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Potassium hydroxide pulping of four non-woods

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Abstract

Four non-woods such as, dhaincha (*Sesbania bispinosa*), jute stick (*Corchorus capsularis*), wheat straw (*Triticum aestivum*) and corn stalks (*Zea mays*) were cooked by potassium hydroxide (KOH) at the optimum conditions of soda pulping. Dhaincha, wheat straw and corn stalks were delignified to kappa number 19.4, 13.6 and 19, respectively, while jute stick was not delignified sufficiently (kappa number 32.5). All these four raw materials maintained good yield in KOH process. Dhaincha produced the highest pulp yield (50.5%) and wheat straw had the lowest pulp yield (44.7). All pulps were bleached by $D_0E_pD_1$ bleaching sequences in identical bleaching conditions. Final pulp brightness reached to above 80% ISO except jute stick pulp. Jute stick pulp reached to 74.9% brightness only after the consumption of 30 kg ClO_2/ ton of pulp. The overall bleaching yields were 92.6%, 88.4%, 90.1 and 90.8% for dhaincha, jute stick, wheat straw and corn stalks pulps, respectively. The °SR of these four non-wood bleached pulps was above 20, consequently improved papermaking in the unrefined state. Beating rapidly increased papermaking properties, as for example, the tensile index of dhaincha pulps increased from 49 N.m/g in the unrefined pulp to 90 N.m/g in the beaten 50 °SR. It can be seen that KOH is a good substitute to soda process for non-wood.

Keywords: Non-wood; Potassium hydroxide pulping; Bleaching; Beating; Papermaking properties

Introduction

World expected GDP growth in 2018 is 3.6% (OECD 2017), while the growth in Bangladesh is much higher, 7.1%, consequently cellulose, paper and paperboard consumption will increase significantly. Therefore, Bangladesh needs more fibrous raw materials to meet the demand. Lignocellulosic raw materials come from forest. But the forest area in Bangladesh is very limited and population density is extremely high, which facilitates conversion of forest land into agricultural land.

In this context, substantial amounts of agricultural wastes are generated every year that can be an alternative substitute for lignocellulosic raw materials (*Jahan et al*., 2016). Jahan *et al*., (2016) also showed that main crop residue generated in Bangladesh is rice straw, which accounts 78.3 million MT, followed by wheat straw (2 million MT). Corn stalks produce about 1.5 million MT. Jute is one of the most important natural fibers in Bangladesh. It generates about 3.5 million MT jute stick in the year of 2013 (FAOSTAT 2016). These can be used as alternative lignocellulosic raw materials. To exploit these wastes, our research group has carried out extensive research on pulping of rice straw, wheat straw, jute stick, dhaincha, mulberry plant, mustard stalks, lentil stalks etc. (Jahan *et al*., 2013, 2013a, 2016a; Matin *et al*., 2015; Rahman *et al*., 2014, 2016; Sarker *et al*., 2017;).

But there are numerous limitations on utilizing agricultural wastes as pulping raw materials. i) Collection of agricultural wastes is difficult as these grow scattered areas, ii) these are bulky compared to wood. iii) contain high silica creating problems in recovery plant and paper machine wet end, iv) high content of fines in the raw material hampers machine running, etc. To overcome these limitations, many attempts have been made, such as organic acid pulping (Jahan *et al*., 2005, 2006; Xu *et. al*., 2006), potassium hydroxide (KOH) pulping (Huang *et al*., 2007, 2008; Rodríguez *et al*., 2008). KOH pulping is suitable for small scale pulping, the black liquor of which can be used as fertilizer in agriculture (Huang *et al*., 2007; Jahan *et al*., 2016a).

Recently our group finds interesting results on potassium hydroxide pulping of kash (*Saccharum sponteneum* (Jahan *et al*., 2016a) and rice straw (Jahan *et al*., 2016b). Kash was easily delignified to kappa number 12.5 with pulp yield of 52.9% at the conditions of 14% KOH expressed as NaOH for 2 h at 150°C. At this condition, pulp yield in soda (NaOH) process was 0.3% lower with higher kappa number. Potassium based pulping black liquor was also applied in soil amendment and found beneficial on soil properties and the growth of Red amaranthus. Compared to non-amended control soil, black liquor increased Red amaranthus growth by 2.7 times (Jahan *et al*., 2016a). At the optimum KOH pulping conditions (alkali charge 12% as NaOH, cooking temperature 150 °C for 2 h and material to liquor ratio, 1:6), rice straw produced pulp yield of 42.4% with kappa number

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10.3. KOH pulp bleached to 85% brightness by D_0EpD_1 bleaching sequences with ClO_2 consumption of 25 kg/ton of pulp (Jahan *et al*., 2016b). Silica and lignin were separated from the black liquor of KOH pulping. The amount of recovered silica, lignin and hemicelluloses were 10.4%, 8.4% and 13.0% (Jahan *et al*. 2016b). The papermaking properties of KOH pulp from rice straw were slightly better than those of corresponding NaOH pulp.

Therefore, in this paper, four non-wood such as dhaincha, jute stick, wheat straw and corn stalks pulping was done with KOH. Pulps were bleached by D_0EpD_1 bleaching sequences and papermaking properties were evaluated.

Materials and methods

Raw materials

Four non-woods : dhaincha, jute stick, wheat straw and corn stalks were collected and cut to 2-3 cm in length. Thickness of jute stick and dhaincha was 2-3 mm in size. After determination of the moisture content of air dried raw materials equivalent to 300 gm o.d. (oven dried) was weighed separately in a polyethylene bag for subsequent cooking experiments.

Pulping

Pulping of dhaincha, jute stick, wheat straw and corn stalks was carried out by KOH process in an electrically heated 5 lit capacity digester. Active alkali charge was fixed at 16 % as NaOH on od raw materials. The following parameters were maintained: i) liquor to fiber ratio: 6:1 for wheat straw and corn stalk and 5:1 for jute stick and dhaincha, ii) temperature: 150 °C for wheat straw and corn stalk and 170 °C for jute stick and dhaincha, iii) Cooking time: 120 min at maximum temperature. After the desired time of cooking, pulp was filtered and black liquor was collected for subsequent experiment. Pulp was washed with tap water till the removal of all chemicals. The yield of the pulp was determined gravimetrically from the oven-dried weight of raw material. The kappa number of the resulting pulp was determined in accordance with Tappi Test Methods (T 236 om-99).

D_0EpD_1 bleaching

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 ClO_2 was 2%. The temperature was 70°C in D_0 stage for 45 min. Pulp consistency was 10%. The pH was adjusted to 2.5 by adding dilute H_2SO_4. In the alkaline extraction stage, pulp was extracted with 2 % NaOH and 0.5% H_2O_2 (on od pulp) for 120 min at 70°C. Pulp consistency was 10 %. The end pH in the D_1 stage was adjusted to 4 on adding dilute NaOH. The ClO_2 charge in the D_1 was 1%. The brightness was determined in accordance with Tappi Test Methods T525 om 92.

Evaluation of pulps

The bleached pulps obtained from dhaincha, jute stick, wheat straw, and corn stalks were beaten in a PFI mill in different revolutions and handsheets of about 60g/m^2 were made in a Rapid Kothen Sheet Making Machine. The papermaking properties determined were according to TAPPI Standard Test Methods. The sheets were tested for tensile (T 494 om-96), burst (T 403 om-97) and tear strength (T 414 om-98) according to TAPPI Standard Test Methods.

Results and discussion

Raw materials

As shown in Table I, α-cellulose content in these four raw materials was above 40%, which is acceptable for pulping. The holocelluose content in these raw materials varied from 66 to 77%, which was within the range of wood and important non-woods (Jimmenez *et al*., 1990). The lowest lignin content was observed in wheat straw and corn stalk that facilitates easier pulping. The ash content was much higher in wheat straw than the other non-woods. The high ash content is disadvantageous in pulping process that creates problems in chemical recovery system.

Pulping

These raw materials were cooked under identical cooking conditions based on our previous cooking conditions in soda process (Jahan *et al*., 2004, 2007, 2016b, 2016c). Temperature and material to liquor ratio for dhaincha and jute stick were 170°C and 1:5 and for wheat straw and corn stalks were 150°C and 1:6, respectively. KOH charge was used as NaOH. As shown in Table II, KOH cooking resulted in a screened yield and total yield of 48.6% and 50.5%, respectively for dhaincha. The pulp had a kappa number of 19.4. The pulp yield was much higher and kappa number lower than the previously studied soda-AQ and kraft processes (Jahan *et al*. 2007). This pulp yield is close to formic acid-peroxyformic acid process (Jahan *et al*. 2007a). Screened pulp yield and total pulp yield from jute stick were 48.4 and 48.8%, respectively at a kappa number of 32.5. The higher kappa number can be explained by higher lignin content in jute stick (Table I). But the pulp yield and kappa number in KOH process were higher than the kraft process (Jahan *et al*., 2016c). This result indicates that jute stick needs more alkali charge in KOH process. No reject was observed for wheat straw and corn stalks in the employed cooking conditions. Pulp yield in wheat straw was 44.7%

Table I. Characteristics of dhaincha, jute stick, wheat straw and corn stalks

Parameter	Jute stick (Rahman *et al*., 2016)	Dhaincha (Sarker *et al*.,2017)	Wheat straw (Jahan *et. al*., 2016b)	Corn stalks (Li *et al.*, 2012)
Hollo Cellulose,%	76.9	66 -75	65.6	-
Alpha Cellulose, %	40.8	40 -44	40.1	39.4
Extractive, %	2.2	0.4 -0.6	0.9	2.5
Ash, %	0.74	1-2	9.7	9.9
Klason lignin, %	25. 3	21 -23	15.0	18.1
Pentosan, %	18. 1	16 -19	21.9	16.0

Table II. Pulping of four non-woods by KOH process

Sample	M:L	Temperature (^{O}C)	Screened yield (%)	Reject (%)	Total pulp yield (%)	Kappa no
Dhaincha	1:5	170	48.6	1.93	50.5	19.4
Jute stick	1:5	170	48.4	0.38	48.8	32. 5
Wheat Straw	1:6	150	44.7	0	44.7	13. 6
Corn Stalk	1:6	150	45.8	0	45.8	19.0

kappa number 13.6, which were close to the previous results (Jahan *et al*., 2016a). In that study pulp yield from wheat straw in soda process was 44.0% at a kappa number 12.0 in the same cooking conditions. Pulp yield in corn stalks was 44.7% at a kappa number 19.0. Byrd *et al*. (2006) also showed that screened pulp yield and total pulp yield of corn stalks were 44.5% and 46.6% at kappa number 16.5 in soda-AQ process. Sun *et al*. (2012) also investigated corn stalk pulping by KOH and NH_4OH. The combined alkaline system effectively removed lignin during pulping. Wheat straw and corn stalks respond better to delignification in KOH process, resulting lower kappa number and higher pulp yield than other non-woods (Khristova *et al*., 2002, Hurter and Byrd 2017). Approximately 90% delignification was achieved at the temperature of 150°C for over 30 min. From the pulp yield and kappa number data, it can be inferred that pulp yield from dhaincha in KOH process is similar or higher than hardwoods in conventional process (Francis *et al*., 2008).

Bleaching

All pulps were bleached by $D_0E_pD_1$ bleaching sequences in identical bleaching conditions. The residual ClO_2 data are not shown because of 100% of the ClO_2 consumption in D_0 and D_1 sequences. As shown in Table III, final pulp brightness reached to above 80% ISO except jute stick pulp. Jute stick pulp reached to 74.9% brightness only after the consumption of 30 kg ClO_2/ ton of pulp. This can be explained of higher initial kappa number (Table II). To achieve 80% brightness, jute stick pulp needs more ClO_2 charge. Variation of pulp viscosity among these four different pulps was not prominent. The highest viscosity after Ep stage was 21.3 mPa.s for dhaincha pulp and the lowest viscosity was 18.4 mPa.s for wheat straw pulp. The final pulp viscosity was 17-19, which indicates that the pulp viscosity did not decrease significantly on the applied bleaching conditions. The final kappa number of dhaincha, wheat straw and corn stalks pulp reached to 1.1-1.2, which indicated almost fully bleached pulp. But the same for jute stick pulp was 3.7. Therefore, jute stick was not delignified sufficiently during

Table III. Bleaching of non-wood KOH pulps

Raw material	Satge	Kappa number	Viscosity (mPa.s)	Brightness (% ISO)	Yield (%)
Dhaincha	D_0	-	-	-	-
	E_p	4.1	21.3	61.5	-
	D_1	1.2	19.2	81.7	92.6
Jute stick	D_0	-	-	-	-
	E_p	12.3	20.6	43.2	-
	D_1	3.7	18.7	74.9	88.4
Wheat straw	D_0	-	-	-	-
	E_p	3.5	18.4	60.6	-
	D_1	1.1	17.0	81.3	90.1
Corn stalks	D_0	-	-	-	-
	E_p	3.6	21.1	58.8	-
	D_1	1.1	18.8	80.9	90.8

cooking or D_0 stage to get fully bleached pulp. The overall bleaching yields were 92.6, 88.4, 90.1 and 90.8% for dhaincha, jute stick, wheat straw and corn stalks pulps, respectively. Hurter and Byrd (2017) indicated a total bleaching loss of 6 - 7% with typical non-wood fiber at kappa number of 15. The authors further anticipated a bleaching loss of 9-11% at a kappa number of 20. Therefore, the bleaching yields are within the expected range.

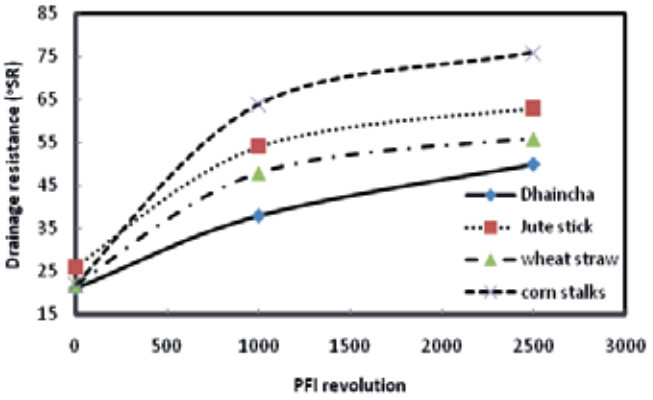

Fig. 1. Increase of drainage resistance of KOH pulps with PFI revolution

Papermaking properties

The refining behaviour of the pulps is shown in Fig. 1 in relation to drainage resistance (°SR) development. The °SR of these four non-wood pulps was above 20, unrefined jute stick pulp had already 26 °SR. With increasing PFI revolution, °SR value of corn stalks and jute stick pulps increased faster compared with dhaincha pulp. At the beating degree of 2500 PFI revolution, °SR value increased from 22 in unrefined state to 76 for corn stalks, while °SR value increased from 21 in unrefined state to 50 for dhaincha pulp. The higher °SR value can be explained by the presence of pith, vessel, and parenchyma in the starting raw materials, which generate fines and increase hydration.

Figs 2-5 show tensile, burst, tear and elongation development in relation to beating degree. Dhaincha and jute stick pulp showed the highest tensile index. The high yield and consequently high-hemicelluloses content in these pulps resulted in good fiber bonding ability and hence high tensile and burst strength. Beating increased the strength properties like tensile and burst strength and elongation. For instance, the tensile index of dhaincha and jute stick pulps increased from 49 N.m/g in the unrefined pulp to 90 N.m/g and 94

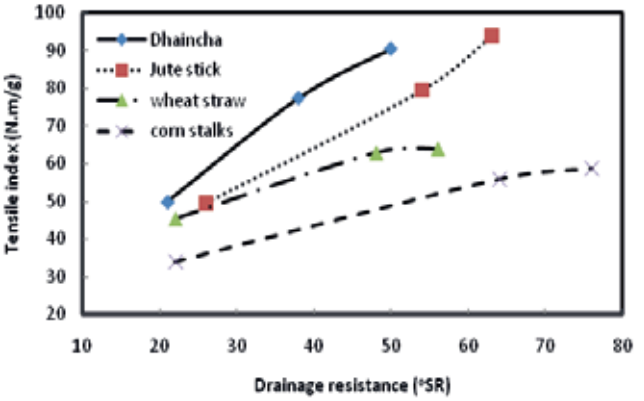

Fig. 2. Tensile index development of KOH pulps with °SR

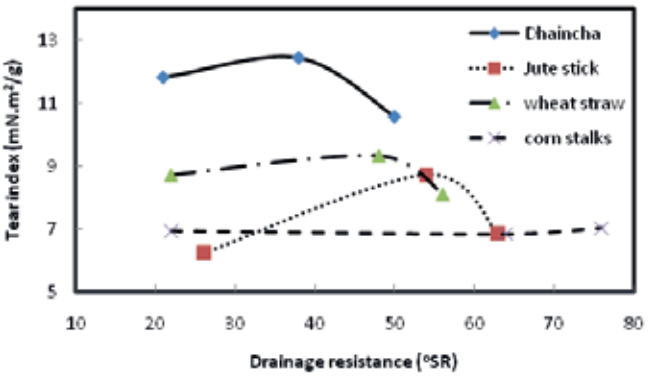

Fig. 3. Tear index development of KOH pulps with °SR

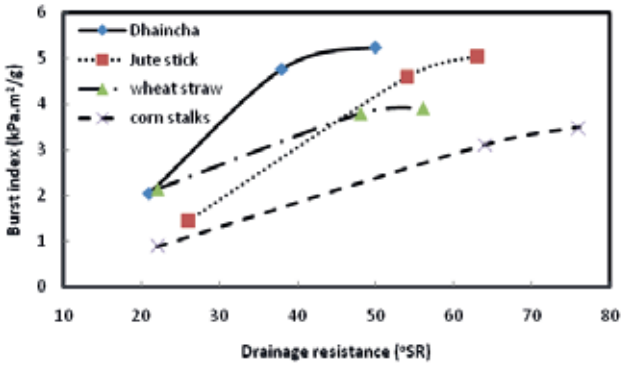

Fig. 4. Burst index development of KOH pulps with °SR

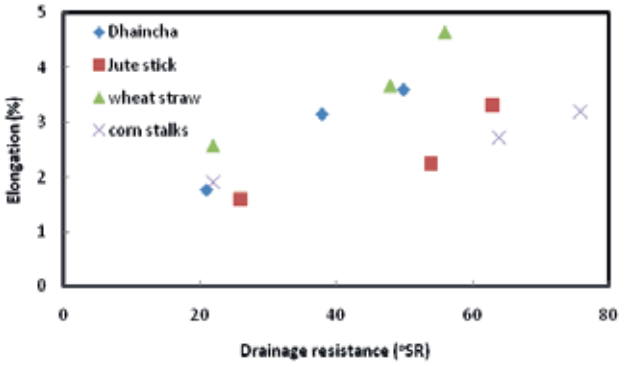

Fig. 5. Elongation development of KOH pulps with °SR

N.m/g in the beaten degree 50 and 63°SR, respectively. Wheat straw and corn stalks pulp also showed good tensile index (58-63 N.m/g). Dhancha pulp showed the highest tear index of 12.4 mN.m^2/g, which was 42.9%, 33.3% and 81.7% higher than jute stick, wheat straw and corn stalks pulps, respectively. Tear index of corn stalks pulp was independent with beating grade (Fig. 4). Thus, properties of papers obtained from these four non-wood pulps in KOH process are considerably better than those of other non-wood pulps (Dutt *et al*., 2008, Enayati *et al*., 2009). As shown in Fig. 5, elongation of dhaincha and wheat straw pulps showed better results than jute stick and corn stalks pulps.

Conclusion

Dhaincha, wheat straw and corn stalks was delignified satisfactorily by KOH in the optimum cooking conditions of soda process on preserving the pulp yield. Dhaincha, wheat straw and corn stalks pulps were bleached to brightness above 80 %. The overall bleaching yield of KOH pulps was 90-93%. But jute stick was not delignified as desired in applied cooking conditions, consequently showed poor bleachability and lower overall bleaching yield. A good papermaking properties were observed for these four non-wood bleached pulps. The obtained data show that potassium hydroxide (KOH) process could be considered as a promising alternative process for non-wood.

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