RICE STRAW AS A DUAL-PURPOSE FEEDSTOCK: INTEGRATED SUGAR RECOVERY AND CELLULOSIC FIBER PRODUCTION FOR PAPERMAKING

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The utilization and management of lignocellulosic waste for production of valuable products is a great challenge for the scientific community. Rice straw offers an opportunity for diversifying application to generate valuable resources from waste in this regard. The present study demonstrates the optimal utilization of rice straw for the production of sugars and paper simultaneously. The pretreatment of rice straw was conducted under different alkali charge and variable reaction conditions. A maximum of 12.80% sugars were extracted with 4% NaOH treatment at 160 °C and retention time of 120 min. The pretreated and untreated biomasses were further subjected to pulping under different sets of reaction conditions for the production of pulp. Then, 60 gsm handsheets from each variety of pulp were prepared and paper properties were evaluated. The morphological changes of untreated and pretreated rice straw were examined by FESEM, showing the intact structure of untreated biomass, and the disrupted and fragmented structure of alkali pretreated biomass. The HPLC analysis of extracted liquor confirmed the presence of three monosugars: glucose (14.10%), xylose (55.66%) and arabinose (20.14%). Conclusively, the overall study opens a new avenue for the utilization of an underutilized waste biomass for production of valuable products and explores the optimal practices for management of waste biomass.

Keywords: waste biomass, pretreatment, sugars, pulping, paper properties

INTRODUCTION

The rapid increase in the global population has resulted in an intensified demand for food production, which in turn has led to a significant rise in the cultivation of crops. Among these, rice is one of the most widely grown cereals, particularly in Asia.[1] Rice straw, a by-product of rice farming has become an abundant lignocellulosic waste material.[2,3] Traditionally, rice straw is discarded by burning the straw in the fields.[4,5] This contributes to environmental pollution and loss of potential resources. However, with the growing need for sustainable practices and the search for renewable materials, rice straw would become a promising feedstock for various value-added applications. The increased global population has put immense pressure on natural resources to fulfill its energy requirements.[6] Due to very limited conventional energy resources, it is crucial to explore alternative, sustainable solutions. In this respect, abundantly available lignocellulosic biomass could become a sustainable alternative to feed the energy demand across the globe. Recently, significant efforts have been undertaken to utilize the underutilized natural resources for the production of biofuels so as to reduce the unwanted pressure on natural resources.

Lignocellulosic biomass is a rich source of natural carbohydrates that can be utilized as a potential resource for various end use applications. The extracted carbohydrates may be utilized in pharmaceuticals, pulp and paper, textiles, biofuels, biocomposites, food additives, animal feeds, cosmetics and in many other sectors. Cellulose and hemicelluloses are the major polysaccharides present in lignocellulosic biomass, along with lignin.[7] The structural complexity of lignocellulosic biomass makes the overall process of extraction of carbohydrates very challenging.

However, various pretreatment methods, such as chemical, physical, and biological approaches, may be employed to break down the complex lignin-carbohydrate matrix, which may enhance the accessibility of biomass for the extraction of sugars.[8]

In comparison to cellulose, hemicelluloses having branched structure can be more easily hydrolyzed by making them more soluble under milder conditions during chemical processes. Milder conditions help preserve the structural integrity of other biomass components, allowing for more efficient utilization of overall biomass. Prior extraction of hemicelluloses, first leaves cellulose and lignin largely intact, allowing for their further use in fiber production, bio-composites, or lignin valorization. This approach certainly may support the integrated biorefinery models where all biomass components are efficiently utilized.

At present, the availability of quality raw materials for the production of various products is a serious issue. Industries are facing an acute scarcity of sustainable raw materials driven by factors such as depletion of natural resources, supply chain disruptions and increasing demand. This crisis is more severe in energy-intensive sectors, such as pulp and paper, textiles, chemicals, plastics, and manufacturing, which heavily depend on limited resources. In such a scenario, the integrated utilization of a single raw material for the production of two or more end products with high commercial value may provide a solution, as various industries are competitive for a single raw material. Hence, it is the need of the hour to identify new routes of utilization for a single raw material covering the need of two or more industries within a single production unit.

The paper industry is one of the largest consumers of natural raw materials, traditionally reliant on wood and agro-based raw materials. The increasing global demand for paper products has intensified pressure on natural resources, leading to concerns about raw material scarcity, environmental impact, and sustainability. In view of this, the biorefinery concept offers a transformative approach by integrating biomass valorization strategies, such as the pre-extraction of hemicelluloses before pulping.[9-11] During pulping, most of the hemicelluloses are released into the black liquor and subsequently combusted in the recovery furnace of the pulp mill.[11-13] These hemicelluloses provide less than 20% of the total energy output when burnt in the recovery furnace, as most of the energy is generated from the combustion of lignin. Burning of any of the natural potential resource must be the last solution until it finds its utility for other purposes. In view of this, the utilization of hemicelluloses in the recovery furnace is not the ideal route. Pre-extraction of hemicelluloses prior to pulping offers an opportunity for their optimal utilization.[14,13]

Hemicelluloses can be selectively extracted before pulping to serve as a valuable feedstock for biofuels, biochemicals, and biomaterials, thereby enhancing resource efficiency and sustainability. This pre-extraction process not only enables the integrated utilization of wood components, but also improves pulp quality by reducing the presence of hemicelluloses that can interfere with fiber bonding. Pre-extraction of hemicelluloses can be achieved through different approaches under an optimal set of reaction conditions. Recently various methodologies, *e.g.* aqueous pre-extraction, steam explosion, alkali extraction, acid pretreatment, organosolvent extraction, supercritical fluid pretreatment, microwave-assisted treatment, ultrasound assisted extraction, hydrothermal processing have been extensively employed for the extraction of hemicelluloses.[15-25] Among all, the pretreatment of lignocellulosic materials with alkali is considered as one of the most viable options.[26,27] Alkali prehydrolysis of lignocellulosic biomass is a crucial pretreatment step that enhances sugar extraction by selectively breaking down hemicelluloses into soluble sugars. This process improves the overall efficiency of biomass conversion by increasing sugar yield, reducing the complexity of the lignin-carbohydrate structure, and enhancing the susceptibility of the remaining biomass for further treatments. Apart from this, mild reaction conditions during alkali prehydrolysis reduce sugar degradation and the formation of unwanted by-products, making it an environmentally friendly and efficient method for sugar extraction.

Although research has already been done on this, it has been mainly focused on the strength properties of paper prepared from pre-extracted biomass.[28] In view of the above, efforts have been undertaken for optimal pre-extraction of sugars from rice straw under alkaline conditions, followed by investigation of pulping and papermaking characteristics of pretreated biomass. Such an approach may enhance the overall efficiency of the pulp mill by valorizing a greater fraction of the biomass, while reducing waste and the environmental burden of the process. The

objectives of the present study were (i) to optimize alkali pretreatment conditions for the extraction of sugars; (ii) perform pulping of pretreated biomass; (iii) evaluate the pulp and (iv) assess the physical strength properties of paper. Structural changes in the rice were evaluated through FESEM. In addition, HPLC was applied to confirm the presence of reducing sugars. The present study not only facilitates the efficient separation of sugars for potential valorization, but also improves the fiber quality for paper production to some extent.

EXPERIMENTAL

Materials

Rice straw was collected from Dehradun (India), air-dried, screened and stored in a dry environment before processing. Initially, rice straw was cut to 2-3 cm in length. The chopped rice straw was then kept into airtight bags and stored for further experiments. Pulping and papermaking chemicals were of laboratory grade, whereas the chemicals used for pretreatment and sugar estimation were of analytical grade. All stock solutions for carrying out the experiments were freshly prepared.

Methods

Chemical composition of untreated and pretreated raw material

The chemical composition of untreated and alkali pretreated raw material was determined with respect to various chemical parameters. All the parameters were examined according to standard methods of the Technical Association of Pulp and Paper Industry (TAPPI). Moisture content, ash content, hot-water and cold water solubility, 1% NaOH solubility, alcohol-benzene solubility, acid-insoluble lignin (Klasson lignin) and holocellulose content were analyzed as per TAPPI methods T 412 om-16,[29] T 211 om-02,[30] T 207 cm-99,[31] T 204 cm-97,[32] T 212 om-02,[33] T 222 om-02,[34] and method 249, respectively. All the experiments were done in triplicate and the results reported represent mean values.

Alkali pretreatment

Alkali pretreatment is an effective method for modifying the lignocellulosic structure of rice straw for sugar extraction and improve its suitability for papermaking. In the present study, sodium hydroxide (NaOH) was used as the alkali reagent to disrupt the lignin-carbohydrate complex, facilitating the removal of lignin and increasing cellulose accessibility for improved papermaking characteristics. The alkali pretreatment of rice straw was conducted using an oil bath digester having six vessels of equal capacity. A fixed amount of 100 g of rice straw was treated with varying alkali charges of 2%, 3%, and 4% (w/w) NaOH, maintaining a bath ratio of 1:10 (solid:liquid). The reaction was carried out at different temperatures (100 °C, 120 °C, 140 °C, and 160 °C), with residence times ranging from 20 to 120 minutes (20, 40, 60, 80, 100, and 120 min). After the completion of the pretreatment, the overall content was extracted using a spin dryer machine for the collection of the sugar rich liquor and the biomass residue. The extracted liquor was kept in sample bottles for immediate analysis of sugars, whereas the biomass left after pre-extraction was further washed thoroughly until a neutral pH was attained and sequentially processed for proximate chemical analysis for various components as per TAPPI standard methods mentioned above.

Estimation of total reducing sugars (TRS)

The estimation of sugars was performed using the 3,5-dinitrosalicylic acid (DNS) method, a widely used colorimetric method for quantifying reducing sugars.[35] A standard curve was generated using xylose as the reference sugar, enabling the quantification of reducing sugars in the samples. The pretreated rice straw hydrolysate was centrifuged and the supernatant part was taken. The supernatant liquid was further hydrolysed with concentrated H_2SO_4 at 121 °C for 60 minutes in an autoclave. Post-hydrolysis, the solution was neutralized to pH 7 using a $BaCO_3$ slurry. A 100 µL aliquot of the hydrolysate was diluted 30-fold with deionized water, followed by the addition of 3 mL DNS reagent. The mixture was then heated at 100 °C in a water bath for 5 minutes for colour development and cooled to room temperature. To stabilize the colour, 1 mL of Rochelle salt was added. Absorbance was measured at 510 nm using a UV-Vis spectrophotometer (UV-2600, Shimadzu).

High-performance liquid chromatography analysis

The hydrolysate obtained under optimal pretreatment conditions (alkali charge: 4%; reaction temperature: 160 °C; reaction time: 120 min) was further analyzed through high-performance liquid chromatography (HPLC) technique, with an Agilent Technologies 1260 Infinity II system. Prior to the HPLC analysis, the sample and standards were filtered through a Cole-Parmer PTFE Nylon HPLC Syringe Filter (13 mm filter diameter, 0.45 µm pore size) and left undiluted. Formic acid was separated on a BIO-RAD Aminex® HPX-87H HPLC column (7.8 mm x 300 mm) operated at ambient temperature with an overall flow rate of 0.5 mL per min of a 0.05% sulphuric acid mobile phase and detected using a RID. A 10 µL sample volume was injected, and the results were compared to a calibration curve created with different concentrations of formic acid standard. The analysis was completed within 45 min, and data were recorded using OpenLAB CDS Chemstation Edition Chromatography software. The formic acid standard and CO_2 hydrogenated product showed peaks at a retention time of 16.443 minutes, respectively.

Field emission gun scanning electron microscopy analysis

Field emission gun scanning electron microscopy (FESEM) study was performed to investigate the impact of alkali treatment on rice straw. The FESEM of untreated and pretreated rice straw was done using a Hitachi-PU field emission scanning electron microscope. The images of untreated and pretreated rice straw were captured with an accelerating potential difference of 10 kV within a working range of 3-200 μm.

Pulping

Pulping of treated and untreated rice straw samples was carried out in a rotary oil bath digester containing six vessels to evaluate the impact of alkali charge, temperature, and reaction time on fiber yield and quality. In each case, 100 g of sample was treated with different alkali charges of 10%, 12%, and 14% (on oven-dry raw material basis). The cooking temperature was maintained within the range of 140–160 ºC, with a reaction time varying between 30 and 50 minutes to optimize delignification. A bath ratio of 1:4.5 (solid to liquor) was kept constant during the pulping. At the end of the cooking, the vessels were removed from the digester and placed in a cold-water container. After cooking, the pulp was subjected to mechanical squeezing using a spin dryer machine to remove excess black liquor. The residual pulp was then thoroughly washed with lukewarm water to eliminate any remaining chemicals and impurities before further processing.

Pulp screening

After pulping, the obtained pulp was subjected to a screening process to separate fibers from oversized debris, shives, and other unwanted materials. Pulp screening is a critical step in the pulping process aimed at removing oversized fibers, shives, and other unwanted contaminants to ensure uniform fiber distribution and improve the final paper quality. The separation of contaminants from the pulp is a significant step in the evaluation and improvement of the pulping process. The untreated and pretreated pulps were subjected to screening in a laboratory Somerville type pulp screening machine (Lorentzen & Wettre, Canada) to remove the uncooked and unwanted particles like knots, shives, *etc*. Initially, the pulp was disintegrated and diluted to pulp consistency of 1% with water. The pulp slurry was then agitated using a heavy duty overhead stirrer to maintain uniform consistency within the slurry without changing the nature of contaminants. The overall agitated mass was then passed through the pulp screening machine for removal of contaminants present in the pulp.

Pulp yield determination

The pulp yield was determined by calculating the ratio of the oven-dry weight of the pulp obtained after pulping to the initial oven-dry weight of the raw material. The yield was expressed as a percentage using the following equation:

$$Pulp\ yield\ (\%) = \frac{X}{Y} \times 100 \quad (1)$$

where X is the oven-dry weight of the obtained pulp (g), and Y is the oven-dry weight of the raw material (g).

To determine the oven-dry weight, samples of both raw material and pulp were weighed before and after drying in an oven at 105 ± 2 °C until a constant weight was achieved. The dried samples were then cooled in a desiccator before final weighing. The yield calculations were performed in triplicate to ensure accuracy and repeatability.

Residual lignin determination

Residual lignin content in the pulp obtained after pulping untreated and pretreated samples was further determined in terms of kappa (K) number. For this, at first, a pad was made from the screened pulp and was air dried. The pad sample was torn into small pieces. The test specimen was then disintegrated in 500 mL of water. The disintegrated pulp was transferred to a 2 litre reaction beaker. The beaker was placed in a temperature regulated bath adjusted at 25 °C and continuously stirred with a stirrer. 100 mL of potassium permanganate solution and 100 mL of 4N sulphuric acid solution were introduced into the 2 litre beaker and 300 mL of distilled water was added, so that the total volume became 1000 mL. After 10 minutes, the reaction was stopped by adding 20 mL of 1 N potassium iodide. A few drops of starch indicator were added into the reaction beaker and free iodine was titrated with 0.2 N sodium thiosulphate. A blank titration was also performed using the same method. The residual lignin in the pulp samples was finally calculated as per the following formulas:

$$Kappa\ no.\ (K) = p \times \frac{f}{w} \quad (2)$$

$$p = (b - a)N/0.1 \quad (3)$$

where f – correction factor to a 50% permanganate consumption depending upon the value of p, w – weight of moisture free pulp in g, p – amount of 0.1N permanganate consumed by the pulp sample in mL, b – amount of thiosulfate consumed in blank titration in mL, a – amount of thiosulfate consumed by the pulp specimen, N – normality of thiosulfate.

Preparation of handsheets

Handsheets of 60 gram per square meter (gsm) were prepared according to TAPPI T 205 sp-02[36] standard procedure to evaluate the strength properties of the paper. Initially, the pulp was disintegrated in a standard laboratory disintegrator to ensure uniform fiber dispersion. The pulp suspension was then diluted and thoroughly mixed before being transferred to a Rapid Kothen paper sheet making machine. The sheets were formed using a controlled drainage process, followed by couching onto blotter papers and pressing to remove excess water. The pressed sheets were then air-dried to prevent shrinkage and ensure uniform fiber bonding.

Determination of paper properties

The handsheets prepared from untreated and pretreated pulps of rice straw were subjected to conditioning at a temperature of 27±1 °C and a relative humidity of 65 ± 2% prior to testing of paper properties. The grammage, tear index, tensile index, burst index and brightness were determined as per TAPPI standard methods T410 om-02; T 414 om-12; T494 om-01, T403 om-97 and T452 om-02, respectively. Grammage of paper was determined with a grammage tester, tear index was calculated using an Elmendorf type tearing tester (Testing Machines Inc., USA), tensile index was determined by using a vertical type tensile tester (Lorentzen & Wettre, Sweden); burst index was calculated using a burst tester (Lorentzen & Wettre, Sweden) and brightness was estimated with a brightness tester (Global Eng. Corp. India).

RESULTS AND DISCUSSION

Proximate chemical analysis

The investigation of any biomass with respect to various chemical components is essential prior to its processing. In the present study, the proximate chemical composition of rice straw revealed a high holocellulose content (58.9%), representing a considerable occurrence of carbohydrate polymers, mainly cellulose and hemicelluloses, which shows its utility as a potential raw material for various bio-based applications. The presence of alpha-cellulose (36.6%) suggests a substantial proportion of pure cellulose in rice straw, which is essential for applications requiring high cellulose content, such as bioethanol production or pulp and paper industries. The lignin content (16.4%) in rice straw was recorded lower than that of hardwood and softwood. The lower lignin content in rice straw may require mild cooking conditions, with lower chemical charge during pulping. The ash content in rice straw was comparatively higher than in wood-based raw materials commonly used for production of paper and paper products. Such a high ash content (16.3%), deriving from the silica content of rice straw, may further cause problems during refining and recovery of the cooking liquor.

The water solubility analysis indicated that the hot water solubility (18.2%) was higher than cold water solubility (13.1%), highlighting the presence of thermally sensitive compounds, such as simple carbohydrates, phenolics, and extractives. The 1% NaOH soluble fraction (45.8%) represents a considerable amount of low-molecular-weight hemicelluloses, pectins, and other alkali-soluble components, which can affect the digestibility and processing efficiency of the biomass. A high solubility value indicates the significant presence of these components, suggesting improved chemical accessibility in bioconversion processes like pulping and bioethanol production. The ethanol–benzene extractives (2.78%) imply a relatively low content of non-polar compounds, including waxes, resins, and lipophilic components. These findings provide an important insight into the composition of rice straw, highlighting both its potential and limitations in various industrial applications, such as biofuel production, paper manufacturing, and agricultural amendments.

The proximate chemical analysis of pretreated rice straw showed a holocellulose content of 66.20%, which is higher than that of untreated rice straw. This increase could be attributed to the loss of some hemicelluloses during pretreatment, resulting in a higher cellulose content per gram of the material. The lignin content of the alkali pretreated biomass was 11.80%, indicating a significant decrease due to removal of some lignin during alkali pre-extraction. The alcohol-benzene extractives in the pretreated biomass represented 1.80%, indicating a slight reduction after the pretreatment. Additionally, there was a notable decrease in solubility in cold water, hot water, and 1% NaOH, with values recorded up to 6.40%, 10%, and 21%, respectively. The reduction in solubility of rice straw may be due to the loss of water-soluble low molecular weight polysaccharides, phenols, proteins, and starch during the pretreatment. Such decreases in solubility following pretreatment have been also reported previously.[37] The results of the present study are in good agreement with the reports published earlier.[5]

Alkali pretreatment of rice straw

Alkali pretreatment of rice straw was performed as per the conditions mentioned above. During the experiments, it was observed that chemical charge and temperature with retention time collectively play an important role in the extraction of reducing sugars. Figure 1 (A)-(L) illustrates the effect of temperature and chemical charge on the extraction of sugars. For 2% alkali pretreatment, at maximum retention time (120 min), the maximum reducing sugars extracted were 4.48% (Fig. 1(A)), 7.48% (Fig. 1(B)), 11.56% (Fig. 1(C)), and 12.44% (Fig. 1(D)) at 100 °C, 120 °C, 140 °C, and 160 °C, respectively. When the alkali charge was increased to 3% under a retention time of 120 minutes, the reducing sugars extracted were 4.86% (Fig. 1(E)),

7.98% (Fig. 1(F)), 11.56% (Fig. 1(G)), and 12.56% (Fig. 1(H)) at 100 °C, 120 °C, 140 °C, and 160 °C, respectively. As the chemical charge increased from 2% to 4% and the temperature from 100 °C to 160 °C, more sugars were released during the pretreatment. For 4% alkali pretreatment, at maximum retention time (120 min) and temperature (160 °C), reducing sugars up to 12.80% were recovered.

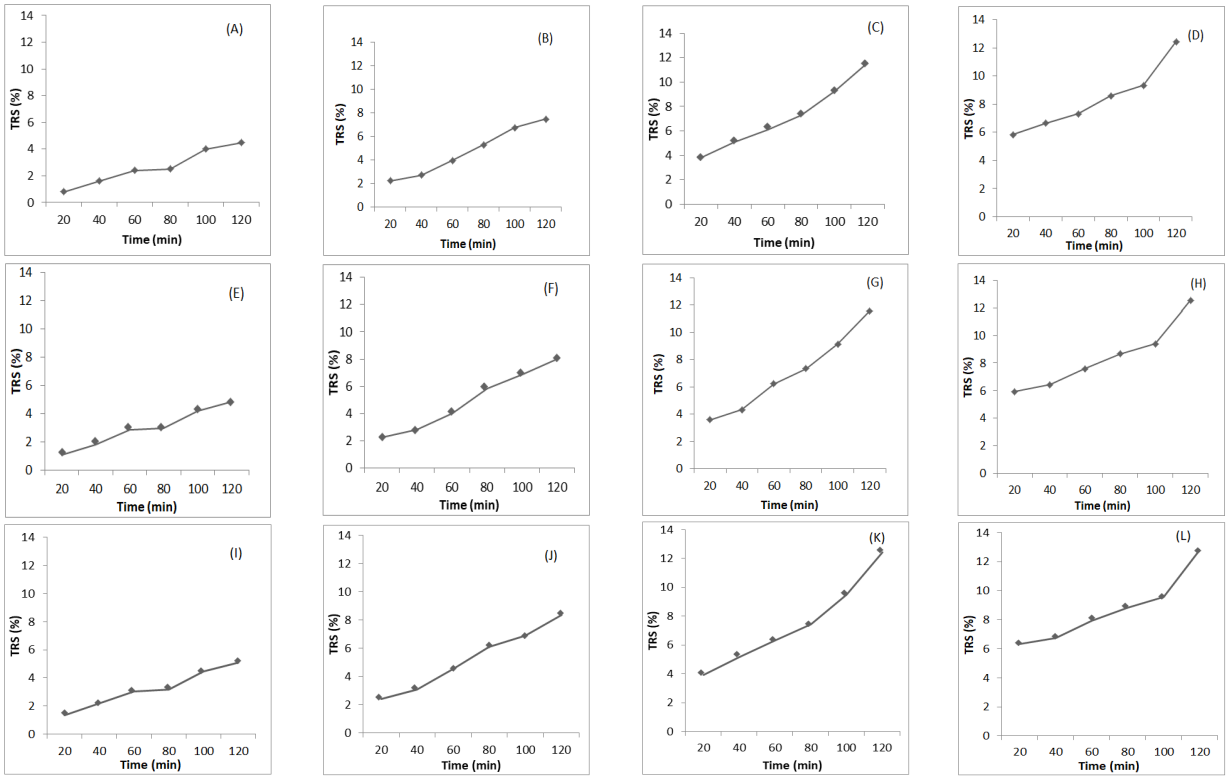


Figure 1: Effect on total reducing sugars during pretreatment at (A) 100 °C; (B) 120 °C; (C) 140 °C; (D) 160 °C at 2% alkali charge; (E) 100 °C; (F) 120 °C; (G) 140 °C; (H) 160 °C at 3% alkali charge; (I) 100°C; (J) 120 °C; (K) 140 °C; (L) 160 °C at 4% alkali charge

Thus, an increase in alkali charge from 2 to 4%, in reaction temperature from 100 to 160 °C and in reaction time from 20 to 120 min during the pretreatment promotes the breakdown of complex polysaccharides, such as cellulose and hemicelluloses, into simpler reducing sugars. The higher alkali charge disrupts the hydrogen bonds and ester linkages within the lignocellulosic matrix, leading to lignin solubilization and improved accessibility of cellulose and hemicelluloses to hydrolysis. Furthermore, alkali promotes the swelling of cellulose fibers, reducing crystallinity and facilitating cleavage of glycosidic bonds. This results in the release of more monosaccharides and oligosaccharides, thereby increasing the overall reducing sugar content. The increase in temperature from 100 to 160 °C may further facilitate the breaking of glycosidic bonds, leading to significant depolymerization of polysaccharides into reducing sugars. The increase in temperature provides the necessary activation energy to break covalent bonds, thereby reducing the structural complexity of biomass, leading to efficient release of reducing sugars. Additionally, extended reaction time facilitates the diffusion of hydrolyzed sugars into the reaction medium, reducing steric hindrance and enhancing overall sugar recovery. The prolonged exposure of polysaccharides to hydrolytic conditions allows for more extensive breakdown of complex carbohydrates, resulting in higher sugar yields.

High performance liquid chromatography analysis

The high performance liquid chromatography (HPLC) analysis (Fig. 2) of the treated biomass revealed the presence of three major monosaccharides: xylose, arabinose, and glucose. The quantification results showed that xylose was the predominant sugar, constituting 55.66% of the

total sugar content, followed by arabinose at 20.14% and glucose at 14.10%. The presence of these sugars indicates the effectiveness of the biomass pretreatment in hydrolyzing hemicellulosic components into fermentable sugars. In the present study, xylose was the most abundant sugar detected, showing extensive hemicellulose degradation during the biomass pretreatment. Hemicelluloses, primarily composed of xylan, undergo hydrolysis during pretreatment, releasing xylose as the major product. The high xylose yield demonstrates the effectiveness of the pretreatment in breaking down xylan-rich biomass components.

The second most prevalent sugar, arabinose, accounted for 20.14% of the total sugars. Arabinose is a basic component of arabinoxylans, which are present in biomass. The moderate yield of arabinose in the present study suggests that the treatment process was able to cleave arabinose side chains from hemicelluloses effectively. However, its lower concentration compared to xylose indicates that arabinose-rich linkages may have been more resistant to complete hydrolysis or were present in lower amounts in the original biomass.

Glucose was detected at a lower concentration (14.10%), which could be attributed to partial cellulose hydrolysis during the treatment. Since cellulose is more resistant than hemicelluloses, its conversion to glucose usually necessitates more severe pretreatment conditions. The relatively lower glucose yield suggests that the conditions primarily targeted hemicellulose degradation, leaving the cellulose fraction largely intact. This is advantageous for further processing of the left-over biomass, as the retained cellulose can be utilized for the production of paper and paper products. The high content of xylose present in the alkali pretreated pre-extracted liquor makes it suitable for pre-extraction, which can be further processed for fermentation and used for value-added products, like biofuel *etc*.

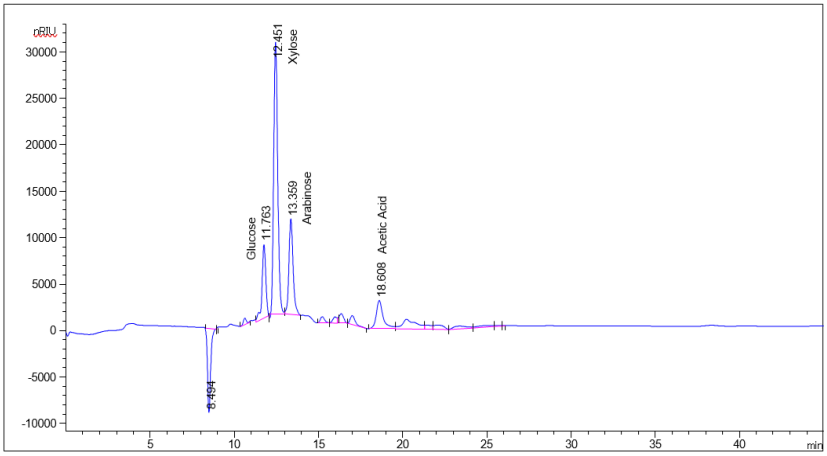


Figure 2: HPLC spectrum of pre-extracted liquor

Field emission gun scanning electron microscopy (FESEM)

Using FESEM, the study delved into the morphological differences between the fibrous structures of natural biomass and alkali-pretreated biomass. The micrographs provide a visual comparison of these structural variations, highlighting distinct changes due to the pretreatment process.

In Figure 3A, the untreated or native rice straw is shown. These images clearly depict the raw biomass with a smooth, intact structure, characterized by very hard and rigid fibrillar morphology. The fibrils appear tightly bound and well-organized, indicating the robust nature of the untreated biomass. This structural integrity suggests minimal external interference, maintaining its natural composition and rigidity.

Figure 3B displays the alkali pretreated rice straw. These images reveal significant morphological transformations resulting from the alkali pretreatment. The fibrillar structure of the biomass appears to be disrupted and fragmented. The once compact and finely divided surfaces are now unsettled, indicating a breakdown of the rigid fibrillar framework. This disruption is a clear sign of the impact of the alkali pretreatment, which aims to make the biomass more amenable to further processing. Additionally, the SEM images of pretreated biomass show the presence of clusters of

spherical micrograins. These micrograins suggest a substantial fragmentation of hemicelluloses during the pretreatment process.

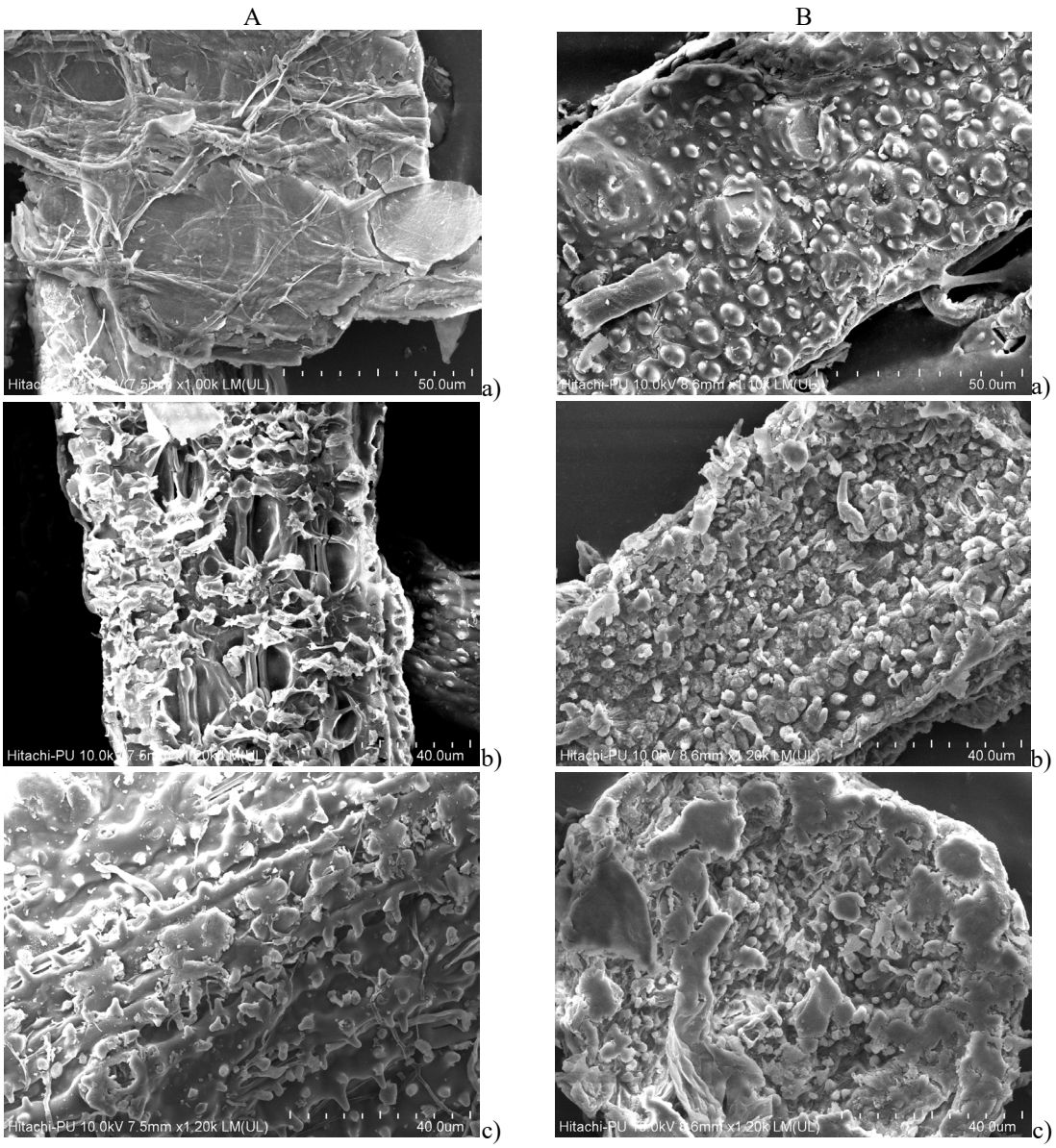


Figure 3: FESEM images of (A) untreated rice straw; (B) alkali pretreated rice straw

Assessment of pulping operations

The pulping of untreated and alkali pretreated rice straw was carried out under different reaction conditions and the pulp was characterised for various properties. Figure 4 (A-L) shows the effect of process parameters on different properties, *viz.* pulp yield, Kappa number, tear index, tensile index, burst index, and brightness for both untreated and alkali pretreated rice straw samples.

Pulp yield and Kappa number

The effect of alkali pretreatment and cooking conditions on pulp yield was investigated by varying cooking temperatures (140 °C, 150 °C, and 160 °C), alkali concentrations (10%, 12%, and 14%), and retention times (30 and 50 min) (Fig. 4A and 4B). The results clearly indicate the influence of pretreatment method, cooking temperature, alkali concentration, and retention time on pulp yield. In general, pulp yield decreased with

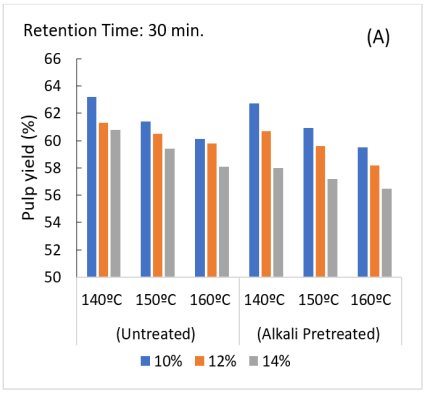
increasing alkali concentration, higher cooking temperatures, and longer retention times in both untreated and alkali-pretreated samples. For the untreated samples, it was observed that pulp yield decreased with increasing alkali concentration and temperature. At 140 °C, the pulp yield decreased from 63.2% to 60.8% with an increment in alkali charge from 10% to 14% for a 30-minute retention time. A similar pattern was also observed at 150 °C and 160 °C, with pulp yield decreasing from 61.4% to 59.4% and 60.1% to 58.1%, respectively, for the same time period (Fig. 4A). The lowest pulp yield was recorded at 160 °C with 14% alkali concentration, indicating that at higher temperature and higher alkali charge, efficient delignification and dissolution of hemicelluloses took place, thereby reducing the overall yield. When the retention time was extended to 50 minutes by varying cooking temperatures (140 °C, 150 °C, and 160 °C), alkali concentrations (10%, 12%, and 14%), a further reduction in pulp yield was observed with yields decreasing from 62.1% to 58.4% attributed to increased degradation of carbohydrates due to prolonged exposure, leading to additional loss of fibrous material (Fig. 4B).

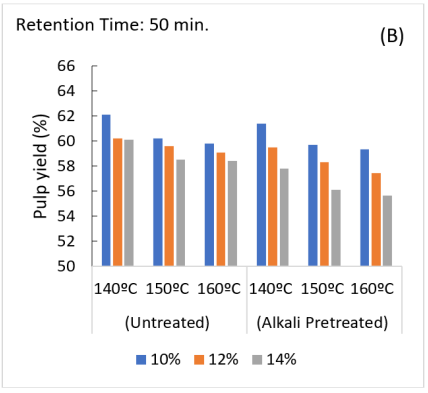
Compared to the untreated samples, alkali pretreated samples exhibited slightly lower pulp yields under the same conditions, especially at higher alkali concentrations and temperatures. In the case of alkali pretreated samples, at 140 °C and 30 minutes, pulp yield declined from 62.7% at 10% alkali to 58% at 14% (Fig. 4A), and a similar trend was observed at 50 minutes, where the yield dropped from 61.4% to 57.8% with a successive increase of alkali charge (Fig. 4B). Further increment in cooking temperature (150 °C and 160 °C) did not bring any improvement in pulp yield and it significantly decreased from 57.2% to 55.64% at 30 and 50 min retention time and 14% chemical charge (Fig. 4A and 4B).

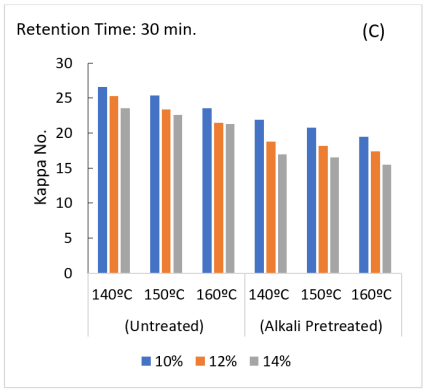
In the present study, pretreatment appears to enhance delignification, thereby reducing pulp yield further due to more efficient removal of non-cellulosic components. Notably, the lowest pulp yield (55.64%) was recorded at 160 °C, 14% alkali, and 50-minute retention time for alkali-pretreated samples, highlighting the collective effect of harsh treatment conditions (Fig. 4B). In contrast, the maximum yield (63.2%) was achieved under milder conditions (140 °C, 10% alkali, 30-minute retention, untreated), indicating that milder processing parameters favour enhanced pulp yield (Fig. 4A).

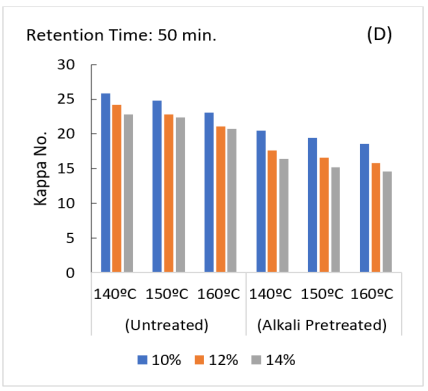
The impact of cooking temperature, cooking time, and alkali pretreatment on Kappa number is presented in Figure 4 (C) and 4(D). The results of the study report a consistent decreasing trend in Kappa number with an increase in temperature, alkali concentration, and cooking time, indicating enhanced delignification under more severe pulping conditions. For untreated samples, the Kappa number decreased from 26.6 to 21.3 at 30 minutes (Fig. 4C) and from 25.8 to 20.7 at 50 minutes (Fig. 4D) when both temperature and alkali concentration were increased. A similar trend in Kappa number was also reported for alkali pretreated rice straw samples. The alkali-pretreated samples demonstrated significantly lower Kappa numbers under all conditions, highlighting the effectiveness of pretreatment in facilitating lignin degradation. At 160 °C and 14% alkali concentration, the lowest Kappa number of 15.5 was observed at 30 minutes (Fig. 4C), which further decreased to 14.6 at 50 minutes (Fig. 4D).

These results clearly suggest that alkali pretreatment in conjunction with higher cooking temperature and prolonged cooking time substantially improves delignification efficiency, thereby enhancing pulp quality and reducing chemical consumption in subsequent bleaching processes. As the chemical charge increases, the β-aryl ether bonds are cleaved more effectively, causing greater alkaline degradation of lignin. This leads to more bond cleavage between lignin and carbohydrates, resulting in a reduced amount of residual lignin (indicated by a lower Kappa number) in the pulp. It is also hypothesized that at higher cooking temperature and prolonged reaction time the enhanced removal of reducing sugars from rice straw during pretreatment makes the remaining biomass more prone to the diffusion of active molecules deep inside the cell wall. This process seems to enlarge the size of the pores in the cell wall by removing reducing sugars, especially hemicelluloses, and these larger pores play a key role in the rate at which lignin is removed, ultimately leading to a lower Kappa number in the pulp.

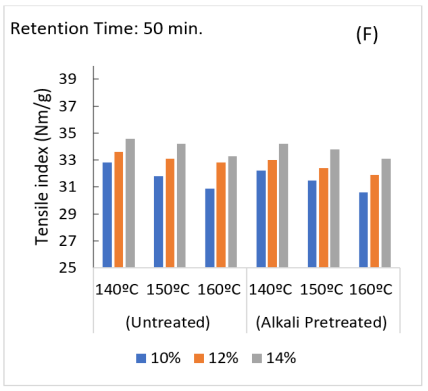

Retention Time: 30 min.
(A)
Pulp yield (%)
66
64
62
60
58
56
54
52
50
140ºC 150ºC 160ºC 140ºC 150ºC 160ºC
(Untreated)
(Alkali Pretreated)
10% 12% 14%

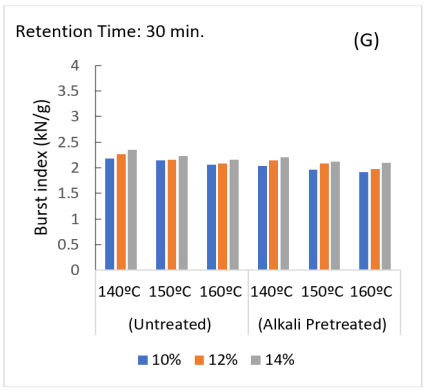

Retention Time: 50 min.
(B)
Pulp yield (%)
66
64
62
60
58
56
54
52
50
140ºC 150ºC 160ºC 140ºC 150ºC 160ºC
(Untreated)
(Alkali Pretreated)
10% 12% 14%

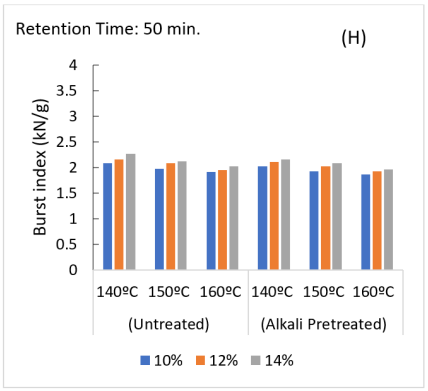

Retention Time: 30 min.
(C)
Kappa No.
30
25
20
15
10
5
0
140ºC 150ºC 160ºC 140ºC 150ºC 160ºC
(Untreated)
(Alkali Pretreated)
10% 12% 14%


Retention Time: 50 min.
(D)
Kappa No.
30
25
20
15
10
5
0
140ºC 150ºC 160ºC 140ºC 150ºC 160ºC
(Untreated)
(Alkali Pretreated)
10% 12% 14%


Retention Time: 30 min.
(E)
Tensile index (Nm/g)
39
37
35
33
31
29
27
25
140ºC 150ºC 160ºC 140ºC 150ºC 160ºC
(Untreated)
(Alkali Pretreated)
10% 12% 14%


Retention Time: 50 min.
(F)
Tensile index (Nm/g)
39
37
35
33
31
29
27
25
140ºC 150ºC 160ºC 140ºC 150ºC 160ºC
(Untreated)
(Alkali Pretreated)
10% 12% 14%


Retention Time: 30 min.
(G)
Burst index (kN/g)
4
3.5
3
2.5
2
1.5
1
0.5
0
140ºC 150ºC 160ºC 140ºC 150ºC 160ºC
(Untreated)
(Alkali Pretreated)
10% 12% 14%


Retention Time: 50 min.
(H)
Burst index (kN/g)
4
3.5
3
2.5
2
1.5
1
0.5
0
140ºC 150ºC 160ºC 140ºC 150ºC 160ºC
(Untreated)
(Alkali Pretreated)
10% 12% 14%

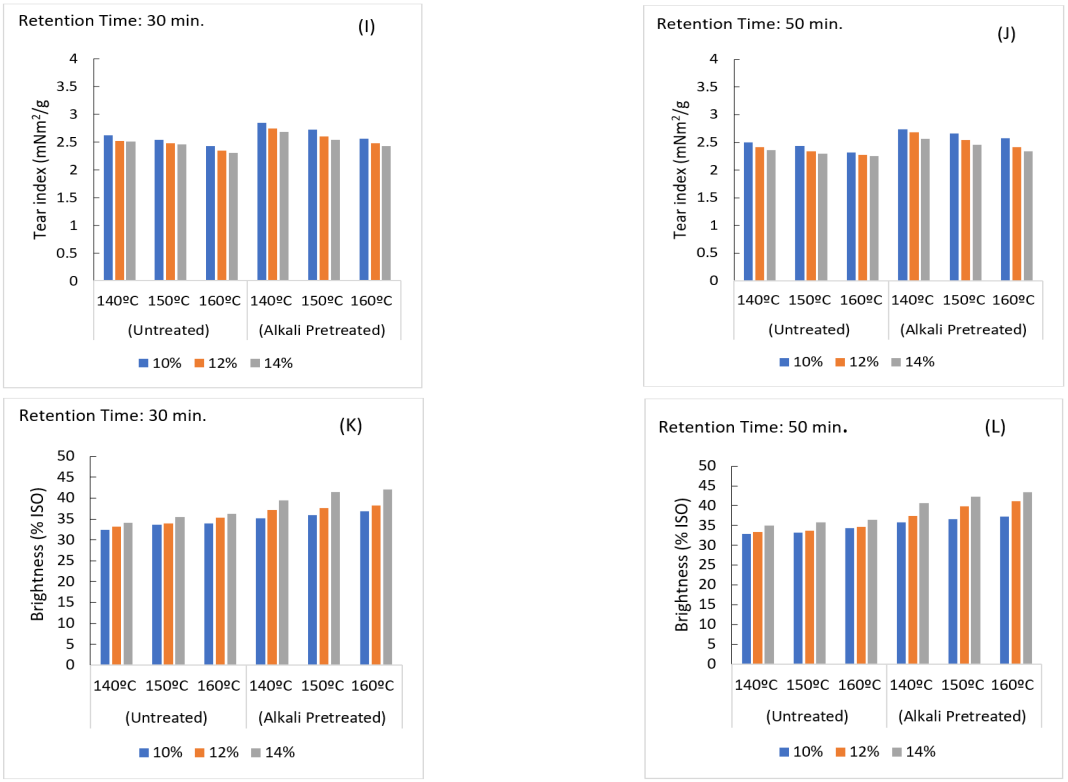


Figure 4: Pulp yield for untreated rice straw pulp at (A) 30 min, (B) 50 min; Kappa number of pulp produced at (C) 30 min, (D) 50 min reaction time; Tensile index of handsheets from pulp produced at (E) 30 min, (F) 50 min reaction time; Burst index of handsheets from pulp produced at (G) 30 min, (H) 50 min reaction time; Tear index of handsheets from pulp produced at (I) 30 min, (J) 50 min reaction time; Brightness of handsheets from pulp produced at (K) 30 min, (L) 50 min reaction time

Assessment of paper properties

In the present study, the properties of untreated rice straw and alkali pretreated rice straw handsheets were examined in terms of tensile index, tear index, burst index and brightness. Figures 4E and 4F present the tensile index of paper produced from untreated rice straw and alkali pretreated rice straw pulp samples obtained at 30 and 50 minutes pulping time, respectively. It was observed that with an increment in alkali charge (10 to 14%) at a particular temperature, tensile index increases however; a slight decrease in tensile index was recorded with an increase in temperature and retention time at a fixed chemical charge. The maximum tensile index up to 35.8 Nm/g (Fig. 4E) was recorded for untreated rice straw pulp obtained at 30 min reaction time, 14% alkali charge and 140 °C temperature, whereas it was recorded maximum up to 34.6 Nm/g (Fig. 4F) for the pulp obtained at 50 min reaction time, 14% alkali charge and 140 °C temperature.

On the other hand, handsheets prepared from alkali pretreated rice straw recorded maximum tensile index up to 34.9 Nm/g (Fig. 4E) at 30 min reaction time, 14% alkali charge and 140 °C temperature, whereas it was recorded maximum up to 34.2 Nm/g (Fig. 4F) for the pulp obtained at 50 min reaction time, 14% alkali charge and 140 °C temperature. The tensile strength of paper is primarily influenced by the quality of the raw material used, fiber length, the degree of fiber bonding and fiber orientation.[38] Longer fibers, such as those from wood pulp may contribute to the higher tensile strength due to better fiber entanglement and bonding, whereas agricultural residues give a comparatively lower tensile strength of the end product. The pretreatment of the raw material can significantly affect the tensile index of paper by altering the physical and chemical characteristics of the fibers.

Figure 4E shows that with successive increment in alkali charge from 10% to 14% for a retention time of 30 minutes, the tensile index of paper increases from 32.9 to 35.8 Nm/g (at 140 °C), from 32.5 to 35.4 Nm/g (at 150 °C) and from 31.3 to 34.1 Nm/g (at 160 °C). A similar trend was observed for alkali pretreated rice straw, where the tensile index of paper increased from 32.6 to 34.9

Nm/g (at 140 °C), from 32.1 to 34.4 Nm/g (at 150 °C) and from 30.9 to 33.6 Nm/g (at 160 °C), respectively, on varying the chemical charge from 10% to 14%. The increase in tensile index may be attributed to enhanced delignification with the increase in chemical charge. The increase in tensile index is also supported by the declining trend of kappa number with the increase of chemical charge, as discussed above. In addition, Figure 4E also depicts that at a fixed chemical charge and retention time, an increase in temperature from 140 °C to 160 °C resulted in a consistent decrease in tensile index, which may be attributed to the degradation of cellulose fibers at higher temperatures, resulting in weaker fiber-to-fiber bonding in the final paper sheet. This compromises the overall tensile strength of the paper, as the structural integrity of the fibers is reduced. An analogous pattern of tensile index was also observed in respect of paper prepared from pulp obtained at 50 minutes retention time (Fig. 4F). The results of the study presented in Figure 4F clearly reveal that at 140 °C, the tensile index of untreated pulp gradually increased with the increase in alkali charge from 32.8 to 34.6 Nm/g, whereas alkali-pretreated samples followed a parallel trend, but with slightly lower values, reaching 34.2 Nm/g at 14% alkali charge. As the temperature increased to 150 °C, tensile index declined slightly in both cases, with untreated pulp showing values from 31.8 to 34.2 Nm/g and alkali-pretreated pulp from 31.5 to 33.8 Nm/g, showing a marginally lower range. At the highest temperature (160 °C), a further decline in tensile index was observed, with untreated pulp reporting 30.9 to 33.3 Nm/g and pretreated pulp reporting 30.6 to 33.1 Nm/g.

The burst index of paper prepared from untreated and alkali pretreated pulp samples produced under different cooking conditions, specifically varying cooking temperatures (140 °C, 150 °C and 160 °C), retention times (30 and 50 min) and different alkali charge (10%, 12% and 14%), is presented in Figure 4G and 4H. In all the samples, a common trend of decreasing burst index was observed with increasing temperature, despite alkali pretreatment or cooking time. For untreated rice straw samples at 30 minutes cooking time, the burst index decreased from 2.18 (140 °C) to 2.06 kN/g (160 °C) at 10% alkali concentration, whereas it decreased from 2.27 (140 °C) to 2.08 kN/g (160 °C) at 12% alkali concentration, and from 2.35 (140 °C) to 2.16 kN/g (160 °C) at 14% alkali concentration (Fig. 4G). A similar trend was observed in paper samples prepared from pulp produced at 50 minutes cooking time (Fig. 4H). The burst index decreased from 2.08 kN/g (140 °C) at 10% alkali charge to 2.02 kN/g (160 °C) at 14% alkali charge. This decline in burst index can be attributed to the degradation of cellulose fibers at higher temperatures, which weakens the fiber bonding capability and thus reduces the burst strength of the paper. Besides this, a noticeable impact of the increase in alkali charge (10% to 14%) leading to a slight improvement in burst index at each corresponding temperature and cooking time was also observed, suggesting that increased alkali concentrations at a particular temperature and fixed cooking time may help in better lignin removal, enhancing fiber bonding and contributing to improved burst strength.

In the case of alkali pretreated samples, the burst index values were generally lower than for untreated samples under similar conditions. At 140 °C, 10% alkali charge and 30 min cooking time, the burst index for alkali pretreated rice straw samples was 2.04 kN/g, which reduced to 1.92 kN/g at 160 °C under the same alkali charge and cooking time (Fig. 4G). A similar pattern leading to a decline in burst index from 2.14 (150 °C; 12% alkali charge) to 2.1 kN/g (160 °C; 14% alkali charge) was achieved for the other pretreated samples obtained at 30 min cooking time. An analogous trend was also recorded for the alkali pretreated rice straw samples produced at 50 min retention time. For alkali pretreated rice straw samples at 50 minutes cooking time, the burst index decreased from 2.02 (140 °C) to 1.86 kN/g (160 °C) at 10% alkali concentration, whereas it decreased from 2.1 (140 °C) to 1.92 kN/g (160 °C) at 12% alkali concentration and 2.16 (140 °C) to 1.96 kN/g (160 °C) at 14% alkali concentration (Fig. 4H). The results of the study reveal that although alkali pretreatment is effective in the removal of lignin, it may also lead to the exposure of fiber to further degradation because of the breakdown of hemicelluloses and partial depolymerization of cellulose, especially under high temperature and extended exposure, reducing fiber strength and other paper properties.

Besides tensile and burst indexes, tear index is also considered as one of the most important properties to assess in paper and paper products. Determining the tear index of paper and paperboards is crucial for quality assessment because it measures the material's resistance to tearing, which directly reflects its strength, durability, and suitability for various applications.

A higher tear index indicates better structural integrity, confirming the product can withstand handling, processing, and end-use stress without damage. In the present study, tear index of paper prepared from untreated and alkali pretreated pulp samples produced under different cooking conditions is presented in Figure 4I and 4J. The results of the study clearly demonstrate that cooking temperature, alkali charge, and cooking time significantly influence the tear index, thereby affecting fiber strength and the quality of the final paper product.

In untreated samples, the tear index showed a decline with increasing cooking temperature and alkali charge. At 30 minutes cooking time, the highest tear index (2.62 mNm^2/g) was observed at 140 °C with 10% alkali charge, while the lowest (2.30 mNm^2/g) was recorded at 160 °C with 14% alkali charge (Fig. 4I). A similar decreasing trend was observed at 50 minutes cooking time, where the tear index decreased from 2.50 mNm^2/g (140 °C, 10% alkali) to 2.25 mNm^2/g (160 °C, 14% alkali) (Fig. 4J). This reduction may be attributed to depolymerisation at higher temperatures and alkali concentrations, leading to shortening of fiber length and reduced tear resistance. The shorter fibers may create a less interconnected structure, making the paper more prone to tearing and less durable. In the case of alkali pretreated samples, the tear index was recorded higher than that of untreated samples for corresponding temperature and alkali charge. At 140 °C, 10% alkali charge and 30 min cooking time, the tear index for alkali pretreated rice straw sample was 2.84 mNm^2/g, which reduced to 2.56 mNm^2/g at 160 °C under the same alkali charge and cooking time (Fig. 4I). A similar pattern leading to a decline in tear index from 2.74 mNm^2/g (150 °C; 12% alkali charge) to 2.42 mNm^2/g (160 °C; 14% alkali charge) was achieved for the other alkali pretreated samples obtained at 30 min cooking time (Fig. 4I). An analogous trend was also recorded for the alkali pretreated rice straw samples produced at 50 min retention time. Herein, tear index decreased from 2.74 mNm^2/g (140 °C) to 2.58 mNm^2/g (160 °C) at 10% alkali concentration, whereas it decreased from 2.68 mNm^2/g (140°C) to 2.42 mNm^2/g (160 °C) at 12% alkali concentration and from 2.56 mNm^2/g (140 °C) to 2.34 mNm^2/g (160 °C) at 14% alkali concentration (Fig. 4J).

The improvement in tear index in comparison to untreated samples at similar reaction conditions is attributed to the partial delignification and fiber swelling induced by alkali pretreatment, which enhances fiber flexibility and bonding ability during sheet formation. In general, with a continuous increase in cooking temperature and alkali concentration, tear index values slightly decreased in both untreated and pretreated samples. This reduction can be explained by fiber degradation at harsher pulping conditions, which leads to a reduction in fiber length and bonding strength. The tearing index is influenced by factors such as fiber length, fiber quality, and the strength of the bonds between fibers in the paper.[39] Of these factors, fiber length and fiber bonding are the most important. Longer fibers enhance tear strength by distributing stress across fiber length, while short fibers concentrate stress in a smaller area. In this study, it is anticipated that higher alkali charge and reaction temperature during pulping will lead to shorter fiber lengths due to the peeling of end-reducing groups, resulting in a weaker fiber network in the paper.

Following the analysis of tear, tensile, and burst index, the brightness, which is considered one of the most important optical properties, was also determined in the current work. The brightness of paper is a vital optical property that directly affects its appearance and suitability for end use applications. The brightness values recorded in this study varied significantly with changes in cooking time, cooking temperature and alkali charge. The results are collectively presented in Figure 4K and 4L. For the untreated samples, brightness increased moderately with rising cooking temperature and alkali charge. At a cooking time of 30 minutes, the brightness improved from 32.4% ISO to 36.2% ISO as both the alkali charge and temperature increased from 10% at 140 °C to 14% at 160 °C, respectively. Similarly, with an extended cooking time of 50 minutes, brightness increased from 32.8% ISO to 36.5% ISO for the same reaction conditions. The increase in brightness is attributed to enhanced delignification at higher temperatures and alkali concentrations, which reduce the presence of chromophoric groups in the pulp, thereby increasing brightness. A more prominent increase in brightness was recorded in alkali pretreated samples, representing the considerable positive effect of pretreatment on pulp quality. At 140 °C and 30-minute cooking time, brightness increased from 35.2% ISO (at 10% alkali charge) to 39.4% ISO (at 14% alkali charge), while at 160 °C, brightness reached up to 42.0% ISO (at 14% alkali charge), indicating a significant improvement over untreated samples under comparable conditions. The same trend was

observed at 50 minutes, with brightness attainment up to 43.4% ISO (at 14% alkali charge; 160 °C cooking temperature). This improvement can be ascribed to the fact that alkali pretreatment facilitates more effective lignin removal during cooking, thereby yielding a pulp with lower residual lignin content and higher brightness. Additionally, the influence of cooking time was comparatively less impactful than that of pretreatment and temperature, suggesting that although extended cooking time contributes to further delignification, its effect on brightness is relatively less substantial compared to other parameters.

Impact assessment of alkaline and hydrothermal (aqueous) pretreatments on sugar recovery and papermaking: a comparative study

The present study focusing on an alkaline medium was conceived as a successive extension of our previously published report on simultaneous recovery of sugars and papermaking authored by Sharma *et al*.[5] In the preceding work, aqueous pretreatment of rice straw was performed at temperatures ranging from 100 to 160 °C for 20–120 min reaction time, sequentially followed by pulping and assessment of paper properties. Under optimal reaction conditions, a maximum TRS recovery of 12.38% was achieved in the case of aqueous pretreatment, whereas the present study recorded a maximum sugar recovery up to 12.80% with 4% NaOH corresponding to an increase of approximately 3.4% compared to the previously reported value. This difference can be attributed to the distinctive mechanisms functioning during aqueous and alkaline pretreatments separately. Aqueous pretreatment of biomass usually supports hydrolysis of the hemicellulosic fraction in the acidic environment generated during the treatment, while the pretreatment in an alkaline medium firstly promotes swelling of the biomass matrix, deacetylation, breakdown of lignin–carbohydrate linkages and then the release of sugars.[40] Therefore, these two approaches may report a comparable sugar recovery, but the pretreatment in alkaline medium changes the characteristics of the residual biomass matrix to a greater extent, making a different downstream pulping and paper response. Alkaline pretreatment also had a significant impact on the subsequent papermaking stage.

In comparison to the previously reported aqueous pretreatment, the present alkali-pretreated rice straw recorded approximately 3.56% (34.9 vs. 33.7 N·m/g) higher tensile index, 5.77% (2.20 vs. 2.08 kN/g) higher burst index and 13.15% (2.84 vs. 2.51 mN·m²/g) higher tear index. A more noticeable enhancement was observed in optical properties, with brightness increasing by 20.89% (43.4 vs. 35.9% ISO). These outcomes demonstrate that the nature of the pretreatment not only influences sugar recovery, but also the strength properties of the residual biomass during the subsequent stage of pulping and papermaking.

CONCLUSION

Rice straw, an abundantly available underutilized lignocellulosic agricultural waste, has always posed serious challenges for its proper utilization and management. Conventional burning of rice straw in the fields emerged as a serious threat to the environment. Optimal utilization and management of rice straw, without disturbing ecosystems, is the need of the hour. In view of this, the present study explored the possibility of optimal utilization and management of rice straw for production of high-value end products. The outcomes of the present study report the extraction of 12.80% sugars with 4% NaOH pretreatment at 160 °C and retention time of 120 min. The pretreatment comes out as a crucial step for the recovery of sugars and enhanced yield of the subsequent processes.

The pulp produced from the alkali pretreated biomass has shown comparable strength characteristics to those of the pulp produced from untreated biomass. The maximum tensile index up to 35.8 Nm/g was recorded for untreated rice straw pulp obtained at 30 min reaction time, 14% alkali charge and 140 °C temperature, whereas handsheets prepared from alkali pretreated rice straw recorded maximum tensile index up to 34.9 Nm/g under identical conditions. The handsheets prepared from untreated rice straw showed a maximum burst index of 2.35 kN/g at 30 min reaction time, 14% alkali charge and 140 °C temperature; however, the maximum burst index of handsheets prepared from alkali pretreated rice straw was 2.20 kN/g. Alkali pretreatment also affected the optical properties of paper. There was a significant difference in the brightness of handsheets prepared from untreated and alkali pretreated rice straw. The maximum brightness of untreated rice straw was 36.5% ISO with alkali charge of 14% at 160 °C for 50 min retention time, whereas that of alkali pretreated biomass was 43.4% ISO under identical conditions.

In conclusion, incorporating a method to remove sugars before pulping could streamline the entire process, reduce costs, and make paper production more economic.

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