Enhancing the Fractionation Efficiency of Hemicellulose from Agricultural Waste using Expansion Pretreatment

Miao Wu,[a] Jin-Hui Pang,[b] Ping-Ping Song,[c] Xue-Ming Zhang,[c,*] and Jian-Jun Peng [a,*]

Hemicellulosic fractions isolated from agricultural wastes (rice straw and rice husk) were investigated using expansion pretreatment and subsequent alkali extraction, which is a method that combines the advantages of extrusion and milder steam explosion. The structure of the obtained hemicellulosic samples was determined by high-performance anion-exchange chromatography (HPAEC), Fourier transform infrared spectroscopy (FT-IR), 2D heteronuclear single quantum coherence nuclear magnetic resonance (NMR) spectroscopy, and thermogravimetric analysis (TGA). The expansion pretreatment resulted in a remarkable increase in the hemicellulose extraction efficiency from the rice straw compared with that of the controlled sample, while that from the rice husk was relatively unnoticeable. It was concluded from the FT-IR, molecular weight, sugar analysis, and NMR spectra results that the molecular weights of the hemicellulosic fractions extracted with this process significantly decreased and then rose, which was probably due to the prominent degradation and then generation of condensation substances. Moreover, the obtained hemicelluloses of the rice husk had a relatively more linear polymer structure than the rice straw. Considering the extraction efficiency and composition of each component, the expansion pretreatment was confirmed to be a promising method for the comprehensive separation and utilization of agricultural wastes.

Keywords: Expansion pretreatment; Agricultural waste; Hemicellulose; 2D HSQC NMR

*Contact information: a: National Engineering Laboratory for Pulp and Paper, China National Pulp and Paper Research Institute, Beijing, 100102, P. R. China; b: College of Marine Science and Biological Engineering, Qingdao University of Science and Technology, Qingdao, 266042, P. R. China; c: Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing, 100102, P. R. China; * Corresponding author: xm_zhang@bjfu.edu.cn; jjpeng@163.com*

INTRODUCTION

To meet the energy demand and need for global climate stability, research has focused on renewable resources, particularly agricultural crop wastes (Luque *et al.* 2008). Only a minor portion of agricultural crop wastes is reserved for animal feed or household fuel, while a huge quantity is mainly burnt in fields (Xiao *et al.* 2001). Rice is the second largest cereal crop in the world after wheat and produces the largest amount of crop residues (approximately 330 million MT) (Van Soest 2006). Hence, the main residues from rice (rice straw and rice husk) are abundant and potential resources for the utilization of carbon dioxide-neutral renewable energy, fuels, chemicals, and biomaterials (Westbye *et al.* 2008).

Similar to wood, agricultural wastes also mainly consist of polysaccharides (cellulose and hemicellulose) and lignin. Hemicellulose is the second most abundant polysaccharide after cellulose (Sun *et al.* 2001). Unlike cellulose, hemicelluloses are heterogeneous polymers with pentoses (D-xylose and L-arabinose), hexoses (D-mannose,

D-glucose, D-galactose, and L-rhamnose), and sugar acids (D-glucuronic acid, D-galacturonic acid, and 4-*O*-methyl-D-glucuronic acid) that are arranged in different proportions with different substituents (Bian *et al.* 2010b; Wang *et al.* 2010b). Generally, xylan represents the most common hemicellulose constituent and possesses a backbone of *β*-(1→4)-linked D-xylosyl units. While specific hemicellulose compositions vary remarkably in different plants, softwood hemicelluloses primarily contain galactoglucomannans, hardwood hemicelluloses mostly contain glucuronoxylans, and herbaceous crop hemicelluloses mainly contain glucuronoarabinoxylans (Izydorczyk and Biliaderis 1995; Bian *et al.* 2010a). Because of structural varieties and diversities, hemicelluloses can be utilized as hydrogels, thickeners, emulsifiers, stabilizers, and binders in various industries, including the food, pharmaceutical, agricultural, and cosmetic industries (Spiridon and Popa 2008). Moreover, hemicelluloses have been efficiently converted to a large number of chemicals, such as xylitol, furfural, levulinic acid, lactic acid, succinic acid, and others *via* chemical and biotechnological methods (Neureiter *et al.* 2004). However, hemicelluloses are closely associated with cellulose and lignin by hydrogen bonds and covalent bonds (mainly R-benzyl ether linkages), and are simultaneously linked with acetyl units and hydroxycinnamic acids by ester linkages, which restrict the release of hemicellulosic components from cell wall matrices (Peng *et al.* 2009). Therefore, to realize the wide application of hemicellulose, appropriate processes are needed for the effective and integrated extraction of hemicellulose.

Currently, various extraction methods have been developed to separate hemicellulosic components from plant materials, such as alkaline extraction, alkaline peroxide extraction, organic solvent treatment, mechanical-chemical treatment, liquid hot water extraction, steam explosion-based extraction, *etc.* (Peng *et al.* 2012). Among these different techniques, steam explosion has been confirmed to be a potential pretreatment method for fractionating lignocellulosic materials into three major components, which is effective not only for wood, but also for agricultural residues (Emmel *et al.* 2003; Sun *et al.* 2005). During this process, hemicelluloses are partially degraded into soluble sugars by organic acids, mainly acetic acid derived from the acetylated hemicelluloses in straw (Sun *et al.* 2005). In the previous work by the authors, a relatively mild and continuous new expansion pretreatment method using an expanding and softening device was studied to treat agricultural waste, during which the cell wall can be completely destroyed, and the extensive degradation of sugars and polymerization of lignin can be avoided (Wu *et al.* 2013). The procedures of this treatment method are as follows: firstly, the material is fed by feeding screw and the moisture is adjusted by constant monitoring. The compression screw is fitted with a motor to control the screw speed. The transition zone and die section temperature increases during the extrusion of the biomass samples due to the compression and friction. When the treated materials finally reach the die section, the pressure is released and the treated materials are exploded. During this process, the water content is one of the important parameters, which not only affects the production index, but also the extrusion effect of materials (Chinnaswamy and Hanna 1988; Zhang *et al.* 2010). The remarkable advantage of this treatment method is that both the screw extrusion and mild steam explosion are combined into a single process. This process is more environmentally friendly by not adding chemicals or generating waste water, and it has relatively lower energy costs (22 W/kg to 27.5 W/kg) compared with steam explosion because it does not need a steam generator or pressurized container (Zhu and Pan 2010).

Moreover, the results of the previous study also confirmed that the expansion pretreatment resulted in an increased lignin extraction efficiency, which indicated it is a promising pretreatment method for the separation of lignin, though it was accompanied by mild condensation (Wu *et al.* 2013). Therefore, the purpose of the present study was to explore the effect of the expansion treatment on hemicellulosic fractions, which can assist in integrally analyzing the reaction course and promoting the further utilization of hemicellulosic fractions. Specifically, the hemicellulosic samples obtained from the raw and expanded agricultural residues (rice straw and rice husk) were comparatively characterized with spectroscopic and chromatographic techniques, *i.e.* Fourier transform infrared spectroscopy (FT-IR), high-performance anion exchange chromatography (HPAEC), 2D heteronuclear single quantum coherence (2D HSQC) NMR spectroscopy, and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

The rice straw and rice husk used in this experiment were obtained from the suburban area of Anhui province, China, and were preliminarily treated in the manner that was previously reported by Wu *et al.* (2013). The raw material was extracted with acetone for 24 h and then dried at 60 °C for 16 h. All of the chemical reagents used were of analytical grade.

Expanding Pretreatment Procedures

The expansion pretreatment process was performed using a rub stone device (PX-30E, Maywa Co. Ltd., Ishikawa, Japan), as reported in the previous literature (Wu *et al.* 2013). The specific procedure involved three steps: (i) the moisture content of the material was adjusted to 15% to 20% (wt.%); (ii) the material was treated with extrusion, while the temperature increased to the range of 120 °C to 150 °C because of compression and friction; and (iii) the extruded material expanded as the pressure was released.

Fractionation of the Hemicellulosic Fractions

After the expansion pretreatment, the hemicellulosic fractions from the raw and expanded rice straw, and rice husk were isolated following the previously published method (Wu *et al.* 2013), as described in Fig. 1. Specifically, the expanded samples were extracted with 1 M NaOH at 50 °C for 3 h with a solid-to-liquid ratio of 5% (w/v). Afterwards, the filtered liquid was neutralized to a pH of 5 to 6 with 6 M HCl. It was then concentrated under vacuum and precipitated with three volumes of 95% ethanol. Finally, the hemicellulose obtained was filtered, dialyzed for removing salts, concentrated, and freeze-dried.

Similarly, the hemicellulosic fractions isolated from the unexpanded raw rice straw and rice husk were also isolated with the same procedure as described above. The hemicellulosic samples extracted from the raw rice straw, expanded rice straw with a 15% water content, expanded rice straw with a 20% water content, raw rice husk, and expanded rice husk with a 15% water content were labeled as RS, RS_{15}, RS_{20}, RH, and RH_{15}, respectively.

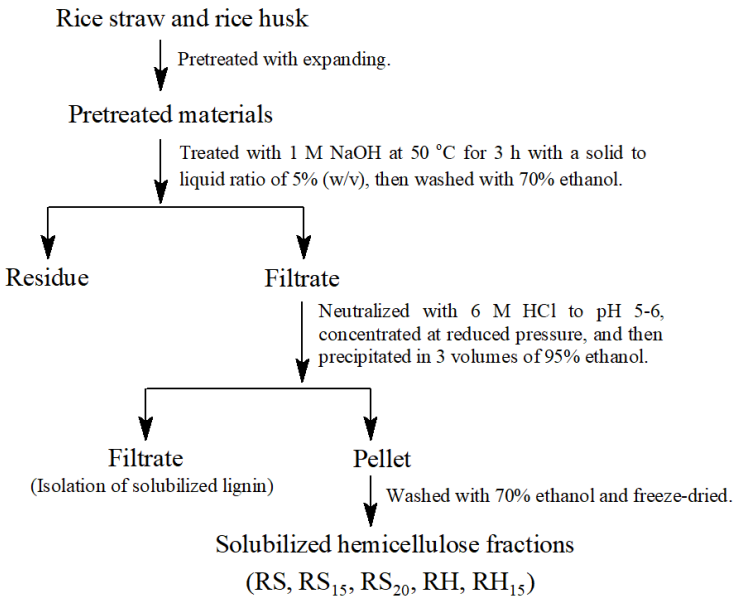


Fig. 1. Scheme for the extraction of the alkali hemicellulosic fractions from the rice straw and rice husk

Characterization of the Isolated Hemicellulosic Fractions

Yield analysis

The extraction efficiency of the isolated hemicellulosic samples was calculated by the following formula.

$$\text{Yield (\%)} = \frac{m_1}{m_2 \times H_x} \times 100 \quad (1)$$

where m_1 and m_2 are the amounts of the obtained hemicellulosic fractions and raw materials added in the NaOH extraction, respectively. H_x is the corresponding hemicellulose content of all the raw and expanded materials, which is determined by a standard method of National Renewable Energy Laboratory's (NREL) (Sluiter *et al.* 2011).

Molecular weight determination

The molecular weights of the hemicellulosic fractions were determined by gel permeation chromatography on a PL aquagel-OH 50 column (300×7.7 mm, Polymer Laboratories Ltd.). The specific parameters were referred to the previous literature (Peng *et al.* 2011b).

Sugar analysis

The composition of the neutral sugars and uronic acids in the isolated hemicellulosic fractions was determined by high-performance anion exchange chromatography (HPAEC) coupled with pulsed amperometric detection, as was described in a previous study (Peng *et al.* 2010). Briefly, the monomeric sugars and uronic acids in the hemicellulosic subfractions were first liberated by hydrolysis with 1 M H_2SO_4 at 105 °C for 2.5 h, and then diluted 50-fold, filtered, and injected into the HPAEC system (Dionex, ICS-3000, Sunnyvale, CA, USA) equipped with a Dionex ICS3000 gradient pump, amperometric detector, AS50 autosampler, and Carbopac^{TM} PA-20 column (4 mm × 250 mm; Dionex). In this system, the neutral sugars and uronic acids were separated in 5 mM

NaOH (carbonate free and purged with nitrogen) for 20 min, followed by a 0 mM to 75 mM NaAc gradient in 5 mM NaOH for 15 min. Afterwards, the column was washed with 200 mM NaOH for 10 min to remove the carbonate, which was followed by a 5-min elution with 5 mM NaOH to re-equilibrate the column before the next injection. The temperature and time of the total analytic process was 30 °C and 50 min, respectively, and the flow rate was 0.4 mL/min. Calibration was performed with standard solutions of L-arabinose, D-glucose, D-xylose, D-galactose, D-mannose, glucuronic acid, and galacturonic acid.

FT-IR spectra

The FT-IR spectra were obtained using a Thermo Scientific Nicolet iN10-MX FT-IR microscope (Thermo Nicolet Corporation, Madison, WI, USA) equipped with a liquid nitrogen cooled MCT detector. The dried samples were ground and pelletized with BaF_2, and the spectra were recorded in the range of 4000 cm^{-1} to 650 cm^{-1} at 8 cm^{-1} resolution with 64 scans per sample.

NMR spectra

The 2D HSQC NMR spectra were recorded on a Bruker AVIII 400 MHz spectrometer (Karlsruhe, Germany) using 50 mg of hemicellulose samples dissolved in 1.0 mL of D_2O. The spectra were obtained over a t_1 spectral width of 20000 Hz and a t_2 width of 3600 Hz. The specific operation conditions as described in the previous procedures (Peng *et al.* 2009; Peng *et al.* 2011b) were employed. Data processing was performed using the standard Bruker Topspin-NMR software. The central solvent (D_2O) peak was used as an internal chemical shift reference point (δ_H = 4.7 ppm).

TGA

The thermal behavior of the hemicelluloses was determined using TGA and differential thermogravimetric (DTG) analysis on a simultaneous thermal analyzer (DTG-60, Shimadzu, Kyoto, Japan). Samples that weighed 8 mg to 13 mg were heated from room temperature to 600 °C at a rate of 10 °C/min under a continuous nitrogen flow of 30 mL/min.

RESULTS AND DISCUSSION

Fractional Hemicellulose Yield

A previous study confirmed that the new treatment method (expanding pretreatment) can make a contribution to delignification because of the decomposition of the three-dimensional cell wall structure, which results in an increase in the lignin extraction efficiency (Wu *et al.* 2013). Therefore, the effect of the expanding pretreatment in this process on the extraction efficiency of the hemicellulose components and their structure was also investigated. The contents of hemicelluloses in the raw rice straw, expanded rice straw with a 15% water content, expanded rice straw with a 20% water content, raw rice husk, and expanded rice husk with a 15% water content were 25.6, 24.2, 22.1, 22.5, and 20.8%, respectively, as determined by the NREL standard analytical procedure (Sluiter *et al.* 2011). Thus, the yields of RS, RS_{15}, RS_{20}, RH, and RH_{15} (based on the hemicelluloses in the raw and expanded materials) are listed in Table 1. For the yields of the hemicelluloses extracted from the unexpanded and expanded rice straw, the most prominent result was that the extraction efficiency increased from 23.5% to 45.7%

and 54.2%, with an increase in the water content during the expanded pretreatment, which was apparently higher than that from steam explosion pretreatment (Wang *et al.* 2010a). This was in accordance with the increasing trend of the lignin component reported previously (Wu *et al.* 2013). The relatively high yield was attributed to the fact that extrusion and explosion processing can break up cell walls and partial linkages between lignins and/or carbohydrates, which contributed to the subsequent effect of the hydroxyl ions, including the swelling of celluloses, disruption of hydrogen bonds between the celluloses and hemicelluloses, and hydrolysis of ester bonds most likely connecting cell wall polysaccharides. Consequently, this resulted in the substantial solubilization of hemicelluloses. This same phenomenon was also observed with the rice husk, while all of the yields obtained with the rice husk was higher than that with the rice straw, which led to the smaller growth rate of the former. Overall, the extraction efficiency of the alkali-dissolved hemicellulose was improved by the expansion pretreatment, which was more effective for the rice straw.

Table 1. Neutral Sugar and Uronic Acid Contents in the Hemicellulosic Fractions

	Hemicellulosic Fraction[a]				
	RS	RS_{15}	RS_{20}	RH	RH_{15}
Yield (%)[b]	23.5	45.7	54.2	60.1	68.1
Molecular weights					
M_w	104,429	75,308	96,663	ND[c]	ND
M_n	25564	29373	41610	ND	ND
M_w/M_n	4.09	2.56	2.32	ND	ND
Sugars (%)[d]					
Arabinose	12.86	11.62	10.67	7.09	7.83
Galactose	1.83	1.93	1.64	1.16	1.01
Glucose	4.18	6.20	16.91	17.74	1.29
Xylose	78.89	78.02	68.57	71.78	87.38
Uronic acid	2.24	2.23	2.21	2.23	2.49
Arabinose/xylose	0.16	0.15	0.16	0.10	0.09
Uronic acid/xylose	0.03	0.03	0.03	0.03	0.03

[a] RS, RS_{15}, RS_{20}, RH, and RH_{15} represent hemicellulosic fractions extracted from raw rice straw, expanded rice straw (15% water content), expanded rice straw (20% water content), raw rice husk, and expanded rice husk (15% water content), respectively; [b] Yields are based on the hemicellulose content in the samples; [c] ND, the molecular weights of the hemicellulosic fractions extracted from rice husk were not detected; [d] Neutral sugar and uronic acid contents are the relative percent of the hemicellulosic samples

Distribution of Molecular Weight

The weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (M_w/M_n) of the hemicellulosic fractions extracted from the rice straw were determined by gel permeation chromatography (GPC). As shown in Table 1, all the samples exhibited high M_w ranging between 75,300 and 104,400 g/mol. It was obviously observed that when the water content increased to 15% during the expanding process, the molecular weight significantly decreased from 104,400 to 75,300, this indicated that the more water produced the more mild acid hydrolysis, promoting the cleavage of glycosidic ether linkages between sugar units in the macromolecular structure of hemicelluloses; thus the relative low molecular weight fragments were obtained. However, with the further increase of water content to 20%, the molecular weight increased again, which was probably due to the generation of condensation substances between the hemicellulose degradation products. In addition, RS_{15} and RS_{20} had a lower polydispersity (2.32 to 2.56) compared with RS (4.09); this result implied that the expansion process produced the more homogeneous hemicellulosic polymers. The molecular weights of the hemicellulosic fractions extracted from the rice husk were not detected in this study, possibly due to the low solubility or more ash impurities. This could be investigated in the future.

Neutral Sugar Composition of the Hemicellulosic Fractions

Hemicellulose is a branched polymer that is composed of several types of monosaccharides. The compositions can vary depending on the isolation method, type of plant, and part of the plant that is used. The neutral sugar and uronic acid contents of the five hemicellulosic fractions are listed in Table 1. Notably, xylose was the primary sugar component and comprised 68.6% to 87.4% of the total neutral sugars, while arabinose was the second most abundant sugar component (7.1% to 12.9%). A certain amount of glucose (1.29% to 17.7%) and minor quantities of uronic acid (2.21% to 2.49%) and galactose (1.01% to 1.93%) were also detected in the five hemicellulosic preparations. This preliminary data indicated that the main constituent of the hemicelluloses obtained by the expanding pretreatment combined with alkali extraction was xylan as the backbone and arabinose as the major branch, followed by uronic acid. Table 1 shows that all of the samples in this work had a similar composition.

The comparison of the neutral sugar and uronic acid contents of the isolated hemicellulosic fractions, obtained from the unexpanded and expanded rice straw, demonstrated that the content of xylose decreased from 78.9% to 68.6% with an increase in the water content in the rice straw material, while the amount of glucose increased from 4.2% to 16.9%. This implied the potential decomposition of cellulose and degradation of hemicelluloses *via* the expanding pretreatment with more water. The opposite tendency was observed in the hemicelluloses from the rice husk. The rice husk hemicellulosic fraction extracted from the 15% water content expansion had a higher xylose amount (87.4%) compared with the previously reported data for agricultural residues (Xiao *et al.* 2001). Furthermore, all of the samples had nearly equal arabinose to xylose and uronic acid to xylose ratios in the rice straw and rice husk hemicelluloses, respectively, which were consistent with the general values in the literature (Peng *et al.* 2011b). This demonstrated the similar degree of hemicellulose branching. In contrast, the hemicelluloses of the rice husk had a relatively more linear polymer structure than the rice straw.

FT-IR Spectra

The FT-IR spectra of the five hemicellulosic samples are illustrated in Figs. 2 and 3, and the signals were assigned using the literature (Kačuráková *et al.* 2000; Rao and Muralikrishna 2004; Jin *et al.* 2009). There were no remarkable differences in the main absorption peaks among the spectra from the rice straw (Fig. 2) and rice husk (Fig. 3). Simultaneously, a specific band in the 1200 cm^{-1} to 1000 cm^{-1} region that is typical of xylan was observed in all five spectra, which indicated the much higher content of xylose than the other sugars, as was shown in the sugar analysis.

In particular, Fig. 2 shows a strong band at 1040 cm^{-1}, which was attributed to the *β*-glycosidic linkage C-O-C contributions in the xylans, and an absorption peak at 1162 cm^{-1}, which was assigned to the arabinose substitutions at C-3 in the xylans. The signals at 1458 cm^{-1}, 1420 cm^{-1}, 1377 cm^{-1}, and 1317 cm^{-1} were because of -CH_2 symmetric bending, C-H and O-H bending, O-H in-plane bending, and –C-H wagging in the hemicelluloses, respectively.

An absorption peak at 897 cm^{-1} derived from the C-1 group frequency or ring frequency was clearly visible, which indicated the presence of *β*-glycosidic linkages between the sugar units in these hemicellulosic fractions.

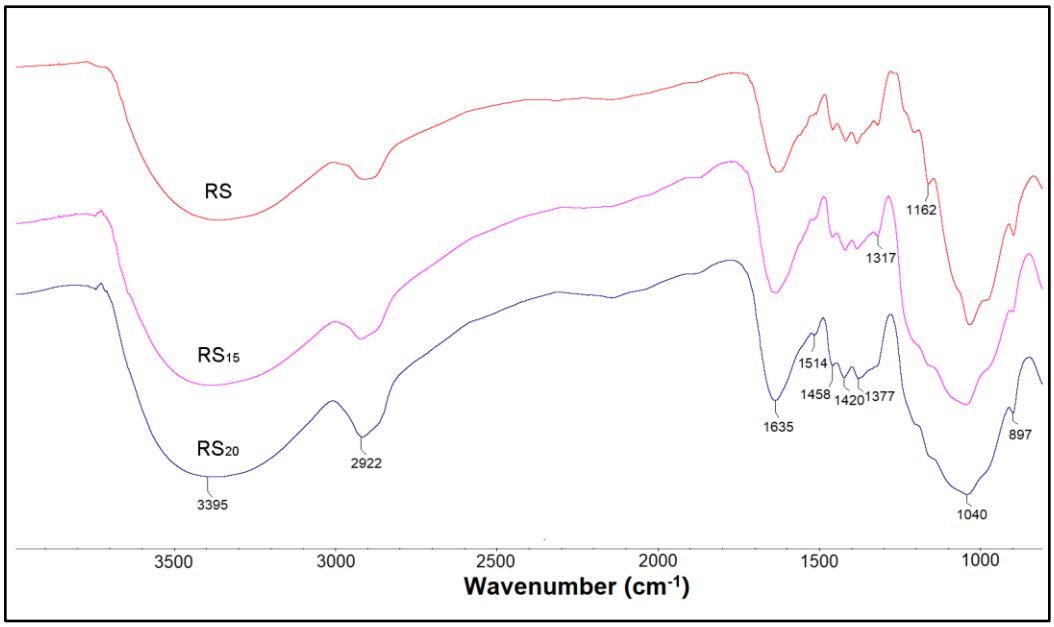


Fig. 2. FT-IR spectra of the hemicellulosic fractions RS, RS_{15}, and RS_{20}

Additionally, the absorption peaks at 3395 cm^{-1} related to the stretching vibration of O-H groups and at 2922 cm^{-1} related to C-H stretching were observed. The absorbed water gave an intensive signal at 1635 cm^{-1} because of the strong affinity hemicelluloses have for water. A small peak at 1514 cm^{-1} appeared in Fig. 2, which was caused by aromatic skeleton vibration in the associated lignin, which demonstrated that the NaOH-soluble hemicellulose samples contained trace amounts of lignin; this signal was barely present in Fig. 3.

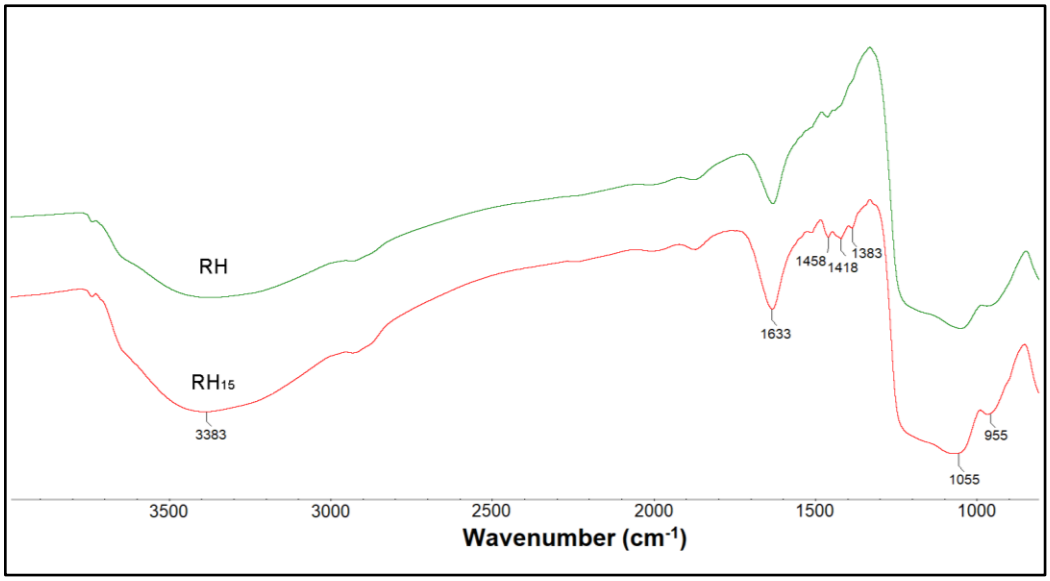


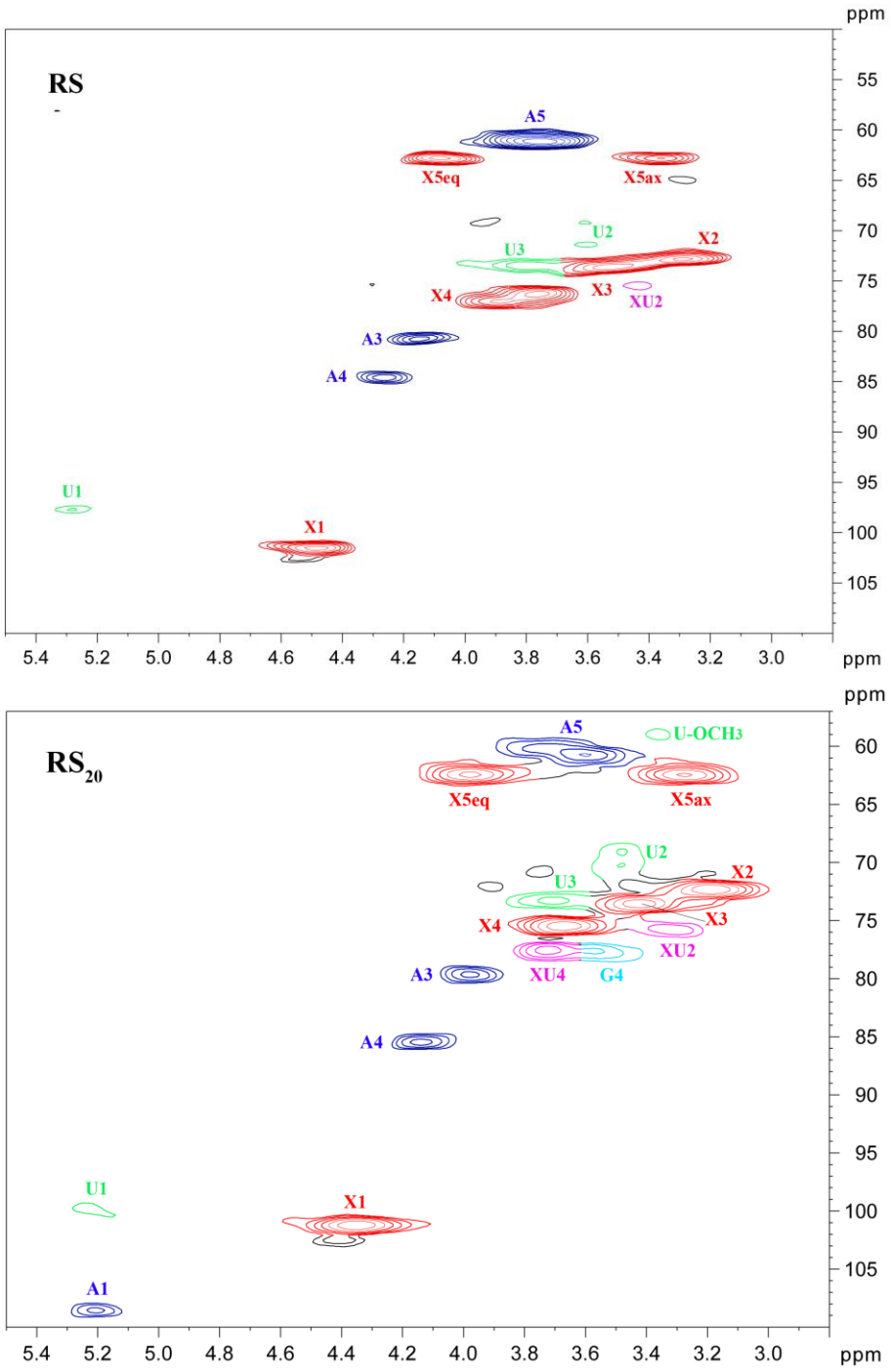
Fig. 3. FT-IR spectra of the hemicellulosic fractions RH and RH_{15}

2D HSQC NMR Spectroscopy

Figure 4 shows the 2D HSQC spectra of the alkali-extracted hemicellulosic fraction RS, RS_{20} from the rice straw and RH, RH_{15} from the rice husk. Most of the major resonances were assigned according to the literature data (Kardošová *et al.* 2004; Habibi and Vignon 2005; Bendahou *et al.* 2007; Peng *et al.* 2011a), and listed in Table 2.

As shown in the representative spectrum of RS_{20}, the specific $^{13}C/^{1}H$ cross-peaks of the five main signals of the (1→4)-linked *β*-D-xylopyranosyl units ((1→4)-*β*-D-Xyl*p*, X) were observed at δ_C/δ_H 102.3 ppm/4.37 ppm, 75.9 ppm/3.67 ppm, 74.8 ppm/3.42 ppm, 73.2 ppm/3.18 ppm, and 63.1 ppm/3.95 ppm and 3.25 ppm, which were assigned to the C-1, C-4, C-3, C-2, and C-5 positions of (1→4)-*β*-D-Xyl*p*, respectively. Some relatively weak signals at δ_C/δ_H 109.5 ppm/5.21 ppm, 86.4 ppm/4.13 ppm, 80.3 ppm/3.98 ppm, and 60.7 ppm/3.59 were also detected and were attributed to the C-1, C-4, C-3, and C-5 positions of the *α*-L-arabinofuranosyl residues (*α*-L-Ara*f*, A) linked to *β*-D-xylans, respectively. Additionally, the correlations for the C-1, C-3, C-2, and O-CH_3 of the 4-*O*-methy-*α*-D-glucuronic acid unit (4-*O*-Me-α-D-Glc*p*A, U) were also observed at δ_C/δ_H values of 99.7 ppm/5.23 ppm, 73.5 ppm/3.71 ppm, 70.0 ppm/3.47 ppm, and 59.2 ppm/3.35 ppm, respectively. Other signals detected at δ_C/δ_H values of 77.9 ppm/3.72 ppm and 75.9 ppm/3.32 ppm were characteristic of the C-4 and C-2 of (1→4)-*β*-D-Xyl*p*-2-*O*-(4-*O*-Me-*α*-D-Glc*p*A) residues (XU), respectively. A small signal ascribed to the C-4 position of the glucose was also present at δ_C/δ_H 77.9 ppm/3.57 ppm. Comparing the spectra of RS and RS_{20}, it could be found that the obtained hemicellulosic fractions from the raw and expanded rice straw were both similar, except the presence of glucose after expansion treatment, which was possibly due to the potential decomposition of cellulose. Thus, from the sugar analysis results and the FT-IR and NMR spectra, it was speculated that the hemicellulosic fraction extracted from the expanded rice straw in this process was composed of a main chain of (1→4)-linked *β*-D-xylopyranosyl residues, with *α*-L-arabinofuranosyl and 4-*O*-methyl-*α*-D-glucuronic acid linked as the side chains, accompanied by a certain amount of (1→4)-*β*-D-xylopyranosyl-2-*O*-(4-*O*-methyl-*α*-D-glucuronic acid).

Likewise, the hemicellulosic fractions from the raw and expanded rice husk were also similar. As shown in the spectrum of RH, (1→4)-*β*-D-Xyl*p* was present as the main unit, accompanied by the weak glucose signal, while in that of RH_{15}, (1→4)-*β*-D-Xyl*p* were also detected followed by *α*-L-Ara*f* residues, which were all consistent with the sugar analysis results. Therefore, combined with the sugar analysis data, it indicated that the hemicellulosic fraction extracted from the expanded rice husk through this process mainly consisted of a linear (1→4)-linked *β*-D-xylopyranosyl backbone decorated with branches of *α*-L-arabinofuranosyl or 4-*O*-methyl-*α*-D-glucuronic acid unit.



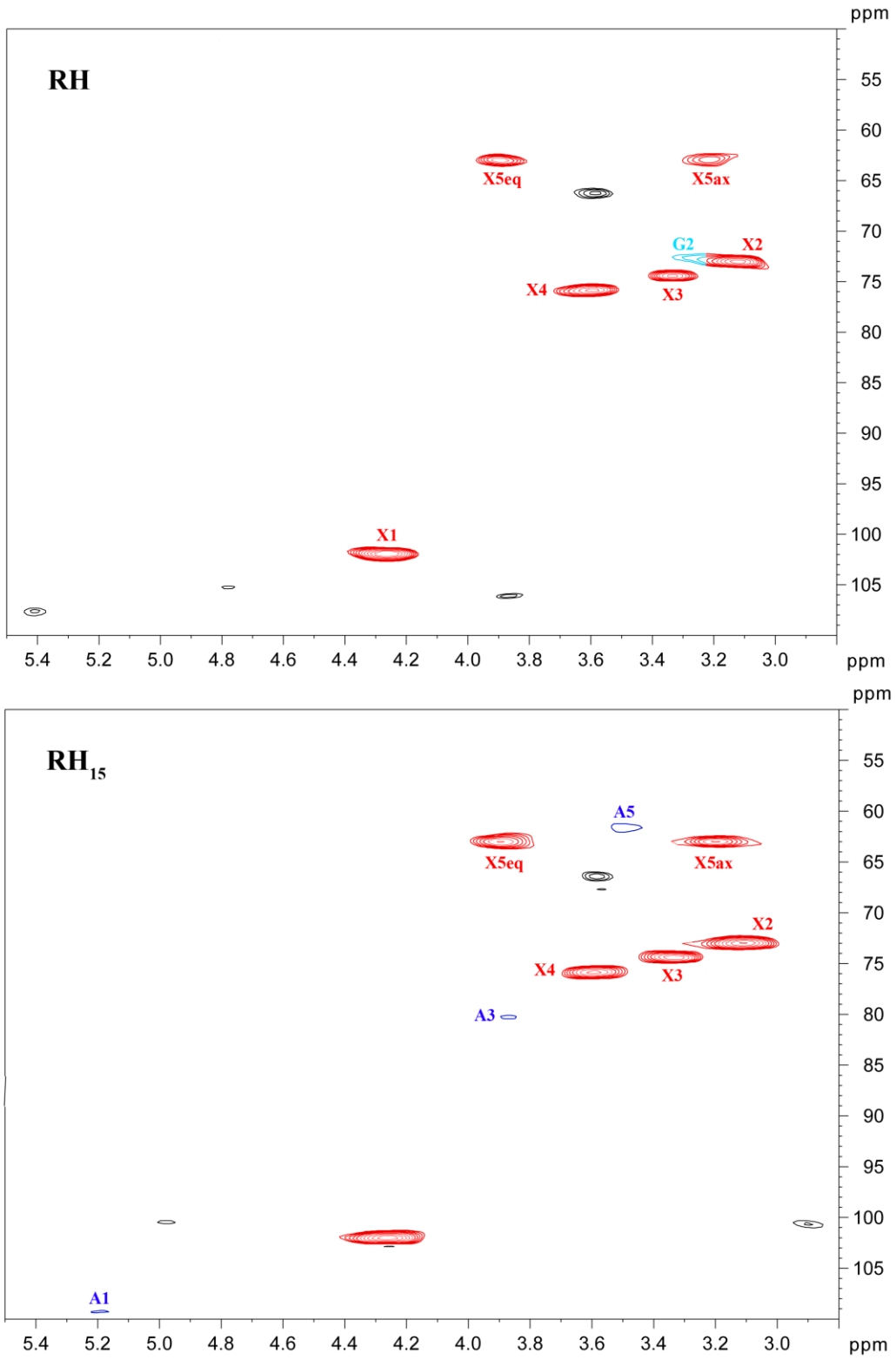


Fig. 4. 2D HSQC spectra of the hemicellulosic fractions RS, RS_{20}, RH, and RH_{15}: X - (1→4)-*β*-D-Xyl*p*; A - *α*-L-Ara*f*; U - 4-*O*-Me-*α*-D-Glc*p*A; XU - (1→4)-*β*-D-Xyl*p*-2-*O*-(4-*O*-Me-*α*-D-Glc*p*A); and G - Glucose

Table 2. Chemical Shifts of the Signals in the 2D HSQC NMR Spectrum of the Hemicellulosic Fractions

	Position	^{13}C (ppm)	^{1}H (ppm)
X	1	102.3	4.37
	2	73.2	3.18
	3	74.8	3.42
	4	75.9	3.67
	5ax	63.1	3.25
	5eq	63.1	3.95
A	1	109.5	5.21
	3	80.3	3.98
	4	86.4	4.13
	5	60.7	3.59
U	1	99.7	5.23
	2	70	3.47
	3	73.5	3.71
	O-CH_3	59.2	3.35
XU	2	75.9	3.32
	4	77.9	3.72
G	2	73.0	3.29
	4	77.9	3.57

Thermal Analysis

The thermal properties of biomass components are of vital importance for their application in thermochemical conversion into energy and chemicals, which is affected by the specific structures of different components from lignocellulosic materials (Wu *et al.* 2014). Thermogravimetric analysis (TGA) is one of the most common techniques to investigate the thermal properties, supplementing the physicochemical properties of biomacromolecules (Sun *et al.* 2005). Therefore, the TGA and corresponding DTG analysis were performed to study the thermal stability of the hemicellulosic fractions isolated with the expanding pretreatment and sequential NaOH post-treatment from the rice straw and rice husk. Figure 5 shows that the TGA curves of the pyrolysis process exhibited three weight-loss phases. The weight loss in the beginning (mainly < 150 °C) was ascribed to the evaporation of water because of the affinity of the hemicelluloses for water. The second weight loss stage occurred between 250 °C and 380 °C, during which the thermal decomposition of hemicelluloses was ascribed to the cracking of the main chains and fragmentation of the branched chains, which was also accompanied by decarboxylation and decarbonylation. These processes decomposed the hemicelluloses into CO, CO_2, CH_4, HCOOH, and other compounds. Eventually, when the temperature was above 400 °C, the weight loss was almost negligible (Hu *et al.* 2000; Bian *et al.* 2012).

In Fig. 6, it was observed that with the increase of water content during the expanding process, the maximum decomposition temperatures of the hemicellulose samples obtained from the rice straw (RS_{15} = 319 °C and 368 °C, RS_{20} = 315 °C and 366 °C) and rice husk (RH_{15} = 326 °C) were both higher than the corresponding control samples

(RS = 306 °C; RH = 319 °C). This was probably due to the presence of both degraded low molecular weight hemicelluloses and the condensation substances during the expansion pretreatment. Furthermore, it was also found in Fig. 5 that the contents of the solid residues were 30% to 47% for the rice straw hemicellulose (RS = 42%; RS_{15} = 47%; RS_{20} = 30%) and 82% to 83% for the rice husk hemicellulose (RH = 82%; RH_{15} = 83%). In combination with the molecular weight analysis, RS_{15} of the minimum molecular weight had the maximum solid residue content, which was probably attributable to some co-precipitated and condensed lignin in it (Wen *et al.* 2013).

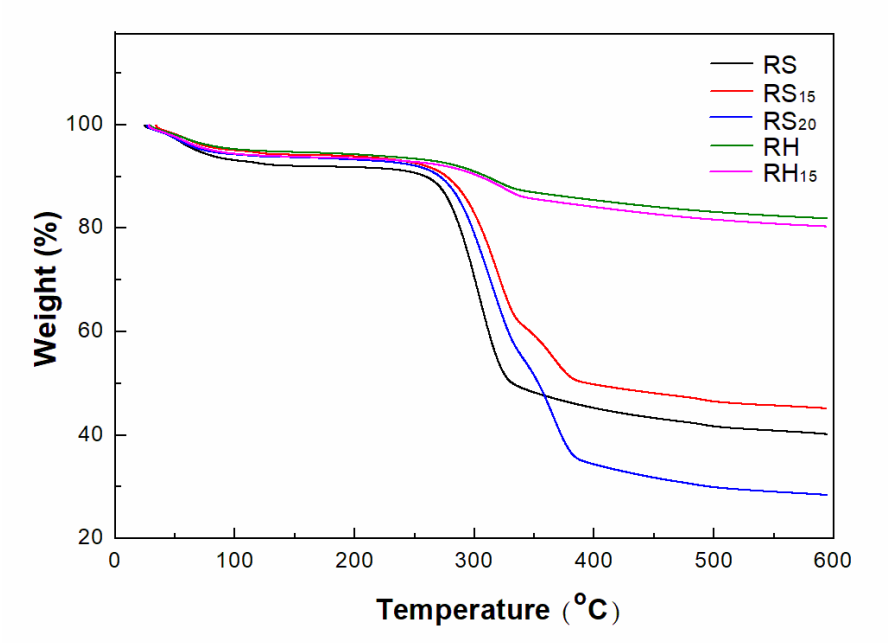


Fig. 5. TGA curves of the hemicellulosic fractions RS, RS_{15}, RS_{20}, RH, and RH_{15}

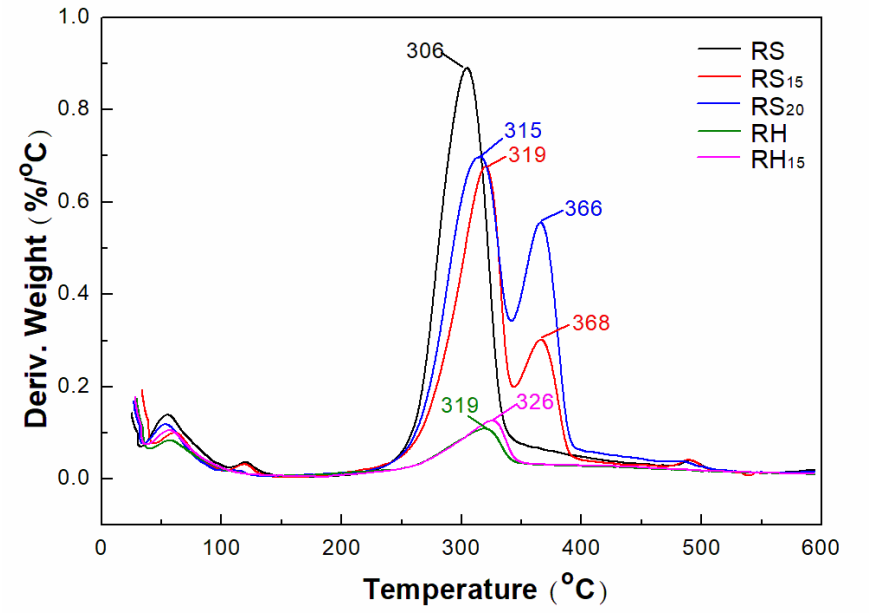


Fig. 6. DTG curves of the hemicellulosic fractions RS, RS_{15}, RS_{20}, RH, and RH_{15}

Notably, the hemicellulosic fractions of the rice husk had a higher content of residue than those of the rice straw. This was possibly because of the end-products of the decomposition of the hemicelluloses, which were carbonaceous residues formed in an inert atmosphere and the salts formed during the extraction processes (Devallencourt *et al.* 1996). Also, more ash remained in the rice husk. Another reason for this higher residue content was presumed to be the higher thermal stability of the hemicellulosic fractions of the rice husk than that of the rice straw.

CONCLUSIONS

1. The extraction efficiency of the alkali-dissolved hemicellulose was dramatically improved by the expansion pretreatment, which was more effective for the rice straw compared with the rice husk.
2. From the FT-IR, molecular weight, sugar analysis, and NMR spectra results, it was found that with the more water content during the expansion treatment, the molecular weights of the obtained hemicelluloses significantly decreased and then rose, which was probably due to the prominent degradation and then generation of condensation substances. Moreover, the extracted hemicelluloses of the rice husk had a relatively more linear polymer structure than the rice straw.
3. With an increase in the water content during expansion processing, the thermal stability of the extracted hemicellulosic fraction increased.

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