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Potassium hydroxide pulping of rice straw in biorefinery initiatives

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HIGHLIGHTS

- KOH pulping of rice straw and wheat straw were carried out.
- Pulp was bleached and papermaking properties were evaluated.
- Pulp yield and bleachability were better than the corresponding soda pulp.
- Silica and lignin were separated from the black liquor of KOH black liquor.
- Silica, lignin and hemicelluloses separated waste water can be used in irrigation.

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ABSTRACT

Rice straw is supposed to be one of the most important lignocellulosic raw materials for pulp mill in Asian countries. The major problem in rice straw pulping is silica. The present research is focused on the separation of silica from the black liquor of rice straw pulping by potassium hydroxide (KOH) and pulp evaluation. Optimum KOH pulping conditions of rice straw were alkali charge 12% as NaOH, cooking temperature 150 °C for 2 h and material to liquor ratio, 1:6. At this condition pulp yield was 42.4% with kappa number 10.3. KOH pulp bleached to 85% brightness by D_0EpD_1 bleaching sequences with ClO_2 consumption of 25 kg/ton of pulp. 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%. The papermaking properties of KOH pulp from rice straw were slightly better than those of corresponding NaOH pulp.

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 (FAO, 2016). 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) (Quader, 2011). To reach the paper and board consumption to Asia level, our consumption will increase to 10 times of current consumption. So Bangladesh needs alternative fibrous raw materials as forest resources is very limited. Rice straw and wheat straw are the most abundant agriculture residues those are produced in large quantity in Asian countries. Non-wood materials, particularly wheat straw, rice straw, bagasse, bamboo are exploited as the main raw material for papermaking in China and India. The main problem that hinders the intensive use of non-wood raw materials in papermaking industry is the environmental pollution caused by black liquor.

The major agricultural waste in Bangladesh is rice straw, which produced around 34.4 million tons of rice in FY 2013-14 (FAO, 2016). Every kilogram of grain harvested is accompanied by production of 1–1.5 kg of the straw (Maiorella, 1985). As a result 34–52 4 million tons of rice straw is produced in Bangladesh. Like many other lignocellulosic biomass, rice straw is mainly composed of cellulose (32–47% by dry weight), hemicellulose (19–27%), and lignin (15–24%) (Binod et al., 2010). The abundance of carbohydrates in straw renders it as a potential source for biofuel and biochemicals in addition to pulp production. Silica is a problem

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specific to straw pulp production when using the soda or kraft process. In the pulp production from straw, the recovery of chemicals and energy from the spent cooking liquor is very much difficult due to the presence of silica in the liquor, which causes fouling of heat transfer surfaces and high viscosity when the liquor is evaporated. By lowering the liquor pH, the silica can be precipitated and separated.

To overcome these problems of straw pulping many new technologies have been studied. In the organic acid pulping, the major portion of silica remains on the fiber, therefore, spent liquor recovery problem would be solved (Jahan et al., 2006; Seisto and Poppius, 1997). Silica retained on the pulp fiber can be dissolved by alkaline extraction; subsequently silica can be separated from the alkaline extracted liquor by reducing pH to 7 and used for industrial purpose (Jahan et al., 2015). Huang et al. (2006, 2007a, b) explored wheat straw pulping without generating black liquor waste. The cooking liquor was aqueous ammonia mixed with a small amount of potassium hydroxide (KOH), which enriched the black liquor with nutrients such as potassium and nitrogen as a fertilizer. Rodríguez et al. (2008) studied rice straw pulping in different process and obtained highest pulp yield in KOH process. Pulping of corn stover using KOH and NH4OH was investigated by Sun et al. (2012). The combined alkaline system could effectively remove lignin during pulping. Approximately 90% delignification was achieved at the temperature of 150 °C for over 30 min. But those studies did not mention alkalinity of the black liquor. The liquor with pH above 8 cannot be used in soil. In this paper new technology has been proposed in biorefinery concept. During alkaline pulping process lignin, part of hemicellulose and silica were dissolved. Silica can be precipitated from the alkaline liquor by reducing pH to 7 (Jahan et al., 2015; Minu et al., 2012). Ultrafiltration (UF) and nanofiltration can separate and recover lignin and hemicellulosic sugars from the black liquor (Ahsan et al., 2014; Toledano et al., 2010). After the separation of silica and dissolved biomass, potassium rich liquor can be used in irrigation purposes.

The main aim of this work was to produce pulp from rice straw and wheat straw by KOH process, which comprises i) characterization of rice straw and wheat straw, ii) pulping of rice straw and wheat straw by KOH and soda (NaOH) processes with varying alkali charge, iii) bleaching of the produced pulps $D_0E_pD_1$ bleaching sequences, iv) evaluation of papermaking properties, v) characterization of spent liquor and recovery of silica and lignin from the spent liquor by reducing pH, specifically.

2. Materials and methods

2.1. Raw materials

Rice and wheat straw were collected and cut to 2–3 cm in length. After determination of the moisture content of air dried raw materials equivalent to 300 g o.d. (oven dried) was weighed separately in a polyethylene bag for subsequent cooking experiments.

2.2. Chemical analysis

The chemical compositions of rice straw and wheat straw were carried out by following Tappi Test Methods: the extractive (T204 om88), water solubility (T207 cm99), Klason lignin (T211 om83). The Holocellulose was prepared by treating extractive free bagasse meal with $NaClO_2$ solution (Browining, 1967). The pH of the solution was maintained at 4 by adding CH_3COOH-CH_3COONa buffer and α-cellulose was determined by treating holocellulose with 17.5% NaOH (T203 om 93).

2.3. Pulping

Pulping of rice straw and wheat straw was carried out by KOH and NaOH process in a electrically heated 5 lit capacity digester. Active alkali charge was varied from 12, 14, and 16% on od raw materials. The following parameters were kept constant: i) Liquor to fiber ratio: 6:1, ii) Temperature: 150 °C, iii) Cooking time: 120 min at 150 °C. After desire 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).

2.4. Evaluation of pulps

The produced pulps at the optimum conditions from rice straw and wheat straw were beaten in a PFI mill in different revolution and handsheets of about 60 g/m^2 were made in a Rapid Köthen Sheet Making Machine. The papermaking properties 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.

2.5. Silica and lignin separation from the black liquor

The pH of the black liquor was reduced to pH 7 by adding 4N sulfuric acid or carbon dioxide purging with constant stirring by magnetic bar. After adjusting the pH to the desired value, the conical flask was kept undisturbed for settling of the flocs. After complete precipitation, the content in the flask was centrifuged. After silica separation, the pH of the black liquor was again reduced to pH 2 by 4N sulfuric acid to precipitate lignin. The silica and lignin precipitate were then air-dried overnight followed by oven drying at 105 °C overnight to obtain constant weight. The solid content and ash of silica and lignin free black liquor were measured by TAPPI Standard Test Methods.

2.6. 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 Do 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, temperature was 70 °C for 60 min in a water solution of 2% NaOH and 0.5% H_2O_2 (on od pulp). Pulp consistency was 10%. The end pH in the D_1 stage was adjusted to 4 adding dilute NaOH. The ClO_2 charge in the D_1 was 0.5%. The brightness (T525 om 92), for tensile (T 494 om-96), burst (T 403 om-97) and tear strength (T 414 om-98) were determined in accordance with Tappi Test Methods.

3. Results and discussion

3.1. Characteristics of rice straw and wheat straw

Table 1 shows chemical characteristics of rice straw and wheat straw and compared with previously reported data. The content in acetone extracts of rice straw and wheat straw is lower than other agricultural residues and alternative raw materials (Jiménez et al., 1990). Some substances including resins, wax, fat and acetone extractables can precipitate upon pulping and leave stains in the