

Supplementary Materials

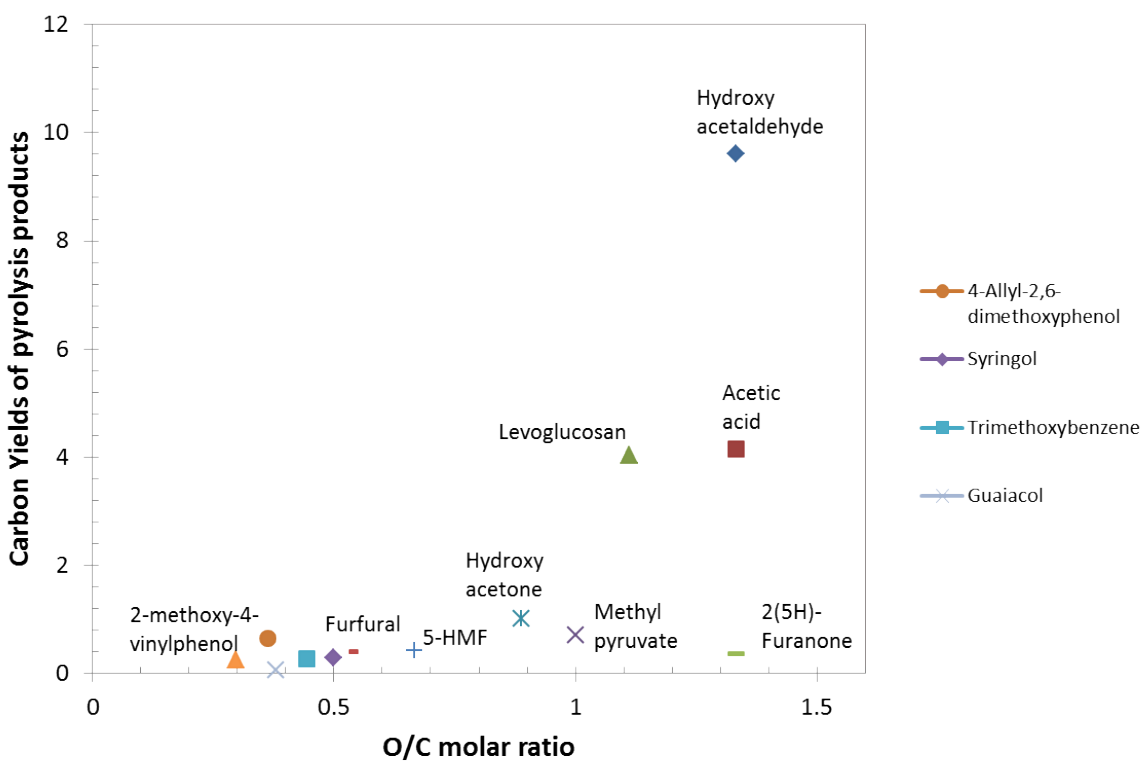


Figure S1. A plot of carbon yields versus O/C molar ratio showing the role of individual compounds from the hybrid poplar on the oxygenated nature pyrolysis oil.

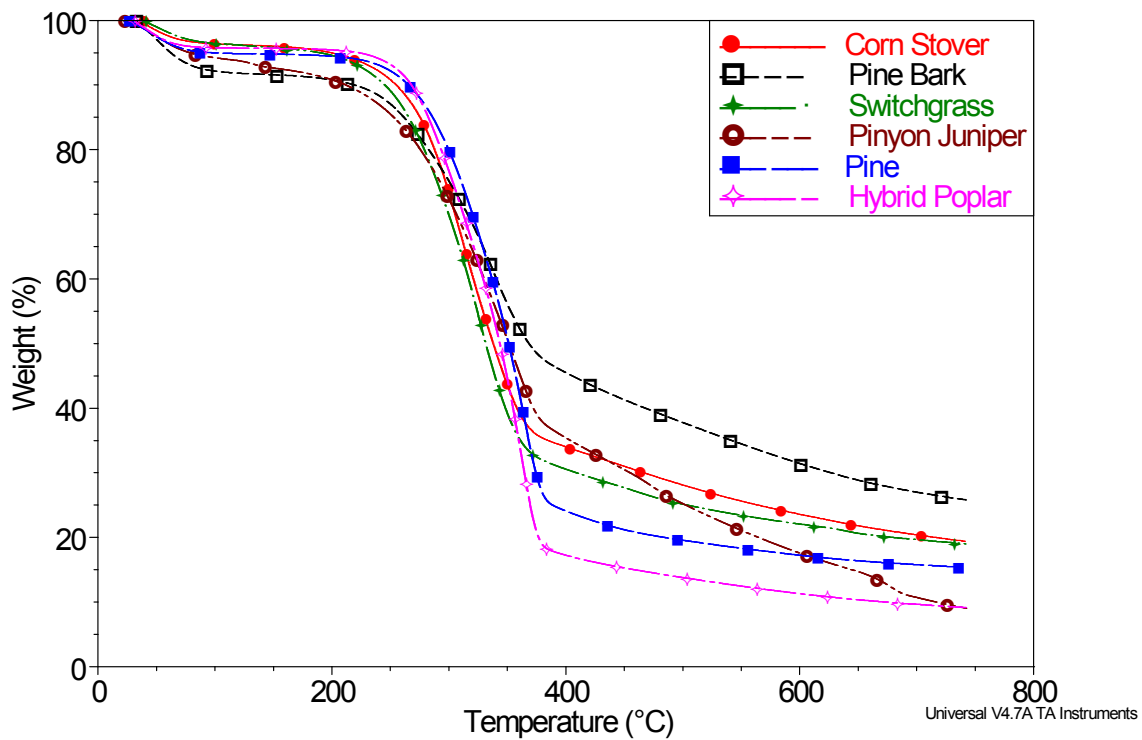


Figure S2. TG curves of corn stover, pine bark, switchgrass, pinyon-juniper, pine, and hybrid poplar

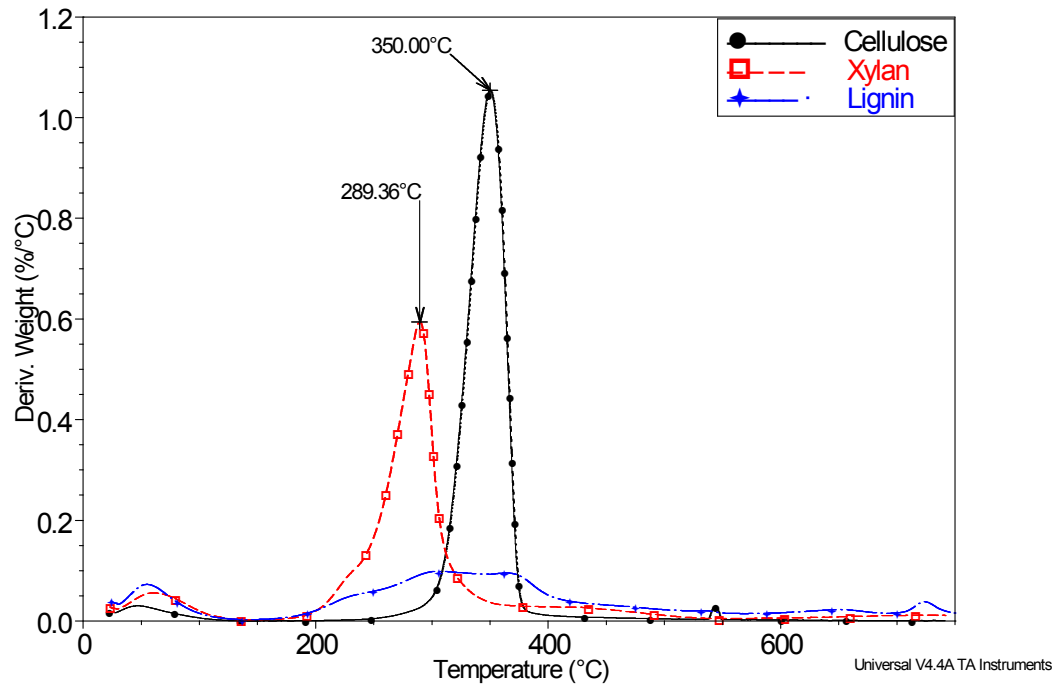


Figure S3a. DTG curves model biopolymer: xylan, cellulose and kraft lignin

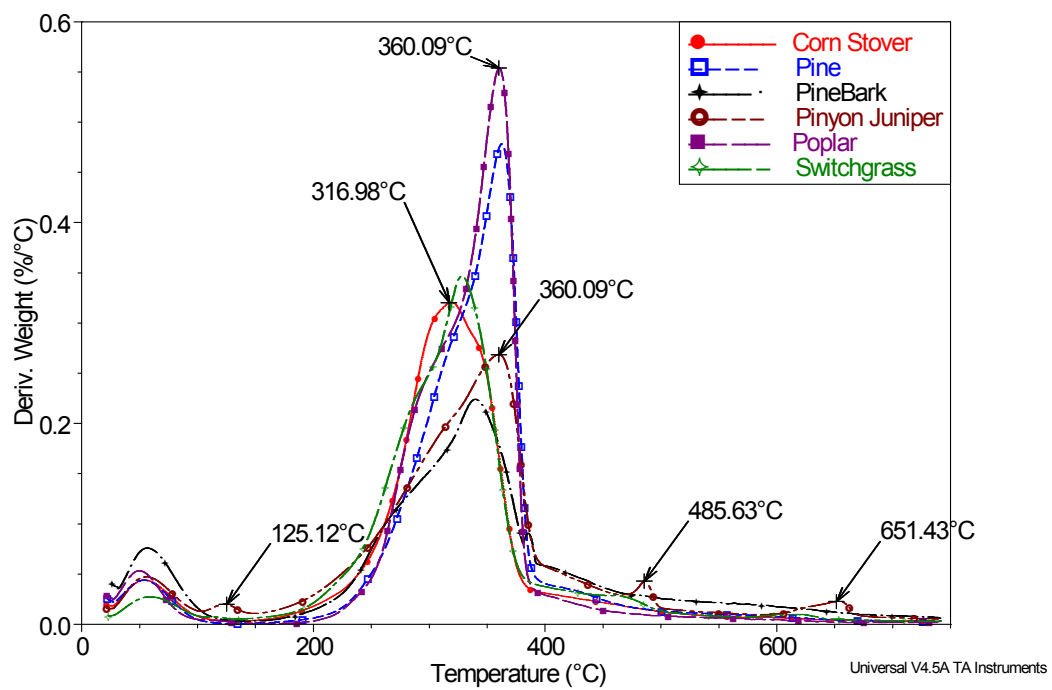


Figure S3b. DTG curves of corn stover, pine, pine bark, pinyon-juniper, poplar and switchgrass

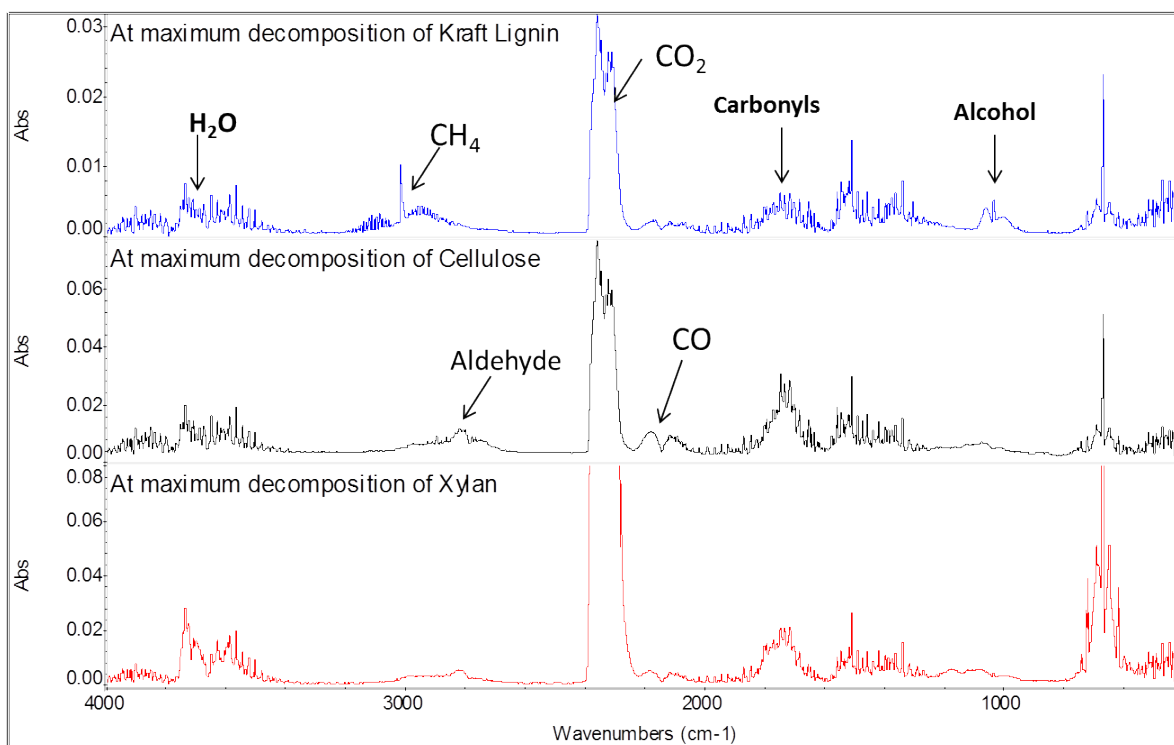


Figure S4a. FTIR spectra of evolved gases at the maximum rate of decomposition for xylan, microcrystalline cellulose and kraft lignin

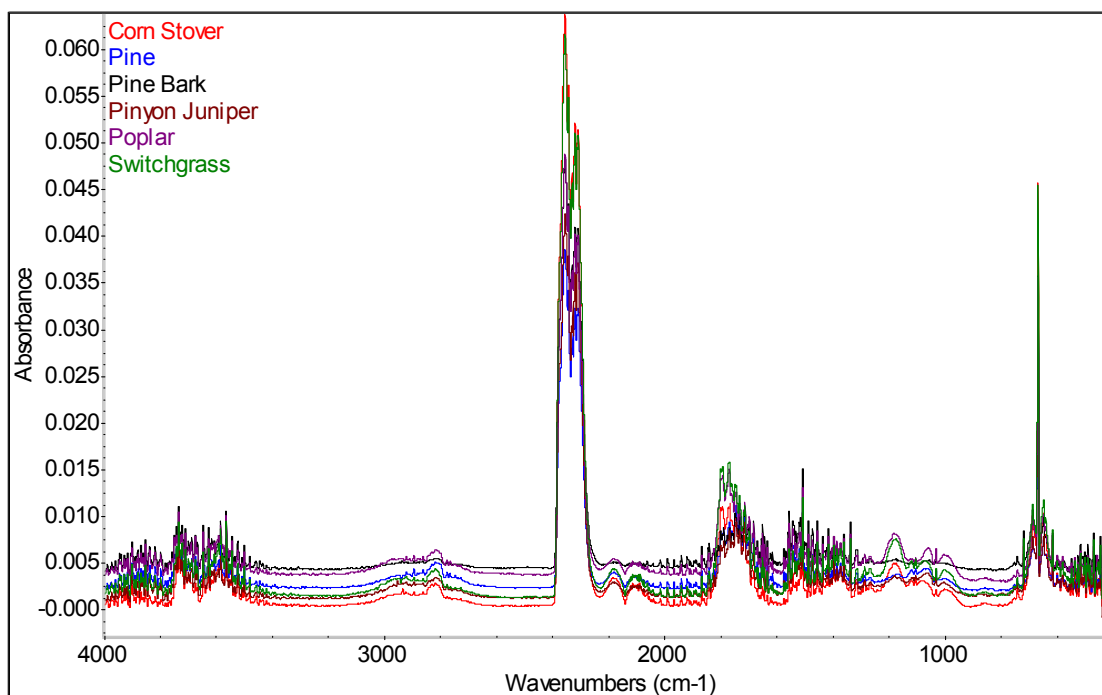


Figure S4b. FTIR spectra of evolved gases at 290°C from the thermal degradation of corn stover, pine, pine bark, pinyon-juniper, poplar and switchgrass

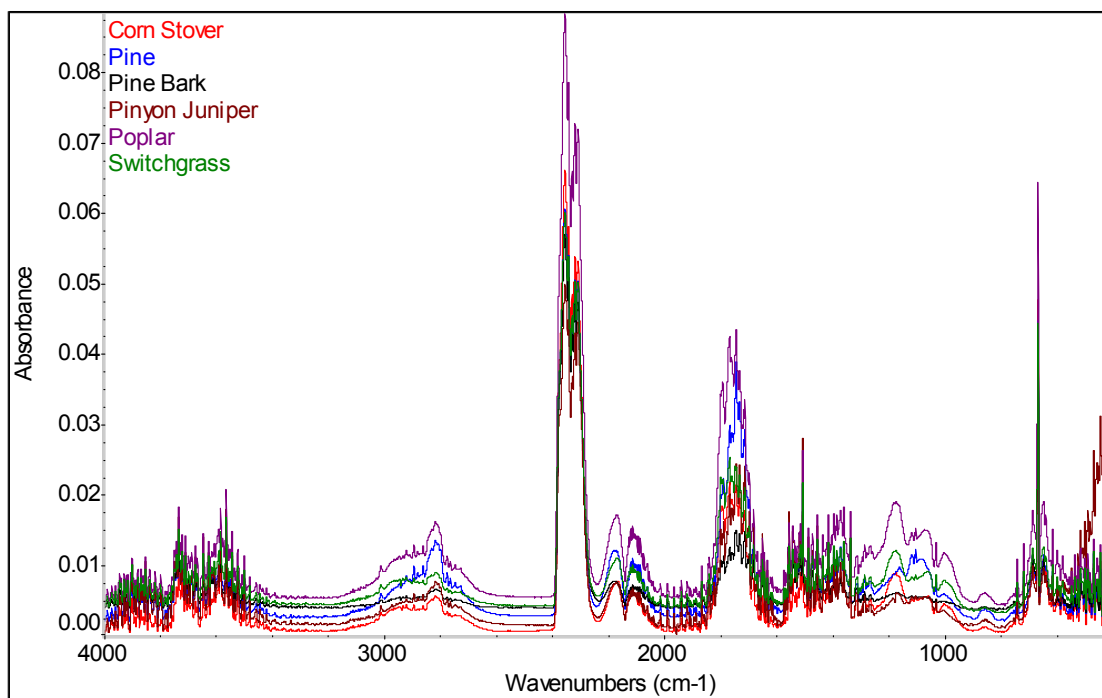


Figure S4c. FTIR spectra of evolved gases at 350 °C from the thermal degradation of corn stover, pine, pine bark, pinyon-juniper, poplar and switchgrass

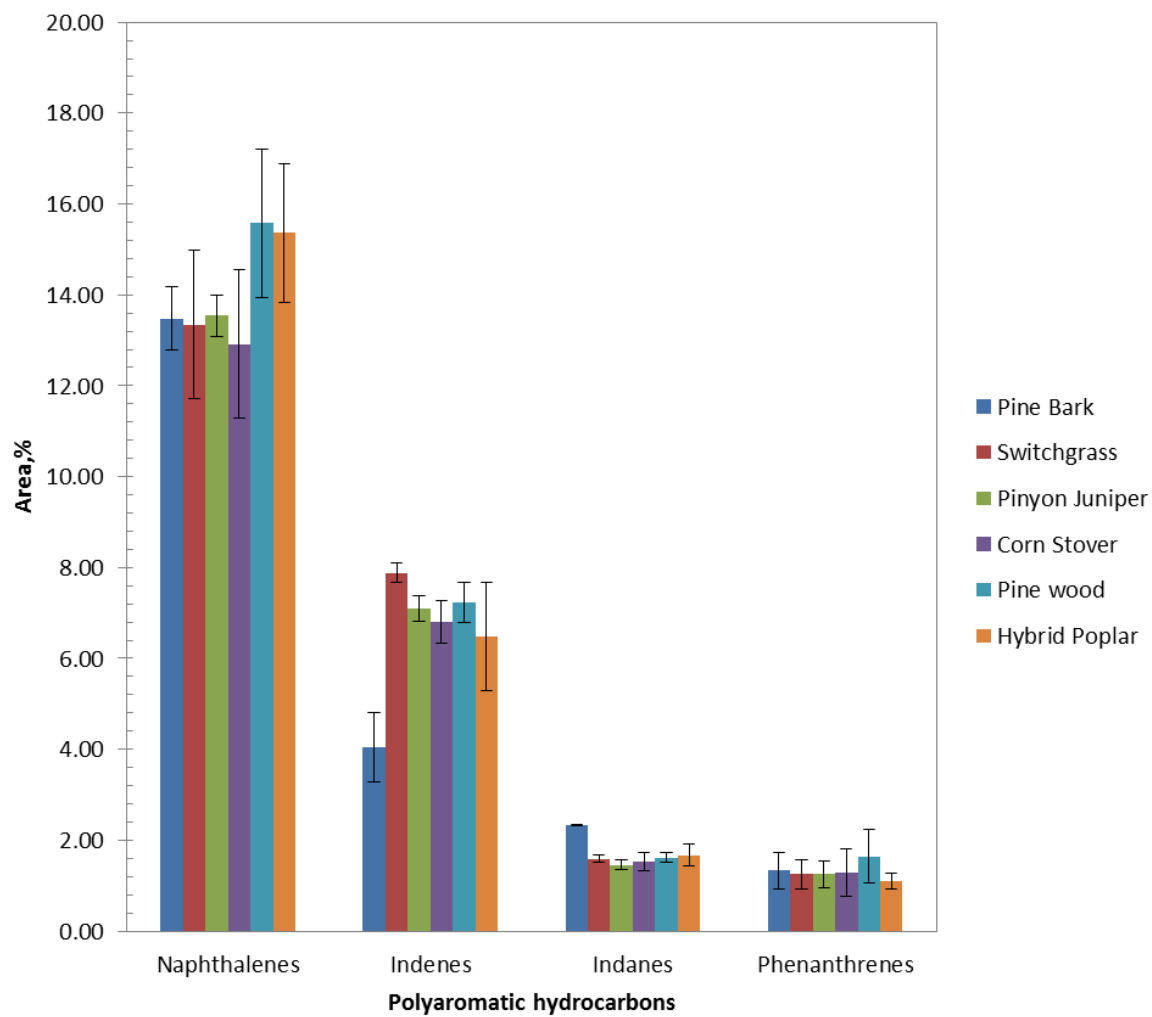


Figure S5. Comparison of polyaromatic hydrocarbons produced in the catalytic pyrolysis with ZSM- at 550 °C and C/F ratio of 10 (w/w)

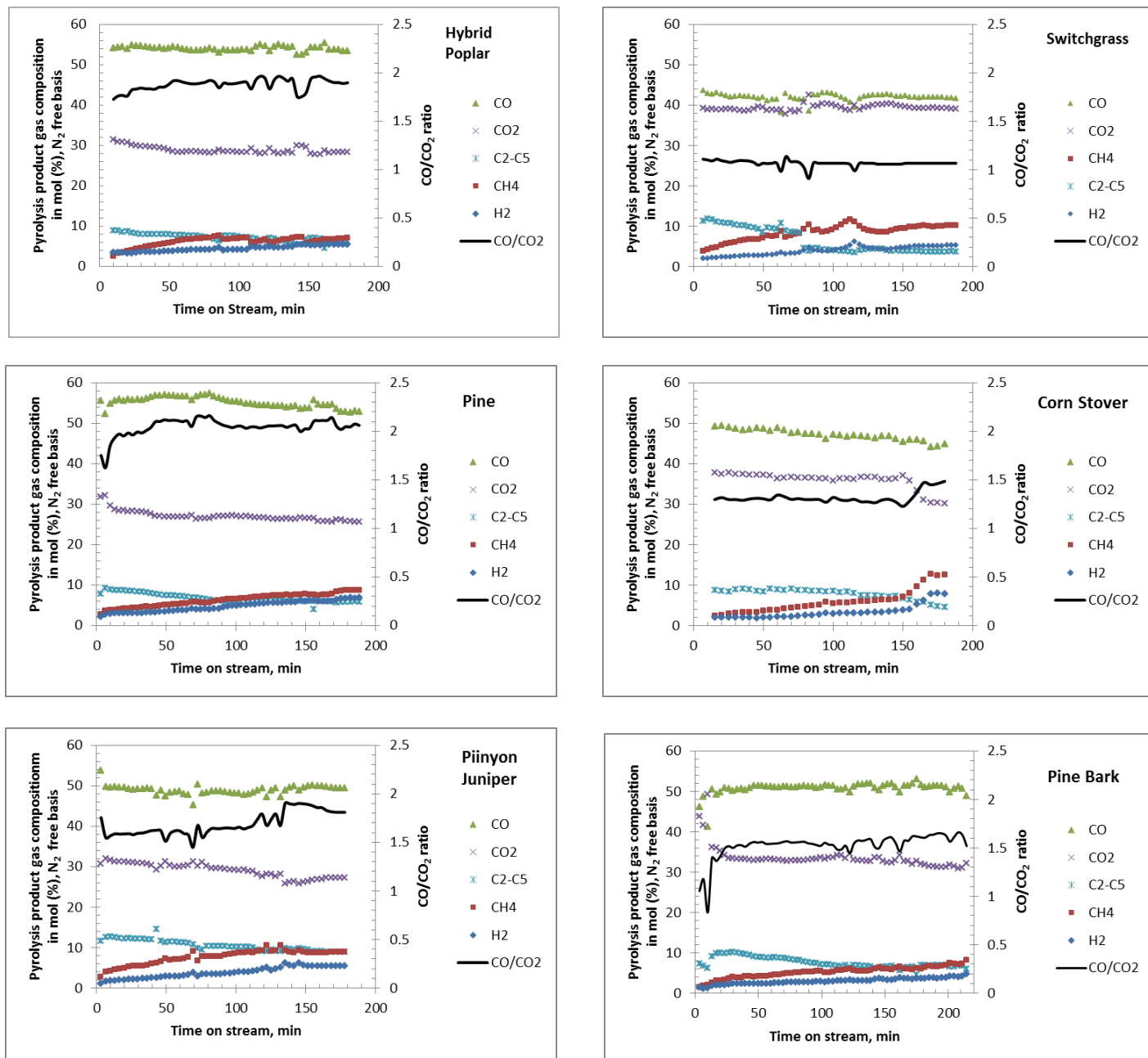


Figure S6. Gas evolution plot showing the composition of NCG produced from the various feedstocks sampled after the coalescing filter at time interval of 3.25 mins during the 3 hour run of catalytic pyrolysis experiments.

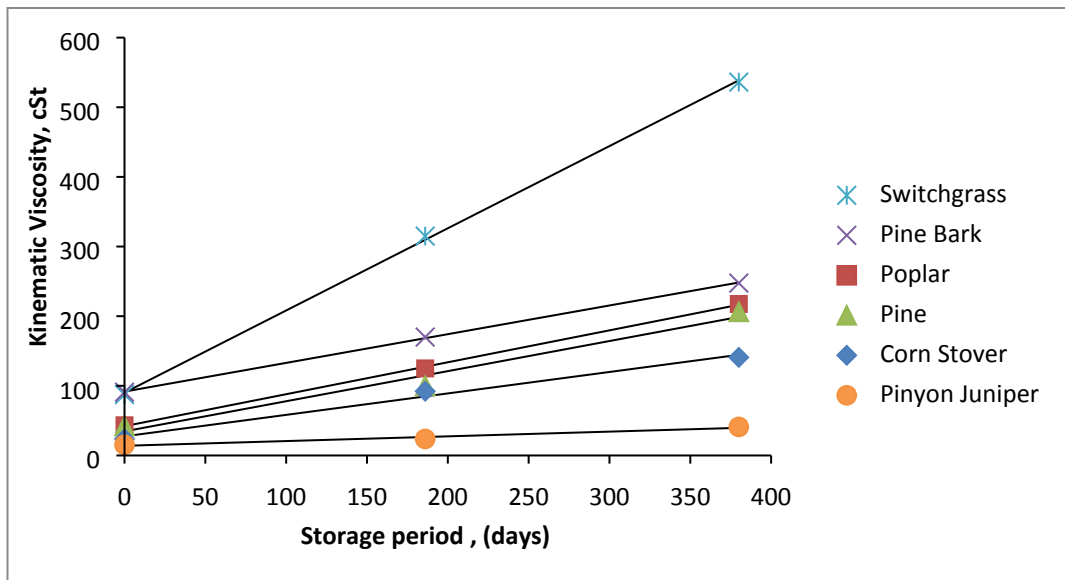


Figure S7. Storage stability curves showing the change in the viscosity of the various biocrude oils measured over a period of one year at a six month interval.

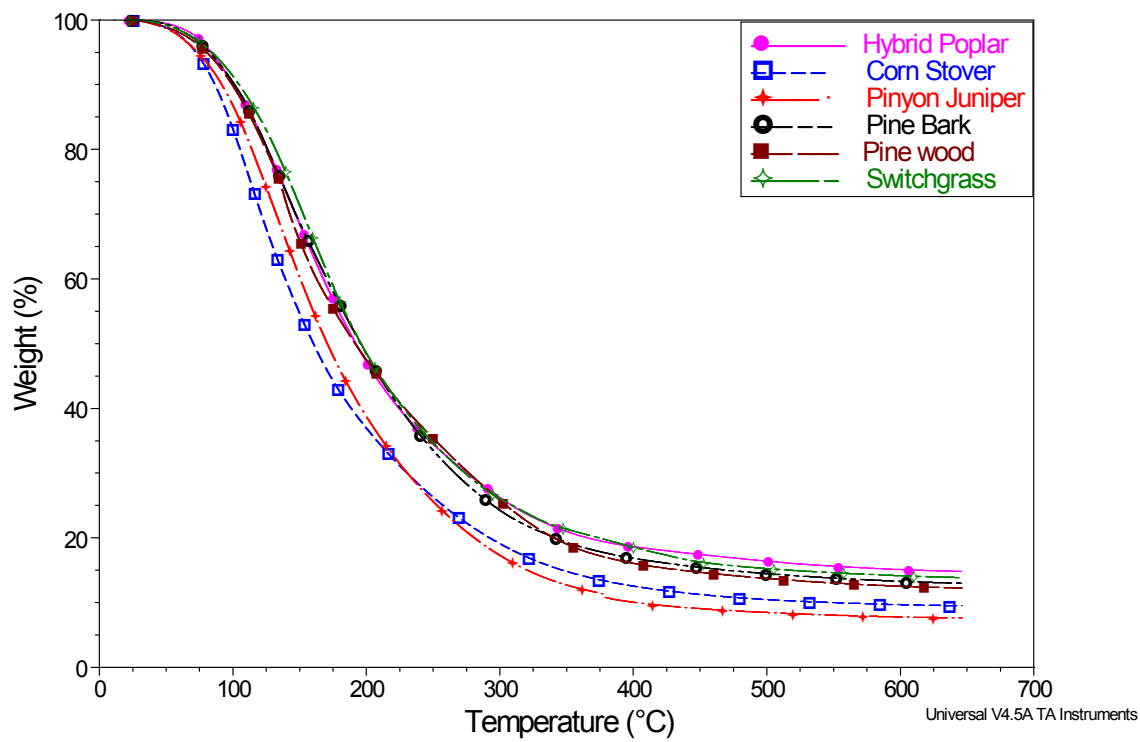


Figure S8. TG curves of biocrude oils from poplar, corn stover, pinyon-juniper, pine bark, pine and switchgrass.

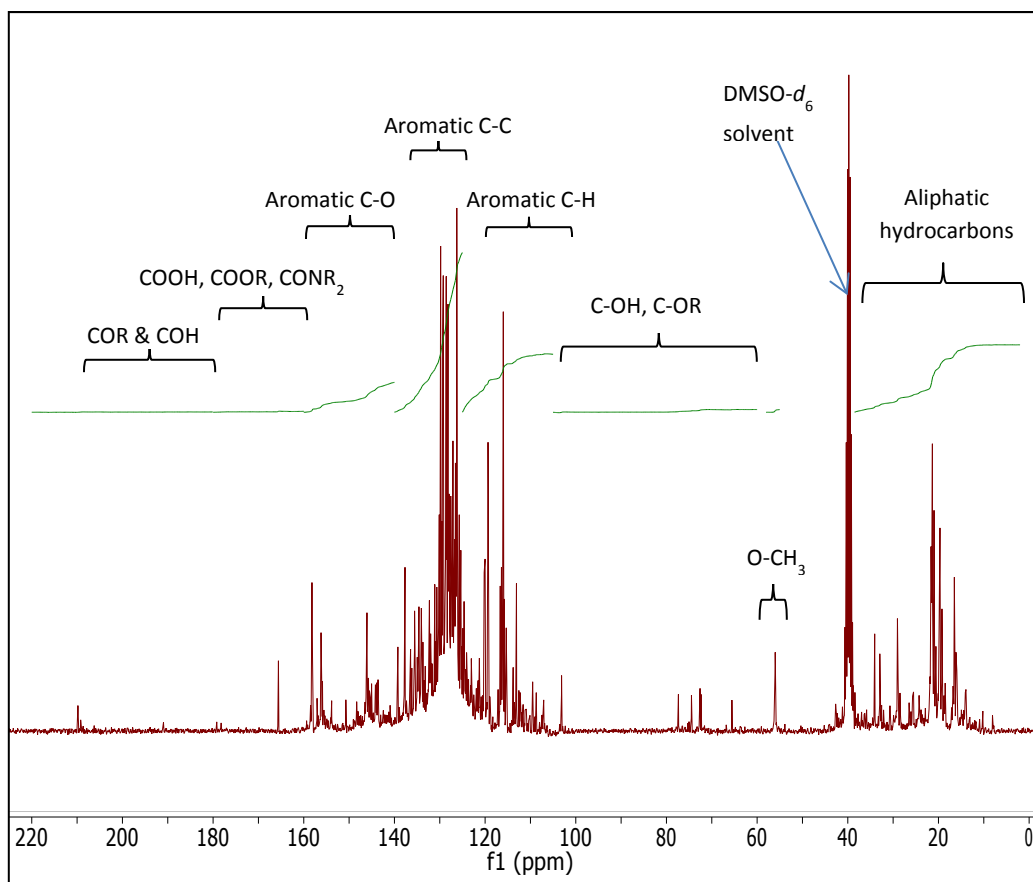


Figure S9. ^{13}C -NMR spectrum of biocrude oil produced from pinyon juniper

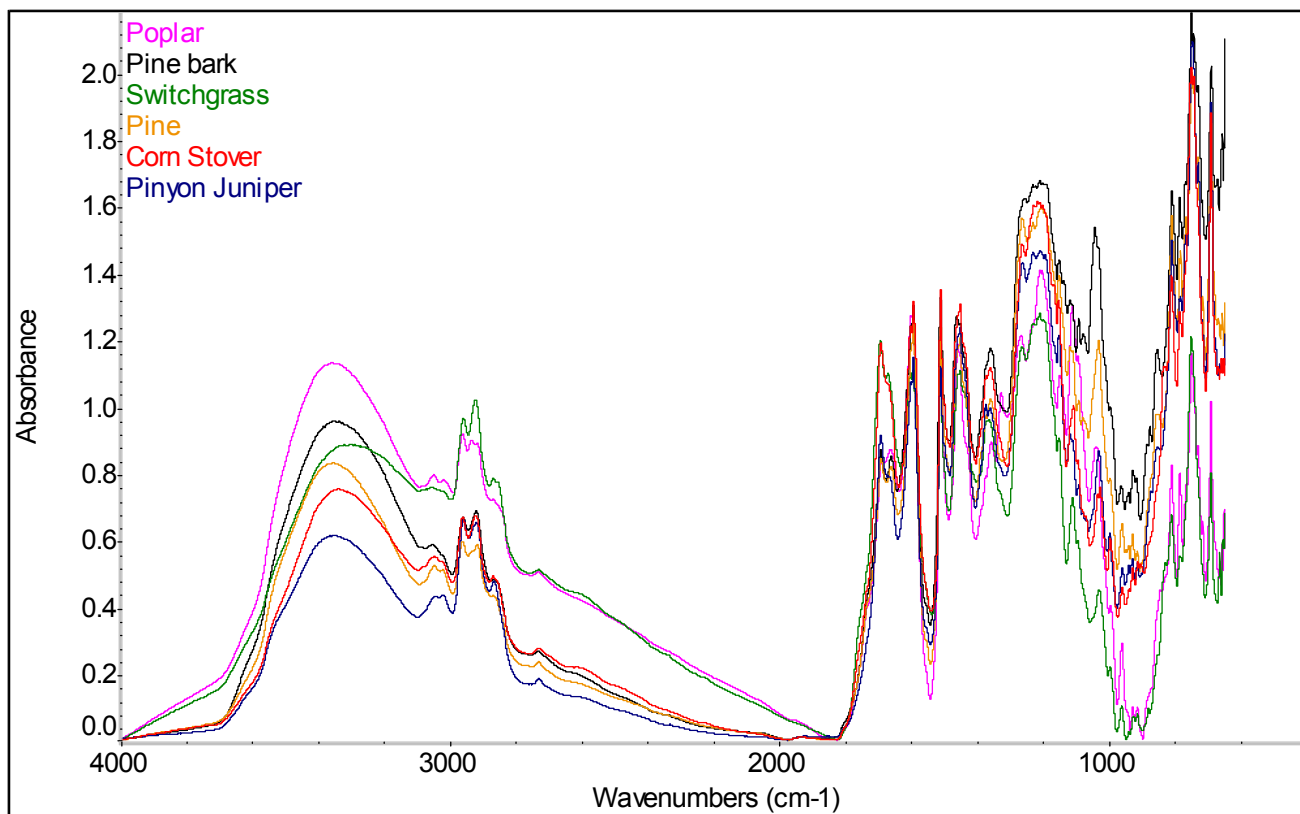


Figure S10. FT-IR spectra of biocrude oils from poplar, pine bark, switchgrass, pine, corn stover and pinyon juniper.

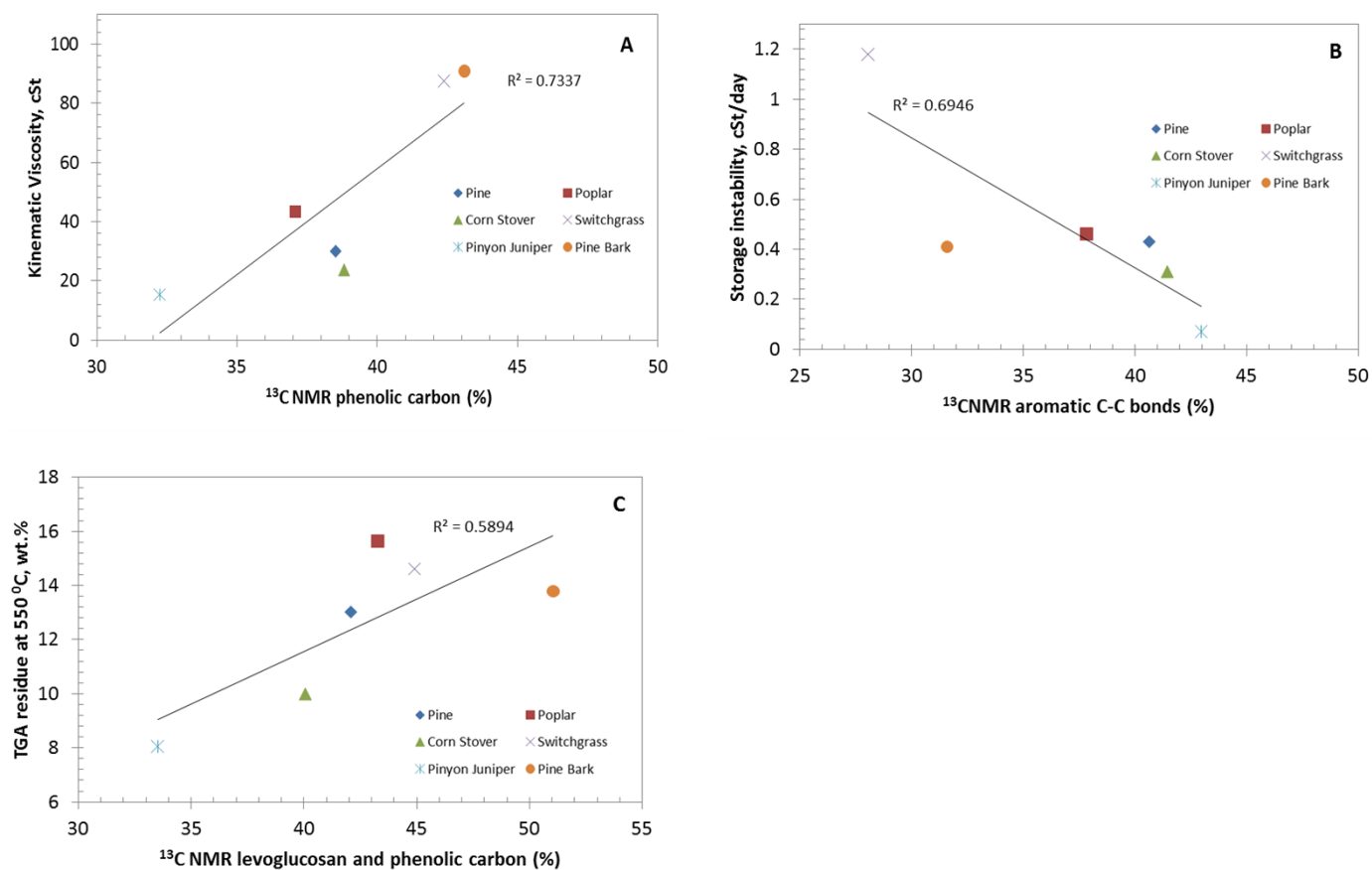


Figure S11. Correlation plots showing the relationship between the chemical composition of the biocrude oils and selected physical properties: (A) correlation between kinematic viscosity and phenolic carbons; (B) correlation between aromatic C-C bonds and storage stability; (C) correlation between levoglucosan/phenolics carbons and TGA solid residue.

Table S1. Comparison of the physico-chemical properties of raw bio-oil and upgraded bio-oils*

Analysis	Raw bio-oil	Upgraded bio-oil A	Upgraded bio-oil B
Elemental (Moisture free basis)			
C	60.67	81.83	75.29
H	6.67	7.84	6.87
O	32.94	9.83	17.69
N	< 0.5	< 0.5	< 0.5
S	< 0.5	< 0.5	< 0.5
Ash	< 0.08	< 0.06	< 0.07
H/C molar ratio	1.32	1.15	1.09
O/C molar ratio	0.41	0.10	0.18
pH	2.60	4.05	3.52
Density (g/cm ³)	1.21	0.96	1.06
Gravity, °API	-14.6	15.9	2.0
Viscosity (at 40 °C, cSt)	285	4.90	18.60
HHV (MJ/kg)	24.48	36.87	33.98
Karl Fischer moisture (wt.%)	2.95	0.83	1.99
Thermal stability at 90 °C for 24 h (Rate of viscosity change, cP/h)	53.08	0.003	0.364
Viscosity of 310 days stored oil (at 40 °C, cP)	N/A	5.15	23.8
Distillate fractions, wt.%			
≤ 220 °C	51.20	91.23	N/A
≤ 440 °C	-	-	76.37

Adapted from Mante, O. and F. Agblevor ²

Table S2. Elemental and ash analysis of the various biomass feedstocks

Elemental Composition (wt.%)^{d,b}	Biomass Feedstock					
	Poplar	Pine	Pinyon-Juniper	Switchgrass	Corn Stover	Pine Bark
C	50.31	52.11	51.59	48.07	46.49	53.41
H	6.02	5.03	5.33	5.028	5.30	4.88
N	0.02	0.07	0.34	0.65	0.43	0.22
O*	43.18	42.36	42.34	40.93	38.81	40.47
Ash	0.46	0.43	0.40	5.32	8.97	1.02

[d.b]-dry basis, *by difference

Table S3. Structural composition of various feedstocks from literature

Reference Source sample ID	Biomass Feedstock	Cellulose	Hemicellulose	Lignin	Ash	Reference
78-Switchgrass (Alamo)	Switchgrass	33.03	26.51	17.63	5.21	70
		37.00*	29.00*	19.00*	6.00*	71
45-Corn Stover (Zea mays)	Corn Stover	35.82	23.04	17.77	9.82	70
		38.00*	26.00	19.00	6.00	71
Hybrid Poplar (DN-34)	Hybrid Poplar	44.65	22.59	23.91	0.85	70
	Hybrid Poplar	40.80	19.21	27.17	0.43	
153-Monterey Pine (Pinus Radiata)	Pine	41.7	20.5	25.9	0.3	70
	Loblolly pine bark	23.1	14.1	43.5	1.1	68

*Average values

Table S4. ^{13}C NMR distribution of the various carbons in the biocrude oils (percentage carbon total)

Type of carbon	Chemical Shift, δ (ppm)	Biocrude oils					
		Pine	Poplar	Corn Stover	Switchgrass	Pinyon Juniper	Pine Bark
Aliphatic C-C	55-0	16.49	17.32	17.52	25.17	22.82	16.66
Methoxy C (-OCH ₃) in lignin	57-55	1.17	4.62	1.05	1.89	1.10	1.47
Aliphatic C-O (including levoglucosan)	103-60	3.57	6.20	1.25	2.53	1.28	7.95
Aromatic C-H	125-105	27.36	21.83	28.59	29.01	21.17	29.56
Aromatic C-C (carbons in aromatic hydrocarbons further from an O atom)	140-125	40.63	37.82	41.44	28.06	42.96	31.59
Aromatic C-O	160-140	10.11	10.62	8.67	10.88	9.97	12.07
Carbonyl (carboxylic acids and derivatives)	180-160	0.18	0.64	0.89	1.60	0.38	0.19
Carbonyl (aldehydes, ketones)	220-180	0.49	0.96	0.59	0.86	0.33	0.51

Table S5. Pearson Correlation Coefficients

Property	Carbons types determined by ¹³ CNMR								Elemental	
	Total C-C carbons	Phenolic Carbons	Levoglucosan Carbons	Phenolics and levoglucosan	Carbonyls	Oxygenates	Aromatic C-C	Aromatic C-O	C	N
pH	0.20	0.05	-0.64	-0.27	0.56	-0.20	-0.31	-0.22	0.70	0.90
Density (g/cm ³)	-0.93	0.76	0.94	0.95	0.02	0.94	-0.62	0.77	-0.87	-0.20
Gravity, °API	0.94	-0.76	-0.94	-0.95	-0.04	-0.94	0.63	-0.76	0.88	0.19
Kinematic Viscosity (at 40 °C, cSt)	-0.88	0.86	0.59	0.85	0.38	0.88	-0.98	0.82	-0.47	0.43
Dynamic Viscosity (at 40 °C, cP)	-0.89	0.86	0.61	0.86	0.36	0.89	-0.97	0.83	-0.48	0.40
Storage Stability	-0.54	0.64	0.05	0.45	0.82	0.54	-0.83	0.33	-0.34	0.74
TGA amount degraded below 400 °C, wt.%	0.81	-0.69	-0.65	-0.77	-0.48	-0.81	0.72	-0.60	0.88	-0.13
TGA residue at 550 °C, wt.%	-0.81	0.66	0.70	0.77	0.43	0.81	-0.68	0.61	-0.91	0.04

Values in bold are different from 0 with a significance level $\alpha=0.05$