Markedly different decomposition temperature and products of biomass pyrolysis at low temperature – differentiation of acids in their effects on pretreatment

Peifang Yan, Xiumei Liu, Zhanwei Xu, and Zongchao Conrad Zhang*

State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China.

*E-mail: zczhang@yahoo.com.

Dedicated to the 70th anniversary of Dalian Institute of Chemical Physics, CAS

Table S1. Characterization of raw and acids pretreated biomass.

Entry	Samples	Cell-wall components (wt.% dry basis)[a]					Ultimate analysis (wt.% dry basis)				
		Cellulose	Hemicell.	Lignin	Ash	Others	N	C	H	S	O
1	Pine	40.9	23.0	27.5	0.7	7.9	0.26	49.4	6.4	0.40	43.8
2	Pine_ H_3PO_2	38.9	21.0	24.2	0.3	6.8	0.19	49.3	6.6	0.02	44.0
3	Pine_ H_3PO_4	38.3	20.8	25.7	0.2	6.5	0.21	49.2	6.7	0.06	44.1
4	Pine_ HCl	36.4	10.9	19.3	0.1	1.5	0.20	49.5	6.5	0.10	43.9
5	Poplar	41.5	19.4	23.7	0.8	14.6	0.30	49.4	6.5	/	44.1
6	Poplar_ H_3PO_2	41.4	20.0	20.1	0.2	10.7	0.31	48.7	6.8	/	44.4
7	Poplar_ H_3PO_4	40.6	19.0	21.3	0.1	13.7	0.25	49.0	6.8	/	44.1
8	Poplar_ HCl	39.7	7.3	10.1	0.2	2.1	0.21	47.2	6.7	/	46.0

a: Cell-wall compositions, corrected for the measured solid recovery rate.

Pretreatment conditions: 3g biomass, 28ml 1,4-dixane and 2 ml water, 15 mmol H_3PO_2, 80°C, 5.0 h. Hemicell.: Hemicellulose

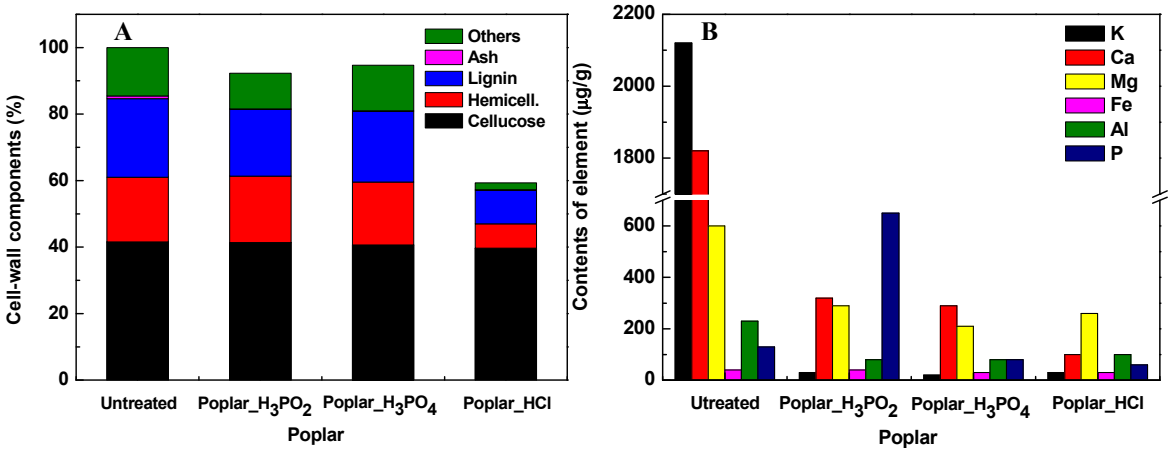

Figure S1. (A) Cell-wall compositions of untreated and acids pretreated poplar, corrected for the measured solid recovery rate and (B) Mineral species and contents of untreated and acids pretreated poplar.

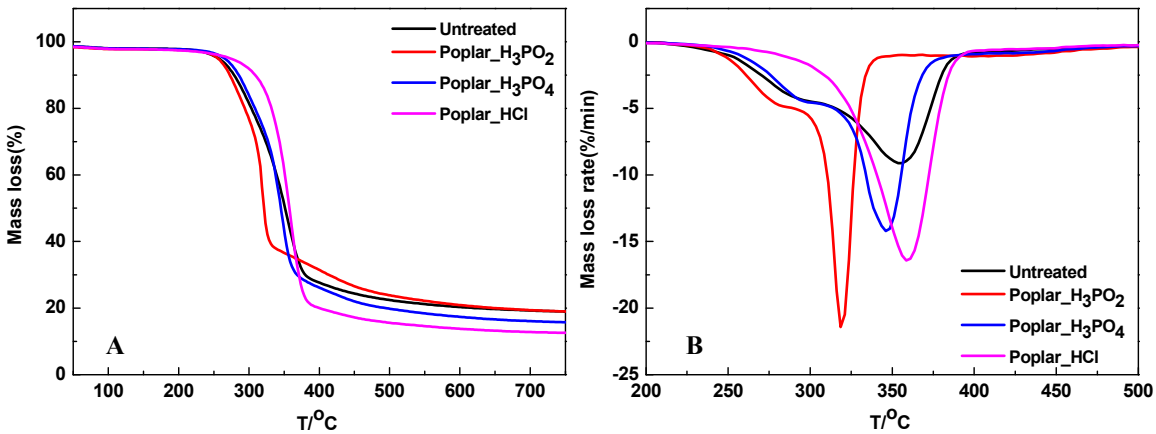

Figure S2. (A) TG profiles and (B) DTG profiles of untreated and acids pretreated poplar.

Table S2. Characteristic parameters from thermogravimetric analysis.

Entry	Samples	T_i	T_f	T_{max}	$(dW/dt)_{max}$
		°C			%/min
1	Poplar	199	405	361	9.1
2	Poplar_ H_3PO_2	**214**	**347**	**318**	**21.2**
3	Poplar_H_3PO_4	210	400	347	14.1
4	Poplar_HCl	211	403	360	16.3

T_i : initial decomposition temperature; T_f : final decomposition temperature (in this study, it is the termination temperature of maximum weight loss peak); T_{max} : the temperature at which maximum mass loss; $(dW/dt)_{max}$: the maximum mass loss rate.

Table S3. Yields of the products obtained from pyrolysis of untreated and acids pretreated poplar.

Entry	Samples	Solid recovery/ wt.%	T[a]/ °C	Liquid/ wt.%	Bio-char/ wt.%	Gas/ wt.%
1	Poplar	100	400	50.9	23.3	25.8
			330	42.5	27.8	27.8
2	Poplar_ H_3PO_2	92	400	50.9	25.8	23.3
			330	44.3	35.1	35.1
3	Poplar_H_3PO_4	95	400	54.9	18.3	26.8
			330	45.4	26.7	26.7
4	Poplar_HCl	59	400	67.4	15.9	16.8
			330	54.8	19.8	19.8

a: pyrolysis temperature.

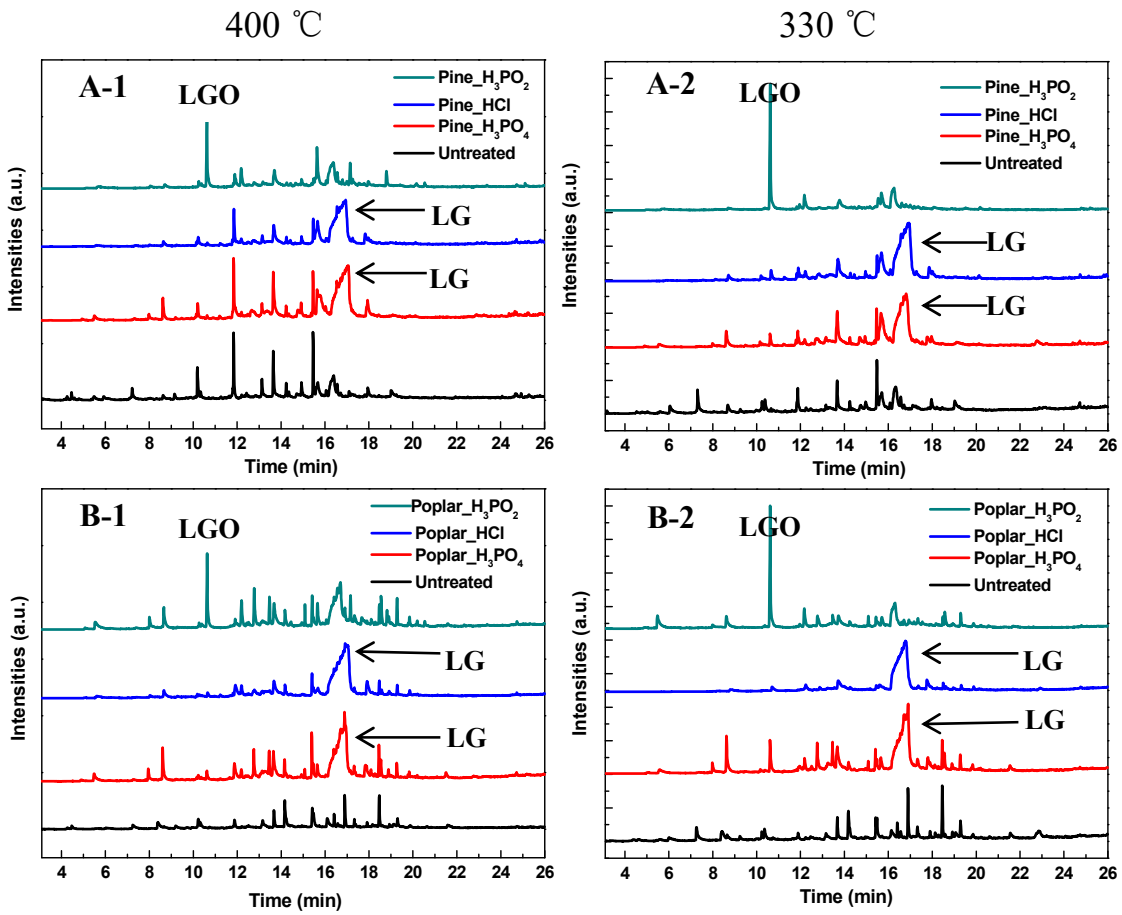

Figure S3. GC−MS chromatograms of liquid products from untreated and acids pretreated biomass pyrolysis, (A) Pine, (B) Poplar.

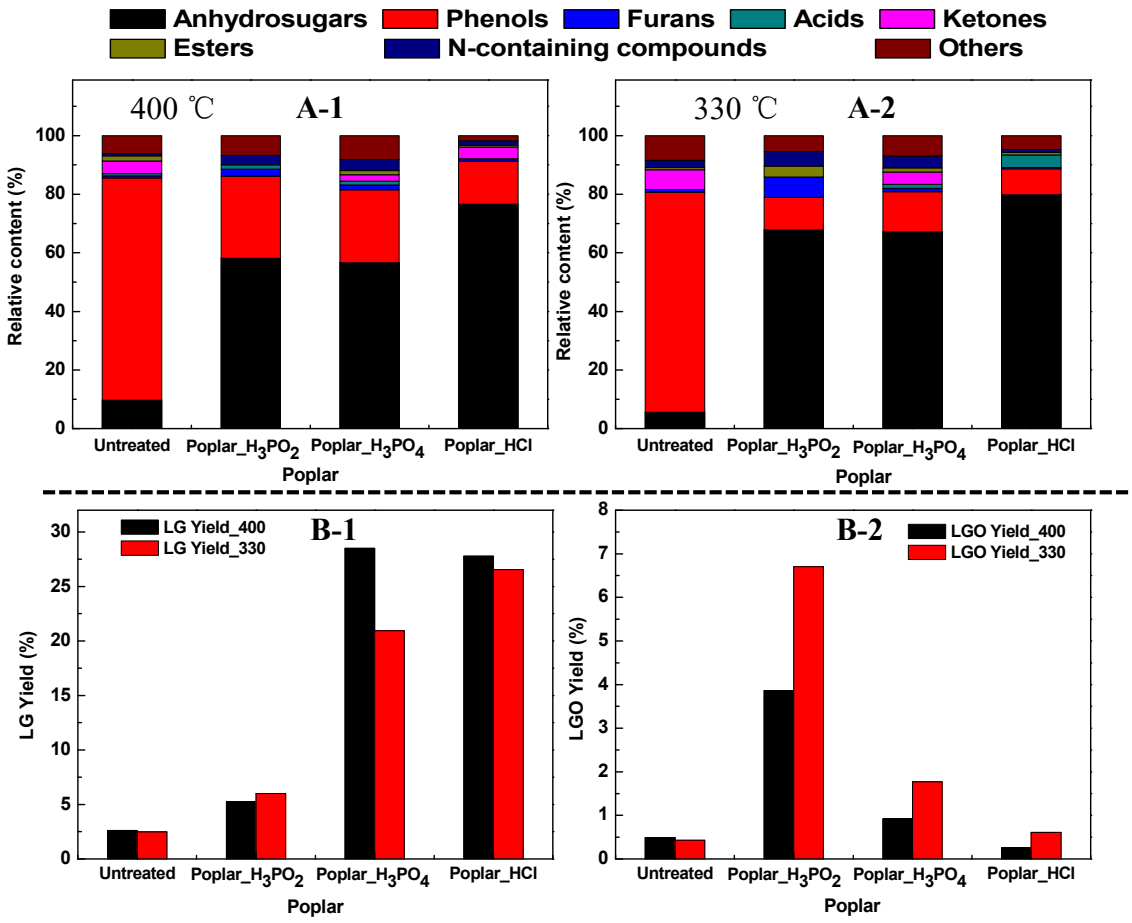

Figure S4. (A) Relative content of main groups of bio-oil from pyrolysis of untreated and acids pretreated poplar. (The data are also given in Tables S5, S7) (B) Levoglucosan (LG) and levoglucosenone (LGO) yields of liquid products from pyrolysis of untreated and acids pretreated poplar. The yields of LG and LGO are calculated mass ratio of the products to the masses of corresponding cellulose fractions in the biomass feedstocks on dry basis.

Table S4. GC/MS analysis of bio-oil obtained from the fixed-bed pyrolysis of untreated and acids **pretreated pine** samples, pyrolysis temperature: **400℃**.

Compounds	Peak area/%			
	Pine	Pine_HCl	Pine_H_3PO_4	Pine_H_3PO_2
Furans				
Furfural	1.69	0.50	0.99	0.86
2-Furanmethanol	0.97	—	—	—
Total	**2.66**	**0.50**	**0.99**	**0.86**
Phenols				
2-Methoxyphenol	5.87	1.75	1.39	1.34
Creosol	12.01	4.14	4.60	3.79
4-Ethyl-2-methoxyphenol	3.92	1.74	2.25	1.50
2-Methoxy-4-vinylphenol	9.22	6.14	7.16	7.72
Eugenol	2.38	0.95	0.97	0.98
α-Ethyl-4-methoxy-benzenemethanol	8.99	8.81	3.32	—
Vanillin lactoside	2.69	0.87	1.60	1.95
2-Methoxy-4-(1-propenyl)-, (Z)phenol	9.56	2.68	3.25	1.42
2-Methoxy-4-propylphenol	—	—	—	10.17
1-(4-Hydroxy-3-methoxyphenyl)ethanone	1.47	1.34	1.85	—
1-(4-Hydroxy-3-methoxyphenyl)-2-propanone	2.72	—	—	3.04
4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol	0.74	1.41	—	4.05
2,6-Dimethoxy-4-(2-propenyl) phenol	—	—	—	1.43
4-(Ethoxymethyl)-2-methoxyphenol	—	—	2.66	1.18
2-(4-Hydroxy-3-methoxyphenyl)ethanoic acid	2.66	—	—	—
3-(4-Hydroxy-3-methoxyphenyl)-2-propenal	2.22	1.20	—	—
Total	**64.45**	**31.83**	**29.05**	**38.57**
Anhydrosugars				
Levoglucosenone	0.20	0.50	0.30	13.65
1,4:3,6-Dianhydro-α-D-glucopyranose	0.80	1.16	0.81	5.52
D-(+)-Melezitose	2.17	3.02	4.52	11.701
D-Mannose	0.58	—	—	—
6-Acetyl-β-D-mannose	—	—	—	—
D-Allose	—	—	7.11	—
Levoglucosan	16.85	53.85	46.21	20.64
Total	**20.60**	**58.53**	**58.95**	**51.51**
Acids				
Propanoic acid	0.50	—	—	0.50
Homovanillic acid	2.66	—	—	—
Total	**3.16**	**—**	**—**	**—**
Ketones				
2-Hydroxy-2-cyclopenten-1-one	3.94	—	—	—
2-Hydroxy-3-methyl-2-cyclopenten-1-one	1.38	—	—	—
2-(Hydroxymethyl) -cyclohexanone	0.69	—	—	—
Total	**6.01**	**—**	**—**	**—**

Esters				
Carbonic acid, ethyl 2-propenyl ester	1.02	—	—	—
Total	**1.02**	**—**	**—**	**—**
N-containing compounds				
2,2-Diethyl-3-methyl-oxazolidine	1.07	0.95	2.11	1.10
Total	**1.07**	**0.95**	**2.11**	**1.10**
Others	1.03	8.19	8.90	7.96

Table S5. GC/MS analysis of bio-oil obtained from the fixed-bed pyrolysis of untreated and acids **pretreated poplar** samples, pyrolysis temperature: **400℃**.

Compounds	Peak area/%			
	Poplar	Poplar_HCl	Poplar_H_3PO_4	Poplar_ H_3PO_2
Furans				
Furfural	0.65	0.79	1.56	2.48
Total	**0.65**	**0.79**	**1.56**	**2.48**
Phenols				
Phenol	3.36	—	—	—
2-Methoxyphenol	3.61	0.50	0.51	0.62
Creosol	3.35	2.87	2.85	0.87
4-Ethyl-2-methoxyphenol	3.61	1.29	1.44	—
3-Methoxy-1,2-benzenediol	—	—	—	1.30
2-Methoxy-4-vinylphenol	5.14	—	5.06	—
2,6-Dimethoxyphenol	10.89	1.68	1.69	2.10
3,4-Dimethoxyphenol	—	—	—	—
1,2,4-Trimethoxybenzene	5.20	1.85	2.65	2.09
2-Methoxy-4-(1-propenyl)-, (Z) phenol	5.31	1.00	1.31	1.05
2-Methoxy-4-propylphenol	—	—	1.92	2.94
α-Ethyl-4-methoxy-benzenemethanol	—	2.2	—	—
1-(4-Hydroxy-3-methoxyphenyl)ethanone	—	—	—	0.73
1-(4-Hydroxy-3-methoxyphenyl)-2-propanone	4.77	—	—	—
3',5'-Dimethoxyacetophenone	8.71	—	—	2.42
2,6-Dimethoxy-4-(2-propenyl)phenol	10.41	1.22	3.89	5.79
4-(Ethoxymethyl)-2-methoxyphenol	1.35	—	—	—
4-Hydroxy-3,5-dimethoxybenzaldehyde	—	—	1.09	0.71
2,4,6-Trimethoxytoluene	1.38	—	—	2.52
1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone	1.22	0.65	0.63	2.13
4-(3-Aminobutyl)-2-methoxyphenol	2.00	—	—	—
1-(2,6-Dihydroxy-4-methoxy-phenyl)-butan-1-one	3.06	0.89	1.11	2.00
3,5-Dimethoxy-4-hydroxycinnamaldehyde	2.54	—	0.81	—
2-(Benzoyloxy)-1-[1,1'-biphenyl]-4-yl- ethanone	—	0.56	—	0.71
Total	**75.91**	**14.71**	**24.96**	**27.98**
Anhydrosugars				
Levoglucosenone	—	0.44	0.89	7.11
6-Acetyl-β-D-mannose	—	—	—	0.714
1,4:3,6-Dianhydro-α-D-glucopyranose	0.81	1.67	1.07	3.59
D-(+)-Melezitose	2.26	7.79	3.79	12.11
1,3-Di-O-acetyl-α-β-D-ribopyranose	—	—	—	3.23
D-Mannose	—	4.75	3.18	1.38
Levoglucosan	6.63	61.96	47.68	29.99
Total	**9.70**	**76.61**	**56.61**	**58.12**

Acids				
Propanoic acid	0.76	—	—	—
Butanedioic acid	—	—	1.35	1.44
Total	**0.76**	**—**	**1.35**	**1.44**
Ketones				
2-Hydroxy-2-cyclopenten-1-one	3.12	—	—	—
2-Hydroxy-3-methyl-2-cyclopenten-1-one	1.24	—	—	—
3,5-Dihydroxy-2-methyl-4H-pyran-4-one	—	2.87	—	—
4-Hydroxy-3-pentyl-cyclohexanone	—	1.10	2.13	—
Total	**4.36**	**3.97**	**2.13**	—
Esters				
Carbonic acid, ethyl 2-propenyl ester	1.70	—	—	—
(2Z,4Z)-Dimethyl 3,4-diethylhexa-2,4-dienedioate	—	0.63	1.50	—
Total	**1.70**	**0.63**	**1.50**	**—**
N-containing compounds				
2,2-Diethyl-3-methyl-oxazolidine	0.81	1.55	3.74	3.19
Total	**0.81**	**1.55**	**3.74**	**3.19**
Others	6.11	1.74	8.15	6.78

Table S6. GC/MS analysis of bio-oil obtained from the fixed-bed pyrolysis of untreated and acids **pretreated pine** samples, pyrolysis temperature: **330℃.**

Compounds	Peak area/%			
	Pine	Pine_HCl	Pine_H_3PO_4	Pine_ H_3PO_2
Furans				
Furfural	0.50	0.51	1.08	0.56
2-Furanmethanol	3.35	—	—	—
5-Hydroxymethylfurfural	—	—	2.98	—
Total	**3.85**	**0.51**	**4.06**	**0.56**
Phenols				
2-Methoxyphenol	2.68	—	0.51	—
Creosol	6.04	1.46	1.78	1.86
4-Ethyl-2-methoxyphenol	1.19	—	—	—
2-Methoxy-4-vinylphenol	7.63	—	7.94	—
Eugenol	1.38	—	0.87	—
Vanillin lactoside	3.75	2.55	1.25	—
2-Methoxy-4-(1-propenyl)-, (Z)phenol	8.56	—	2.90	9.36
2-Methoxy-4-propylphenol	7.04	9.54	—	—
1-(4-Hydroxy-3-methoxyphenyl)ethanone	1.41	1.59	—	—
1-(4-Hydroxy-3-methoxyphenyl)-2-propanone	2.94	—	—	2.03
4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol	0.79	—	—	—
4-(Ethoxymethyl)-2-methoxyphenol	2.88	0.94	1.31	—
2,6-Dimethoxy-4-(2-propenyl)phenol	0.59	—	—	—
4-Hydroxy-2-methoxycinnamaldehyde	3.66	—	1.46	—
Total	**50.54**	**16.08**	**18.02**	**13.25**
Anhydrosugars				
Levoglucosenone	0.62	1.31	1.37	34.67
1,4:3,6-Dianhydro-α-D-glucopyranose	1.03	1.32	1.54	5.97
D-(+)-Melezitose	10.31	9.69	4.64	9.12
D-Mannose	—	—	3.36	5.56
6-Acetyl-β-D-mannose	—	—	—	0.83
D-Allose	—	—	13.07	2.36
Levoglucosan	15.92	62.15	45.32	22.37
1,6-Anhydro-α-D-galactofuranose	—	1.93	1.49	
Total	**27.88**	**76.40**	**70.79**	**80.88**
Acids				
Propanoic acid	—	—	0.52	—
Butanedioic acid	—	—	—	—
Total	**—**	**—**	**0.52**	**—**
Ketones				
1,2-Cyclopentanedione	6.17	—	—	—
2-Hydroxy-3-methyl-2-cyclopenten-1-one	0.96	—	—	—
2,5-Dimethyl-4-hydroxy-3(2H)-furanone	—	0.53	—	—

Total	**7.13**	**0.53**	**—**	**—**
N-containing compounds				
2,2-Diethyl-3-methyl-oxazolidine	2.35	1.06	2.53	—
Total	**2.35**	**1.06**	**2.53**	**—**
Others	8.25	5.37	4.08	5.36

Table S7. GC/MS analysis of bio-oil obtained from the fixed-bed pyrolysis of untreated and acids **pretreated poplar** samples, pyrolysis temperature: **330℃**.

Compounds	Peak area/%			
	Poplar	Poplar_HCl	Poplar_H_3PO_4	Poplar_ H_3PO_2
Furans				
Furfural	0.35	0.50	1.16	6.87
2-Furanmethanol	0.60	—	—	—
Total	**0.95**	**0.50**	**1.16**	**6.87**
Phenols				
Phenol	5.19	—	—	—
2-Methoxyphenol	2.53	—	—	—
Creosol	2.15	—	—	—
4-Ethyl-2-methoxyphenol	1.93	—	—	—
2-Methoxy-4-vinylphenol	4.28	—	—	—
2,6-Dimethoxyphenol	8.24	2.73	1.19	—
3,4-Dimethoxyphenol	—	—	—	1.61
1,2,4-Trimethoxybenzene	3.34	0.59	2.39	—
2-Methoxy-4-(1-propenyl)-, (Z)phenol	—	—	—	1.92
2-Methoxy-4-propylphenol	4.70	1.21	1.97	4.11
5-tert-Butylpyrogallol	2.62	—	—	—
3',5'-Dimethoxyacetophenone	8.45	—	—	—
4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol	2.53	—	—	
2,6-Dimethoxy-4-(2-propenyl)-phenol	11.87	2.50	4.06	—
4-Hydroxy-3,5-dimethoxy-benzaldehyde	1.56	—	0.81	—
2,4,6-Trimethoxytoluene	—	0.52	—	—
1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone	1.08	0.54	0.80	1.08
4-Hydroxy-2-methoxycinnamaldehyde	2.47	—	—	
1-(2,4,6-trihydroxyphenyl)-2-pentanone	—	0.71	—	2.41
1-(2,6-Dihydroxy-4-methoxy-phenyl)-butan-1-one	3.56	—	0.94	—
2-(Benzoyloxy)-1-[1,1'-biphenyl]-4-yl- ethanone	0.86	—	0.56	—
3,5-Dimethoxy-4-hydroxycinnamaldehyde	2.20	—	1.00	—
3,7(3,9or7,9)-dihydroxy-9(7or3)-methoxy-1-methyl-6H-Dibenzo[b,d]pyran-6-one	5.56	—	—	—
Total	**75.14**	**8.80**	**13.72**	**11.13**
Anhydrosugars				
Levoglucosenone	0.61	1.24	2.91	25.97
1,4:3,6-Dianhydro-α-D-glucopyranose	0.60	2.17	1.90	5.60
D-(+)-Melezitose	—	3.57	11.48	16.09
D-Mannose	—	—	2.93	—
Levoglucosan	4.34	68.82	47.92	20.19
1,6-Anhydro-α-D-galactofuranose	—	4.01	—	—
Total	**5.55**	**79.81**	**67.14**	**67.85**

Acids				
Propanoic acid	—	—	1.30	—
3-Propylglutaric acid	—	4.30	—	—
Total	**—**	**4.30**	**1.30**	**—**
Ketones				
2-Hydroxy-2-cyclopenten-1-one	5.70	—	—	—
2-Hydroxy-3-methyl-2-cyclopenten-1-one	1.01	—	—	—
3,5-Dihydroxy-2-methyl-4H-pyran-4-one	—	—	1.30	—
2-(Hydroxymethyl)-cyclohexanone	—	—	2.95	—
Total	**6.71**	—	**4.25**	—
Esters				
(2Z,4Z)-Dimethyl 3,4-diethylhexa-2,4-dienedioate	0.81	0.81	1.43	3.80
Total	**0.81**	**0.81**	**1.43**	**3.80**
N-containing compounds				
2,2-Diethyl-3-methyl-oxazolidine	2.43	1.03	4.03	4.90
Total	**2.43**	**1.03**	**4.03**	**4.90**
Others	8.41	4.74	6.97	5.45

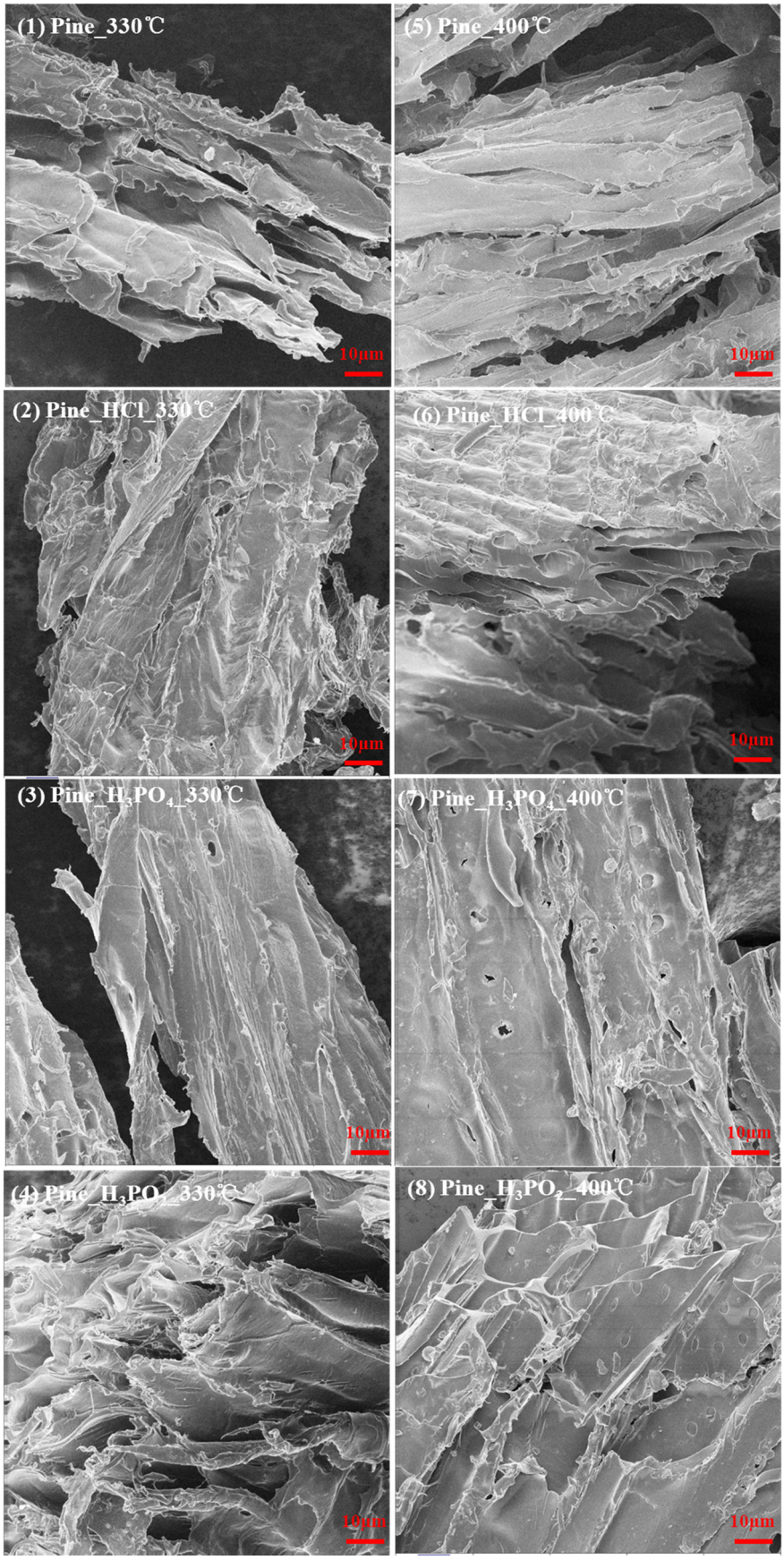

Figure S5. Helium ion microscope (HIM) images of biochar from untreated and acids pretreated pine. (1)~(4): pyrolysis at 330℃; (5)~(8): pyrolysis at 400℃.