A BIOREFINERY INITIATIVE IN PRODUCING DISSOLVING PULP FROM DHAINCHA (*SESBANIA ACULEATA*) – A SHORT-ROTATION CROP

M. SARWAR JAHAN and M. MOSTAFIZUR RAHMAN

Pulp and Paper Research Division, BCSIR Laboratories, Dhaka, Dr. Qudrat-i-Khuda Road, Dhaka 1205, Bangladesh

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Dhaincha (*Sesbania aculeata*) is a short-rotation crop cultivated for its nutritional value to soil. Dhaincha chips were pre-extracted with acidic and alkaline solutions at 165 °C for 60 min to produce dissolving pulp. The pH of the pre-extracted liquor reached a near-neutral value (pH 6.8), when 3% NaOH was added. Pre-extraction dissolved 17-20% biomass from dhaincha. From the pre-extraction liquor, 1.6-2.6% lignin, 1.5-1.7% acetic acid and about 7% sugars (on o.d. dhaincha) were extracted. Pre-extracted dhaincha was cooked by the kraft process. Pre-extraction with alkaline solution produced higher pulp yield and lower kappa number than simple water and H_2SO_4-water pre-extraction. After D_0EpD_1 bleaching, the pre-extracted pulp showed almost similar pulp brightness. The pulp obtained after alkaline pre-extraction exhibited higher pulp viscosity and higher α-cellulose content. It can be concluded that pre-extraction at near-neutral pH produces pulp with higher yield, purity and viscosity with good brightness.

Keywords: Dhaincha, pre-extraction, pulp yield, viscosity, pulp brightness

INTRODUCTION

Today, the vast majority of paper pulp and other pulp products (viscose, cellulose derivatives, etc.) are produced from wood originating from forests. As a result, the forest area diminishes by 7317000 ha each year on a global scale, consequently fuelling global warming.[1] As forests can no longer meet the demand, the use of cellulose fiber from annual plants or short-rotation trees is inevitable.

Dhaincha (*Sesbania aculeata*) is a crop generally cultivated for its nutritional value to soil. It is cultivated in the monsoon season almost throughout Bangladesh and grows well in loamy, clayey, black and sandy soil. Dhaincha is an annual plant with a straight stem, which can reach 6 m in height and produce a dry stem yield of up to 20 t/ha.

The dhaincha stem has the following composition: 22-23% Klason lignin, 34-38% α-cellulose and 19-20% pentosans.[2] Its fiber length (1.0-1.3 mm) and chemical characteristics are comparable to those of hardwood.[3] In the authors' previous investigation, it was observed that dhaincha is a potential raw material for kraft liner grade paper pulp.[4]

Current research demostrates growing interest in biomass as a potential renewable source of biofuels and biochemicals, to replace petroleum products and reduce green house gas emissions. Combustion of fossil fuels is considered the major factor responsible for global warming, as it releases 7.0 billion tons of carbon/year into the atmosphere, equalling 82% of net green house gas emissions.[5] Considering climate change and the need for biofuels and bioproducts, the existing pulp industry has manifested considerable interest in promoting the development of forest product biorefineries. Recently, pulp mills are considering pre-extraction of hemicelluloses prior to traditional pulping processes in integrated forest biorefineries.[6,7] In the commercial chemical pulping process, hemicelluloses are partly degraded and subsequently combusted in the recovery furnace of the pulp mill. But hemicelluloses provide lower heating value than lignin.

Pre-extraction of hemicelluloses prior to pulping would make these polysaccharides available for other applications, such as fermentation to ethanol or butanol (feedstock for bioenergy) or for conversion to other bioproducts.[8,9]

Most of the cellulose or dissolving pulp comes from wood using the prehydrolysis kraft or acid sulfite processes.[10,11] Dissolving wood pulp is a chemically refined bleached pulp composed of more than 90 percent pure α-cellulose. The end uses of dissolving pulp include making of cellophane and rayon, cellulose esters (acetates, nitrates, etc.), cellulose ethers (carboxymethyl cellulose, etc.), graft and cross-linked cellulose derivatives.[12]

The present study focuses on fast-growing biomass utilization in producing dissolving pulp, in order to obtain economic and high-quality feedstock for bioenergy and bioproducts. The objective of this study was to pre-extract dhaincha in acidic and alkaline media, prior to kraft pulping, in order to produce dissolving pulp. The pre-extracted liquor and produced pulp were then characterized.

EXPERIMENTAL

Materials

Dhaincha was collected from the Savar, Dhaka. It was sun-dried and the leaves and dirt were removed manually. Then it was cut to 2-3 cm in length by a hand cutting machine. After determining the moisture content, air dried dhaincha equivalent to 100 g oven dried (o.d.) product was weighed separately in a polyethylene bag for subsequent cooking experiments.

The lignin (T211 om83) and pentosans (T223) of the raw material were analysed according to Tappi Test Methods. Holocellulose was determined by treating the extractive-free wood meal with a NaClO2 solution. The pH of the solution was maintained at 4 by adding CH3COOH-CH3COONa buffer and α-cellulose was determined by treating holocellulose with 17.5% NaOH.

Prehydrolysis

Dhaincha was pre-extracted by water, water with 0.2% H_2SO_4, water with 1% NaOH and water with 3% NaOH in oil-heated bomb digesters. Pre-extraction was carried out at 165 °C for 60 min. The dhaincha to liquor ratio was of 1:6. The time required to reach maximum temperature was 50 min. After completing pre-extraction, the digester was cooled by circulating cold water. For determining pH, solid content, lignin and acetic acid, the samples were collected from the drained off liquor. The percentage of dissolved components was measured gravimetrically.

Lignin analysis

The dissolved lignin in the prehydrolysate was measured by the UV/Vis spectrometric method at 205 μm wavelength (TAPPI UM 250).[13]

Acetic acid determination

Acetic acid in the prehydrolysate liquor (PHL) was dehydrated by anhydrous sodium sulphate. 1 μL of the dehydrated sample was injected into GC. Pure glacial acetic acid (GAA) was used as reference standard. The analysis of GAA was carried out on a gas chromatograph model 14B, Shimadzu, Japan, provided with software Class GC-10 (version 20). The GC was equipped with flame ionization detector (FID) and a FAMEWAX RESTEC capillary column (15 m x 0.25 mm). Before injection, the column was conditioned at 180 °C for about 2 h for attaining thermal stability before use. The temperatures of the column oven, injection port and detector were of 180 °C, 240 °C and 250 °C, respectively.

Solid content

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

Pulping

Pulping of pre-extracted dhaincha was carried out by the kraft process in the same digester as the pre-hydrolysis. Pulping conditions were as follows:

- Active alkali: 18% on oven dry (o.d.) raw material as Na_2O
- Sulphidity: 30%
- Cooking time: 120 min at maximum temperature of 170 °C; time to reach maximum temperature from room temperature – 90 min
- Liquor to material ratio: 6:1.

After digestion, the pulp was washed till free from residual chemicals, and screened on a flat vibratory screener (Yasuda, Japan). The screened pulp yield, total pulp yield and screened reject were determined gravimetrically as percentage of o.d. raw material. The kappa number of the resulting screened pulp was determined in accordance to Tappi Test Methods (T 236 om-99).

D_0EpD_1 bleaching

The pulps were bleached by D_0EpD_1 bleaching sequences (where D represents chlorine dioxide and Ep represents peroxide reinforced alkaline extraction). In the first stage (D_0) of D_0EpD_1 bleaching sequences 2% ClO_2 was used, a temperature of 70 °C, for 60 min. Pulp consistency was of 10%. The pH was adjusted to 2.5 by adding dilute H_2SO_4. In the alkaline extraction stage, the following conditions were applied: temperature – 70 °C, time – 60 min, a water solution of 2% NaOH and 0.5% H_2O_2 (on o.d. pulp). Pulp consistency was of 10%. In the D_1 stage, the final pH value was 4 and the ClO_2 charge was of 1.0%. The brightness, viscosity and α-cellulose of the bleached pulp were determined in accordance with Tappi Test Methods T525 om-92, T 230 om-89 and T 203 om-88, respectively.

RESULTS AND DISCUSSION

Chemical composition

The results of the chemical analysis of the dhaincha samples used in this study are shown in Fig. 1. According to them, dhaincha had a Klason lignin content of 21.9% and an α-cellulose content of 41.4%, values that are similar to those of hardwood,[3,14] as well as a pentosans content of 23.4%. The chemical composition of dhancha depends on the age of the plant.[2]

Pre-hydrolysis

Pulp mills may increase revenue by producing biofuels and chemicals, in addition to pulp, in an Integrated Forest Biorefinery (IFBR). Pre-hydrolysis is an important part in the dissolving pulp production process used to remove hemicelluloses. Besides, furfural and acetic acid are extracted from PHL. Table 1 represents the effects of pre-hydrolysate pH on biomass residue and PHL characteristics. As can be noted in Table 1, pre-hydrolysis with pure water results in an acidic condition (pH 3.5), which is caused by the release of acetic acid from acetylated hemicelluloses.[15] The mechanism of hot-water extraction depends in part on the cleavage of *O*-acetyl and uronic acid substitutions, which result in the formation of acetic acid and other organic acids. This acid catalyzes the hydrolysis of the hemicelluloses to a soluble oligomer and monomers.[16] A similar observation was made for the auto-hydrolysis of birch wood.[17] The final pH of alkaline pre-hydrolysis varied from acidic (1% NaOH) to near-neutral (3% NaOH). The biomass weight loss during pre-hydrolysis increased from 17%, under acidic conditions, to 20%, under near-neutral conditions. Yoon *et al.* showed that the wood dissolution during alkaline pre-extraction increased with NaOH charge.[18] The sum of the recovered biomass after pre-hydrolysis and solid content in the PHL is close to 97%, which is relatively low, because of the formation of degraded products from sugars, like furfural or other products. This finding concurs with that of Leschinnsky *et al.*[19] and Tunc and van Heiningen.[20] The solid content represents mostly sugars and lignin.[21] The lignin content in the PHL was the maximum (2.61% on o.d. dhaincha) when pre-extraction was carried out by water alone (pH 3.5). Alkaline pre-extraction in pH 4.6 and 6.8 dissolved only 1.6% lignin. Following the biorefinery concept, Yoon *et al.*[22] extracted loblolly pine in hot water prior to pulping and obtained 5.11% lignin in the prehydrolysate. The lignin content in the hot-water extract of sugar maple was of 3.27%.[23]

Lignin, as a non-toxic, low-cost and renewable resource, has been considered for substituting some petrochemical products to deal with petroleum resources crisis and lessen environment pollution caused by non-biodegradable polymers.[24,25] For instance, lignin as part of the starting material, has been studied to produce different polymers, such as polyurethane[24] and phenol-formaldehyde resin.[26] Due to its value-added applications, lignin not only helps to boost the economic viability of biorefinery, but also serves as a source of renewable materials.

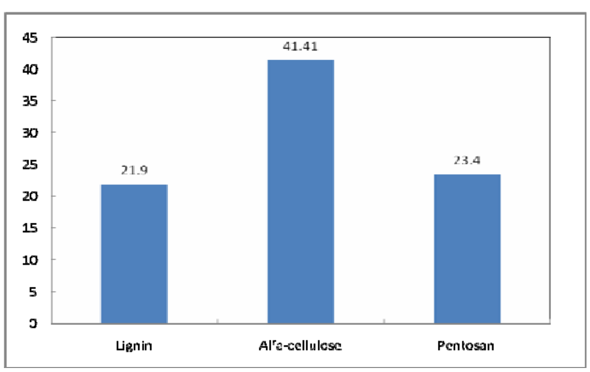

Figure 1: Chemical analysis of dhaincha

Table 1
Chemical composition of pre-hydrolysis liquor of dhaincha

Pre-extraction conditions	Yield (%)	pH	Solid content in PHL (% on dhaincha)	Lignin (% on dhaincha)	Acetic acid (%)
Acid water	82.5	2.0	14.4	1.93	1.49
Water	82.1	3.5	14.6	2.61	1.32
Alkaline-1% NaOH	81.3	4.6	15.5	1.64	1.56
Alkaline-3% NaOH	80.2	6.8	17.8	1.63	1.71

Acetic acid is an important by-product of the hemicelluloses extraction process. At a lower pH, the acetyl groups lead to the formation of acetic acid. The amount of acetyl groups liberated from the hemicelluloses during pre-extraction depends upon the pH of pre-extraction. The acetic acid in the PHL increased to 1.49% in acidic pre-extraction from 1.32% in simple water pre-hydrolysis. At near-neutral pH pre-extraction conditions (3% NaOH), acetic acid increased to 1.71%.

In our earlier studies,[21] it was observed that the total sugars content in the PHL represented 49% of the solid content, which allows to assume that about 6-8% (on o.d. dhaincha) sugars were present in the PHL. During the biorefinery process, sugars can be transformed into building-block chemicals by fermentation, as well as by enzymatic and chemical transformations. The key building-block chemicals will include ethanol, C3 to C6 carboxylic acids (e.g., hydroxypropanoic acid, glucaric acid), and alcohols, such as glycerol and sorbitol. Xylose/xylan can be converted into xylitol, yeast, furfural and others by chemical or enzymatic processes. The U.S. Department of Energy recently published a comparative study on the top 12 chemicals from carbohydrate biomass, identifying several particularly promising compounds, including sorbitol, levulinic acid and glycerol.[27]

Pulping

To find a suitable pre-hydrolysis pH, in order to obtain high-purity dissolving pulp from dhaincha, the prehydrolysate fibrous materials were cooked under identical cooking conditions by the kraft process. From Table 2, it may be seen that near-neutral pH produced a higher pulp yield and lower kappa number. The pulp yield was 2.6% higher when the pre-hydrolysis was carried out with 3% NaOH (pH 6.8) than in simple water pre-hydrolysis (pH 3.5). The delignification was also better with the 3% NaOH prehydolysate materials, kappa number was lower by 9.2 points than that of water prehydrolysate. It was also observed that the addition of H_2SO_4 in the pre-hydrolysis liquor decreased kappa number and increased α-cellulose content in the pulp.[28] The dissolving pulp produced by alkaline pre-extraction or 0.2% H_2SO_4 pre-hydrolysis showed better α-cellulose content than the water pre-hydrolysis (Table 2).

Considering the yield, kappa number and viscosity of the pulp, alkaline pre-extraction under near-neutral conditions showed the best results.

Bleaching

Bleaching of dissolving pulp is primarily a purification process. All the pulps produced were bleached by D_0EpD_1 bleaching sequences under identical conditions. Bleaching improved the α-cellulose content in the pulp (Table 3).

The purity of the bleached pulp was dependent on the pre-hydrolysis conditions. When using a charge of 30 kg/MT chlorine dioxide, all the pulps showed almost similar brightness.

Table 2
Effect of pre-hydrolysis conditions on the pulping of dhaincha*

Prehydrolysis conditions	Total pulp yield (%)	Kappa number	Cellulose in pulp (%)
Acid water	43.6	20.4	91.0
Water	43.9	18.8	89.8
Alkaline-1% NaOH	46.2	13.4	91.2
Alkaline-3% NaOH	46.5	11.2	91.6

*Alkali charge 18% on o.d. raw material, 120 min at 170 °C

Table 3
Effect of pre-hydrolysis conditions on the bleaching of dhaincha pulp

Prehydrolysis conditions	Brightness (%)	Viscosity (mPa*s)	α-cellulose (%)
Acid water	89.1	15.7	96.3
Water	89.2	16.8	93.7
Alkaline-1% NaOH	89.2	17.2	95.8
Alkaline-3% NaOH	89.5	17.8	96.2

The addition of 0.2% H_2SO_4 in the pre-hydrolysis increased α-cellulose content by 2.6%, at the expense of final pulp viscosity (1.1 mPa*s).
The α-cellulose content in the alkaline pre-extracted (3% NaOH) bleached pulp increased to 96.2%, showing better viscosity than the water pre-hydrolysed bleached pulp.

CONCLUSIONS

The pH of the pre-extracted liquor reached a near-neutral value (6.8) on prehydrolysis of dhaincha with 3% NaOH solution. Under such pre-extraction conditions, 1.6% lignin, 1.7% acetic acid and 8% sugars (on o.d. dhaincha) were extracted from the pre-extracted liquor. Alkaline pre-extraction produced a higher pulp yield and lower kappa number than the acidic pre-extraction. All the pre-extracted pulps showed good bleachability. Improved viscosity and high purity pulp were obtained from the alkaline pre-extraction (3% NaOH). As a conclusion, dhaincha can be used a suitable source for producing dissolving pulp in a biorefinery initiative.

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