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ARTICLE TYPE

Selective Dissociation and Conversion of Hemicellulose in *Phyllostachys Heterocycla* cv. var. *Pubescen*s to Value-added Monomers via Solvent-thermal Methods Promoted by $AlCl_3$†

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Selective dissolution of hemicellulose from *Phyllostachys heterocycla* cv. var. *pubescen*s (short for *pubescens* afterwards), and conversion of dissolved hemicellulose into value-added monomers (such as furfural and levulinic acid) promoted by $AlCl_3$ under solvent-thermal conditions were investigated. Solid biomass samples were characterized by chemical titration and XRD techniques. Liquid products were analyzed by GC-FID, HPLC, and GPC. In the $AlCl_3$ promoted dissociation of hemicellulose from *pubescens*, the conversion of hemicellulose reached to 72.6 wt% without significant degradation of cellulose and lignin (only 10.4 wt% and 13.3 wt%, respectively) after hydrothermal treatment at a rather low temperature of 120 ºC for 4 h. The extracted hemicellulose could be divided mainly into two parts, that is, monomers (such as xylose, furfural and acetic acid, about 36.1%) and oligomers (about 63.9%). THF and SiO_2 were added, forming SiO_2-$AlCl_3$-H_2O/THF system, for the further conversion of the oligomers and monomers derived from hemicellulose. The selectivity to total monomers could reach 97.6% based on the converted *pubescens*. High selectivity to value-added monomers (39.1% furfural and 48.3% levulinic acid) was obtained at 160 °C.

1. Introduction

The conversion of biomass has attracted worldwide increasing interest with the depletion of fossil resource and the concern of environmental protection, because it is the only organic carbon renewable resource that can be converted into carbon-based liquid fuels and chemicals by multiple ways[1], such as pyrolysis[2,3], fermentation[4,5] and hydrolysis[6,7]. Lignocellulosic biomass is mainly composed of three components with complicated structure: hemicellulose, cellulose, and lignin. The complex structure of biomass brings big challenges for the synthesis of fuels and chemicals from biomass.

Solvent-thermal conversion of raw biomass has been proposed currently as one of the efficient approaches to obtain chemicals from biomass[4,8]. Many researchers paid much attention to the simultaneous decomposition of the three components in biomass in solvent-thermal process, which was efficient to improve the conversion of biomass[9, 10]. However, the complexity in structure and composition of biomass inevitably results in the complicacy of liquid products obtained, a mixture composed of many kinds of carboxylic acids, furans, phenols and some oligomers, then caused the difficulty in product separation and in the further use of the products.

A fractional route is believed to be an effective method to improve the product selectivity[11-13]. Hemicellulose that accounts for 15~35% of biomass is a heteropolymer consisting of different five- and six-carbon monosaccharide units[14,15]. The removal of hemicellulose from biomass is generally accompanied by the conversion of lignin and cellulose, because the structure of hemicellulose-lignin complex coating on cellulose is destroyed and then makes the degradation of lignin and cellulose easy[16]. Therefore, the selective removal of hemicellulose avoiding significant influence on other components preserves a big challenge. Various solvent-thermal methods had been investigated to conduct the selective dissolution of hemicellulose from biomass including water treatment[17], DMSO or DMSO/water treatment[18], combination of water treatment and water/acetone extraction, and formic acid/acetic acid/H_2O co-organic solvent treatment and so on[19]. These treatments were shown to be effective in removing hemicellulose without affecting the cellulose and lignin. In our previous work, a two-step hydrothermal conversion of *pubescens*[20] and the separation of hemicellulose in *pubescens* in water-cyclohexane solvent had been achieved[21]. These researches suggested that the stepwise conversion of *pubescens* was possible, and the hemicellulose contained could be converted at moderate temperature of about 160 °C. Therefore, developing high efficient method is crucial in facilitating the selective dissolution of hemicellulose and needs to be further investigated.

Metal chlorides, one kind of environmentally friendly catalysts with low toxicity, were used to convert effectively carbohydrates into value-added chemicals in recent years[22-25]. $AlCl_3$ was a promising Lewis acid catalyst for the selective conversion of carbohydrates with the addition of inorganic acid, organic solvents or ionic liquid[26-29]. In a biphasic medium of water and tetrahydrofuran (THF), $AlCl_3$ could effectively catalyze the conversion of C_5 and C_6 sugars respectively to obtain high yields of furfural and 5-hydroxymethyl furfural (5-HMF)[30,31]. Peng and Kamireddy et al studied the reaction mechanism of Lewis acid catalyst on hemicellulose dissolution, it was discovered that $AlCl_3$ was an excellent choice to produce chemicals such as furfural[32,33]. $AlCl_3$ was also found to be effective for the selective conversion of hemicellulose in corn stover[34]. The excellent performance of $AlCl_3$ is promising to play a vital role in the selective dissolution of hemicellulose in raw biomass under hydrothermal conditions.

Currently, synchronous isolation and selective conversion of hemicellulose remain one interesting issue for the effective use of hemicellulose in biomass. Considerable research efforts had been made to convert hemicellulose selectively from biomass to sugars or water-soluble oligomers, while the yields of value-added monomers obtained from hemicellulose were not high[35-37]. For the production of value-added monomers with high yield, another key challenge was the further degradation and conversion of the oligomers obtained from hemicellulose. Carrasquillo-Flores *et al.*[28] showed that water-soluble oligosaccharides were useful feedstocks for high-yield production of 5-HMF and furfural in a biphasic reaction system. Sahu *et al.*[38] developed a biphasic reaction system (water + *p*-xylene) for the selective conversion of oligomers from hemicellulose in biomass to obtain high-yield furfural. Although the improvement in the degradation of oligomers has been studied, the development of novel deploymerization processes for production of value-added monomers from lignocellulosic biomass with high yield is still required.

As a typical lignocellulosic biomass, *pubescens* shows potential for industrial exploitation because of its worldwide distribution and fast growth. Herein, in this work, a new two-step method was applied to selectively dissolve hemicellulose in *pubescens* and convert the dissolved hemicellulose into value-added monomers (such as furfural and levulinic acid) promoted by $AlCl_3$ under solvent-thermal conditions. Furthermore, the origin of liquid products was also investigated.

2. Experimental

2.1 Materials

Pubescens sample, purchased from Anji county of Zhejiang Province in China, was ground to 80 meshes, washed by distilled water for three times and dried at 110 ºC in an oven overnight before use. The main components of dried *pubescens* were 17.9 wt% hemicellulose, 46.5 wt% cellulose, and 25.4 wt% lignin. D(+)-Xylose (Merck Serono), xylan from beechwood (Japan Tokyo Chemical Industry Co), microcrystalline cellulose (Shanghai Chemical Reagent Factory) and anhydrous glucose (Chengdu Kelong Chemical Reagent Factory) were used without further treatment. Precursor catalyst $AlCl_3·6H_2O$ (AR, Chengdu Kelong Chemical Reagent Factory) was dried in a vacuum oven at 60 ºC for 10 h before use. SiO_2 purchased from Qingdao Xinchanglai Silicone Co (40-60 meshes, S_{BET} = 478 m^2/g) was calcined at 525 ºC in a muffle furnace for 4 h before use. All reagents (dichlormethane, THF) used in the experiment were purchased commercially and used without further purification.

2.2 Methods

2.2.1 Selective dissolution of hemicellulose in *pubescens*

Hydrothermal conversion of *pubescens* was conducted in a 250 mL stainless steel sealed autoclave. In a typical run, 5.00 g *pubescens* with 1.00 g $AlCl_3$ (The amount of $AlCl_3$ was chosen according to previous work[31,34] and literature[33]) and 100 mL water was loaded in the reactor. Then the reactor was sealed and the inner air was replaced by nitrogen. The initial pressure was added to 2.0 MPa with nitrogen. The reactor was heated from room temperature to desired temperature and then kept at the desired temperature for different time. After reaction, the reactor was cooled down to room temperature by cooling water. The gaseous products were collected in a pre-vacuumed gas-bag and then analyzed using gas chromatography (GC) with a thermal conductivity detector (TCD). A small amount of gaseous products (C_2H_6, CO_2, H_2, and CO) were detected, thus the gaseous products were not discussed in detail. For the further conversion of the oligomers and monomers, the mixture was poured out and the reactor was washed with distilled water for three times. The mixture was fully collected and filtered through a pre-weighed filter paper. The obtained liquid was noted as filtrate liquid (FL). For the product analysis and yield calculation, the mixture was poured out and the reactor was washed with distilled water and dichloromethane successively for three times. Solid residues obtained were dried at 110 ºC in an oven overnight and weighed to calculate the conversion of *pubescens*. Liquid products were extracted by dichlormethane and then were divided into organic phase and water phase which were analyzed by GC-FID and HPLC, respectively. The selectivity to liquid product was the sum of organic phase and water phase, and was defined as the weight percentage of product based on the converted *pubescens* feedstock. The selectivity to total monomers was defined as the summation of the selectivity to all the monomers obtained based on the converted *pubescens* feedstock. The selectivity to converting hemicellulose was calculated through the conversion of hemicellulose divided by the total conversion of the three components.

2.2.2 The degradation and conversion of FL

In order to investigate the degradation and conversion of the extracted components from *pubescens*, the FL was filtrated from the product mixture in the first-step reaction at 120 ºC for 4 h, then put in a 250 mL stainless steel sealed autoclave to complete the second-step reaction. The effects of SiO_2, THF, and the co-existence of SiO_2 and THF on the distribution of products at different temperature were studied. The influences of different volume ratios of FL to THF were researched at 160 ºC for 1 h. When the volume ratio of FL to THF was 1:3 or 1:4, the effect of reaction time was also studied at 160 ºC. The procedure for

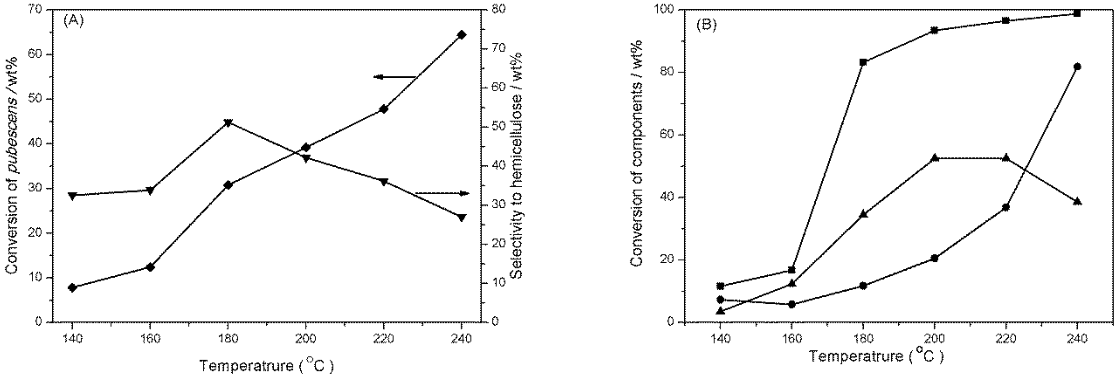

Fig. 1 Effect of different reaction temperature for 0.5 h in hydrothermal reaction: (A) the conversion of *pubescens* feedstock (-◆-) and the selectivity to hemicellulose (-▼-); (B) the conversions of the three components (hemicellulose: -■-; cellulose: -●-; lignin: -▲-) in *pubescens*.

treatment and analysis of the products in the second-step reaction was the same as that in the first-step reaction. Here, the selectivity to liquid product was also defined as the weight percentage of product based on the converted *pubescens* feedstock.

2.2.3 Analysis of liquid products

Products in water phase were analyzed by Dionex U-3000 High Performance Liquid Chromatography (HPLC) equipped with dionex PG-3000 pump, an aminex HPX-87 column (Bio-Rad) and shodex 101 Refractive Index Detector (RID). The temperature of column oven and detector were 50 ℃ and 35 ℃, and the mobile phase was 0.005 M H_2SO_4 solution at a flow rate of 0.6 mL/min. The content of products in water phase was quantified by external standard method.

Products in organic phase were analyzed by Fuli 9750 Gas Chromatography (GC) equipped with Flame Ionization Detector (FID) and a HP-innowax column (30 m×0.25 mm×0.25μm). The temperature of both the detector and injector were 280 ℃. The oven was heated from 50 ℃ to 250 ℃ at a rate of 5 ℃/min, then held at 250 °C for 10 min. The content of products was quantified by internal standard method and phenylacetonitrile was used as internal standard. Every sample was tested for three times to confirm the reproducibility of reported results.

The molecular weight distribution of liquid products was determined by Gel Permeation Chromatography (GPC) equipped with Waters 515 pump, 2410 refractive index detector and UL column (300×7.8 mm). The sample was dissolved in 1% NaCl solution at a final concentration of 5 mg/mL before measurement. 1% NaCl solution was used as eluent at a flow rate of 0.6 mL/min and the injection volume was 15 μL. Dextranum was used as the standard for molecular weight calibration.

2.2.4 Characterization of the solid biomass samples

The conversions of the three components in *pubescens* were determined through a typical chemical titration method. The details could be obtained in reference[39]. The average deviation of titration was less than ±0.5 wt%.

The crystalline structure of *pubescens* feedstock and residues after hydrothermal treatment at different temperature was characterized by X-Ray Diffraction (XRD) on DANDONG FANGYUAN DX-1000 instrument with monochromatic Cu K_α radiation (λ=1.542 Å) operated at 40 kV and 25 mA. The crystallinity index of cellulose in the samples, which could determine the relative crystallinity, was calculated using Segal's method as the following equation[40].

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

Where I_{002} is the intensity of diffraction peak at 2θ =22° corresponding to (002) plane of cellulose Ⅰ, and I_{AM} is the intensity of diffraction peaks at 2θ =18°. I_{002} represents both crystalline and amorphous material while I_{AM} represents amorphous material only[41].

3. Results and discussion

3.1 Selective dissolution of hemicellulose in *pubescens*

3.1.1 The influence of reaction temperature

The influence of reaction temperature on the hydrothermal conversion of *pubescens* was firstly investigated. As shown in Fig. 1(A), elevated temperature remarkably boosted the decomposition of *pubescens* from low conversion of only 7.8 wt% at 140 °C to high value of 64.4 wt% at 240 °C. The conversions of the three components in *pubescens* exhibited obviously different tendency with elevating temperature, as shown in Fig. 1(B). The conversions of the three components were all below 10.0 wt% at 140 °C. When the temperature increased from 140 °C to 160 °C, the conversion of hemicellulose and lignin gradually increased, while the conversion of cellulose almost remained. When the temperature increased from 160 °C to 200 °C, the degradation of hemicellulose and lignin were boosted observably, while that of cellulose increased slowly. When the temperature

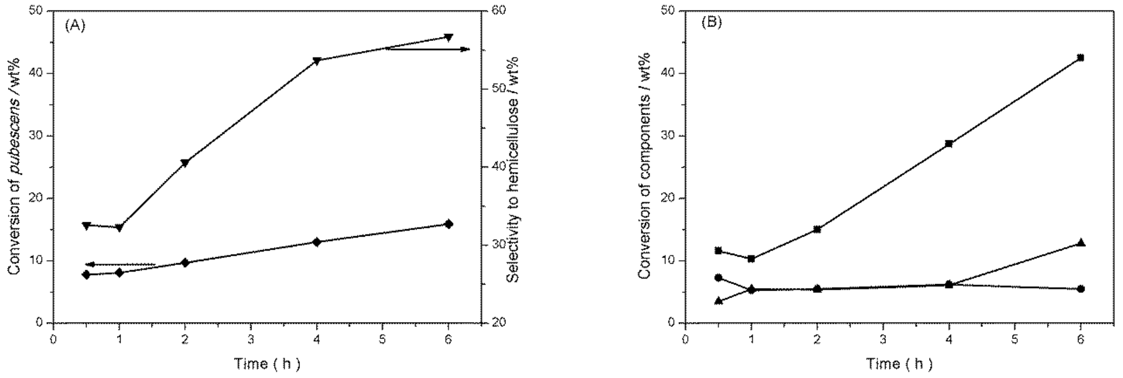

Fig. 2 Effect of different reaction time at 140 ºC in hydrothermal reaction: (A) the conversion of *pubescens* feedstock (-◆-) and the selectivity to hemicellulose (-▼-); (B) the conversion of the three components (hemicellulose: -■-; cellulose: -●-; lignin: -▲-) in *pubescens.*

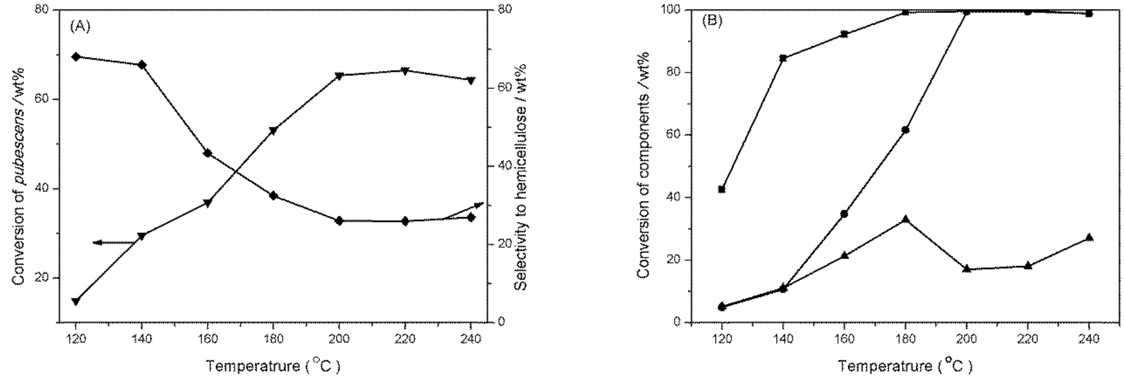

Fig. 3 The influence of reaction temperature in the presence of $AlCl_3$ for 0.5 h: (A) the conversion of *pubescens* feedstock (-◆-) and the selectivity to hemicellulose (-▼-); (B) the conversion of the three components (hemicellulose: -■-; cellulose: -●-; lignin: -▲-) in *pubescens.*

was above 200 °C, the three components presented different trends. The conversion of hemicellulose slightly increased to reach almost complete degradation. Nevertheless, as pointed out by Patil *et al*[42], the titration method could not give accuracy data for lignin beacause of the comtaminant of carbon decomposion from the conversion of hemicellulose and cellulose. Thus the varication of lignin content above 200 °C was not discussed. The degradation of cellulose increased significantly. As reported by Singh[43], most of the hemicellulose and part of the lignin were removed below 200 °C, thus increasing the accessibility of water to cellulose molecules under hydrothermal conditions. Therefore, the conversion of cellulose increased. The selectivity to hemicellulose increased gradually to a maximum value of only 51.2 % at 180 °C with increasing temperature. The low value indicated that the selective dissolution of hemicellulose was not easy under hydrothermal conditions. However, it was observed that the conversion variation of the three components in *pubescens* was different with varying temperature. So reaction temperature was one of the main factors to realize the stepwise conversion of *pubescens*.

3.1.2 The influence of reaction time

In the above mentioned results (Fig. 1(B)), the conversions of cellulose and lignin were low at 140 ºC. Therefore, in order to obtain selective dissolution of hemicellulose from *pubescens*, the influence of reaction time on the hydrothermal conversion of *pubescens* and the three components at 140 ºC was studied. As depicted in Fig. 2, the degradation of *pubescens* slightly increased from 7.8 wt% for 0.5 h to 15.9 wt% for 6 h. The degradation of hemicellulose displayed an obvious increasing tendency with prolonged time, while the degradation of lignin and cellulose remained almost unchanged. The increment of *pubescens* conversion should be mainly attributed to the increase of hemicellulose dissociation. Therefore, the selectivity to hemicellulose increased gradually to 56.7 % for 6 h.

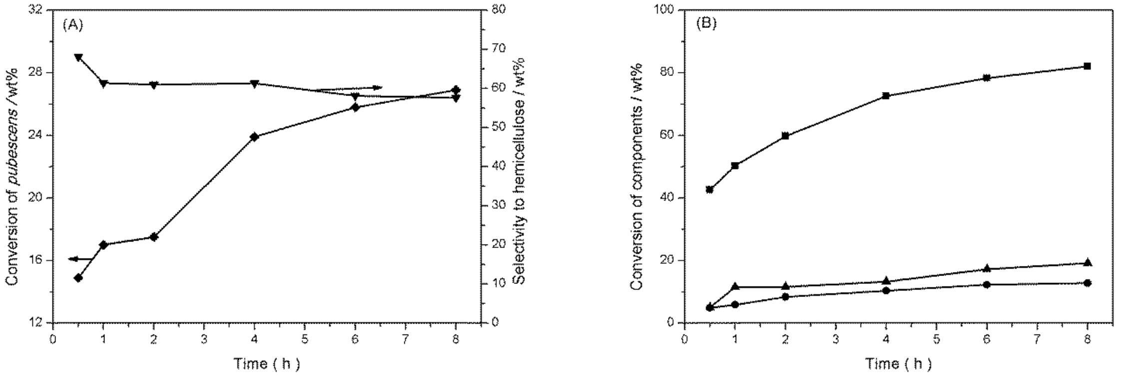

Fig. 4 The influence of reaction time in the presence of $AlCl_3$ at 120 ºC: (A) the conversion of *pubescens* feedstock (-◆-) and the conversion of the selectivity to hemicellulose (-▼-); (B) the conversion of the three components (hemicellulose: -■-; cellulose: -●-; lignin: -▲-) in *pubescens*.

The results suggested that reaction time had an impact on the selective dissolution of hemicellulose from *pubescens*. However, under the present conditions, the conversions of *pubescens* and hemicellulose were excessively low and the selectivity to hemicellulose conversion needed to be promoted. So it was necessary to optimize reaction conditions for the selective dissolution of hemicellulose from *pubescens*.

3.2 Selective dissolution of hemicellulose in *pubescens* in the presence of $AlCl_3$

3.2.1 The influence of reaction temperature in the presence of $AlCl_3$

$AlCl_3$ is a promising Lewis acid catalyst for the selective conversion of carbohydrates to obtain high yields of value-added chemicals[26-29]. Previous results indicated that the selective separation of hemicellulose from corn stover could be promoted by $AlCl_3$ under hydrothermal conditions[34]. Therefore, $AlCl_3$ was added into hydrothermal reaction to selectively dissolve hemicellulose in *pubescens*, and the results were shown in Fig. 3. The results showed that the conversion of *pubescens* was accelerated by $AlCl_3$, which increased from 7.8 wt% (in the absence of $AlCl_3$) to 29.5 wt% at 140 ^{o}C. With the temperature decreased to 120 ^{o}C, the conversion of *pubescens* was 14.9 wt% in the presence of $AlCl_3$ which was higher than 12.4 wt% obtained in the absence of $AlCl_3$ at 160 ^{o}C. With temperature increasing, the conversion of *pubescens* gradually increased.

The effect of reaction temperature on the conversions of the three components was shown in Fig. 3(B). When the temperature varied from 120 ^{o}C to 140 ^{o}C, the conversion of hemicellulose was facilitated sharply from 42.6 wt% to 84.5 wt%, while only small amount of cellulose (10.7 wt%) and lignin (11.1 wt%) were converted at 140 ^{o}C. Therefore, the stripping of hemicellulose from *pubescens* promoted by $AlCl_3$ could be observed clearly. When the temperature increased from140 ^{o}C to 240 ^{o}C, the conversion of hemicellulose gradually increased and reached almost complete conversion at about 180 ^{o}C. The conversion of cellulose significantly increased from 10.7 wt% at 140 ^{o}C to 99.4 wt% at 200 ^{o}C and kept almost constant till 240 ^{o}C. The variation trend of lignin degradation was the same as the above-mentioned results in the absence of $AlCl_3$. Therefore, in the presence of $AlCl_3$, the conversion of hemicellulose significantly increased within 140 ^{o}C. When the temperature varied from 140 ^{o}C to 200 ^{o}C, the conversion of cellulose was boosted observably. While the degradation of lignin needed higher temperature. The selectivity to hemicellulose conversion could reach a high value of 68.1 % at 120 ^{o}C. With elevated temperature, the conversions of the three components were all improved. The increment of cellulose conversion was obvious, leading to the gradual decline of the selectivity to hemicellulose.

Compared to the results in the absence of $AlCl_3$ (Fig. 1), the degradation of hemicellulose increased from 41.6 wt% in the absence of $AlCl_3$ to 84.5 wt% in the presence of $AlCl_3$ at 140 ^{o}C, and the selectivity to hemicellulose increased from 32.6 wt% in the absence of $AlCl_3$ to 66.0 wt%. The results suggested that $AlCl_3$ catalyst could accelerate remarkably the degradation of hemicellulose, especially at low temperature. As shown by Peng and Kamireddy et al[32,33], the mechanisms for the $AlCl_3$ catalyzed conversion of C6 oligomers and C5 oligomers in hemicellulose were shown in Fig. S3† and Fig. S4†. The aluminium acted as the Lewis acid and aided in cleaving of the glycosidic linkages, with the coordinated water molecules from the hydrated $AlCl_3$ participating as a nucleophile to form glucose and xylose, thus metal chlorides played a major role in the hemicellulose hydrolysis. It was revealed that the selective dissolution of hemicellulose from *pubescens* at low temperature could be achieved with $AlCl_3$ promotion.

3.2.2 The influence of reaction time in the presence of $AlCl_3$

As indicated by the above-mentioned results (Fig. 3), lower temperature was beneficial for the selective dissolution of hemicellulose. Since keeping the reaction system at low temperature was energy saving, the effect of reaction time on the selectivity to hemicellulose conversion from *pubescens* feedstock

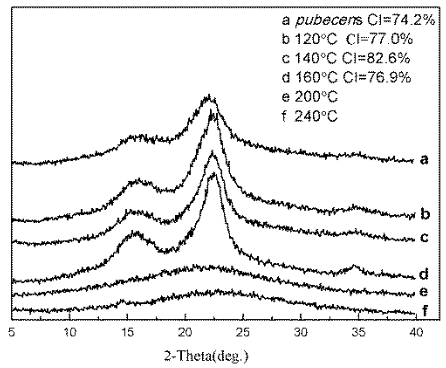

Fig. 5 XRD patterns of *pubescens* and residues after hydrothermal treatment at different temperature in the presence of $AlCl_3$ for 0.5 h

and on the conversion of the three components in the presence of $AlCl_3$ was studied at 120 ºC. As shown in Fig. 4(A), the conversion of *pubescens* feedstock was gradually improved with the reaction time increased from 0.5 h to 8 h. Compared with the result in the absence of $AlCl_3$ (Fig. 2(A)), the conversions of *pubescens* feedstock were significantly improved. In the absence of $AlCl_3$ (Fig. 2(A)), the selectivity to hemicellulose increased from 32.6 wt% to 56.7 wt% by prolonging time to 6 h at 140 ºC. While in the presence of $AlCl_3$, the selectivity to hemicellulose conversion displayed a decreasing tendency from 68.1 % to 58.3 wt% by prolonging time to 6 h at 120 ºC. The contrary trend and higher value of the selectivity demonstrated that $AlCl_3$ accelerated the degradation of hemicellulose. This accelerating effect favored the selective dissolution of hemicellulose from *pubescens* feedstock. Fig. 4(B) showed that the conversion of hemicellulose rose and most hemicellulose was transformed by prolonging time to 8 h (82.1 wt% conversion). The conversion of hemicellulose in the presence of $AlCl_3$ was 78.3 wt% at 120 ºC for 6 h which was much higher than 42.5 wt% obtained in the absence of $AlCl_3$ at 140 ºC for 6 h. The conversions of cellulose and lignin increased slightly and kept low values within 12.8% and 19.2% respectively. It was worthy to note that $AlCl_3$ particularly accelerated the dissociation of hemicellulose and then made its conversion much higher than those of cellulose and lignin. Therefore, the stripping of hemicellulose from the other two components in *pubescens* could be observed clearly. When the reaction was carried out at 120 ºC for 4 h, most of hemicellulose (72.6 wt%) was selectively isolated from *pubescens* without significant degradation of cellulose and lignin (only 10.4 wt% and 13.3 wt%, respectively). In order to verify the catalytic effect of Al^{3+}-species, HCl was used as catalyst at 120 ºC for 4 h. The results were shown in Table S7†. The results suggested that the selective dissolution of hemicellulose with HCl was not better than $AlCl_3$.

3.3 XRD analysis

The crystalline structure of *pubescens* feedstock and the residues after hydrothermal treatment under different reaction temperature in the presence of $AlCl_3$ were characterized by XRD. The XRD patterns and calculated crystallinity index were given in Fig. 5. *Pubescens* is a lignocellulosic complex in which hemicellulose,

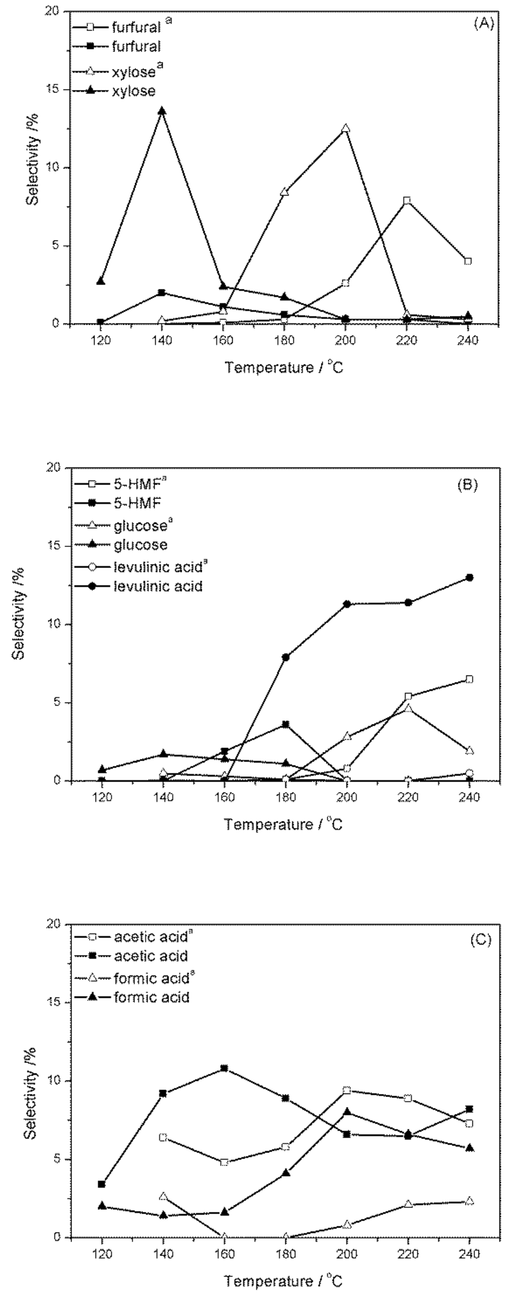

Fig. 6 The influence of reaction temperature on the distribution of liquid products carried out for 0.5 h without $AlCl_3$[a] and with $AlCl_3$. The amount of products (2,3-2H-benzofuran, 4-ethyl-2-methoxyl phenol, 4-ethyl phenol, vanillin and syringaldehyde) from the degradation of lignin in *pubescens* was very small (total less than 0.5 wt %) and was not discussed in this paper

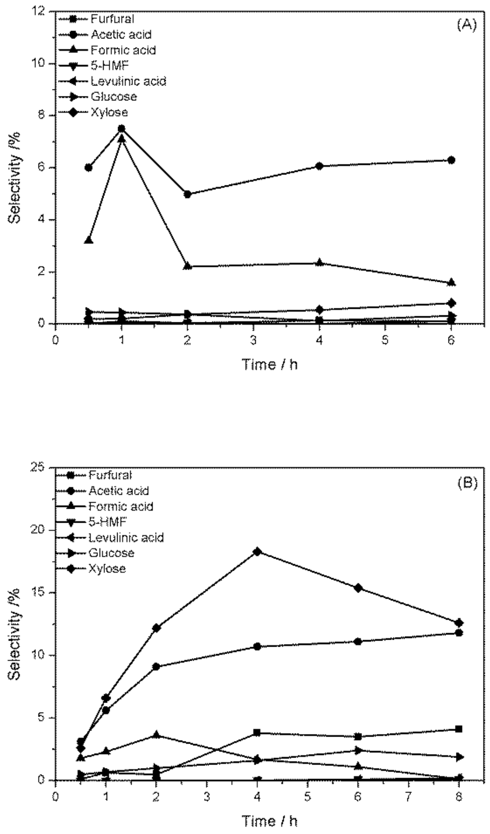

Fig. 7 The influence of reaction time on the product distribution in the hydrothermal conversion of *pubescens*: (A) at 140 ºC without $AlCl_3$; (B) at 120 ºC with $AlCl_3$

cellulose and lignin are connected to each other by ether links and/or glucosidic linkage[21]. For *pubescens* feedstock and the residues obtained within 160 ºC, there were four characteristic diffraction peaks at 2θ=14.6°, 16.5°, 22.4° and 34.6° corresponding to (110), (1$\bar{1}$0), (002) and (004) lattice planes of cellulose Ⅰ, respectively[44,45]. A slight increase in crystallinity index from 74.2% for the original material to 77.0% for that treated at 120 °C was observed. The results suggested that hydrothermal treatment at low temperature of 120 °C would not destroy obviously the crystalline structure of cellulose and maintained cellulose Ⅰ well, even most of hemicellulose and easily degradable lignin were removed after $AlCl_3$ promoted hydrothermal conversion. With the elevation of temperature to 140 °C, the enhanced diffraction peaks and increased crystallinity index (CI) of the residues indicated that cellulose crystallite became more ordered. It might be the result of the conversion of amorphous cellulose after the removal of hemicellulose[46]. When the temperature was elevated to 160 °C, the accessible surface of cellulose under hydrothermal conditions increased after the complete removal of hemicellulose, hence the degradation of cellulose was facilitated and the CI value declined. At high temperature above 200 °C, the disappearance of diffraction peaks resulted from the complete conversion of cellulose. The results matched well with the results of chemical titration.

3.4 The influence of reaction conditions on the distribution of liquid products

3.4.1 The influence of reaction temperature and $AlCl_3$ on the product distribution

The influence of reaction temperature on the distribution of liquid products in the hydrothermal conversion of *pubescens* for 0.5 h in the absence of $AlCl_3$ was shown in Fig. 6. Xylose, furfural, 5-HMF, formic acid, and acetic acid were the predominant products. The amount of isomerization products such as fructose, xylulose and lactic acid was small, and was not discussed in detail in this paper. The selectivity to xylose originated from the degradation of pentose units in hemicellulose got the maximum value at 200 ºC, followed by the maximum selectivity to furfural as the product of xylose dehydration at higher temperature of 220 °C. Whereas, the selectivity to glucose got maximum value at 220 ºC and the selectivity to 5-HMF from the hydration of hexose units increased monotonically with reaction temperature. A trace amount of levulinic acid was detected. It indicated that the degradation of pentose was easier than that of hexose. The selectivity to acetic acid got the maximum value at 200 ºC, while the selectivity to formic acid decreased from 140 ºC to 160 ºC and increased monotonically with reaction temperature raised to 240 ºC. As shown in Table S1†, the selectivity to total monomers was low below 160 ºC. With the raise of temperature to 240 ºC, the maximum selectivity to total monomers reached only 29.7% at 220 ºC. It meant that the converted *pubescens* mainly existed in the form of water-soluble oligomers[28].

When $AlCl_3$ was added, as shown in Fig. 6, the conversion of monomers was promoted. The maximum selectivity to xylose and furfural appeared at lower temperature of 140 ºC. The same phenomenon was observed for glucose and 5-HMF, while their maximum values occurred at 140 ºC and 180 ºC, respectively. The selectivity to levulinic acid and formic acid were significantly increased. It revealed that at higher temperature $AlCl_3$ could accelerate the hydrolysis of 5-HMF to generate levulinic acid and formic acid, which existed only in trace amount in liquid products without $AlCl_3$. The formation of acetic acid was also promoted by $AlCl_3$ which got the maxmuim selectivity at a lower temperature of 160 ºC. While the maxmuim selectivity to acetic acid obtained at a higher temperature of 200 ºC in the absence of $AlCl_3$**.** As shown in Table S2†, the selectivity to total monomers increased slightly when $AlCl_3$ was added, though $AlCl_3$ promoted remarkably the degradation of *pubescens* as mentioned above in Fig. 3. The results illustrated that the liquid products might contain mainly oligomers.

3.4.2 The influence of reaction time and $AlCl_3$ on the product distribution

As indicated by the results (Fig. 2(A) and Table S3†), the conversion of *pubescens* and the selectivity to total monomers were low at 140 ºC even when the reaction time prolonged to 6 h in the absence of $AlCl_3$. Therefore, the influence of reaction time at a lower temperature than 140 ºC on the distribution of liquid products was not discussed. Thus, the results obtained at 140 ºC (Fig. 7(A)) were used for comparision to discuss the influence of

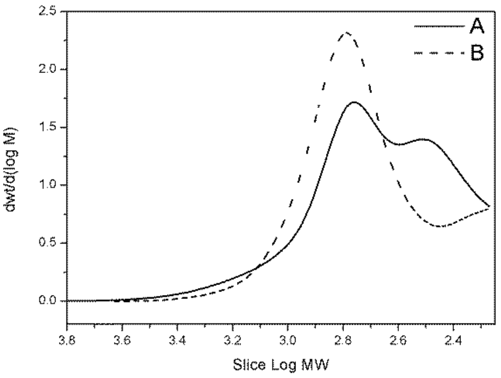

Fig. 8 The variation curves of different molecular weight detected by GPC for two different samples (A: The FL obtained at 120 ºC for 4 h; B: The FL obtained at 120 ºC for 4 h was directly heated to160 ºC for 1 h)

Table 1 Weight-average (*Mw*) and number-average (*Mn*) molecular weights and polydispersity (*Mw/Mn*) of the liquild fractions

Samples	M_W (g/mol)	M_n (g/mol)	polydispersity
FL (120 ºC 4.0 h) [a]	578	419	1.38
Liquid (160 ºC 1.0 h) [b]	614	477	1.29

[a] The FL obtained at 120 ºC for 4 h. [b] The FL obtained at 120 ºC for 4 h was directly heated to160 ºC for 1 h

reaction time on the distribution of liquid products in the presence of $AlCl_3$ at 120 ºC.

The typical compounds in liquid products and their dependence on reaction time at 140 ºC were presented in Fig. 7(A). The main products were acetic acid and formic acid, followed with a trace amount of xylose, glucose and furfural. 5-HMF and levulinic acid were almost not detected. The maximum selectivity to total monomers was only 15.4% (Table S3†) by prolonging reaction time to 1 h. The results suggested that the liquid products might contain oligomers. The influence of reaction time at 120 ºC in the presence of $AlCl_3$ was shown in Fig. 7(B). Compared with Fig. 7(A), the selectivity to liquid products was greatly promoted by $AlCl_3$ and the distribution of liquid products was changed. The main products changed from acetic acid and formic acid in the absence of $AlCl_3$ (Fig. 7(A)) to xylose and acetic acid in the presence of $AlCl_3$. A large amount of xylose was obtained from the hydrothermal conversion of hemicellulose in *pubescens* catalyzed by $AlCl_3$. The selectivity to xylose reached a maximum of 18.3% detected for 4 h. The selectivity to acetic acid increased gradually with increasing time and reached 11.8% after 8 h. Acetic acid was considered mainly coming from the hydrolysis of acetyl groups in O-acetyl-4-O-methylglucuronoxylan in hemicellulose[47]. It mainly rooted in the degradation of hemicellulose, so the selectivity increased with facilitated degradation of hemicellulose by prolonging time. The variation trend of formic acid in the presence of $AlCl_3$ was similar to that in the absence of $AlCl_3$. The selectivity to furfural and glucose were obviously promoted by $AlCl_3$ which increased gradually with prolonging time. 5-HMF was still almost not detected, while levulinic acid was detected when the time prolonged to 8 h. The results suggested that $AlCl_3$ significantly promote the synchronous dissolution and conversion of oligomers and monomers from hemicellulose. The promotion of $AlCl_3$ exhibited better performance on the hydrolysis of xylose oligomers to xylose followed by the further dehydration of xylose to furfural. Meanwhile, $AlCl_3$ was effective for the hydrolysis of glucan to glucose and then its further conversion to 5-HMF. The hydrolysis of 5-HMF to levulinic acid was also promoted by $AlCl_3$. However, the maximum selectivity to total monomers was only 36.1% obtained at 4.0 h. Based on the result, it could be deduced that the liquid products contained oligomers. Therefore, the large amount of xylose and the oligomers obtained at 120 ºC for 4 h needed to be further converted to value-added monomers for an effective use of the hemicellulose.

3.5 Molecular weight distribution of liquid products

GPC was used to estimate the degradation extent of *pubescens* feedstock after reaction catalyzed by $AlCl_3$. The variation trend of molecular weight detected by GPC for the two different samples was shown in Fig. 8. The distribution of molecular weight in FL obtained at 120 ºC for 4 h could be divided into two major peaks (line A). When the FL obtained at 120 ºC for 4 h was directly heated to 160 ºC for 1 h, only a shaper peak corresponding to large molecular weight was observed (line B).

The weight-average (*Mw*), number-average (*Mn*) molecular weights and the polydispersity (*Mw/Mn*) of liquid fractions determined by GPC were presented in Table 1. In FL obtained at 120 ºC for 4 h, *Mw* was 578 g/mol and *Mn* was 419 g/mol, which were near to the weight of three or four molecules of xylose. The results confirmed the formation of oligomers with the polydispersity of 1.38. The molecular weight (*Mw*) of 578 g/mol was much lower than the reported data of hemicellulose treated with organic solvent (1786 g/mol[48], 2020–4574 g/mol[49]). This implied that the degradation of oligomers was improved in the presence of $AlCl_3$. In FL obtained at 120 °C for 4 h with HCl as catalyst (Table S8†), *Mw* was about 1120-1160 g/ mol, which was much higher than that of FL with $AlCl_3$ as catalyst. This suggested that $AlCl_3$ was better for the degradation of oligomers compared with HCl. When the FL obtained at 120 ºC for 4 h was directly heated to 160 ºC for 1 h, M_W increased from 578 g/mol to 614 g/mol, and *Mn* increased from 419 g/mol to 477 g/mol. The polydispersity varied from 1.38 to 1.29. This indicated that depolymerization was not promoted by directly heating to 160 ºC. On the contrary, reploymerization occurred and the distribution of molecular weight was concentrated by directly heating to 160 ºC.

3.6 The second-step reaction: the conversion of oligomers and monomers in the FL

3.6.1 The catalytic performance of SiO_2

In the above mentioned results, 72.6 wt% hemicellulose was separated from *pubescens* at 120 ºC for 4 h promoted by $AlCl_3$, while cellulose and lignin remained a little change. HPLC results indicated that the main liquid products were 18.3% xylose and 10.7% acetic acid. The selectivity to total monomers was only 36.1%, as shown in Table 2. GPC results proved the existance of

Table 2 The influence of solvent, SiO_2 catalyst and temperature on the product distribution for 1 h

Items		Selectivity / %							S_{Total} / %[f]
		Fur	AA	FA	5-HMF	LA	Glu	Xyl	
FL[a]		3.8	10.7	1.7	-	-	1.6	18.3	36.1
FL[b]	160 °C	4.4	13.5	2.8	0.2	0.6	-	-	21.6
FL/THF[c]	160 °C	8.3	3.6	1.9	0.1	0.5	0.1	0.1	14.7
	180 °C	10.1	5.7	4.2	0.2	2.3	0.1	0.4	23.1
	200 °C	9.2	4.6	2.3	0.2	2.0	-	0.4	18.8
SiO_2-FL[d]	160 °C	13.0	12.9	2.1	-	1.3	7.2	0.5	37.0
	180 °C	8.9	12.9	2.5	-	1.7	10.1	-	36.2
	200 °C	4.0	12.0	2.5	-	1.7	12.9	0.5	33.6
SiO_2-FL/THF[e]	160 °C	13.8	9.4	8.6	0.1	6.1	6.0	0.6	44.7
	180 °C	12.2	8.5	9.0	0.1	7.9	7.7	0.1	45.5
	200 °C	11.7	7.9	9.3	0.1	7.7	7.9	0.3	44.9

[a] FL= the filtrated liquid obtained at 120 °C for 4 h. [b] The 100 mL FL obtained at 120 °C for 4 h was directly heated to 160 °C for 1 h. [c] The further reaction was carried out with FL (50 mL) and THF (50 mL). [d] The further reaction was carried out with SiO_2 (1.00 g) and FL (100 mL). [e] The further reaction was carried out with SiO_2 (1.00 g), FL (50 mL) and THF (50 mL). [f] the selectivity to total monomers. Fur, AA, FA, 5-HMF, LA, Glu and Xyl were the abbreviation of furfural, acetic acid, formic acid, 5-hydroxymethyl furfural, levulinic acid, glucose and xylose.

some oligomers in the liquid products. The conversion of the oligomers and monomers to value-added chemicals remained one interesting issue for the effective use of biomass[28,38]. Therefore, the second-step reaction was applied to convert the oligomers and monomers originated from hemicellulose to value-added chemicals. As described in Table 2, when the FL was directly heated to 160 °C and kept for 1 h, xylose in the FL was nearly converted, while no significant increase in the selectivity to other products (such as furfural, AA and FA) was observed. Therefore, the selectivity to total monomers declined to only 21.6%. The decrease in selectivity to total monomers suggested that directly heating to 160 °C resulted in repolymerization of liquid products, which matched well with GPC results.

Compared with water solvent, organic solvent such as 2-butanol, acetone, methyl isobutyl ketone (MIBK) and gamma-valerolactone (GVL) were deemed to exhibit better performance for the transformation of hemicellulose to value-added products (such as furfural and levulinic acid) with high yield, especially THF was highly desirable which was identified as a biomass-derived green solvent[12, 31,50,51]. Thus the influence of FL/THF co-solvent on the product distribution was studied. The results were illustrated in Table 2. Compared with FL obtained at 120 °C for 4 h, the selectivity to glucose and xylose significantly decreased, while the formation of acetic acid was inhibited with THF solvent. The selectivity to furfural increased from 3.8% to 8.3%. The selectivity to formic acid remained a little change. Levulinic acid and 5-HMF were detected even though the selectivity was only 0.5% and 0.1%, respectively. The selectivity to total monomers was only 14.7%. With increasing temperature, the selectivity to monomers (furfural, AA et al) was still low. The selectivity to total monomers was only about 20.0% even when the temperature was raised to 200 °C. The low values indicated that repolymerization occurred and some oligomers from hemicellulose were still not converted. As reported by Xing[51], THF exhibited better performance on the conversion of monomers. This result suggested that THF was not beneficial for the conversion of oligomers in the reaction system.

Recently, Zhou reported that H-USY zeolite catalyst with pore structure was beneficial for the high yield of monosaccharides from oligosaccharides[36]. Dhepe *et al.* used microporous zeolites (H-USY, H-Beta and H- MOR) and mesoporous molecular sieves (Al-MCM-41 and Al-SBA-15) to catalyze the hydrolysis of dimmers and trimers from hemicellulose to monomer sugars[52]. Mochizuki *et al.* pointed out that SiO_2 catalysts with a certain pore size played an important role in the inhibition of polymerization reactions thus effectively reduce the content of undesirable compounds in the catalytic fast pyrolysis of Jatropha residues[53]. In order to improve further the selectivity to monomers in liquid products, SiO_2 catalyst was used in the present work. The results were shown in Table 2. At 160 °C for 1h, the selectivity to xylose decreased from 18.3% to 0.5% and the selectivity to furfural increased from 3.8% to 13.0%. A large amount of glucose was obtained with the selectivity increased from 1.6% to 7.2%. Levulinic acid began to be detected, although the selectivity was not high. There was also slight increase in the selectivity to acetic acid and formic acid. When the temperature increased from 160 °C to 200 °C, the selectivity to furfural decreased gradually and the selectivity to formic acid increased, which indicated that furfural was further degraded to formic acid. The selectivity to glucose significantly increased from 7.2% to 12.9% with increasing temperature, while the

Table 3 The effect of volume ratio of FL to THF and reaction time on the products distribution in the presence of SiO_2 at 160 °C

Volume ratio	Time (h)	Selectivity/ %							S_{total} / %[b]
		Fur	AA	FA	5-HMF	LA	Glu	Xyl	
1:0	1	13.0	12.9	2.1	-	1.3	7.2	0.5	37.0
1:1	1	13.8	9.4	8.6	0.1	6.1	6.0	0.6	44.7
1:3	1	21.3	9.0	27.5	0.5	18.0	4.3	3.4	84.0
	2	24.8(45.6)[a]	9.4	27.3	0.2	16.9(31.1)[a]	3.9	0.6	83.1
	4	24.1	8.7	25.8	0.1	16.6	3.9	-	79.1
1:4	1	19.8	10.2	28.8	0.1	23.5	4.9	4.9	92.3
	2	23.0	8.7	35.8	0.4	23.1	3.8	2.7	97.6
	4	21.3(39.1)[a]	9.5	33.9	1.9	26.3(48.3)[a]	4.0	0.3	97.3
1:5	1	18.8	8.8	30.3	0.7	20.3	4.3	10.0	93.2

[a] The selectivity to liquid product in bracket was defined as the weight percentage of product based on the converted hemicellulose in *pubescens* feedstock. [b] the selectivity to total monomers.

selectivity to levulinic acid slightly increased. The selectivity to acetic acid remained a little change even when the temperature was raised to 200 °C. The results suggested that SiO_2 catalyzed the conversion of xylose to furfural, and the degradation of oligomers of hexose to glucose. So the distribution of monomers in liquid products was changed with the addition of SiO_2 catalysts. However, the selectivity to total monomers was only 37.0% at 160 °C for 1 h which was similar to that of FL (36.1%), and then reduced to 33.2% gradually when the temperature was raised to 200 °C. The results suggested that SiO_2 catalysts were not particularly good for the conversion of some monomers and oligomers, while repolymerization of liquid products still occurred. Therefore, some oligomers still existed in the liquid products.

As known from the results, repolymerization occurred and large part of extracted hemicellulose still existed as oligomers in FL in the presence of SiO_2 catalyst or FL/THF co-solvent. Therefore, the further degradation of oligomers in FL with co-addition of SiO_2 catalyst and FL/THF co-solvent was studied. The results were shown in Table 2. It could be seen that the selectivity to levulinic acid and formic acid significantly increased in SiO_2-FL/THF system. The formation of acetic acid was inhibited and the selectivity to acetic acid decreased from 12.9% obtained in the presence of SiO_2 catalyst system to 9.4% in SiO_2-FL/THF system. A trace amount of 5-HMF and xylose was detected. The selectivity to glucose significantly increased from 0.1% in FL/THF co-solvent system to 6.0% in SiO_2- FL/THF system. The selectivity to furfural increased from 8.3% in FL/THF co-solvent system to 13.8% in SiO_2- FL/THF system.

The selectivity to levulinic acid and glucose increased with temperature elevated. Conversely, higher temperature led to a significant reduction of furfural selectivity which decreased from 13.8% at 160 ºC to 11.7% at 200 ºC. Xing *et al.* showed that higher temperature might lead to other side reactions which were not benefit for the enhancement of furfural[51]. The result of present work was consistent with their report. Increasing temperature exhibited unconspicuous effect on the selectivity to acetic acid and 5-HMF. The selectivity to total monomers remained a value of 45.5% which was higher than the selectivity to total monomers in SiO_2 catalyst (37.0%) and THF/FL co-solvent single system (14.7%). The results suggested that the great improvement of monomer selectivity might be ascribed to the synergistic effects of SiO_2 and THF. In the reaction system, a large amount of glucose was obtained when SiO_2 was added, thus it significantly promoted the further conversion of oligomers to monomer sugars, especially for the conversion of hexose oligomers to glucose. THF as a miscible co-solvent promoted the hydrolysis reaction and helped to protect products from degradation in catalytically-active phase, significantly enhanced the production of furfural and LA. THF limited the possible side reactions because of the lack of hydroxyl groups, resulting in higher selectivity[54,55]. So the addition of THF exhibited better performance on the further conversion of monomer sugars. Therefore, it was beneficial for the inhibition of polymerization, and the conversion of oligomers was also promoted with the co-addition of SiO_2 and THF.

3.6.2 The influence of volume ratio of FL to THF and reaction time

Based on the results above, the oligomers formed were converted to monomers improved by the co-existence of SiO_2 and THF. However, about 55.0% of converted *pubescens* still existed as oligomers and the selectivity to value-added chemicals (such as furfural and levulinic acid) were not high. To obtain complete degradation of oligomers to monomers in SiO_2- FL/THF system, the effect of different volume ratios of FL/THF on the product distribution at 160 °C for 1 h was carried out. The results were shown in Table 3. With increasing volume of THF in SiO_2-FL/THF system, the selectivity to furfural was facilitated sharply from 13.0% without THF to a maximum value 21.3% at the volume ratio of 1:3, and then reduced to 18.8%. The selectivity to

Table 4 The effect of different substrate on the product distribution in SiO_2-$AlCl_3$- H_2O/THF (1:4) at 160 °C for 1 h

Samples	Yield[a] / %							Y_{Total}[b] / %
	Fur	AA	FA	5-HMF	LA	Glu	Xyl	
Xylose	38.9	1.1	20.0	-	11.3	-	13.3	71.3[c]
Xylan	39.6	1.3	18.4	-	8.1	-	9.0	76.4
Glucose	-	0.3	3.9	10.6	2.7	29.2	-	16.5[d]
Microcrystalline cellulose	-	0.7	5.3	2.6	3.6	4.0	-	16.2

Reaction conditions: 0.2g substrate (xylose, xylan, glucose and microcrystalline cellulose), 1.00 g SiO_2, 0.08 g $AlCl_3$, 80 mLTHF, 20 mL water. [a] Yield was calculated based on the weight of samples. [b] The total yield was the summation of liquid products obtained. [c] The yield of xylose was not contained for the calculation of the total yield. [d] The yield of glucose was not contained for the calculation of the total yield.

formic acid significantly increased from 2.1% without THF to 30.3% at the volume ratio of 1:5. It was found that the selectivity to levulinic acid was promoted obviously, and the maximum value of 23.5% was obtained at the volume ratio of 1:4. The selectivity to acetic acid and glucose decreased gradually, while the selectivity to xylose gradually increased. However, the selectivity to 5-HMF was slightly changed. The selectivity to total monomers increased from 37.0% to 93.2% (a small amount of phenols was not contained) at FL/THF volume ratio of 1:5 for 1 h. It suggested that the further degradation of oligomers from hemicellulose was promoted with THF and SiO_2, and the oligomers were almost all degraded into monomers.

Though monomers with selectivity to total monomers of 93.2% at FL/THF volume ratio of 1:5 for 1 h were obtained, the main liquid product was formic acid with a selectivity of 30.3%, while the selectivity to furfural and levulinic acid were only 18.8% and 20.3%, respectively. In order to obtain more value-added chemicals, the effect of time on the product distribution at 160 °C at the volume ratios of 1:3 and 1:4 were studied. The results were also illustrated in Table 3. When the volume ratio of FL to THF was 1:3, the xylose was converted gradually with time, and reached almost complete conversion at 4 h. The selectivity to acetic acid and levulinic acid were reduced slightly. The selectivity to furfural firstly increased at 2 h and then kept almost constant till 4 h. The selectivity to total monomers decreased gradually from 84.0% to 79.1% with the time prolonged. When the volume ratio of FL to THF was 1:4, the selectivity to furfural and formic acid reached a maximum of 23.0% and 35.8% for 2 h, respectively. The selectivity to 5-HMF and levulinic acid increased gradually with time. The variation trend of the selectivity to xylose and acetic acid was the same as the volume ratio of 1:3. The selectivity to total monomers increased from 92.3% to 97.3%. When the volume ratio of FL to THF was 1:3, the highest selectivity to value-added chemicals (24.8% furfural and 16.9% levulinic acid) was obtained at 160 °C for 2 h. If all the furfural and levulinic acid came from the conversion of hemicellulose, the selectivity to furfural and levulinic acid could be 45.6% and 31.1% based on the converted hemicellulose, respectively. The maximum selectivity to value-added chemicals (21.3% furfural and 26.3% levulinic acid) was obtained at 160 °C for 4 h when the volume ratio of FL to THF was 1:4. If all the furfural and levulinic acid came from the conversion of hemicellulose, the selectivity to furfural and levulinic acid could be 39.1% and 48.3% based on the converted hemicellulose, respectively. Therefore, the second-step reactions were essential for the conversion of oligomers to value-added monomers.

Mineral acids (such as HCl and H_2SO_4) were usually used as catalysts to produce chemicals from biomass. Yang[56] et al used H_2SO_4 to convert of cotton straw to sugars and levulinic acid via 2-stage hydrolysis. Hirokazu Kobayashi[57] et al used activated carbons and 0.012% HCl in water to obtain high selectivity to glucose from real biomass, while the selectivity to value-added monomers was not high. Although the highest selectivity to chemicals from biomass was obtained, the conversion of cellulose and lignin was not avoided. Compared with the existing reports involving mineral acids, the simultaneously extraction and decompostion of the hemicellulose in *pubescens* selectively was achieved. In the FL, the $AlCl_3$ contained which might exihibit catalytic performance with the existence of SiO_2 and THF. In order to verify the catalytic effect of the $AlCl_3$, a comparsion with HCl was studied. As shown in Table. S9†, the results suggested that Lewis acid played an important role in the selective dissolution of hemicellulose and conversion of dissolved hemicellulose into value-added monomers. The effect of the Brönsted acid obtained by the hydrolyzation of $AlCl_3$ in aqueous systems was little. Therefore, the results also demonstrated that it was an efficient route to convert the hemicellulose in *pubescens* to furfural and levulinic acid selectively in the SiO_2-$AlCl_3$-H_2O/THF system.

3.7 The origin of liquid products

In order to further study the origin of liquid products from biomass, the conversion of some carbohydrates with typical structure like xylose, glucose, microcrystalline cellulose, and xylan were investigated in SiO_2-$AlCl_3$-H_2O/THF (1:4) at 160 °C for 1 h. The results were shown in Table 4. Using xylose as raw material, a small amount of acetic acid and about 39.0% furfural were obtained, accompanied with 20.0% formic acid and 11.3% levulinic acid, and the total yield was 71.3%. It suggested that most xylose was converted to monomers although 13.3% xylose was remained. When xylan was used, the distribution of products was similar to that obtained from xylose. 18.4% formic acid and 8.1% levulinic acid were obtained. 9.0% xylose remained and the total yield was 76.4%. The main product of glucose conversion was 10.6% 5-HMF, accompanied with the formation of levulinic acid. Formic acid with a trace amount of acetic acid was detected. The total yield was only 16.5% because a large amount of glucose (29.2%) was not converted. It suggested that side reactions for conversion of glucose (about 50%) might occur in this system. The yields of liquid products were low that the total yield was only 16.2% when starting from microcrystalline cellulose. This clearly indicated that under the reaction conditions employed in this study, the cellulose in *pubescens* was hardly converted, and the liquid products mainly come from xylan and xylose from hemicellulose in *pubescens*.

Therefore, the results implied the degradation of xylan to xylose and then further dehydration to furfural. The formic acid formed mainly came from the acid hydrolysis of formylated xylose oligomers and the acid hydrolytic fission of the aldehyde group in furfural[51], because the yield from xylose and xylan was higher than that from glucose and cellulose. A trace amount of acetic acid was obtained when xylose and xylan were used. So the formation of acetic acid in SiO_2-$AlCl_3$-H_2O/THF may be from the first-step reaction catalyzed by $AlCl_3$. The production of levulinic acid has been reported via two possible pathways[58]. One is via the hydrolysis of 5-HMF which came from the dehydration of hexose in hemicellulose or extracted cellulose to levulinic acid and formic acid, and the other one is via the reduction of furfural to furfuryl alcohol which was further hydrolyzed to levulinic acid. In this system, hydrogen was detected in gaseous products. Considering the fact that the reactor is made of stainless steel containing metals like nickel, the hydrogenation of furfural is possible. Thus, furfural can be hydrogenated to furfural alcohol and levulinic acid formation through furfurly alcohol is possible. The formation of furfuryl alcohol was also identified by GC-MS, which was in low content in our experiments when starting from xylose and xylan. In order to verify this possibility, we used furfural as raw material in the $AlCl_3$-SiO_2-H_2O/THF (1:4) system with 0.5MPa H_2, a small amount of levulinic acid and formic acid were obtained. Therefore, the formation of levulinic acid was through two possible pathways in the present reaction system. The result also suggested that levulinic acid and furfural mainly came from hemicellulose because the above-mentioned results proved cellulose hardly be converted. So value-added chemicals (39.1% furfural and 48.3% levulinic acid based on the converted hemicellulose) with high selectivity at 160 ^{o}C for 4 h were obtained in SiO_2-$AlCl_3$-H_2O/THF (1:4) system.

4. Conclusions

A new two-step process was developed for the selective dissolution and conversion of dissolved hemicellulose in *pubescens* to value-added monomers. $AlCl_3$ catalyst strongly promoted the selective dissolution of hemicellulose from *pubescens* without significant degradation of cellulose and lignin. The addition of SiO_2 and THF, forming SiO_2-$AlCl_3$-H_2O/THF system, promoted the complete degradation and conversion of dissolved hemicellulose oligomers to monomers. The selectivity to total monomers could reach 97.6% at volume ratio of FL to THF of 1:4 at 160 ^{o}C for 4 h. High selectivity to value-added monomers (39.1% furfural and 48.3% levulinic acid based on the converted hemicellulose) with high selectivity to total value-added monomers (87.4%) was obtained in SiO_2-$AlCl_3$- H_2O/THF (1:4) system at 160 ^{o}C. The method provided a significant guidance to complete degradation of hemicellulose in biomass to value-added monomers, while the reaction residue contained mainly cellulose (89.6%) and lignin (86.9%) could be further used as feedstock to produce fuels and chemicals.

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Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

1. H. Olcay, L. J. Xu, Y. Xu and G. W. Huber, *ChemCatChem*, 2010, **2**, 1420.
2. A. Demirbas, *Energy Convers. Manage.*, 2000, **41**, 633.
3. A. Demirbas, *Fuel Process. Technol.*, 2007, **88**, 591.
4. S. Brethauer and C. E. Wyman, *Bioresour. Technol.*, 2010, **101**, 4862.
5. F. Talebnia, D. Karakashev and I. Angelidaki, *Bioresour. Technol.*, 2010, **101**, 4744.
6. F. Jin and H. Enomoto, *Energy Environ. Sci.*, 2011, **4**, 382.
7. Z. G. Yang, H. Y. Kang, Y. F. Guo, G. Q. Zhuang, Z. H. Bai, H. X. Zhang, C. X. Feng and Y. P. Dong, *Ind Crop. Prod.*, 2013, **46**, 205.
8. F. M. Jin and Z. Y. Zhou, *Energy Environ. Sci.*, 2005, **39**, 1893.
9. S. S. Toor, L. Rosendahl and A. Rudolf b, *Energy,* 2011*,* **36**, 2328.
10. T. Etcheverry and C. B. Xu, *Fuel,* 2008, **87**, 335.
11. C. W. Hu, J. Luo, Y. Xu, Y. Zeng and D. M. Tong, *petrochem techno*, 2012, **41**, 245.
12. D. M. Alonso, S. G. Wettstein, M. A. Mellmer, E. I. Gurbuz and J. A. Dumesic, *Energy Environ. Sci.*, 2013, **6**, 76.
13. E. S. Kim, S. Liu, M. M. Abu-Omar and N. S. Mosier, *Energy Fuels*, 2012, **26**, 1298.
14. F. M. Gírio, C. Fonseca, F. Carvalheiro, L. C. Duarte, S. Marques and R. Bogel-Łukasik, *Bioresour. Technol.*, 2010, **101**, 4775.
15. E. M. Rubin, *Nature*, 2008, **454**, 841.
16. M. Stöcker, *Angew. Chem. Int. Ed.*, 2008, **47**, 9200.
17. P. Azadi, R. Carrasquillo-Flores, Y. J. Pagán-Torres, E. I. Gürbüz, R. Farnoodb and J. A. Dumesic, *Green Chem.*, 2012, **14**, 1573.
18. G. Hu, *J. A. Heitmann and O. J. Rojas,* BioResources, 2008, **3**, 94.
19. F. Xu, C. F. Liu, Z. C. Geng, J. X. Sun, R. C. Sun, B. H. Hei, L. Lin, S. B. Wu and J. Je, *Polym. Degrad. Stab.*, 2006, **91**, 1880.
20. J. Luo, Y. Xu, L. J. Zhao, L. L. Dong, D. M. Tong, L. F.Zhu and C. W. Hu, *Bioresour. Technol.*, 2010, **101**, 8873.
21. Y. Xu, L. B. Hu, H. T. Huang, D. M. Tong and C. W. Hu, *Carbohydr. Polym.*, 2012, **88**, 1342.
22. L. Liu, J. S. Sun, C. Y. Cai, S. H. Wang, H. S. Pei and J. S. Zhang, *Bioresour. Technol.*, 2009, **100**, 5865.
23. V. Choudhary, S. I. Sandler and D. G. Vlachos, *ACS Catal.*, 2012, **2**, 2022.
24. Z. H. Zhang and Z. K. Zhao, *Bioresour. Technol.*, 2010, **101**, 1111.
25. X. N. Lv, G. Li, F. Yang, P. Gao, Z. H. Liu, L. Meng and X. Q. Yu, *Ind. Eng. Chem. Res.*, 2013, **52**, 297.
26. L. X. Zhang, H. B. Yu, P. Wang, H. Dong and X. H. Peng, *Bioresour. Technol.*, 2013, **130**, 110.
27. S. De, S. Dutta and B. Saha, *Green Chem.*, 2011, **13**, 2859.
28. R. Carrasquillo-Flores, M. Käldström, F. Schüth, J. A. Dumesic and R. Rinaldi, *ACS Catal.*, 2013, **3**, 993.
29. Y. Yang, C. W. Hu and M. M. Abu-Omar, *Bioresour. Technol.* 2012, **116**, 190.
30. Y. Yang, C. W. Hu and M. M. Abu-Omar, *ChemSusChem.*, 2012, **5**, 405.

31. Y. Yang, C. W. Hu and M. M. Abu-Omar, *Green Chem.*, 2012, **14**, 509.
32. L. C. Peng, L. Lu, J. H. Zhang, J. P. Zhuang, B. X. Zhang and Y . Gong. Molecules, 2010, **15**, 5258.
33. S. R. Kamireddy, J. B. Li, M. Tucker, J. Degenstein and Y. Ji, Ind. Eng. Chem. Res. 2013, **52**, 1775.
34. J. Yi, T. He, Z. C. Jiang, J. M. Li and C. W. Hu, *Chin. J. Cata.*, 2013, **34**, 2146.
35. I. Hasegawa, K. Tabata, O. Okuma and K. Mae, *Energy Fuels*, 2004, **18**, 755.
36. L. P. Zhou, M. T. Shi, Q. Y. Cai, L. Wu, X. P. Hu, X. M. Yang, C. Chen and J. Xu, *Microporous Mesoporous Mater.*, 2013, **169**, 54.
37. Y. M. Kim, R. Hendrickson, N. Mosier and M. R. Ladisch, *Energy Fuels*, 2005, **19**, 2189.
38. R. Sahu and P. L. Dhepe, *ChemSusChem.*, 2012, **5**, 751.
39. W. Y. Qi, C. W. Hu, G. Y. Li, L. H. Guo, Y. Yang, J. Luo, X. Miao and Y. Du, *Green Chem.*, 2006, **8**, 183.
40. L. Segal, J. J. Creely, A. E. Martin and C. M. Conrad, *Text. Res. J.*, 1959, **29**, 786.
41. S. Kumar and R. B. Gupta, *Energy Fuels*, 2009, **23**, 5151.
42. P. T. Patil, U. Armbruster, M. Richter and A. Martin, *Energy Fuels*, 2011, **25**, 4713.
43. R. Singh, T. Bhaskar, S. Dora and B. Balagurumurthy, *Bioresour. Technol.*, 2013, **149**, 446.
44. J. K. Zhang and D. P. Kamdem, *Holzforschung*, 2000, **54**, 27.
45. Y. M. Nishio and R. S. John Manley, *Macromolecules*, 1988, **21**, 1270.
46. A. Emsley and G. C. Stevens, *Cellulose*, 1994, **1**, 26.
47. X. Lu, K. Yamauchi, N. Phaiboonsilpa and S. Saka, *J. Wood Sci.*, 2009, **55**, 367.
48. J. Yip, M. Chen, Y. S. Szeto and S. Yan, *Bioresour. Technol.*, 2009, **100**, 6674.
49. J. B. Shi, Q. L. Yang, L. Lin and L. C. Peng, *Ind. Crop. Prod.*, 2013, **44**, 542.
50. H. Amiri, K. Karimi and S. Roodpeyma, *Carbohydr. Res.*, 2010, **345**, 2133.
51. R. Xing, W. Qi and G. W. Huber, *Energy Environ. Sci.*, 2011, **4**, 2193.
52. P. L. Dhepe and R. Sahu, *Green Chem.*, 2010, **12**, 2153.
53. T. Mochizuki, D. Atong, S. Y. Chen, M. Toba and Y. Yoshimura, *Catal. Commun.*, 2013, **36**, 1.
54. C. M. Cai, T. Y. Zhang, R. Kumar and C. E. Wyman, *Green Chem.*, 2013, **15**, 3140.
55. M. H. Tucker, R. Alamillo, A. J. Crisci, G. M. Gonzalez, S. L. Scott and J. A. Dumesic, *ACS Sustainable Chem. Eng.* 2013, **1**, 554
56. Z. G. Yang, H. Y. Kang, Y. F. Guo, G. Q. Zhuang, Z. H. Bai, H. X. Zhang, C. X. Feng and Y. P. Dong, *Ind Crop. Prod.*, 2013, **46**, 205.
57. H. K. Kobayashi, M. Z. Yabushita, T. Komanoya, K. J. Hara, I. Fujita, and A. Fukuoka, *ACS Catal.*, 2013, **3**, 581.
58. E. I. Gürbüz, S. G. Wettstein and J. A. Dumesic, *ChemSusChem.*, 2012, **5**, 383.