with paper type. Generally, mineral fillers comprise at least 12% of paper. Toner and mineral fillers removal efficiency of lesser printed waste paper with different pH values (4–10) was studied by Azevedo et al. [12]. Removed hemicelluloses give access to a sugar-rich feedstock, which can be used as downstream feed stock for producing bio-based products.

In this paper, an effort has been made to produce dissolving pulp from white press cuttings. Mineral fillers from waste paper were removed by acidification, and hemicelluloses were extracted by cold and hot alkaline extraction. The produced dissolving pulp was characterized in terms of purity, viscosity, pentosan, alkali solibilities, and brightness.

EXPERIMENTAL

Materials

White press cuttings were collected from a local printing press and torn and immersed in water for 24 h, followed by pulping in a hydropulper. A portion of pulp was taken for moisture determination for the subsequent experiment. A portion of pulp was kept before screening for chemical analysis. Analysis was carried out according to the TAPPI Standard Test Methods: ash (T211 om-02 "Ash in wood, pulp, paper and paperboard: combustion at 525°C"), pentosans (T 223 cm-84 "Pentosans in wood and pulp"), and α-cellulose (T 203 om-88 "Alpha-, beta- and gamma-cellulose in pulp").

Acid treatment

Acid treatment of waste pulp was done in polyethylene bags at 25°C, 50°C, and 90°C for 120 min. The pH values were maintained during acid treatment at 2, 4, and 6 by adding dilute sulfuric acid. The pulp consistency in the acid treatment was 10%. After acid treatment, the pulp was washed with tap water until neutrality, which was followed by screening in a 100 mesh screener to remove the filler. Pulp was filtered, shredded, air dried, and kept in the polyethylene bag. The pulp yield was determined gravimetrically. Ash, pentosane, and α-cellulose content were determined by TAPPI Standard Test Methods as mentioned previously.

Alkaline extraction

Alkaline extraction of acid treated pulp was carried out in polyethylene bags with 8%, 10%, and 12% sodium hydroxide charge (w/w based on pulp) at 25°C, 70°C, and 90°C for 120 min. The pulp consistency was 10%. After alkali treatment, the pulp was washed with water. The pulp yield was determined gravimetrically. Ash, pentosane, and α-cellulose content were determined following TAPPI Standard Test Methods as mentioned previously. The Fock reactivity of the produced pulp was determined by modified method, which is described by Tian et al. [13]. The sodium hydroxide concentration, xanthation temperature, xanthation time, and carbon disulfide dosage were 9%, 19°C, 3 h, and 1.3 mL, respectively.

Analysis of alkaline extracted liquor

The total solids content in the alkaline extracted liquor was determined gravimetrically by drying a 50 ml sample at 105°C to constant weight. Ash content in the alkaline extracted liquor was determined following TAPPI Standard Test Method T 211 om-02. Total organics were determined by subtracting ash content from total solids content.

Evaluation of pulps

After alkaline extraction, pulp tests were performed according to TAPPI Standard Test Methods: brightness (T 452 om-92 "Brightness of pulp, paper, and paperboard [directional reflectance at 457nm]"); viscosity (T 230 om-89 "Viscosity of pulp [capillary viscometer method]"); pentosan (T 223 cm 84), α-cellulose (T 203 om-88), and alkali solubility R10 and R18 (T 235 cm-85 "Alkali solubility of pulp at 25°C").

RESULTS AND DISCUSSION

A sample was collected from a local printing press to investigate the feasibility of producing dissolving pulp from white press cuttings. Its chemical composition was determined as shown in **Table I**, which shows that the ash content was 11.5% and pentosan content was 11.4%. These must be removed from the white press cuttings to make it dissolving pulp. In order to remove the fines and filler, acid treatment of press cutting pulp was done at different pH and temperature, followed by screening. The ash content in pulp decreased with decreasing pH, as shown in Table II. Consequently, the proportion of α-cellulose content increased. The temperature effect was marginal on filler removal. At pH 2, ash content was 0.5% at 25°C, which further decreased to 0.29% at 90°C. The proportion of pentosan slightly increased due to the removal of fillers. The pentosan content increased to 12%–14% from 11.5% in the starting pulp. Acid treatment followed by screening decreased pulp yield due to the removal of fillers as indicated by ash content in the pulp. The pulp yield at pH 2 was 89%. Therefore, acid treatment at pH 2 and 25°C was considered optimum for subsequent alkaline extraction.

Alkaline extraction

White press cutting pulp obtained from acid treatment at pH 2 and 25°C was taken for alkaline extraction. Alkaline extraction of acid treated pulp was carried out with varying sodium hydroxide charge and temperature, as shown in Table III. Pentosan content decreased with increasing alkali charge. This is a common phenomenon of cold alkali

Chemical	%
Ash	11.5
α-cellulose	79.4
Pentosan	11.4

I. Chemical composition of white press cutting sample.

pH	Temperature, °C	Ash Content, %	Pulp Yield, %	α-cellulose, %	Pentosan, %
2	25	0.50	89.3	84.1	13.7
2	50	0.33	89.0	85.4	13.0
2	90	0.29	88.8	85.6	13.2
4	25	0.58	89.4	83.5	13.0
4	50	1.04	89.2	83.3	12.8
4	90	0.69	89.5	83.7	13.1
6	25	7.09	95.7	81.3	12.4
6	50	6.61	94.3	81.4	12.6
6	90	6.11	93.6	81.4	12.7

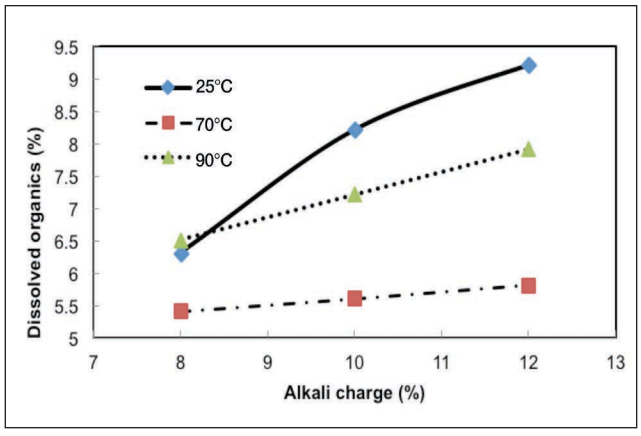
II. Ash content after acid treatment of white press cuttings at various temperatures.

Temperature, °C	NaOH Charge, %	Pulp Yield, %		α-cellulose, %	Pentosan, %
		Alkaline Extraction	Overall		
25	8	89.3	79.7	89.8	9.8
	10	87.0	77.7	90.5	8.2
	12	85.8	76.6	89.2	8.0
70	8	90.3	80.6	85.2	10.1
	10	90.0	80.4	86.2	9.8
	12	89.5	79.9	86.7	9.7
90	8	90.0	80.4	91.1	8.7
	10	89.1	79.6	89.9	8.3
	12	88.0	78.6	89.7	8.2

III. Alkaline extraction of acid-treated white press cutting pulp.

extraction [1]. The pentosan content decreased to 9.8% from 13.7% by alkaline extraction with 8% alkali charge at 25°C, which was further decreased to 9% with increasing alkali charge to 12%. The interaction between alkali and cellulose also affects the supramolecular structure of cellulose. Increasing alkali concentration at room temperature gradually leads to a change from the native cellulose I structure into the Na-cellulose I structure. Thus, the plane distance of the 101-lattice planes is widened due to incorporation of the sodium hydrate ion. This structure gives rise to a better reactivity with chemical reactants due to better accessibility of the hydroxyl groups on C_6 and C_2 (e.g., CS_2 in the case of the viscose process) [1]. But at high alkali concentration, cellulose mercerization occurs. Mercerization consists in the conversion of cellulose I polymorph (native cellulose) into cellulose II. Formation of cellulose II is the result of the swelling of cellulose. The cellulose II was reported to be detrimental to dissolving pulp reactivity [14].

Temperature was less effective in removing hemicellulose (Table III). It is seen that the pentosan dissolution decreased with the increase of temperature to 70°C and increased again when temperature increased to 90°C. This observation can be explained by the opposite effect of two phenomena. One, cellulose swelling is enhanced at room temperature, which favors hemicelluloses removal. It is well established that lower temperatures cause a high degree of swelling, and this enhances the solubility of hemicelluloses. It was observed that an increase in temperature from 30°C to 50°C of cold caustic extraction (CCE) of eucalyptus prehydrolysis kraft pulp at a constant NaOH concentration of 70 g L^{-1} decreased removal of xylan content of 0.4% (from 1.5% to 1.9% in the residue) [1]. Secondly, at 90°C, peeling reaction may be started and part of hemicelluloses degradation and dissolution occurred. Similar results were observed in alkaline extraction of hemicelluloses



1. Effect of temperature and alkali charge on the dissolved organics acid-treated white press cuttings.

from softwood bleached kraft pulp [14]. Arnoul-Jarriault et al. [14] separately heated pulps and NaOH solution and then mixed them together and found that no cellulose II occurred at 90°C and a low hemicelluloses extraction was obtained. An increase of temperature decreases pulp swelling [1]. The same observations can be done for cellulose II content, since cellulose II formation is the result of swelling.

Pulp yield decreased with increasing alkali charge that was mainly due to removal of hemicelluloses. At 25°C, pulp yield decreased from 89.3% to 85.8% with increasing alkali charge from 8% to 12%. Consequently, overall pulp yield (considering acid treatment and alkaline extraction) decreased from 79.6% to 76.6%. An insignificant difference in pulp yield was observed with varying alkali charge at 70°C due to less removal of hemicellulose. Considering overall pulp yield and pentosan content, room temperature (25°C) and 12% alkali charge were allowed as optimum conditions for dissolving pulp properties evaluation.

Alkaline extracted liquor

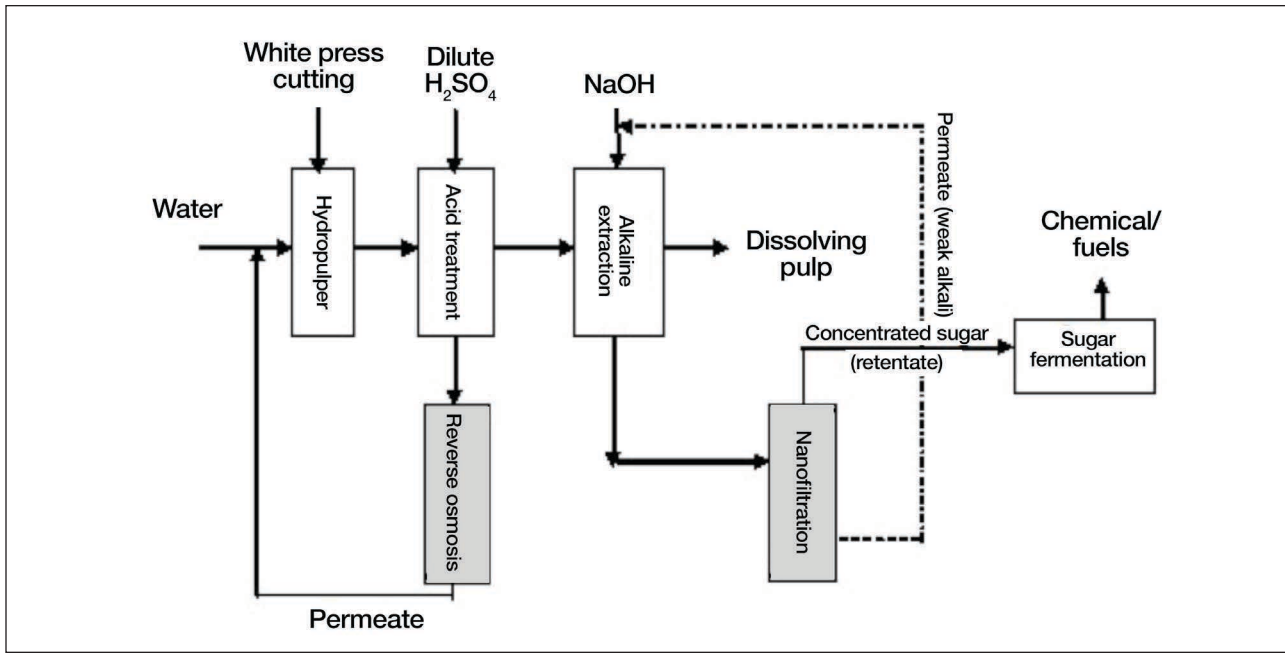
Solids content and ash content in the alkaline extracted liquor were determined. Ash content consists of inorganics, which includes NaOH used in the alkali extraction. This subtraction of ash content from solids content represented organics dissolved from the pulp during the alkaline extraction process. This is mostly lignin and hemicellulosic sugars. As shown in **Fig. 1**, total organics in the alkaline extracted liquor increased with the alkali charge. This effect was pronounced in the alkaline extraction at 25°C. It can be noted that extraction was minimum at 70°C. Dissolved organics increased from 6.3% to 9.2% with the increase of alkali charge from 8% to 12% at 25°C, whereas at 70°C, dissolved organics only increased from 5.4% to 5.6%. This was due to fiber swelling at 25°C, which facilitated hemicelluloses removal. Total organics increased at the extraction temperature of 90°C, which is consistent with pentosan content data. This can be attributed to the peeling reaction started at this temperature and contributed hemicelluloses degradation and dissolution. From these results, it can be inferred that maximum hemicelluloses were extracted with 12% alkali charge at 25°C.

Pulp evaluation

Alkaline extracted pulp obtained from the extraction conditions of 12% alkali charge at 25°C was selected for dissolving pulp evaluation. The results are compared with the data reported earlier with jute stick and commercial hardwood dissolving pulp obtained by prehydrolysis kraft and acid sulfite process (**Table IV**) [15-16]. The purity of pulp reached 91.1% α-cellulose, which was slightly lower than the dissolving pulp produced from jute stick by the prehydrolysis kraft process [15] and acid sulfite commercial pulp [16]. The residual pentosan in the alkaline extracted pulp was too high for dissolving grade pulp but is suitable for some rayon grade pulp. The R_{18} - R_{10} values indicate the content of degraded cellulose with

	White Press Cuttings	Jute Stick [15]	Commercial Dissolving Pulp [16]	
			Prehydrolysis Kraft	Acid Sulfite
α–cellulose, %	91.1	92.3	94.7	92.9
Pentosan, %	8.7	7.8	3.66	2.86
R_{10}, %	88.9	88.8	93.12	90.65
R_{18}, %	92.4	92.9	96.41	95.55
R_{18} - R_{10}, %	3.5	4.1	3.29	4.9
Viscosity, mPa.s	4.33	3.2	587 (ml/g)	498 (ml/g)
Brightness, % ISO	85.3	88.3	-	-
Fock reactivity, %	68.8	-	55.3	92.3

IV. Final dissolving pulp properties.



2. Proposed biorefinery based on white press cutting into dissolving pulp

a degree of polymerization between approximately 50 and 150 [3]. Pulp from white press cuttings showed better R_{18} - R_{10} value than the pulp from jute stick by the prehydrolysis kraft process. These results are consistent with the viscosity. Brightness of the dissolving pulp from white press cuttings in this study was 85.4%. The Fock reactivity of the produced dissolving pulp was 68.8%, which was better than that of commercially produced hardwood kraft dissolving pulp and inferior to that of acid sulfite hardwood pulp [16].

Proposed biorefinery concept in dissolving pulp production from white press cuttings

A biorefinery initiative based on upgrading of white press cuttings into dissolving pulp has been proposed in **Fig. 2**. It is known that acid treatment removed mineral fillers from the waste paper [12]. This acid water can be reused in the system through reverse osmosis (RO). In order to maximize resource use and to minimize residual environmental effects of discharged effluents, Dubé and MacLatchy [17] studied RO treatment of evaporator and digester clean condensates to reduce or remove the effluent load of bleached kraft pulp mills.

Residual hemicelluloses in the acid treated pulp can be removed by alkaline extraction. Dissolved hemicelluloses can be separated from the alkaline extracted liquor for biochemicals and biofuel production. The concentration of the dissolved hemicelluloses is weak and needs to be concentrated to make a viable resource for a downstream process. The theoretical conversion rate of pentoses to ethanol is approximately 50% [18]; the resulting ethanol concentration after fermenting the hydrolysate would be weaker. It is known that one of the most energy-intensive steps in the ethanol production process is the recovery of ethanol from the fermentation broth by distillation [19]. The cost of distillation decreases as ethanol concentration increases, and a starting concentration of around 5% ethanol is generally considered the minimum. Therefore, an additional process step for increasing sugar concentrations after pre-extraction is required. It was observed that nanofiltration (NF) increased sugar concentration significantly [20]. NF can separate/recover hemicellulosic sugars, and it has been used to separate and concentrate saccharides in the fermentation broth [21-23]. In principle, NF is suited for the recovery, separation, and purification of sugars from prehydrolysis liquor of a hardwood kraft-based dissolving pulp production process [20]. NF pre-concentrated hemicellulosic sugars into 344.36 g/L [24]. The concentrated oligo sugars can be fermented by *Pitichia stipitis* to ethanol [21]. The hemicelluloses can also be used for furfural production [25-26]. Permeate of NF can be reused in an alkaline extraction process.

CONCLUSIONS

Acidification of white press cutting pulp at pH 2 at 90°C followed by screening by 100 mesh screener reduced ash content to 0.25% from 11.5%. Increasing pH value decreased mineral fillers removal. Alkaline extraction of acid treated pulp at 25°C reduced hemicelluloses content in pulp. The pentosan content decreased to 9.8% from 13.7% by alkaline extraction with 8% alkali charge at 25°C, which further decreased to 9.0% with increasing alkali charge to 12%. Temperature was less effective in removing hemicelluloses. The yield after alkaline extraction was 85.8%; consequently, overall pulp yield reached to 76.6% at the extraction conditions of 12% alkali charge at 25°C. The purity of pulp reached to 91.1%. Such low purity pulp can be used in rayon production. The alkaline

extracted liquor contained 9.2% total organics — mostly pentose sugars, which can be utilized in biochemical or bioethanol production. **TJ**

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Raw material for pulping is scarce in Bangladesh, and the price of dissolving pulp is high. Therefore, discovery of a new, cheap raw material for dissolving pulp is of prime interest.

Much research has been carried out on upgrading paper pulp into dissolving pulp. However, our research is unique in that we examine the use of white press cuttings rather than pulp.

The technology used here is very easy and simple, but removal of residual xylan is difficult. This can be done by mechanical and chemical treatment prior to alkaline extraction.

The most interesting thing we discovered was that temperature is less effective in removing hemicellulose. We found that pentosan dissolution decreased with the increase of temperature to 70°C from room temperature of 25°C.

Small pulp mills can set up this process with low capital investment, as it only involves two steps: 1) acid treatment and screening, and 2) alkaline extraction.

To improve the purity of the dissolving pulp from this process, mechanical and enzymatic treatment prior to alkaline extraction will be studied next.

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