

Supplementary Information

Effect of Torrefaction on Biomass Structure and Hydrocarbons Production from Fast Pyrolysis

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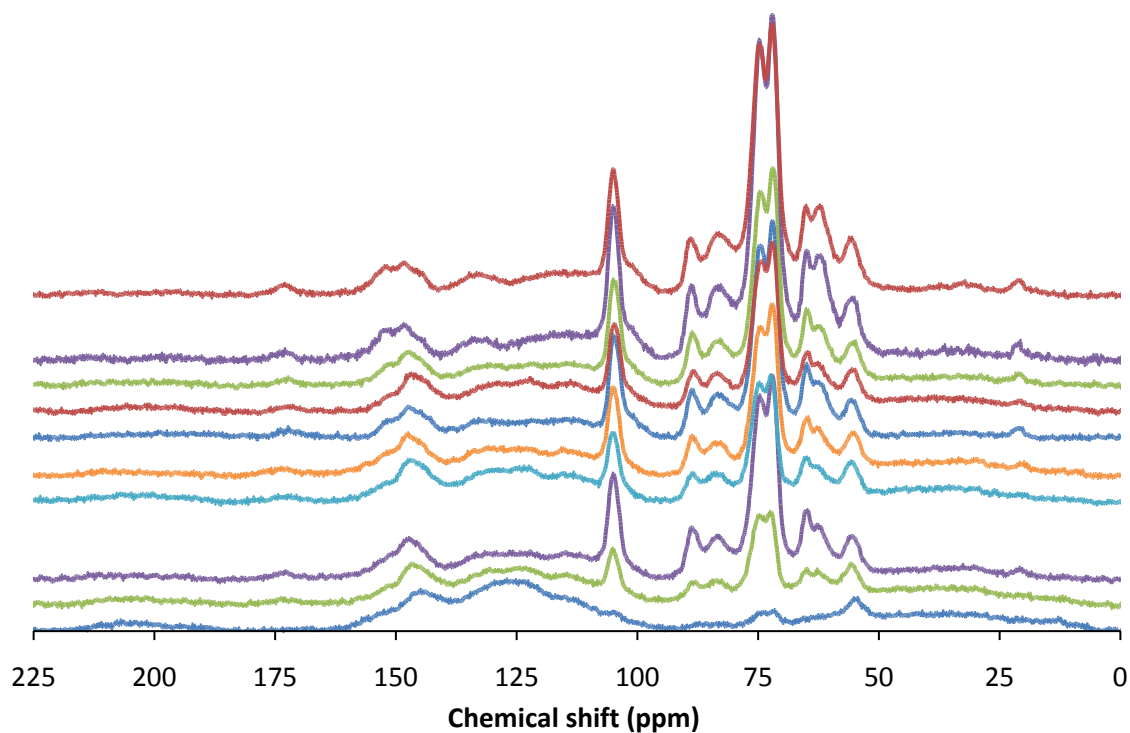
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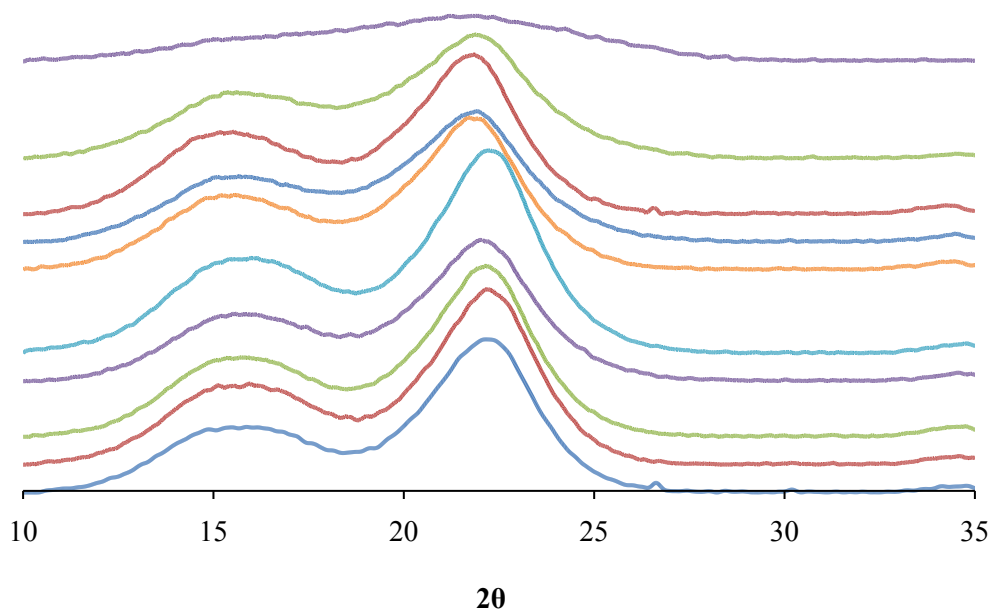
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S1: Assignment of signal from CP/MAS ^{13}C NMR ^{17, 31-33}

Chemical shift (ppm)	Bond assignment
206	Ketone
173	Acetyl carboxyl (Hemicellulose)
152	Ether linked - Guaiacyl, C-3/4
148	Guaiacyl non-ether linked, C-3/4
110-140	Aromatic C-C and C-H
105	Cellulose/xylan C-1
89	Crystalline cellulose C-4
83	Amorphous cellulose C-4/ xylan
72 and 74	Cellulose C-2/3/5; xylan C-2/3
65	Crystalline cellulose C-6
62	Amorphous cellulose C-6/xylan C-5
56	Lignin methoxyl
32	Aliphatic
21	Acetyl methyl (hemicellulose)



S2: ^{13}C NMR spectra (from top to bottom): control, 225°C-15min, 225°C-30min, 225°C-45min, 225°C-15min, 250°C-30min, 250°C-45min, 275°C-15min, 275°C-30min, 275°C-45min



S3: XRD spectra (from bottom to top): control, 225°C-15min, 225°C-30min, 225°C-45min, 225°C-15min, 250°C-30min, 250°C-45min, 275°C-15min, 275°C-30min, 275°C-45min

S4: List of compounds quantified for non-catalytic pyrolysis

Aromatic	Phenolic	Guaiacol	Furan	Ketone
Benzene	Phenol	Phenol, 2-methoxy-	Furan, 2-methyl-	2-Cyclopenten-1-one, 2-methyl
Toluene	Phenol, 2-methyl-	Phenol, 2-methoxy-4-methyl	Furan, 2,5-dimethyl-	2-Cyclopenten-1-one, 3-methyl
Ethylbenzene	Phenol, 2,3-dimethyl-	Phenol, 4-ethyl-2-methoxy	Furfural	2-Cyclopenten-1-one, 2,3 - dimethyl-
P-xylene	Phenol, 4-methyl	2-Methoxy-4-vinylphenol	Furan, 2-ethyl-5-methyl-	
o-xylene	Phenol, 2,4-dimethyl-	Eugenol	2-Furancarboxaldehyde, 5-methyl	
Styrene	Phenol, 2,3,6-trimethyl-	Phenol, 2-methoxy-4-(1-propenyl)-	2 (5H) - Furanone	
Benzene, 1,3,5-trimethyl	Phenol,3,5-dimethyl-	Phenol, 2-methoxy-4-(1-propenyl)-(Z)-		
Benzene, 1-ethyl-3-methyl	Phenol, 4-ethyl	Vanillin		
Benzene, 1,2,3-trimethyl	Phenol, 3,4-dimethyl	Ethanone, 1-(4-hydroxy-3methoxyphenyl)-		
Naphthalene	Phenol, 4-ethyl-3-methyl-			

S5: List of compounds quantified for catalytic pyrolysis

Aromatic	Poly-aromatic	Phenolic	Oxygenates (benzofurans and guaiacol)
Benzene	Naphthalene	Phenol	Benzofuran, 2-methyl
Toluene	Naphthalene, 1-methyl-	Phenol, 2-methyl-	Phenol, 2-methoxy-4-methyl
Ethylbenzene	Naphthalene, 2-ethyl-	Phenol, dimethyl	Dibenzofuran
p-Xylene	Naphthalene, 2,7-dimethyl-		
o-Xylene	Naphthalene, trimethyl		
Styrene	Fluorene		
Benzene, 1-ethyl-2-methyl-; Benzene, 1-ethyl-3-methyl	Fluorene, 1-methyl-		
Benzene, trimethyl-	Phenanthrene		
Benzene, 1-ethenyl-2-methyl- (Alpha methyl styrene); Benzene, 1-ethenyl-3-methyl-	Anthracene		
2,3 Benzofuran	Anthracene, 9-methyl-		
Indane	Phenanthrene, 2-methyl		
Indene			
Benzene, tetramethyl			
2-Methylindene			
Biphenyl			

S6: Summary of the effect of torrefaction on biomass components

Sample	Difference hemicellulose			Difference in cellulose			Difference in lignin				Aromatic Compon ents	Aliphatic Compon ents
	wt %	Acetyl methyl	Acetyl carboxyl	wt %	Glycosidic components	CrI	AIL wt%	Ether linkage	Non-ether linkage	Lignin methoxyl		
225°C-15min	7.04	-50.17	-46.92	7.49	3.51	0.56	-0.61	-6.38	-7.80	-15.39	-8.32	-17.99
225°C-30min	-21.18	-47.66	-51.67	13.85	-22.85	-2.81	-17.37	-33.69	13.93	-28.44	4.09	3.86
225°C-45min	-70.07	-59.70	-60.13	-3.75	-36.93	-7.26	70.34	-54.24	4.81	-35.21	39.35	52.09
250°C-15min	-14.11	-46.60	-49.32	13.74	-27.34	-5.38	-0.73	-23.53	-25.24	-42.70	-13.49	-53.12
250°C-30min	-74.21	-47.72	-50.49	7.49	-40.11	-7.46	56.26	-15.16	40.34	-29.34	33.19	70.87
250°C-45min	-90.29	-56.31	-55.65	-24.83	-53.79	-15.57	120.97	-25.91	62.99	-34.42	51.68	53.29
275°C-15min	-53.35	-51.11	-51.74	10.52	-28.41	-8.74	65.90	-16.95	41.92	-30.35	28.52	24.69
275°C-30min	-100.00	-60.87	-62.72	-36.04	-61.79	-19.85	148.69	-35.24	53.09	-29.64	68.87	99.32
275°C-45min	-100.00	-100.00	-100.00	-90.05	-84.16	-52.71	228.9	-55.98	56.42	-37.53	117.36	101.37

Note: Positive sign represents increase % and negative sign represents decrease % as compared to control sample.

S7: Results of component analysis (not normalized by mass loss) on weight percentage (dry basis)

Sample	Cellulose % (Glucan)	Hemicellulose %					Lignin %		Extractives %
		Xylan	Galactan	Arabinan	Mannan	Total	AIL	ASL	
Control	39.08	6.88	2.94	1.87	12.51	24.21	30.29	1.00	2.99
225°C-15min	42.01	8.01	2.86	1.25	13.79	25.91	30.10	0.98	2.53
225°C-30min	44.49	5.26	1.78	0.60	11.44	19.08	25.99	0.98	3.48
225°C-45min	37.61	1.73	0.26	0.00	5.26	7.25	51.60	0.99	2.60
250°C-15min	44.45	5.96	1.96	0.72	12.15	20.79	30.07	0.95	3.21
250°C-30min	42.01	1.36	nd	nd	4.88	6.24	47.33	0.90	2.66
250°C-45min	29.38	0.41	nd	nd	1.94	2.35	66.93	0.82	1.93
275°C-15min	43.19	3.15	0.53	0.26	7.35	11.29	50.25	0.89	2.09
275°C-30min	24.99	nd	nd	nd	nd	nd	75.33	0.75	1.81
275°C-45min	3.89	nd	nd	nd	nd	nd	99.64	0.26	0.90

Cellulose, hemicellulose and lignin are in extractive free basis

nd: not detected

S8: ¹³C NMR Area (not normalized by mass loss)

Sample	Acetyl Carboxyl	Acetyl Methyl	Glycosidic	Ether linkage	Non-ether Linkage	Lignin Methoxly	Aromatic	Aliphatic
Control	6.97E+07	6.60E+07	3.75E+09	2.31E+08	1.53E+08	3.13E+08	5.65E+08	2.12E+08
225°C-15min	3.47E+07	4.90E+07	3.88E+09	2.04E+08	1.31E+08	2.65E+08	5.18E+08	1.73E+08
225°C-30min	3.65E+07	5.89E+07	2.89E+09	1.20E+08	2.26E+08	2.24E+08	5.88E+08	2.20E+08
225°C-45min	2.81E+07	5.15E+07	2.36E+09	9.76E+07	3.18E+08	2.03E+08	7.87E+08	3.22E+08
250°C-15min	3.72E+07	3.50E+07	2.72E+09	1.78E+08	1.34E+08	1.79E+08	4.69E+08	9.92E+07
250°C-30min	3.65E+07	3.65E+07	2.25E+09	1.30E+08	3.87E+08	2.21E+08	7.52E+08	3.61E+08
250°C-45min	3.05E+07	2.16E+07	1.73E+09	1.03E+08	3.96E+08	2.05E+08	8.57E+08	3.24E+08
275°C-15min	3.41E+07	3.27E+07	2.68E+09	1.90E+08	2.76E+08	2.18E+08	7.26E+08	2.64E+08
275°C-30min	2.73E+07	0.00E+00	1.43E+09	1.18E+08	4.09E+08	2.20E+08	9.54E+08	4.22E+08
275°C-45min	0.00E+00	0.00E+00	5.94E+08	1.23E+08	4.74E+08	1.96E+08	1.23E+09	4.26E+08

S9: Nomenclature used for samples torrefied at different conditions

Nomenclature	Torrefaction Temperature (°C)	Torrefaction Residence Time (min)
Control	Non-torrefied (raw) pine	
225°C-15min	225	15
225°C-30min	225	30
225°C-45min	225	45
250°C-15min	250	15
250°C-30min	250	30
250°C-45min	250	45
275°C-15min	275	15
275°C-30min	275	30
275°C-45min	275	45