PRETREATMENT OF LIGNOCELLULOSIC WHEAT STRAW IN ETHANOL-WATER CO-SOLVENTS

MINGYU ZHANG, K. S. HUI,[*] GUIFEN GONG,[**] K. N. HUI[***] and LIZHU LIU[**]

Electronic and Communication Engineering Department, Suzhou Institute of Industrial Technology, Suzhou, China
[*]*School of Mathematics, University of East Anglia, Norwich, United Kingdom*
[**]*School of Materials Science and Engineering, Harbin University of Science and Technology, Xiangfang, Harbin, China*
[***]*Institute of Applied Physics and Materials Engineering, University of Macau, Macau*
✉ *Corresponding authors: K. S. Hui, k.hui@uea.ac.uk*
K. N. Hui, bizhui@umac.mo

Received June 2, 2015

Pretreatment is the key process for lignocellulosic biomass conversion, which is necessary to alter the structure of biomass to make cellulose and hemicellulose more accessible to the enzymes that convert the carbohydrate polymers into fermentable sugars. The present study reports the use of 15 ml ethanol-water co-solvents (1:1, v/v) for the pretreatment of lignocellulosic biomass (1.5 g) to produce cellulosic residual solid under varying conditions of temperature (220-310 °C) and time (20-100 min). Kinetic analysis was performed to examine the decomposition behavior of biomass in the co-solvents. The results showed that the optimal conditions for the pretreatment were 250 °C and 40 min. The maximum yield of residual solid under the optimized pretreatment conditions was 49.6% (0.744 g), which consisted of 91.4% holocellulose (cellulose and hemicellulose). Microstructure analysis showed that the compact monolithic structure of biomass had decomposed into a loose filamentous structure.

Keywords: lignocellulosic biomass, pretreatment, ethanol-water co-solvents, holocellulose, lignin

INTRODUCTION

Excessive consumption of fossil fuels has resulted in the generation of high levels of pollution over the last few decades. Therefore, it is essential to develop clean biomass energy.[1-6] Lignocellulosic biomass, such as wheat straw, is a potential biofuel source. Statistical data show that China has considerable lignocellulosic biomass. Approximately 0.7 billion tons of lignocellulosic biomass is produced in China annually.[7] For the conversion of lignocellulosic biomass to energy, the saccharification of holocellulose (cellulose and hemicellulose) followed by fermentation is one of the methods to obtain liquid fuel.[8-11] On the other hand, it is difficult to hydrolyze the holocellulose in lignocellulosic biomass directly because the crystalline structure of cellulose is difficult to break up into a monomer.[10,12-15] In addition, the lignin that wraps the holocellulose fiber prevents the cellulose from being digested by enzymes.[15,16]

Pretreatment is an important tool for practical biomass conversion and it is required to alter the structure of cellulosic biomass to make holocellulose more accessible to the enzymes that convert the carbohydrate polymers to fermentable sugars.[17-20] The goal of pretreatment is to break the lignin seal and disrupt the structure of holocellulose, as shown in Figure 1. Thus far, the available technologies for biomass pretreatment include liquid hot water pretreatment, steam explosion, acid pretreatment, and alkaline pretreatment, but none of the known methods is cost-effective for large-scale applications.[21] For example, acid and alkaline pretreatments have high operating costs and cause significant environmental pollution. Removing the lignin is difficult with a liquid hot water pretreatment; rather, hemicelluloses are transformed in the degradation product, which inhibits fermentation. Steam explosion is not cost effective.[18]

Considerable attention has been focused on the pretreatment of biomass using some ionic liquids, because these liquids have good solubility for holocellulose.[22,23] On the other hand, the high cost and viscosity of ionic liquids impede the commercialized application of such a pretreatment.[24]

It is still necessary to develop advanced pretreatment technologies and control mechanisms tuned to the unique characteristics of different types of biomass and to minimize costs. The ultimate goal is the efficient fractionation of lignocellulose into multiple streams that contain value-added compounds in concentrations that make purification, utilization, and/or recovery economically feasible. A better understanding of the physical and chemical mechanisms that occur during the pretreatment of wheat straw and finding the relationship between the chemical composition and the physico-chemical structure of lignocellulose are needed for developing better predictive pretreatment models. Predictive pretreatment models can enable the selection, design, optimization, and process control of pretreatment technologies that match the biomass feedstock with the appropriate method and process configuration.[25,26] Therefore, an effective pretreatment is characterized by several criteria. This avoids the need to reduce the size of the biomass particles, preserves the hemicellulose fractions, limits the formation of degradation products that inhibit the growth of fermentative microorganisms, minimizes the energy demands, and limits the cost. These properties, along with the others, including low pretreatment catalyst cost or inexpensive catalyst recycling, and the generation of a higher-value lignin co-product form the basis for a comparison of various pretreatment options.

Recently, some studies suggested that ethanol-water co-solvents are an effective solution for degrading lignin into the monomeric form, even without a catalyst from 200 to 350 °C.[27] A previous study showed that the ethanol–water co-solvent would have a synergistic effect on the biomass treatment process.[28] Although hot compressed water was found to be quite effective in promoting ionic, polar non-ionic and free-radical reactions, ethanol, as an extraction solvent, can dissolve relatively high-molecular-weight products from lignin due to its lower dielectric constant than that of water.[29] The addition of ethanol can act as both reaction substrate and hydrogen-donor in the pretreatment process. A combination of these advantages may break the lignin seal and explore the structure of biomass.[30] The lignin in biomass can be extracted effectively using ethanol and water co-solvents, and cellulose and hemicellulose can be preserved.[31] H^+ ions (from water) act as a catalyst to break the lignin seal and the ethanol increases the dissolution ability of cellulose and hemicellulose. In this study, the experiments were carried out at different temperatures (220-310 °C) and times (20-100 min) with a solid-liquid ratio of 100 g/L in ethanol-water co-solvents (1:1, v/v) to pretreat the wheat straw and produce a cellulosic residual solid. Kinetic analysis was performed to examine the decomposition behavior of the wheat straw in the co-solvents.

EXPERIMENTAL

Samples and chemicals

Wheat straw (Jimai 22, authorization number: CNA20060015.X) was obtained from the Shangdong province of China and was used as lignocellulosic biomass in this study. The straw was cut to lengths of 3 to 6 cm, and dried in an oven at 105 °C for 24 h prior to use.

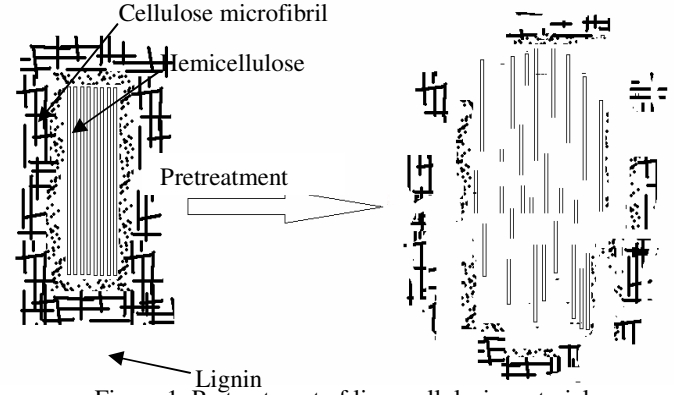


Figure 1: Pretreatment of lignocellulosic material

Table 1 lists the chemical compositions of the wheat straw. Filter paper, with pore size of 20-25 μm, was received from the Hangzhou Special Paper Co. Ltd. The co-solvents used in the pretreatment tests were distilled water and ethanol (1:1, v/v).

Pretreatment system

The experiments were carried out in a batch system. The reactor was made from stainless steel with an inner volume of 22 ml. The salt bath, which was controlled by a heater and a temperature controller, was filled with $NaNO_2$ and KNO_3 (1:1 w/w), providing an operative temperature ranging from 200 to 400 °C with an accuracy of ±1 °C.

Experiment process

In each test, the reactor was loaded with 1.5 g wheat straw and 15 ml ethanol-water co-solvents (1:1, v/v). The solid-liquid ratio was 100 g/L. The reactor was then sealed and immersed vertically into a salt bath that had been preheated to the reaction temperature (220-310 °C). After the desired reaction time, the reactor was removed from the salt bath and immersed in iced water immediately. The reaction time is defined as the duration that the reactor was kept in the salt bath. Subsequently, the liquid mixture was filtered through the filter paper to obtain the residual solid. The residual solid was dried to remove water at 105 °C for 12 h prior to analysis. The reaction pressures inside the reactor were calculated based on the temperature, density and pressure of the ethanol-water co-solvents, as shown in Table 2.[16] The yield of the residual solid, Y (%), was evaluated by Eq. (1) as follows:

$$Y = \frac{W_s}{W_0} \times 100\% \quad (1)$$

where W_0 is the weight of the wheat straw (g) and W_s is the weight of the residual solid (g).

Table 1
Composition of wheat straw

Composition (wt%)	
Extractives	4.92
Ash	8.22
Lignin	19.03
Holocellulose	67.83

Table 2
Reaction pressure inside the reactor at different temperatures

Temperature (^oC)	Pressure (MPa)
220	4.29
250	25.38
280	26.84
310	28.30

Analytical methods

Solvent extraction (60 ml ethanol-toluene solution (1:2, v/v) for 1 g of dried sample) was used to determine the amount of extractives in the wheat straw, and the temperature was held at 100 °C for 6 h. The sample was dried at 105 °C until a constant weight was obtained. The weight difference before and after extraction is the amount of the extractives.[32] To determine the amount of ash, 1 g of extractive-free dried wheat straw was burned at 750 °C for 24 h in air. The difference between the sample weight before and after this treatment is the ash content. The lignin content was analyzed using the 72% (w/w) H_2SO_4 method.[32] The holocellulose (hemicelluloses and cellulose) content was calculated by the difference assuming that the extractive, lignin, ash, and holocellulose are the only components of the wheat straw. After the pretreatment at 220-280 °C, the color of the solid residue was a pale white. The amounts of extractives and ash were difficult to detect in the residual solid because the contents are too small. Therefore, it was assumed that the residual solid contains only lignin and holocellulose at temperatures ranging from 220 to 280 °C. On the other hand, the color of the solid residue was a pale black when the reaction temperature was up to 310 °C, which indicated that the wheat straw was partly carbonized. Therefore, the component analysis of the residue solid was not performed at 310 °C. The morphology of the pristine wheat straw and the residual solid were observed by optical microscopy.

RESULTS AND DISCUSSION

Figure 2 shows the variation of the residual solid and the lignin as a function of the reaction

time at different reaction temperatures (220, 250 and 280 °C). Figure 2a shows that the yields of the residual solid decreased with increasing reaction time and the lignin content decreased with increasing reaction time between 20 and 60 min at 220 °C. From 80 to 100 min, the lignin content increased with increasing reaction time, which was attributed to cellulose hydrolysis. Figure 2b shows the variation of the residual solid and the lignin with different reaction times at 250 °C. The lignin content in the residual solid was reduced to 8.64 wt% for a reaction time of 40 min and 8.27 wt% for a reaction time of 80 min. About 4 wt% of the lignin of the wheat straw had been removed as the amount of the residual solid was about 50%, which indicated that approximately 15 wt% of the lignin had been removed from the wheat straw. The lignin content of the residual solid after a reaction time of 80 min (44.7%) was slightly lower than that at a reaction time of 40 min (49.6%). This indicated that more holocellulose was hydrolyzed during a reaction time of 80 min than during a reaction time of 40 min at 250 °C. Therefore, the proper reaction time is 40 min at 250 °C. Figure 3c shows the variation of the residual solid and lignin with different reaction times at 280 °C. The results indicated that the amount of lignin increased with increasing reaction time due to the decomposition of more cellulose and hemicelluloses at higher temperature. As a result, it is proposed that the lignin content of the wheat straw can be removed effectively at 250 °C for 40 min.

Figure 3 shows the variation of the yield of residual solid with different reaction times at 310 °C. Component analysis was not performed at this temperature because the color of the solid residue was a pale black, which indicated that the wheat straw has been partly carbonized. The results indicated that approximately 85% of biomass conversion was achieved at 310 °C for 100 min. These results suggest that ethanol-water co-solvents had synergistic effects on the direct liquefaction of the wheat straw at 310 °C. The critical temperature of the ethanol-water co-solvents (1:1, v/v) was approximately 314 °C.[27,28] Therefore, the test was carried out under near critical conditions at 310 °C. The hydrogen donor capability of ethanol was promoted under the near critical conditions. Ethanol acted as both reaction substrate and hydrogen-donor in the degradation of the wheat straw.

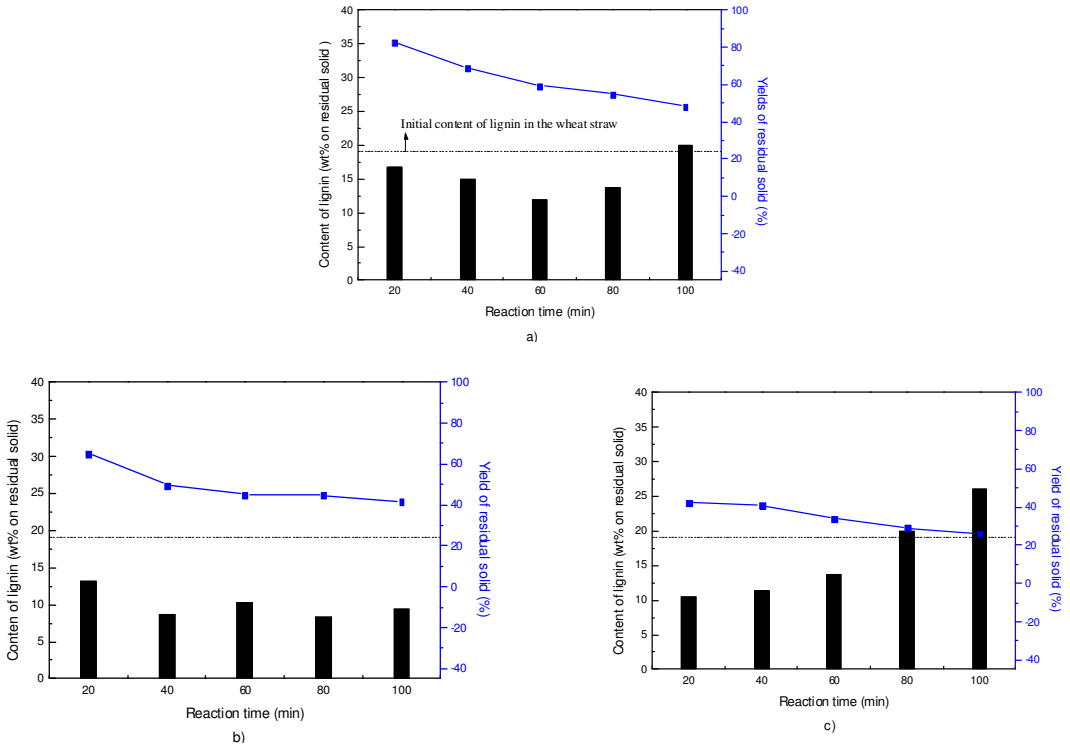


Figure 2: Variation of residual solid and lignin with pretreatment time at different temperatures; a) 220 °C; (b) 250 °C; (c) 280 °C

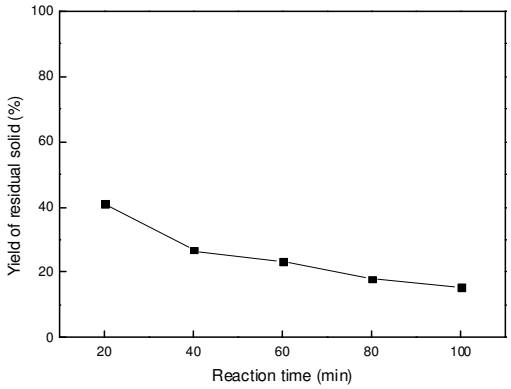
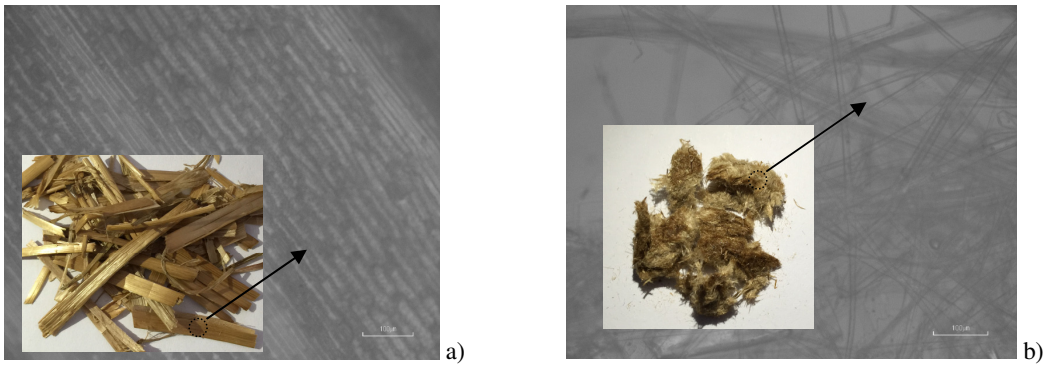


Figure 3: Variation of the yield of residual solid with reaction time at 310 °C



a) b)

Figure 4: Microstructural images of pristine wheat straw (a) and residual solid (treated at 250 °C for 40 min) (b)

Figure 3 shows the variation of the yield of residual solid with different reaction times at 310 °C. Component analysis was not performed at this temperature because the color of the solid residue was a pale black, which indicated that the wheat straw has been partly carbonized. The results indicated that approximately 85% of biomass conversion was achieved at 310 °C for 100 min. These results suggest that ethanol-water co-solvents had synergistic effects on the direct liquefaction of the wheat straw at 310 °C. The critical temperature of the ethanol-water co-solvents (1:1, v/v) was approximately 314 °C.[27,28] Therefore, the test was carried out under near critical conditions at 310 °C. The hydrogen donor capability of ethanol was promoted under the near critical conditions. Ethanol acted as both reaction substrate and hydrogen-donor in the degradation of the wheat straw.

A mechanism proposed in the literature stated that ethanol had hydrogen-donor capability to stabilize the free radicals generated and reduced the repolymerization reaction.[27] Low-boiling-point materials were produced in the reaction, which might be vaporized and vented in the rotary evaporator. The formation of high-boiling-point materials (labeled as bio-oil) was promoted when ethanol was diluted with the appropriate amount of water. Previous studies also reported that the critical point and the dielectric constant of the alcohol/water mixture could be lower than that of pure water, which led to milder conditions for the reaction and an increase in the solubility of the relatively high molecular weight products from cellulose, hemicelluloses and lignin.[28] Therefore, 310 °C appears to be the proper temperature for the direct liquefaction of wheat straw to produce bio-oil using the hot-compressed co-solvents of ethanol-water (1:1, v/v).

Morphological characteristics

An effective pretreatment of the wheat straw can remove the hindrance of the lignin wrapped around the cellulose fiber. For this purpose, images of the pristine wheat straw and the residual solid samples were compared. The pristine wheat straw (Fig. 4a) exhibited a regular and compact structure, as well as a highly fibrillar and intact morphology. After the reaction at 250 °C for 40 min, the ethanol-water co-solvents

disrupted the lignocellulosic structure mainly by dissolving the lignin. As a result, as shown in Figure 4b, the major microfibrous cellulose structures were still preserved and completely fibrillated in the residual solid. The microfibers were separated from the initial structure and fully exposed, thereby increasing the external surface area and porosity. The compactly monolithic structure of the wheat straw disappeared. These results indicated that the lignin was removed and broken under the tested conditions. Therefore, the compactly monolithic structure of the wheat straw was disrupted. The residual solid was much softer than the pristine wheat straw.

Reaction kinetics of biomass decomposition

Kinetic analysis of the wheat straw decomposition was performed. The reactions in the co-solvents treatment can be simplified as Eq. 2, in which k is the reaction rate constant of the wheat straw decomposition with a unit of min^{-1}.

$$Biomass(B) \xrightarrow{k} liquid\ \ products(L) \quad (2)$$

The mass of the residual solid, B, is decomposed into soluble liquid or gaseous products with the reaction rate equation shown in Eq. 3. Eq. 4 expresses the integral equation of Eq. 3. Eq. 5 was derived from Eq. 4, representing the linear fitting with the apparent reaction time. The linear and curve fittings were applied to calculate the reaction rate constants.

$$dB / dt = - kB_0 \quad (3)$$

$$B=B_0 \exp(- kt) \quad (4)$$

$$\ln(B_0 / B) = kt' + C \quad (5)$$

where t' is the apparent reactor time (min), B is the mass of the residual solid (g), B_0 is the initial mass of the biomass (g), and C is the constant factor.

Figure 5 shows the fitting curves for the reactions conducted at 220 °C (Figure 5a), 250 °C (Figure 5b), 280 °C (Figure 5c) and 310 °C (Figure 5d). The slope of the fitting line indicates the reaction rate constants (k) of the biomass decomposition.

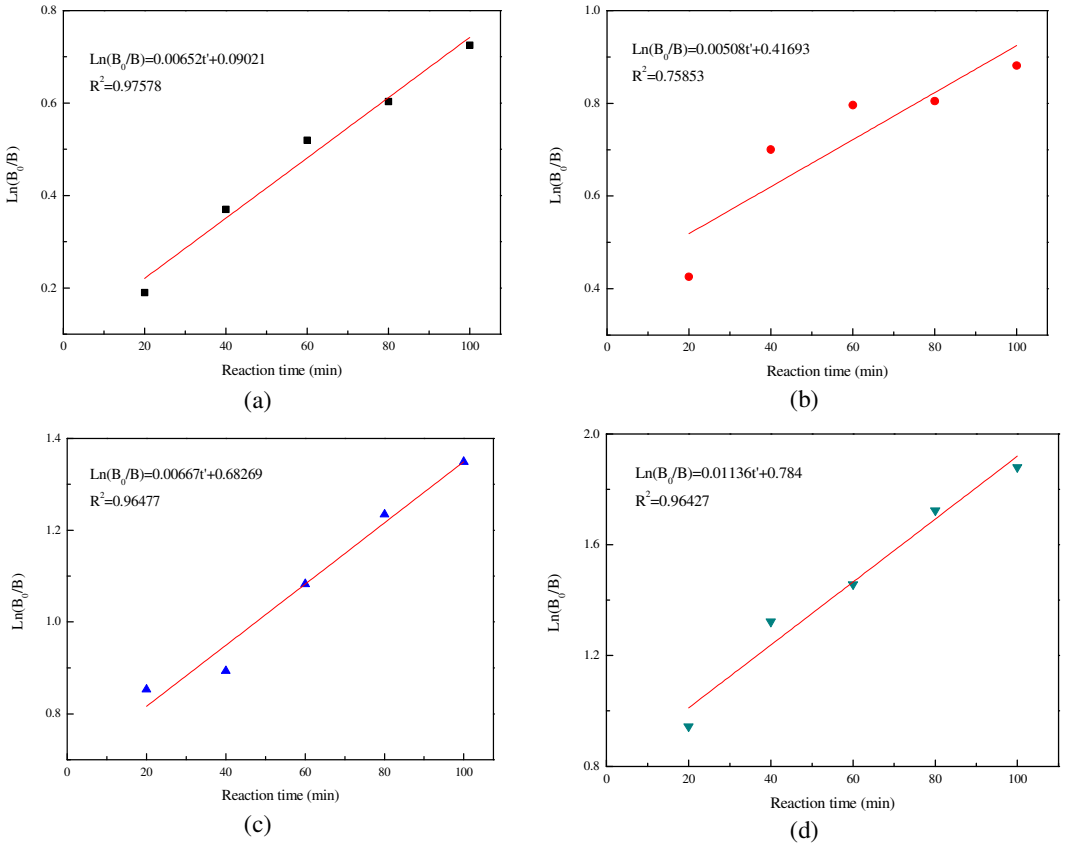


Figure 5: Fitted curves of the reaction rate equations of biomass decomposition at different temperatures; (a) 220 °C, (b) 250 °C, (c) 280 °C, (d) 310 °C

Table 3 lists the reaction rate constants of the biomass decomposition at different temperatures. As expected, the rate constant increased with increasing temperature.[16] The results indicated that the reaction rate constants have a positive correlation with the temperature, except at 250 °C. This is unusual in that the reaction rate constant of the biomass decomposition at 250 °C was smaller than that at 220 °C.

Table 3
Reaction rate constants of biomass at different temperatures

T (^{o}C)	K (min^{-1})
220	0.00652
250	0.00508
280	0.00667
310	0.01136

Based on the results of Figure 2b, this observation can be explained as follows. First, the lignin in the wheat straw was decomposed by the co-solvents rapidly at 250 °C. The lignin barriers were then broken and the cellulose and hemicellulose underwent a slow hydrolysis. Therefore, the reaction rate constant at 250 °C is smaller than that at 220 °C. This indicates that the lignin decomposition took place more rapidly than the holocellulose decomposition, which allows the holocellulose to be preserved at 250 °C. Thus, the co-solvents had a selective ability to decompose the lignin and preserve the holocellulose in the wheat straw at 250 °C. After the treatment of the wheat straw with the co-solvents at 250 °C for 40 min, the wheat straw turned into loose filamentous structural residues that were rich in celluloses and were hydrophilic (Fig. 4b). This process is beneficial for the follow-up treatment of translating it into useful chemicals in water.[20,26,33]

The reaction rate constant of the biomass hydrolysis became much faster at 310 °C. A faster decomposition rate and carbonization are unfavorable for saving cellulose in the biomass. Therefore, the reaction temperature should not exceed 310 °C when utilizing the co-solvents to pretreat biomass. This could be more suitable for further research into the liquefaction or gasification of biomass at temperatures exceeding 310 °C in a short time due to the high reaction rate constant.

CONCLUSION

The pretreatment of the wheat straw by the ethanol-water co-solvents at different reaction temperatures and times was investigated. The results indicated that higher holocellulose content and lower lignin content were obtained at 250 °C for 40 min. The results suggest that the ethanol-water co-solvents can be used to break the pristine structure of the wheat straw while effectively removing the lignin. Ethanol-water co-solvents could be a competitive and effective pretreatment method, especially for a tactical biorefinery, because ethanol is a green solvent and no expensive equipment is required. In addition, ethanol is a product of cellulose fermentation and can be reused in the pretreatment after a distillation process.

ACKNOWLEDGMENTS: This project was funded by the UEA funding, the Science and Technology Project Fund of Suzhou Institute of Industrial Technology (SGYKJ201707), the Science and Technology Research Project of the Education Department of Heilongjiang Province (No. 12511070), the Young Teachers of Vocational Colleges Enterprise Practice Training Project of Jiangsu Province (2017QYSJPX021), the Suzhou Social Science Fund (2017LX122), the National Natural Science Foundation of China (51372128, 11404322).

REFERENCES

[1] M. Balat, H. Balat and C. Öz, *Prog. Energ. Combust. Sci.*, **5**, 34 (2008).
[2] Y. Yu, X. Lou and H. Wu, *Energ. Fuels*, **1**, 22 (2007).
[3] F. Wu and S. Zhou, *J. Energ. Eng.*, **1**, 138 (2011).
[4] V. Panwar, B. Prasad and K. L. Wasewar, *J. Energ. Eng.*, **2**, 137 (2010).
[5] T. R. Brown and G. Hu, *J. Energ. Eng.*, **2**, 138 (2011).

[6] N. Sarkar, S. K. Ghosh, S. Bannerjee and K. Aikat, *Renew. Energ.*, **1**, 37 (2012).
[7] Y. Zhao, W. Lu, J. Chen, X. Zhang and H. Wang, *Front. Environ. Sci. Eng.*, **2**, 8 (2014).
[8] M. Sasaki, B. Kabyemela, R. Malaluan, S. Hirose, N. Takeda *et al*., *J. Supercrit. Fluids*., **1-3**, 13 (1998).
[9] K. Ehara and S. Saka, *J. Wood Sci*., **2**, 51 (2005).
[10] M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri and K. Arai, *Ind. Eng. Chem. Res*., **8**, 39 (2000).
[11] Y. Zhao, W. J. Lu, H. Y. Wu, J. W. Liu and H. T. Wang, *Bioresour. Technol*., **12**, 126 (2012).
[12] Y. Zhao, W. J. Lu, H. T. Wang and J. L. Yang, *Bioresour. Technol*., **23**, 100 (2009).
[13] Y. Zhao, H. T. Wang, W. J. Lu and H. Wang, *Chem. Eng. J*., **3**, 166 (2011).
[14] M. Zhang, G. Gong, K. Hui, K. Hui and L. Liu, *J. Energ. Eng*., **4**, 141 (2014).
[15] A. M. Boudet, C. Lapierre and J. Grimapettenati, *New Phytol*., **2**, 129 (2010).
[16] Y. Zhao, W. J. Lu, H. T. Wang and D. Li, *Environ. Sci. Technol*., **5**, 43 (2009).
[17] C. E. Wyman, B. E. Dale, R. T. Elander, M. Holtzapple and M. R. Ladisch *et al*., *Bioresour. Technol*., **18**, 96 (2005).
[18] N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Lee *et al*., *Bioresour. Technol*., **6**, 96 (2005).
[19] B. Yang and C. E. Wyman, *Biofuel. Bioprod. Biorefin*., **1**, 2 (2008).
[20] P. Kumar, D. M. Barrett, M. J. Delwiche and P. Stroeve, *Ind. Eng. Chem. Res*., **8**, 48 (2009).
[21] C. E. Wyman, *Trends Biotechnol*., **4**, 25 (2007).
[22] L. Xing, Z. Wu and G. Gong, *J. Energ. Eng*., **2**, 140 (2013)
[23] Z. Zhang and Z. K. Zhao, *Bioresour. Technol*., **3**, 101 (2010).
[24] Y. Y. Wu, Z. H. Fu, D. L. Yin, Q. Xu, F. L. Liu *et al*., *Green Chem*., **4**, 12 (2010).
[25] W. Abdelmoez, S. M. Nage, A. Bastawess, A. Ihab and H. Yoshida, *J. Clean. Prod*., **5**, 70 (2014).
[26] P. Alvira, E. Tomás-Pejó, M. Ballesteros and M. Negro, *Bioresour. Technol*., **13**, 101 (2010).
[27] S. Cheng, I. D'cruz, M. Wang, M. Leitch and C. Xu, *Energ. Fuels*, **9**, 24 (2010).
[28] Y. Liu, X. Z. Yuan, H. J. Huang, X. L. Wang, H. Wang *et al*., *Fuel Process. Technol*., **3**, 112 (2013).
[29] S. N. Cheng, C. Wilks, Z. S. Yuan, M. Leitch and C. B. Xu, *Polym. Degrad. Stabil*., **6**, 97 (2012).
[30] H. S. Lu, M. M. Ren, M. H. Zhang and Y. Chen, *Chin. J. Chem. Eng*., **5**, 21 (2013).
[31] D. Pasquini, M. T. B. Pimenta, L. H. Ferreira and A. A. D. Curvelo, *J. Supercrit. Fluids*, **1**, 36 (2005).
[32] I. De Bari, D. Barisano, M. Cardinale, D. Matera, F. Nanna *et al*., *Energ. Fuels*, **4**, 14 (2000).
[33] L. Lin, R. Yan, Y. Liu and W. Jiang, *Bioresour. Technol*., **21**, 101 (2010).