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Valorization of Wheat Straw for the Paper Industry: Pre-extraction of Reducing Sugars and Its Effect on Pulping and Papermaking Properties

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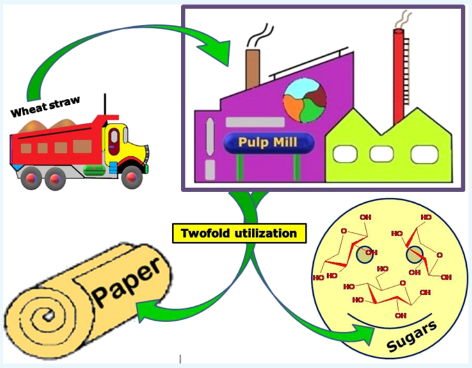

ABSTRACT: Cleaner production of sugars and pulp from renewable feedstocks has captured significant scientific attention in the recent past because they can be used for various end applications. In the papermaking industry, a major fraction of hemicellulosic sugars is lost during the pulping. The present study aims at retrieving these hemicellulosic sugars through alkali-, hot-water-, and acid-mediated extraction prior to pulping, which otherwise would have been lost during pulping and washing of pulp. These retrieved sugars can be used as feedstocks for renewable energy and value-added products. Different pretreatments were applied, aided with varying temperature, chemical concentrations, and time. Substantial amounts of total reducing sugars (TRSs) up to 21.98, 13.2, and 15.01% were extracted prior to pulping by acid, alkali, and hot-water pretreatments. Compositions of mono sugars present in the treated liquor were also characterized and confirmed by high-performance liquid chromatography analysis. The morphological changes in the wheat straw after pre-extraction were studied using the field emission gun scanning electron microscopy technique. Pulping of untreated and pretreated wheat straw was carried out at different alkali charges (12, 14, and 16% NaOH). Among all, acid-pretreated straw showed an increase in pulp yield by 10.9% at a 16% alkali charge. Physical strength properties of different pulps were further examined. Alkali- and hot-water-pretreated straw pulp retained 94.26 and 83.16% tensile indices and 92.43 and 87.02% burst indices, respectively. An increase in tear index up to 4.32, 2.01, and 2.30% for alkali-, hot-water-, and acid-pretreated straw pulp was achieved, respectively. Hot-water- and alkali-pretreated wheat straw was observed to be conducive for paper production. The integrated use of wheat straw for extraction of underutilized sugars and pulp production in this way may serve as a key stepping stone for future biorefinery designs in pulp and paper mills.

1. INTRODUCTION

Complete utilization of available resources is the most inherent parameter for a cleaner production technology in any industry. Recovery and utilization of wasted components of main raw materials are the key challenge for various industries. Some recent developments in respect of value-added products from underutilized waste are providing the solution toward green and clean technologies.[1−5] The concept of waste management has been applied over the years in all the commercial activities including pulp and paper mills. The ever-increasing demand of energy and the limited availability of conventional energy sources have fostered pulp and paper industries to develop the integrated production of pulp, paper, and other valuable byproducts such as bioethanol.[6,7] Agricultural waste, preferably wheat straw, a major contributor in the pulp and paper sector, which is rich in carbohydrate content, would be an attractive feedstock that can be channelized for the production of bioenergy and various bioproducts in near future.[8−10] While processing a raw material for pulp production through different chemical treatments, a major proportion of carbohydrates, predominantly hemicelluloses, are wasted, thereby reducing the pulp yield as well. Hemicellulose is considered as a potential feedstock for industrial production of biofilms, bioethanol, and additives in papermaking.[7,11] However, hemicelluloses, which are branched in structure, are fairly reactive in nature and can be pre-extracted through liquid hot-water pretreatment and mild acidic and alkaline hydrolysis prior to pulping and could be converted into soluble sugars which can successively be utilized for the production of bioethanol and other value-added products.[12,13] Limited lab-scale studies for the effective recovery of hemicellulose prior to pulping leading to an integrated biorefinery pulp mill have been done previously, but none of them have been

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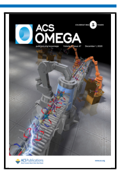

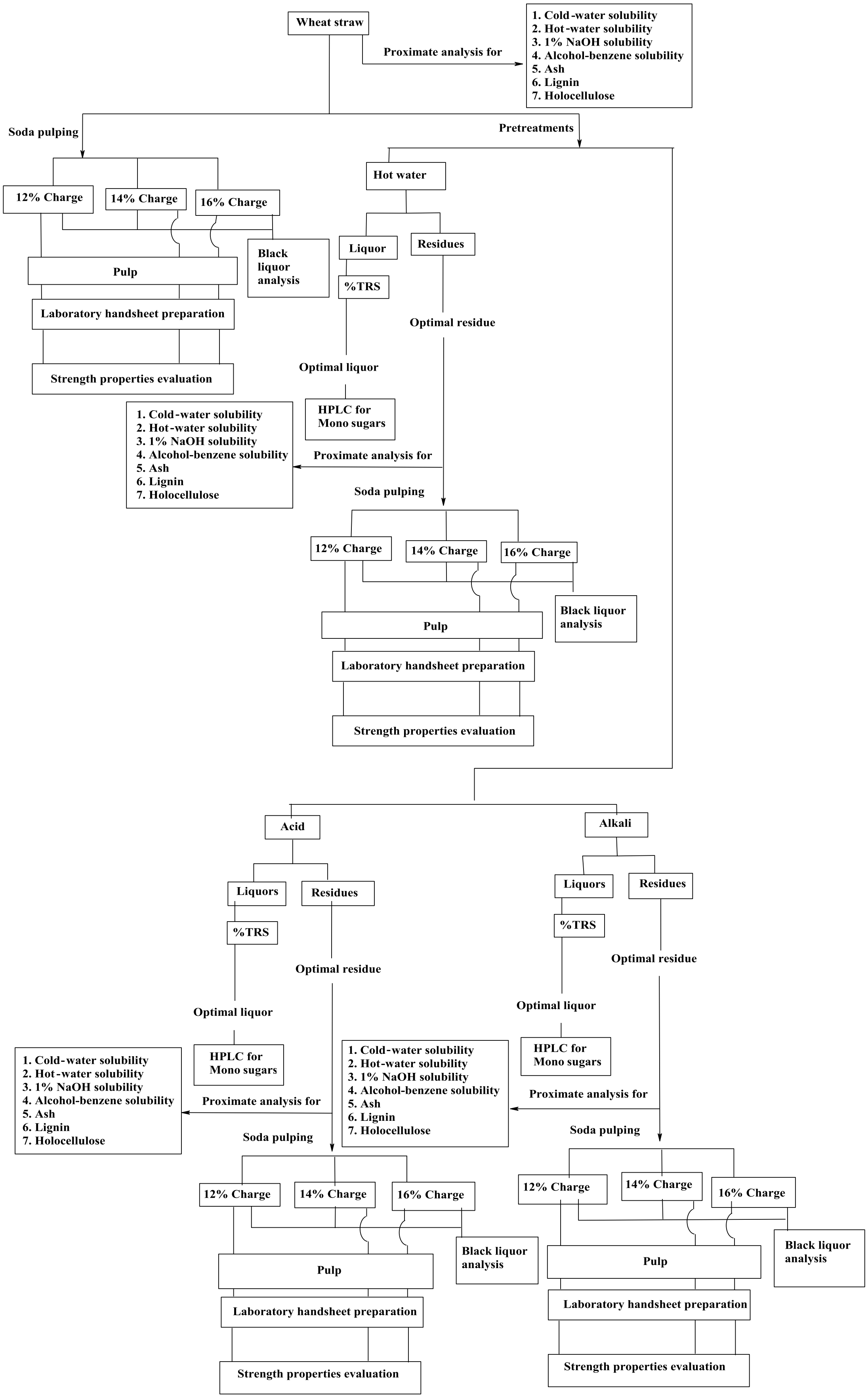

Figure 1. Schematic representation of experimental design for utilization of wheat straw.

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Table 1. Chemical Analysis of Untreated and Pretreated Wheat Straw[a]

parameters (%)	untreated	hot-water-pretreated[a]	acid pretreated[b]	alkali pretreated[c]
cold-water solubility	11.38	2.07	4.52	2.12
hot-water solubility	14.85	3.20	6.51	4.21
1% NaOH solubility	38.99	37.65	35.02	14.37
alcohol-benzene solubility	1.30	1.20	1.10	0.91
ash content	9.58	5.72	3.53	5.64
Klason lignin (after ash correction)	22.38	21.33	25.67	17.12
holocellulose (after residual lignin and ash correction)	70.11	73.61	71.60	77.32

[a]*a* = 150 °C for 120 min; *b* = 0.1 N H_2SO_4, 125 °C for 120 min; *c* = 6% (w/w) NaOH, 150 °C for 120 min.

commercialized so far.[14] The main focus of the integrated biorefinery approach is to produce value-added products in an existing chemical pulp mill, to meet the growing demand of pulp and paper products, and to supply mono sugars for bioethanol production, which may provide a long-term profitability for the pulp and paper industry as well.[15] The worldwide production of wheat straw is 850 million metric tons (MMT), and it is used as a raw material for pulp and papermaking in many countries.[10,16] In view of this, wheat straw, an agro-based biomass extensively utilized by the pulp and paper sector, could play a vital role to achieve the goals of an integrated approach toward production of various value-added products of commercial importance. It is well reported previously that during the pulping process, substantial loss of hemicellulose and some amorphous cellulose along with lignin occurs, thereby reducing the overall pulp yield on one hand and increasing the organic load in the black liquor on the other hand.[17] In the conventional chemical recovery process, this black liquor is burnt in recovery boilers to generate power or energy for mill operations.[18] However, it is inefficient to burn hemicelluloses as they have lower heating values than lignin.[19] Extraction of hemicellulose from agro and agro-industrial residues through hot-water pretreatment (up to 21.8%),[15,20−24] alkaline pretreatment (up to 10%),[21,24−26] and from woody biomass (up to 21.3%)[7] through mild acid pretreatment has been reported in previous studies. In addition, recovery of wasted hemicellulosic sugars from wheat straw as well as utilization of wheat straw in bio-based industries through conventional treatment methods has also been demonstrated by various authors,[10,27−29] but a holistic approach comprising different effective pretreatment methods for extraction of reducing sugars prior to pulping and assessment of pulped mass for physical strength properties successively, followed by black liquor characterization studies with prime emphasis on total reducing sugars (TRSs) as presented herein is completely missing. The present study was embarked with the prime focus on optimization of the pretreatment method for controlled extraction of TRSs from wheat straw, mainly hemicellulose, prior to pulping, which are usually burned along with lignin in the chemical recovery boiler. The physical strength properties of pulped mass in terms of tear index, tensile index, and burst index were further examined. To the best of our knowledge, this is the first report on complete optimization of various parameters with regard to prior extraction of sugars through different pretreatment approaches in a single platform, sequentially followed by pulping and strength behavioral and black liquor characterization studies in every aspect. The comprehensive approach undertaken for accomplishment of prime objectives of the present study is shown in Figure 1. The outcomes of the study may serve to open the future paths of the biorefinery concept in an integrated way.

2. RESULTS AND DISCUSSION

2.1. Chemical Analysis of Wheat Straw.

Table 1 summarizes the results of the chemical composition of untreated and pretreated wheat straw. The cold- and hot-water solubilities for untreated wheat straw were found to be 11.38 and 14.85%, respectively. The hot-water solubility is very much similar to the value reported by García et al.[25] The cold- and hot-water solubilities decrease after pretreatments (hot water, acid, and alkali). This is primarily due to the loss of most of the water-soluble low-molecular-weight polysaccharides, phenols, starch, and proteins. The 1% NaOH solubility for untreated straw was 38.99%, which is lower as compared to the values reported by various authors.[30,31] The NaOH solubility is significantly decreased up to 14.37% in the case of alkali pretreatment as most of the alkali-soluble material is removed during the pretreatment. A marginal decrease up to 37.65% in the case of hot-water pretreatment and 35.02% in the case of acid pretreatment was also recorded. NaOH solubility indicates the degree of fungal decay or degradation by heat, light, oxidation, etc. As the biomass decays or degrades, the NaOH solubility increases. It is also an indicative of degraded cellulosic substrates during the pulping and bleaching processes. The alcohol-benzene solubility, which generally reports the presence of wax, tannins, resins, etc., in the raw material was noted to be 1.30% for untreated wheat straw. A marginal decrease in alcohol-benzene solubility was observed for all the three pretreated wheat straw biomasses. For untreated wheat straw, the ash content was 9.58%, which is in close agreement with the value reported earlier;[32] however, it is higher in comparison to most woody and nonwoody biomasses (1−3%).[33] Higher ash content indicates the presence of higher inorganic substances and it may cause inconvenience during chemical recovery. The ash content is reduced for all pretreated wheat straw biomasses, which may be helpful for the smoother working of the chemical recovery operation in sequential stages of papermaking. This decrease in ash content after pretreatments may be due to the efficient washing of wheat straw after pretreatments. The Klason lignin content in untreated wheat straw was recorded as 22.38%, which increased up to 25.67% in case of acid pretreated straw as most of the hemicelluloses were removed, leaving high cellulose and lignin per gram of the material. However, unlike acid pretreatment, the lignin content was reduced up to 17.12% in the case of alkali-pretreated straw as lignin is fragmented under alkaline conditions; hence, some part of lignin present in the native wheat straw will be solubilized in the alkaline medium, leading to lowering of lignin content in alkali-pretreated wheat straw in comparison to hot-water- and

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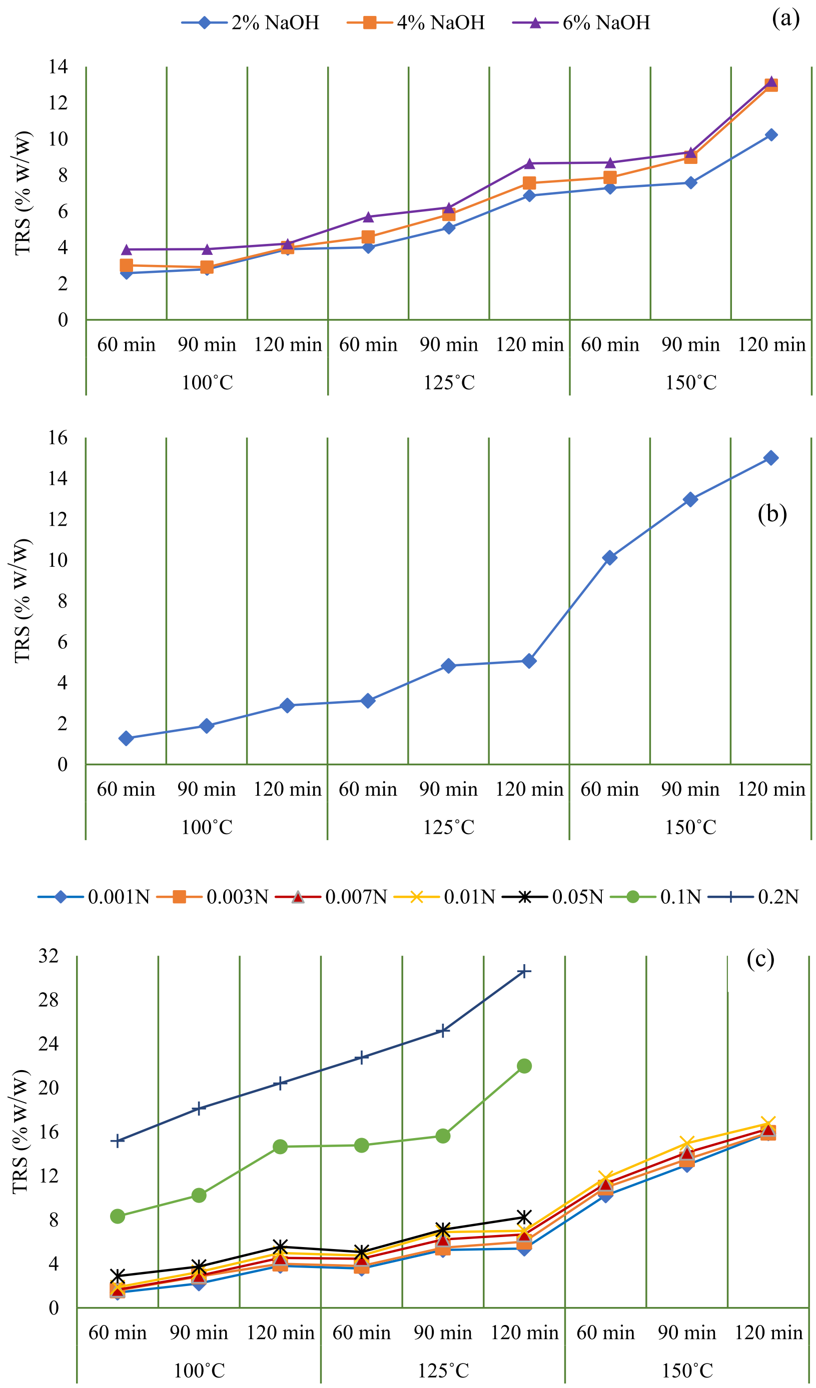

Figure 2. TRSs extracted via (a) alkali, (b) hot-water, and (c) acid pretreatment of wheat straw.

acid-pretreated wheat straw. A low Klason lignin content ensures low chemical demand during pulping and consequently in bleaching. The holocellulose content in untreated wheat straw was 70.11%, which increased in hot-water- and alkali-pretreated wheat straw up to 73.61 and 77.32%, respectively. A high holocellulose content in pretreated wheat straw confirms the suitability of biomass for pulping and papermaking.

2.2. Effect of Different Pretreatments on TRS Extraction. The effect of different pretreatment conditions on extraction of TRSs is shown in Figure 2a−c. In the case of alkali pretreatment (Figure 2a), alkali charge and reaction temperature play a vital role in the extraction of TRSs. As the alkali charge increased from 2 to 6% and the reaction temperature increased from 100 to 150 °C, there was a significant increase in the TRS. A higher alkali charge during alkali pretreatment would be helpful in swelling of the internal fibrillar structure of the biomass, thereby leading to the loosening of the accessible bonds. In addition, in the presence of an alkali at a higher temperature, the minimum amount of energy required to beak the existing bonds is met, leading to discharge of reducing sugars to a greater extent. Hot-water pretreatment efficiently extracted TRSs when the reaction was carried out at 100−150 °C temperatures for 60−120 min reaction times (Figure 2b). During hot-water pretreatment, a marginal increase in TRSs was achieved when the reaction was

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carried out at 100 and 125 °C for different reaction intervals, that is, 60−120 min. Beyond this, a considerable increment in TRSs was recorded when pretreatment was performed at 150 °C. This significant increase in TRSs may be due to the pronounced effect of reaction temperature on hot-water pretreatment. The assessment of alkali and hot-water pretreatment demonstrates that alkali pretreatment at 6% NaOH charge extracted a maximum of 13.2% reducing sugars at a 150 °C reaction temperature for a 120 min reaction time, whereas hot-water pretreatment extracted a maximum of 15.01% reducing sugars at the same reaction time and temperature. Such an increase in reducing sugars in the case of hot-water pretreatment may be due to discharge of more free sugars in the liquor. Figure 2c shows the effect of acid pretreatment on extraction of TRSs. It is clear from Figure 2c that acid pretreatment was able to extract comparatively higher reducing sugars at the same reaction time and temperature as compared to the pre-extraction studies carried out with alkalies and hot water. Acid concentration showed an influential behavior during pre-extraction of TRSs prior to pulping. The present study reports that as the concentration of H_2SO_4 increased from 0.001 to 0.05 N, there was a marginal increase in TRSs. However, a significant increment in TRSs was observed when the concentration of H_2SO_4 increased from 0.05 to 0.2 N. This increase in TRSs is attributed to greater availability of H^+ ions responsible for cleavage of existing bonds between polysaccharides, leading to higher extraction of reducing sugars. The results in the present study are in good agreement with the previous reports reported by authors.[7] Although maximum extraction of reducing sugars is preferred for ethanol production, with the viewpoint of bioenergy concept, the present study was focused with the prime objective of limited recovery of reducing sugars from wheat straw through pretreatments prior to pulping, followed by papermaking. The controlled removal of reducing sugars will also help to maintain the strength properties of paper in the later stage by facilitating fiber−fiber bonding. In this context, the following three samples of wheat straw were subjected to pulping and papermaking: (i) the sample pretreated with 6% NaOH at 150 °C for 120 min, (ii) the sample pretreated with hot water at 150 °C for 120 min, and (iii) the sample pretreated with 0.1 N H_2SO_4 at 125 °C for 120 min.

2.3. HPLC Analysis. High-performance liquid chromatography (HPLC) analysis of liquor samples obtained from hot-water (150 °C for 120 min), acid (0.1 N H_2SO_4, 125 °C for 120 min), and alkali (6% w/w NaOH, 150 °C for 120 min) pretreatments was performed to confirm the nature and ratio of mono sugars present in pre-extracted liquors. HPLC results confirm the presence of glucose (2.43%), xylose (70.16%), and arabinose (27.39%) in the hot-water-treated liquor, whereas the liquor obtained from alkali pretreatment confirms the presence of three monosaccharides, glucose (3.35%), xylose (68.12%), and arabinose (28.52%). The pre-extracted liquor obtained from acid pretreatment shows the presence of mainly three monosaccharides, namely, glucose (7.24%), xylose (66.66%), and arabinose (26.08%). The increased proportion of glucose moieties in the case of the acid-treated liquor could be due to the partial hydrolysis of the weak or amorphous region of structural cellulose of wheat straw during pretreatments. The presence of a high xylose content in all the pretreated liquors further confirmed the suitability of pretreatments for extraction of reducing sugars, which can be utilized for bioethanol production through fermentation.

2.4. FESEM Analysis. To analyze the structural changes between pretreated and untreated wheat straw, field emission gun scanning electron microscopy (FESEM) analysis was performed. The morphological features of untreated wheat straw are shown in Figure 3a,b, respectively, which is

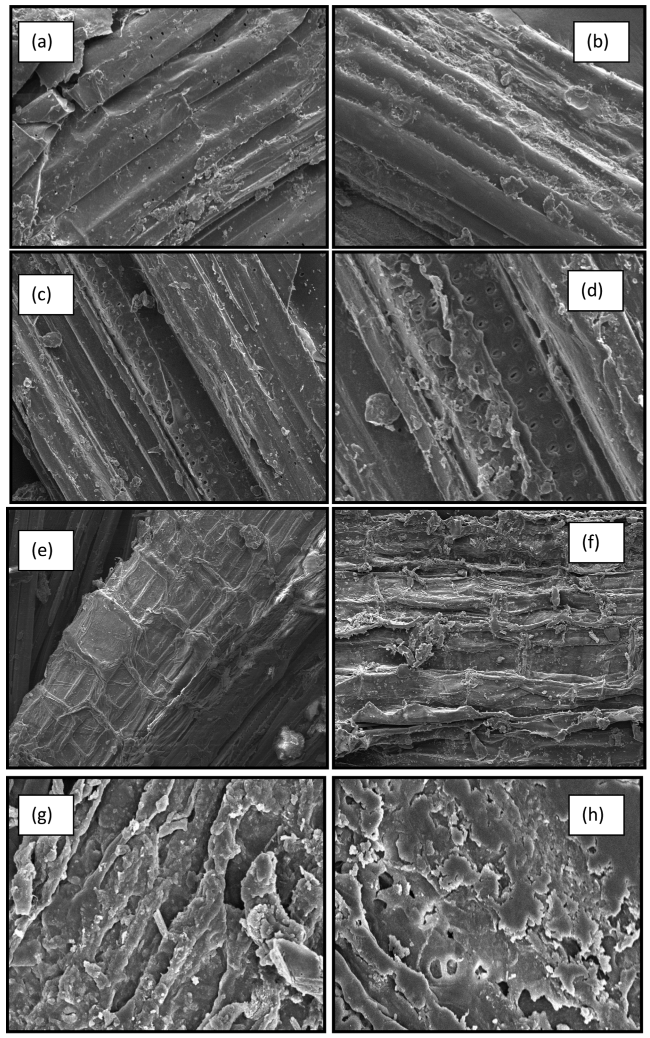

Figure 3. FESEM images of (a,b) untreated, (c,d) hot-water-treated, (e,f) alkali-treated, and (g,h) acid-treated wheat straw.

characterized by a regular and compact surface structure with tangled arrangements of fibers, resulting in the prohibitive accessibility of cellulose. Figure 3c−h shows the morphological changes which occurred during pretreatment in wheat straw. Figure 3c,d (hot-water-pretreated wheat straw at 150 °C for 120 min) and Figure 3e,f (alkali-pretreated wheat straw at 6% w/w NaOH, 150 °C for 120 min) show that the surface of wheat straw is partially destroyed after hot-water and alkali pretreatment. Only few changes in the case of hot-water-pretreated wheat straw were recorded, which would be due to the partial removal of hemicellulose moieties from the structure. In the case of alkali-pretreated wheat straw, more open structures of fibers were recorded, which would be due to the initiation of lignin degradation under mild alkaline conditions. Under an alkaline medium, the fiber swells by loosening of chemical bonds, resulting in more insertion of reactive moieties responsible for disruption of the regular cell structure. Acid pretreatment (0.1 N H_2SO_4, 125 °C, 120 min)

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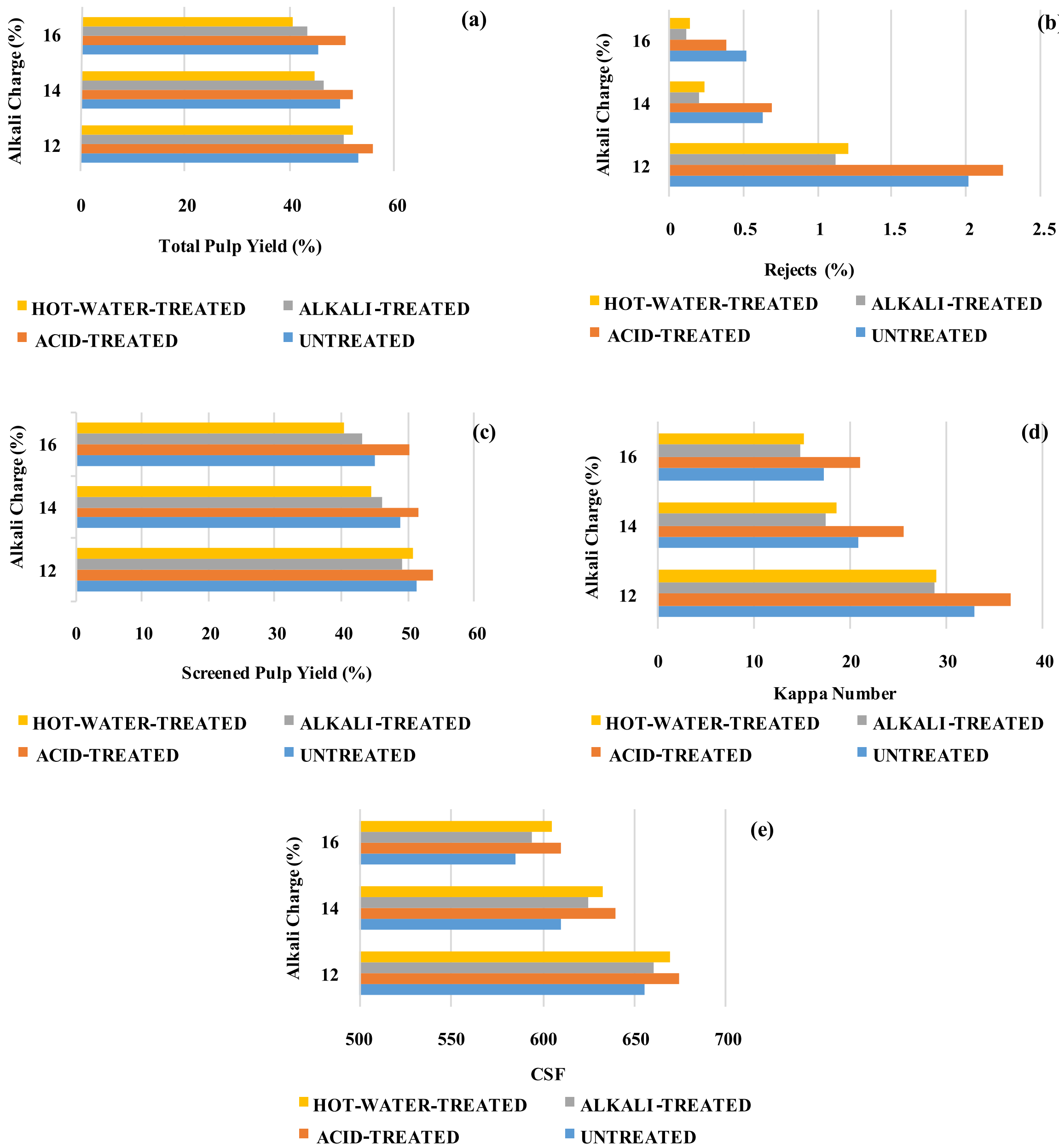

Figure 4. Pulping properties of untreated and pretreated wheat straw. (a) Total pulp yield, (b) rejects, (c) screened pulp yield, (d) Kappa number, and (e) CSF.

on wheat straw resulted in scattered fibers exposing internal structures (Figure 3g,h) as most of the hemicelluloses were removed. The removal of hemicelluloses will minimize the effective bonded area within the fiber network, thereby resulting in opening of the internal fibrillar structure. In addition, it could be linked with the strength properties of paper as well, where the strength properties were significantly decreased after pulping for acid-pretreated wheat straw. The structural components (hemicellulose and lignin) of cell wall were partially removed predominantly in the case of alkali pretreatment, resulting in the exposure of internal structures. This indicates that pretreatment could distort the cellulose–hemicellulose–lignin network, resulting in the exposure of internal structures.

2.5. Pulping of Untreated and Pretreated Wheat Straw. Alkali pretreated (6% alkali, 150 °C, 120 min) and hot-water-pretreated (150 °C, 120 min) wheat straw samples were selected for pulping and papermaking based on maximum reducing sugar recovery during pretreatments. In the case of acid pretreatment, wheat straw pretreated under controlled conditions (0.1 N H_2SO_4, 125 °C, 120 min) was selected for pulping and papermaking as it was expected that under harsh acidic conditions, the cellulose may get degraded or hydrolyzed, which can be linked with poor pulping and paper strength properties. Alkaline pulping of pretreated and untreated (control) wheat straw was carried out at 12, 14, and 16% NaOH. The H-factor during the pulping of pretreated and untreated wheat straw was 1175. Figure 4a–e shows the results of total pulp yield, pulp rejects, screened pulp yield, kappa number, and freeness of pretreated and untreated wheat straw samples. Figure 4a shows the effect of different alkali (NaOH) charges on total pulp yield of pretreated and untreated wheat straw pulp. The highest pulp yield of 55.97% was achieved for acid pretreated wheat straw pulped

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at a 12% alkali charge, while the lowest pulp yield of 40.41% was recorded for hot-water-pretreated wheat straw subjected to pulping at a 16% alkali charge. It is noticed that on increasing the alkali charge from 12 to 16%, the total pulp yield successively decreases because of the higher rate of delignification at a higher alkali charge. Figure 4b shows the pulp rejects present in pretreated and untreated wheat straw pulp. Pulp rejects were maximum at the 12% alkali charge for all pretreated and untreated wheat straw samples, which show that at a low alkali charge, the raw material was not cooked properly. However, when the alkali charge was increased from 12 to 16%, there was a considerable decrease in pulp rejects. Minimal rejects were achieved at a 16% alkali charge for all pretreated and untreated wheat straw pulps because of effective cooking of wheat straw. Figure 4c shows the screened pulp yield of pretreated and untreated wheat straw samples pulped at different alkali charges. It is observed that the screened pulp yield was higher in the case of the acid-pretreated wheat straw sample as compared to that of the untreated, hot-water-pretreated, and alkali-pretreated wheat straw samples. An increase in the pulp yield after pretreatment is also reported by various authors as well.[20,34] Acid-pretreated wheat straw recorded the highest screened pulp yield of 53.73% at the 12% alkali charge. This could be linked to the more loading of cellulose and lignin per unit of raw material. Similar observation was also recorded during the proximate chemical analysis of pretreated wheat straw. Figure 4d shows the Kappa number of pretreated and untreated wheat straw biomasses pulped at different alkali charges. The study reports that the Kappa number successively decreases on increasing the alkali charge from 12 to 16% during pulping. The highest Kappa number was found to be 36.70 at the 12% alkali charge for the acid-pretreated wheat straw sample, which could be linked with reduced delignification during pulping. This may be due to the formation of pseudolignin during acid pretreatment, which is difficult to oxidize and solubilize during pulping.[11] Unlike the acid-pretreated wheat straw sample, the hot-water- and alkali-pretreated wheat straw samples show a decrease in Kappa number because of better delignification at the time of pulping. The minimum Kappa number 14.9 was recorded for the alkali-pretreated sample at the 16% alkali charge. This is primarily due to partial removal of lignin during alkali pretreatment of wheat straw. Previously, researchers have also reported the positive impact of pretreatment on pulping conditions, leading to better delignification of biomass.[18,35] Figure 4e shows the effect of different alkali charges on Canadian standard freeness (CSF) of untreated and pretreated wheat straw pulp. A decrease in CSF on increasing the alkali charge from 12 to 16% was recorded for both the categories. In the case of untreated wheat straw pulp, the CSF decreased from 655 to 585, whereas a decrease in CSF from 674 to 610, 660 to 594, and 669 to 605 was recorded for acid-, alkali-, and hot-water-pretreated wheat straw pulp samples, respectively. This decrease in CSF may be due to the generation of more fines at a higher alkali charge during pulping.

2.5.1. Black Liquor Analysis. After completion of pulping, all the pulp samples were washed to remove the black liquor from the pulp. The black liquor is an aqueous dark-colored solution comprising dissolved and colloidal organic (lignin and carbohydrate degradation products) and inorganic (sodium hydroxide and sodium carbonates) components. Table 2 summarizes the results of black liquor analysis comprising total solids, residual active alkali (RAA), and TRSs. It is seen that on increasing the alkali charge during pulping from 12 to 16%, the solid content increases for the untreated sample as well as for all the three pretreated samples. This is due to the higher rate of delignification and degradation of carbohydrates at a higher alkali charge during pulping. The total solid content in the black liquor decreased for all the three pretreated samples as compared to that for the untreated wheat straw black liquor sample. Among all, the acid-pretreated sample reported a maximum percentage decrease in total solid content up to 32.61 at the 12% alkali charge, 28.54 at a 14% alkali charge, and 30.93 at a 16% alkali charge. This decrease in total solids is attributed to the removal of hemicellulose prior to pulping during the pretreatment process. The total solid content in the black liquor is an important parameter as it governs the steam economy in evaporators during the chemical recovery process. The black liquor having low total solids will demand less steam in evaporators, leading to an energy-efficient chemical recovery process. Table 2 also lists the RAA in the black liquors obtained after pulping of all pretreated and untreated wheat straw samples. RAA is an indicator of free NaOH in the black liquor, and it is also considered as an important parameter of the black liquor for its colloidal stability. The maximum RAA of 4.2 g/L black liquor is reported for untreated wheat straw pulp at the 16% alkali charge. The decrease in RAA in the black liquor for all the pretreated samples may be due to more consumption of NaOH during pulping as compared to that in the black liquor obtained after pulping of untreated wheat straw. This in turn results in better delignification and a reduced Kappa number as observed in the case of alkali- and hot-water-pretreated wheat straw pulp. A higher RAA demands a greater amount of water for washing of pulp. A lower RAA in the black liquor as reported in the present study for pretreated wheat straw samples will lead to a higher washing efficiency. TRS estimation in all the black liquor samples was also done. The maximum TRS of 3.6% was achieved in the black liquor obtained after pulping of untreated wheat straw at the 16% alkali charge. In the case of black liquor samples obtained after pulping of different pretreated wheat straws, the maximum TRS of 3.4% was found in the black liquor of alkali pretreated wheat straws at the 16% alkali charge. A minimum TRS of 0.9% was noted in the black liquor obtained after pulping of acid-pretreated wheat straw at the 12% alkali charge. A continuous increase in TRS of the black liquor was observed with the increase of alkali charge from 12 to 16% during

Table 2. Analysis of Pretreated and Untreated Straw Black Liquors

treatment	alkali charge (%)	black liquor properties		
		total solids (%)	RAA (gm/L) as NaOH	TRS (%)
untreated	12	10.21	2.98	2.2
	14	11.07	3.56	2.6
	16	11.93	4.2	3.6
acid-pretreated	12	6.88	2.71	0.9
	14	7.91	3.11	1.7
	16	8.24	3.98	2.3
alkali-pretreated	12	8.9	2.28	2.6
	14	9.88	3.17	2.6
	16	10.15	3.55	3.4
hot-water-pretreated	12	8.7	2.35	1.9
	14	9.74	3.14	2.8
	16	9.98	3.42	3.0

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pulping under each category of pretreated and untreated wheat straw. This may be due to the more release of hemicelluloses at a higher charge of alkali during pulping.

2.5.2. Paper Strength Properties. Paper handsheets of 60 g/m^2 (gsm) were prepared from pretreated and untreated wheat straw pulps for the assessment of strength properties. Figure 5a–c shows the effect of different alkali charges on the tear, tensile, and burst indices of pretreated and untreated wheat straw. Figure 5a shows that the tear index of handsheets prepared from all pretreated and untreated wheat straw pulps increased on increasing the alkali charge from 12 to 16% during pulping. The tear index increased from 4.98 to 6.94 mN m^2/g in the case of untreated wheat straw, whereas it increased from 4.26 to 7.1 mN m^2/g in the case of acid-pretreated wheat straw. Moreover, an increase in tear index from 4.72 to 7.24 mN m^2/g for alkali-pretreated wheat straw and from 4.44 to 7.08 mN m^2/g for hot-water-pretreated wheat straw was observed. Among all these, a maximum tear index was reported for alkali-pretreated wheat straw at the 16% alkali charge. The results show a marginal increment in tear index as the individual fiber strength is more responsible rather than the fiber-to-fiber bonding for the tear strength of paper. Figure 5b shows the tensile index of handsheets prepared from pretreated and untreated wheat straw pulp at different alkali charges. The tensile index of handsheets prepared from all pretreated and untreated wheat straw pulps increased on increasing the alkali charge from 12 to 16% during pulping. The tensile index increased from 26.87 to 32.44 Nm/g in the case of untreated wheat straw, whereas it increased from 20.63 to 24.7 Nm/g in the case of acid-pretreated wheat straw. Moreover, an increase in tensile index from 23.41 to 30.58 Nm/g for alkali-pretreated wheat straw and from 21.26 to 26.98 Nm/g for hot-water-pretreated wheat straw was observed. Among all, the highest tensile index was achieved in the case of untreated wheat straw pulp at the 16% alkali charge. This may be due to the better fibrillation of fibers when the biomass was subjected to pulping at a higher alkali charge, which in turn results in greater hydrogen bonding between the cellulosic fibers. The results show that the tensile index decreased marginally for the handsheets prepared from pretreated wheat straw as compared to that prepared from the untreated wheat straw. This would be due to the loss of the low-molecular-weight polysaccharides during the pretreatment process as they are responsible to some extent for greater bonding between the fibers after pulping. Figure 5c shows the burst index of handsheets prepared from pretreated and untreated wheat straw pulp samples at different alkali charges. The burst index also increased for pretreated and untreated wheat straw pulp, particularly on increasing the alkali charge from 12 to 16% during pulping. At a low alkali charge, because of insufficient delignification, the creation of new bonding sites for development of hydrogen bonding will be limited, leading to lower strength properties. In this respect, a higher alkali charge during pulping having a better delignification rate will enhance the effective bonded area, thereby improving the strength properties as well. The burst index increased from 1.49 to 1.85 KPa m^2/g in the case of untreated wheat straw, whereas it increased from 0.71 to 1.10 KPa m^2/g in the case of acid-pretreated wheat straw. Moreover, an increase in burst index from 0.91 to 1.71 KPa m^2/g for alkali-pretreated wheat straw and from 0.88 to 1.61 KPa m^2/g for hot-water-pretreated wheat straw was recorded. Like tensile index, the burst index also decreased for the pretreated wheat straw pulp as compared to that for the untreated wheat straw pulp. The decrease in the tensile and burst indices is attributed to the loss of hemicelluloses during pretreatment.[23,36] Because of the loss of hemicelluloses, pretreated pulp had a higher cellulose-to-hemicellulose ratio than the untreated wheat straw pulp, which results in the decrease of the tensile and burst indices.[37] Previous reports also demonstrate the adverse effect of hemicellulose removal on strength properties of paper prior to pulping.[21] The hemicelluloses are responsible for the swelling tendency of fibers as well. Studies in recent past also recorded a decrease in tensile index and an increase in tear

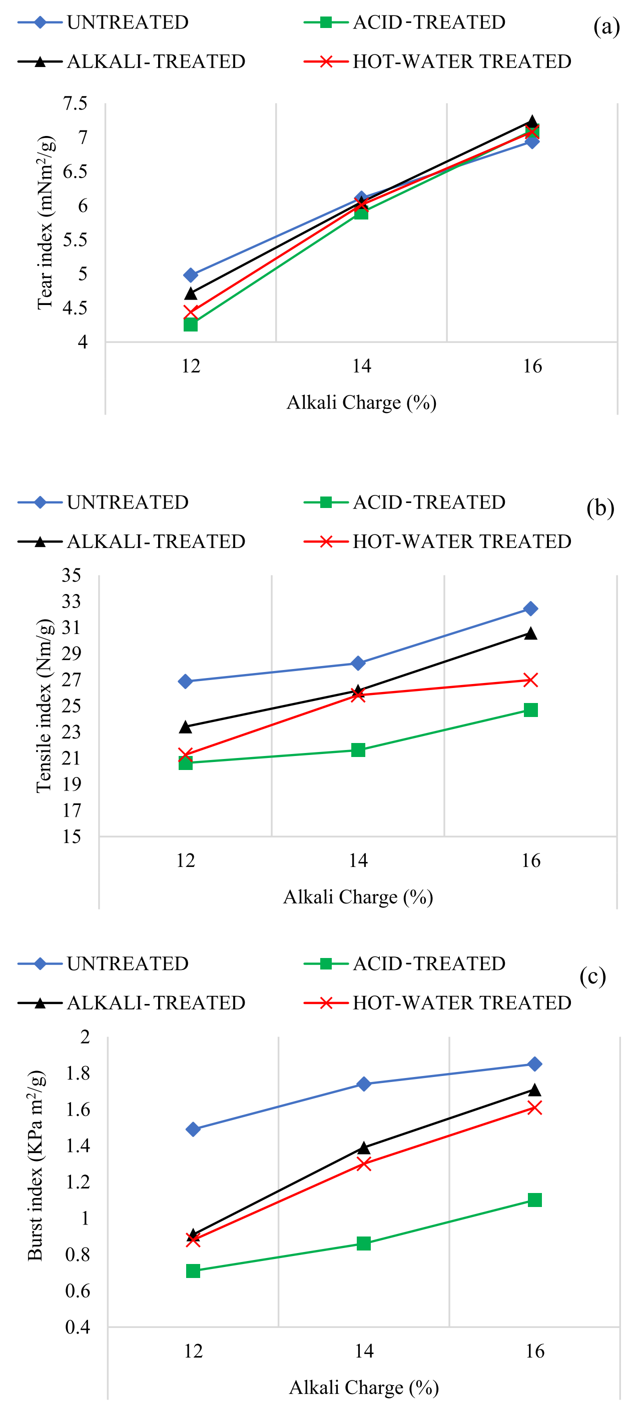

Figure 5. Strength indices of paper. (a) Tear index, (b) tensile index, and (c) burst index.

index because of the reduced hemicellulose content in the pulp.[23,38,39]

3. CONCLUSIONS

The present study demonstrates an integrated approach by recovery of reducing sugars prior to pulping, which otherwise would have been wasted in the black liquor. A simultaneous recovery of hemicelluloses on one hand and pulp production on the other hand may provide a long-term profitability for the pulp and paper industry. Overall, the present study deals with the three pretreatment approaches, namely, hot-water, alkali, and acid pretreatments, for the recovery of reducing sugars prior to pulping of wheat straw. Alkali and hot-water treatments were able to extract 13.2 and 15.01% TRSs, respectively, at a 150 °C reaction temperature and a 120 min reaction time, whereas acid (0.1 N H_2SO_4) pretreatment at a 125 °C reaction temperature and a 120 min reaction time significantly extracted 21.98% TRSs prior to pulping of wheat straw. These retrieved sugars in the pre-extracted liquor can effectively be utilized for the production of bioethanol and various commercially viable products. Papermaking studies on different pretreated residues were further executed successfully. While undergoing pulping treatments, acid-pretreated straw showed an increase in pulp yield by 10.9% at the 16% alkali charge. However, a decrease in pulp yield by 5.02 and 11.22%, respectively, was recorded in the cases of alkali- and hot-water-pretreated biomasses at the 16% alkali charge. The impact of different pretreatments on strength properties of pulp was also studied. The outcomes of the study reveal that alkali- and hot-water-pretreated biomasses retained the tensile index by 94.26 and 83.16%, respectively, whereas acid-pretreated biomass retained only 76.14%. In addition, alkali- and hot-water-pretreated biomasses retained the burst index by 92.43 and 87.02%, while the acid-pretreated one retained only 59.45%. An increase in tear index by 4.32, 2.01, and 2.30%, respectively, was recorded for alkali-, hot-water-, and acid-pretreated wheat straw biomasses. From the results, it is evident that the hot-water and alkali pretreatments are conducive for retaining the strength of paper as compared to the acid pretreatment. Conclusively, pretreatment approaches for prior removal of sugars with considerable retention of strength properties in sequential stages may successfully be applied to produce paper, paperboards, etc., in near future.

4. MATERIALS AND METHODS

4.1. Materials. Wheat straw was procured from Dehradun, Uttarakhand, India, in the month of August. The procured material was cut into the desired size (3−5 cm) using a chopper. The chopped material was air-dried at room temperature (25−31 °C). The material was kept in airtight plastic bags and stored for further use. All standard chemicals were procured from Merck, India, and were of high purity and analytical grade.

4.2. Methods. *4.2.1. Raw Material Processing and Chemical Composition Analysis.* Untreated wheat straw and alkali-, hot-water-, and acid-pretreated wheat straw biomasses under the study were examined for chemical parameters. All the samples for chemical composition analysis were prepared according to the Technical Association of the Pulp and Paper Industry (TAPPI) standard method T 257 cm-02. The moisture content, ash content, hot-water and cold-water solubility, 1% NaOH solubility, alcohol-benzene solubility, acid-insoluble lignin, and holocellulose were determined according to methods T 264 cm-9, T 211 om-02, T 207 cm-99, T 212 om-02, T 204 cm-97, T 222 om-02, and useful method-249, respectively. The chemical composition of the pretreated straw was analyzed according to the same methods as mentioned above. All tests were performed in triplicate, and the results reported are their mean values.

4.2.2. Pretreatments. In the present study, prior to pulping different pretreatments, namely, the hot-water, alkali, and acid pretreatments, were performed for extraction of TRSs from wheat straw under different reaction conditions as enlisted in Table 3. All the pretreatments were conducted in an oil-bath digester (Universal, India) provided with pressure-tested six autoclaves of a capacity of 2.5 L each. For each pretreatment, the bath ratio was fixed at 1:10 (solid:liquor). All the pretreatments were carried out individually at different temperatures (100−150 °C) for different time periods (60−120 min); while processing alkali and acid pretreatments, the NaOH and H_2SO_4 concentrations were varied from 2 to 6% (w/w) and from 0.01 to 0.2 N, respectively.

Table 3. Pretreatment Parameters for Wheat Straw

pretreatment	concentration	temperature (°C)	time (min)
alkali (NaOH)	2%	100, 125, 150	60, 90, 120
	4%	100, 125, 150	60, 90, 120
	6%	100, 125, 150	60, 90, 120
acid (H_2SO_4)	0.001 N	100, 125, 150	60, 90, 120
	0.003 N	100, 125, 150	60, 90, 120
	0.007 N	100, 125, 150	60, 90, 120
	0.01 N	100, 125, 150	60, 90, 120
	0.05 N	100, 125	60, 90, 120
	0.1 N	100, 125	60, 90, 120
	0.2 N	100, 125	60, 90, 120
hot water		100, 125, 150	60, 90, 120
		100, 125, 150	60, 90, 120
		100, 125, 150	60, 90, 120

4.2.3. Liquor Processing and Estimation of TRSs. All pretreated wheat straw samples were processed using a laboratory spin dryer to separate the liquor and residual wheat straw biomass. The residual wheat straw was washed with distilled water until neutral pH and air-dried for further use. The liquor obtained was centrifuged to obtain a clear supernatant. The hot water and alkali supernatant were further hydrolyzed with concentrated H_2SO_4 at 121 °C for 60 min in an autoclave. The hydrolysates were neutralized to pH 7 using the $BaCO_3$ slurry (72% w/v), followed by filtration through a Whatmann no. 1 filter paper. The concentration of TRSs in the filtrate was determined using the 3, 5-dinitrosalicylic acid (DNS) colorimetry method with xylose as the standard.[40] To follow this, 100 μL of the sample was diluted 30 times with deionized water, and 3 mL of the DNS reagent was added to 3 mL of the diluted sample. The mixed solutions (6 mL) were then digested at 100 °C for 5 min, followed by cooling to ambient temperature. Rochelle salt (1 mL) was added into the solution for color stability. The absorbance of the solutions was measured at 510 nm with a UV−visible spectrophotometer (UV-2600, Make Shimadzu). All the hydrolysis experiments and TRS estimations were carried out in triplicate.

4.2.4. High-Performance Liquid Chromatography. The quantitative analysis of sugars present in the liquor after pretreatment was performed through HPLC (Make-Shimadzu)

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using an Aminex HPX-87H300 mm × 7.8 mm column with a 9 μm particle size (Bio-Rad, California, USA). The instrument was equipped with an autoinjector facility (SIL-20AC HT, Shimadzu Corporation, Japan) and a detector (RID-10A; Shimadzu Corporation, Japan). The analysis was carried out at 55 °C under isocratic conditions with 5 mM H_2SO_4 as the mobile phase at a flow rate of 0.55 mL/min with an injection volume of 20 μL.

4.2.5. Field Emission Gun Scanning Electron Microscopy. The morphological changes between the untreated wheat straw and pretreated wheat straw were studied using a Hitachi-PU field emission scanning electron microscope. The images were captured with an accelerating potential difference of 5 kV within a working range of 3−200 μm.

4.3. Pulping and Papermaking. *4.3.1. Pulping of Untreated and Pretreated Wheat Straw.* The pretreated wheat straw sample with 0.1 N sulfuric acid at 125 °C for 120 min, with hot water at 150 °C for 120 min, and with 6% alkali at 150 °C for 120 min was further subjected to pulping. Pulping of pretreated wheat straw was carried out in an oil-bath digester having pressure-tested six autoclaves. Pulping was carried out at a 1:5 (solid:liquor) bath ratio, with different alkali charges of 12, 14, and 16% (w/w) at 166 °C for 180 min. The time taken to reach 100 °C from 28 °C was 60 min. After the temperature reached at 100 °C, there was an increase of 11 °C for every 15 min. The H-factor of 1175 was maintained throughout the pulping. Pulping of all the samples of pretreated wheat straw and untreated wheat straw was carried out under the same pulping conditions. After completion of pulping, the autoclaves were quickly removed from the digester and were put in cold water to stop the reaction. Washing of each pulp was done thoroughly with lukewarm water, and the excess black liquor was removed from the pulp using a spin dryer. Each pulp was then subjected to screening.

4.3.2. Pulp Screening and Pulp Yield. Untreated and pretreated pulps were screened in a laboratory Noram vibrating pulp screening machine (Lorentzen & Wettre, Canada) to remove the uncooked material (knots, shives, etc.). After screening, screened pulp was then shredded in a laboratory shredder to avoid the pulp clump formation and was further utilized for handsheet preparation. The pulp rejects which remain over the screen were collected and dried in an oven at 105 ± 2 °C. The pulp yield (%), rejects (%), and screened pulp yield (%) in the case of each processed sample were calculated as per the following formulas

$$\text{pulp yield (\%)} = P \times \frac{\text{pulp dryness (\%)}}{\text{initial weight of straw taken}}$$

$$\text{rejects (\%)} = \frac{\text{O. D. weight of rejects}}{\text{raw material cooked}} \times 100$$

$$\text{screened pulp yield (\%)} = \text{total pulp yield (\%)} - \text{rejects (\%)}$$

where P is the total weight of the pulp.

4.3.3. Kappa Number Determination. The Kappa number of each pulp sample was determined according to the TAPPI standard method T 236 om-99. The pulp sample (2 g) was disintegrated with 500 mL of distilled water. Disintegrated pulp was transferred to a 2000 mL beaker, and the apparatus was rinsed with enough distilled water to make a total volume of 795 mL and stirred thoroughly. Hundred milliliters of 0.1 N $KMnO_4$ and 100 mL of 4 N H_2SO_4 solution were added to disintegrated pulp simultaneously at 25 °C. Beakers containing $KMnO_4$ and H_2SO_4 solutions were rinsed with 5 mL of water, and the aliquot was added to the reaction mixture to make final volume 1000 mL. Twenty milliliters of 1 N KI solution was added into the reaction mixture after 10 min to stop the reaction. Free iodine was titrated with 0.2 N $Na_2S_2O_3$ using the starch indicator at the end of the reaction. A blank determination was also carried out using exactly the same procedure as mentioned above.

4.3.4. Pulp Freeness Determination. The CSF of pulps was determined according to the TAPPI standard T 227 om-04 using a freeness tester (Messmer Instruments Ltd.).

4.3.5. Black Liquor Analysis. Black liquor samples of untreated and pretreated wheat straw pulps were analyzed for solid content, RAAs, and TRSs. Total solids and RAA were determined according to the TAPPI standards T 650 om-05 and T 650 pm-84, respectively, whereas TRS was determined as per the method described under Section 4.2.3. In brief, 100 mL of the black liquor was separated and neutralized (pH = 7) by the slow addition of dilute acetic acid (1:1) to precipitate lignin. The lignin was separated by centrifugation. The supernatant was separated and processed for TRS estimation.

4.3.6. Preparation of Laboratory Handsheets. Laboratory handsheets of 60 gsm of untreated and pretreated wheat straw pulps were prepared for assessment of strength properties according to the TAPPI standard method T 275 sp-02 using a Rapid Kothen paper sheet making machine.

4.3.7. Physical Testing of Handsheets. The prepared laboratory handsheets were conditioned prior to testing at a temperature of 27 ± 1 °C and a relative humidity of 65 ± 2%. The grammage of handsheets was calculated according to the TAPPI standard T 220 sp-06 using a Universal make (India) gsm tester. Tear index was determined according to the TAPPI standard T 414 om-04 using an Elmendorf-type tearing tester (Testing Machines Inc., USA). The tensile and burst indices were determined according to the TAPPI standards T 494 om-06 and T 403 om-10 using a vertical-type (12−30) tensile tester (AB Lorentzen & Wettre, Sweden) and a burst tester (type 14-2, AB Lorentzen & Wettre, Sweden), respectively.

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Notes

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