Supplementary Materials

Development of Quantitative ^{13}C NMR Characterization and simulation of C, H, O contents for pyrolysis oils based on the ^{13}C NMR analysis

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Table S1. Certified value for standard #1 (ASTM-P-0050)

Analyte	CAS Number	Target Concentration (w_t %)	Formula
n-Pentane	109-66-0	6.66	C_5H_{12}
n-Hexane	110-54-3	6.66	C_6H_{14}
n-Heptane	142-82-5	6.66	C_7H_{16}
n-Octane	111-65-9	6.66	C_8H_{18}
n-Nonane	111-84-2	6.66	C_9H_{20}
n-Decane	124-18-5	6.66	$C_{10}H_{22}$
n-Undecane	1120-21-4	6.66	$C_{11}H_{24}$
n-Dodecane	112-40-3	13.33	$C_{12}H_{26}$
n-Tetradecane	629-59-4	6.66	$C_{14}H_{30}$
n-Pentadecane	629-62-9	6.66	$C_{15}H_{32}$
n-Hexadecane	544-76-3	6.66	$C_{16}H_{34}$
n-Heptadecane	629-78-7	6.66	$C_{17}H_{36}$
n-Octadecane	596-45-3	6.66	$C_{18}H_{38}$
n-Eicosane	112-95-8	6.66	$C_{20}H_{42}$

Table S2. Certified value for standard #2 (D-5443-93-HTM)

Analyte	CAS Number	Certified Value (w_t %)	Formula
Cyclopentane	287-92-3	1	c-C_5H_{10}
n-Pentane	109-66-0	1	n-C_5H_{12}
Cyclohexane	110-82-7	2	c-C_6H_{12}
2,3-Dimethylbutane	79-29-8	2	C_6H_{14}
n-Hexane	110-54-3	2	C_6H_{14}
1-Hexene	592-41-6	1.5	C_6H_{12}
Methylcyclohexane	108-87-2	4.25	C_7H_{14}
4-Methyl-1-hexene	3769-23-1	1.5	C_7H_{14}
n-Heptane	142-82-5	3.5	C_7H_{16}
1,2-Dimethylcyclohexane	583-57-3	5	C_8H_{16}
Isooctane	540-84-1	5	C_8H_{18}
n-Octane	111-65-9	5	C_8H_{18}
1,2,4-Trimethylcyclohexane	2234-75-5	4.25	C_9H_{18}
n-Nonane	111-84-2	4.5	C_9H_{20}
n-Decane	124-18-5	4.25	$C_{10}H_{22}$
n-Undecane	1120-21-4	3.5	$C_{11}H_{24}$
n-Dodecane	112-40-3	3.25	$C_{12}H_{26}$
Benzene	71-43-2	3.25	C_6H_6
Toluene	108-88-3	2.25	C_7H_8
trans-Decahydronaphthalene	493-02-7	4.25	$C_{10}H_{18}$
n-Tetradecane	629-59-4	4.5	$C_{14}H_{30}$
Ethylbenzene	100-41-4	4.5	C_8H_{10}
o-Xylene	95-47-6	4.25	C_8H_{10}
n-Propylbenzene	103-65-1	5	C_9H_{12}
1,2,4-Trimethylbenzene	95-63-6	4.5	C_9H_{12}
1,2,3-Trimethylbenzene	526-73-8	5	C_9H_{12}
1,2,4,5-Tetramethylbenzene	95-93-2	5	$C_{10}H_{14}$
Pentamethylbenzene	700-12-9	5	$C_{11}H_{16}$

Table S3. The feed types of industrial fluid catalytic cracking units

Feed	Sample	Composition
1	KO105	kerosene + oak wood (1) pyrolysis oil (5 w_t %)
2	VO105	vacuum gas oil + oak wood (1) pyrolysis oil (5 w_t %)
3	KO110	kerosene + oak wood (1) pyrolysis oil (10 w_t %)
4	VO110	vacuum gas oil + oak wood (1) pyrolysis oil (10 w_t %)
5	KO205	kerosene + oak wood (2) pyrolysis oil (5 w_t %)
6	VO205	vacuum gas oil + oak wood (2) pyrolysis oil (5 w_t %)
7	KO210	kerosene + oak wood (2) pyrolysis oil (10 w_t %)
8	VO210	vacuum gas oil + oak wood (2) pyrolysis oil (10 w_t %)

Table S4. ^{13}C NMR chemical shift assignment ranges for pyrolysis oils (on the basis of reference[30]).

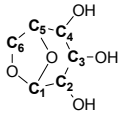
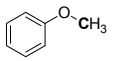
Type of carbons	Range (ppm)	Structure
Carbonyl	215.0-166.5	
Aromatic C-O	166.5-142.0	
Aromatic C-C	142.0-125.0	
Aromatic C-H	125.0-95.8	
Levoglucosan	C1 102.3, C2 72.0 C3 73.7, C4 71.7 C5 76.5, C6 64.9	
Aliphatic C-O	95.8-60.8	
Methoxyl	60.8-55.2	
Aliphatic C-C	55.2-0.0	
Methyl – Aromatic	21.6-19.1	
Methyl – Aromatic’	16.1-15.4	

Table S5. The influences for concentrations of relax reagent on the T_1 of bio-oils.

	C=O	Aromatic carbons	Aliphatic C-O	Aliphatic C-C
	230 - 166.5 ppm	166.5 - 95.8 ppm	95.8 - 53.5 ppm	53.3 - 0.0 ppm

5 mg/ml $Cr(acac)_3$	459.268ms	211.380ms	277.742ms	269.905ms
1 mg/ml $Cr(acac)_3$	893.397ms	1244.000ms	2246.000ms	785.890ms

Table S6. In-situ aging test for quantitative ^{13}C NMR for bio-oil sample produced from oak wood with 5mg/ml relax reagent, the results shown as carbon ***mol***%.

Functional groups	Integration					
	8 hs	16 hs	24 hs	32 hs	40 hs	48 hs

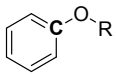
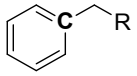
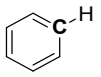
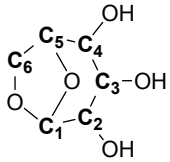
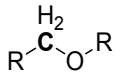
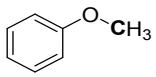
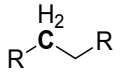
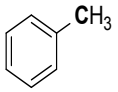
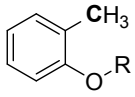
	16.4	16.4	15.6	16.8	16.7	16.1
	7.5	7.4	7.2	7.2	7.5	6.2
	1.8	1.2	2.3	2.0	1.7	3.1
	12.0	11.7	12.1	12.3	11.6	13.3
	43.0	44.7	43.9	42.3	42.5	42.1
	31.4	30.6	29.5	30.4	31.4	30.7
	3.1	3.2	3.3	3.1	3.2	3.2
	16.3	15.4	15.6	16.3	16.7	16.1
	7.5	7.0	6.7	7.2	7.4	7.3
	1.0	1.0	0.9	0.9	0.9	0.9

Table S7. In-situ aging test for quantitative ^{13}C NMR for bio-oil sample produced from cottonwood with 5mg/ml relax reagent, the results shown as carbon ***mol***%.

Functional groups	Integration				
	0 hs	12 hs	24 hs	36 hs	48 hs

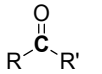
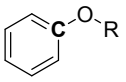
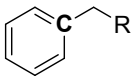
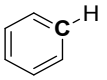
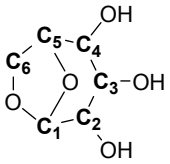
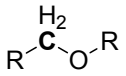
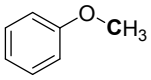
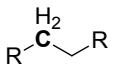
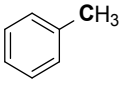
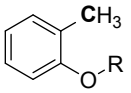
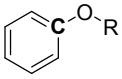
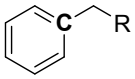
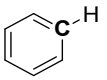
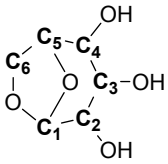
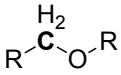
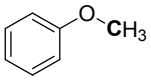
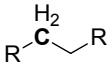
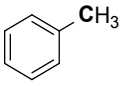
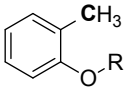
	9.6	7.2	6.5	3.6	4.2
	7.4	8.5	7.8	7.4	8.6
	3.6	6.0	6.0	4.6	6.7
	9.9	12.1	15.0	13.0	15.2
	1.4	1.6	1.7	1.9	1.6
	25.2	24.6	24.2	26.5	24.5
	8.7	8.6	8.5	8.7	8.4
	34	33.1	32.1	34.0	31.8
	4.4	4.2	4.1	4.5	4.0
	4.7	4.7	4.5	5.1	4.5

Table S8. In-situ aging test for quantitative ^{13}C NMR for bio-oil sample produced from the mixture of cottonwood and coal with 5mg/ml relax reagent, the results shown as carbon ***mol***%.

Functional	Integration

groups	0 hs	12 hs	24 hs	36 hs	48 hs
	3.9	2.2	4.4	3.6	7.1
	2.6	2.5	4.6	5.8	3.3
	16.3	16.2	16.6	17	15.8
	15.1	15.1	15.8	16	12.6
	1.8	1.4	1.5	1.9	1.3
	20.6	18.8	18.3	18.6	16.5
	8.1	7.4	7.6	7.3	5.6
	34.1	36.6	33.8	32.1	36.7
	5.3	5.7	5.2	4.8	3.7
	2.3	2.1	2.2	2.1	2.1

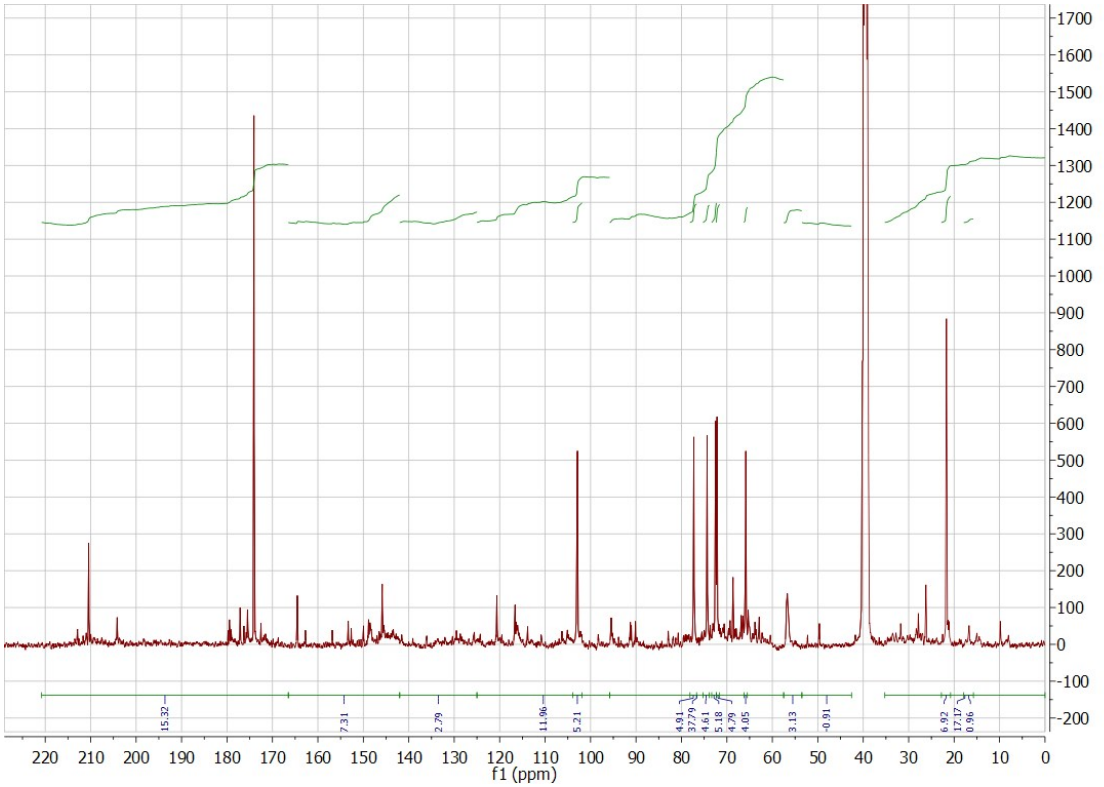


Figure S1. Quantitative ^{13}C NMR for pyrolysis oil sample without relax reagent, pulse delay was set as 60 s.

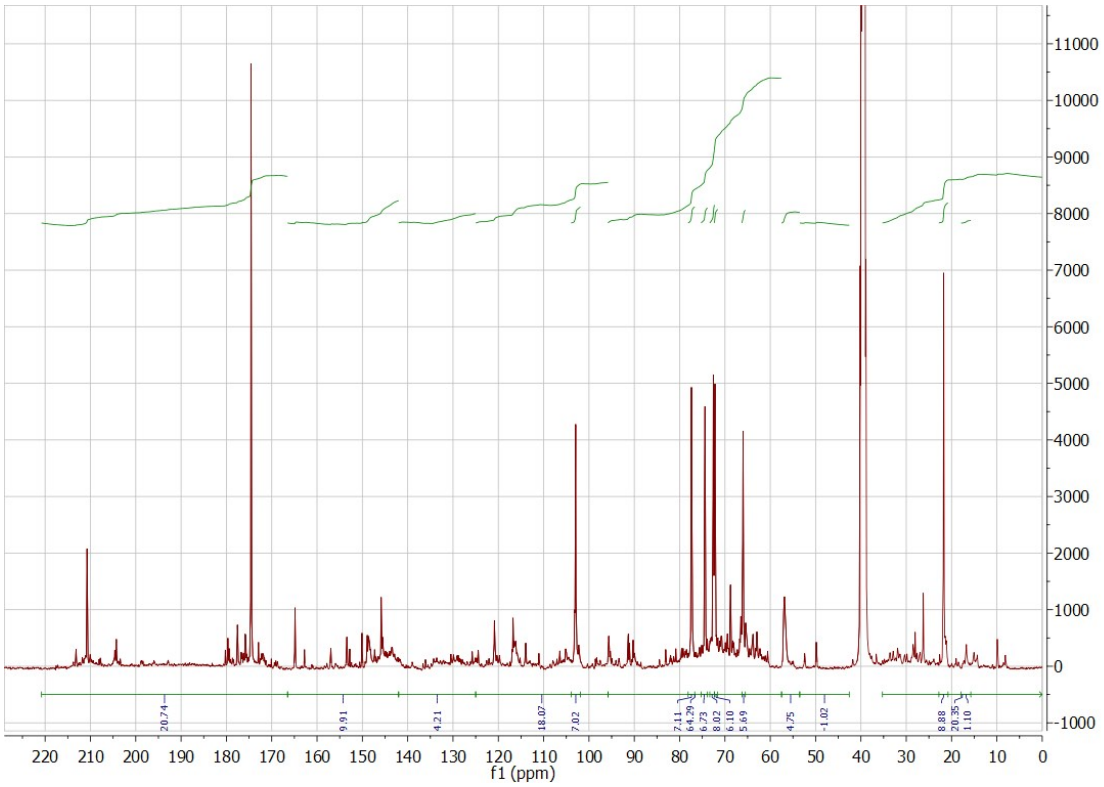


Figure S2. Quantitative ^{13}C NMR for pyrolysis oil sample with 1 mg/ml relax reagent, pulse delay was set as 15 s.

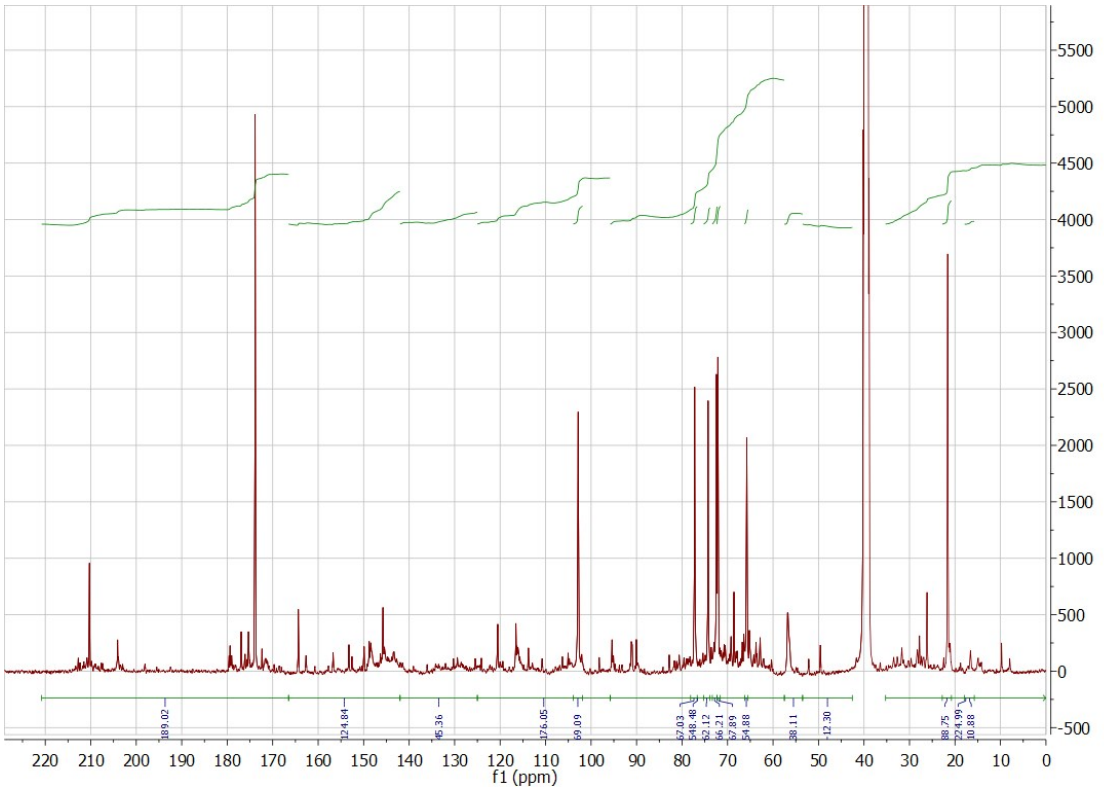


Figure S3. Quantitative ^{13}C NMR for pyrolysis oil sample with 5 mg/ml relax reagent, pulse delay was set as 15 s.

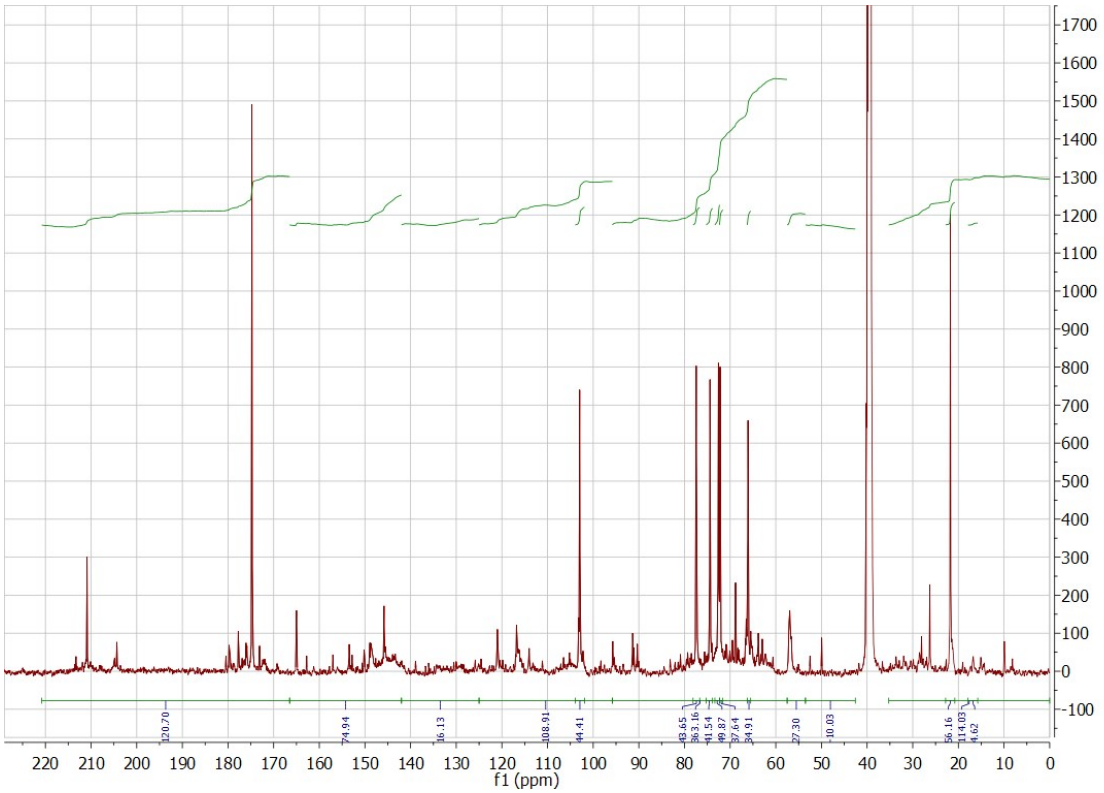


Figure S4. Quantitative ^{13}C NMR for pyrolysis oil sample with 5 mg/ml relax reagent, pulse delay was set as 3 s.

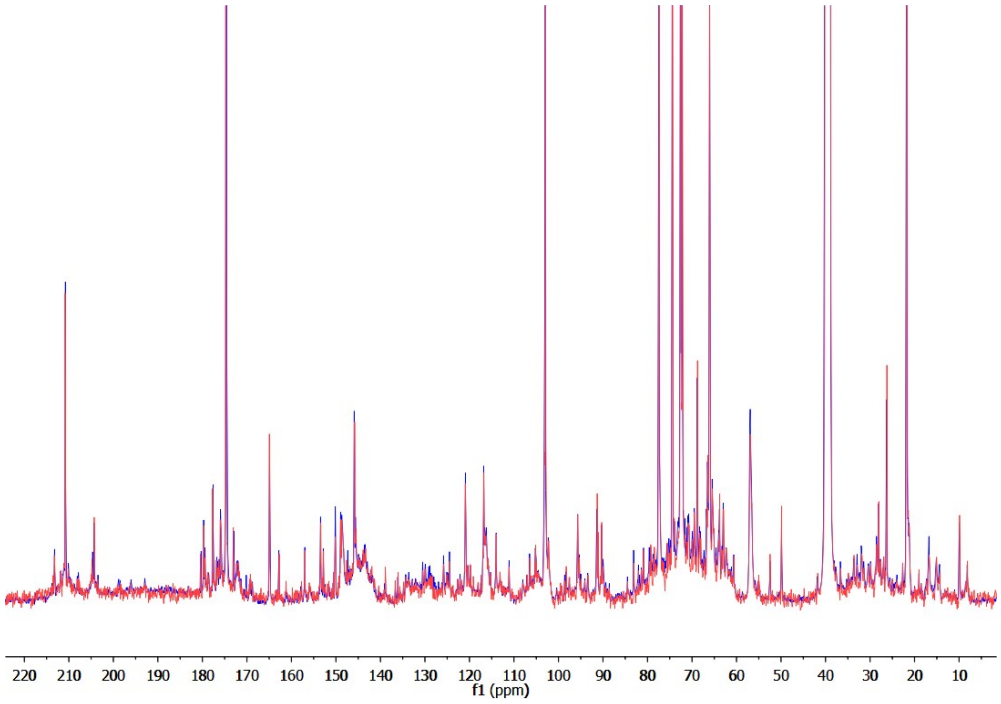


Figure S5. Quantitative ^{13}C NMR for bio-oil samples produced from oak wood with 5 mg/ml relax reagent, pulse delay was set as 3 s with 8 k scans (blue) and 1 k scans (red).

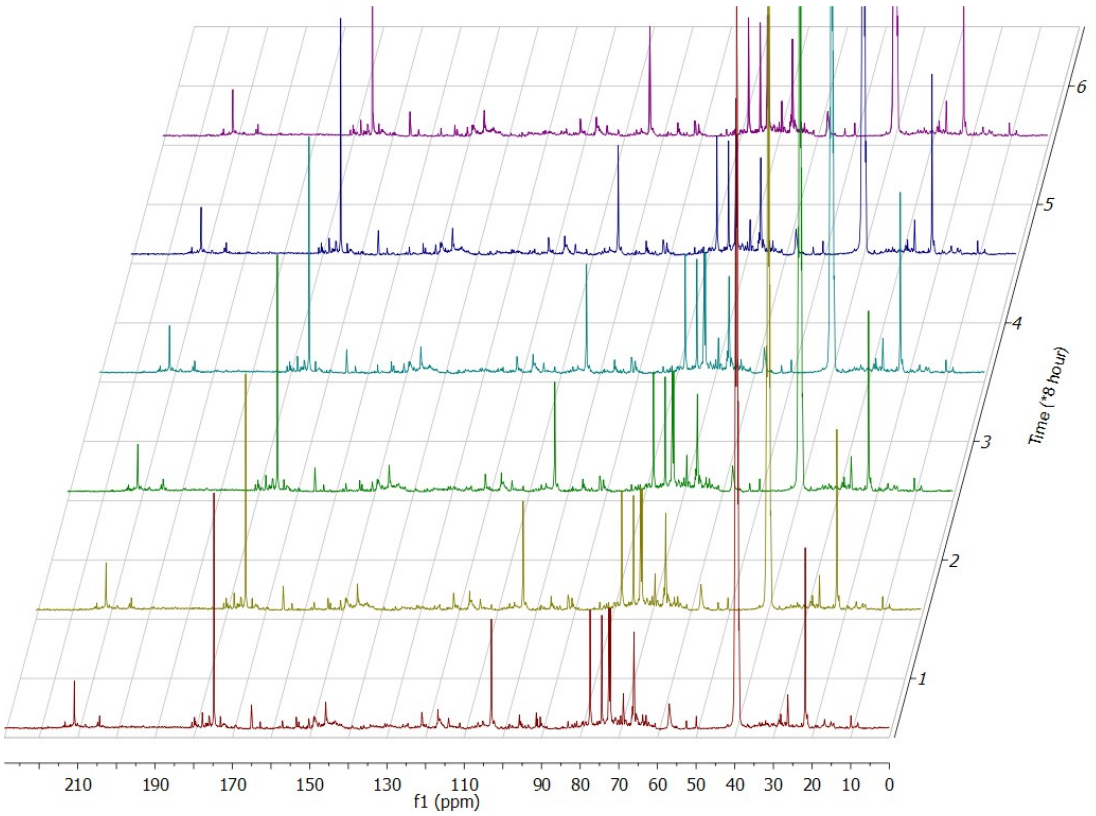


Figure S6. In-situ aging test for quantitative ^{13}C NMR for bio-oil sample produced from oak wood with 5 mg/ml relax reagent.

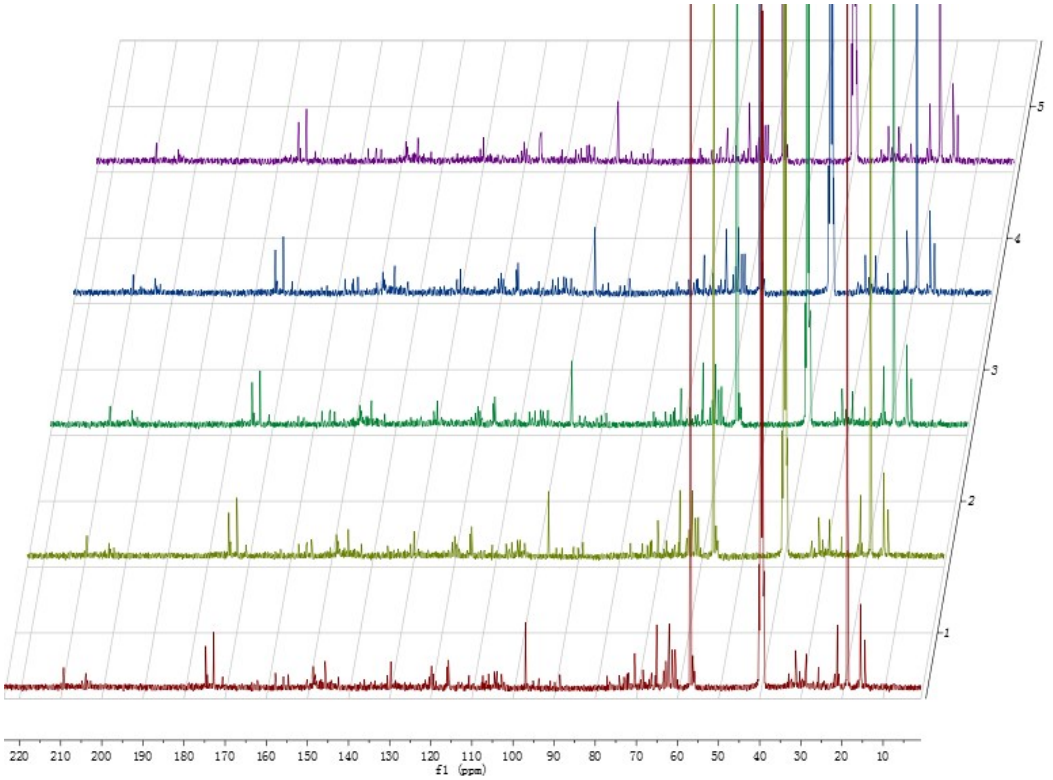


Figure S7. In-situ aging test for quantitative ^{13}C NMR for bio-oil sample produced from cottonwood with 5 mg/ml relax reagent.

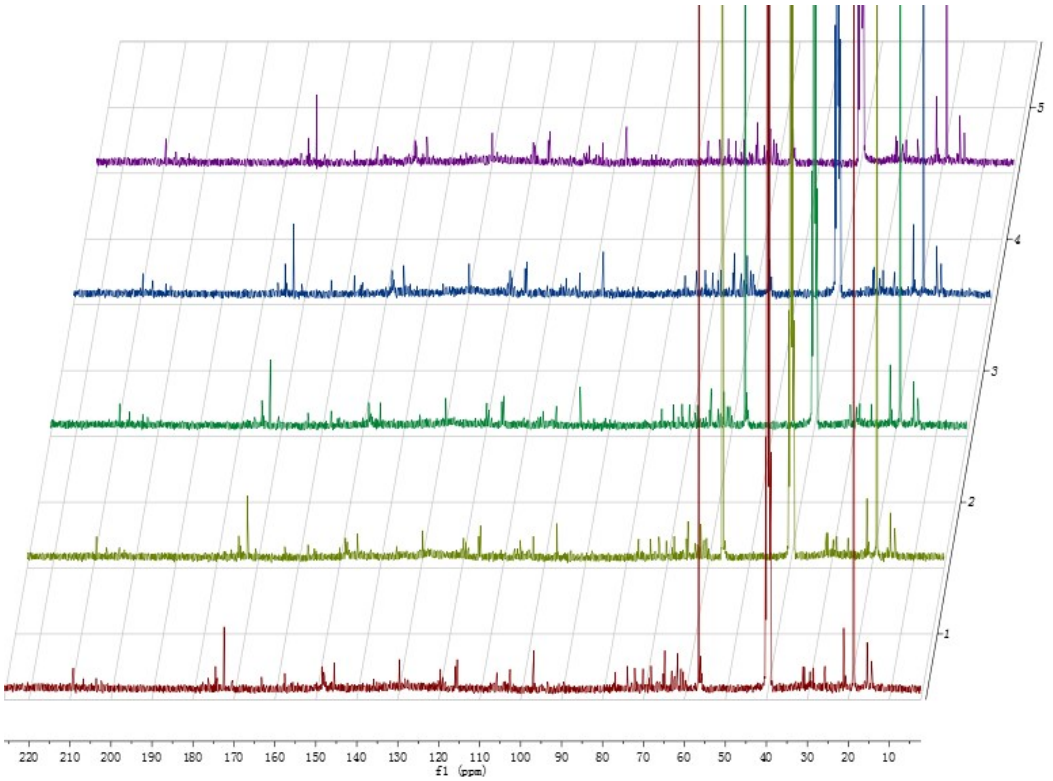
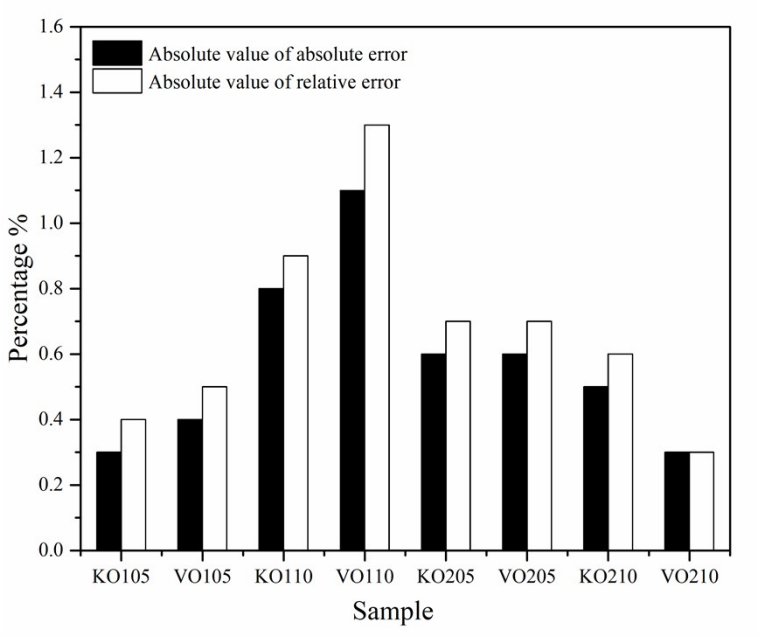
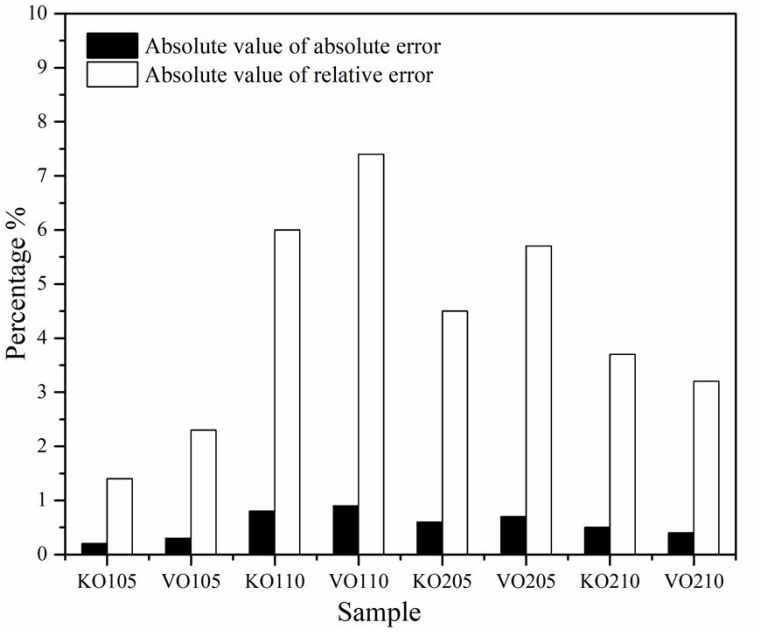


Figure S8. In-situ aging test for quantitative ^{13}C NMR for bio-oil sample produced from the mixture of cottonwood and coal with 5 mg/ml relax reagent.



(**a**)



(**b**)

Figure S9. The absolute value of absolute error and relative error for oxygen-deficient compounds: (**a**) Carbon; (**b**) Hydrogen.

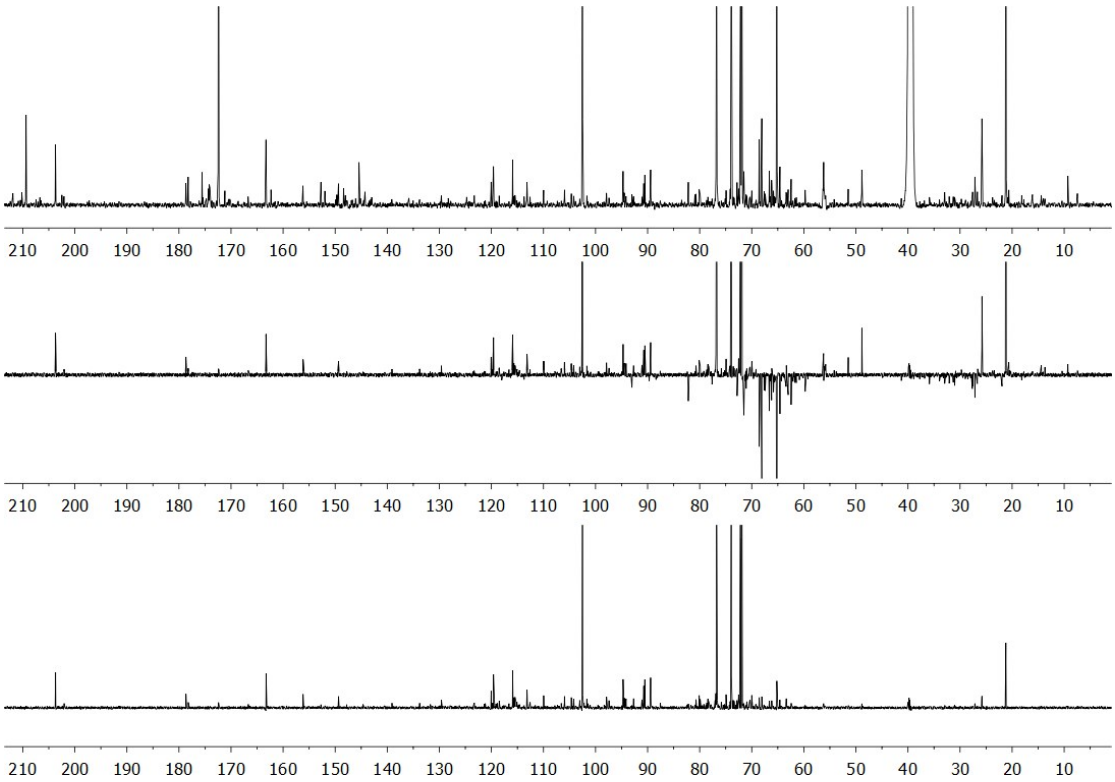
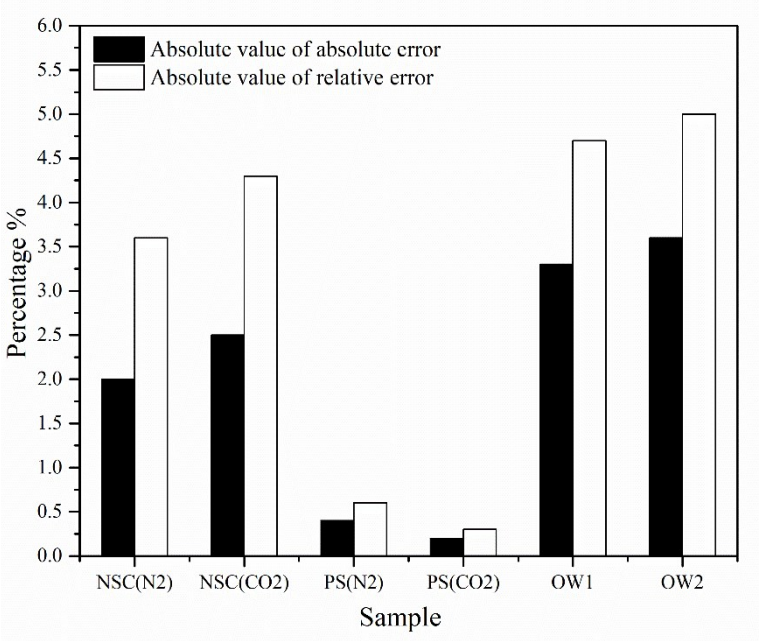
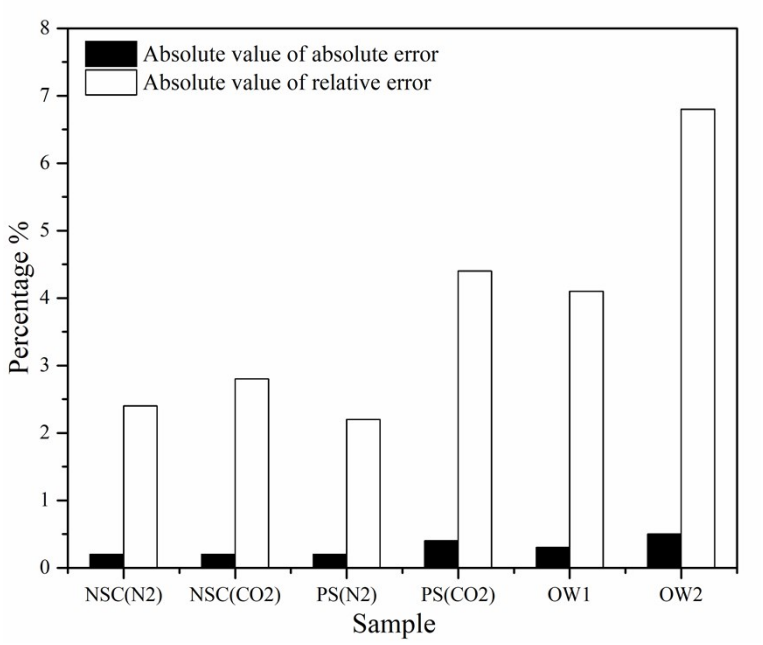


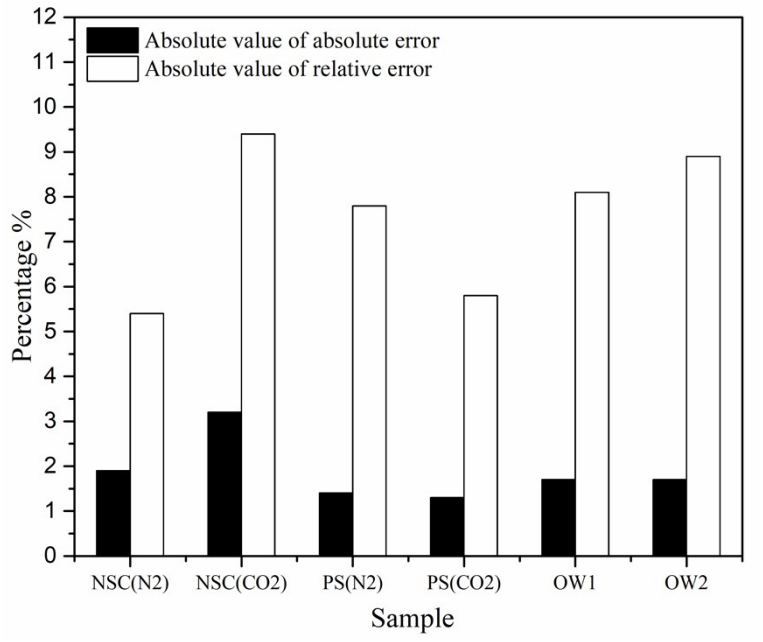
Figure S10. Quantitative ^{13}C NMR and DEPT 135 and DEPT 90 (from top to bottom) for the pyrolysis oil of oak wood 1.



(**a**)



(**b**)



(c)

Figure S11. The absolute value of absolute error and relative error for oxygen-rich pyrolysis oils: (**a**) Carbon; (**b**) Hydrogen; (**c**) Oxygen.

References

(30) Ben, H.; Ragauskas, A. J. NMR Characterization of Pyrolysis Oils from Kraft Lignin. *Energy Fuels* **2011,** 25 (5), 2322–2332.

doi:10.1021/ef2001162.