Consecutive Organosolv and Alkaline Pretreatment: An Efficient Approach toward the Production of Cellulose from Rice Straw

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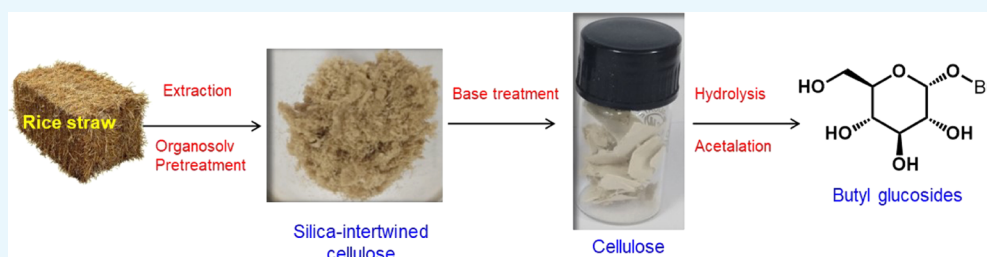
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ABSTRACT: The efficient removal of silica from rice straw and separation of its major components is essential for further valorization to produce value-added products. With regard to this, the isolation of cellulose (CEL), hemicellulose (HEM), and lignin (LIG) is imperative but quite challenging. Among several pretreatments of lignocellulosic biomass, the organosolv approach is deemed as one of the promising methods. Here, we present two different two-step approaches for the removal of silica and disintegration of significant components from rice straw, especially CEL; (i) base pretreatment, followed by organosolv treatment in the presence of organic acid, and (ii) organosolv pretreatment in the presence of organic acid, followed by base treatment. After each treatment, the recovered solid components are confirmed by various characterization techniques such as Fourier-transform infrared spectroscopy, X-ray diffraction, field emission scanning electron microscopy, and thermogravimetric analysis. Method 2 demonstrates 82% total removal of HEM and LIG along with 90.4% of silica removal from rice straw to obtain CEL. Furthermore, the obtained crude CEL is found to be with a purity of 78%. Excellent removal of silica (90.4%) reflects that in a test study, the crude CEL obtained from method 2 gives a higher yield of butyl glucosides (59.6%) than rice straw, which affords 45.0% of butyl glucosides.

1. INTRODUCTION

A steady decline of limited fossil resources demands alternative, sustainable resources, which can potentially substitute existing commodity chemicals and fuels to keep the current value chain.[1] With regard to this, lignocellulosic biomass can be employed as feedstock to produce a wide array of value-added chemicals and fuels.[2] Among lignocellulosic biomass, the valorization of agricultural residues, such as rice straw, encounters a significant problem due to the presence of a high silica content, apart from the recalcitrant nature of lignocellulosic components.[3] The worldwide production of rice was estimated to be 760 million tons (MT) in 2017, which gave rise to 1.1−1.3 times straw as the agro-residue.[4] Of which, India produced approximately 112 MT of rice straw, which was generally underutilized.[5] On the other hand, rice straw cannot be fed to animals due to the presence of nondigestible components such as lignin (LIG) and silica.[6] Presently, there is no economical way of disposal and commercial value for rice straw after being harvested from the field, accentuating the importance of transforming rice straw into potential bioproducts, such as bio-based surfactants, which not only diminish the underutilization of valuable constituents but also mitigate environmental issues.[7]

The foremost challenges of valorizing rice straw are the efficient removal of silica and developing a feasible process for isolating its major constituents, especially cellulose (CEL).[3,8,9] Thus, it is essential to find out a suitable pretreatment process for separating the biopolymers from silica in rice straw. Various bases such as Na_2CO_3, NaOH, and KOH were employed for the removal of silica.[8,10,11] Ajula et al. reported that silica could be removed in the form of sodium silicate in aqueous NaOH solution when having pH > 10.[12] In line with this, Khaleghain et al. employed sodium dodecyl sulfate and sodium acetate as the base separately at 90 °C, achieving the maximum of 10% silica removal due to lower pH in the medium.[8]
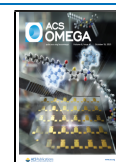
Tang et al. reported the recovery of CEL (76%, w/w) in the form of solid residue (SRD) from rice straw using a mixture of ethylene glycol and aluminum chloride at 150 °C.[13] The CEL-containing SRD also possessed 10 and 12% hemicellulose (HEM) and LIG, respectively. CEL was also extracted from rice straw in the form of nanofibers using a chemomechanical approach, yielding 79.3% CEL along with 4.8% HEM and 15.9% LIG.[14] However, this method entailed a complicated sequential procedure (swelling of rice straw in aq. NaOH solution, acid hydrolysis, alkaline treatment, bleaching, and sonication). Rice straw was also pretreated with dilute nitric acid, followed by treating with NaOH and sodium hypochloride, affording 26.0% of CEL.[15] Rice straw was also pretreated with dilute KOH solution at 40−90 °C, followed by soaking in an acidic solution having a pH between 3 and 4, giving 86% yield of crude CEL.[16]

The isolation of CEL from rice straw was also performed by following a multistep approach, including steam-explosion pretreatment (235−265 °C; 40 bar), delignification, and bleaching, yielding 96% CEL.[17] Jiang et al. reported the isolation of CEL from rice straw using sequential steps, including steam explosion, extraction of CEL using ionic liquids, obtaining 64.8% CEL-rich fraction, which increased further to 95.6% after bleaching with H_2O_2.[18] To overcome the major drawbacks of the processes mentioned above, recent studies showed that organosolv pretreatment could be a promising approach for fractioning biomass components.[19,20]

Luo et al. reported CEL production from rice straw using the organosolv approach, followed by bleaching with Na_2CO_3/ H_2O_2 and then treating with hydrochloric acid, obtaining a fraction with a CEL content of 92.4%.[21] Nie et al. reported a comparative study of rice straw using the organosolv process containing 60% n-butanol, n-propanol, ethanol, and methanol in water at 75 °C for 3 h, achieving 89% of the CEL-rich residue.[22] Amiri et al. also reported that using 75% ethanol with 1% H_2SO_4 at 180 °C for 60 min resulted in 66.9% solid recovery, containing 62.3% CEL out of 49.2% CEL present in untreated rice straw.[23] Similarly, Raita et al. explored a comparative study with acetone and ethanol in the presence of 5% NaOH at 80 °C, yielding 76.0 and 71.0 in terms of sugars recovered from the solid fraction of rice straw, respectively.[24] These studies demonstrated that adding an acid or a base as a catalyst could enhance CEL yield.[25] In line with this, Momayez et al. showed a comparative study for pretreating rice straw in 1 and 4% (v/v) of lactic acid, propionic acid, acetic acid, and butyric acid in water at 100 °C, resulting in the liberation of sugar components more efficiently with lactic acid with a loss of 64.0% SRD.[26] Similarly, Morone et al. investigated the pretreatment of rice straw in 2-methyltetrahydrofuran in the presence of oxalic acid, yielding 55.7% of CEL.[27]

Here, we report the CEL production from rice straw by adopting two different two-step approaches. The first one (method 1) is base pretreatment for the removal of silica from rice straw, followed by organosolv treatment to obtain CEL in the presence of organic acid. The second one (method 2) is organosolv pretreatment of rice straw in the presence of organic acid, followed by post-treatment with a base for the removal of silica from the crude CEL. The obtained crude CEL from the best method is converted to butyl glucoside to signify the removal of silica, and the results are compared with those obtained for rice straw and silica-intertwined cellulose (S-ICEL) as substrates.

2. MATERIALS AND METHODS

2.1. Feedstock and Chemicals. Rice straw was received from the Mohali region, Punjab, India. Glucose, lactic acid, oxalic acid, acetic acid, levulinic acid, galactose, and arabinose were purchased from Sigma-Aldrich. Formic acid, fructose, xylose, sodium bicarbonate, and sodium hydroxide were purchased from CDH. Ethanol was received from Changshu Hongsheng fine chemical. Co. Ltd. Sodium carbonate and urea were purchased from TCI.

2.2. Characterization. Field-emission scanning electron microscopy (FESEM) images were captured using a Hitachi SU8010. Fourier-transform infrared (FTIR) spectra were recorded using a Fourier transform infrared-attenuated total reflectance spectrophotometer (PerkinElmer Spectrum Two). Thermogravimetric analysis (TGA) was performed using a simultaneous thermal analyzer STA-8000 (Perkin Elmer) in the range of 30−800 °C with a heating rate of 10 °C/min under N_2 or air atmosphere. X-ray diffraction (XRD) analysis was performed using PAN analytical Xpert Pro. equipped with an x'Celerator solid-state detector under the following conditions: 45 kV, 40 mA, and Cu Kα (λ = 1.54056 Å). The measured 2θ range was between 10 and 90° with a rate of 2°/min. The crystallinity index was calculated using the equation given below.[28]

$$CrI(\%) = \left[\frac{I_{002} - I_{am}}{I_{002}} \right] \times 100$$

where CrI represents the crystallinity index of the sample, I_{002} represents the intensity of the peak that appeared at 2θ of 22.2 (crystalline region), and I_{am} represents the intensity of the peak appeared at 2θ of 18.4 (amorphous region). After the organosolv pretreatment, the degraded products (e.g., glucose, xylose, and formic acid), if formed, were analyzed and quantified using an Agilent HPLC 1200 (column: Rezex ROA-Organic Acid H^+; column temperature: 60 °C; detector: refractive index; eluent: 5 mM H_2SO_4; flow rate: 0.6 mL/min).

2.3. Preparation of the Rice Straw Sample. Native rice straw was initially soaked in deionized water overnight, thoroughly washed with a copious amount of water for removing dust and dried in an oven at 40 °C. Dried rice straw was then ground well to a size of less than 3 mm using a super mass colloider grinding machine (Masuko sangyo co. Ltd) and dried in a vacuum oven at 40 °C until no change in weight. Finally, it was stored in an air-tightened bag in a desiccator prior to use.

2.4. Pretreatment with Base. Initially, native rice straw sample was subjected to removal of extractives (waxes, chlorophyll, and other minor components) in ethanol in a soxhlet assembly by continuously refluxing for 6 h (four to five siphon cycles per hour). The solid fraction was filtered off, washed with water and ethanol, and dried at 40 °C in an oven. All the experiments were performed with extractive free rice straw denoted as "rice straw".

The influence of base treatment for the removal of silica from rice straw and S-ICEL was studied with various bases, such as sodium carbonate, sodium bicarbonate, sodium hydroxide, and urea. 100 mg of rice straw was suspended in 0.07 M aqueous solution of a base (10 mL) in an ace pressure tube and heated to the required temperature and time at a stirring speed of 600 rpm in an oil bath. The solution was then cooled to room temperature, filtered off, and washed with water until the filtrate reached neutral pH. The solid sample

was then dried in a vacuum oven at 40 °C for 24 h and then kept in a desiccator. The obtained solid sample was denoted as an "SRD". The quantification of SRD was done as follows; the amount of solid sample recovered after the treatment divided by the amount of dried rice straw taken. The amount of silica present in the rice straw and the SRD was quantified based on TGA analysis. The post-treatment of S-ICEL, obtained from the first step of method 2, was performed under the conditions optimized in the first step of method 1 to obtain "base-treated cellulose (B-TCEL)".

2.5. Organosolv Pretreatment. Organosolv experiments were performed in an acid digestion vessel with a 45 mL thick-walled PTFE liner from Parr equipped with a pressure safety disc. The maximum operating temperature and pressure of this acid digestion vessel are 250 °C and 120 bar, respectively. A suspension of rice straw (500 mg) in 15 mL of 0.1 M organic acid in an ethanol/water (1:1) mixture was taken in a Teflon-lined vessel and tightly closed. The vessel was placed on a magnetic stirrer with a hot plate and heated to the set temperature (100−160 °C) for 4 h under constant stirring (600 rpm). After treatment, the vessel was cooled down to room temperature, and the reaction mixture was then filtered off to collect both solid fraction and the filtrate. Subsequently, the solid part was washed with 60 mL of ethanol/water (1:1) mixture. An aliquot of the filtrate portion was subjected to high-performance liquid chromatography (HPLC) analysis to confirm whether sugar and/or other downstream products from CEL and HEM formed. The filtrate was diluted further by adding 120 mL of deionized water for improving LIG separation from HEM. The collected solid part was S-ICEL, and the filtrate contained HEM and LIG. The filtrate portion was stored in a refrigerator until LIG precipitated, centrifuged, and quantified after dried at 40 °C. The leftover supernatant liquid portion was HEM along with a minor amount of organic acid, which was quantified after removing the solvent using a rotary evaporator. The S-ICEL was washed and dried in a vacuum oven at 40 °C for 24 h. The yields of all isolated components were calculated by measuring their masses on a weighing scale based on vacuum oven-dried samples. Similarly, the obtained SRD from the first step in method 1 was subjected to organosolv treatment under the conditions optimized in the first step of method 2.

2.6. Conversion of CEL to Butyl Glucosides. An appropriate amount of rice straw or crude CEL obtained from the best method and the required amount of sulfuric acid in butanol were taken in a 100 ml stainless steel vessel (Amar Equipment Pvt Ltd). The vessel was then flushed with N_2, pressurized to 20 bar N_2, and heated to the desired reaction temperature for a specific reaction time. After the completion of the reaction, the vessel was cooled down to room temperature, and then aliquots of the reaction mixtures were analyzed in HPLC as mentioned above.

2.7. Quantification of CEL, HEM, LIG, and Silica Plus Ash. To determine the silica plus ash (SPA) content, an appropriate amount of dried rice straw, S-ICEL, SRD, and B-TCEL was calcined in a muffle furnace at 575 °C for 24 h in static air. The weight percentage of SPA and CEL recovered from rice straw was quantified as per the formula given below. The quantification of HEM and LIG was done according to the NREL procedure. The percentage of silica removal in the sample was calculated based on the weight loss obtained from TGA analysis by subjecting the sample at 800 °C for 10 min

with a ramp rate of 10°C/min under air. The formulae are given below.

wt % of SPA

= [(wt of crucible plus sample left after thermal treatment

− wt of empty crucible)/wt of sample taken] × 100

% of silica removal

= [(wt of sample taken − wt of sample after treatment)

/wt of sample taken] × 100

CEL recovered from rice straw

= (amount of CEL obtained/

actual amount of CEL present in rice straw(NREL)

× 100

3. RESULTS AND DISCUSSION

3.1. Determination of Rice Straw Composition. The composition of rice straw was determined by following the National Renewable Energy Laboratory (NREL) protocol,[29] and the results are summarized in Table 1. The obtained

Table 1. Rice Straw Composition Based on the NREL Procedure

components	composition (wt %)
CEL	42.9 ± 1.3
HEM	23.9 ± 0.7
LIG (ASL + AIL)	16.7 ± 0.2
SPA	11.5 ± 0.3[a]
extractives	2.2 ± 0.03

[a]Rice straw calcined at 575 °C for 24 h to obtain SPA. ASL = acid-soluble LIG; AIL = acid-insoluble LIG.

results were the mean value of three experiments. It was found that the employed rice straw is composed of 42.9 wt % CEL, 23.9 wt % HEM, 16.7 wt % LIG, 11.5 wt % SPA, and 2.2 wt % extractives, accounting for a mass balance of 97.1 wt %.

The removal of silica from rice straw to obtain CEL was performed by adopting two different two-step approaches, as shown in Scheme 1. The first method adopted was pretreatment of rice straw with a base to obtain SRD, followed by organosolv treatment with a mild organic acid in an ethanol−water mixture to obtain CEL. The second one was the organosolv pretreatment of rice straw with a mild organic acid in the ethanol−water combination to isolate S-ICEL, followed by base treatment to obtain CEL.

3.2. Base-Organosolv Treatment (Method 1). *3.2.1. In-fluence of Base (Step 1).* Apart from the recalcitrant nature of rice straw due to its complex structure of components, the outer surface is predominately covered with a silica layer, thus emphasizing that silica removal is imperative. It is known that bases are generally being used in the desilication processes.[8,10] The rice straw was initially treated with an aqueous solution of various bases, such as NaOH, $NaHCO_3$, Na_2CO_3, and urea, and the results are presented in Table 2.

Among the bases employed, NaOH with a concentration of 0.07 M was found to be suitable for removing silica efficiently from rice straw without compromising the degradation of significant components at 70 °C for 4 h, as confirmed by

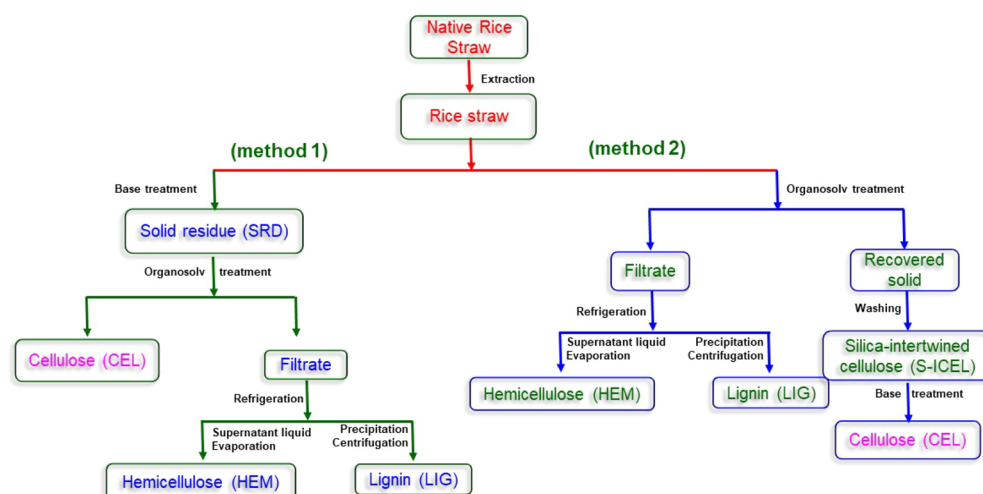**Scheme 1. Schematic Representation of Rice Straw Treatment with Two Different Two-Step Approaches**

Table 2. Effects of Different Bases on the Removal of Silica from Rice Straw[a]

base	SRD (wt %)	SPA (wt %)[b]	silica (wt %)[c]	silica removal (%)[c]
rice straw		11.3	10.5	
Na$_2$CO$_3$	74.4	4.9	6.6	37.1
NaHCO$_3$	67.9	5.6	9.8	6.6
urea	67.9	6.5		
NaOH	69.8	2.8	2.8	73.3

[a]Pretreatment conditions: 100 mg rice straw, 0.07 M base, 10 mL water, 70 °C, and 4 h. [b]After calcination of SRD. [c]Based on TGA analysis.

subjecting the supernatant liquid samples to HPLC and UV−visible spectroscopy analysis for sugar components and LIG, respectively. The amount of silica present before and after the base treatment (SRD) was quantified by subjecting the samples to TGA analysis in air and found that NaOH favored the highest removal of silica (73.3%) compared to other bases. The corresponding TGA thermograms are present in Figure S1. After the treatment, SRD composed of CEL, HEM, and LIG was calcined at 575 °C for 24 h and the leftover was predominantly ash, suggesting that the base treatment removed silica efficiently.

3.2.2. Optimization of Other Parameters. To optimize the pretreatment process for the efficient removal of silica from rice straw, the influence of temperature, time, and concentration was investigated. Figure 1a shows the effect of NaOH concentration on the rice straw. No significant difference in the degradation of rice straw was observed between 0.02 and 0.07 M aq. NaOH solution, but the weight loss increased by 10.0 wt % when increasing the NaOH concentration to 0.1 M, indicating the partial degradation of rice straw, confirmed by HPLC analysis (2−3 wt % unidentified products). In all cases, the SPA content (derived by treating at 575 °C for 24 h) was found between 2.8 and 6.5 wt %.

Similarly, the influence of temperature was also examined and observed that there was a significant effect of increasing the pretreatment temperature (100 °C) on the degradation of rice straw, leading to a decrease in the SRD significantly (37.2 wt %) (Figure 1b). The filtrate part was analyzed in HPLC and found that 10.0 wt % of the unidentified product was formed, revealing the degradation of significant components of rice

straw. The influence of temperature studied between 40 and 70 °C did not show a significant difference in terms of the recovered solid content; however, the results obtained from 70 °C showed a slightly higher removal of silica. Figure 1c shows that as the treatment time increased with 0.07 M NaOH solution from 1 to 24 h, the solid recovery of rice straw decreased from 74.4 to 57.1 wt %, but no significant changes in the recovered SPA content. The optimal time required for removing silica from rice straw was 4 h with 0.07 M NaOH at 70 °C.

The influence of the amount of rice straw and various treatment techniques were also investigated, and the results are presented in Figures 1d and S2, respectively. As the amount of rice straw increased, the solid recovery improved. The recovered SRD was subjected to TGA analysis to determine the silica removal and observed that employing 100 mg of rice straw offered the highest removal of 73.3% silica (Table S1). The corresponding TGA thermograms are presented in Figure S3.

The removal of silica from rice straw was subjected to various treatment such as water bath shaking and sonication and no significant difference in terms of SRD recovered was observed (Figure S2).

3.2.3. Characterization of SRD. Analyzing SPA-derived from rice straw and SRD would indicate the degree of silica removal from rice straw. Figure 2 shows the FTIR spectra of SPA-derived from various base-treated rice straw. The peaks appearing at 1071 cm^{-1} are ascribed to Si− O−Si, which significantly shifted to a lower wavenumber when using NaOH for desilication compared to other bases.[11] The treatment with different bases, such as sodium carbonate (pH-10), sodium bicarbonate (pH-8), and urea (pH-7), showed a significant amount of silica might have remained intact with rice straw and deposited on the surface, which could be challenging to be removed.[12] It is known that NaOH can efficiently react with silica on the surface of rice straw to form potentially sodium silicate compared to other bases to form their corresponding salt.[12]

The effective removal of silica from rice straw using base treatment was substantiated further by calcining the rice straw samples at 575 °C for 24 h. The FTIR spectrum of NaOH-treated rice straw clearly showed silica removal compared to rice straw (Figure 3). The FTIR spectra of NaOH-treated rice
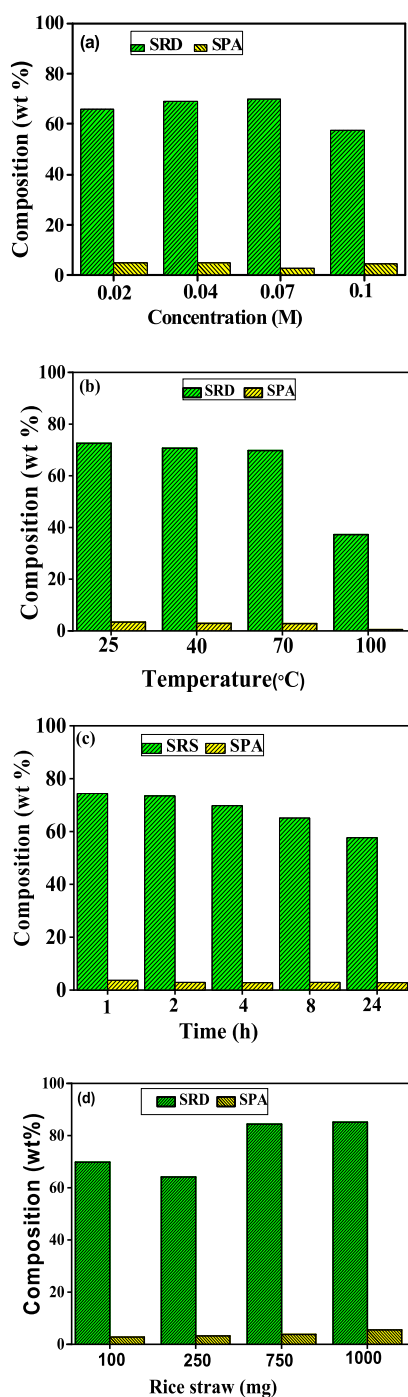
Figure 1. Influence of various parameters on the recovery of SRD after base treatment. Treatment conditions: 100 mg rice straw, 10 mL water (a) NaOH, 70 °C, 4 h, (b) 0.07 M NaOH, 4 h, (c) 0.07 M NaOH, 70 °C, and (d) 0.07 M NaOH, 70 °C, 4 h.

Figure 2. FTIR spectra of (a) SPA-derived from rice straw and the SRD obtained after base treatment of rice straw (b) NaOH, (c) Na_2CO_3, (d) $NaHCO_3$, and (e) urea.

Figure 3. FTIR spectra of (a) rice straw, (b) SRD, (c) SPA derived from rice straw after thermal treatment, and (d) SPA-derived from the SRD after thermal treatment.

straw displayed peaks corresponding to the −OH groups of CEL and HEM (3200−3400 cm^{-1}), −CH stretching of CEL, HEM, and LIG (2900 cm^{-1}), C−O and O−CH$_3$ stretching of LIG (1268−1470 cm^{-1}) compared to rice straw (Figure 3a,b), suggesting that the silica removal enhanced the corresponding characteristic peak of the major components, leaving behind the peaks predominately corresponding to ash. For instance, all the peaks corresponding to organic moieties present in the rice straw samples (3400, 1720, 1619, 1268, and 901 cm^{-1}) disappeared after calcination. Moreover, the peak at 1071 cm^{-1}
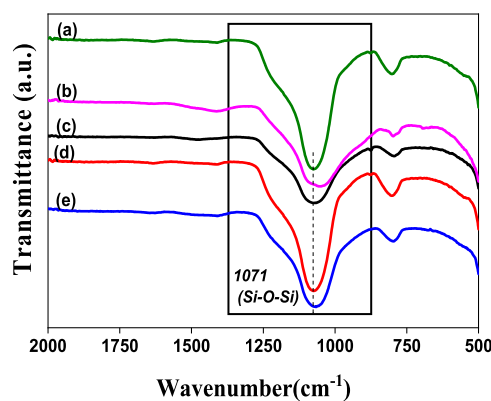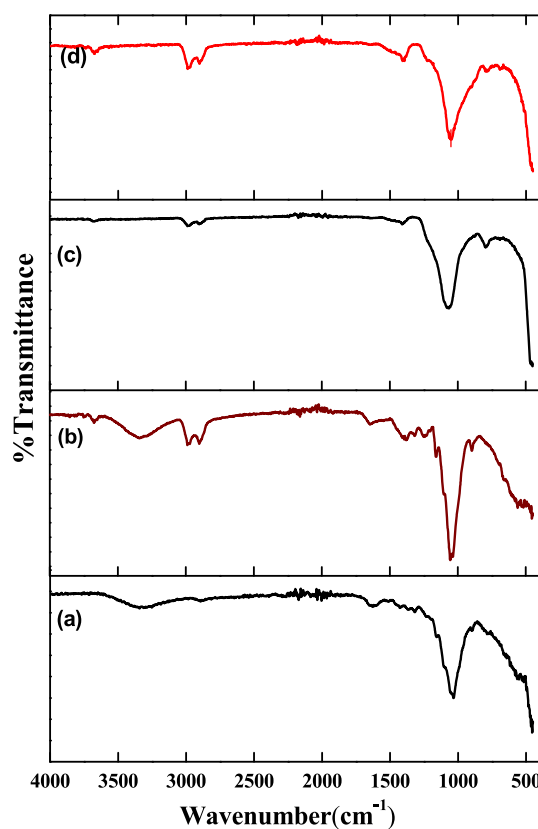
ascribed to Si−O−Si stretching significantly shifted to a lower frequency of 1042 cm^{-1}, suggesting the removal of silica from rice straw (Figure 3c,d).[11,30]

Figure 4a,b shows the FESEM images of rice straw covered with silica, which has a rough surface, and the SRD has a smooth surface and a permeable structure due to the removal of silica from the surface, respectively.[31] The FESEM images of SPA derived from rice straw after calcination and SPA-derived from the SRD are shown in Figure S4 and found no significant differences in their morphology due to elimination of all organic components (CEL, HEMs, and LIG) at a higher temperature (575 °C, 24 h), only left with SPA.
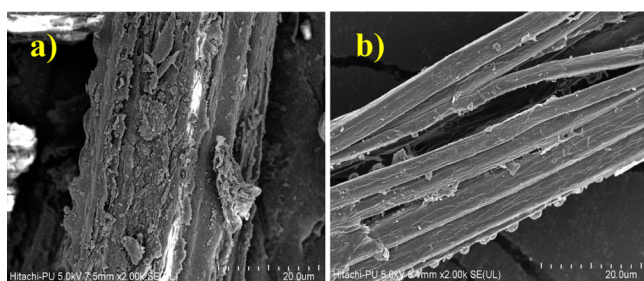
Figure 4. FESEM images of (a) rice straw and (b) SRD.

The XRD patterns of SPA derived from rice straw, SPA derived from SRD, and the reference silica are shown in Figure 5. Figure 5a shows a very broad peak centered at a 2θ value of
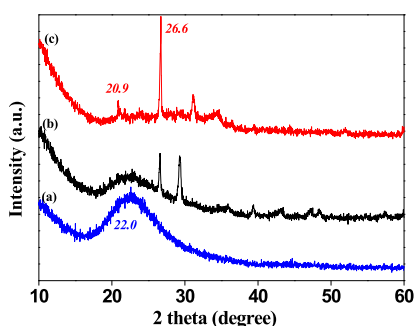

Figure 5. X-ray diffraction patterns of (a) silica reference, (b) SPA-derived from rice straw, and (c) SPA-derived from SRD.

22° ascribed to amorphous silica. Likewise, Figure 5b exhibits a very broad peak at 2θ of 22° and a sharp peak at 26.6° corresponding to amorphous and crystalline silica present in the rice straw, respectively. In the XRD patterns, the disappearance of a broad peak at 22.0° confirmed the effective removal of amorphous silica[30] and two other peaks at 20.9 and 26.6° indicated the complete removal of amorphous silica but leaving behind a minimal amount of crystalline silica in the SRD (Figure 5c).[32,33]

3.2.4. Organosolv Treatment of SRD (Step 2). It has been shown that base pretreatment effectively influenced silica removal from rice straw (vide supra). As treating rice straw with NaOH showed efficient removal of silica, SRD was subjected to the optimized organosolv treatment conditions, as shown in method 2. Treating rice straw with aq. NaOH, followed by the organosolv approach (ethanol−water mixture as a solvent and lactic acid as a catalyst) afforded only 28.3 wt % CEL, 16.4 wt % HEM, 2.5 wt % LIG, and 6.0 wt % SPA (Table 3). According to the NREL procedure, rice straw possessed 42.9 wt % CEL, 23.9 wt % HEMs, 16.7 wt % LIG, and 11.5 wt % SPA. These results indicated that NaOH followed by organosolv treatment significantly decreased the yield of CEL emphasizing adopting an alternative approach to enhance the yield of CEL.

3.3. Organosolv-Base Treatment (Method 2). *3.3.1. Influence of Organic Acid (Step 1).* Method 1 (base-organosolv treatment) showed relatively a low yield of CEL obtained from rice straw compared to the actual amount assessed by the NREL procedure. Thus, it was set to explore method 1 other way around: first organosolv pretreatment, followed by base treatment (method 2). The organosolv pretreatment of rice straw with various organic acids was initially investigated in an

Table 3. Effect of Combined Treatment on Rice Straw[a]

method	treatment	SRD (wt %)	CEL (wt %)	HEM (wt %)	LIG (wt %)	SPA (wt %)[b]
NREL	rice straw	NA	42.9	23.9	16.7	11.5
method 1	step 1: NaOH	70.6				
	step 2: organosolv	NA	28.3	16.4	02.5	06.0

[a]Reaction conditions: 500 mg rice straw. Base treatment conditions (step 1): 0.07 M NaOH, 50 mL, 70 °C, 4 h; organosolv conditions (step 2): 15 mL of 0.1 M lactic acid in the ethanol/water (1:1), 160 °C, 4 h. Composition percentage calculation is based on the oven-dried weight of each sample. [b]On the basis of SRD calcined at 575 °C for 24 h.

ethanol−water mixture at 160 °C for 4 h, and the results are summarized in Table 4. Among the organic acids employed,

Table 4. Isolation of Major Components in the Presence of Various Organic Acids[a]

organic acid	S-ICEL (wt %)[b]	HEM (wt %)[c]	LIG (wt %)[c]
lactic acid	49.9	26.0	7.2
levulinic acid	51.5	37.2	0.4
formic acid	61.0	29.8	0.4
acetic acid	67.3	27.9	1.9
oxalic acid	45.5	44.7	0.4

[a]Reaction conditions: 500 mg rice straw, 15 mL of 0.1 M organic acid in an ethanol/water mixture (1:1), 160 °C, 4 h. [b]SRD obtained after organosolv treatment. [c]See the experimental procedure for the separation of HEM and LIG.

lactic acid was found to be yielding an optimal amount of major components; S-ICEL (49.9 wt %), HEM (26.0 wt %), and LIG (7.2 wt %). This could be due to the intermittent pK_a (acid dissociation constant) value of lactic acid and the order of pK_a of used organic acid as follows: levulinic acid > acetic acid > lactic acid > formic acid > oxalic acid: 4.78 > 4.76> 3.86 > 3.75>1.2.[34] The amount of HEM (26.0 wt %) obtained from rice straw was slightly higher than the actual amount, indicating that the catalytic amount of organic acid could also partly contribute to the slight excess of HEM content. Moreover, a part of LIG is still intact with HEM (Figure S7c); corresponding peaks appeared at 1507 and 1420 cm^{-1}, which could also partly contribute to enhance the yield of HEM than the actual amount according to the value obtained from the NREL procedure.

It is known that the lower the pK_a of acid, the higher the strength of the Bronsted acid, which readily gives up the protons and could facilitate the disintegration of the major components in rice straw. With regard to this, oxalic acid has lower pK_a than lactic acid, inferring that oxalic acid can readily donate protons into the solution, which could efficiently catalyze the disintegration process. However, lactic acid afforded optimum yields of S-ICEL, HEM, and LIG, suggesting that having a moderate pK_a value would be appropriate for disintegrating these three major components. In addition to this, lactic acid has a hydroxyl group that could facilitate the hydrogen bonding network between lactic acid and the hydroxyl moiety present in rice straw components, thus improving the disintegration, compared to other organic acids employed (Figures S5 and S6).[26] Moreover, this organosolv pretreatment in the presence of lactic acid resulted in the liberation of a hemicellulosic content (26.0 wt %) and

LIG (7.2 wt %) as ethanol acts as a delignification solvent to some extent,[35] and no other acids yielded more than 2.0 wt % LIG.

3.3.2. Influence of Organosolv Pretreatment Parameters. The other pretreatment parameters were also optimized based on the amount of S-ICEL recovered from organosolv pretreatment in the presence of lactic acid. The concentration of lactic acid was studied between 0.05 and 0.15 M, and 0.1 M was found to be optimal to obtain maximum S-ICEL (Figure 6a). Figure 6a shows as the concentration of lactic acid
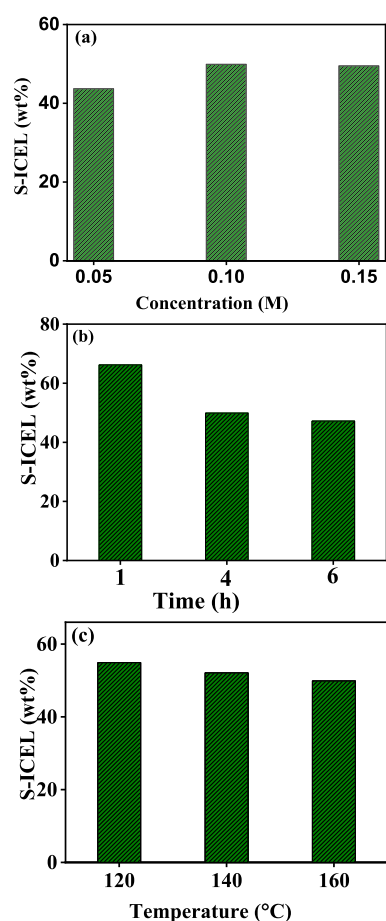

Figure 6. Optimization of organosolv treatment parameters of rice straw to obtain S-ICEL. Treatment conditions: 500 mg rice straw, 15 mL of ethanol/water (1:1) mixture (a) lactic acid, 160 °C, 4 h; (b) 0.1 M lactic acid, 160 °C; and (c) 0.1 M lactic acid, 4 h.

increases from 0.05 to 0.1 M, the yield of S-ICEL increases from 44 to 49.9 wt % and slightly decreases to 49.5 wt % when increasing the concentration of lactic acid to 0.15 M, indicating the role of organic acid as a catalyst during the pretreatment. The influence of other parameters, such as time and temperature, were also explored, and the results are illustrated in Figure 6b,c. The effect of time indicated that after 1 h pretreatment, the S-ICEL was relatively high (66.2 wt %), which exceeds the total content of CEL and SPA according to the adopted NREL procedure. The obtained high amount of SRD displayed the suppression of the structural alteration, resulting in an increasing CEL content and implying that HEM and LIG fraction might still predominantly be intact with CEL. When prolonging the treatment time to 4 h, the yield of S-ICEL was about 50.0 wt % (Figure 6b), as no notable increase

was observed in terms of the S-ICEL content after 6 h pretreatment. The optimum S-ICEL recovered was achieved at 160 °C, and no significant changes were found at 120 and 140 °C (Figure 6c).

3.3.3. Characterization of Rice Straw Components after Organosolv Treatment. The effect of organosolv pretreatment in the presence of lactic acid on the structural changes of rice straw and its components was examined using FTIR to understand the efficiency of the treatment procedure, based on the characteristic peaks of the major components. Rice straw is predominantly composed of CEL, HEM, LIG, and silica, containing various functional groups (e.g., −OH, −C=O, −CHO, −C=C−, and Ar) and can be monitored by FTIR analysis. Figure S7 shows the spectra of S-ICEL, HEM, LIG, and rice straw with characteristic peaks assigned to a particular functional group of the major component. Broadbands at 3200−3400 and 2900 cm^{-1} were assigned to O−H and C−H stretching of CEL, respectively (Figure S7b).[36] It is known that glucose units in CEL are bridged by a β-1,4 glycosidic linkage, and the corresponding characteristic peaks of C−H bending (rocking vibration) and C−O−C bridging (antisymmetric) stretching bands at 902 and 1157 cm^{-1}, respectively, were observed.[37] The sharp peak that appeared at 1057 cm^{-1} can be ascribed to the stretching frequency of secondary alcohol with a −C−O− group and ether functions in CEL.[38] The absorption bands at 2900 and 1373 cm^{-1} can be ascribed to C−H stretching (glucose unit) and to C−H deformation vibrations in CEL, respectively.[36,38] The intactness of silica with CEL was confirmed by the appearance of a peak at 786 cm^{-1} for Si−O−Si.[33] However, the FTIR spectrum of S-ICEL is not the complementary technique to substantiate the complete removal of HEM and LIG as it has been very challenging to distinguish between the functional groups of components.

In the cases of HEM and LIG fractions, a peak at 1720 cm^{-1} was observed and ascribed to the C=O (unconjugated keto group) group present in these components (Figure S7c,d).[39] As HEM is primarily composed of xylan, the corresponding absorption peak was observed at 1040 cm^{-1} for both linear and branched (1−4)-β−xylan (arabinoxylans and glucuronoxylan). The separation of LIG from other components was confirmed by the appearance of a peak at 1507 cm^{-1}, which can be ascribed to the C=C aromatic skeleton vibration, which was absent in CEL and HEM fractions.[40] A band at 1420 cm^{-1} can be assigned to C−H deformation of methyl and methoxy groups. LIG is comprised of mainly syringyl (C−O), guaiacyl (C−O aryl group), and the corresponding peaks appearing at 1328 and 1268 cm^{-1}, respectively (Figure S7d).[41] All the characteristic peaks of the major components obtained from FTIR spectra are in line with the characteristic peaks of rice straw. However, the FTIR spectra of these major components do not provide substantial evidence for their complete isolation.

The isolated components of S-ICEL, HEM, and LIG were subjected to TGA to understand their thermal decomposition, and the corresponding thermographs and their derivative thermographs are shown in Figure 7. At a low-temperature region of 50 to 250 °C, S-ICEL showed a peak that could be assigned to a loss of hydrophilic water. A significant weight loss can be seen from 250 to 340 °C that could be ascribed to the decomposition of CEL with a maximum weight loss at 340 °C according to the derivative thermogravimetric (DTG) curve.[42] Upon increasing temperature to 800 °C, the leftover residue
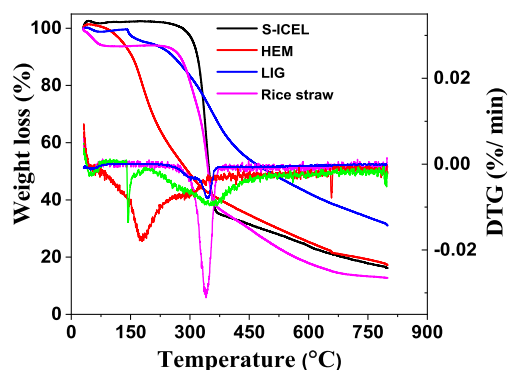
Figure 7. TGA (solid line) and DTG thermographs (dotted line) of S-ICEL, HEM, and LIG.

Figure 8. X-ray diffraction patterns of rice straw and S-ICEL.

was equivalent to 16.2%, which corresponded to SPA. Compared to S-ICEL, the decomposition of HEM began gradually from a relatively lower temperature of 140 °C up to 350 °C, with a maximum weight loss at 176 °C, according to the DTG thermograph. The leftover residue was equivalent to 18.0% belonging to unconverted carbonaceous species formed under N_2 atmosphere.

In the case of the LIG sample, there was no peak corresponding to the significant decomposition temperatures of CEL (340 °C) and HEM (176 °C), suggesting that LIG possessed no impurities of CEL and HEM, according to the TGA and DTG thermographs. LIG has an entirely different thermograph pattern and showed a broad peak from 200 to 400 °C (DTG thermograph) and showed a slow weight loss rate of up to 30%. The peak appeared at 350 °C was assigned to LIG, confirming the disintegration of its components as in line with previous studies.[43,44] These results indicate that the decomposition of HEM initially took place, followed by CEL and LIG decomposition (Figure 7).

The native rice straw, rice straw and its separated components were subjected to FESEM analysis to visualize the physical changes that occurred before and after the treatment. Figure S8a shows the intact and compact structure of rice straw covered with silica on its outer surface before subjecting it to the organosolv pretreatment. The FESEM image of rice straw after the ethanol extraction displays small changes in the morphology (Figure S8b). Figure S8c–e exhibits the FESEM images of S-ICEL, HEM, and LIG isolated from rice straw after the organosolv pretreatment, respectively. A packed and intact morphology of rice straw distorted into the open matrix, more accessible to S-ICEL having a bundle like structure (Figure S8c)[24] and, in the cases of HEM and LIG, the FESEM images display an irregular shape and size (Figure S8d,e). Apart from S-ICEL, HEM showed an enclosed and somewhat twisted angular pattern-like structure, and LIG showed an agglomerated and cluster-like structure.[45]

XRD patterns of rice straw and S-ICEL are shown in Figure 8. The characteristic peaks of CEL can be seen at 2θ of 15.5, 22.2, and 34.7°.[30,46] It is known that CEL is composed of both crystalline and amorphous phases.[30] The crystalline and secondary amorphous CEL peaks appeared at 2θ of 22.2 and 15.5°, respectively.[46] Moreover, the crystallinity index (CrI) of CEL was calculated from the characteristic peaks using the equation mentioned in Section 2.2. The rice straw showed a crystallinity index of 47.0%. After subjecting rice straw to organosolv pretreatment, the isolated S-ICEL afforded a crystallinity index of 59.4%.
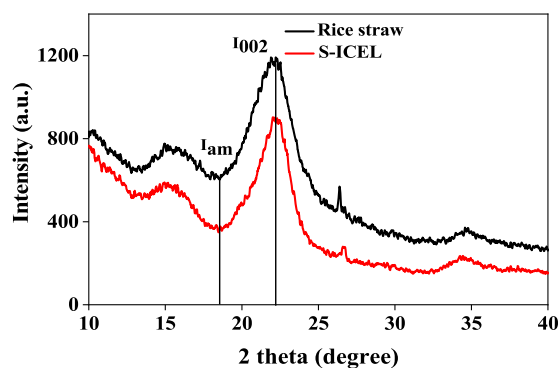
3.3.7. Base Treatment of S-ICEL.
As it has been shown that base pretreatment influenced effectively the removal of silica from rice straw (step 1 in method 1, vide supra), experiments have been performed accordingly after the organosolv pretreatment. Moreover, treating rice straw with base (NaOH), followed by the organosolv approach led to an efficient removal of silica. However, significant loss of carbohydrate (2−3 wt %) and LIG (5.1 wt %) based on HPLC and UV analysis, respectively, was observed due to its solubility in the basic medium. Thus, it is worth performing organosolv pretreatment, followed by base treatment to alleviate CEL, HEM, and LIG degradation, and the results are presented in Table 5. According to the NREL procedure, rice straw possessed 42.9 wt % CEL, 23.9 wt % HEM, 16.7 wt % LIG, and 11.5 wt % SPA. The treatment of rice straw with NaOH, followed by the organosolv approach (ethanol−water mixture as a solvent and lactic acid as a catalyst) afforded only 28.3 wt % CEL, 16.4 wt % HEM, 2.5 wt % LIG, and 6.0 wt % SPA.

Interestingly, the silica removal was performed by the other way around, that is, organosolv pretreatment, followed by base treatment, gave 36.6 wt % CEL, 26.1 wt % HEM, 7.2 wt % LIG, and 5.9 wt % SPA, inferring that this reverse approach ultimately lessens the degradation of CEL (36.6 wt %) (Table 5), which is only 8.3 wt % lower than the CEL content obtained using the NREL procedure. In addition, the recovered amount of HEM and LIG improved, inferring that using the base during the second step could diminish the degradation of CEL, thus enhancing the CEL content. Hence, this approach (method 2) was found to be more suitable than prebase treatment (method 1) for the disintegration of rice straw and gave high amount of total carbohydrates. As the obtained LIG content was relatively low from both methods 1 and 2, the other fractions such as CEL and HEM were subjected to NREL and UV analyses and found that altogether, 88.0 and 78.4% of LIG was accountable, respectively. Moreover, method 2 discloses that 82% total removal of LIG and HEM along with 90.4% of silica removal from rice straw were achieved to obtain a high yield of CEL (Table 5).

On subjecting B-TCEL to XRD analysis, the crystallinity index increased to 61.8% from 59.4% after NaOH treatment (Figure 9). It has been speculated that base treatment led to an increase in the pore ratio and surface area of CEL, thus enhancing the CrI, as in line with the previous report.[41] B-TCEL was also subjected to FESEM analysis and found that after NaOH treatment, the FESEM image displayed a smooth surface and permeable structure (Figure 10).[31]

Table 5. Effects of Pre- and Postbase Treatment on Rice Straw[a]

method	treatment	CEL (wt %)	HEM (wt %)	LIG (wt %)	SPA (wt %)	silica removal (%)[e]
NREL	rice straw (NREL)	42.9	23.9	16.7	11.5[c]	10.5
method 1	step 1: NaOH					
	step 2: organosolv	28.3 (19.8)[d]	16.4	02.5	06.0	87.6
method 2	step 1: organosolv	49.9[b]	26.1	07.2		
	step 2: NaOH	36.6 (28.3)[d]			05.9	90.4

[a]Reaction conditions: 500 mg rice straw. Organosolv conditions: 15 mL of 0.1 M organic acid in ethanol/water (1:1), 160 °C, 4 h and base treatment conditions: 0.07 M NaOH, 50 mL water, 70 °C, 4 h. Composition percentage calculation is based on the oven-dried weight of each sample. [b]S-ICEL. [c]On the basis of rice straw calcined at 575 °C for 24 h. [d]The actual amount of CEL present in the CEL fraction is based on the NREL procedure. [e]Based on TGA analysis.
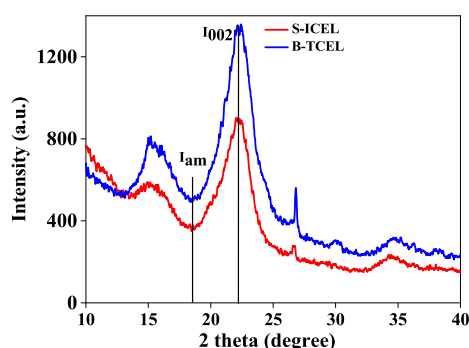

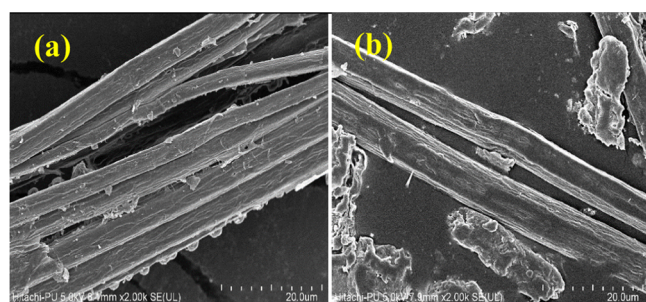**Figure 9.** XRD patterns of CEL before and after NaOH treatment.

Figure 10. FESEM images of (a) S-ICEL and (b) B-TCEL.

4. QUANTIFICATION OF CEL

The components present in the CEL fraction obtained from method 2, as the better one, were quantified. The B-TCEL derived from method 2 was subjected to a slightly modified NREL procedure, in which 50 mg of B-TCEL was taken along with 0.5 mL of 72% sulfuric acid in a 15 mL ace pressure tube and treated for 1 h at room temperature. 5.7 mL of deionized water was then added to the solution, kept in an oil bath at 80 °C, and stirred for 5 h. The aliquots of the sample were thoroughly analyzed in HPLC (mainly sugars) and found that the SRD was composed of 78.0 wt % CEL, 14.4 wt % HEM, 2.4 wt % LIG, and 4.5 wt % SPA with a mass balance of 99.3%. The calculation and quantification of LIG and SPA were done according to the NREL procedure. Moreover, CEL recovered from the employed rice straw using method 2 was 66.0 wt % with respect to rice straw. Similarly, CEL obtained from method 1 was found to be composed of 70.3 wt % CEL and 15.1 wt % HEM, 6.0 wt % LIG and 3 wt % SPA. CEL recovered from method 1 was only 46.2 wt %. Thus, the recovered cellulosic component from rice straw using method 2 is a promising approach; however, the recovery of cellulosic components needs to be improved for achieving near-quantitative recovery.

5. CONVERSION OF CEL TO BUTYL GLUCOSIDES

To emphasize the importance of disintegration and the removal of silica, which could interfere during the catalytic transformation and decrease the yield of the target product, from rice straw, the crude CEL obtained from method 2 (better than method 1 in terms of CEL yield) was subjected to hydrolysis−acetylation reaction as a probe reaction. The hydrolysis of CEL followed by acetylation of glucose is an important reaction to form alkyl glucosides (nonionic surfactants) in corresponding alcohols, which have potential applications in washing and cleaning[47] and pharmaceutical and cosmetic products.[48,49] Generally, microcrystalline CEL has been used as a substrate for the production of alkyl glucoside,[50,51] and producing directly from lignocellulosic biomass-based substrates was scarcely reported.[52,53]

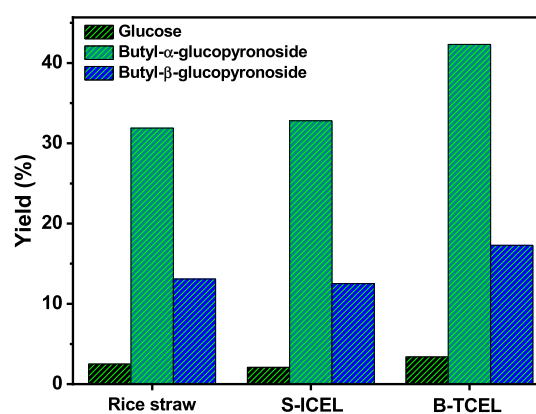Figure 11 shows the results obtained from rice straw and S-ICEL and B-TCEL (before and after the removal of silica).

Figure 11. Production of butyl glycosides from treated and untreated CEL; conditions: CEL = 50 mg, 20 ml butanol, conc of H_2SO_4 = 0.12 M, time = 15 min, temp = 140 °C.

The rice straw yielded 2.5% glucose, 31.9% butyl-α-glucopyranoside, and 13.1% butyl-β-glucopyranoside. Similarly, S-ICEL obtained from method 2 after step 1 gave pretty much the same product distribution (2.1% glucose, 32.8% butyl-α-glucopyranoside, and 12.5% butyl-β-glucopyranoside), indicating the presence of silica lowered the yields of butyl glucosides, though CEL predominantly disintegrated from HEM and LIG (see Table 5 and Section 4). On the other hand, B-TCEL (crude CEL obtained from method 2 after the step) afforded an improved yield of butyl glucosides (42.3% butyl-α-glucopyranoside and 17.3% butyl-β-glucopyranoside) along with 3.4% glucose, demonstrating the significance of the removal of silica from CEL for enhancing the yield of the target product. The crude CEL obtained from method 2 gave 15.5%

higher total yield (Figure 11) than what was obtained from rice straw.

6. CONCLUSIONS

We have demonstrated the removal of silica and disintegration of major components of rice straw with two different two-step approaches in an ethanol−water system in the presence of organic acid. Method 1 (base pretreatment, followed by organosolv treatment with an organic acid) showed not only a lower recovery of CEL but also the substantial decomposition of the major components such as CEL, HEM, and LIG compared to method 2 (organosolv pretreatment with an organic acid, followed by base treatment), revealing a suitable strategic approach for the removal of silica from rice straw and that its disintegration was essential. In method 1, after treating rice straw with an aqueous solution of 0.07 M NaOH at 70 °C for 4 h, the solid recovered was only 70.6 wt %. After the second step of method 1, that is, organosolv treatment with 0.1 M lactic acid in a 1:1 mixture of ethanol/water at 160 °C for 4 h, the recovered solid component was only 28.3 wt % (crude CEL) along with 16.4 wt % HEM and 2.5 wt % LIG from other fractions.

On the other hand, after the first step, method 2 yielded 49.9 wt % S-ICEL along with 26.1 wt % HEM and 7.2 wt % LIG (Table 5), revealing the importance of employing the organosolv pretreatment first for improving the HEM and LIG content. After the second step (base treatment), method 2 yielded 36.6 wt % CEL, which was 8.3 wt % higher than the CEL obtained from method 1. The crude CEL recovered from method 2 was subjected to NREL treatment and found that the crude CEL was composed of 78.0 wt % CEL, 14.4 wt % HEM, 2.4 wt % LIG, and 4.5 wt % SPA with a mass balance of 99.3%, clearly disclosing that treating rice with the organosolv approach first, followed by base treatment improved not only the CEL content but also the mass balance. In a nutshell, CEL recovered from the employed rice straw using method 2 was 66.0 wt % out of the actual CEL (42.9 wt %) content in rice straw. The removal of silica from CEL after the base treatment in method 2 favored improving the yield of butyl glucosides (59.6%) than that from S-ICEL (45.3% butyl glucosides) and rice straw (45.0% butyl glucosides).

◼ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04030.

TGA thermographs; FE-SEM images; FTIR spectra; and determination of silica removal (%) after treating rice straw with aqueous NaOH (PDF)

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Notes

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◼ ABBREVIATIONS

SRD, solid residue; CEL, cellulose; HEM, hemicellulose; LIG, lignin; SPA, silica plus ash; S-ICEL, silica-intertwined cellulose; B-TCEL, base-treated cellulose; ASL, acid-soluble lignin; AIL, acid-insoluble lignin

◼ REFERENCES

(1) World Energy Scenarios 2019. https://www.worldenergy.org/assets/downloads/Scenarios_Report_FINAL_for_website.pdf/ (accessed on 2020-03-20).

(2) Corma, A.; Iborra, S.; Velty, A. Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* **2007**, *107*, 2411−2502.

(3) Van Soest, P. J. Rice straw, the role of silica and treatments to improve quality. *Anim. Feed Sci. Technol.* **2006**, *130*, 137−171.

(4) Food and Agriculture Organization of the United Nations. *Rice Market Monitor*; FAO: Washington, DC, 2017. http://www.fao.org/3/I9243EN/i9243en.pdf/.

(5) Devi, S.; Gupta, C.; Jat, SL.; Parmar, M. S. Crop residue recycling for economic and environmental sustainability: The case of India. *Open Agric.* **2017**, *2*, 486−494.

(6) Sharma, D. D.; Joshi, A. L.; Schiere, J. B.; Ibrahim, M. N. M. Treatment of crop residues: A review, Handbook for straw feedback system in livestock production. *XXXIXTH EAAP General Assembly*; ICAR, 1995; Vol. *44*; pp 263−264.

(7) Wang, W.; Wu, X.; Chen, A.; Xie, X.; Wang, Y.; Yin, C. Mitigating effects of ex situ application of rice straw on CH4 and N2O emissions from paddy-upland coexisting system. *Sci. Rep.* **2016**, *6*, 37402.

(8) Khaleghian, H.; Molaverdi, M.; Karimi, K. Silica removal from rice straw to improve its hydrolysis and ethanol production. *Ind. Eng. Chem. Res.* **2017**, *56*, 9793−9798.

(9) Binod, P.; Sindhu, R.; Singhania, R. R.; Vikram, S.; Devi, L.; Nagalakshmi, S.; Kurien, N.; Sukumaran, R. K.; Pandey, A. Bioethanol production from rice straw: an overview. *Bioresour. Technol.* **2010**, *101*, 4767−4774.

(10) Pekarovic, J.; Pekarovicova, A.; Fleming, III, P. D. Two-step straw processing—a new concept of silica problem solution. *Engineering Pulping and Environmental Conference*; TAPPI, 2006.

(11) Nandiyanto, A. B. D.; Rahman, T.; Fadhlulloh, M. A.; Abdullah, A. G.; Hamidah, I.; Mulyanti, B. Synthesis of silica particles from rice

straw waste using a simple extraction method. *IOP Conf Ser J. Mater. Sci. Eng.*; IOP Publishing, 2016; Vol. *128*; p 01204.

(12) Aujla, M. I.; Rahman, I.; Javaid, A. Mechanism of silica precipitation by lowering pH in chemi-thermomechanical pulping black liquors. *1st WSEAS Int Conf on Comp Chem.*; ACM, 2007; pp 58−62.

(13) Tang, S.; Dong, Q.; Fang, Z.; Miao, Z.-d. Complete recovery of cellulose from rice straw pretreated with ethylene glycol and aluminum chloride for enzymatic hydrolysis. *Bioresour. Technol.* **2019**, *284*, 98−104.

(14) Nasri-Nasrabadi, B.; Behzad, T.; Bagheri, R. Extraction and characterization of rice straw cellulose nanofibers by an optimized chemo mechanical method. *J. Appl. Polym. Sci.* **2014**, *131*, 40063.

(15) Krishania, M.; Kumar, V.; Sangwan, R. S. Integrated approach for extraction of xylose, cellulose, lignin and silica from rice straw. *Bioresour. Technol. Rep.* **2018**, *1*, 89−93.

(16) Fan, G.; Wang, M.; Liao, C.; Fang, T.; Li, J.; Zhou, R. Isolation of cellulose from rice straw and its conversion into cellulose acetate catalyzed by phosphotungstic acid. *Carbohydr. Polym.* **2013**, *94*, 71−76.

(17) Mu, C.; Jiang, M.; Zhu, J.; Zhao, M.; Zhu, S.; Zhou, Z. Isolation of cellulose from steam-exploded rice straw with aniline catalyzing dimethyl formamide aqueous solution. *Renewable Energy* **2014**, *63*, 324−329.

(18) Jiang, M.; Zhao, M.; Zhou, Z.; Huang, T.; Chen, X.; Wang, Y. Isolation of cellulose with ionic liquid from steam exploded rice straw. *Ind. Crops Prod.* **2011**, *33*, 734−738.

(19) Zhao, X.; Cheng, K.; Liu, D. Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis. *Appl. Microbiol. Biotechnol.* **2009**, *82*, 815−827.

(20) Borand, M. N.; Karaosmanoğlu, F. Effects of organosolv pretreatment conditions for lignocellulosic biomass in bio refinery applications: a review. *J. Renewable Sustainable Energy* **2018**, *10*, 033104.

(21) Luo, K.; Wang, Y.; Xiao, H.; Song, G.; Cheng, Q.; Fan, G. Preparation of convertible cellulose from rice straw using combined organosolv fractionation and alkaline bleaching. *IOP Conf Ser Earth Environ. Sci.* **2019**, *237*, 052053.

(22) Nie, X. N.; Liu, J.; She, D.; Sun, R. C.; Xu, F. Physicochemical and structural characterization of hemicelluloses isolated by different alcohols from rice straw. *BioResources* **2013**, *8*, 3817−3832.

(23) Amiri, H.; Karimi, K.; Zilouei, H. Organosolv pretreatment of rice straw for efficient acetone, butanol, and ethanol production. *Bioresour. Technol.* **2014**, *152*, 450−456.

(24) Raita, M.; Denchokpraguy, N.; Champreda, V.; Laosiripojana, N. Effects of alkaline catalysts on acetone-based organosolv pretreatment of rice straw. *3 Biotech* **2017**, *7*, 340.

(25) Zhang, K.; Pei, Z.; Wang, D. Organic solvent pretreatment of lignocellulosic biomass for biofuels and biochemicals: A review. *Bioresour. Technol.* **2016**, *199*, 21−33.

(26) Momayez, F.; Karimi, K.; Karimi, S.; Horváth, I. S. Efficient hydrolysis and ethanol production from rice straw by pretreatment with organic acids and effluent of biogas plant. *RSC Adv.* **2017**, *7*, 50537−50545.

(27) Morone, A.; Pandey, R. A.; Chakrabarti, T. Evaluation of OrganoCat process as a pretreatment during bioconversion of rice straw. *Ind. Crops Prod.* **2017**, *99*, 7−18.

(28) Park, S.; Baker, J. O.; Himmel, M. E.; Parilla, P. A.; Johnson, D. K. Cellulose crystallinity index: Measurement techniques and their impact on interpreting cellulase performance. *Biotechnol. Biofuels* **2010**, *3*, 10.

(29) Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. *Determination of structural carbohydrates and lignin in biomass*; Laboratory. Analytical Procedure. 2008; Vol. *1617*; pp 1−16.

(30) Rafiee, E.; Shahebrahimi, S.; Feyzi, M.; Shaterzadeh, M. Optimization of synthesis and characterization of nanosilica produced from rice husk (a common waste material). *Int. Nano Lett.* **2012**, *2*, 29.

(31) Talib, N. A.; Ahmed, A.; Setapar, S. H.; Khamis, A. K.; Lokhat, D.; Rafatullah, M. Removal of silica from rice straw by using alkaline hydrogen peroxide solution in a fixed bed column. *J. Mater. Environ. Sci.* **2018**, *9*, 864−872.

(32) Okoronkwo, E. A.; Imoisili, P. E.; Olubayode, S. A.; Olusunle, S. O. O. Development of silica nanoparticle from corn cob ash. *Adv. Nanopart.* **2016**, *05*, 135−139.

(33) Xiao, X.; Chen, B.; Zhu, L. Transformation, morphology, and dissolution of silicon and carbon in rice straw-derived biochars under different pyrolytic temperatures. *Environ. Sci. Technol.* **2014**, *48*, 3411−3419.

(34) Schowen, R. L.; Lehninger, A. L.; Nelson, D. L.; Cox, M. M. Principles of biochemistry 2nd ed. (Lehninger, Albert L.; Nelson, David L.; Cox, Michael M.). *J. Chem. Educ.* **1993**, *70*, A223.

(35) Huijgen, W. J. J.; Reith, J. H.; den Uil, H. Pretreatment and fractionation of wheat straw by an acetone-based organosolv process. *Ind. Eng. Chem. Res.* **2010**, *49*, 10132−10140.

(36) Binod, P.; Satyanagalakshmi, K.; Sindhu, R.; Janu, KU.; Sukumaran, R. K.; Pandey, A. Short duration microwave assisted pretreatment enhances the enzymatic saccharification and fermentable sugar yield from sugarcane bagasse. *Renewable Energy* **2012**, *37*, 109−116.

(37) Cao, Y.; Tan, H. Structural characterization of cellulose with enzymatic treatment. *J. Mol. Struct.* **2004**, *705*, 189−193.

(38) Dinh Vu, N.; Thi Tran, H.; Bui, N. D.; Duc Vu, C.; Viet Nguyen, H. Lignin and Cellulose Extraction from Vietnam's Rice Straw Using Ultrasound-Assisted Alkaline Treatment Method. *Int. J. Polym. Sci.* **2017**, *2017*, 1−8.

(39) Nath Barman, D.; Haque, M. A.; Kang, T. H.; Kim, G. H.; Kim, T. Y.; Kim, M. K.; Yun, H. D. Effect of mild alkali pretreatment on structural changes of reed (Phragmites communisTrinius) straw. *Environ. Technol.* **2014**, *35*, 232−241.

(40) Nanayakkara, M. P. A.; Pabasara, W. G. A.; Samarasekara, A. B.; Amarasinghe, D. A. S.; Karunanayake, L. Synthesis and character-ization of cellulose from locally available rice straw. *Moratuwa Engineering Research Conference*; MERCon, 2017; pp 176−181.

(41) He, Y.; Pang, Y.; Liu, Y.; Li, X.; Wang, K. Physicochemical characterization of rice straw pretreated with sodium hydroxide in the solid state for enhancing biogas production. *Energy Fuels* **2008**, *22*, 2775−2781.

(42) Yeng, L. C.; Wahit, M. U.; Othman, N. Thermal and flexural properties of regenerated cellulose (RC)/poly (3-hydroxybutyrate) (PHB) bio composites. *J. Teknol.* **2015**, *75*, 107−112.

(43) Zhou, H.; Long, Y.; Meng, A.; Chen, S.; Li, Q.; Zhang, Y. A novel method for kinetics analysis of pyrolysis of hemicellulose, cellulose, and lignin in TGA and macro-TGA. *RSC Adv.* **2015**, *5*, 26509−26516.

(44) Yang, H.; Yan, R.; Chen, H.; Zheng, C.; Lee, D. H.; Liang, D. T. In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin. *Energy Fuels* **2006**, *20*, 388−393.

(45) Mohtar, S. S.; Tengku Malim Busu, T. N. Z.; Md Noor, A. M.; Shaari, N.; Mat, H. An ionic liquid treatment and fractionation of cellulose, hemicellulose and lignin from oil palm empty fruit bunch. *Carbohydr. Polym.* **2017**, *166*, 291−299.

(46) Fu, G.; He, A.; Jin, Y.; Cheng, Q.; Song, J. Fabrication of hollow silica nanorods using nanocrystalline cellulose as templates. *BioResources* **2012**, *7*, 2319−2329.

(47) Von Rybinski, W. Alkyl Glycosides and Poly alkyl glycosides. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 587−597.

(48) Kahre, J.; Tesmann, H. Alkylpolyglycosides - a new concept for care and compatibility in cosmetic products. *SOFW J.* **1995**, *121*, 598−611.

(49) Busch, P.; Hensen, H.; Tesmann, H. Alkylpolyglycoside - eine neue Tensidgeneration für die Kosmetik / Alkyl Polyglycosides - a New Generation of Surfactants for Cosmetics. *Tenside, Surfactants, Deterg.* **1993**, *30*, 116−121.

(50) Bouxin, F.; Marinkovic, S.; Bras, J. L.; Estrine, B. Direct conversion of xylan into alkyl pentosides. *Carbohydr. Res.* **2010**, *345*, 2469−2473.

(51) Villandier, N.; Corma, A. Transformation of Cellulose into Biodegradable Alkyl Glycosides by Following Two Different Chemical Routes. *ChemSusChem* **2011**, *4*, 508−513.

(52) Boissou, F.; Sayoud, N.; De Oliveira Vigier, K.; Barakat, A.; Marinkovic, S.; Estrine, B.; Jérôme, F. Acid-Assisted Ball Milling of Cellulose as an Efficient Pretreatment Process for the Production of Butyl Glycosides. *ChemSusChem* **2015**, *8*, 3263−3269.

(53) Ma, Y.; Tan, W.; Wang, K.; Wang, J.; Jiang, J.; Xu, J. An Insight into the Selective Conversion of Bamboo Biomass to Ethyl Glycosides. *ACS Sustainable Chem. Eng.* **2017**, *5*, 5880−5886.