Supporting Information

for:

A Fundamental Study of Lignin Reactions with Formaldehyde and Glyoxal

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This file (8 pages) contains:

Supporting Figures S1 – S6

Supporting Tables S1 – S2

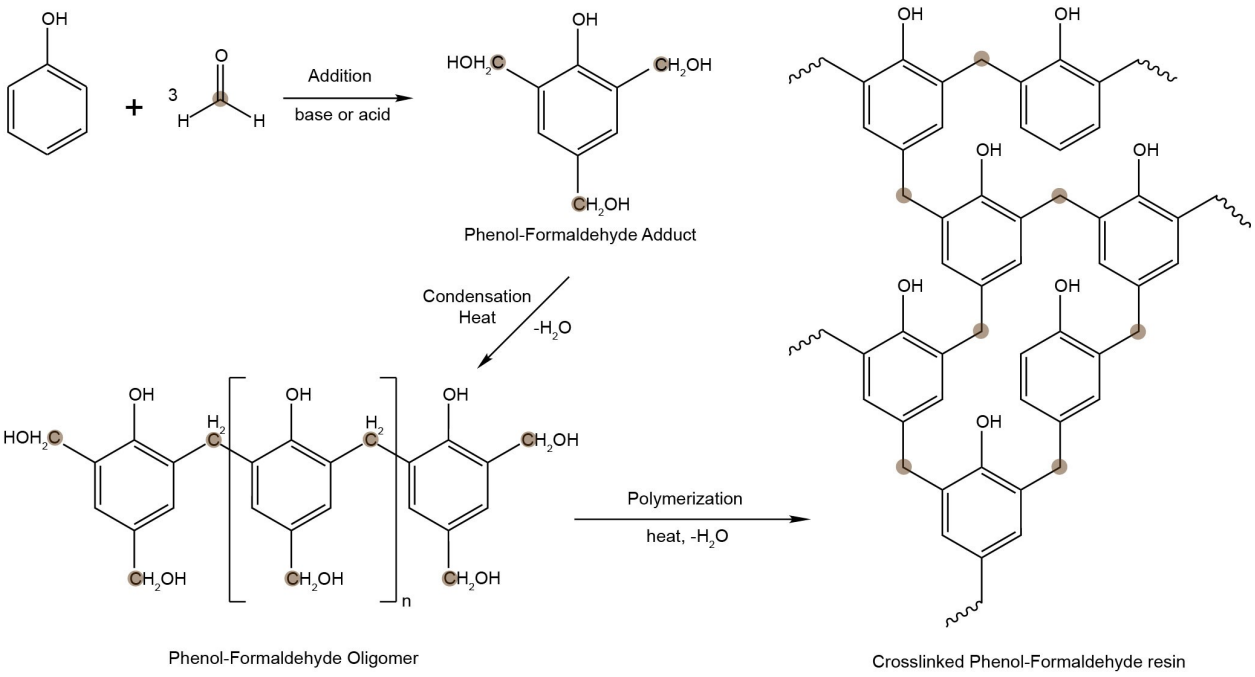


Figure S1: Schematic representation of the Phenol-Formaldehyde resin formation.

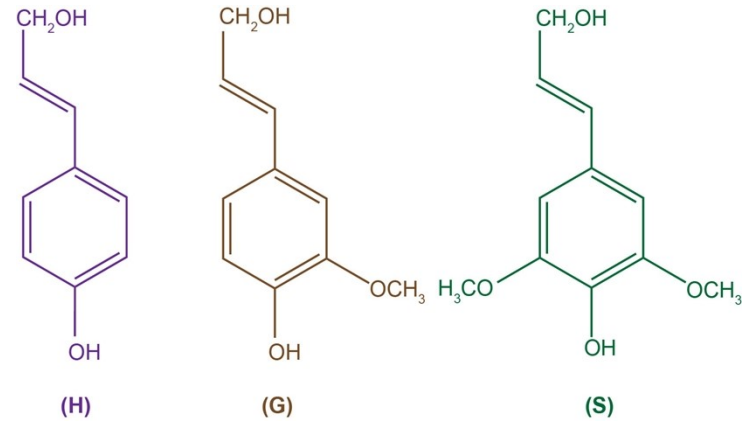


Figure S2: Major phenylpropanoid units of lignin.

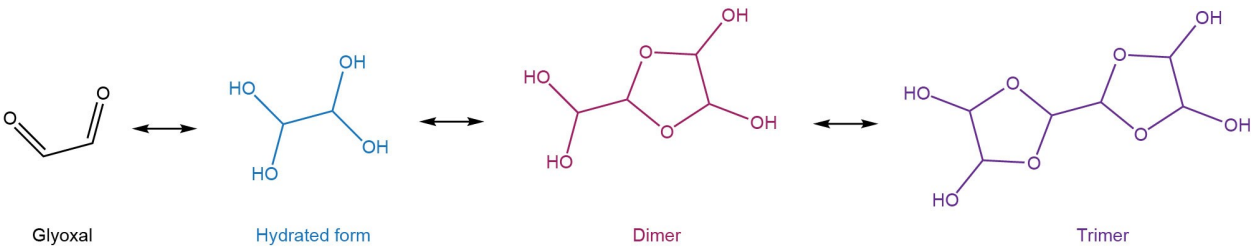


Figure S3: Structure of glyoxal and major hydrated oligomers.

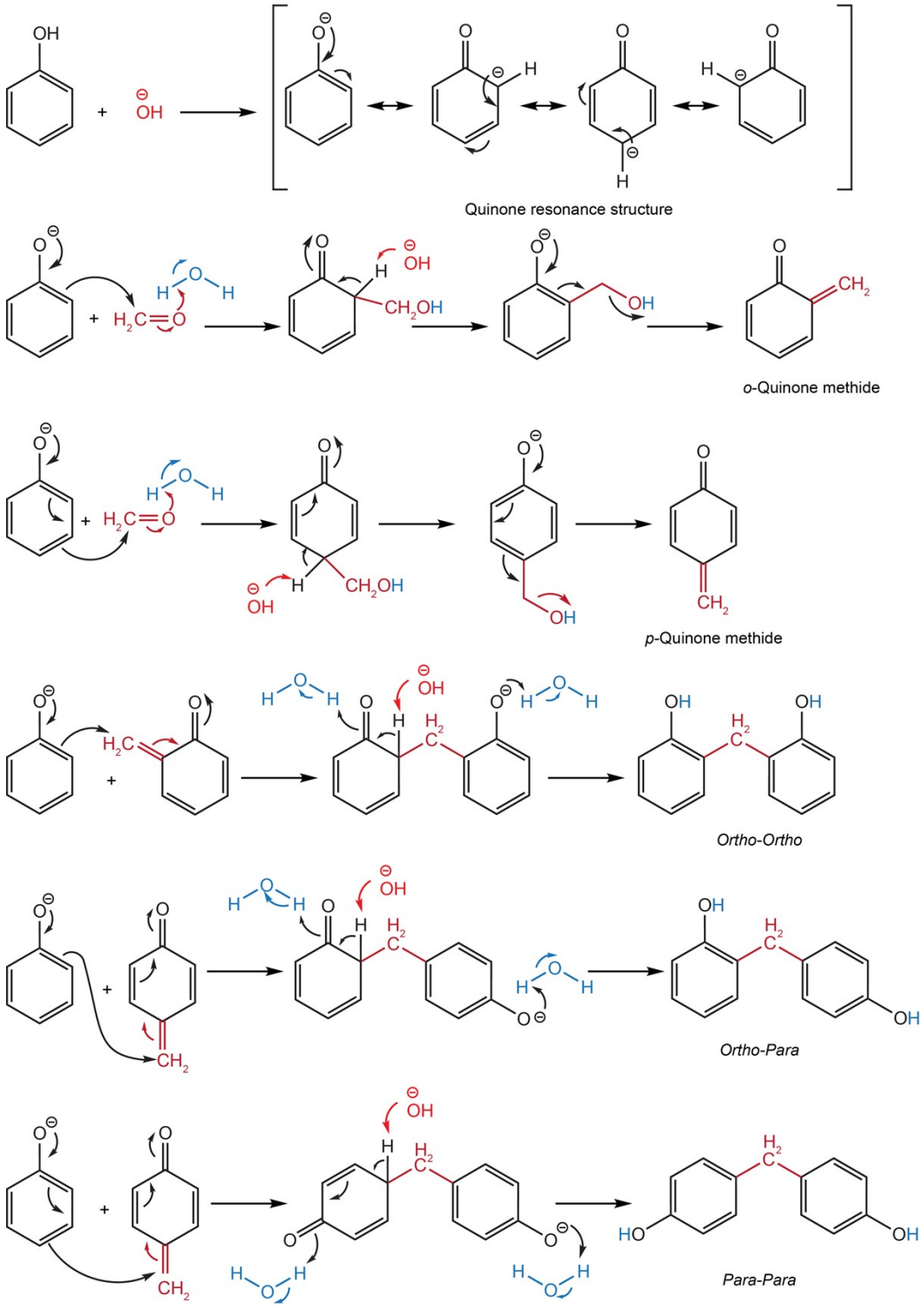


Figure S4: Mechanism of dimer formation through quinone methide intermediate.

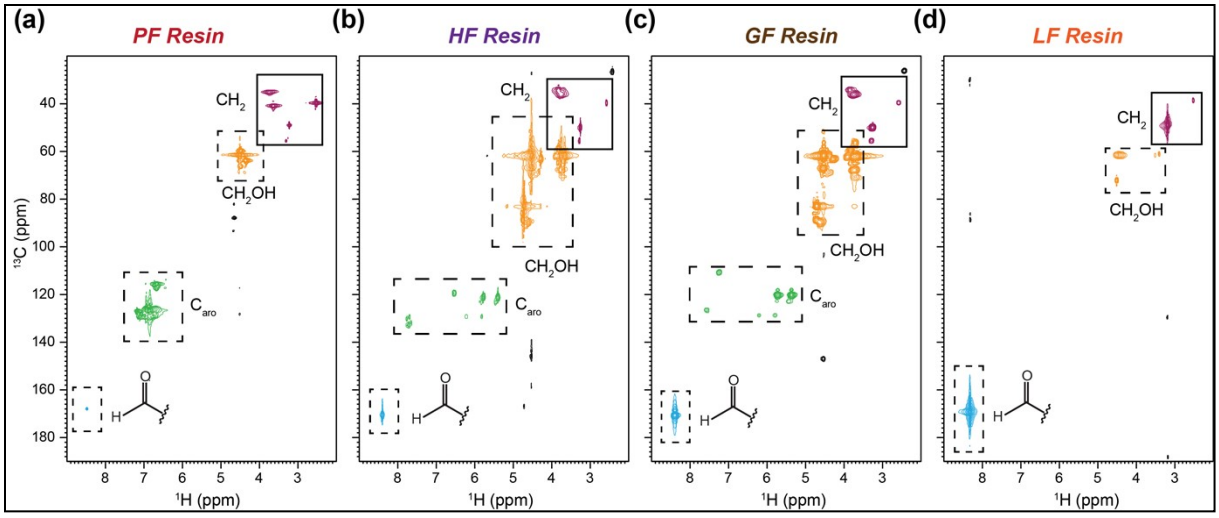


Figure S5: HSQC spectra of formaldehyde resins. (a) PF resin with C_{aro}, CH_2OH, and CH_2 peaks. (b) HF resin and (c) GF resin have similar peaks. (d) LF resin has two major peaks of formate ester and CH_3OH, along with CH_2OH.

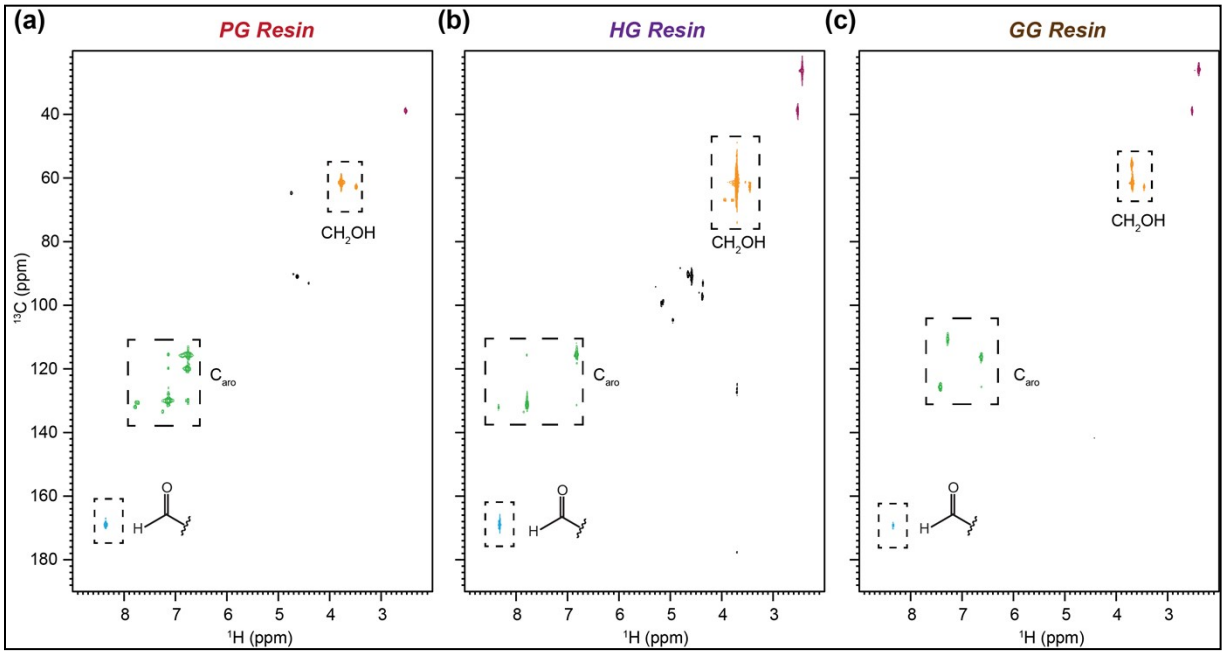
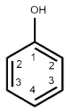
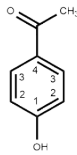
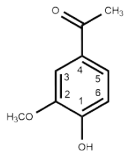


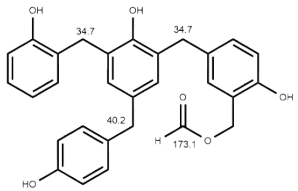
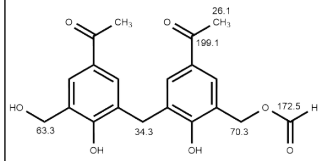
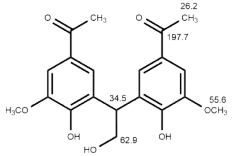
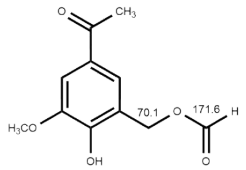
Figure S6: HSQC spectra of glyoxal resins. (a) PG resin with -CHO, $C_{aro,}$ and CH_2OH peaks, (b) HG resin, and (c) GG resin have similar peaks of -CHO, Caro, and CH_2OH.

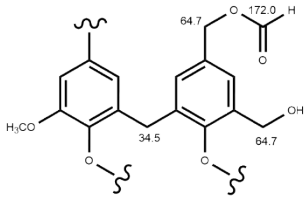
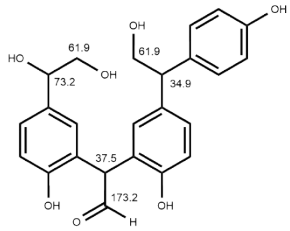
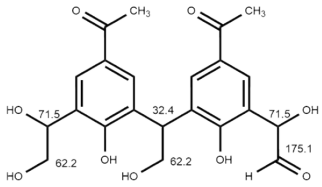
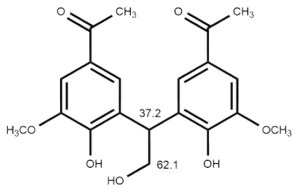
Table S1: ^{13}C Chemical shifts (in ppm) of precursor compounds. Not applicable (/).

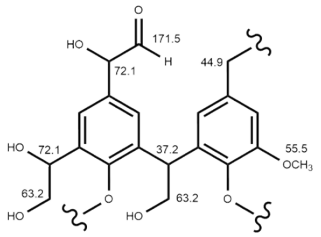
Compounds	C 1*	C2	C3	C4	C 5	C6	Carbonyl	Methyl (CH_3)	Methoxy (OCH_3)	Structure
Phenol	157.3	115.2	129.4	118.8	/	/	/	/	/	
H-monomer	162.0	115.2	130.7	128.6	/	/	196.0	26.2	/	
G-monomer	151.7	147.5	111.1	128.9	123.4	114.9	196.0	26.2	55.6	

*Aromatic carbon attached to -OH group

Table S2: ^{13}C Chemical shifts (in ppm) of cured resins acquired by 3.2 mm probe in 400 MHz solid-state NMR. Not applicable (/). Unidentified (-).

Compounds	C_{aro}	CH_2OH	Ether and -CHOH	$-CH_2-^a$	$-CH_2-^b$	Carbonyl#	Quinonoid	Methyl (CH_3)	Methoxy (OCH_3)	Unreacted formaldehyde	Structure
PF* resin (cured)	C**: 156.6; 117.7; 130.3	63.2	70	34.7	40.2	173.1	184.3	/	/	-	
HF* resin (cured)	120.6; 129.0	63.3	70.3	34.3	/	172.5; Cα: 199.1	-	26.2	/	-	
GF* resin (cured)	119.9; 125.9	62.9	70.1	34.5	/	171.6, Cα: 197.7	-	26.2	55.6	89.5, 84.3	 

LF* resin (cured)	128.7; 123.5; 111.4	64.7	75.7	34.5	41.31	172.0	-	23.7	-	94.1	
PG*** resin (cured)	C*: 165.5; 130.4; 116.1; 104.5; 102.7	61.9	73.2	37.5, 34.9	-	172.9	181.2	/	/	-	
HG*** resin (cured)	133.4; 131.1; 128.3; 116.4; 101.8	62.2	71.5	32.4, 30.8	/	175.1	182.1	25.3	/	-	
GG*** resin (cured)	C*: 149.8; 128; 123.3; 116.4; 112.1; 108.4	62.1	71.6	37.2	/	175.6	182.2	25.6	54.1	-	

LG*** resin (cured)	C*: 150.4; 119.8; 111.7	63.2	72.1	37.2	44.9	171.5	181.8	-	55.5	-	

*PF (Phenol-Formaldehyde), HF (Lignin H Monomer-Formaldehyde), GF (Lignin G monomer-Formaldehyde), and LF (K-SW Lignin-Formaldehyde) resins were prepared under identical synthesis procedures.

**Aromatic carbon attached to -OH group

***PG (Phenol-Glyoxal), HG (Lignin H monomer-Glyoxal), GG (Lignin G monomer-Glyoxal), and LG (K-SW Lignin-Glyoxal) resins were prepared under identical synthesis procedures.

[#]Carbonyl groups are arising due to formate (HCOO-) formation and -$COCH_3$ group of H and G-lignin monomers which has ^{13}C chemical shifts of 172-176 ppm and 196-199 ppm, respectively.

[a] ortho-ortho, ortho-para methylene linkage.

[b] para-pare methylene linkage.