# Conversion of paper-grade pulp from rice straw into dissolving pulp

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**ABSTRACT:** About 1,165 million metric tons of rice straw is generated every year worldwide, which can be a good source for the circular bioeconomy. In this research paper, the paper-grade pulp from rice straw was converted to dissolving-grade pulp by fractionation in a biorefinery initiative. Rice straw was cooked at an optimum condition of 8% potassium hydroxide (KOH) charge for 120 min at 150°C and produced a pulp yield of 47.2% with a kappa number of 18.5. Subsequently, $D_0(EP)D_1$ bleaching was carried out for the produced pulp, and the brightness of the pulp reached to 82.4%. From the black liquor, 16.5% of the lignin and 11.9% of the hemicellulose were isolated for producing biobased products and chemicals, and then the spent liquor was used for soil amendment. The bleached pulp was fractionated in a Bauer McNett fiber classifier. The pulp fibers retained on 16-, 30-, and 50-mesh screens were used as a longer fiber fraction pulp, and pulp fibers retained on 100- and 200-mesh screens were used as a shorter fiber pulp. The longer and shorter fiber fraction pulps were analyzed for cellulose, $R_{10}$, pentosan, and viscosity. The long fiber fraction pulps were characterized by higher cellulose (88.2% vs. 83.1%) and lower pentosan (11.3% vs. 13.0%) content than the shorter fiber fraction pulps. The longer fiber fraction was further treated with cold KOH to remove residual hemicellulose. The KOH extraction reduced pentosan content in pulp to 6.3% and increased α-cellulose content to 91.3%. The short fiber fraction was converted to monomeric sugars using cellulase enzymes with varying reaction time, temperature, and consistency. The efficiency of cellulase activity was assessed through glucose yield and residual dry weight. A temperature of 45°C, 5.0 pH, 5% consistency, and 6 filter paper units/gram (FPU/g) o.d. pulp resulted in maximum sugar conversion of 85.7%.

***Application:*** In this paper, dissolving pulp was produced in a cost-effective way, where KOH paper-grade pulp from rice straw was fractionated into shorter and longer fractions. The longer fraction pulp was further KOH extracted to reduce residual hemicellulose. The 16.5% of lignin and 11.9% of hemicellulose were isolated from the KOH liquor for producing biobased products and chemicals, and then the spent liquor was used for soil amendment.

The main raw material for the production of rayon fiber for textiles is dissolving pulp. For developing a circular bioeconomy, synthetic textile fiber needs to be replaced by cellulose-based rayon fiber [1]. Therefore, dissolving pulp production increased globally from 4.18 million metric tons in 2010 to 8.62 million metric tons in 2022, which was valued at US$5,563.60 million in 2022 and is expected to have a value of US$7,623.47 million in 2032 [2].

Dissolving pulp contains high α-cellulose and a minimum amount of hemicellulose with no or trace amount of lignin, extractives, and ash [3]. Therefore, the cost of dissolving pulp is higher than paper-grade pulps due to lower yield, higher capital investment, additional chemical costs, lower production rates, and high control of the inventory and storage spaces [4]. Conventionally, dissolving pulp is produced by the pre-hydrolysis kraft and acid sulfite processes. Apart from these processes, conversion of paper-grade pulp into dissolving pulp through purification has been tried.

In order to reduce the cost of dissolving pulp production, a number of researchers have explored the possibility of converting paper-grade pulps into dissolving-grade pulps through purification [5-8]. Köpcke et al. [6] removed hemicellulose from the paper-grade pulp by enzymatic treatment followed by alkaline extraction. The pulp reactivity was enhanced by an endoglucanase treatment, and the converted pulp's characteristics ultimately corresponded with those of a commercial dissolving pulp. Hyatt et al. [9] also investigated combined pretreatments using xylanases and alkaline extraction. Janzon et al. [10-11] extracted hemicellulose from the paper pulp by using nitren (a metal complex of tris-(2-aminoethyl) amine and nickel(II) hydroxide) to convert to dissolving pulp. The nitren charge was a crucial factor for xylan removal and pulp purity.

Fiber fractionation is an option to get the desired pulp properties in both dissolving-grade and paper-grade pulp. Therefore, fiber fractionation of pulp was done by a number of researchers. A high tensile index, energy absorption capacity, and high porosity are prerequisites for sack paper. Olson [12] observed that fractionated longer fiber pulp had a significantly higher porosity after beating in a PFI mill to a target tensile energy absorption (TEA). Abubakr et al. [13] investigated the fractionation of mixed office waste fibers to enhance fiber quality. Their study revealed that

fractionation effectively improved the long-fiber component, resulting in increased strength indices of paper.

In another study, Duan et al. [5] examined kraft-based dissolving pulp fractionated and treated with cellulase. They found that the short fiber fraction exhibited the highest accessibility, lowest viscosity, and greatest cellulase adsorption capacity, whereas the long fiber fraction showed the opposite characteristics.

Duan et al. [14] explored a combined process for converting paper-grade pulp into dissolving pulp. This process involved mechanical refining, followed by a low-alkali extraction. The combined treatment removed hemicellulose and significantly increase the Fock reactivity from 62.2% to 81.0%.

Bamboo, being a nonwood material, contains a high proportion of non-fiber cells that complicates dissolving pulp production using conventional methods. To address this issue, Liu et al. [15] proposed a new process concept involving the separation of hemicellulose through fiber fractionation. In their approach, the long fiber fraction, rich in cellulose, was further purified and transformed into dissolving pulp through acid hydrolysis and cold caustic extraction. Rice straw is similar to bamboo and contains a lot of nonfibrous cells. Rice straw is the largest amount of crop residue available in Bangladesh, and about 1,165 million metric tons were generated in 2022 [16].

In an earlier investigation, it was observed that agriculture residues, such as straws and bagasse, require mild cooking conditions [17,18]. Rice straw could be pulped using a weak KOH charge [18].

Longer fiber fractions contain higher cellulose and lower pentosan levels vs. the shorter fiber fractions [19]. On the other hand, shorter fiber fractions always contain a high amount of ash and nonfibrous parenchymatic cells, which are detrimental for the pulping process [20,21].

The pre-hydrolysis KOH process was evaluated for dissolving pulp production from different nonwoods [22]. It was seen that the pulp yield from rice straw was only 32.4%. The alkaline pulping process with chemical recovery systems requires high capital investment, making it less suitable for straw pulping due to its high silica content and other associated technical challenges [23].

Therefore, rice straw was cooked at the mild conditions with KOH, and the produced pulp was bleached by $D_0(EP)D_1$ bleaching sequences. The bleached pulp was fractionated to longer and shorter fiber fractions by Bauer McNett fiber classifier. The longer fiber fractions were further cold alkali extracted by KOH, and shorter fiber fractions were converted into glucose for ethanol production by adjusting pH, consistency, and treatment time. The KOH-extracted longer fiber fractions were characterized for dissolving pulp properties.

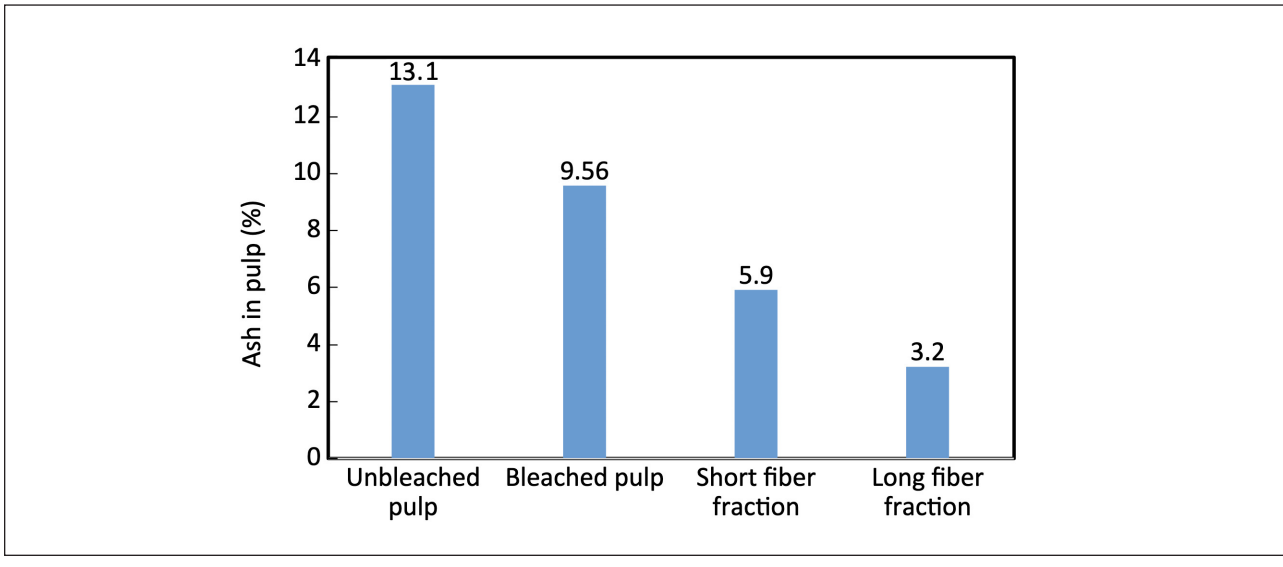
## MATERIALS AND METHODS

### *Raw materials*

Rice straw was collected from the Rajbari district of Bangladesh, which was planted in July/August 2020 and harvested in November/December 2020. After collection at the laboratory, it was chopped into 2–3 cm lengths. The composition of the rice straw was analyzed, revealing cellulose content at 38.5%, pentosan at 19.1%, lignin at 12.7%, and ash at 17.2% [18]. The moisture content of the rice straw was measured, after which it was stored in an airtight plastic bag for future pulping.

### *Pulping*

Rice straw was subjected to cooking with an 8% KOH solution at 150°C for 120 min and dry material-to-liquor ratio of 1:6 based on previous investigation [18]. The cooking experiment was done thrice to get a reproducible result. After the cooking process, the biomass was filtered and washed with water. The collected filtrate was reserved for subsequent experiments. Lignin was precipitated from




*1. Ash content in pulp after different treatment*

the filtrate by adjusting the pH to 2.5 with sulfuric acid ($H_2SO_4$), and separation of lignin was achieved through centrifugation. The detailed fractionation of the black liquor is illustrated in **Fig. 1**.

The pulp yield, precipitated lignin, and solids content in the filtrate were determined gravimetrically at 105°C based on the oven-dried rice straw. The pulp kappa number was measured according to TAPPI Standard Test Method T 236 om-99 "Kappa number of pulp," while the ash content in both the pulp and filtrate was evaluated using TAPPI Standard Test Method T 211 om-07 "Ash in wood, pulp, paper and paperboard: combustion at 525°C."

### $D_0(EP)D_1$ bleaching

Pulps were bleached using the $D_0(EP)D_1$ sequence in plastic bags. In this process, $D_0$ and $D_1$ refer to chlorine dioxide ($ClO_2$) in the first and second stages, respectively, while EP denotes hydrogen peroxide ($H_2O_2$) reinforced alkaline extraction. In the first stage ($D_0$), the $ClO_2$ charge was 2.0%, with the initial pH adjusted to 2.5 using dilute $H_2SO_4$. During the alkaline extraction stage, sodium hydroxide (NaOH) and $H_2O_2$ charges were 2% and 0.5% (on o.d. pulp), respectively, at a temperature of 70°C for 60 min with a pulp consistency of 10%. In the $D_1$ stage, the final pH was 4, with a $ClO_2$ charge of 0.5%.

### Fractionation of the bleached pulp

The bleached pulp was fractionated in a Bauer McNett fiber classifier, following TAPPI T 233 cm-95 "Fiber length of pulp by classification" into five different fractions. The weight percentage of each fraction was determined gravimetrically. The fiber fractions retained on 16-, 30-, and 50-mesh screens were marked long fiber fraction, and fiber retained on 100- and 200-mesh screens was marked as short fibers.

### Fiber quality analysis

The fiber quality parameters of the whole pulp and fractionated long and short fiber fractions were analyzed using a Fiber Quality Analyzer – 360 (OpTest Equipment; Hawkesbury, ON, Canada).

### KOH extraction

The longer fraction pulp was further treated with 12% KOH at 25°C for 120 min. Then, the pulp was filtered and washed with distilled water, and the filtrate was collected for sugar analysis.

### Evaluation of Pulps

The dissolving pulp properties were determined according to the following TAPPI Standard Test Methods:

- Brightness: TAPPI T 452 om-92 "Brightness of pulp, paper, and paperboard (directional reflectance at 457 nm)"
- Viscosity: TAPPI T 230 om-89 "Viscosity of pulp (capillary viscometer method)"
- α-cellulose: TAPPI T 203 om-88 " Alpha-, beta- and gamma-cellulose in pulp"
- Alkali solubility $S_{10}$ and $S_{18}$: TAPPI T 235 cm-85 "Alkali solubility of pulp at 25°C test method"
- Pentosan in pulp: TAPPI T 223 cm-23 "Pentosans in wood and pulp"

Fock reactivity was assessed using a modified method by Tian et al. [24].

### Isolation of lignin and hemicellulose from the KOH spent liquor

The lignin from the KOH spent liquor was precipitated by reducing the pH to 2.5 with the addition of dilute $H_2SO_4$ and separated by centrifugation. The isolated lignin from the KOH spent liquor was purified by dissolution in dioxane: water (9:1) solution and precipitated in diethyl ether followed by vacuum drying under phosphorus pentoxide ($P_2O_5$) for analysis.

The supernatant mainly contained hemicellulose, which was concentrated in a rotary evaporator, and the pH of the concentrated solution was increased to 3.5 by dilute NaOH. The hemicellulose in the concentrated solution was precipitated by adding three volumes of absolute ethanol. The resulting precipitate was then separated by centrifugation and dried under vacuum at 40°C.

### Lignin analysis

Carbon (C), hydrogen (H), oxygen (O), sulfur (S), and nitrogen (N) analyses were carried out in Central Analytical Research Laboratory of Bangladesh Council of Scientific and Industrial Research (BCSIR) in Dhaka. The methoxyl content in KOH lignin was determined in accordance with the Zeisel–Viebock–Schwappach method [25].

In this method, the lignin sample of 0.03 g, 0.6 mL (0.5 g) phenol ($C_6H_5OH$), six drops of acetic anhydride ($(CH_3CO)_2O$), and 3.5 mL of hydroiodic acid (HI) was taken into a reaction flask, which was fitted with condenser. The upper head of the condenser was fitted with two absorption tubes, which were filled with 15 mL of bromine solution. The bromine solution was prepared by adding six drops bromine in 15 mL water. The reaction flask was heated at 140°C by oil bath for 30 min. Water at 50°C was circulated through the condenser by a forced circulation water bath. Carbon dioxide gas was passed through reaction vessel to the absorber to carry away reaction product. The absorption solution was transferred quantitatively to a 250 mL conical flask, shaken vigorously with 25 mL of 20% sodium acetate solution, and then 4% formic acid was added drop by drop until the solution was decolorized. Two more drops of methyl red were then added, a pink color was observed, and then 20 mL of 10% $H_2SO_4$ and 5 mL of 10% potassium iodide (KI) were added. The flask was closed with a glass ground stopper and allowed to stand for 5 min. The iodine formed was titrated with 0.1 N sodium thiosulfate solutions

| Pulp Yield, % | Kappa Number | Spent Liquor Composition, % based on rice straw | | |
|---|---|---|---|---|
| | | Lignin | Hemicellulose | Solids Content |
| 47.2 ± 1.3 | 18.5 ± 0.9 | 16.5 ± 1.2 | 11.9 ± 1.0 | 10.8 ± 1.2 |

***I. Potassium hydroxide (KOH) pulping of rice straw.***

($Na_2S_2O_3$) using a starch indicator, as follows:

Methoxy group, [$OCH_3$] (%) == [($a$*$f$*0.5172)/$A$]*100

where $a$ is the volume of 0.1 N $Na_2S_2O_3$; $f$ is the titer factor for 0.1 N $Na_2S_2O_3$; 0.5172 is the quantity of $OCH_3$ groups, corresponding to 1 mL of 0.1 N $Na_2S_2O_3$; and $A$ is the milligram amount of the lignin sample.

### *Fourier transformed infrared (FTIR) spectroscopy*

The Fourier transform infrared (FTIR) spectrum of KOH lignin was taken by a Frontier FTIR spectrometer (PerkinElmer; Waltham, MA, USA) equipped with a GaAs detector. The spectra were recorded in the absorption band mode in the range 4000–400 $cm^{-1}$. For each sample, 32 scans were collected at a spectral resolution of 16 $cm^{-1}$ with an interval of 4 $cm^{-1}$, and then 32 scans were averaged and stored as transmittance percentage (% T). Here, PerkinElmer Spectrum (Version 10.4.4) software was used for spectral data processing.

### *Enzymatic hydrolysis and sugar analysis*

The saccharification of shorter fiber pulps from rice straw was carried out using cellulase at a concentration of 6 filter paper units/gram (FPU/g) o.d. pulp. Reactions were conducted at 35°C, 40°C, and 45°C, with pulp consistencies of 4%, 5%, and 6%, and incubation times of 2 h, 3h, 4 h, and 5 h. The pH was maintained at 4.8 using a 0.1 M sodium citrate buffer. Novozymes A/S (Bagsværd, Denmark) supplied a commercial endoglucanase-rich cellulase (FiberCare D, EG), which exhibited a cellulase activity of 460 U/mL, determined as sodium carboxymethyl cellulose (CMC-Na) activity. Upon completion of the enzymatic reaction, it was halted by immersing the reactor in boiling water for 1 h. The resulting glucose was quantified using high-performance liquid chromatography (HPLC) with an amino-bonded column and a refractive index (RI) detector. The analysis was performed with a Shimadzu (Kyoto, Japan) Prominence-I LC-2030C 3D HPLC system equipped with an RI detector, and data processing was conducted using Shimadzu Lab Solutions software.

### *Lignin acetylation*

For lignin acetylation, 100 mg KOH lignin was added to 1.5 mL of dry pyridine-acetic anhydride (1:1), kept for 72 h, and then centrifuged. The solution was added to a 10-fold volume of ice-cold water, and the acetylated sample was recovered as a precipitate, which was purified by successive washing with water and dried under vacuum over $P_2O_5$.

### *Molecular weight*

The weight average (Mw) and number average molecular (Mn) weight of acetylated KOH lignins were determined by gel permeation chromatography (GPC) using a Shimadzu LC-20A. The 10 mg lignin samples were dissolved in tetrahydrofuran (THF) and 10 µL was injected. The column was operated at 30°C and eluted with THF at a flow rate of 1 mL/min. The column was calibrated using eight polystyrene standards of weights 162; 2400; 4050; 9880; 17,900; 27,500; 46,300; and 172,400 g/mol.

## RESULTS AND DISCUSSION

### *Rice straw pulping with KOH*

Rice straw was cooked with KOH using the optimum conditions in our earlier investigation [18]. As shown in **Table I**, the pulp yield was 47.2%, which was higher than the pulp yield from rice straw in other studies [26,27]. The higher pulp yield can be attributed to the retention of silica on the pulp fibers [18]. The ash content in whole unbleached pulp was 13.1% (Fig. 1). A high ash content, consisting mainly of silicates, is typical of grasses. Tutuş and Eroğlu [28] also found that soda-oxygen pulping of wheat straw produced pulp with a high amount of ash (containing 80.4% of the total silica), with a minimal transfer of silica to the spent liquor. The addition of 3% aluminum oxide ($Al_2O_3$) in the soda-oxygen process increased silica retention on the pulp to 96.5%. Seisto and Poppius-Levlin [29] showed that the unbleached pulps in MILOX process from tall fescue and reed canary grass had a high content of silica. The results were also verified by determining the silicon content of the pulping spent liquors of less than 0.01% on grass. However, the presence of silica and other minerals is detrimental to dissolving pulp. It could be reduced by fiber fractionation and alkaline extraction in subsequent processes. The dissolved biomass from the spent liquor was separated, and it was found that 16.5% lignin and 11.9% hemicellulose were precipitated. The precipitated lignin was not purified and thus contained more impurities than the original Klason lignin extracted from the rice straw. Previous research has shown that precipitated lignin from KOH liquor at pH 3.25 contained 10.0% ash, composed of

| Fraction | 16 mesh | 30 mesh | 50 mesh | 100 mesh | 200 mesh |
|---|---|---|---|---|---|
| Pulp, % | 1.31 | 16.38 | 17.43 | 40.02 | 13.64 |
| Ash in pulp, % | 1.1 | 1.13 | 4.31 | 5.11 | 11.11 |

***II. Fractionation of KOH pulp from rice straw.***

| Fraction | Length Weighted, mm | Fiber Width, µm | Curl Index, % | Kink Index, $Nm^{-1}$ | Fines Content, % | Degree of Fibrillation, % |
|---|---|---|---|---|---|---|
| Whole pulp | 0.79 ± 0.07a | 13.9 ± 0.20a | 0.181 ± 0.01a | 2.56 ± 0.13a | 51.6 ± 2.80ab | 1.75 ± 0.39a |
| Longer fraction | 1.09 ± 0.18a | 13.7 ± 2.50a | 0.150±0.02a | 1.82 ± 0.11a | 27.8 ± 0.70c | 1.13 ± 0.04a |
| Short fraction | 0.34 ± 0.037b | 11.1 ± 0.50b | 0.139±0.10a | 1.86 ± 0.09a | 66.9 ± 18.30a | 1.42 ± 0.79a |
| Means containing the same letter ("a, b, c") do not differ significantly at 5% level of significance. | | | | | | |

***III. Fiber quality analysis of fractionated rice straw pulp by Fiber Quality Analyzer – 360 (OpTest Equipment; Hawkesbury, ON, Canada).***

| Pulp Type | α-cellulose, % | $R_{10}$, % | $R_{18}$, % | Viscosity, mPa.s | Pentosan, % | Fock Reactivity, % |
|---|---|---|---|---|---|---|
| Whole pulp | 81.5 | 79.9 | 81.6 | 4.05 | 17.87 | - |
| Shorter fiber | 83.1 | 78.0 | 82.7 | 7.51 | 13.04 | - |
| Longer fiber | 88.2 | 81.5 | 87.6 | 4.86 | 11.31 | 13.8 |
| Long fiber (KOH extraction) | 91.3 | 83.8 | 91.4 | 2.33 | 6.25 | 41.8 |

***IV. Pulp properties of fractionated and KOH-extracted rice straw pulp.***

65.2% potassium oxide ($K_2O$), 2.21% ferric oxide ($Fe_2O_3$), and 1.3% silicon dioxide ($SiO_2$) [18]. This precipitated lignin also likely contained carbohydrates.

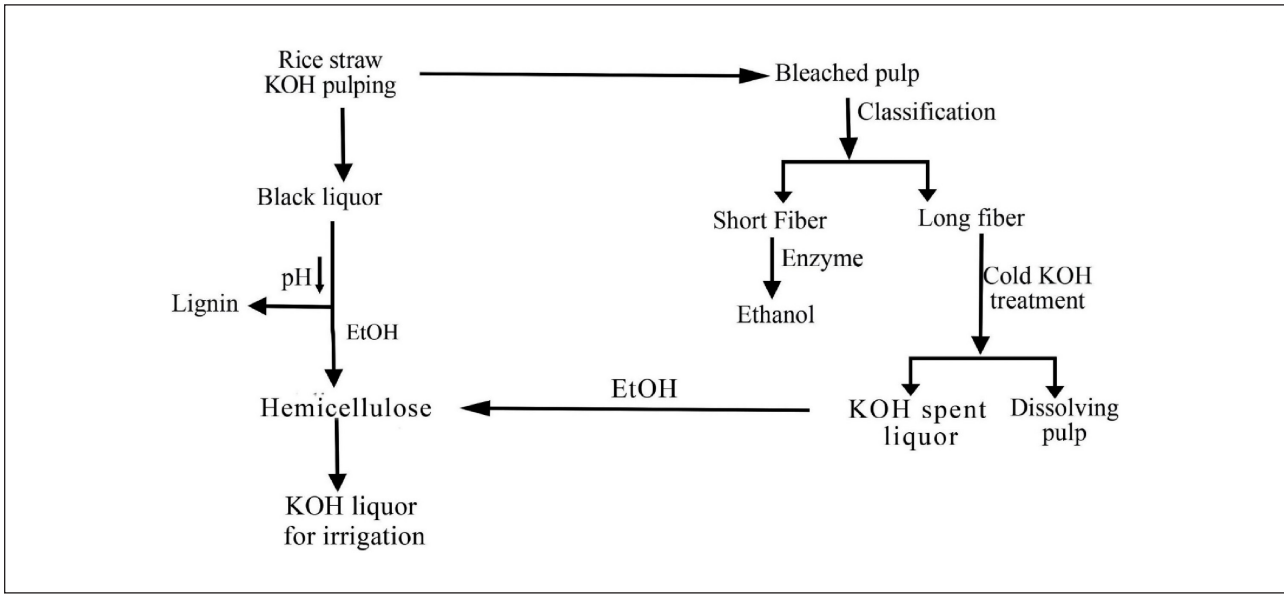
The KOH lignin was characterized with higher phenolic hydroxyl group levels and lower molecular weight [30]; therefore, the lignin can be used in resin preparation [31] and also can be used in co-polymer preparation [32]. After lignin was separated from the liquor, hemicellulose was precipitated with ethanol. The hemicellulose consisted mainly of xylan, which could be converted to furfural [33]. In our earlier investigation, it was observed that the dissolved xylan in the prehydrolysis liquor was easily converted to furfural with high yield [34]. The lignin and hemicellulose separated liquor had 10.8% solids content, which represented mainly organics and potassium [18]. Therefore, potassium-rich filtrate can be utilized as a soil amendment. In a previous study, potassium-rich black liquor was used as a soil amendment, showing positive effects on soil properties and significantly boosting the growth of red amaranthus. Notably, the application of black liquor increased crop growth compared to the non-amended control soil [35]. Additionally, Popy et al. [17] reported that the weight of a vegetable increased almost three time with the application of K-rich black liquor.

### *Pulp bleaching and fractionation*

The pulp was bleached by $D_0(EP)D_1$ sequences and reached a final brightness of 82.4%, where pulp viscosity was 10.4 mPa.s. The bleached pulp was fractionated in a Bauer McNett fiber classifier. The pulp fiber retained on 16-mesh, 30-mesh, and 50-mesh screens was considered long fiber fraction, and pulp fiber retained on 100-mesh and 200-mesh screens was considered as short fiber fraction. As shown in **Table II**, the longer fiber fractions were 35.12% and shorter fiber fractions were 53.66%, which means the fiber retained 88.78% and passed 11.22%. The ash content in the pulp fiber retained in each mesh of Bauer McNett fiber classifier was determined based on the fiber retained on the individual screen. Table II shows an increase in ash content with a decrease in particle size, corresponding to an increase in screen mesh number. However, some mineral particles were observed to pass through the 200-mesh screen. The FQA results reveal that the fiber fractionation decreased the fines content from 51.5% in whole pulp to 27.8% in longer fraction pulp, while the average fiber length increased from 0.79 mm to 1.09 mm (**Table III**).

### *Dissolving-grade pulp properties*

As shown in **Table IV**, the α-cellulose content in whole




*2. Biorefinery initiative in producing dissolving pulp from paper-grade pulp from rice straw (EtOH: ethanol; KOH: potassium hydroxide).*

pulp was 81.5%, while the same for the fractionated longer fraction pulps was 88.2%, and for the shorter fraction pulps, it was 83.1%. The higher α-cellulose content in fractionated pulps than in the whole pulp can be explained by the loss of fines during the fractionation process, which was reflected by lower ash in fractionated pulps (Table II). The ash content in the unbleached pulp was 13.1%, which was decreased to 9.56% on bleaching (**Fig. 2**). The high ash content in pulp could be decreased by fiber fractionation and alkali extraction. Further, fiber fractionation decreased ash content in the longer fiber fraction to 3.2% and decreased the shorter fiber fraction to 5.9% (Fig. 1). The proportion of pentosan decreased during the pulp fractionation. The pentosan content in the whole pulp was 17.9%, which decreased to 13.0% for the shorter fraction and 11.3% for the longer fraction pulp. Nayeem et al. [19] showed that the α–cellulose content in long fiber fraction pulp was higher than short fiber fraction pulp, and the pentosan content did not vary significantly. The solubilities at 10% NaOH represent the degraded cellulose and hemicellulose in pulp, while the solubilities at 18% NaOH represent only hemicellulose [36]. Therefore, $R_{18}$ was very close to α–cellulose, and $R_{10}$ was lower than $R_{18}$. As shown in Table IV, degraded cellulose ($R_{18}$-$R_{10}$) in longer fraction and shorter fraction pulps was 4.7% and 6.1%, respectively.

The Fock reactivity of dissolving pulp is highly important in the production of viscose rayon. The measurement techniques closely simulate the commercial viscose-rayon process [37]. Fock reactivity of longer fraction pulp was only 13.8%. The KOH extraction of longer fraction pulp increased accessibility of reactant by swelling, and consequently increased reactivity to 41.8%. Still, the reactivity was not as high as desired. Nayeem et al. [38] showed that the Fock's reactivity for jute cutting pulp, as well as for the caddis and cutting-caddis mixed pulp obtained from prehydrolysis at 140°C, was measured at 66.7%, 66.9%, and 66.8%, respectively, which increased to 69.9%, 68.7%, and 68.8% from the prehydrolysis at 170°C. Strunk [39] illustrated that the pulp with higher "$R_{18}$-$R_{10}$" increased the physical ability of reactants/solvents to reach the hydroxyl groups and overcome steric hindrance in the fiber structure. The degraded cellulose in the KOH-extracted pulp was 7.6%. Miao et al. [40] demonstrated that only 6 min cellulase treatment of pulp increased the Fock reactivity to about 70%. Miao et al. [41] also showed that the fiber fibrillation by PFI refining of the dissolving pulp increased Fock reactivity. Therefore, further treatment of KOH-extracted pulp increased the reactivity of the produced pulp.

### *Alkaline extraction*

The cold alkali extraction of longer fraction pulp was done by KOH to further reduce the hemicellulose content. The α-cellulose content and reactivity of dissolving pulp after alkaline extraction are shown in Table IV. The residual pentosan in long fiber fraction pulp was 6.2% which corresponds to 44.2% pentosan removal from the longer fraction pulp. In an earlier study, a significant amount of pentosan was decreased in white press cutting pulp by alkaline extraction [42]. The α-cellulose content in the pulp increased due to the removal of pentosan; its content in the alkali extracted pulp was 91.3%. The interaction between alkali and cellulose significantly influences the overall cellulose structure. Increasing alkali concentration at room temperature initiates a transition from the original cellulose I structure to the Na-cellulose I structure. This transition causes an expansion of the plane distance of the 101-lattice planes due to the incorporation of sodium hydrate ions, thus facilitating reactivity. However, at high

| Sample | C, % | H, % | O, % | N, % | S, % | $CH_3O$, % | $C_9$ Formula |
|---|---|---|---|---|---|---|---|
| Rice straw | 59.50 | 5.75 | 26.41 | 4.59 | 3.75 | 17.5 | $C_9H_{8.33}O_{2.25}(OCH_3)_{1.15}$ |
| Corn stalk* | 55.67 | 4.447 | 39.12 | 0.77 | - | 17.12 | $C_9H_{6.14}O_{4.17}(OCH_3)_{1.21}$ |
| Dhaincha* | 51.06 | 4.39 | 44.23 | 0.325 | - | 22.24 | $C_9H_{5.70}O_{5.70}(OCH_3)_{1.82}$ |

C: carbon; H: hydrogen: O: oxygen: S: sulfur; N: nitrogen; $CH_3O$: methoxide.
*Nayeem et al. [30].

***V. Elemental analysis and methoxyl content of KOH spent lignin from rice straw.***

alkali concentrations, cellulose undergoes mercerization. Mercerization involves transforming the native cellulose I polymorph into cellulose II. This transformation occurs as cellulose swells, but it is noted to adversely affect the reactivity of dissolving pulp.

The highest amount of low molecular weight degraded cellulose ($R_{18}$-$R_{10}$) in the short, long, and KOH-extracted long fiber pulps were 4.7%, 6.1%, and 7.6%, respectively (Table IV). The results were consistent with the viscosity lowering trend. The low molecular weight degraded cellulose in the dissolving pulp from rice straw by the prehydrolysis KOH was 5.27% [22].

The KOH-extracted liquor contained 2.7% xylose (based on pulp). Additionally, a considerable amount of glucose and fructose was also detected, which originated from the lower degree of polymerization (DP) cellulose. The conversion of hemicellulose into fuels and chemicals has been extensively investigated by numerous researchers [31,43]. The detailed process is illustrated in Fig. 2. In this study, 11.9% hemicellulose from the KOH liquor and 1.27% xylose (based on rice straw) from the KOH extraction of pulp were isolated. These compounds can be further converted into furfural and bioethanol, as discussed in the earlier section [32,44]. Consequently, the proposed concept demonstrates the potential to utilize each fraction of biomass efficiently, achieving near-zero emissions.

### *Characterization of lignin of KOH lignin from rice straw*

Elemental analysis

Elemental analysis and methoxyl content of lignin from KOH spent liquor of rice straw was carried out, and results along with some data from the literature are shown in **Table V**. The results showed that KOH lignin from rice straw had a similar methoxyl content to corn stalk KOH lignin (17.1% vs. 17.5%), but higher N content, and consequently, lower O contents. Zhao and Liu [45] reported that the methoxyl and N contents of milox lignin from Siam weed stem were 17.14% and 1.15%, respectively. Nitrogen was mainly derived from the protein–lignin complexes during the KOH delignification process. Pan and Sano [46] also obtained a higher amount of N content in acetic acid spent liquor lignin. The $C_9$ empirical formula of KOH lignin from rice straw was $C_9H_{8.33}O_{2.25}(OCH_3)_{1.15}$, which indicated a lower syringyl unit content compared to corn stalk and dhaincha KOH lignin (Table V). Since syringyl units contain two methoxyl groups, a higher –($OCH_3$) per $C_9$ ratio would suggest a higher syringyl unit content in the lignin. The –($OCH_3$) per $C_9$ in corn stalk and dhaincha was 1.21 and 1.82, respectively [30].

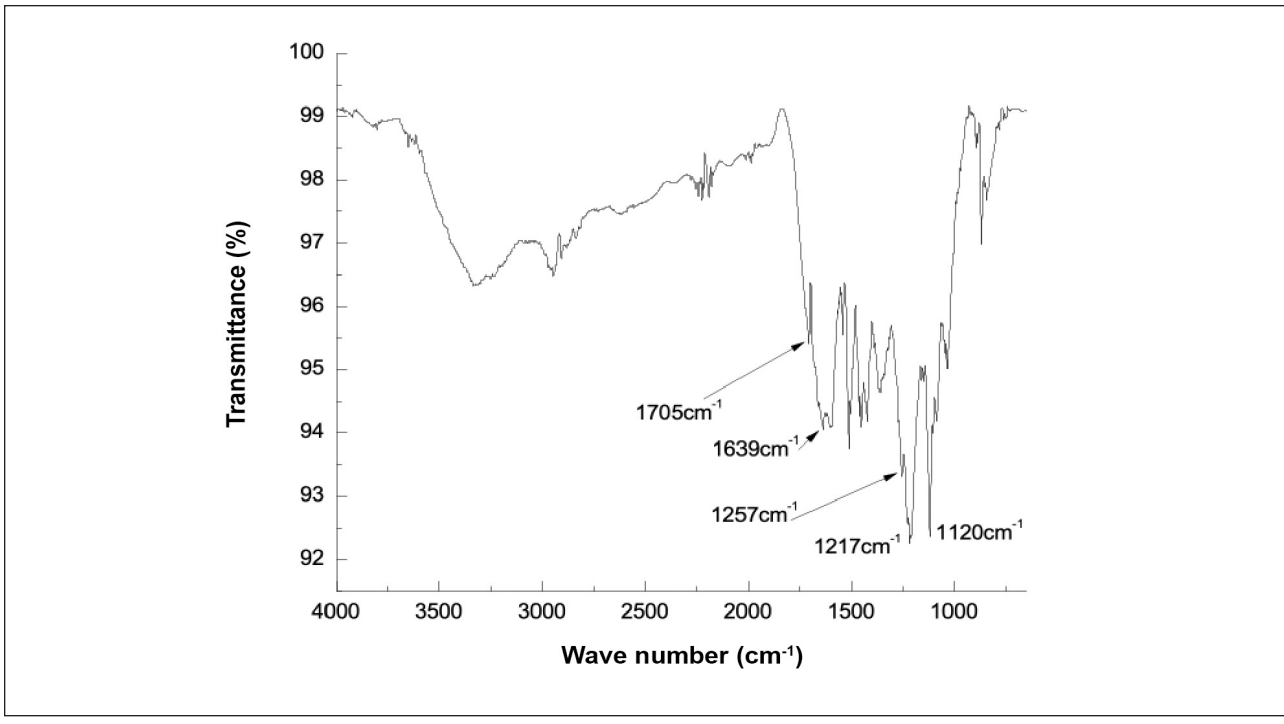
FTIR analysis

The species, geographic location, and isolation method changes the characteristics of lignin. Herbaceous straw lignins differ from wood lignins in their composition. Straw lignins contain p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) monomeric units, whereas wood lignins are primarily composed of either G units or a combination of G and S units [47]. **Figure 3** presents the FTIR spectrum of KOH spent liquor lignin derived from rice straw. The band at 1510 $cm^{-1}$, associated with aromatic skeletal vibrations, serves as a reference for evaluating the relative intensities of other bands. The peak around 3322 $cm^{-1}$ corresponds to the stretching of O–H groups, which include R–OH and Ar–OH. Additionally, the region between 2955 $cm^{-1}$ and 2842 $cm^{-1}$ is attributed to C-H stretching vibrations from methyl and methylene groups. A weak signal at 1705 $cm^{-1}$ was observed due to unconjugated C=O stretching. Other straw lignin from the acetic acid process obtained a strong signal at the unconjugated C=O stretching due to the introduction of acetyl group [45]. The lignin had a strong band at 1639 $cm^{-1}$ due to the conjugated C=O stretching.

The strong signals at 1217 $cm^{-1}$ for p-coumaryl unit and at 1120 $cm^{-1}$ for S units were clearly found. A weak shoulder at 1257 $cm^{-1}$ was also observed, indicative of G units [48]. A strong band at 1359 $cm^{-1}$ was assigned to syringyl ring breathing combined with CAr-$OCH_3$ stretching [49]. The KOH lignin from rice straw shows the HgS-type spectral features.

Molecular weight of lignin

The weight-average (Mw) and number-average (Mn) molecular weights and the polydispersity (Mw/Mn) of lignin from KOH spent liquor of rice straw was carried out, and results, along with some data from the literature of




*3. Fourier transform infrared (FTIR) spectrum of KOH lignin from rice straw.*

| Raw Material | Mw | Mn | Mw/Mn |
|---|---|---|---|
| Rice straw | 10054 | 4800 | 2.09 |
| Corn stalk* | 10613 | 4943 | 2.15 |

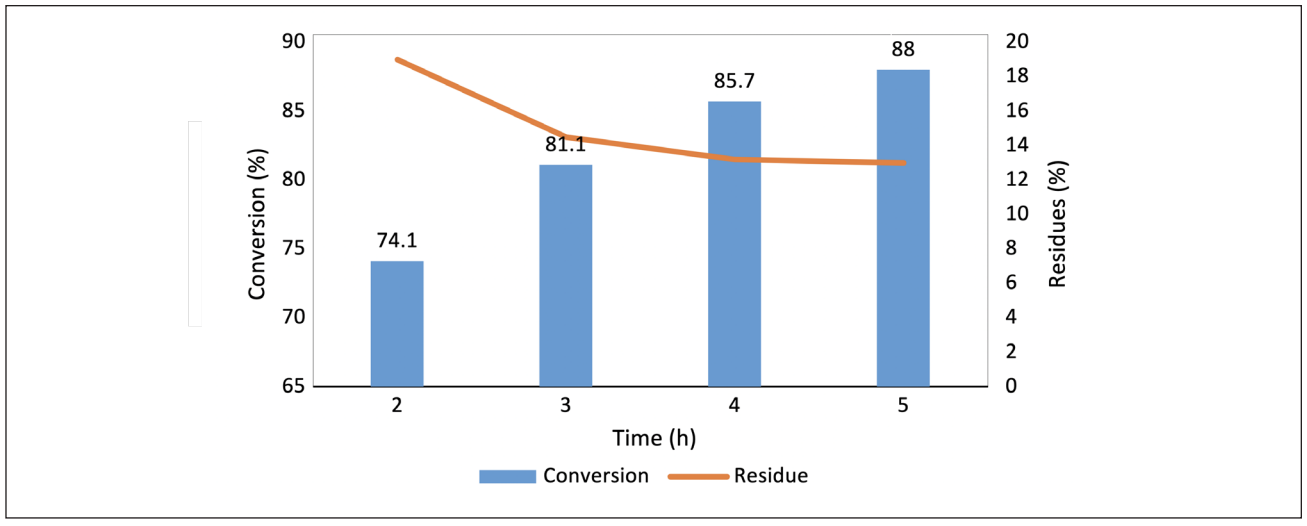
Mw: weight-average molecular weight; Mn: number-average molecular weight; Mw/Mn: lignin polydispersity.
*Nayeem et al. [30].

*VI. Molecular weight of KOH lignin from rice straw*

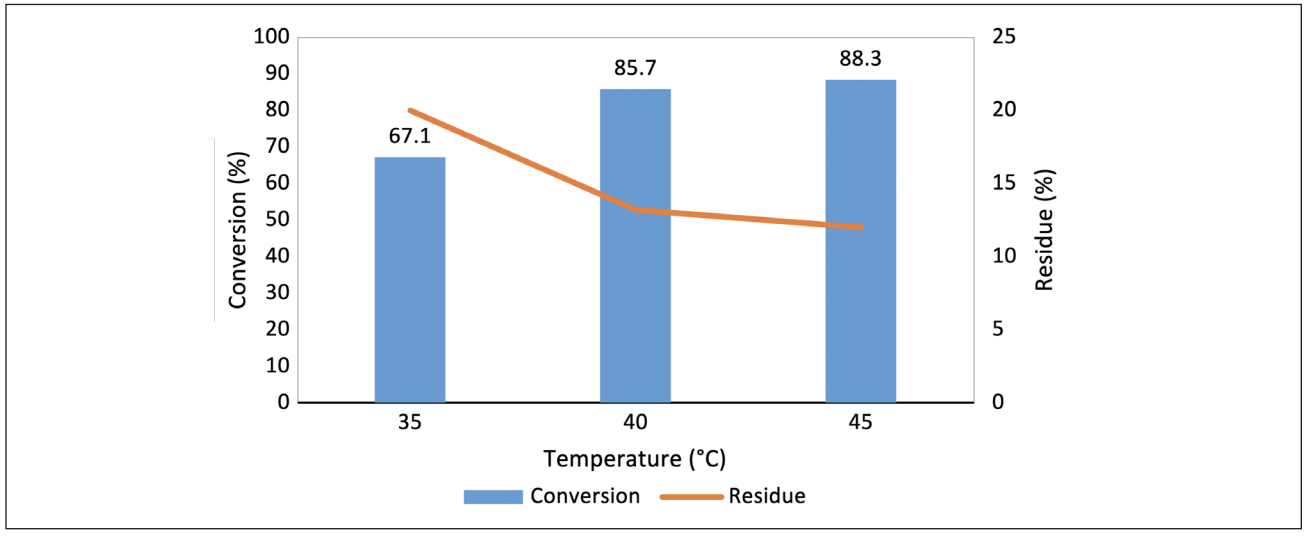
KOH lignin from corn stalk, are shown in **Table VI**. It is observed that KOH lignin from rice straw had similar Mw, Mn, and polydispersity as KOH lignin form corn stalk. The Mw was higher than that of the organic acid spent liquor lignin from Siam weed stem [43]. It is always observed that the Mw and Mn of dioxane lignin is higher than the spent liquor lignin due to the depolymerization and degradation of lignin, particularly through the cleavage of β-O-4 and α-O-4 linkages, and this generates numerous non-etherified phenolic OH groups in the lignin [31]. The molecular weight distribution/polydispersity varies depending on the biomass source, pretreatment conditions, and isolation method. As shown in Table VI, the polydispersity of KOH lignin from rice straw was 2.09, which was close to the KOH lignin from the corn stalk (2.15). In an earlier investigation, it was observed that the polydispersity of dhaincha lignin was 2.79 and 1.98 by acidic dioxane and in KOH, respectively [30]. Therefore, technical lignin (spent liquor lignin) is better for producing new products [32,50].

### *Conversion of shorter fiber fraction pulp into glucose*

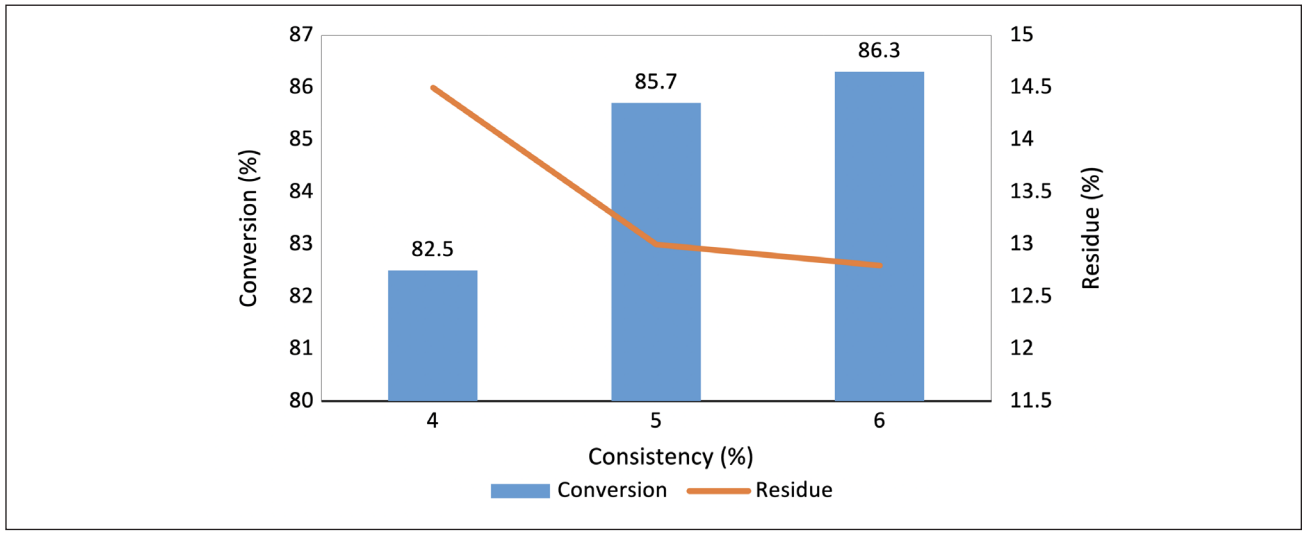
An evaluation was conducted on the one-stage enzymatic saccharification of shorter fiber fraction pulp obtained from rice straw. The study investigated the conversion of shorter fiber fraction pulp to monomeric sugars using cellulase enzyme by varying cellulase dose, treatment time, consistency, and 6 FPU/g o.d. pulp. The efficacy of cellulase activity was assessed by measuring the yield of sugars and the residual dry weight. Glucose was mainly released during the hydrolysis, but a considerable amount of xylose was also present in hydrolysate, which was not encountered. It is observed from **Figs. 4–6** that the higher the glucose yield is, the lower the residual mass is. Figure 4 shows that the glucose conversion increased from 74.1% to 88.0% and the residue decreased from 19.0% to 13.0% with increasing saccharification time from 2 h to 5 h. Saccharification temperature had a pronounced effect on glucose conversion. Glucose conversion increased to 85.7% from 67.1% with the rise of temperature of 5°C from 35°C, and with a further rise of 5°C, glucose conversion increased only 2.6%. A minor effect on glucose conversion was observed with consistency. Ladeira Ázar et al. [51] showed a higher glucose conversion in relatively low lignin content bagasse than in the high lignin content bagasse. In an earlier investigation, it was observed that bleached pulp had higher conversion efficiency and higher glucose yield than the unbleached pulp due to the removal of lignin during bleaching and increased contact of cellulose with enzyme [52].




*4. Effect of treatment time on the conversion into glucose (temperature, 40°C; pH 4.8; consistency, 5%).*




*5. Effect of temperature on the conversion into glucose (time, 4 h; pH 4.8; consistency, 5%).*




*6. Effect of consistency on the conversion into glucose (time, 4 h; pH 4.8; temperature, 40°C).*

## CONCLUSIONS

Bleached pulp could be produced from rice straw at the cooking conditions of 8% KOH at 150°C for 120 min followed by D(EP)D bleaching with a yield of 47.2% and 82.4% brightness. The pulp was fractionated into longer and shorter fiber fractions with fiber length of 1.09 mm and 0.34 mm, respectively. The α-cellulose content in the longer fiber fraction was 88.2% with 11.3% residual pentosan, which increased to 91.3% with residual pentosan of 6.3% by 12% KOH extraction at room temperature. The shorter fiber fraction with 83.1% α-cellulose and 13.0% residual pentosan was saccharified by cellulase enzyme at the conditions of 4 h of treatment at 40°C with 5% consistency. During the KOH pulping process, the dissolved biomass in the spent liquor was separated as 16.5% of lignin and 11.9% of hemicellulose, which can also be used for biomaterials and biochemicals, and the remaining liquor can be used for soil amendment. Therefore, paper-grade pulp from rice straw can be converted into dissolving pulp and glucose for bioethanol by fractionation, and dissolved lignin and hemicellulose in the black liquor can be used for biomaterial and biochemical production. **TJ**

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## ABOUT THE AUTHORS

We studied this topic because Bangladesh is a forest deficient country and needs alternative raw material. The topic here certainly generates new ideas in this respect. The idea was very simple, and we did not face any problems with implementing it.

Through our study, we discovered that grass can be a good source for pulping if a different technology/concept is applied. We also found that a small-scale biorefinery with low capital investment is possible using rice straw. The step is to scale up this concept.


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