Biomass Conversion and Biorefinery
https://doi.org/10.1007/s13399-021-01728-y

ORIGINAL ARTICLE

Conversion of rice straw into disposable food-serving bowl via refiner mechanical pulping: an environmentally benign approach to mitigate stubble burning and plastic pollution

Shashank Saini[1] · **Ashish A. Kadam**[1] · **Vivek Kumar**[2] · **Kirtiraj K. Gaikwad**[1] · **Surendra Pratap Singh**[1] · **Dharm Dutt**[1]

Received: 20 March 2021 / Revised: 17 June 2021 / Accepted: 3 July 2021

Abstract

Rice straw, a leftover vegetative part of rice plant, is neither efficiently composted nor used as a feed in India. Moreover, due to the need for quick disposal, operational difficulties in small-scale pulp and paper mills and lack of logistical convenience rice straw doesn't find other large-scale commercial applications, and therefore is burnt openly in fields causing tremendous air pollution in parts of India. In the present work, a prospective commercially viable small-scale on-field utilization of rice straw was identified for the first time through an environmentally benign process. Refiner mechanical pulping was successfully used for converting rice straw into paperboard and a food-serving bowl. The prepared rice straw paperboard was found equivalent to grade-III Kraft paper as specified in IS 1397:1990, when compared for tensile and burst index. The molded bowl could become an environment friendly alternative for the presently used disposable food-serving containers made of plastics. Three different chemical treatments were attempted to impart water- and grease-resistance to the rice straw paperboard and bowl as demanded by the conceived application. Water absorption was reduced from 387 to 3 $g \cdot m^{-2}$ as measured by $Cobb_{60}$ test and grease-resistance was improved from 0 to 10 as measure by Kit test. Moreover, the sizing process didn't render the bowls harmful to consumers' health in terms of toxicity. Summarily, the utilization of rice straw pulp for making value-added products holds promise in mitigating air pollution, reducing plastic-based disposables, and in promoting entrepreneurship in rural areas.

Keywords Rice straw burning · Eco-friendly pulping · Paper-making · Bio-based food-serving disposable containers · Water-resistance · Grease-resistance

1 Introduction

Every year, about 120 million tons of rice straw remains in the fields after rice grain harvesting in India [1, 2]. The farmers resort to open burning of rice straw in the fields to dispose it off, especially in northern India because: (a) commercial value of the rice straw is not realized, and (b) shorter time available between rice harvesting and sowing of the successive crop. For example, about 80% of the 20 million tons of rice stubble is burnt in the fields of the state of Punjab alone in order to be quickly disposed [3], giving rise to air pollution. As reported by Satyendra et al. [4], open burning of 1 kg dry rice straw in India emits 1460 g CO_2, 1.20 g CH_4, 0.07 g N_2O, 34.70 g CO, 3.10 g NO_X, 2.0 g SO_2, and 12.95 g PM2.5, which severely affects health of the people, animals, and birds [1, 5]. Therefore, it is imperative to encourage farmers to consider economical utilization of rice straw. Some of the known uses of rice straw are its conversion to biofuel including biogas and bioethanol [6, 7]; animal feed, paper, and construction material [8, 9]; and composting [1]. Rice stubble management options like animal feeding and composting are challenging due to digestibility issues [10, 11] and slow composting, [1] respectively. Further, for commercially viable conversion into energy or any other products, rice straw needs to be transported to large-scale centralized industrial set ups, which may not be always feasible considering the time-, logistics-, and economy-related

✉ Ashish A. Kadam
ashishkadam.pkgg@gmail.com

[1] Department of Paper Technology, Indian Institute of Technology Roorkee, Roorkee 247667, Uttarakhand, India

[2] Center for Rural Development and Technology, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India

constraints. Hence, exploring decentralized, e.g. on-field processing of rice straw could provide a feasible solution to the stubble burning issue, while providing a source of income to the farmers.

Paper-making from rice straw using chemical pulping is already in practice. However, certain problems discourage the extensive large-scale usage of rice straw in papermaking, in spite of being one of the major agro-residues and a great source of cellulosic fiber. Although it produces stronger and aesthetically better pulp but chemical pulping methods give lower yield, i.e. 40% of the original raw material [12]. Problems specific to chemical pulping of rice straw include deposition of silica on the recovery equipment causing scaling, inefficient recovery of black liquor, etc. [1]. Consequently, liquid effluent is generated and needs to be discharged without treatment. Such an untreated or poorly treated discharge of chemical pulp wastewater poses threat to the ecosystem by increasing toxicity, color, suspended solids, chemical oxygen demand (COD), and biochemical oxygen demand (BOD) of the receiving water body [13]. An environmentally sustainable process, refiner mechanical pulping (RMP) is already in use for making paper for newsprint, magazines, and books; which produces pulp with higher yield, i.e. 85–95% of the original raw material [12] when used with water as the pulping media. Also, such a RMP effluent is far less harmful to the environment as compared to chemical pulping effluent. For example, typical RMP wastewater contains 91 mg/L soluble solids, 2440 mg/L COD; whereas Kraft mill wastewater has 3620 mg/L soluble solids and 4112 mg/L COD [13]. In spite of these advantages, RMP has restricted applications, which may be due to production of weaker fibers [12].

Thus, the use of rice straw in less demanding applications should be explored to widen the scope for its utilization. One such application is disposable food-serving containers, production of which has become recognizable these days in the wake of replacing non-biodegradable disposables. Such articles are being widely marketed, but only a few of them are known to be made from rice straw. For example, Sain, M. [14] reported that Kriya Labs in Indian Institute of Technology Delhi, India has successfully prepared tableware from rice straw. Inevitably, the material has to be adequately sized to develop water-resistance. Drastic reduction in water absorbance by paper sheets has been reported by Bildik et al. [15] and Shen et al. [16], and many others by means of a well known process, alkyl ketene dimer (AKD) sizing.

The present work is focused on turning rice straw into food-serving containers, e.g. a bowl, using refiner mechanical pulp. This judiciously chosen technique is less resource-intensive, free of harmful chemicals; and thus is relatively simple to implement in the vicinity of rice straw field. Moreover, utmost utilization of rice straw with minimum wastage is focused in the present work. The bowl is proposed to serving foodstuffs expected to be consumed over a short period of time, such as snacks. The foods including liquid are expected to be held into the bowl during consumption, therefore the water absorption may be assumed to be as minimum as about 10 $g\cdot m^{-2}$.

2 Materials and methods

The rice straw obtained from the state of Haryana, India was pulped using RMP process with water as a media at seven different temperatures (hydrothermal treatment) from 65 to 155 °C. The pulping temperature was optimized based on physicochemical and mechanical properties of the paperboards prepared. For further work, the pulp was prepared by hydrothermal treatment of the rice straw at the optimum temperature. The laboratory handmade paperboard sheet was a water leaf paper as it had a $Cobb_{60}$ value of 380 $g\cdot m^{-2}$. The water- and grease-resistance of the prepared paperboard needed a significant improvement for the proposed application. To impart water- and grease-resistance to satisfy the requirement toward the proposed application, the paperboard was subjected to sizing process. Kraft pulping of the rice straw was carried out and the sheets made thereby were tested as control for comparison with the ones made using RMP process. The overall flow chart of the process is shown in Fig. 1.

2.1 Characterization of the raw material

Long strands of rice straw were cut into 2 to 4 cm long pieces and were used as raw material in this work. The raw material was grinded in a ball mill to size 40–85 mesh and was used for chemical analyses. Alcohol-benzene soluble content, hot water soluble content, lignin content, and ash content were determined as per TAPPI standard methods TAPPI T 204 cm-97, TAPPI T 207 cm-99, TAPPI T 222 om-02, and TAPPI T 211 om-02, respectively. Holocellulose was determined as per method given by Wise et al. [17].

2.2 Pulping

2.2.1 Refiner mechanical pulping (RMP)

Hydro-thermal treatment. An optimum temperature was found out by treating the chopped rice straw with water at temperatures ranging from 65 to 155 °C and at a water to raw material ratio 5:1 for 180 min in an electrically heated, rotating batch digester of capacity 1.5 l (Model No. UEC-2015, Universal Engineering Corporation, Saharanpur, India). The hydro-thermal treatment conditions are reported in Table 1.

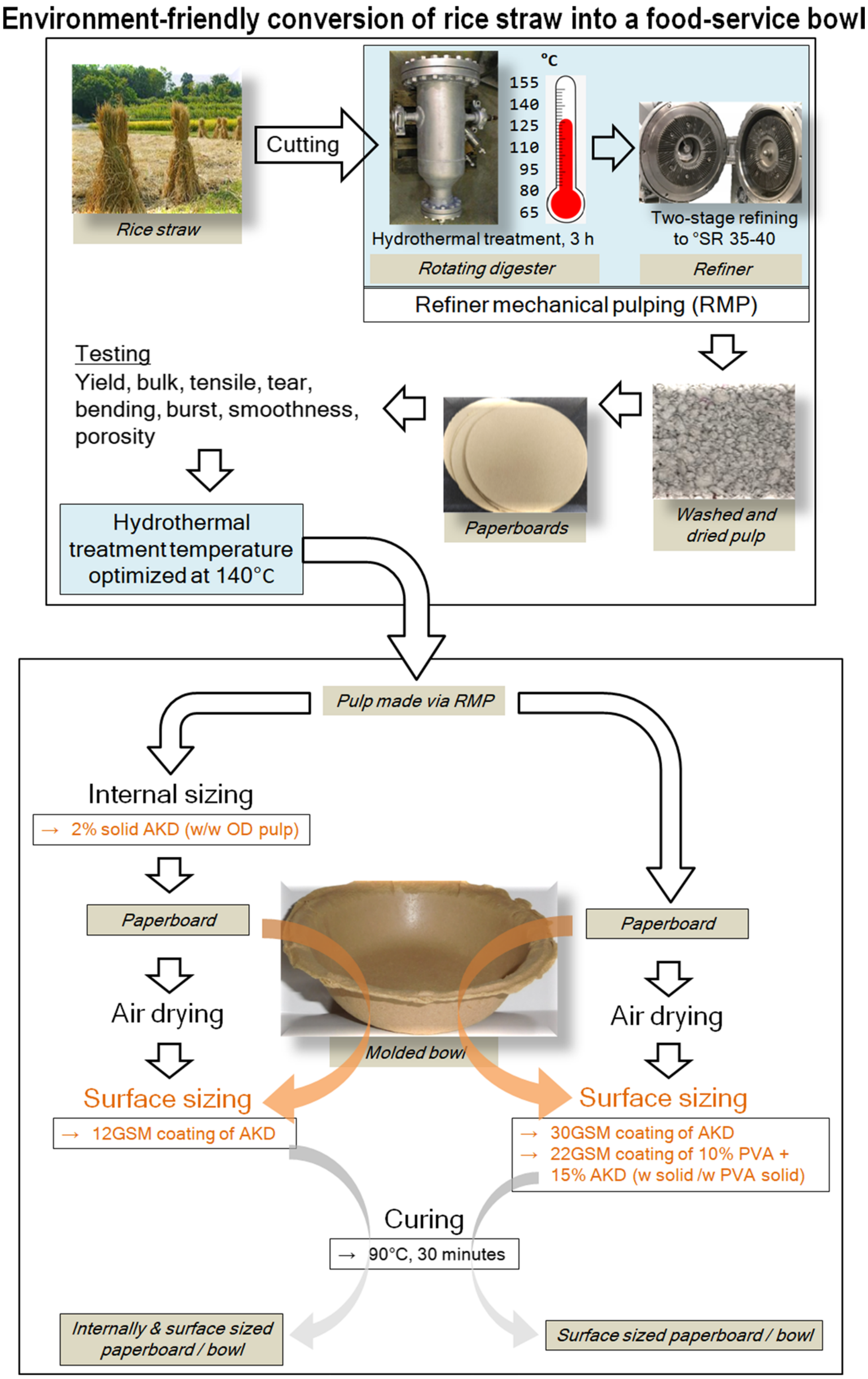

Fig. 1 Overall process flowchart

The optimum temperature was determined based on various properties tested as mentioned further.

Mechanical treatment (refining). The hydro-thermally treated rice straw was refined in a 12-in. single disc atmospheric laboratory refiner (Model number 105A, Sprout Bauer Combustion Engineering, Inc., Muncy, PA, USA) in a two-stage operation to obtain °SR between 35 and 40. The clearance between rotor and stator refiner plates was 15 and 8 thou respectively in two consecutive stages. Finally, the

Table 1 Digester conditions for hydro-thermal treatment

Temperature (°C)	Time to temperature (minutes)	Gauge pressure ($kg \cdot cm^{-2}$)
65	16	-
80	20	-
95	33	-
110	40	0.52
125	50	0.8
140	90	6.5
155	120	7.5

pulp was washed using tap water and muslin cloth, squeezed, crumbled and air-dried in atmospheric conditions.

2.2.2 Chemical pulping (CP)

The chopped rice straw was cooked in the digester by Kraft pulping process using 8% active alkali ($NaOH + Na_2S$), time to maximum temperature (160 °C) 60 min, time at temperature 90 min and liquor to raw material ratio 5:1 in the digester. The conditions selected entailed minimum possible alkali charge, temperature, and time for satisfactory pulp and sheet formation. An alkali concentration of 10% at 170 °C for 60 min has been reported by Rodriguez et al. [18] for Kraft pulping of rice straw. The cooked pulp was washed using tap water and muslin cloth, squeezed, crumbled and air-dried in atmospheric conditions. The laboratory handmade paperboard sheets were prepared in the same way.

2.3 Making of paperboard and bowl

The laboratory handmade paperboard sheets of grammage 200 $g \cdot m^{-2}$ were prepared from the RMP pulp at the optimum hydrothermal treatment temperature as per TAPPI standard method (TAPPI T 205 sp-02) using a laboratory hand-sheet former (Model number 1092, MAVIS Engineering Corporation Limited, India). The wet pulp pad (i.e. paperboard before drying) was cushioned with blotter paper (200–250 $g \cdot m^{-2}$ with a capillary rise of 50 to 100 mm of water in 10 min) on one side, and was sandwiched between two stainless steel bowls each of 230 ml capacity for molding the sheet and squeezing out the extraneous water for 24 h. The bowl-shaped wet pulp pad was then removed and air-dried for 24 h. The bowl making process is shown in Fig. 2.

2.4 Determination of physicochemical and mechanical properties of rice straw paperboard

All the specimens were conditioned at 23 °C and 50%RH for 48 h prior to testing. Grammage was determined for 6 replicates and rest of the tests in triplicate. Thickness of the paperboard was determined with the help of a Lorentzen and Wettre instrument (Stockholm, Sweden). Bulk ($cm^3 \cdot g^{-1}$) was calculated using Eq. (1):

$$Bulk = Thickness \bullet GSM^{-1} \tag{1}$$

Tensile index was determined using a tensile strength tester (Model number F81.50200, Frank-PTI, Germany). Bending stiffness values (N·mm) were obtained by using a two-point bending stiffness tester (Model number F58.56601, FRANK-PTI, Germany). Bursting strength of the paperboard was tested as per (TAPPI T 403 om-97,) using a bursting strength tester (Lorentzen and Wettre, Stockholm, Sweden). An Elmendorf type tear strength tester (Model number 327, Lorentzen and Wettre, Stockholm, Sweden) was used according to (TAPPI T 414 om-98,). Bending stiffness index (BSI), burst index, and tear index were calculated using Eqs. (2), (3), and (4) respectively.

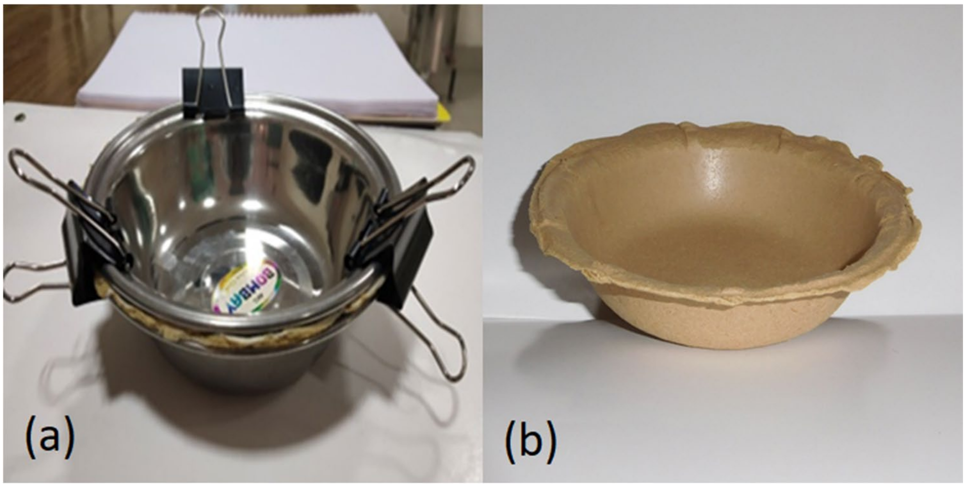

Fig. 2 Bowl making process

$$BSI\left(N \bullet m^2 \bullet kg^{-3}\right) = Bending\ stiffness(N \bullet mm) \times 10^6 \times Grammage^{-3}\left(\left(g \bullet m^{-2}\right)^{-3}\right) \tag{2}$$

$$Burst\ index\left(kPa \bullet m^2 \bullet g^{-1}\right) = Burst\ strength\left(kg \bullet cm^{-2}\right) \times 10^3 \times 0.098 \times Grammage\left(g \bullet m^{-2}\right) \tag{3}$$

$$Tear\ index\left(mN \bullet m^2 \bullet g^{-1}\right) = Tear\ strength(gf) \times 2 \times 9.81 \times Grammage\left(g \bullet m^{-2}\right) \tag{4}$$

Water-resistance of the coated and uncoated paperboard sheets was determined via Cobb$_{60}$ value according to (TAPPI T 441 om-09,) standard test method using a water absorption device. Grease-resistance was determined via Kit test as per (TAPPI T 559,). The Kit test is useful in quantifying performance of papers and paperboards used in food-contact (TAPPI T 559 cm-12).

The hydrothermal treatment at 140 and 155 °C yielded paperboard with higher smoothness than at the other temperatures. Further, the hydrothermal treatment temperature of 140 °C was selected for pulping and bowl-making as it produced better sheets than at 155 °C, in terms of bulk and %yield, and was equivalent in terms of tear index, bending stiffness, smoothness, and porosity.

2.5 Developing water- and grease-resistance in the rice straw paperboard and bowl

Alkyl ketene dimer (AKD, 15% solids, particle size 1.49 µm, viscosity 13 cp at 25 °C) and poly(vinyl alcohol) (PVA, hot-water soluble, 98–100 mol% hydrolyzed, molecular weight 125,000 g·mol^{-1}, maximum viscosity 21 cp at 20 °C for 4% aqueous solution) were used in preparing sizing formulations. The AKD solution was courteously provided by Star Paper Mill, Saharanpur, India. AKD is considered safe by United States Food and Drug Administration (USFDA) when used in contact with food according to 21CFR176.120 [19]. PVA is also declared safe by USFDA for food packaging. The sizing was done in three different ways: (i) four-layer coating of AKD (Size 1), (ii) two-layer coating of mixture of 10% PVA and 15 wt.% AKD w. r. t. PVA (Size 2), and (iii) internal sizing using 2% (w/w OD pulp) AKD followed by two-layer coating of AKD (Size 3). Alum, (potassium aluminium sulphate) was added to the pulp slurry during internal sizing to promote retention of AKD with the pH maintained at 6.5. Multiple coating layers were administered as single layer is often not sufficient to cover the surface of the substrate to achieve the sizing effect. The brush used was of flat shape having soft bristles of length 70 mm (protruded) and average thickness of 145 µm. Coating was done by using a brush as it is a simple method and is effective for shaped articles like bowl in the present work. The sized paperboards were stored in an oven at 90 °C for 30 min for drying and curing.

2.6 Release of sizing chemicals

As mentioned earlier, the chemicals used in the sizing treatment of rice straw articles prepared in the present work are approved for direct food contact. Yet, the consumers could be concerned of these chemicals getting released into the foodstuffs in direct contact in quantities that could pose health risks. Therefore, the release of AKD and PVA from bowls into water was studied. Each bowl having treated with sizing chemicals was filled with 150 ml distilled water covering 132 cm^2 area of the bowl, stored at 30 °C, and the water was tested for the presence of both sizing chemicals using a UV–VIS spectrophotometer (UV-1800, Shimadzu). After time intervals of 10, 20, and 30 min, water in the bowl was stirred and a 4-ml aliquot was drawn into a quartz cuvette. The spectrophotometric analysis was carried out at 450 nm for AKD and between 200 and 700 nm for PVA. The quantities of the chemicals were determined using calibration curves.

3 Results and discussion

3.1 Chemical characterization of the raw material

Table 2 displays chemical composition of the rice straw. Holocellulose content in the rice straw as determined in the present work is corroborated by other reports in the literature, especially [1, 20]. Holocellulose includes cellulose of high degree of polymerization and hemicelluloses of lower molecular weight. Total holocellulose content contributes to pulp yield and overall paper strength.

Lignin content in rice straw found out in the present work was close to that reported by many authors. It is comparable to wheat straw and is less than that in woody raw materials [1]. A raw material having lower lignin content requires milder treatment for its conversion into pulp [21, 22] as was observed in the present work as well.

Table 2 Chemical composition of rice straw

Reference	Component (%)			
	Holocellulose	Lignin	Ash	Hot water extractives
Present study	66.92	15.09*	14.10	11.84
Kaur et al. [1]	66.40	13.00*	NA	NA
Davachi et al. [20]	66.89	18.9	14.21	NA
Kaur et al. [23]	66.40	13.00*	12.60	10.50
Rodriguez et al. [24]	60.70	21.90	9.20	7.30

**, Ash-free*

NA, Not Available

However, considerably higher ash content in rice straw as compared to other agricultural residues has been reported in literature.

Water soluble components usually include starch and proteins and their higher content causes more consumption of pulping reagents. Rice straw, as studied in the present work, contains hot water extracts higher than other reports, however is close to that reported by Kaur et al. [23]. The difference in the values may be attributed to the rice variety used in various studies and/or the location at which the rice was grown.

3.2 Physical and mechanical properties of rice straw paperboard

Table 3 shows different physical and mechanical properties of rice straw paperboard made by refiner mechanical and chemical pulping.

3.2.1 Pulp yield

As expected, there was a significant ($p < 0.05$) drop in the pulp yield when soaking temperature increased from 65 to 155 °C. The yield of rice straw pulping in this study was higher than chemical pulping found in literature. For instance, rice straw pulp yield achieved by using chemicals like potassium hydroxide [24] and soda-anthraquinone [11] was 42.82% and 45.2%, respectively. Yield values similar to the ones in our study are found, such as 53.0% using ethylene glycol [25]; 60.0% using tetrahydrofurfuryl alcohol [26]; 84.7% using acetic acid [27].

3.2.2 Smoothness and porosity

As hydrothermal treatment temperature increased, smoothness of the paperboard improved tremendously and porosity reduced significantly ($p < 0.05$). Paper consists of capillary system in which pores of irregular size and shape are interconnected. There are large inter-fiber and small intra-fiber pores. The large inter-fiber pores allow penetration through them [28]. These pores might have been reduced in number due to increased inter-fiber bonding caused by removal of extractives facilitated by higher soaking temperatures, impact of which may be seen on the gradually reducing bulk (from 2.20 to 1.20 $cm^3 \cdot g^{-1}$). This could be why the paperboard became increasingly smoother and less porous at higher temperatures.

3.2.3 Tensile index

There was significant ($p < 0.05$) increase in tensile index for soaking temperatures from 65 to 80 °C, 110 to 125 °C, and 140 to 155 °C. Tensile index of paper made from rice straw pulp prepared in a similar way has not been sufficiently discussed in the literature. Both, the individual fiber strength and inter-fiber bonding strength contributes to tensile strength of a paper sheet [29]. The already existing network of inter-fiber hydrogen bonding is made stronger by developing more such bonds when the inter-fiber gaps are filled by shorter fibers. Generation of shorter fibers is facilitated by beating/refining, and in the present study, soaking of the raw material at higher temperatures may have made the beating and refining more effective, thereby strengthening the paper than at lower temperatures. Tensile index of the paperboard in our work increased along the soaking temperature. However, the pulp made in our study could not be as strong as chemical pulp found in literature. For instance, tensile index achieved by pulping using acetic acid and formic acid followed by alkaline extraction was 40.1 and 48.8 $N \cdot m \cdot g^{-1}$, respectively [27], 45.7 and 77.32% higher respectively than in the present work. In another work, Jani and Rushdan [29] reported high value of tensile index i.e. 79.57 $N \cdot m \cdot g^{-1}$ for the paper made of rice straw after NaOH pretreatment.

3.2.4 Bending stiffness

Bending stiffness is the resistance to force causing a material to bend and is one of the very important mechanical properties for applications such as bowls, cups and plates. In the present work, bending stiffness was almost gradually decreased through the range of soaking temperatures, but a decisive decrease could only be seen at 155 °C. This decrease in bending stiffness could be because lignin, which imparts stiffness to paper, was increasingly removed at higher temperatures. Among very few reports in the literature, bending stiffness index of steam exploded wheat straw pulp came out to be 0.96 $N \cdot m^7/kg^3$ [30]. According to Schott et al. [30], bending stiffness index of rice straw pulp cooked by 40% acetic acid and blended with recycled duplex pulp in a ratio 1:9 was 0.79 $N \cdot m^7/kg^3$ [31], which was slightly higher

Table 3 Properties of paperboard made from refiner mechanical pulp of rice straw

Hydrothermal treatment temperature (°C)/ Treatment	Beating level (°SR)	Grammage (g·m^{-2})	Yield (%)	Bulk (cm^3·g^{-1})	Tensile index (Nm·g^{-1})	Tear index (mN·m^2·g^{-1})	Bending stiffness index (N·m^7·kg^{-3})	Burst index (kPa·m^2·g^{-1})	Smoothness (ml·min^{-1})	Porosity (ml·min^{-1})
Sample ↓	Hydrothermally treated at various temperatures									
65	37	205 ± 14	73.99 ± 2.18 a	2.20 ± 0.14 a	11.10 ± 0.06 a	0.83 ± 0.16 a	0.68 ± 0.04 a	0.40 ± 0.09 a	867 ± 76 a	550 ± 50 a
80	38	200 ± 10	70.26 ± 1.96 ac	2.15 ± 0.11 ab	14.28 ± 0.43 b	0.88 ± 0.16 ab	0.60 ± 0.03 ab	0.49 ± 0.04 ab	750 ± 50 ab	500 ± 50 ab
95	37	210 ± 5	68.71 ± 0.82 bf	1.95 ± 0.05 bc	15.08 ± 0.84 bc	1.24 ± 0.16 b	0.56 ± 0.12 abc	0.63 ± 0.05 b	650 ± 50 b	433 ± 29 bc
110	37	210 ± 12	65.37 ± 1.88b ac	1.90 ± 0.01 c	17.10 ± 0.20 c	1.65 ± 0.16 c	0.52 ± 0.02 bc	0.57 ± 0.00 b	500 ± 50 c	383 ± 29 cd
125	37	205 ± 12	63.44 ± 2.25 bd	1.86 ± 0.12 cd	21.48 ± 1.12 d	1.81 ± 0.16 cd	0.56 ± 0.03 abc	0.87 ± 0.05 c	483 ± 58 cd	327 ± 12 de
140	39	205 ± 11	56.32 ± 2.07 cf	1.81 ± 0.10 cd	21.95 ± 0.45 d	1.94 ± 0.16 cd	0.51 ± 0.07 bc	1.23 ± 0.05 d	463 ± 23 cd	280 ± 20 ef
155	40	190 ± 5	52.68 ± 0.63 d	1.63 ± 0.02 d	27.52 ± 1.44 e	2.10 ± 0.16 d	0.45 ± 0.02 bc	1.55 ± 0.07 e	420 ± 20 de	240 ± 10 fg
Chemical pulp	37	200 ± 16	41.61 ± 1.72 e	1.20 ± 0.01 e	36.72 ± 1.22 f	7.90 ± 0.09 e	0.42 ± 0.02 c	2.23 ± 0.11 f	300 ± 12 e	190 ± 10 g
Sample ↓	Hydrothermally treated at 140 °C and sized									
Size 1	-	230 ± 15	-	1.76 ± 0.02 h	20.50 ± 1.20 h	1.58 ± 0.14 h	0.49 ± 0.04 h	0.87 ± 0.07 h	283 ± 29 h	190 ± 10 h
Size 2		222 ± 11		1.78 ± 0.01 h	23.95 ± 0.32 i	1.98 ± 0.18 i	0.48 ± 0.07 h	1.41 ± 0.07 i	203 ± 6 i	120 ± 5 i
Size 3		210 ± 9		1.81 ± 0.04 h	18.27 ± 0.84 j	1.06 ± 0.10 j	0.53 ± 0.02 h	0.95 ± 0.07 h	320 ± 26 h	88 ± 3 i
Unsized		206 ± 12		1.81 ± 0.10 h	21.95 ± 0.45 hi	1.94 ± 0.11 hi	0.51 ± 0.07 h	1.23 ± 0.05 j	463 ± 23 j	280 ± 20 j

Mean of three replicates is reported along with standard deviation. Different lowercase letters across rows indicate significantly ($p < 0.05$) different values than that of our paperboard. In another work, bending stiffness index of mechanical pulp of rapeseed straw was found to be 1.43 $N{\cdot}m^7/kg^3$ [32].

3.2.5 Burst index

Bursting strength of paper or paperboard is a composite strength property that is affected by various other properties of the sheet, principally tensile strength and stretch. Generally, bursting strength depends upon the kind, proportion, and amount of fibers present in the sheet; their method of preparation, degree of beating and refining; and the use of additives.

The burst index of rice straw paperboard made in this work was drastically ($p < 0.05$) improved between successive soaking temperatures between 100 and 155 °C. However, the maximum burst index of the paperboard made in our work was lower than that found in most of the relevant literature. For instance, burst index of rice straw paper made from KOH and soda-AQ pulping was 0.96 and 2.51 $kPa{\cdot}m^2{\cdot}g^{-1}$ respectively as determined by Rodriguez et al. [24]. The rice straw paper made from chemi-mechanical (NaOH pretreated and refined) pulp resulted into a strong paper with burst index of 5.70 $kPa{\cdot}m^2{\cdot}g^{-1}$ [29], which is 2.7 times higher than for our paper made from refiner mechanical pulp. Burst index of rice straw paper made from the pulp obtained by hydrothermal and then diethanolamine treatment could not be more than 1.01 $kPa{\cdot}m^2{\cdot}g^{-1}$ [18]. In another study by Rodriguez et al. [11], burst index of rice straw paper made from soda-AQ pulp was 2.40 $kPa{\cdot}m^2{\cdot}g^{-1}$.

3.2.6 Tear index

In our study, tear index significantly ($p < 0.05$) increased with rising soaking temperature. These values are higher than reported by Rodriguez et al. [24] for rice straw paper made by soda and kraft pulping methods, respectively. In a study by Rodriguez et al. [18], the tear index of rice straw paper made from hydrothermal-diethanolamine pulp was 0.42 $mN{\cdot}m^2{\cdot}g^{-1}$. According to another study by Rodriguez et al. [11], tear index of rice straw paper made from soda-AQ pulp was only 0.61 $mN{\cdot}m^2{\cdot}g^{-1}$, which is 2.4 times lower than that found in the present study. In comparison with those results, our process yielded a paperboard with higher tear strength.

3.2.7 Effect of sizing

Mechanical properties such as tensile and tear indices of the sized paperboards were unaffected by size 1 and size 2, but reduced by size 3, i.e. internal sizing followed by surface sizing. The reduction in the values can mainly be due to the internal sizing as the hydrogen bonding may be weakened during the process. Burst index of the size 1 and size 3 paperboards was reduced. Varshoei et al. [33] observed similar trend with old corrugated container (OCC) pulp was internally sized with AKD. Burst index in our work however, was significantly ($p < 0.05$) improved by size 2 which could be attributed to the excellent film-forming of PVA; while decreased for size 1 and size 3. Shen et al. [16] reported improvement in tensile strength after surface sizing by PVA/AKD formulations. Bending stiffness index and bulk was not affected by the sizing processes. Smoothness and porosity were favorably improved by virtue of the continuous film of PVA formed on the board surface.

3.2.8 Properties of chemical vs. refiner mechanical pulp

Table 3 also shows comparison between properties of refiner mechanical and chemical pulp. Except bending stiffness, the paperboard made from refiner mechanical pulp was found to be weaker than the chemical pulp. Paperboard made from chemical pulp had lower bending stiffness than that made from the refiner mechanical pulp. This may be due to the presence of silica, a large part of which does not get removed during refiner mechanical pulping process. The paperboard made from refiner mechanical pulp showed better smoothness and porosity than that made from chemical pulp. The paperboard made from chemical pulp of rice straw had roughness and porosity higher than that made from refiner mechanical pulp after hydrothermally treating at 155 °C. Taken as a whole, when compared with the values of tensile index and burst index as specified in [34], our paperboard made from refiner mechanical pulp of rice straw was found to be equivalent to grade-III Kraft paper. In spite of having lower mechanical strength, it is worthwhile to say that the pulp is suitable for the targeted applications such as food serving containers as mentioned earlier as one of the value-added products with little or no harmful effluents.

3.2.9 Water- and grease-resistance

Cobb value is a function of various characteristics of paper or board such as sizing, porosity, etc. (TAPPI T 441 om-09,). Higher the Cobb value, the faster the water absorption rate of the sheet. As shown in Table 4, $Cobb_{60}$ value of the paperboard in our work decreased tremendously after 30 $g{\cdot}m^{-2}$ AKD coating and curing. AKD contains two different groups: (a) long-chain alkyl that contains 12 to 20 carbon atoms which imparts hydrophobicity to AKD and (b) the four-membered lactone ring [35] which forms β-keto ester bonds with cellulose. During the curing process, AKD reacts with cellulose on the paperboard surface while orienting the hydrophobic group outwards, making the sheet surface water-resistant [36]. Similar results were achieved by several other authors. For instance, the $Cobb_{60}$ of Whatman filter paper sheet was reduced from 110 to 10 $g{\cdot}m^{-2}$ by means of surface sizing with 0.5% AKD

Table 4 Water- and grease-resistance of the rice straw paperboard

Rice straw paperboard sample	GSM of AKD coating ($g{\cdot}m^{-2}$)	$Cobb_{60}$ value ($g{\cdot}m^{-2}$)	Water contact angle (°)	Kit rating
Size 1	30.3 ± 3.7	3.33 ± 0.58	119.19	10
Size 2	22.7 ± 1.5	20.67 ± 1.53	94.90	12
Size 3	12.2 ± 1.2	15.33 ± 0.58	111.32	10
Unsized	0	387.0 ± 9.6	10.19	0

Mean of three replicates is reported along with standard deviation

solution prepared in n-heptane [15]. Water contact angle (WCA) is also used as a measure of hydrophobicity. In our work, WCA of the size 1 paperboard was highest, i.e. 119.19°, among the sized sheets; followed by size 3. The sizing process caused tremendous enhancement in water-resistance of the unsized sheet, which had a WCA value of merely 10.19°. Similar improvements are found in literature. For example, WCA of bleached kraft paper was increased from 11 to 137° due to hydrophobicity imparted by AKD coating of 7.7 $g{\cdot}m^{-2}$ [16].

Grease-resistance as determined by Kit test was improved via the surface sizing process. Unsized paperboard had Kit rating of 0 (zero), which was improved to 10 for size 1 and size 3, and to 12 for size 2. The outstanding improvement in grease-resistance due the formulation 'size 2' can be ascribed to the use of PVA and sufficient coverage of the paperboard's surface by means of two-layer coating. Shen et al. [16] also achieved Kit rating of OCC paperboard by sufficiently covering surface with multiple layers of PVA or PVA/AKD coating.

3.2.10 Release of AKD and PVA from bowls into water

The release of AKD and PVA from bowls into the water filled in them was quantitatively analyzed using UV–VIS spectrophotometry. The minimum quantity of AKD released into the water was from Size 1 (four-layer coating of AKD) specimen and was 0.125 ppm (mg $AKD{\cdot}ml^{-1}$ water) i.e. 0.0014 $\mu g{\cdot}dm^{-2}$ (w $AKD{\cdot}area^{-1}$ of bowl covered with water). While the maximum quantity of AKD released was 13.250 ppm i.e. 0.1506 $\mu g{\cdot}dm^{-2}$, which corresponded to the Size 2 (two-layer coating of mixture of 10% PVA and 15 wt.% AKD w. r. t. PVA) specimen. The toxicity level of AKD has been reported to be low, the LD_{50} oral value as tested in rats is 40000 ppm ($mg{\cdot}kg^{-1}$ body weight) [37]. Thus, the AKD released into the water in the present study during a 30 min period was far less than the quantity that can cause toxic effects. The PVA couldn't be detected in the water at any time interval. Summarily, the chemical treatment done on rice straw in order to impart water- and grease-resistance doesn't compromise health safety of consumers. Therefore, the prepared materials are less likely to pose toxicity risks in humans and may be considered safe in food contact for serving for about 30 min.

4 Conclusion

Rice straw was successfully converted into paperboard and a food serving bowl using refiner mechanical pulping. The refiner mechanical pulping was proved to be a competent process for rice straw conversion into the value-added product. The tensile and burst index of the paperboard made from refiner mechanical pulp of rice straw was equivalent to that of grade-III Kraft paper (IS 1397:1990). Water- and grease-resistance of the rice straw articles was greatly enhanced (water contact angle from 10.19 to 119.19° and Kit rating from 0 to 12) by sizing process using poly(vinyl alcohol) (PVA) and Alkyl Ketene Dimers (AKD). Optimum results in terms of water- and grease-resistance were obtained with internal sizing using 2% AKD followed by 12 $g{\cdot}m^{-2}$ coating of the same. The present study suggested that the chemicals used in sizing of the rice straw bowl do not pose health risk to consumers during short-term food service at ambient conditions, as their release from bowls into aqueous foods seems to be far lower than toxicity thresholds found in rats. Summarily, the simple and environmentally benign process can potentially be an alternative to stubble burning and plastic pollution.

Acknowledgements The authors gratefully acknowledge the Ministry of Human Resource Development (MHRD), Govt. of India for financial support.

References

1. Kaur D, Bhardwaj NK, Lohchab RK (2017) Prospects of rice straw as a raw material for paper making. Waste Manag 60:127–139. https://doi.org/10.1016/j.wasman.2016.08.001
2. Sood J (2015) Not a waste until wasted - Punjab farmers burn straw after harvest. It is time to exploit the potential of this agro-waste. https://www.downtoearth.org.in/coverage/not-a-waste-until-wasted-40051. Accessed 06 Nov 2020
3. Datta A, Emmanuel MA, Ram NK, Dhingra S (2020) https://www.teriin.org/article/impact-stubble-burning-and-poor-air-quality-india-during-time-covid-19. Accessed 06 Nov 2020

4. Satyendra T, Singh RN, Shaishav S (2013) Emissions from crop/biomass residue burning risk to atmospheric quality. Int Res J Earth Sci 1:1–5
5. Haile A, Gebino G, Tesfaye T, Mengie W, Ayele M, Abuhay A, Yilie D (2021) Utilization of non-wood biomass for pulp manufacturing in paper industry: case of Ethiopia. Biomass Conv Bioref. https://doi.org/10.1007/s13399-021-01424-x
6. Sasaki K, Okamoto M, Shirai T et al (2016) Toward the complete utilization of rice straw : methane fermentation and lignin recovery by a combinational process involving mechanical milling, supporting material and nanofiltration. Bioresour Technol 216:830–837. https://doi.org/10.1016/j.biortech.2016.06.029
7. Kadam S, Sharma A, Islam S et al (2020) Utilization of rice straw as a source of biomolecules for sustainable multifunctional finishing vis a vis dyeing of wool utilization of rice straw as a source of biomolecules for sustainable multifunctional finishing vis a vis dyeing of wool. J Nat Fibers 17:1508–1518. https://doi.org/10.1080/15440478.2019.1581120
8. Lou R, Wu SB, Lv GJ, Guo DL (2010) Pyrolytic products from rice straw and enzymatic/mild acidolysis lignin (EMAL). BioResources 5:2184–2194. https://doi.org/10.15376/biores.5.4.2184-2194
9. Munshi S, Sharma RP (2019) Utilization of rice straw ash as a mineral admixture in construction work. Mater Today Proc 11:637–644. https://doi.org/10.1016/j.matpr.2019.03.021
10. Jackson MG (1978) Rice straw as livestock feed. In: Ruminant nutrition: selected articles from the World Animal Review. http://www.fao.org/3/X6512E/X6512E07.htm. Accessed 06 Nov 2020
11. Rodríguez A, Sánchez R, Requejo A, Ferrer A (2010) Feasibility of rice straw as a raw material for the production of soda cellulose pulp. J Clean Prod 18:1084–1091. https://doi.org/10.1016/j.jclepro.2010.03.011
12. Singh AK, Chandra R (2019) Pollutants released from the pulp paper industry: aquatic toxicity and their health hazards. Aquat Toxicol 211:202–216. https://doi.org/10.1016/j.aquatox.2019.04.007
13. Pokhrel D, Viraraghavan T (2004) Treatment of pulp and paper mill wastewater — a review. Sci Total Environ 333:37–58. https://doi.org/10.1016/j.scitotenv.2004.05.017
14. Sain M (2020) Production of bioplastic and sustainable packaging materials from rice straw to eradicate stubble burning (a mini review). Environ Conserv J 21:1–5. https://doi.org/10.36953/ecj.2020.21301
15. Bildik AE, Hubbe MA, Gürboy KB (2016) Alkyl ketene dimer (AKD) sizing of paper under simplified treatment conditions. TAPPI J 15:545–552
16. Shen Z, Kwon S, Oh K et al (2019) Facile fabrication of hydrophobic cellulosic paper with good barrier properties via PVA/AKD dispersion coating. Nord Pulp Pap Res J 34:516–524. https://doi.org/10.1515/npprj-2019-0040
17. Wise LE, Murphy M, Adieco AAD (1946) A chlorite holocellulose, its fractionation and bearing on summative wood analysis and studies on the hemicelluloses. Pap trade J 2:35–40
18. Rodriguez A, Moral A, Sánchez R et al (2009) Influence of variables in the hydrothermal treatment of rice straw on the composition of the resulting fractions. Bioresour Technol 100:4863–4866. https://doi.org/10.1016/j.biortech.2009.04.030
19. U.S. Food and Drug Administration (2019) 21CFR176.120. Substances for Use Only as Components of Paper and Paperboard. https://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=176.120. Accessed 06 Nov 2020
20. Davachi SM, Bakhtiari S, Pouresmaeel-Selakjani P et al (2018) Investigating the effect of treated rice straw in PLLA/starch composite: mechanical, thermal, rheological, and morphological study. Adv Polym Technol 37:5–16. https://doi.org/10.1002/adv.21634
21. Jakate DN, Rao V, Swamy VSR et al (1981) Soda-AQ [anthraquinone] pulping of rice straw. TAPPI J Tech Assoc Pulp Pap Ind 6:124–125
22 Shao S, Wu C, Chen K (2017) Refining, dewatering, and paper properties of soda-anthraquinone (soda/AQ) pulp from rice straw. BioResources 12:4867–4880. https://doi.org/10.15376/biores.12.3.4867-4880
23. Kaur D, Bhardwaj NK, Lohchab RK (2018) A study on pulping of rice straw and impact of incorporation of chlorine dioxide during bleaching on pulp properties and effluents characteristics. J Clean Prod 170:174–182. https://doi.org/10.1016/j.jclepro.2017.09.111
24. Rodriguez A, Moral A, Serrano L et al (2008) Rice straw pulp obtained by using various methods. Bioresour Technol 99:2881–2886. https://doi.org/10.1016/j.biortech.2007.06.003
25. Rodríguez A, Serrano L, Moral A, Jiménez L (2008) Pulping of rice straw with high-boiling point organosolv solvents. Biochem Eng J 42:243–247
26. Ho CL, Wang EIC, Su YC (2009) Tetrahydrofurfuryl alcohol (THFA) pulping of rice straw. J Wood Chem Technol 29:101–118. https://doi.org/10.1080/02773810902796138
27. Jahan MS, Lee ZZ, Jin Y (2006) Organic acid pulping of rice straw. I: Cooking. Turkish J Agric For 30:231–239. https://doi.org/10.3906/tar-0505-4
28. Casey JP (1960) Pulp and paper-Chemistry and Chemical Technology, 2nd edn. Interscience Publishers Inc, New York, p 1027
29. Jani SM, Rushdan I (2016) Mechanical properties of beating pulp and paper from rice straw. J Trop Agric Fd Sc 44:103–109
30. Schott S, Chaussy D, Mauret E et al (2003) Valorisation of different agricultural crops in papermaking applications. In: Baudin G, Fellegi J, Gellerstedt G et al (eds) Proceedings of the international conference "Chemical technology of wood, pulp and paper." Slovak University of Technology, Bratislava, pp 168–170
31. Nassar MA, Ibrahim S, Attia M, Refaat Y (2017) Improving the performance of local manufactured paperboard. Egypt J Chem 60:435–442. https://doi.org/10.21608/EJCHEM.2017.3595
32. Potucek F, Rihova M, Gurung B (2013) Chemic-mechanical pulp from rapeseed straw. Cellulose Chem Technol 50:489–496
33. Varshoei A, Javid E, Rahmaninia M, Rahmany F (2013) The performance of alkylketene dimer (AKD) for the internal sizing of recycled OCC pulp. Lignocellulose 2:316–326
34. BIS (1999) Kraft paper - Specification Bur. Indian Stand, New Delhi
35. Chen F, Song X, Liu F, Liu D (2013) Calculation of the reactivity of alkyl ketene dimer with ethanol and the characterization of reaction products. Asian J Chem 25:1182–1186
36. Lindström T, Larsson PT (2008) Alkyl Ketene Dimer (AKD) sizing – a review. Nord Pulp Pap Res J 23:202–209
37. SIAM 20 (2005) SIDS Initial assessment profile. UK/ICCA. https://hpvchemicals.oecd.org/ui/handler.axd?id=e74fc6e7-fef5-4661-b424-23de896ce75b#:~:text=Cross%20reading%20from%20a%20newly,experimental%20animal%20and%20human%20studies. Accessed 10 June 2021