ORIGINAL PAPER

Variation of chemical characteristics and pulpability of dhaincha (*Sesbania bispinosa*) on location

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ABSTRACT

Dhaincha (*Sesbania bispinosa* (Jacq.) Wight) is a crop generally cultivated for improving soil quality. Due to the lack of forest worldwide, alternative source of raw materials for cellulose industries is the main concern today. In this investigation, dhaincha samples of 21 accessions were collected from different districts of Bangladesh in order to study the variation of chemical characteristics and its pulpability. The lignin, pentosan and α–cellulose content were varied from 21 to 23%, 16 to 18% and 38 to 43%, respectively. The highest and lowest α–cellulose contents were found in two location of Mymensingh district. There was no correlation was found among the districts. Therefore, pulping of dhaincha from selected seven districts was carried out in kraft process at the conditions of 18% active alkali at 170° C for 2 h. But the pulping properties did not show any mentionable distinction for place variation. Average pulp yield is 42.9% with kappa number 11. The highest brightness 85% was reached with $D_0E_pD_1$bleaching. The papermaking properties were very close to the conventional raw materials used in Bangladesh. Therefore, dhaincha can be used as a raw material for pulp production in Bangladesh.

Keywords: Dhaincha, Accession number, α-cellulose, Lignin, Pentosan, Pulp yield, Brightness

1. INTRODUCTION

Bangladesh is very small country with high population density. But GDP growth rate in Bangladesh is above 6 since last 10 years except 2009-10, consequently living standard of people is increasing. Global production of paper and paperboard in 2014 was 400.2 million tones. The per capita paper and board consumption in Bangladesh is about 3.5~4 kg, which is much lower than the advanced countries (300 kg/capita), the world average (≅50 kg/capita) and the Asian average (≅50 kg/capita). To reach the paper and board consumption to Asia level, our consumption will increase to 10 times of current consumption. Therefore, Bangladesh needs alternative fibrous raw materials as forest resources is very limited. Dhaincha (*Sesbania* spp.) can be an alternative raw material for pulping.[1] Picture of dhaincha shoot is shown in Fig. 1.

Fig. 1. Photograph of dhaincha plant

It is well known that dhaincha is used as a green manure crop.[2-4] As for example, Kurdali et al.[3] studied a field trial on a salt-affected soil to determine the effect of application of three types of dhaincha residues on the performance of sorghum. Dhaincha residues used as green manures significantly increased grain yield, dry matter production, N uptake, and water use efficiency of sorghum.

As a lignocellulosic fibrous material, dhaincha has been studied for paper and boards. Islam et al.[5] studied dhaincha for particleboard manufacturing and found acceptable strength properties. Islam et al.[6] investigated wood–cement boards from dhaincha (*Sesbania aculeata*). Calcium chloride and sodium hydrogen carbonate were used as cement setting accelerator and board properties were studied. Authors concluded that dhaincha with cement setting accelerator can be an alternative source to produce cement board with satisfactory properties. Singh and Rani[7] extracted harsh, coarse and shiny fibres from dhaincha stem after 15 days retting. Extracted fiber was suitable for nonwoven fabric.

In our research group, a lot of researches were carried out on the pulping of dhaincha both for paper and dissolving pulp. Soda-anthraquinone, kraft and alkaline-sulphite-anthraquinone-methanol pulping of dhaincha were evaluated and recommended for unbleached packaging grade paper could be produced from dhaincha pulp.[1] The chemical, morphological, pulp, and papermaking properties and its bleachability harvesting age of dhaincha were studied.[8] The alpha-cellulose content in dhaincha increased and pentosan decreased with increasing age. Pulp yield (43-45 per cent) and kappa number (26-30) did not follow direct correlation with plant age. The bleachability of pulp improved with the

age.

Dhaincha was studied for dissolving pulp.[9] Dhaincha chips were pre-extracted with acidic and alkaline solutions at 165 °C for 60 min to produce dissolving pulp. 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 and bleached by $D_0E_pD_1$ bleaching. It was accomplished that pre-extraction at near-neutral pH produces pulp with higher yield, purity and viscosity with good brightness.

Dhaincha has a yield potential of up 20t DM ha^{-1} $year^{-1}$ under appropriate cultivation.[10] However, in Bangladesh condition, dhaincha produces only 1.5t DM ha^{-1} in a period on 90 days.[4] Along with the native *Sesbania* spp., an exotic species *S. rostrata* Bremek. & Oberm. is also used as green manure crop in Bangladesh. National Seed Board of Bangladesh did not recommend any dhaincha cultivar for specific use. For genetic improvement and high yielding cultivar development, morphological characterization of native dhaincha germplasms was studied by Sarwar et al.[11] for specific purpose(s) e.g., green manure, animal feed, pulp production, reclamation saline and/or sodic soil, etc. As a part of this effort to collect the native plant genetic resources of the genus *Sesbania*, 110 accessions were collected from 11 districts of Bangladesh (Sarwar, unpublished data). After a preliminary screening based on the biomass yield, 20 accessions belong to two *Sesbania* species *viz*. *S. bispinosa* and *S. cannabina* (Re tz.) Poir. along with one accession of exotic *S. rostrata* were included in this experiment.

In this study, dhaincha samples from 21 accessions were chemically characterized in order to evaluate pulping potential. Finally pulping and bleaching experiment were conducted under identical cooking and bleaching conditions based on our previously established cooking conditions.

2. EXPERIMENTAL

2.1 Materials

Dhaincha samples of 21 accessions (*S. cannabina* – Accession # 25, 27 & 28, *S. rostrata* – Accession #105. *S. bispinosa* – rest of the Accessions) were collected from different location of the country and sun dried to remove dirt and leaves. These were cut to 2-3 cm in length, and parts of it were ground (40/60 mesh) in a Wiley mill for chemical analysis.

2.2 Chemical analysis

The hot water solubility (T207 cm99), 1% alkali solubility, extractives (T204 om88), Klason lignin (T222 om98), viscosity (T230 om99) and ash content (T211 om93) were determined in accordance with Tappi Test Methods. Holocellulose was determined by treating extractive-free wood meal with $NaClO_2$ solution. The pH of the solution was maintained at 4 by adding acetate buffer.

2.3 Pulping

Kraft pulping was done in a 5 *l* capacity thermostatically controlled electrically heated rotary digester under constant cooking conditions. The active alkali was constant 18 % as Na_2O on oven dried (o.d.) sample in the liquor ratio of 1:6. The cooking was continued for 120 min at the maximum temperature (170° C). At the end of pulping, pressure was relieved to atmospheric pressure; pulp was taken out from the digester, disintegrated and washed by continuous flow of water. Pulp was screened in a Yasuda flat vibratory screener yield and reject determined gravimetrically. Pulp yield was determined as dry matter obtained on the basis of o. d. raw material. Kappa number was determined in accordance with T 236 cm-85. Three replicates were carried out for each experiment. Pulping selectivity was calculated by dividing pulp yield by kappa number.

2.4 $D_0E_pD_1$ bleaching

Dhaincha pulps were bleached by D_0EpD_1 bleaching sequences (where D represents chlorine dioxide and Ep represents peroxide reinforced alkaline extraction). The ClO_2 charge was 2% and temperature was 70 °C for 45 min in the D_0 stage. The pH was adjusted to 2.5 by adding dilute H_2SO_4. Alkaline extraction was carried out with 2% NaOH and 0.5% H_2O_2, at 70° C for 120 min. In the D_1 stage, ClO_2 charge was 1.0%, and the pH was adjusted to 4.5 by adding dilute alkali. The pulp consistency was 10% in all stages. The brightness (T452 om-08) and viscosity (T 230 om-99) of the bleached pulp were determined in accordance with Tappi Methods. All pulps were beaten in a PFI mill to 2000 revolution and handsheets of about 60 g/m^2 were made in a Rapid Köthen Sheet Making Machine according to German Standard Methods. The physical properties of handsheets were determined by the method of T 220 sp-96.

2.5 Statistical analysis

Descriptive statistics have been computed to see the average behavior of the properties of dhaincha and dispersion of the data. Next, Analysis of Variance (ANOVA) has been performed to test the equality of means. Finally, Post Hoc Duncan Multiple Range Test (DMRT) has been carried out to test the homogeneity of means of the parameters of dhaincha grown in different location of Bangladesh. Statistical software SPSS of its version 22.0 have been used for all calculations.

3. RESULTS AND DISCUSSION

3.1 Chemical characteristics

Dhaincha plants were collected from twenty one accessions in different location of Bangladesh in order to assess the variation of chemical characteristics and ultimately its impact on pulping. The chemical composition, quantity, and distribution also affect the agro industrial uses of plant material. Digestibility and dietary conversion of

herbaceous crops are affected by differences in lignin content and composition.[12-15]

The chemical composition of dhaincha is fairly well known although some results are available with some variation. The chemical compositions of dhaincha from different location are listed in Table 1, which shows that the chemical characteristics of raw material were similar to hardwood.[16-17] A lot of variation was observed in of hot-water soluble (HWS) content (2.4-10.2%) among the dhaincha accessions, which are lower than rice straw and within the range of wheat straw.[18] Hot-water soluble substances in the raw materials include starch and proteins, which could consume chemicals during pulping. The lowest HWS content was found from the dhaincha of Jhinaidaha district. As compared to hardwood, the HWS content in dhaincha from most of the accession was lower, which indicated advantageous for pulping.[19]

Table 1. Chemical properties of different dhaincha accessions

Accession number	Name of District	Extractive (%)	Klasonlignin (%)	Pentosan (%)	HWS (%)	1% AS	Holo-cellulose (%)	α- cellulose (%)	Ash (%)
25	Mymensingh	0.37	23.19	16.02	3.76	20.00	66.10	39.74	1.6
27	Mymensingh	0.55	23.45	17.03	4.31	19.93	67.90	40.56	1.24
28	Mymensingh	0.62	22.91	17.87	2.70	20.35	75.47	40.88	1.67
45	Jhinaidaha	0.58	21.07	18.81	2.35	19.83	73.85	43.70	1.20
50	Jhinaidaha	0.47	22.27	18.72	9.62	25.90	65.98	40.10	1.91
55	Sirajganj	0.45	23.13	17.87	5.08	20.56	73.82	42.27	1.50
73	Sirajganj	0.65	22.71	17.55	5.88	25.02	68.61	40.87	1.81
75	Sirajganj	0.34	26.87	16.89	3.17	21.70	73.38	40.98	1.84
78	Sirajganj	0.47	20.91	16.96	10.22	19.30	74.55	41.76	1.30
79	Sirajganj	0.47	21.87	18.33	4.36	21.50	69.77	40.45	2.00
82	Sirajganj	0.40	21.96	16.80	5.50	21.90	71.20	40.42	1.67
83	Rangpur	0.27	21.73	18.11	6.35	20.10	69.96	41.32	1.20
84	Rangpur	0.47	20.51	17.30	4.58	22.02	70.73	39.65	1.18
85	Rangpur	0.46	22.07	16.20	5.45	25.50	69.87	42.80	2.15
90	Rangpur	0.45	21.97	16.90	8.80	23.94	69.15	42.20	1.80
94	Gaibandha	0.47	21.25	16.71	9.45	20.48	68.20	40.70	1.12
95	Gaibandha	0.60	22.56	17.55	4.15	20.40	66.30	39.50	1.56
96	Gaibandha	0.42	23.62	15.83	9.36	24.36	67.56	38.67	1.73
97	Gaibandha	0.58	21.56	16.93	4.62	20.83	66.97	41.20	1.52
103	Dinajpur	0.46	23.20	17.25	9.70	20.04	67.84	39.63	1.03
105	Nilphamari	0.24	22.96	16.32	3.33	22.12	67.00	38.40	1.88

Note: HWS-Hot water soluble, AS-alkali solubility

As shown in Table 1, 1% alkali solubles in dhaincha were 20-25%. The highest amount of 1% alkali soluble was found in an accession of Rangpur district. The higher NaOH solubility represented low molar mass of carbohydrates and other alkali soluble materials. The 1% soda solubles in dhaincha was higher than softwood and hardwood and lower than agricultural wastes like rice straw, wheat straw, bagasse, etc.[20-21]

Lignocellulosic biomass, such as forestry and agricultural residues, contains a significant amount of lignin, a polyphenolic macromolecule, at up to 20–40% of its dry weight. Lignin is undesirable component for pulping. In the pulping process, lignin is removed. So less amount of lignin is advantageous for pulping. As shown in Table 1, lignin contents in dhaincha samples were close to hardwoods[18] and varied from 20.5% to 23.1% except for a sample from Sirajgong, which had a higher lignin content of 26.9%.

The holocelluose content in dhaincha was varied from 66-75%, which was within the range of wood and important non-wood.[16]The highest amount of holocellulose content was found in the dhaincha accession from Nilphamari. This higher amount of holocellulose in dhaincha from Nilphamari was due to a different species of African origin.

Cellulose is the key component of chemical pulp and α-cellulose content in raw material affects pulp yield and paper strength properties. The cellulose content in dhaincha in different plots of the country was varied from 38.4% to 43.7%. The highest amount of cellulose was found in dhaincha from the accession No. 45 of Jhinaidaha, which was higher than the previously reported data.[9]

The hemicelluloses have much lower molecular weight and degree of polymerization as compared to cellulose. Pentose sugars are the main components of hemicelluloses. In this paper, the pentosan content was measured, and it was found to vary from 16 to 19% with locations. In the chemical pulping, a part of hemicelluloses is dissolved with lignin and a substantial quantity of hemicelluloses remains with the pulp, which affects the swelling behavior of the pulp fiber.[22] Hemicellulose play important role in bonding dependent papermaking properties. As for example, Sitch and

Marshall[23] showed that the tensile strength increased, whereas tearing resistance and fold endurance decreased with the increase of the hemicellulose content. The bursting strength reached a maximum at about 15% alkali-extractable hemicellulose content.

Ash content in a raw material hampers chemical recovery system, consume cooking chemicals ultimately affect pulping process. Ash content in the studied dhaincha was varied from 1.0% to 2.2%, which lower than those of some non-wood, but slightly higher or similar than those of hardwood and softwood.[16]

Table 2 shows the descriptive statistics of chemical characteristics of dhaincha. According to the ANOVA test result, amount of pentosan and holo-cellulose vary significantly for different area (districts) of sample collection ($p<0.05$). On the contrary, all other characteristic studied here do not differ considerably ($p>0.05$) at 5% level of significance.

Further, Post Hoc Duncan Multiple Range Test (DMRT) has been carried out to test the equality of pentosan and holo-cellulose in samples from different districts. It is evident that the pentosan of samples from Mymensingh, Gaibandha, Rangpur, Sirajganj were in a sample group at 5% level of significance, whereas the pentosan of samples from Jhenidah significantly varies from them. Next, holocellulose of samples from Mymensingh, Gaibandha, Jhenidah, Rangpur do not fluctuate significantly, and that of samples from Sirajganj varies from samples of the mentioned districts.

Table 2. Descriptive statistics of chemical properties of dhaincha

Properties	**Range**	**Average**	**Standard Deviation (SD)**
Extractive cont.	0.27-0.65	0.47	0.107
K. Lignin	20.91-23.62	22.27	0.888
Pentosan	16.02-18.81	17.27	0.834
HWS	2.70-10.22	5.84	2.588
1% AS	19.30-23.94	21.70	2.039
Holo-cellulose	66.10-75.47	69.72	2.967
α-cellulose	38.4-43.70	40.75	1.313
Ash	1.03-2.15	1.57	0.322

3.2 Pulping

The difference of chemicals characteristics did not varied significantly. Therefore, seven accessions of different district with higher α–cellulose content were chosen for pulping experiment. Kraft pulping was done with constant cooking conditions based on our previous studies. [1] Yield is the most significant economical factor in pulping processes. The highest pulp yield was obtained from accession number 45, which was collected from Jhinaidaha district. This higher pulp yield can be explained by the higher α–cellulose content in dhaincha (Table 1).

Kappa number represents extent of delignification. It depends on lignin content in the raw material, lignin structure, and accessibility of lignin during pulping processes. The lowest kappa number (8.9) obtained from accession number 105 and the highest from accession number 45 (Table 3). This result indicated that the dhaincha was easier to delignify as compared to other similar non-wood like cotton stalks, jute stick, etc.[24-25] The pulp yield obtained in this study was similar to our previously reported data in our employed cooking conditions, but kappa number was slightly lower.[1] But inferior than data obtained by Dutt et al.[26] where pulp yield was 49.8 % with kappa number 30.4 in kraft pulping of *S. aculeata*, while *S. sesban* showed 47.0 pulp yield with kappa number 31.0.[27] The lower pulp yield of dhaincha in this investigation possibly comes from the low α-cellulose (Table 1).

The selectivity of delignification can be expressed as the weight ratio of the lignin and carbohydrates removed from the wood after a certain cooking time or at a given degree of delignification. A high selectivity thus means low pulp yield and lower kappa number. Table 2 shows the pulp yield to kappa number ratio, which represented selectivity of pulping. As shown in Table 3, the highest selectivity was observed in the dhaincha collected from accession number 78 and 105.

Table 3. Kraft pulping of dhaincha from selected accessions

Accession number	Name of district	Pulp yield (%)	Kappa number	Selectivity
25	Mymensingh	43.72	10.0	4.37
45	Jhinaidaha	43.99	15.1	2.91
78	Sirajganj	42.14	9.3	4.53
85	Rangpur	43.93	10.0	4.39
90	Rangpur	42.65	10.7	3.99
103	Dinajpur	42.67	13.1	3.25
105	Mymensingh	41.40	8.9	4.65

3.3 Bleaching and papermaking properties

All these pulp obtained from the seven dhaincha accessions were bleached by $D_0E_pD_1$ bleaching sequence under identical cooking conditions. Dhaincha pulp showed excellent bleachability and reached to 81 to 85% brightness using 30kg ClO_2 per ton of pulp. The maximum brightness (85.4%) was achieved for dhaincha pulp obtained from accession number 105 and minimum brightness (81.1%) achieved from the dhaincha pulp of accession number 45. This can be explained by lower kappa number of unbleached pulp (Table 2). Better bleachability would certainly reduce bleached effluent load. Gustavsson et al.[25] concluded that a high content of beta-*O*-4 structures in the unbleached residual lignin was found to contribute to a better bleachability of the pulp in ECF and TCF bleaching.

It is clearly seen from the Table 3 that moderate beating of dhaincha pulp leads to remarkable increase in drainage

resistance. The initial drainage resistance was 22-23 °SR. Refining of only 2000 PFI revolutions increased drainage resistance to 51-58 °SR. The tensile index and burst index of dhaincha pulp were improved with minimal amount of energy on beating. There were no significant variations of papermaking properties found among the dhaincha samples. The range of papermaking properties were: tensile index 62-69 N·m/g, tear index 8-9 mN·m^2/g and burst index 5-6 kPa.m^2/g. Maximum tensile index (69.1 N·m/g) was observed from the dhaincha of accession number 28. The papermaking properties dhaincha pulp obtained in this study were slightly lower than the previously reported data.[1] This can be explained by species variation, plant age, etc. It was observed that all papermaking properties are linearly increased with plant age.[8] Mimosa plant pulp also showed better physical properties in mature plant.[29]

Table 4. Bleaching of dhaincha pulp

Accession number	Bleaching yield (%)	Brightness (%)	°SR (2000 Rev)	Tear index mN.m^2/g	Tensile index N. m/g	Busting index kPa.m^2/g
25	93.97	83.1	55	8.8	69.1	5.6
45	94.60	81.1	52	8.3	65.9	5.5
78	94.08	84.0	57	8.1	63.2	5.5
85	95.78	81.5	55	7.9	67.4	6.3
90	96.17	82.7	51	7.7	63.7	6.0
103	96.24	85.2	53	8.6	65.4	5.7
105	94.30	85.4	58	8.7	61.6	5.1

4. CONCLUSIONS

The variation of chemical properties of dhaincha among the accessions in different districts of Bangladesh was studied. The amount of α–cellulose, pentosan and holo-cellulose varied significantly for different areas (districts) of sample collection ($p<0.05$). On the contrary, all other characteristic studied here did not change considerably ($p>0.05$) at 5% level of significance. The highest amount of α–cellulose (43.7%) was found in the No. 45 accession of Jhinaidaha district, and the lowest amount was observed in the No. 105 accession of Nilphamari district, which consequently provided the highest and lowest pulp yield, respectively. A strong positive correlation was noticed between the α–cellulose content and the pulping yield. The obtained Dhaincha pulp showed excellent bleachability, and could be bleached to 81 to 85%ISO brightness using 30kg ClO_2 per ton of pulp. There were no significant variations of papermaking properties observed among the pulps obtained from different dhaincha samples.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the R&D project, 2016-17 of BCSIR.

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