Assessment of Instant Catapult Steam Explosion Treatment on Rice Straw for Isolation of High Quality Cellulose

Guangjun Gou,[a] Qi Wang,[a] Wei Xie,[a] Jing Cao,[a] Man Jiang,[a,*] Jing He,[b] and Zuowan Zhou [a,*]

Instant catapult steam explosion (ICSE) was applied to treat rice straw for isolating high quality cellulose. After ICSE treatment under the condition of maintaining the pressure at 2.0 MPa for 11 min, the hemicellulose content decreased to 3.70% from the original 20.10%, and the content of α-cellulose was 72.02%. The enormous explosion power density provided by ICSE turned rice straw into cellulosic fibers with good accessibility, as well as it protected the cellulose fibers from being over-hydrolyzed. All of the straw cellulosic samples were analyzed by scanning electron microscopy (SEM), Fourier transformation infrared spectrometry (FTIR), and X-ray diffraction (XRD) to collectively examine the impact of ICSE treatment on the structure and morphology of the cellulose components. The recycled lignin was also analyzed by two-dimensional nuclear magnification resonance spectrometry (2D NMR) to understand the mechanisms underlying the ICSE treatment.

Keywords: Rice straw; Instant catapult steam explosion (ICSE); Cellulose isolation; Structure analysis

Contact information: a: Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu, 610031, P.R. China; b: Biogas Institute of Ministry of Agriculture, Chengdu, 610041, P.R. China;
** Corresponding authors: zwzhou@swjtu.edu.cn; jiangman1021@163.com*

INTRODUCTION

Rice straw presents good potential as a sustainable resource in the development of natural polymer materials. This potential comes from the efficient isolation of cellulose that is tightly encapsulated by hemicellulose and intercalated by lignin (Oun and Rhim 2016). Pretreatment is a key step to overcome such lignocellulosic biomass recalcitrance, making it loose and digestible (Travaini *et al.* 2016). To date, several pretreatment technologies have been developed, which can broadly be categorized into biological (Li *et al.* 2016), physical (Karimi and Taherzadeh 2016), chemical, physicochemical methods (Liang *et al.* 2016), and some combinations of these processes (Chen and Liu 2015). Generally, the pretreatment step aims to remove the lignin and/or the hemicellulose, simultaneously disrupting the architecture of the plant cell wall, and thus increasing the surface area and cellulose accessibility (Rabemanolontsoa and Saka 2016; Xu *et al.* 2016; Ramos-Suarez *et al.* 2017). Among those pretreatment methods, steam explosion is designated a physico-chemical process: (a) the rapid pressure release causes mechanical rupture on the texture of the straw; and (b) the steaming with high temperature and high pressure leads to autohydrolyzing of hemicelluloses and partially depolymerizing of lignin (Jacquet *et al.* 2015). Steam explosion has been extensively adopted as a pretreatment for lignocellulosic material to improve its enzymatic digestibility or solvent accessibility

(Zhang *et al.* 2017). Most reported steam explosion pretreatments are conducted in pressure devices with a quick-opening ball valve or butterfly valve, and pressure release is not quick enough because valves with diameters much smaller than that of pressurized vessels are employed (Zhang *et al.* 2013; Kataria *et al.* 2017). The severity factor [logR_0] is commonly used to describe the combined effect of temperature and duration of the steaming process (Zhang *et al.* 2017), which represents only the rigorousness of the chemical reaction during steaming and not the intensity of the mechanical effect of explosion process. Yu *et al*. (2012) reported a new explosion apparatus with catapult mode that is principally composed of cylinders and pistons. During the explosion the piston bursts out of the cylinder, akin to a vessel suddenly and very quickly fractured into two halves, after only 0.0875 s. Through the theoretical explosion power density (EPD) analysis, it is obvious that the heat absorbed by the materials is almost all transferred into mechanical rupture force in such a quick depression process (Yu *et al.* 2012). Therefore, it was reasonably claimed to be "a real explosion". With such a catapult mode steam explosion devices, the chemical-mechanical treatment is suspected to be a promising solution, because the structural integrity of natural cellulose is of significant importance for its high value application. The assessment of ICSE treatment on the composition and structure of lignocellulosic biomass, especially on the structure of cellulose, is necessary to predict its potential application. The authors searched the literature and did not find any published work dealing with the effect of ICSE treatment on the quality of cellulose composition.

In this work, the effect of ICSE treatment on rice straw cellulose was studied through both direct characterization of the cellulosic materials and the structural analysis of the recycled hemicelluloses and lignin, according to the recyclable delignification and bleaching procedures reported (Mu *et al.* 2014). Based on a detailed characterization of the feedstock, inter-stage products, and final cellulose products, the mechanism of the ICSE treatment on the main composition of rice straw biomass was clarified. This inference will play a significant role to control the structure and properties of isolated cellulose from lignocellulosic biomass to meet the requirements of different applications.

EXPERIMENTAL

Materials

Air-dried rice straw was cut into pieces with the size of 2 cm to 3 cm in length before ICSE treatment. The feedstock was collected from the suburb of Deyang City in Sichuan Province, China.

Methods

ICSE treatment and the following delignification and bleaching process

The procedure for the ICSE treatment and the following isolation of cellulose is shown in Fig. 1. The ICSE experiments were conducted in a QBS-200B device with a 500-mL chamber from Hebi Gentle Bioenergy Co., Ltd., Hebi, China. The rice straw samples were treated with ICSE under 2.0 MPa, and different steaming times of 5, 7, 9, 11, and 13 min.

The recycled ICSE-treated rice straw was then delignified using water/N,N-dimethyl formamide (DMF; 2:1, *v*:*v*) at 95 °C for 6 h with 0.3 wt% NaOH as the catalyst. The ratio of the ICSE-treated straw (in dry weight) to delignification solvent was 1:30 (g/mL). The solubilized hemicelluloses were obtained by precipitation of the concentrated

filtrates with three volumes of ethanol, and lignin was recovered by precipitation at pH 2.0 that was adjusted with HCl.

The delignified rice straw, called crude cellulose, was bleached in a three-necked flask contained 2 wt% H_2O_2 aqueous solution with a ratio of solid to liquid of 1:30 (g/mL) under magnetic stirring for 4 h at 55 °C and a regulating pH of 11. The crude cellulose was bleached two times to result in the bleached cellulose.

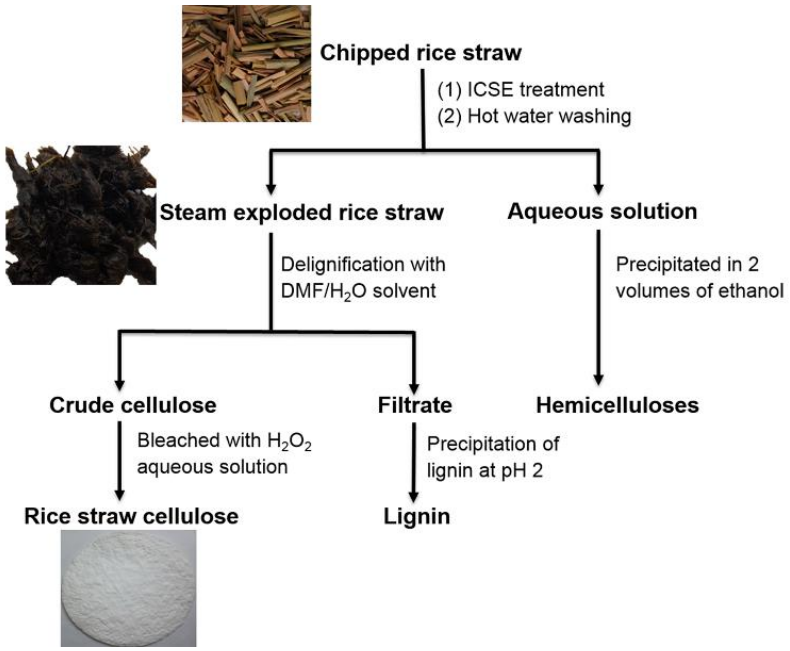

Fig. 1. Flowchart of the ICSE treatment and the following procedures for cellulose isolation

Chemical composition analysis

Acid-insoluble lignin contents in the feedstock, ICSE-treated rice straw, crude cellulose, and bleached cellulose were determined according to the TAPPI T249 cm-85 (1985) standard method. The pentosanes in the original rice straw and the treated samples were analyzed in response to TAPPI T223 cm-01 (2001). The viscosity-average degree of polymerization (DP) of the bleached cellulose was estimated from their intrinsic viscosity ([η]) in cupri-ethylenediamine (CED) solution using the following Eq. 1 (Wang *et al.* 2009):

$$DP^{0.9} = 1.65\ [\eta]/\ mLg^{-1} \quad (1)$$

All of the compositional analyses were conducted in duplicate, and the results were reported as mean values.

Scanning electron microscopy (SEM) analysis

The morphology of the original rice straw and ICSE-treated samples were investigated by a scanning electron microscope (QUANPA200, Philips, Amsterdam, Netherlands). The machine was operated at an acceleration voltage of 20 kV at a working distance of 15 mm to identify the morphological properties of the samples. Before investigation, the samples were sputter-coated with Au to enhance the electrical conductivity.

Fourier transform infrared (FTIR) analysis

The FTIR spectra of all the samples were recorded on a Nicolet 5700 spectrophotometer (Waltham, Massachusetts, USA) in the range of 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1} for 32 scans at 25 °C.

X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) was performed to evaluate the crystalline structure of both the untreated and ICSE-treated samples with a Philips by X'Pert PRO X-ray diffractometer (Philips, Amsterdam, Netherlands) with a Cu Kα radiation, operating at 40 kV voltage and 30 mA current. The diffraction intensities of dried samples placed on a quartz substrate were measured in the range of 5° to 40° 2θ using a step size of 0.02° at a rate of 2°/min. The crystallinity indexes (CrI) of the cellulose samples were calculated according to the method described by Segal *et al*. (1959) using Eq. 2,

$$\text{CrI}\ (\%) = (I_{200} - I_{am}) / I_{200} \times 100 \quad (2)$$

where I_{002} is the maximum intensity of the (002) lattice diffraction peak and I_{am} is the intensity scattered by the amorphous part of the sample. The diffraction peak for the plane (002) is located at a diffraction angle around $2\theta = 22°$ and the intensity scattered by the amorphous part is measured as the lowest intensity at a diffraction angle around $2\theta = 18°$.

2-Dimensional Nuclear Magnetic Resonance Spectroscopy (2D NMR)

The 2D NMR spectra were acquired on a Bruker Avance III 400 MHz instrument (Bruker, Karlsruhe, Germany) equipped with a cryogenically cooled 5-mm TCI gradient probe. Briefly, approximately 40 mg of lignin samples were dissolved in 0.5 mL of dimethyl sulphoxide (DMSO-*d6*), and heteronuclear single quantum coherence (HSQC) experiments were measured using the standard Bruker's "hsqcetgpsisp2.2" pulse program (TopSpin 3.2, Karlsruhe, Germany).

RESULTS AND DISCUSSION

Composition Analysis of the Products During Treatment

Based on the previous optimized operation conditions of 2.5 MPa and 25 min steaming time, using a pilot-scale equipment with a quick opening butterfly valve (the operating pressure releases to atmosphere in 5 s) (Mu *et al.* 2014), the pressure and the steaming duration were decreased to 2.0 MPa and 5 min to 13 min, respectively, in this work. The composition analysis results after ICSE treatment with different steaming times from 5 min to 13 min under 2.0 MPa are included in Table 1.

Table 1. Composition Analysis of the ICSE-treated Rice Straw *

Steaming Time (min)	Hemicellulose (%)	Acid-insoluble Lignin (%)	α-cellulose (%)
0	20.70	15.80	43.12
5	10.44	15.10	68.77
7	7.69	26.62	70.65
9	6.93	25.73	71.12
11	3.70	24.91	72.02
13	3.69	27.90	67.35
*The feedstock was analyzed to contain 20.7% hemicellulose and 15.8% acid-insoluble lignin			

As shown in Table 1, with increased steaming time, the hemicellulose was mainly broken down from the straw texture. The hemicellulose content decreased from 20.7% to 3.69 % with 13 min steaming due to the sufficient hydrolyzing during the high-pressure steaming stage as reported by Zhang *et al*. (2017). During this process, the α-cellulose content increased from 68.8% to 72.0% at first with increased steaming time from 5 min to 11 min, then decreased to 67.4% after 13 min steaming. The acid-insoluble lignin content did not experience as drastic of a change as hemicellulose. During the high-pressure steaming process, autohydrolysis of the hemicellulose component was the main reaction, and lignin-carbohydrate complexes were broken down. At the same time, the content of α-cellulose was comparably increased. From the component analysis of the ICSE-treated rice straw, the chemical function was clearly understood. The ICSE's mechanical rupture effect was further inspected through the delignification experiment and the morphology observation. Table 2 summarizes the component analyses of the delignified samples.

Table 2. Component Analysis of the Crude Celluloses After Delignification

Steaming Time (min)	Acid-insoluble Lignin (%)	Delignification (%) *	Hemicellulose (%)	α-cellulose (%)
0	13.82	12.53	16.62	49.45
5	8.30	45.03	8.30	85.86
7	8.10	69.57	8.10	85.04
9	8.13	68.40	8.13	84.85
11	5.15	79.33	5.15	84.51
13	5.15	81.54	5.15	84.50
* Delignification efficiency was calculated according to: Delignification efficiency (%)=1-lignin content after delignification / lignin content in the ICSE-treated rice straw ×100/100				

As shown in Table 2, the highest delignification reached 90.2% from the ICSE-treated straw under the conditions of 2.0 MPa and 11 min steaming. However, under the same delignification conditions, only 69.0% lignin was removed from the treated straw by the pilot-scale equipment under 2.5 MPa and 25 min (Mu *et al.* 2014). The sudden explosion of ICSE illustrated that the mechanical rupture effect was considerably improved. The contents of hemicellulose and α-cellulose were reasonably increased corresponding to the results shown in Table 1 due to the removal of lignin. To evaluate the ICSE effect on the properties of the straw cellulose, the crude cellulose obtained after delignification was bleached and the component analyses are summarized in Table 3.

Table 3. Component and DP Analyses of the Bleached Cellulose

Steaming Time (min)	Hemicellulose (%)	Acid-insoluble Lignin (%)	α-cellulose (%)	DP *
0	12.64	9.52	55.14	745
5	8.54	4.78	83.82	564
7	7.68	3.54	83.84	550
9	4.24	3.97	83.39	487
11	1.85	2.83	82.13	457
13	1.74	2.42	78.92	442
* DP is degree of polymerization				

The hemicellulose and lignin in the bleached cellulose were further decreased to 1.74% and 2.42%, respectively, from the ICSE-treated straw under the conditions of 2.0

MPa and 11 min steaming. There were no obvious changes in the α-cellulose content for all of the bleached cellulose samples. In previous literature concerning isolated cellulose *via* pilot-scale steam explosion treatment (Mu *et al.* 2014), the DP of bleached cellulose was 549, which was similar to the sample treated with ICSE under the conditions of 2.0 MPa and 7 min.

Morphological Changes After the ICSE Treatment

The SEM images (Figs. 2a through 2f) depict the surfaces of the rice straw before and after ICSE treatment with different steaming times (5, 7, 9, 11, and 13 min, respectively). The treated rice straw with ICSE was washed with hot water with a solid to liquor ratio of 1:20 (g/mL) and dried prior to SEM analysis.

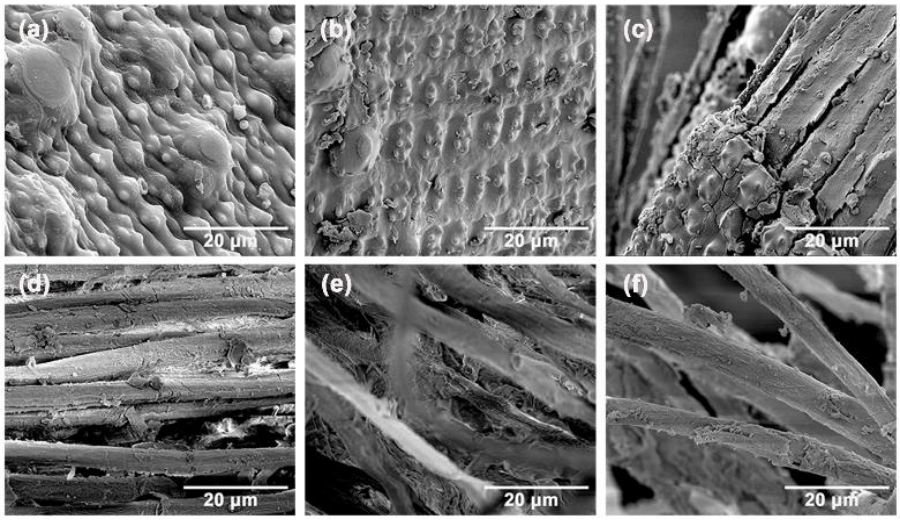

Fig. 2. SEM images of the rice straw before (a) and after ICSE treatment at 2.0 MPa with different steaming time: 5 min (b), 7 min (c), 9 min (d), 11 min (e), and 13 min (f)

As shown in Fig. 2a, the morphology of rice straw exhibited large lumps that were similar to previous reports (Swain and Krishnan 2015). With 3 min or 5 min steaming (Fig. 2b and 2c), the rice straw was not obviously ruptured. By increasing the steaming time to 9 min (Fig. 2d), most of the rice straws began to explode into strips, and when the steaming time was extended to 11 min (Fig. 2e), the straw exploded into thin strips with small fibers scattering. After 13 min steaming (Fig. 2f), the ICSE-treated straw was fibrillary in morphology with clear broken fibers. These results agreed well with the chemical component analyses, of which the α-cellulose content considerably decreased when the steaming time was prolonged to 13 min during the ICSE process, as shown in Table 1.

FTIR Spectra of the ICSE Pretreated Rice Straw and Recycled Hemicellulose

Infrared spectroscopy has been accepted as a useful method to study the physicochemical structures and configurations of carbohydrates (Auxenfans *et al.* 2017). Herein, the FTIR spectra of rice straw before and after ICSE pretreated with different steaming times and the corresponding recycled hemicelluloses are illustrated in Fig. 3.

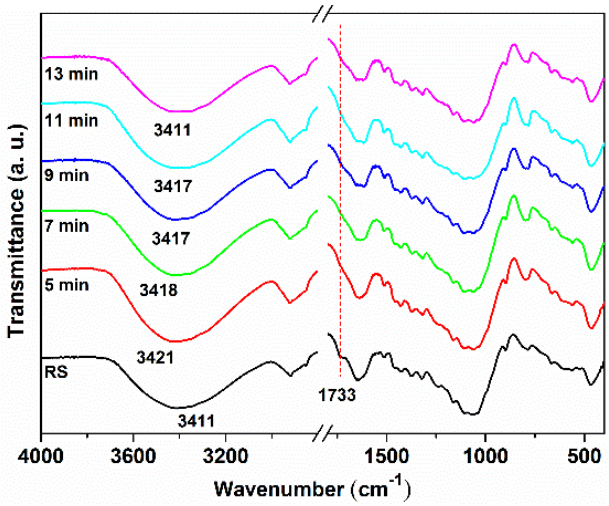

Fig. 3. FTIR spectra of the rice straw before (RS) and after ICSE treatment with different steaming times (5, 7, 9, 11, and 13 min)

Compared with the original rice straw (RS) in Fig. 3, the weak peak at 1733 cm^{-1} that was ascribed to stretching of C=O in hemicelluloses weakened and disappeared in the ICSE-treated samples with increased steaming time. This is due to the reduction of hemicellulose during steam explosion (Swain and Krishnan 2015). The absorptions between 3000 cm^{-1} and 4000 cm^{-1} that were attributed to the stretching of hydroxyl groups, were useful for understanding the formation of hydrogen bond in sugar and glycoside molecules. The red shift associated with intermolecular hydrogen bonds could be observed when -OH acts as both the hydrogen bond donor and acceptor (Kawamoto *et al.* 2014). The 10 cm^{-1} blue shift (from 3411 cm^{-1} to 3421 cm^{-1}) resulted from the weakening of hydrogen bonds between the cellulose and hemicellulose (Dai and Fan 2011; Zhang *et al*. 2011). However, the 10 cm^{-1} red shift (from 3421 cm^{-1} to 3411 cm^{-1}) when steaming time increased from 5 min to 13 min was due to gradual removal of hemicellulose and formation of a new stronger intermolecular hydrogen bonding system among cellulose (Yuan *et al*. 2013). The hemicellulose fractions were analyzed by FTIR spectra, as shown in Fig. 4.

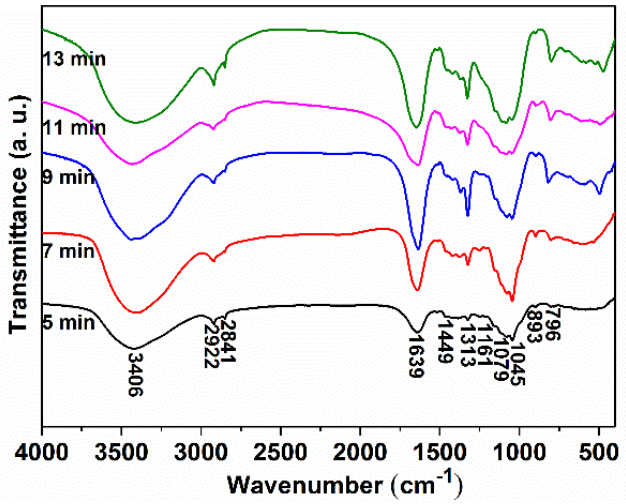

Fig. 4. The recycled hemicellulose fractions with ICSE treatment for different steaming times (5, 7, 9, 11, and 13 min

As shown in Fig. 4, there was no notable difference among these samples. These results provided further evidence that ICSE mainly effected breaking down the hydrogen bonds between hemicellulose and cellulose in rice straw. The signal at 3406 cm^{-1} was associated with the stretching vibration of the hydroxide group. The peaks at 2922 cm^{-1} and 2841 cm^{-1} were attributed to C-H stretching. The adsorption at 1639 cm^{-1} was probably related to the bending mode of absorbed water, because the hemicellulosic polymer usually has strong affinity to water (Zhang *et al.* 2015). The peaks at 1161 cm^{-1}, 1079 cm^{-1}, and 1045 cm^{-1} were assigned to the typical Arabia xylan. A weak sharp absorption band at 893 cm^{-1} was indicative of the *β*-configuration of the 1→4 glycosidic bond between xylopyranose (Xylp) units of the xylan chains in hemicellulose (Bian *et al.* 2012). The adsorption at 793 cm^{-1} was assigned to the C-C stretching of the sugar ring.

The 2D NMR Spectra of the Recycled Lignin

To further reveal the structural transformation of lignin during the ICSE treatment, two recycled lignin samples were selected to be investigated by 2D-HSQC NMR spectra. The side chain (δC/δH 50 to 90/2.5 to 6.0) and the aromatic (δC/δH 100 to 150/5.5 to 8.0) regions of the HSQC spectra of the lignin samples are shown in Fig. 5. The main lignin cross signals assigned in the HSQC spectra are listed in Table 4, and the main lignin substructures present are shown in Fig. 6.

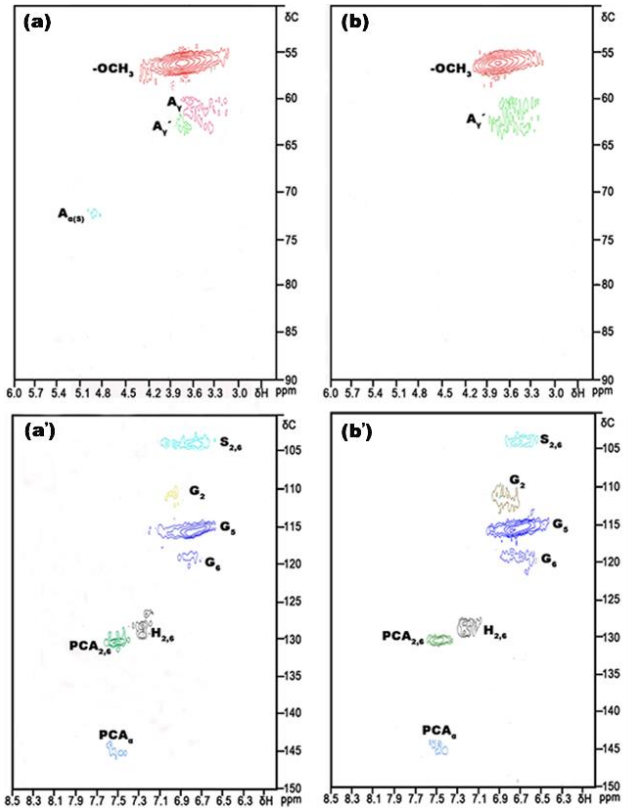

Fig. 5. Side chains (δC/δH 50-90/2.5-6.0) and aromatic/unsaturated regions (δC/δH 100-150/6.0-8.5) in the 2D HSQC NMR spectra of the recycled lignin with different ICSE treatment conditions: (a, a´) 2.0 MPa and 5 min; (b, b´) 2.0 MPa for 13 min

Table 4. Assignments of ^{13}C-^{1}H Correlation Signals in the 2D HSQC Spectra of the Recycled Lignin

Label	δ_C/δ_H (ppm)	Assignment
-OCH_3	56.3/3.72	C-H in methoxyls
A_γ	60.7/3.62	C_γ-H_γ in γ hydroxylated *β*-O-4′ substructures (**A**)
$A_{\gamma'}$	63.4/3.67	C_γ-H_γ in γ-acylated *β*-O-4′substructures (**A′**)
$A_{\alpha(S)}$	72.3/4.89	C_α-H_α in *β*-O-4′ substructures (**A**) linked to a S-unit
$S_{2,6}$	104.2/6.70	C_2-H_2 and C_6-H_6 in etherified syringyl units (**S**)
G_2	111.1/6.92	C_2-H_2 in guaiacyl units (**G**)
G_5	116.0/6.74	C_5-H_5 in guaiacyl units (**G**)
G_6	119.3/6.75	C_6-H_6 in guaiacyl units (**G**)
$H_{2,6}$	128.6/7.23	$C_{2,6}$-$H_{2,6}$ in *p*-hydroxyphenyl units (**G**)
$PCA_{2,6}$	130.7/7.44	C_2-H_2 and C_6-H_6 in p-coumarate (**PCA**)
PCA_α	144.4/7.53	C_α-H_α in *p*-coumarate (**PCA**)

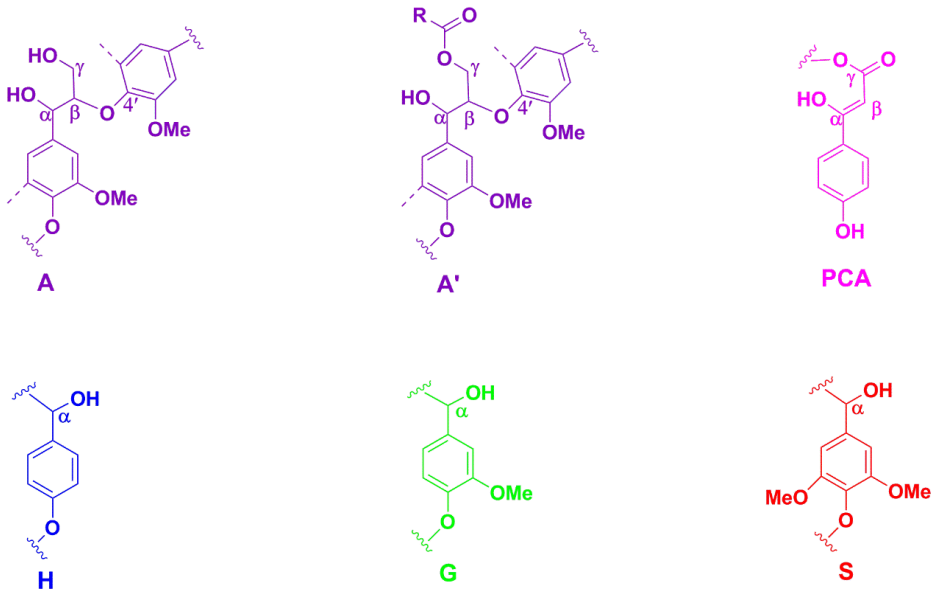

Fig. 6. Main classical substructures, involving different side-chain linkages, and aromatic units identified by 2D NMR of rice straw lignin obtained from various steam explosion conditions: (**A**) β-O-4′ alkyl-aryl ethers; (**A′**) *β*-O-4′ alkyl-aryl ethers with acylated γ-OH; (**PCA**) *p*-coumarates; (**H**) *p*-hydroxyphenyl units; (**G**) guaiacyl unites; and (**S**) Syringyl units

The inter-unit linkages in the lignin *β*-ether (A, *β*-O-4′) were identified due to the presence of cross-peaks at δC/δH 63.4/3.67 (Aγ′). The cross-peaks of methoxy groups in the lignin (-OCH_3, δC/δH 56.3/3.72) were clearly observed. However, the substructure (Aγ) and (Aα(S)) were not found in the HSQC spectrum of lignin isolated from rice straw under 2.0 MPa pressure and 13 min steaming, due to the depolymerization of lignin (Heikkinen *et al.* 2014).

The aromatic lignin units syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) units showed prominent correlations at δC/δH 104.2/6.70 (S2, 6), 111.1/6.92 (G2), 116.0/6.74 (G5), 119.3/6.75 (G6), and 128.6/7.23 (H2, 6), respectively. Therefore, the lignin was guaiacyl-syringyl-*p*-hydroxyphenyl (GSH) type. The signals corresponding to p-coumarate (PCA) and ferulate (FA) structures showed prominent correlations at δC/δH 130.7/7.44

(PCA2, 6), 144.4/7.53 (PCAα), which were typically identified in gramineous plant lignin (del Rio *et al.* 2012; Lan *et al.* 2015; Rencoret *et al.* 2015).

X-ray Diffraction of the Rice Straw Samples Before and After ICSE Treatment

X-ray diffraction (XRD) was further applied to understand the transformation of the crystal structure of cellulose components in the rice straw during the ICSE process, as shown in Fig. 7.

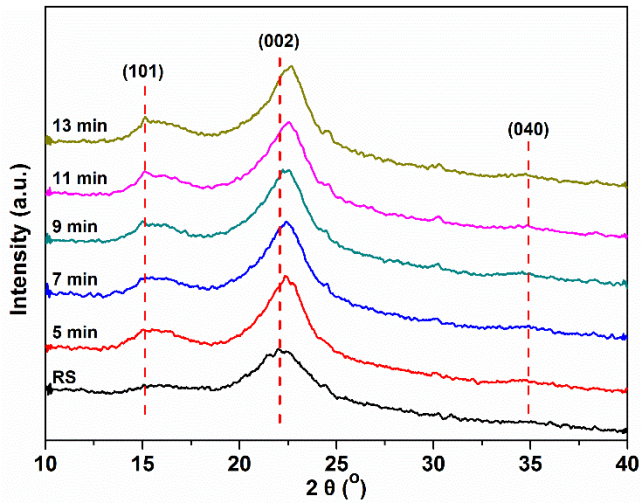

Fig. 7a. X-ray diffraction spectra of the rice straw specimens before and after ICSE treatment with different steaming times (5, 7, 9, 9, 11, and 13 min)

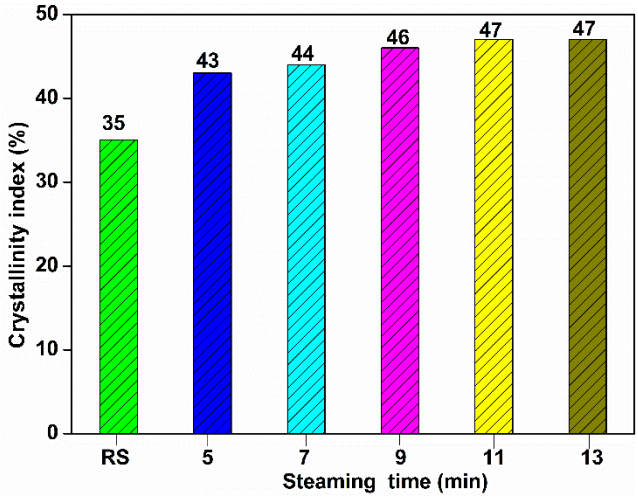

Fig. 7b.The crystallinity index of the rice straw specimens before and after ICSE treatment with different steaming times (5, 7, 9, 9, 11, and 13 min)

Cellulose has a well-pronounced crystalline structure due to hydrogen bonding and Van der Waals' interactions that exist between the adjacent cellulose molecules compared to those amorphous components such as hemicellulose and lignin (Chirayi *et al.* 2014). As shown in the XRD patterns (Fig. 7a), both the original and the ICSE-treated rice straw samples exhibited typical cellulose I crystalline structure, according to the diffraction peaks

around 15.1°, 22.8°, and 34.9°, corresponding to (101), (002), and (004) planes, respectively (Matsumura *et al.* 2000). Compared with the original rice straw, the XRD patterns of the ICSE-treated samples became sharper due to the increase of the degree of crystallinity of cellulose isolated from rice straw.

Figure 7b shows the degree of crystallinity increased from 35% in the original rice straw to 47% in the ICSE-treated sample, which was calculated based on the XRD analysis. The increase in crystallinity of treated rice straw is due to the removal of amorphous components during the ICSE process (Kim *et al.* 2013). It was reported that treatment in some cases would increase the rice straw crystallinity due to the removal or reduction of more easily available amorphous cellulose (Wang *et al.* 2009). Moreover, removal of the amorphous components, lignin and hemicellulose, also contributed to the increase of the crystallinity.

CONCLUSIONS

1. Instant catapult steam explosion provides an effective potential treatment to isolate high quality cellulose from lignocellulose biomass. Such "real explosions" produce enormous explosion power density, which resulted in good accessibility of the treated straw biomass for further delignification.
2. The comparable moderate conditions (2.0 MPa and 11 min), compared with the valve mode apparatus (2.5 MPa and 25 min), were a benefit for protecting the cellulose fibers from being over hydrolyzed and caused some loss in the DP of cellulose.
3. The crystallinity of the cellulose component increased after ICSE treatment, which mainly resulted from the efficient removal of amorphous hemicellulose.

ACKNOWLEDGMENTS

The authors appreciate the financial support from the National Natural Science Foundation of China (Grant No. 51303151), the Sichuan Province Youth Science and Technology Innovation Team (2016TD0026), and the Key Laboratory of Advanced Technologies Materials, Ministry of Education.

REFERENCES CITED

Auxenfans, T., Crônier, D., Chabbert, B., and Paës, G. (2017). "Understanding the structural and chemical changes of plant biomass following steam explosion pretreatment," *Biotechnol. Biofuels* 10(1), 1-16. DOI: 10.1186/s13068-017-0718-z

Bian, J., Peng, F., Peng, X. P., Xu, F., Sun, R. C., and Kennedye, J. F. (2012). "Isolation of hemicelluloses from sugarcane bagasse at different temperatures: Structure and properties," *Carbohyd. Polym.* 88(2), 638-645. DOI: 10.1016/j.carbpol.2012.01.010

Chen, H. Z., and Liu, Z. H. (2015). "Steam explosion and its combinatorial pretreatment refining technology of plant biomass to bio-based products," *Biotechnol. J.* 10(6), 866-885. DOI: 10.1002/biot.201400705

Chirayi, C. J., Joy, J., Mathew, L., Mozetic, M., Koetz, J., and Thomas, S. (2014). "Isolation and characterization of cellulose nanofibrils from *Helicteres isora* plant," *Ind. Crop. Prod.* 59(2), 27-34. DOI: 10.1016/j.indcrop.2014.04.020

del Rio, J. C., Rencorett, J., Prinsen, P., Martinez, A. T., Ralph, J., and Gutierrez, A. (2012). "Structural characterization of wheat straw lignin as revealed by analytical pyrolysis 2D-NMR, and reductive cleavage methods," *J. Agr. Food Chem.* 60(23), 5922-5935. DOI: 10.1021/jf301002n

Heikkinen, H., Elder, T., Maaheimo, H., Rovio, S., Rahikainen, J., Kruus, K., and Tamminen, T. (2014). "Impact of steam explosion on the wheat straw lignin structure studied by solution-state nuclear magnetic resonance and density functional methods," *J. Agr. Food. Chem*. 62(43), 10437-10444. DOI: 10.1021/jf504622j

Jacquet, N., Maniet, G., Vanderghem, C., Delvigne, F., and Richel, A. (2015). "Application of steam explosion as pretreatment on lignocellulosic material: A review," *Ind. Eng. Chem. Res.* 54(10), 2593-2598. DOI: 10.1021/ie503151g

Karimi, K., and Taherzadeh, M. J. (2016). "A critical review of analytical methods in pretreatment of lignocelluloses: Composition, imaging, and crystallinity," *Bioresource Technol.* 200(23), 1008-1018. DOI: 10.1016/j.biortech.2015.11.022

Kataria, R., Mol, A., Schulten, E., Happel, A., and Mussatto, S. I. (2017). "Bench scale steam explosion pretreatment of acid impregnated elephant grass biomass and its impacts on biomass composition, structure and hydrolysis," *Ind. Crop. Prod.* 106, 48-58. DOI: 10.1016/j.indcrop.2016.08.050

Kawamoto, H., Hosoya, T., Ueno, Y., Taeko, S., and Saka, S. (2014). "Thermal stabilization and decomposition of simple glycosides in the presence of aromatic substances in closed ampoules: The role of OH• • • π hydrogen bonding," *J. Anal. Appl. Pyrol.* 109, 41-46. DOI: 10.1016/j.jaap.2014.07.015

Kim, S. B., Lee, S. J., Lee, J. H., Jung, Y. R., Thapa, L. P., Kim, J. S., Um, Y., Park, C., and Kim, S. W. (2013). "Pretreatment of rice straw with combined process using dilute sulfuric acid and aqueous ammonia," *Biotechnol. Biofuels* 6(1), 109-119. DOI: 10.1186/1754-6834-6-109.

Lan, W., Lu, F. C., Regner, M., Zhu, Y. M., Rencoret, J., Ralph, S. A., Zakai, U. I., Morreel, K., Boerjan, W., and Ralph, J. (2015). "Tricin, a flavonoid monomer in monocot lignification," *Plant Physiol.* 167(4), 1284-1295. DOI: 10.1104/pp.114.253757

Liang, L., Li, J., Zeng, J., Ma, N., An, Y., Ju, R., and Wang, Q. (2016). "Effects of steam explosion on bagasse specific surface area and grafting degree of acrylamide-grafted bagasse," *BioResources* 11(3), 6185-6192. DOI: 10.15376/biores.11.3.6185-6192

Li, M., Han, G., Song, Y., Jiang, W., and Zhang, Y. (2016). "Structure, composition, and thermal properties of cellulose fibers from *Pueraria lobata* treated with a combination of steam explosion and laccase mediator system," *BioResources* 11(3), 6854-6866. DOI: 10.15376/biores.11.3.6854-686

Matsumura, H., Sugiyand, J., and Glasser, W. G. (2000). "Cellulosic nanocomposites. I. thermally deformable cellulose hexanoates from heterogeneous reaction," *J. Appl. Polym. Sci.* 78(13), 2242-2253. DOI: 10.1002/1097-4628(20001220)78:13<2242::AID-APP20>3.0.CO;2-5

Mu, C. Y., Jiang, M., Zhu, J., Zhao, M. M., Zhu, S. B., and Zhou, Z. W. (2014). "Isolation of cellulose from steam-exploded rice straw with aniline catalyzing dimethyl formamide aqueous solution," *Renew. Energ.* 63(1), 324-329. DOI: 10.1016/j.renene.2013.09.016

Oun, A. A., and Rhim, J. W. (2016). "Isolation of cellulose nanocrystals from grain straws and their use for the preparation of carboxymethyl cellulose-based nanocomposite films," *Carbohyd. Polym.* 150, 187-200. DOI: 10.1016/j.carbpol.2016.05.020

Rabemanolontsoa, H., and Saka, S. (2016). "Various pretreatments of lignocellulosics," *Bioresource Technol.* 199, 83-91. DOI: 10.1016/j.biortech.2015.08.029

Ramos-Suarez, J. L., Gomez, D., Regueiro, L., Baeza, A., and Hansen, F. (2017). "Alkaline and oxidative pretreatments for the anaerobic digestion of cow manure and maize straw: Factors influencing the process and preliminary economic viability of an industrial application," *Bioresource Technol.* 241, 10-20. DOI: 10.1016/j.biortech.2017.05.054

Rencoret, J., Prinsen, P., Gutierrez, A., Martıńez, A. T., and del Río, J. C. (2015). "Isolation and structural characterization of the milled wood lignin, dioxane lignin, and cellulolytic lignin preparations from brewer's spent grain," *J. Agr. Food Chem.* 63(2), 603-613. DOI: 10.1021/jf505808c

Segal, L., Creely, J. J., Martin, A. E., and Conrad, C. M. (1959). "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer," *Text. Res. J.* 29(10), 786-794. DOI: 10.1177/004051755902901003

Swain, M. R., and Krishnan, C. (2015). "Improved conversion of rice straw to ethanol and xylitol by combination of moderate temperature ammonia pretreatment and sequential fermentation using *Candida tropicalis*," *Ind. Crop. Prod.* 77, 1039-1046. DOI: 10.1016/j.indcrop.2015.10.013

TAPPI T249 cm-85 (1985). "Carbohydrate composition of extractive-free wood and wood pulp by gas chromatography," TAPPI Press, Atlanta, GA.

TAPPI T223 cm-01 (2001). "Pentosans in wood and pulp," TAPPI Press, Atlanta, GA.

Travaini, R., Martin-Juarez, J., Lorenzo-Hernando, A., and Bolado-Rodriguez, S. (2016). "Ozonolysis: An advantageous pretreatment for lignocellulosic biomass revisited," *Bioresource Technol.* 199, 2-12. DOI: 10.1016/j.biortech.2015.08.143

Wang, K., Jiang, J. X., Xu, F., and Sun, R. C. (2009). "Influence of steaming explosion time on the physic-chemical properties of cellulose from Lespedeza stalks (*Lespedeza crytobotrya*)," *Bioresource Technol.* 100(21), 5288-5294. DOI: 10.1016/j.biortech.2009.05.019

Xu, H. F., Li, B., and Mu, X. D. (2016). "Review of alkali-based pretreatment to enhance enzymatic saccharification for lignocellulosic biomass conversion," *Ind. Eng. Chem. Res.* 55(32), 8691-8705. DOI: 10.1021/acs.iecr.6b01907

Yu, Z. D., Zhang, B. L., Yu, F. Q., Xu, G. Z., and Song, A. D. (2012). "A real explosion: The requirement of steam explosion pretreatment," *Bioresource Technol.* 121, 335-341. DOI: 10.1016/j.biortech.2012.06.055

Zhang, P., Dong, S. J., Ma, H. H., Zhang, B. X., Wang, Y. F., and Hu, X. M. (2015). "Fractionation of corn stover into cellulose, hemicellulose and lignin using a series of ionic liquids," *Ind. Crop. Prod*. 76, 688-696. DOI: 10.1016/j.indcrop.2015.07.037

Zhang, X., Yuan, Q., and Cheng, G. (2017). "Deconstruction of corncob by steam explosion pretreatment: Correlations between sugar conversion and recalcitrant structures," *Carbohyd. Polym.*156, 351-356. DOI: 10.1016/j.carbpol.2016.09.044

Zhang, Y. Z., Wang, L., and Chen, H. Z. (2013). "Formation kinetics of potential fermentation inhibitors in a steam explosion process of corn straw," *Appl. Biochem. Biotech.* 169(2), 359-367. DOI: 10.1007/s12010-012-9961-8

Article submitted: November 28, 2017; Peer review completed: January 20, 2018; Revised version received and accepted: January 29, 2018; Published: February 7, 2018.
DOI: 10.15376/biores.13.2.2328-2341