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Simultaneous separation and selective conversion of hemicellulose in Pubescen in water–cyclohexane solvent

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ABSTRACT

The simultaneous separation and selective conversion of hemicellulose in Pubescen samples were investigated in water–cyclohexane solvent at 160 °C. Chemical titration, X-ray diffraction (XRD) and scanning electron microscope (SEM) were used to characterize the samples. The conversion of hemicellulose in Pubescen sample was found rather selectively in the mixed water–cyclohexane solvent, that is, 86.6% hemicellulose conversion was obtained without significant degradation of cellulose. A maximum acetic acid yield of 13.0 wt% was obtained from the conversion of Pubescen. If all the acetic acid comes from the conversion of hemicellulose, the yield would be 90% based on the converted hemicellulose. As compared to water solvent, the mixed solvent played an important role in reducing the conversion rate of hemicellulose, cellulose and lignin. In addition, the reduction of conversion rate of cellulose and lignin was more significant, which benefited the stepwise conversion of different components in raw biomass materials.

1. Introduction

With the depletion of fossil fuel and the concern of environmental protection, the utilization of biomass resources has attracted increasing interests worldwide for their renewability and zero or very low net CO_2 emission. Among the available forestry resources, Pubescen shows good prospect for industrial exploitation and utilization because of their worldwide distribution and short growth period (about one year), which provides an abundant and sustainable supply of raw materials (Qi et al., 2006). Pubescen is a kind of lignocellulosic biomass and composed of three main components: cellulose, hemicellulose, and lignin. Cellulose is a kind of polymer with long chains where the six-carbon glucose is connected end to end linearly through β 1-O-4 glycosidic bonds. Hemicellulose is a collection of heteropolymers of five- and six-carbon sugars with short branched side connections. Lignin is a three-dimensional polymer of phenylpropane units with different degrees of methoxy groups (Liu, 2010). Owing to the complexity in structure and composition of Pubescen materials, their selective conversion to obtain energy materials or chemicals preserves one big challenge.

Multiple ways are adopted to convert raw biomass to fuels or chemical products, such as pyrolysis (Mohan, Pittman, & Steele, 2006; Zhang, Deng, et al., 2010), hydrothermal liquefaction (including hydrolysis liquefaction) (Peterson et al., 2008; Tymchyshyn & Xu, 2010), fermentation (Brethauer & Wyman, 2010) and a combination of hydrolysis and fermentation (Sun, Tang, Iwanaga, Sho, & Kida, 2011). Pyrolysis and hydrothermal liquefaction are the two main kinds of thermo-chemical conversion routes widely used. The three components in Pubescen (cellulose, hemicellulose and lignin) exhibit different reactivity in decomposition and are mainly converted to different chemical species through the thermo-chemical routes respectively. When the decomposition of these three components is carried out by pyrolysis, the obtained pyrolysis oil provides a mixture composed of many kinds of carboxylic acids, furans and phenols (Liu, Hu, et al., 2010; Liu, Hu, Yang, Zhu, & Tong, 2010), which causes the separation difficulty. Hydrothermal liquefaction carried out in sub-/supercritical water is believed to be one of the efficient approaches to improve product selectivity, because the process could be operated at lower temperature than that for pyrolysis and the intermediates in sub-/supercritical water react according to ionic reactions instead of the free-radical mechanism in pyrolysis (Behrendt, Neubauer, Oevermann, Wilmes, & Zobel, 2008). Many researchers devoted to the isolation and extraction of hemicellulose, cellulose or lignin from biomass for further conversion (Buranov & Mazza, 2010; Peng et al., 2011; Rosa, Rehman, de Miranda, Nachtigall, & Bica, 2012; Sun & Sun, 2002; Zhang, Luo, et al., 2010). Furthermore, these three isolated components were converted to fuels or valuable chemicals through different ways (Lavarack, Griffin, & Rodman, 2002; Serrano-Ruiz, Braden, West, & Dumesic, 2010; Yuan, Cheng, Leitch, & Xu, 2010). These reports provided separated two-process way, that is, isolation firstly and

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then conversion of the three typical components of raw biomass. However, as was well-known, the three main components in biomass were connected complexly, and it was hard to isolate one component without affecting the others. Meanwhile, it was difficult to restrain hydrolysis of polysaccharides during the isolation process. Therefore, there would be a loss during the isolation process.

In our previous work (Luo et al., 2010), a new method for stepwise hydrothermal conversion of Pubescen was proposed. The first step performed at a moderate temperature for a shorter time could obtain furan-riched liquid product, while the second step proceeded at a higher temperature for a comparatively longer time could produce more phenol compounds. The results revealed the possibility to convert different components of Pubescen samples stepwise to obtain different kinds of compounds. Furthermore, it was found that 53.4% hemicellulose converted under the hydrothermal circumstance at 160 °C for 30 min, accompanied with the conversion of 7.6% cellulose and 20.9% lignin. It suggested that the stepwise conversion of hemicellulose, cellulose and lignin in Pubescen sample was possible, and hemicellulose was easily to be converted at 160 °C.

In this work, water–cyclohexane solvent was used to study the conversion of hemicellulose in Pubescen sample under solvothermal circumstance, in an attempt to simultaneously separate and convert hemicellulose in Pubescen sample at low temperature.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

Pubescen sample was purchased from Anji county of Zhejiang Province in the southeast of China. For experimental use, it was ground into powder smaller than 80 meshes and dried in an oven at 110 °C overnight. The solvents used in the liquefaction tests were distilled water and cyclohexane (AR).

2.2. Methods

2.2.1. Solvothermal treatment and product separation

The solvothermal treatment of Pubescen was carried out in a 300 ml stainless-steel autoclave reactor equipped with a stirrer. The reactor was charged with 10 g of Pubescen sample, and a mixture solvent composed of 100 ml water and 100 ml cyclohexane was added. The reactor was sealed, and the air contained was displaced by high-purity nitrogen. The reactor was subsequently pressurized to 2.0 MPa with nitrogen and then heated to 160 °C with a rate of 2.5 °C min^{-1}. After reaction, the reactor was cooled down to room temperature. The gaseous product was collected in a pre-vacuumed gas-bag and then analyzed using gas chromatography (GC) with a thermal conductivity detector (TCD). The results showed that only CO_2 was detectable, and thus the gaseous product was not discussed in detail. The liquid products and solid residues (SR) in the reactor were completely rinsed using water and cyclohexane alternatively, and then the resulted suspension was filtered under reduced pressure through a pre-weighed filter paper. The liquid mixture was shaken and then allowed to separate into two layers with separatory funnel. The upper layer was cyclohexane phase and the sub-layer was aqueous phase. The SR products and filter paper were dried at 110 °C over night before weighing.

2.2.2. HPLC analysis

Organic acids (formic acid and acetic acid), furans (5-HMF and furfural) and phenols (phenol, 2-methoxyphenol, 2,6-dimethoxyphenol, 4-ethylphenol, 4-ethyl-2-methoxyphenol) in cyclohexane phase and aqueous phase were quantitatively detected by high performance liquid chromatography (HPLC) using calibration curves of authentic samples. The HPLC system (Agilent Technologies 1200 series) was equipped with a UV detector, and Eclipse XDB-C18 column was used. UV detector at 200 nm was used to detect the organic acid, and 10% acetonitrile–water solvent was used as mobile phase. The flow speed of mobile phase was kept at 0.3 ml min^{-1} for 10 min, and then increased gradually to 3.5 ml min^{-1} at 18 min and retained to the end. For the analysis of furans, UV detector was set at 285 nm for 5 min at the beginning, and then changed to 210 nm and kept herein. Double pump was used, pump A was used to pump 10% acetonitrile–water solvent and pump B for 100% acetonitrile. The ratio of the mobile phase from pump B increased from 0% to 40% in 25 min keeping the total speed at 1.2 ml min^{-1}. On the other hand, ethanol–water system was used to analyze the cyclohexane-phase. UV detector was set at 275 nm for 5 min at the beginning, and then changed to 215 nm and kept herein. Double pump was also used. Pump C was used to pump 10% ethanol–water solvent and pump D for 100% ethanol. The ratio of the mobile phase from pump B decreased from 100% to 60% in 20 min while the total speed decreased from 0.8 ml min^{-1} to 0.6 ml min^{-1}. In the analysis, phenylacetonitrile was used as internal standard. Since the total phenols were only 0.1–0.2 wt%, we did not discuss them in detail. The products were quantified according to the calibration curve constructed previously by the authentic samples. Moreover, the yield of residue or liquid products (summation of the aqueous and cyclohexane phase) was defined as the percentage of the quantity of residue or liquid products to the amount of Pubescen added. All the experiments in this work were conducted for three times parallelly. The yields of various products were the averages of the results from three parallel experiments, with the error less than ±0.5 wt%.

2.2.3. Characterization of the solid residue

The components, that is, hemicellulose, cellulose and lignin in the unconverted part of the samples at different reaction time were analyzed using classical chemical titration methods. The experimental details of the analysis could be obtained from reference (Qi et al., 2006). The averages deviation of titration is less than ±0.4 wt%.

The crystalline forms of Pubescen samples and the residues after liquefaction for different reaction time were examined by XRD measurements on a DANDONG FANGYUAN DX-1000 instrument. The diffracted intensity of Cu Kα radiation ($k = 0.1540$ nm; 40 kV and 25 mA) was measured over the 2θ range from 4° to 80°. The crystallinity index (CI) of cellulose part in samples was determined by the following equation (Segal, Creely, Martin, & Conrad, 1959):

$$\mathrm{CI} = \frac{I_{002} - I_{\mathrm{AM}}}{I_{002}} \times 100\%$$

Here I_{002} was the peak intensity corresponding to the (0 0 2) ($2\theta = 22°$) lattice plane of the cellulose, and I_{AM} was the peak intensity observed at 2θ of 18°. I_{002} represents both crystalline and amorphous material while I_{AM} represented amorphous material only (Kumar & Gupta, 2009).

SEM characterization was performed by INSPECT F, at an acceleration voltage of 20 kV. Samples were coated with gold using a vacuum sputter-coater to improve the conductivity of the samples and thus the quality of the SEM images.

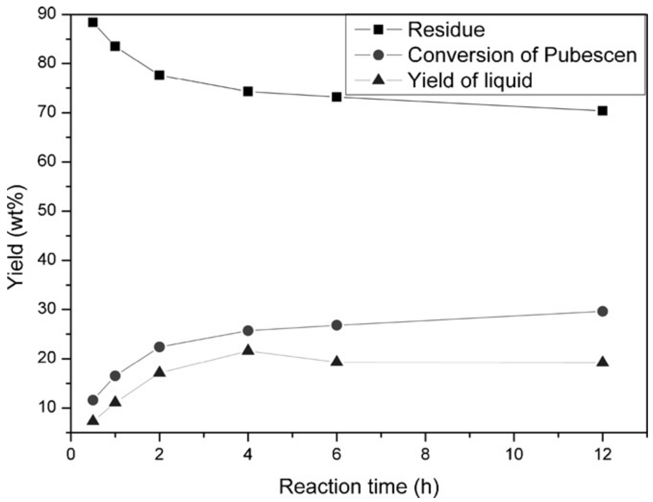

Fig. 1. Effect of reaction time on the conversion of Pubescen as well as the yields of residues and liquids in the liquefaction of Pubescen in water–cyclohexane solvent.

3. Results and discussion

3.1. *The conversion of Pubescen in water–cyclohexane system at 160 °C*

Liquefaction of Pubescen powder for various reaction times (0.5–12 h) was conducted. As illustrated in Fig. 1, the amount of residue decreased continuously with the increasing of reaction time at first, and the conversion rate slowed down after 4 h (74.3 wt% residue left). About 70.4 wt% residue still remained after 12 h. The conversion of Pubescen increased stepwise while the conversion rate decreased gradually with the reaction time. The yield of liquid reached the maximum at 4 h and then fluctuated around almost a constant. As compared to our previous work (Luo et al., 2010), after the reaction at 160 °C for 30 min, the amount of residue was 77.4 wt% in water solvent which was lower than that of 88.4 wt% in water–cyclohexane solvent. Considering the Pubescen samples used were obtained from different area in China compared to our previous work (Luo et al., 2010), another control experiment was carried out using water as the reaction solvent under the same conditions (the same equipment, the same starting material and the same handling procedures as using water–cyclohexane solvent). The amount of residue obtained was 79.5 wt%, which was close to that (77.4 wt%) reported by our previous work (Luo et al., 2010) and much lower than that of 88.4 wt% in water–cyclohexane solvent. It suggested that the water–cyclohexane solvent decreased the conversion rate of Pubescen. It may be helpful to realize the stepwise conversion of Pubescen.

3.2. *The conversion of hemicellulose in water–cyclohexane system*

3.2.1. *The variation of the three main components with time*

The content of hemicellulose, cellulose and lignin in raw Pubescen and its derived residues were analyzed through chemical titration, and the results were summarized in Table 1. The dried Pubescen material contained 17.9 wt% hemicellulose, 51.9 wt% cellulose and 24.0 wt% lignin. The conversion of hemicellulose was 30.2% in the water–cyclohexane solvent while in our previous work (Luo et al., 2010) it reached 59.4% when using water as reaction medium at 160 °C for 0.5 h. It indicated that the water–cyclohexane solvent cut down the conversion rate of hemicellulose. Table 1 also indicated that the cellulose was hardly degraded after the reaction for 0.5 h (only 0.8 wt%), as compared to our previous work (Luo et al., 2010), where 7.6% of cellulose was degraded. In the present work, there was only 5.6% of cellulose degraded when the reaction time was 6 h. It revealed that water–cyclohexane solvent slowed down the degradation rate of cellulose in Pubescen. It was favorable toward stepwise conversion of Pubescen.

The main degradation of lignin took place during the first half-hour, with a degradation percentage of 13.8%. The easy degradation of part of lignin at 160 °C was also observed in our previous work (Luo et al., 2010), using water as reaction medium for 0.5 h, where 20.9% of lignin degraded. It implied that the water–cyclohexane solvent also slowed down the degradation rate of lignin in Pubescen, while the degree of lignin degradation was also lowered. On the other hand, the content of lignin fluctuated around almost a constant after the reaction for 4 h. It implied that the easily degradable part of lignin was converted almost completely at low reaction temperature of 160 °C within 0.5 h.

Various solvents were used to enhance the conversion rate of raw biomass. Yip, Chen, Szeto, and Yan (2009) found that phenol was the optimum solvent for bamboo liquefaction with a yield up to 99%, and cellulose, hemicelluloses and lignin were almost decomposed. Cheng, D'cruz, Wang, Leitch, and Xu (2010) found that the 50 wt% co-solvent of either methanol–water or ethanol–water was the most effective solvent for the liquefaction of eastern white pine sawdust. The 50 wt% aqueous alcohol at 300 °C for 15 min produced a bio-oil yield of approximately 65 wt% and a biomass conversion of more than 95%. However, those literatures were mainly concerning the solvolysis or degradation of total biomass. Hemicellulose, cellulose and lignin were all effectively converted into liquid and gaseous products. It was known that the products from the conversion of these three different components (cellulose, hemicellulose and lignin) were complex, and the main liquid products were different. Therefore, one-pot liquefaction of raw lignocellulosic biomass would be resulted in a more complicated liquid bio-oil, which brought lots of difficulties in the separation and refinement of bio-oil. In our previous work (Luo et al., 2010), the conversion of hemicellulose reached 59.4% while that of cellulose or lignin was 7.6% or 20.9% after hydrothermal reaction at 160 °C for 0.5 h, respectively, which showed the possibility of stepwise conversion of hemicellulose, cellulose and lignin based on the chemical behaviors of the three different components. However, the conversion of cellulose took place even when the reaction time was only 30 min in water medium. In the present work, 86.6% of hemicellulose was converted while only 5.6% of cellulose and 22.5% of lignin degraded after the reaction at 160 °C for 6 h in the water–cyclohexane solvent, which suggested the separation and selective conversion of hemicellulose in Pubescen was realized. It indicated that the mixed solvent played an important role in reducing the conversion rate of Pubescen, and the reduction of conversion rate of cellulose and lignin was more significant, that is, the conversion of hemicellulose in Pubescen could proceed with reduced conversion of cellulose and lignin.

3.2.2. *The XRD measurement*

In order to measure if the crystal structure of cellulose in Pubescen was influenced by solvothermal treatment, XRD analysis of the samples before and after reaction was carried out. Fig. 2 shows the XRD patterns of Pubescen and the solid residues after liquefaction under different reaction times in the water–cyclohexane solvent at 160 °C. Four characteristic peaks at $2\theta = 14.6^\circ$, 16.5°, 22.4°, and 34.6° corresponding to the diffraction of the $(\bar{1}\,1\,0)$, $(1\,1\,0)$, $(0\,0\,2)$, and $(0\,4\,0)$ planes of cellulose I (Cheng et al., 2010; Nishio & Manley, 1988; Zhang & Kamdem, 2000) were clearly observed. The XRD patterns of residues were almost the same after the reaction within 4 h, which suggested that the cellulosic

Table 1
Chemical titration results of Pubescen and its derived residues.

Reaction time (h)	Hemicellulose		Cellulose		Lignin	
	Remained ratio[a] (wt%)	Conversion (%)	Remained ratio[a] (wt%)	Conversion (%)	Remained ratio[a] (wt%)	Conversion (%)
Pubescen	17.9	0	51.9	0	24.0	0
0.5	12.5	30.2	51.5	0.8	20.7	13.8
1.0	8.6	52.0	51.4	1.0	20.1	16.3
2.0	4.9	72.6	50.3	3.1	19.5	18.8
4.0	3.3	81.6	49.3	5.0	18.8	21.7
6.0	2.4	86.6	49.0	5.6	18.6	22.5
12.0	1.8	89.9	46.6	10.2	17.9	25.4

[a] Based on the weight of raw Pubescen materials.

crystalline structures in the residue remained perfectly. This agreed well with the results of chemical titration, that is, the content of cellulose in the residue almost did not change until 4 h. Based on Fig. 2, we also calculated the cellulose crystallinity index of the samples. The cellulose crystallinity index in the residue after the reaction for 4 h (80.2%) was higher than that of initial Pubescen sample (62.9%), which indicated that the crystal structure of cellulose become neater after the conversion of hemicellulose and other easily degradable components at 160 °C. The Pubescen was a lignocellulose complex in which hemicellulose, cellulose and lignin connect with each other via ether link or glucosidic linkage. The structure of lignocellulose complex was damaged when hemicellulose and easily degradable lignin were converted. As reported by Wan, Wang, and Xiao (2010), when hemicellulose was extracted out of paper pulp with 8% NaOH under nitrogen protection, fibrils appeared to aggregate and form a more compact structure. However, the intensities of the cellulose peaks became weak after the reaction for 6 h, which suggested that the structure of cellulose might be hurt. According to the result of chemical titration, part of cellulose was converted. That is to say, it is the conversion of crystalline cellulose caused the decrease of cellulose content.

3.2.3. The SEM measurement

In order to measure if the morphology and structure of Pubescen were influenced by solvothermal treatment, SEM analysis of the samples before and after reaction was carried out. Compared to Fig. 3(a), Fig. 3(b) shows clearly that the cellulose bundle was still perfectly existed. It illustrated that the cellulose was almost the same after the reaction for 4 h. We could observe clearly that the cellulose bundle began to be damaged after the reaction for 6 h from Fig. 3 (c). Fig. 3(d) indicates that although the main skeleton structure of cellulose was kept, cellulose bundles were slightly destroyed into shorter bundles after the reaction for 12 h. Therefore, it could be deduced that cellulose might be protected by outside hemicellulose–lignin composite. As the reaction proceeded, the hemicellulose–lignin composite was degraded, with more cellulose bundles easily exposed in the water–cyclohexane solvent. Therefore, cellulose began to be converted after most of the hemicellulose being converted, although the conversion rate was slow. The results coincided with that of the chemical titration and XRD measurement.

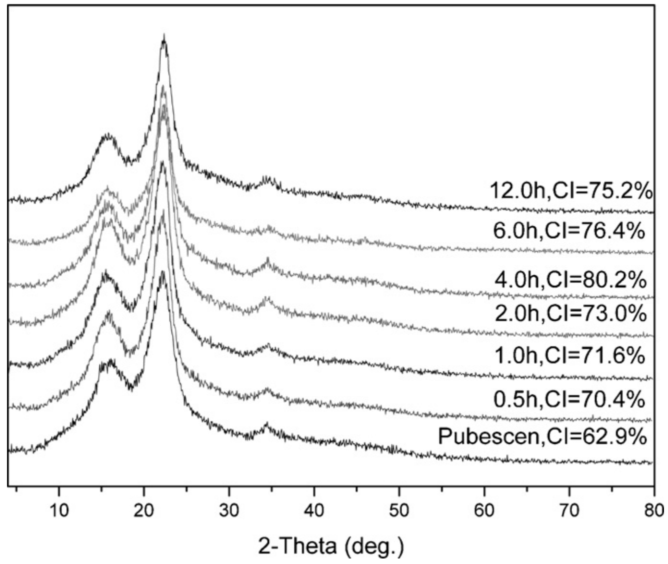

Fig. 2. X-ray diffraction patterns of Pubescen and residues at different reaction times at 160 °C.

3.3. Liquid products from the conversion of Pubescen (especially hemicellulose) at 160 °C

The variation of the amount of different products with reaction time from the liquefaction of Pubescen at 160 °C was given in Fig. 4. As illustrated in Fig. 4, acetic acid and formic acid were the main products. The yield of acetic acid gradually increased with reaction time and reached 13.0 wt% based on the Pubescen when the reaction time was 4 h. If all the acetic acid comes from the conversion of hemicellulose, the yield would be 90% based on the converted hemicellulose. However, acetic acid yield decreased slightly when the reaction time was more than 4 h, suggesting that prolonged reaction time resulted in the decomposition or conversion of acetic acid. The yield of formic acid had the similar tendency with that of acetic acid, with the maximum yield of 5.4 wt% at 6 h. Lu, Yamauchi, Phaiboonsilpa, and Saka (2009) suggested that the acetic acid mainly came from hydrolysis of acetyl groups in O-acetyl-4-O-methylglucuronoxylan in hemicellulose while formic acid proceeded from carboxylic groups of uronic acid (Demirbaş, 2000). Shen, Zhou, Zhou, and Zhang (2011) reported that the decrease of acetic acid was probably due to the decomposition of acetic acid to formic acid. Formic acid could be degraded into gaseous molecules, such as CO_2. Therefore, it was reasonable to deduce that hemicellulose totally converted to the chemicals with smaller molecular weights. The major component was acetic acid, which could further decompose in the reaction. In addition, the yields of furfural and 5-HMF continuously rose with the increase of reaction time, which might be mainly formed from the decomposition of pentoses and hexoses in hemicellulose. The increase of the amount of furfural and 5-HMF after 6 h might mainly be caused by the conversion of cellulose. The results coincided with that of the chemical titration and SEM measurement.

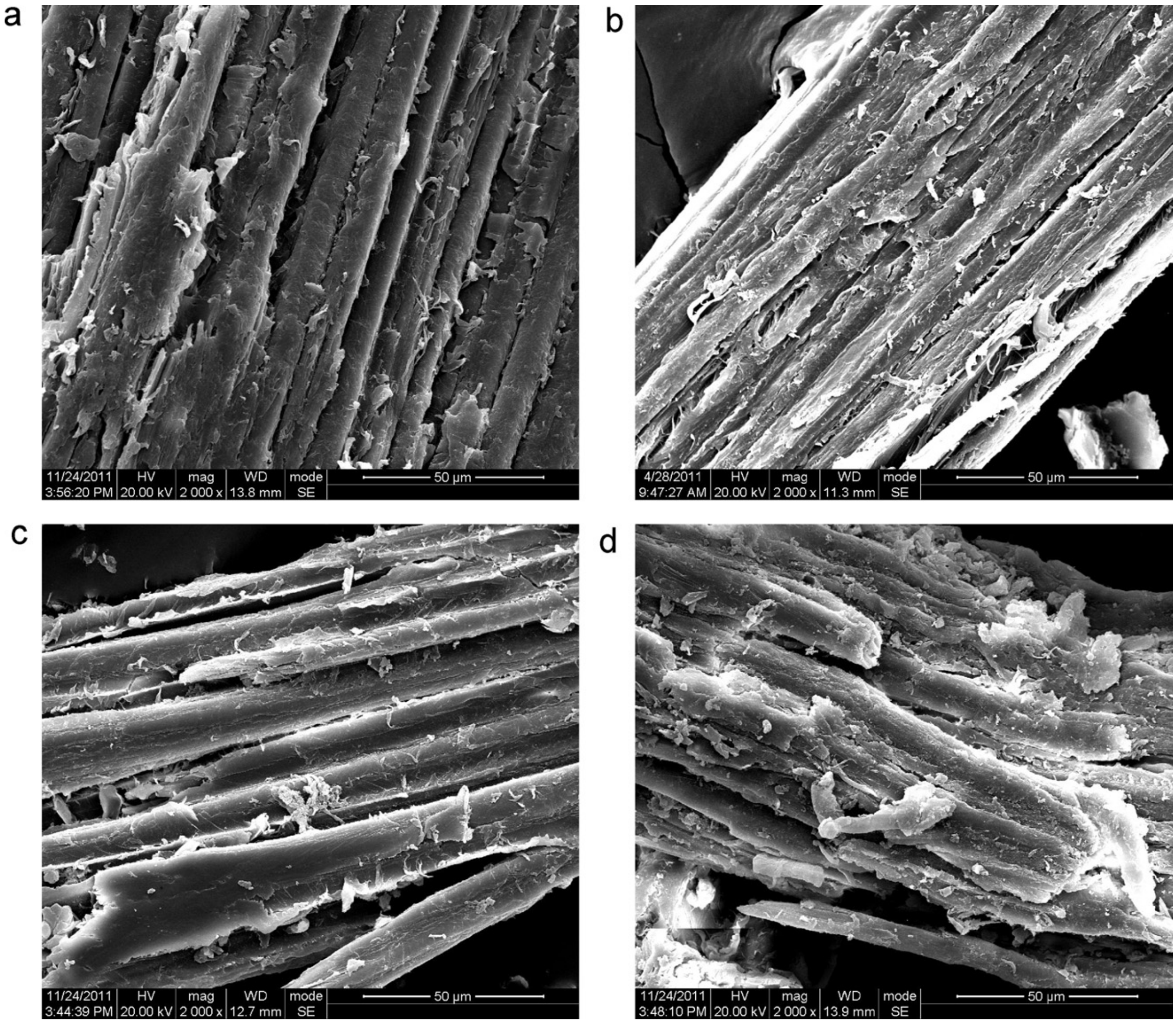

Fig. 3. SEM micrographs of (a) Pubescen feedstock, (b) Pubescen residue after 160 °C reaction for 4 h, (c) Pubescen residue after 160 °C reaction for 6 h, and (d) Pubescen residue after 160 °C reaction for 12 h.

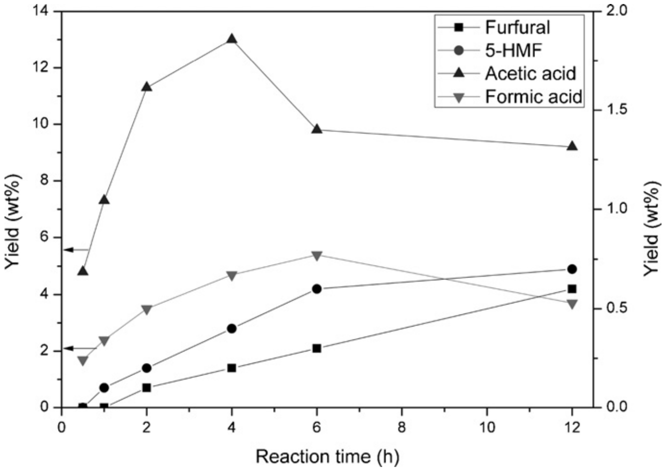

Fig. 4. The variation of the yield of different products from the conversion of hemicellulose in Pubescen at 160 °C (based on Pubescen added) with reaction time.

4. Conclusions

After solvothermal liquefaction with water–cyclohexane mixed solvent at 160 °C for 4 h, a maximum acetic acid yield of 13.0 wt% was obtained from the conversion of Pubescen. If all the acetic acid comes from the conversion of hemicellulose, the yield would be 90% based on the converted hemicellulose. The cellulose was hardly degraded after the reaction for 0.5 h (only 0.8 wt%). Only 5.6% of cellulose was degraded when the reaction time was 6 h while the conversion of hemicellulose reached 86.6%. The easily degradable part of lignin was converted almost completely at low reaction temperature of 160 °C within 0.5 h and the content of lignin fluctuated around almost a constant after the reaction for 4 h. As compared to water solvent, the mixed solvent played an important role in reducing the degradation of hemicellulose, cellulose and lignin, and the reduction of conversion rate of cellulose and lignin was more significant.

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