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ARTICLE TYPE

Supplementary Information for

Selective Dissociation and Conversion of Hemicellulose in *Phyllostachys Heterocycla* cv. var. *Pubescens* to Value-added Monomers via Solvent-thermal Methods Promoted by AlCl₃

5 Yiping Luo^a, Libin Hu^a, Dongmei Tong^{a*}, Changwei Hu^{a*}

^a Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, 29 Wangjiang Road, Chengdu, Sichuan, 610064, China.

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10. References (S1-S5)

1. The influence of reaction temperature and AlCl₃ on the selectivity to total monomers

Table S1 The influence of reaction temperature on the selectivity to total monomers for 0.5 h hydrothermal reaction in the absence of AlCl₃

Temperature (°C)	140	160	180	200	220	240
Selectivity to total monomers /% ^a	9.8	6.1	14.9	28.2	29.7	22.8

5 ^a The selectivity to total monomers was defined as the summation of the selectivity to all the monomers obtained based on the converted *pubescens* feedstock

Table S2 The influence of reaction temperature on the selectivity to total monomers for 0.5 h hydrothermal reaction in the presence of AlCl₃

Temperature (°C)	120	140	160	180	200	220	240
Selectivity to total monomers /% ^a	8.8	27.9	19.2	27.9	26.5	25.1	27.5

10 ^a The selectivity to total monomers was defined as the summation of the selectivity to all the monomers obtained based on the converted *pubescens* feedstock

15 2. The influence of reaction time and AlCl₃ on the selectivity to total monomers

Table S3 The influence of reaction time on the selectivity to total monomers at 140 °C in the absence of AlCl₃

Time (h)	0.5	1.0	2.0	4.0	6.0
Selectivity to total monomers /% ^a	10.0	15.4	8.0	9.3	9.2

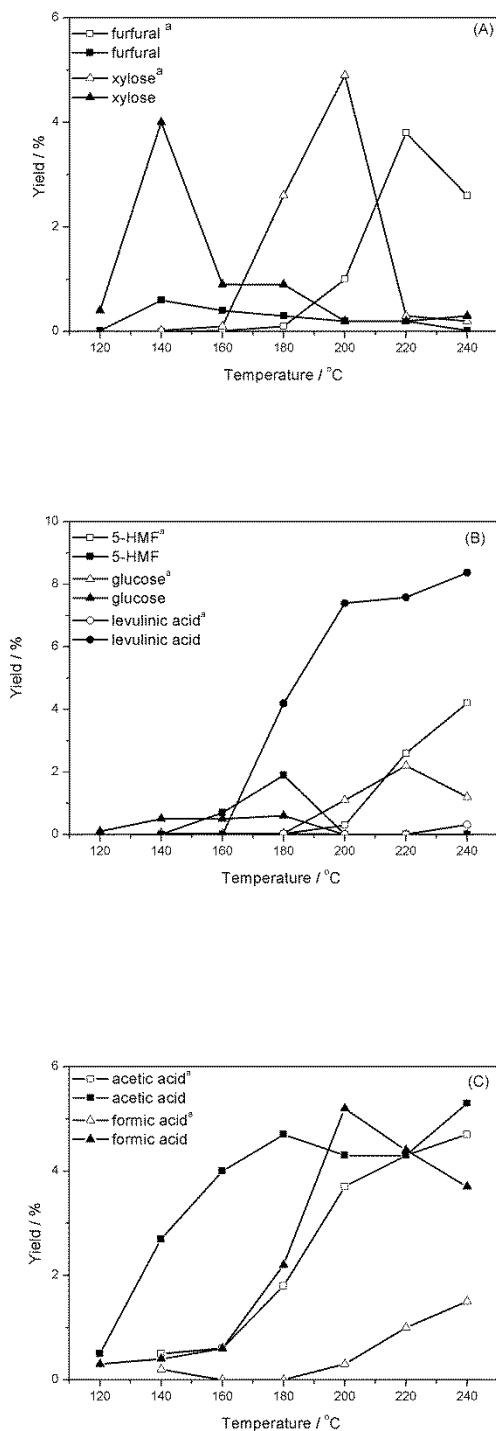
20 ^a The selectivity to total monomers was defined as the summation of the selectivity to all the monomers obtained based on the converted *pubescens* feedstock.

Table S4 The influence of reaction time on the selectivity to total monomers at 120 °C in the presence of AlCl₃

Time (h)	0.5	1.0	2.0	4.0	6.0	8.0
Selectivity to total monomers /% ^a	8.2	15.9	26.4	36.1	33.0	30.8

25 ^a The selectivity to total monomers was defined as the summation of the selectivity to all the monomers obtained based on the converted *pubescens* feedstock

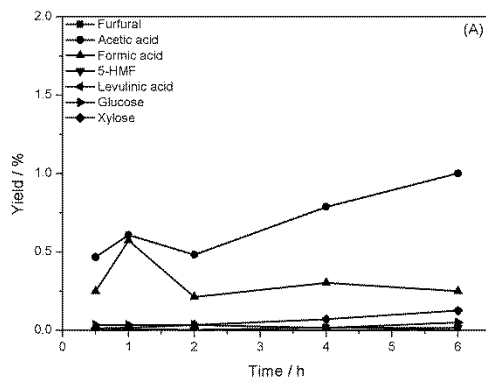
5 3. The influence of reaction temperature on the distribution of liquid products carried out for 0.5 h without AlCl₃ and with AlCl₃



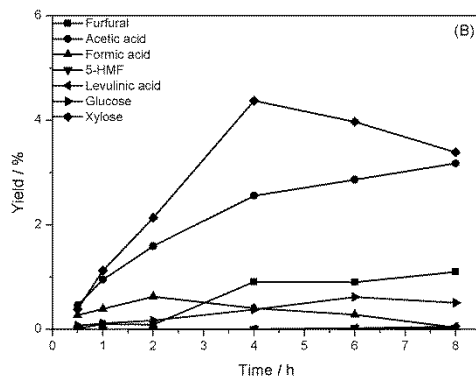
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15 **Fig. S1** The influence of reaction temperature on the distribution of liquid products carried out for 0.5 h without AlCl₃^a and with AlCl₃ (The yield of liquid product was defined as the weight percentage of product based on *pubescens* feedstock) .

4. The influence of reaction time on the product distribution in the hydrothermal conversion of *pubescens*



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10 Fig. S2 The influence of reaction time on the product distribution in the hydrothermal conversion of *pubescens*: (A) at 140 °C without AlCl₃; (B) at 120 °C with AlCl₃ (The yield of liquid product was defined as the weight percentage of product based on *pubescens* feedstock)

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5. The influence of solvent, SiO₂ catalyst and temperature on the product distribution

Table S5 The influence of solvent, SiO₂ catalyst and temperature on the product distribution for 1 h

Items		Yield ^f / %							Y _{total} ^g / %
		Fur	AA	FA	5-HMF	LA	Glu	Xyl	
FL ^a		0.91	2.56	0.41	-	-	0.38	4.37	8.63
FL ^b	160 °C	1.05	3.23	0.67	0.05	0.14	-	-	5.14
FL/THF ^c	160 °C	1.98	0.86	0.45	0.02	0.12	0.02	0.02	3.47
	180 °C	2.41	1.36	1.00	0.05	0.55	0.02	0.10	5.49
	200 °C	2.19	1.10	0.55	0.05	0.48	-	0.10	4.47
SiO ₂ -FL ^d	160 °C	3.10	3.08	0.50	-	0.31	1.72	0.12	8.83
	180 °C	2.12	3.08	0.60	-	0.41	2.41	-	8.62
	200 °C	0.96	2.87	0.60	-	0.41	3.08	0.12	8.04
SiO ₂ -FL/THF ^e	160 °C	3.30	2.25	2.06	0.02	1.46	1.43	0.14	10.66
	180 °C	2.92	2.03	2.15	0.02	1.89	1.84	0.02	10.87
	200 °C	2.80	1.89	2.22	0.02	1.84	1.88	0.07	10.72

^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 SiO₂ (1.00 g) and FL (100 mL). ^e The further reaction was carried out with SiO₂ (1.00 g), FL (50 mL) and THF (50 mL). ^f The yield of liquid product was defined as the weight percentage of product based on *pubescens* feedstock. ^g The total yield was the summation of liquid products obtained. 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.

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6. The effect of volume ratio of FL to THF and reaction time on the products distribution

Table S6 The effect of volume ratio of FL to THF and reaction time on the products distribution in the presence of SiO₂ at 160 °C

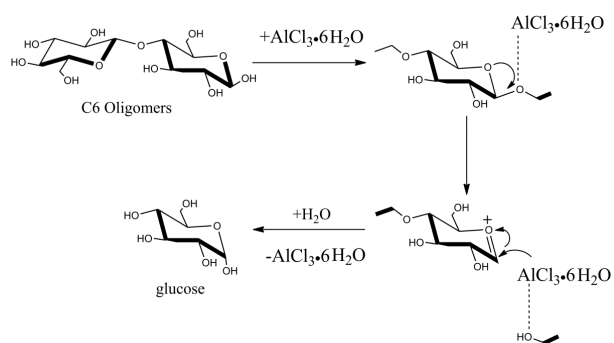
Volume ratio	Time (h)	Yield ^a / %							Y _{total} ^b / %
		Fur	AA	FA	5-HMF	LA	Glu	Xyl	
1:0	1	3.11	3.08	0.50	-	0.31	1.72	0.12	8.84
1:1	1	3.30	2.25	2.06	0.02	1.46	1.43	0.14	10.66
1:3	1	5.09	2.15	6.57	0.12	4.30	1.03	0.81	20.07
	2	5.93	2.25	6.52	0.05	4.04	0.93	0.14	19.86
	4	5.76	2.08	6.17	0.02	3.97	0.93	-	18.93
1:4	1	4.73	2.44	6.88	0.02	5.62	1.17	1.17	22.03
	2	5.50	2.08	8.56	0.10	5.52	0.91	0.65	23.32
	4	5.09	2.27	8.10	0.45	6.29	0.96	0.07	23.23
1:5	1	4.49	2.10	7.24	0.17	4.85	1.03	2.39	22.27

^a The yield of liquid product was defined as the weight percentage of product based on *pubescens* feedstock. ^b The total yield was the summation of liquid products obtained.

7. Analysis of liquid products

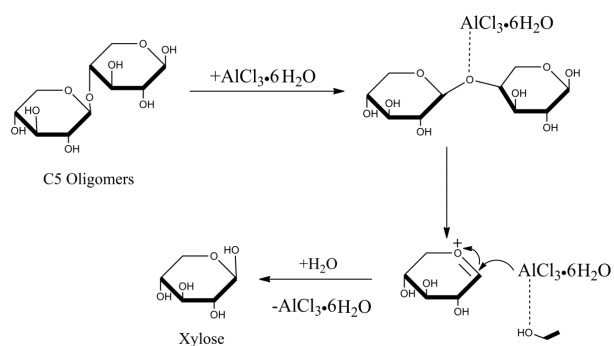
The isomerization products such as fructose and xylulose in the presence of AlCl₃ catalyst were observed. However, the amount of fructose and xylulose was small in the present work. Y. Yang^{S1-S2} showed that the isomerization of glucose to fructose was about 4 times slower than the dehydration of fructose to HMF. V. Choudhary^{S3} showed that the presence of Lewis acid promoted the formation of xylulose, leading to a faster, more selective transformation. In our reaction system, once fructose and xylulose were formed, they quickly participated in the further hydrolysis reaction, thus they were not stably existed. Therefore, the amount of fructose and xylulose was so small that it was not discussed detailedly in manuscript. The formation of lactic acid was also observed. But the yield of lactic acid was low especially with the addition of SiO₂ and THF. So we did not discuss detailedly in manuscript.

8. The mechanism for the AlCl_3 catalyzed conversion of C6 oligomers and C5 oligomers in hemicellulose to glucose and xylose in water^{S4-S5}



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Fig. S3 The mechanism for the AlCl_3 catalyzed conversion of C6 oligomers in hemicellulose to glucose in water.



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Fig. S4 The mechanism for the AlCl_3 catalyzed conversion of C5 oligomers in hemicellulose to xylose in water

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9. The catalytic effect of the Al³⁺-species

Table S7 The effect of different catalysts on the conversion of *pubescens* and the three components in *pubescens*

Samples	Conversion / wt. %				S _H ^d / wt. %
	<i>Pubescens</i>	Hemicellulose	Cellulose	Lignin	
HCl- <i>Pubescens</i> ^a	8.8	0.8	1.2	11.4	4.0
HCl- <i>Pubescens</i> ^b	38.2	98.2	18.4	28.8	52.6
AlCl ₃ - <i>Pubescens</i> ^c	23.9	72.6	10.4	13.3	61.3

⁵ ^a Condition: 5 g *pubescens*, HCl=4.47×10⁻² mmol (the pH of solution was 3.35, which was identical to the pH value of 100 mL aqueous solution with the addition of 1 g AlCl₃), 100 mL H₂O at 120 °C for 4 h. ^b Condition: 5 g *pubescens*, HCl=22.5 mmol (This amount was identical to that could be formed via the complete hydrolysis of 1 g AlCl₃ in 100 mL aqueous solution), 100 mL H₂O at 120 °C for 4 h. ^c Condition: 5 g *pubescens*, 1 g AlCl₃, 100 mL H₂O at 120 °C for 4 h. ^d The selectivity to hemicellulose.

10 Table S8 The GPC result of liquid fractions with different catalysts

Samples	M _w (g/ mol)	Mn(g/ mol)	Polydispersity
HCl- <i>Pubescens</i> ^a	1120	1110	1.01
SiO ₂ -FL/THF ^b	360	313	1.15
HCl- <i>Pubescens</i> ^c	1160	1130	1.03
SiO ₂ -FL/THF ^d	456	421	1.08
AlCl ₃ - <i>Pubescens</i> ^e	578	419	1.38

^a The FL obtained at 120 °C for 4 h with 4.47×10⁻² mmol HCl (the pH of solution was 3.35, which was identical to the pH value of 100 mL aqueous solution with the addition of 1 g AlCl₃). ^b The FL obtained by the further reaction of liquid fraction from *a* in HCl-SiO₂-FL/THF system at 160 °C for 4 h. ^c The FL obtained at 120 °C for 4 h with 22.5 mmol HCl (This amount was identical to that could be formed via the complete hydrolysis of 1 g AlCl₃ in 100 mL aqueous solution). ^d The FL obtained by the further reaction of liquid fraction from *c* in HCl-SiO₂-FL/THF system at 160 °C for 4 h. ^e The FL obtained at 120 °C for 4 h with 1 g AlCl₃.

Table S9 The influence of different catalyst on the product distribution

Items	Selectivity % ^g / %							S _{Total} % ^h
	Fur	AA	FA	5-HMF	LA	Glu	Xyl	
HCl- <i>Pubescens</i> ^a	-	6.2	0.8	-	-	0.1	0.1	7.2
HCl-SiO ₂ -FL/THF ^b	-	-	53.7	0.8	-	-	-	54.5
HCl- <i>Pubescens</i> ^c	3.3	5.4	-	0.1	-	3.9	20.3	33.0
HCl-SiO ₂ -FL/THF ^d	3.5	2.0	10.3	-	-	-	-	15.8
AlCl ₃ - <i>Pubescens</i> ^e	3.8	10.7	1.7	-	-	1.6	18.3	36.1
AlCl ₃ -SiO ₂ -FL/THF ^f	21.3	9.5	33.9	1.9	26.3	4.0	0.3	97.3

^a Condition: 5 g *pubescens*, HCl=4.47×10⁻² mmol (the pH of solution was 3.35, which was identical to the pH value of 100 mL aqueous solution with the addition of 1 g AlCl₃), 100 mL H₂O at 120 °C for 4 h. ^b Condition: 20 mL FL obtained from *a*, 80 mL THF, 1 g SiO₂ at 160 °C for 4 h. ^c Condition: 5 g *pubescens*, HCl=22.5 mmol (This amount was identical to that could be formed via the complete hydrolysis of 1 g AlCl₃ in 100 mL aqueous solution), 100 mL H₂O at 120 °C for 4 h. ^d Condition: 20 mL FL obtained from *c*, 80 mL THF, 1 g SiO₂ at 160 °C for 4 h. ^e Condition: 5 g *pubescens*, 1 g AlCl₃, 100 mL H₂O at 120 °C for 4 h. ^f Condition: 20 mL FL obtained from *e*, 80 mL THF, 1 g SiO₂ at 160 °C for 4 h. ^g The selectivity of liquid product was defined as the weight percentage of product based on the converted *pubescens* feedstock. ^h The selectivity to total monomers was defined as the summation of the selectivity of all the monomers obtained based on the converted *pubescens* feedstock. 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.

The effect of HCl and AlCl₃ catalysts on the conversion of *pubescens* and the three components in *pubescens* was shown in Table S7. Compared with the result of AlCl₃-catalyzed ones, the conversion of *pubescens* and the three components (hemicellulose, cellulose and lignin) was low when 4.47×10⁻² mmol HCl (the pH of solution was 3.35, which was identical to the pH value of 100 mL aqueous solution with the addition of 1 g AlCl₃) was used in 100 mL H₂O. When 22.5 mmol HCl (This amount was identical to that could be formed via the complete hydrolysis of 1 g AlCl₃ in 100 mL aqueous solution) was used in 100 mL H₂O, the conversion of *pubescens* was 38.2 wt% and 98.2 wt% hemicellulose was converted with significant degradation of cellulose and lignin (18.4 wt% and 28.8 wt%). While 1 g AlCl₃ was used in 100 mL H₂O, 72.6 wt% hemicellulose was extracted from *pubescens*, while significant conversion of cellulose and lignin was avoided.

The GPC results were shown in Table S8. In FL obtained at 120 °C for 4 h with HCl as catalyst, M_w was about 1120-1160 g/ mol, which was much higher than that of FL with AlCl₃ as catalyst. When the FL obtained at 120 °C for 4 h with HCl was heated at 160 °C for 4 h in the HCl-SiO₂-FL/THF system, M_w was about 360-456 g/ mol, which were near to the weight of two or three molecules of xylose.

The result suggested oligomers was also existed with HCl as catalyst, while the oligomers in FL were almost converted completely with AlCl₃ as catalyst.

The influence of HCl and AlCl₃ catalysts on the product distribution were shown in Table S9. The selectivity to value-added chemicals (such as furfural and levulinic acid) and the selectivity to total monomers were low with a lower concentration of HCl in the first-step reaction. The results matched well with the low conversion of *pubescens*. Although 53.7% formic acid was obtained in the second-step reaction, the selectivity to total monomers was still low. When a higher concentration of HCl was used, the main product in FL was xylose (20.3%) in the first-step reaction which was similar to the result of AlCl₃-catalyzed. However, when the FL was used for the second-step reaction in HCl-SiO₂-FL/THF system, 10.3% formic acid was obtained and the selectivity to other liquid products was low. The selectivity to total monomers was only 15.8%. The results suggested that some oligomers still existed which was confirmed by the results of GPC.

In conclusion, the results suggested that the selective dissolution of hemicellulose with HCl was not better than AlCl₃, while AlCl₃ was better for the degradation of oligomers compared with HCl. Therefore, 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 Brønsted acid obtained by the hydrolyzation of AlCl₃ in aqueous systems was little.

10. References (S1-S5)

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