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POTASSIUM HYDROXIDE PULPING OF RICE STRAW

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Abstract:

Rice straw is one of the major crop residues in Bangladesh which can be an alternative fibrous raw material for a forest deficient country. Due to high content of silica, rice straw is not a suitable raw material for conventional pulping process with chemical recovery system. The pulping process without chemical recovery is not environmental and economically viable. Therefore, potassium hydroxide (KOH) pulping of rice straw at mild conditions has been explored for packaging paper and spent liquor evaluated for fertilizer. At the conditions of 6% KOH, 2 h of cooking at 150°C and material to liquor ratio of 1:6, pulp yield was 51% with kappa number 23.4. To reduce the energy consumption, two stages KOH pulping of rice straw also carried out at atmospheric conditions. Pulp yield of 45.4 % with kappa numbers 19.7 was obtained at the conditions of 16% KOH charge for 120 min of cooking at 90°C. The papermaking properties of KOH pulp from rice straw in both processes were quite acceptable for kraft liner. In weak KOH pulping, a major part of silica retained on pulp fiber, but most of the silica dissolved in the two stages KOH pulping process. Dissolved silica, lignin, and hemicelluloses were separated from the spent black liquor. The potassium-rich spent liquor was used as a soil amendment (fertilizer).

Keyword: *Weak KOH pulping, Pulp yield, Papermaking properties, Fertilizer,*

Introduction

From the environmental point of views, conventional pulping of crops residues is problematic due to high content of silica and fines. Crops residues are generally bulky in nature. Therefore, the transportation of these raw materials represents a big problem. Crop residues, due to their inherent bulkiness, pose a significant challenge in transportation. However, the volume of crop residues produced in a specific region is often insufficient to support the establishment of a viable pulp mill. Moreover, implementing a small-scale pulp mill is not viable in environmental and economic standpoints. Utilizing crop residues as pulping raw materials presents several drawbacks, including elevated levels of silica and pulp fines, which limit their compatibility with traditional alkaline pulping methods. Consequently, numerous initiatives have been undertaken to address and overcome these limitations. Organic acid fractionation [1], potassium hydroxide pulping, [2-4], nitric acid fractionation [5] etc. have been explored to use crops residues as pulping raw materials in biorefinery concept.

Huang et al. [2, 6] investigated pulping process of wheat straw, aiming to eliminate black liquor waste. They prepared cooking liquor by combining aqueous ammonia with a small quantity of potassium hydroxide (KOH). This cooking liquor not only facilitated the pulping process but also enriched the resultant black liquor with essential inorganic nutrients such as potassium and nitrogen, making it suitable for use as a fertilizer. Sun et al. [7] also investigated the pulping of corn stover using a combination of KOH and NH4OH. This alkaline liquor removed 90% lignin at a temperature of 150°C for over 30 min.

All these processes are energy intensive, which increased capital investment and production cost. Development of a simple environmental friendly and atmospheric pressure pulping process is the interest of this study. Agricultural crop residues like rice straw, wheat straw, corn stalks, kan grass bagasse, etc., are loosely anatomical metrics [8, 9]. Therefore, the delignification and defibering of these raw materials can be achieved by chemical pulping at atmospheric pressure and weak alkali charge.

In this paper, potassium hydroxide (KOH) pulping of rice straw at atmospheric pressure and weak KOH charge are presented and compared with wheat straw, bagasse and kan grass pulping. The strength properties of the produced pulps were also evaluated. The dissolved lignin and silica were separated by reducing pH, and isolated lignin was characterized. The KOH liquor would be used for irrigation purpose, so nothing will be wastes in the proposed process.

Materials and Methods

Raw materials

Rice straw was collected and cut to 2-3 cm in length. The cellulose, pentosan, lignin and ash contents in the rice straw were 38.5 %, 19.1 %, 12.7 % and 17.2 %, respectively. The moisture content in the raw material was determined and kept in an airtight plastic bag for subsequent cooking experiments.

KOH pulping at atmospheric pressure

In this investigation, rice straw was pre-extracted with 12% KOH for 2 h at 90°C. In the first stage, rice or wheat straw was pre-extracted with 16.8% KOH on straw at 90°C for 120 min. Liquor to material was 8:1. After the desired time, the treated biomass was filtered using a Büchner funnel and the solid residue was washed with distilled water. In the second stage, KOH extracted rice straw was further delignified with 16% KOH charge, cooking at 90°C for 120 min. The pulp consistency was 10%. The yield of the pulp was determined gravimetrically from the oven-dried (o.d.) rice straw. The kappa number of the resulting pulp was determined in accordance with TAPPI Test Methods (T 236 om-99). The same experiment was carried out for wheat straw, bagasse and kan grass for comparison.

The obtained black liquor from the both stages were mixed together for further analysis. The pH of the black liquor was reduced to 7 by adding 4N sulfuric acid with constant stirring using a magnetic bar. After adjusting the pH to the desired value, the conical flask was kept undisturbed for the settling of the flocks. After complete precipitation of silica, the contents in the flask were centrifuged. After silica separation, the pH of the black liquor was again reduced to 2 by 4N sulfuric acid addition to precipitate the dissolved lignin. The silica and lignin precipitates were then air-dried overnight followed by oven drying at 105°C overnight to obtain constant mass. The solid (T650 om-99) and ash contents (T211 om-02) in black liquor were measured in accordance with TAPPI Test Methods.

Weak KOH treatment

Pulp was prepared from rice straw by 6, 8 and 10% KOH charge at 150°C for 120 min in a 5 L capacity rotary digester. The pulp consistency was 6%. After the desired time, biomass was filtered in a Buchner funnel and residue was washed with distilled water. The total filtrate was collected for the subsequent experiment. The lignin was precipitated at different pH by adding sulfiric acid. In each pH level, lignin was separated by centrifugation. The detail fractionation of black liquor is shown in Fig. 1. The solid content

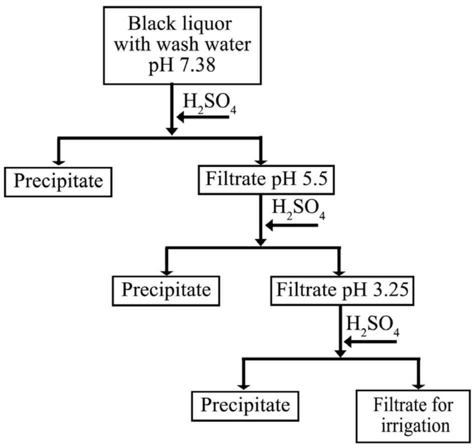

Fig. 1. Fractionation of black liquor of weak KOH pulping of rice straw

in each filtrate, precipitated lignin and the yield of the pulp were determined gravimetrically at 105°C to obtain constant mass based on the oven-dried (o.d.) mass of raw material. The kappa number of the resulting pulp was determined in accordance with TAPPI Test Methods (T 236 om-99). The ash content in pulp, precipitated lignin and filtrate were measured by TAPPI Standard Test Methods (T211 om 07). The SiO_2, K_2O and other inorganic compounds were determined by XRF in IGCRT, BCSIR.

Evaluation of pulp

The produced pulps were beaten in a Valley beater at different times and handsheets (approximately 60 g/m2 grammage) were made using a Rapid Köthen Sheet Making Machine (TAPPI Test Method T 205 cm-88). The pulp strength indices were determined according to TAPPI Standard Test Methods. The sheets were tested for tensile (T 494 om-96), burst (T 403 om-97), and tear (T 414 om-98) strength indices.

Results and discussion

KOH pulping at atmospheric pressure

In order to pre-extract silica and part of the lignin from the raw materials prior to pulping, rice and wheat straws, kan grass and bagasse were pre-extracted with 12% KOH for 2 h at 90°C, and rice straw was pressed to remove maximum liquor. The pre-extracted liquor was kept for further analysis.

Alkaline pre-extracted raw materials were further delignified by 16% KOH charge at 90°C. The overall pulp yield was 45.4% with kappa number 19.7, while the pulp yield for wheat straw, kan grass and bagasse were 52.8, 48.9 and 48.5% with kappa number 20.8, 27.9 and 23.4, respectively (Table 1). In this investigation, the pulp yield at lower temperature than that at higher temperature [3]. In the two stage KOH pulping at atmospheric pressure dissolved most of the silica and lignin, which will be discussed in the later section.

Weak KOH pulping

Pulping at the atmospheric conditions required a very high charge of KOH, therefore, an investigation was also done by weak KOH charge. A weak KOH pulping at 150°C was also carried out to understand the behavior of rice straw. Rice straw pulping was carried out by weak potassium hydroxide (KOH) liquor and results are shown in Table 2. It was found that only 6% KOH at 150°C for 120 min is enough to get defiber rice straw. The pulp yield was 51.0% at 6% alkali charge, which decreased to 43.7% with increasing KOH charge to 10%. The higher pulp yield can be explained by retention of silica present in rice straw. As shown in Table 2, ash in pulp was very high (9.7-13.9%), because KOH was not sufficient to dissolved silica from the rice straw. In another investigation, at higher KOH charge (>17%), pulp yield was lower and most of the silica was dissolved into the cooking liquor [3].

The target of this investigation was to produce brown paper for liner of corrugated board. Therefore, bleachability was not a major fact. For understanding of delignification of at low temperature and weak KOH, kappa number was determined. The kappa number decreased from 23.6 to 16.8 with increasing KOH charge from 6% to 10%. In our previous investigation, the kappa number decreased from 10.3 to 6.2 with increasing KOH charge from 17.9% to 21.8%. In an earlier investigation of two stages KOH pulping of rice straw, pulp produced with kappa number 19.7 at the conditions of 120 min of cooking at 90°C with 15.5% KOH change, the yield of the pulp was 45.4% [10].

Table 1. KOH pulping of crops residues at atmospheric pressure

Raw material	Pulp yield (%) based on raw material	Kappa number
Rice straw	45.4	19.7
Wheat straw	52.8	20.8
Kan grass	48.9*	27.9
Bagasse	48.5	23.4

** 180 min at 90°C*

Table 2. Weak potassium hydroxide pulp of rice straw

KOH charge (%)	Pulp yield (%)	Kappa number	Ash in pulp (%)
6	51.0	23.4	13.9
8	47.0	17.7	13.1
10	43.7	16.8	9.7

Table 3. Papermaking properties of crop residues pulps obtained from low temperature at 40 °SR

Raw material	Tear index (mN·m^2/g)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g
Rice straw	5.2	45.4	2.5
Wheat straw	7.7	52.2	2.7
Kan grass	9.0	58.3	3.0
Bagasse	6.3	63.5	4.2

Table 4. Papermaking of pulp produced from weak KOH

°SR	Tear index (mN·m^2/g)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g
31	4.62±0.23	35.1±1.87	2.0±0.19
36	6.95±0.19	47.16±1.43	2.3±0.21
39	6.84±0.21	47.21±1.23	2.63±0.15
41	6.02±0.24	47.39±2,83	2.69±0.06
47	4.84±0.19	49.08±1.95	2.76±0.22

Table 5. Fractionation of KOH spent liquor

	Rice straw	Wheat straw
Silica (%)	13.2	7.8
Lignin (%)	9.9	15.1
Hemiceluloses (%)	13.2	14.9

Table 6. XRF results of ash of pulp, filtrate and lignin

Ash sample	K_2O, %	SiO_2, %	Fe_2O_3, %
Pulp	0.98	61.8	2.54
Pulping liquor at pH 7.38	80.4	1.85	1.69
Pulping liquor at pH 5.5	76.4	1.92	1.03
Pulping liquor at pH 3.25	56.4	1.51	0.77
Precipitated lignin at pH 7.38	6.7	25.4	0.44
Precipitated lignin at pH 5.5	10.5	35.3	8.19
Precipitated lignin at pH 3.25	65.2	1.3	2.21

Papermaking properties

The papermaking properties of rice straw pulp at 40 °SR (extrapolation) obtained from lower temperature pulping are shown in Table 3. The tensile, tear and burst indexes of the rice straw pulp were inferior than those of wheat straw, kan grass and bagasse pulps. The tensile index of KOH pulp from rice straw was 45.4 N·m/g, while it was 52.2 N·m/g for wheat straw pulp. The tear index of rice straw pulp at low and high temperature was similar at 40°SR (by extrapolation) [10]. The lower strength of pulp obtained at low-temperature KOH pulping can be explained by lower lignin removal and degradation of carbohydrates in the two stages.

Table 4 shows the papermaking properties rice straw pulp obtained by weak KOH pulping at different °SR. The tensile and burst indexes increased with increasing in studied °SR value, while the tear increased up to 41°SR followed by decrease. The maximum tensile (47.2 N.m/g) and tear (6.8 mN.m^2/g) indexes were obtained at 39°SR. These papermaking properties were comparable to our previous investigation at higher KOH charge [3].

Black liquor

Chemical recovery is an important step in chemical pulping process, which makes the process economically and environmentally friendly. The chemical recovery process is based on black liquor evaporation-incineration-lixiviation-causticization operations; but it is difficult to apply this process in pulp mills with straw as the raw material. The most of the silica was dissolved in two stage KOH pulping at atmospheric pressure, which was separated from the black liquor by reducing its pH to 7 by dilute sulfuric acid (4N H_2SO_4) addition. The separated silica from the black liquor of the two-stage KOH pulping was 13.2% for rice straw and 7.8% for wheat straw (Table 5). In our previous study, 10.4% silica was precipitated from the black liquor of KOH pulping of rice straw [3].

Lignin, a potential precursor for valuable renewable polymeric materials, has been explored for high-value applications [11]. The separation of lignin from black liquor was achieved by lowering the pH to a range of 2 to 3 through the addition of diluted H_2SO_4. The resulting lignin yields were 9.9% from rice straw and 15.1% from wheat straw.

Black liquor from the weak KOH pulping of rice straw was also investigated. Although the most of the silica retained in pulp fiber, but still the dissolved silica was a big problem for recovery (Table 3). In this investigation, liquor from 8% KOH pulping was selected. The pH of the black liquor, liquor with wash water was 9.41 and 7.38, respectively. The liquor was settled down for whole night, the part of the lignin was precipitated, and accounted 2.1% based on the rice straw. After separating the precipitate, the solid content of the liquor was 33.1%, which included organics and inorganics based of the starting rice straw. The liquor was acidified to pH 5.5 and 3.25 by adding 4N sulfuric acid (H_2SO_4). The precipitated lignins were 2.5% and 8.5% at pH 5.5 and 3.25, respectively. After separating lignin, the solid content of the filtrate was measured and found 30.5% and 24.6% at pH 5.5 and 3.25, respectively. The ash content of the filtrate was 12.87% at pH 7.38, which decreased to 9.44% at pH 5.5.

Table 6 shows major inorganic compounds present in the ash. The pulp ash contained mainly SiO_2 of 61.8%, which indicated that the silica was not dissolved in weak KOH pulping. As expected, the ash in the liquor at pH 7.38 was a very potassium oxide (K_2O) (80.4%), and decreased with reducing pH. The decrease of K_2O in the filtrate ash can also be reflected by increasing K_2O in precipitated lignin ash with decreasing pH. Therefore, after separating lignin, filtrate can be used in soil amendment. In our earlier communication, potassium based pulping black liquor was applied in soil amendment and found benifical 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 [12]. Popy et al. [10] found that Kolmi sag weight increased from 55.2 g/pot to 170.22 g/pot with the application of KOH liquor.

After separating silica and lignin from the both processes, the black liquor can be neutralized with ammonia, and can be used as soil amendments (fertilizer). The details of this conversion process will be discussed in future communication. Therefore, in the proposed crop residual fractionation, nothing will be wasted.

Conclusions

Rice straw pulping without chemical recovery system in environmental friendly manner is possible, where all fractions can be used in different products. It is easily defibrated by weak KOH charge or two stage KOH pulping at atmospheric conditions. The produced pulp yield in weak KOH pulping was higher (around 50%) than the two stage KOH pulping at atmospheric conditions. Most of the silica retained on the pulp fiber weak KOH pulping, while silica dissolved in two stage KOH pulping. The papermaking properties of produced pulp with weak KOH at 40 °SR were quite similar to the pulp from strong KOH. From the dissolved biomass in the two stage atmospheric pulping, 13.2% silica, 9.9% lignin, and 13.2% hemicelluloses were separated, those can be used for biobased products. The liquor still contained a high amount of K_2O organics, which support to amend soil.

References

[1] T. Ferdous, M. S. Jahan, M. A. Quaiyyum, M. N. Uddin, Biomass Conv. Bioref. 2020, 10 (2), 289–297. DOI: https://doi.org/10.1007/s13399-019-00415-3.

[2] G. Huang, J. X. Shi, T. A. G. Langrish, Bioresource Technology. 2007, 98 (6), 1218–1223. DOI: https://doi.org/10.1016/j.biortech.2006.05.002.

[3] M. S. Jahan, F. Haris, M. M. Rahman, P. R. Samaddar, S. Sutradhar, Bioresource technology. 2016, 219, 445–450.

[4] S. Sutradhar, M. Sarkar, J. Nayeem, M. S. Jahan, C. Tian, Bangladesh Journal of Scientific and Industrial Research. 2018, 53 (1), 1–6.

[5] M. M. Rahman, N.-A.-S. Rafsan, J. Nayeem, R. S. Popy, M. Moniruzzaman, M. S. Jahan, Nordic Pulp & Paper Research Journal. 2023, 38 (2), 243–252. DOI: https://doi.org/10.1515/npprj-2022-0073.

[6] G. Huang, J. X., Shi, T. A. Langrish, Bioresource technology, 2007, 98(15), 2829-2835.

[7] Y. Sun, G. Yang, J. P. Zhang, M. S. Yao, Chemical Industry and Chemical Engineering. Quart/CICEQ, 2012, 18, 137-145.

[8] M. S. Jahan, A. Saeed, Y. Ni, Z. He, Journal of Biobased Materials and Bioenergy, 2009, 3(4), 380-385.

[9] M. S. Jahan, M. M. Rahman, Carbohydrate polymers, 2012, 88(2), 583-588.

[10] R. S. Popy, J. Nayeem, K. M. Y. Arafat, M. M. Rahman, M. S. Jahan, Current Research in Green and Sustainable Chemistry. 2020, 3, 100015.

[11] B. M. Upton, A. M. Kasko, (. Chemical reviews, 2016, 116(4), 2275-2306.

[12] M. S. Jahan, T. Akter, J. Nayeem, P. R. Samaddar, M. Moniruzzaman, J-FOR-Journal of Science & Technology for Forest Products and Processes. 2016, 6 (1), 46–53.