Characterization of Molecular Structure and Interlinkage Network for Seven Representative Biorefinery Lignin

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Introduction:

Along with cellulose and hemicellulose, lignin is one of the three major components of plant biomass, representing up to 40% of the dry weight. Because polysaccharides have been the primary focus for industrial applications, there is already a large amount of lignin being produced annually as a waste product. Therefore, lignin has begun to attract much attention as a potential renewable resource for bio-based materials, fuels, and chemicals. Lignin consists of three major subunits: syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H), and there are a number of lignin sources available, including: wood pulp, corn stover, and wheat straw. However, many factors such as mother biomass source and extraction method result in different physical and chemical lignin properties. In this study, we provide an assembled analysis of seven representative biorefinery lignin.

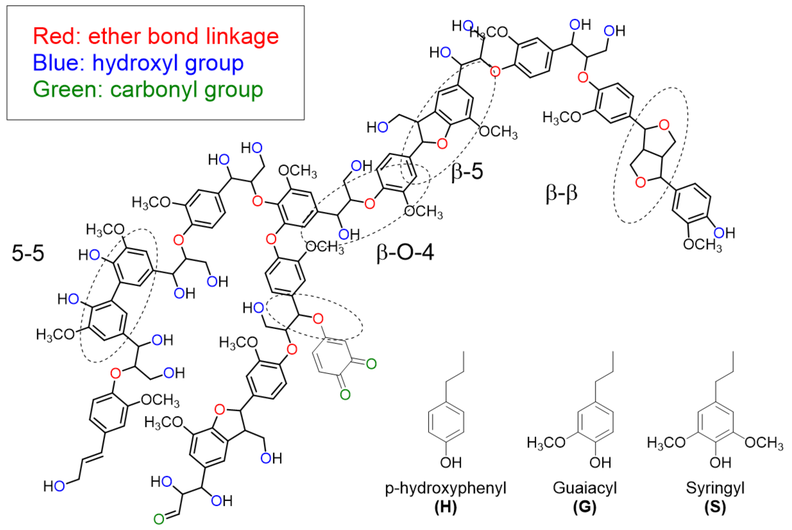

Figure 1: Diagram showing lignin co-polymer structure, interlinkages, and subunits.

Materials and Methods:

Method	Characteristics
Lignin Composition Analysis	
Alkaline Nitrobenzene Oxidation	GHS ratio
Thioacidolysis	GHS ratio
CHNO Elemental Analysis	C9 formula, side-chain oxygen content
Spectroscopic Analysis	
Fourier Transform Infrared Spectroscopy (FT-IR)	Functional groups
UV-Vis Spectroscopy	Quinone quantification
Nuclear Magnetic Resonance Spectroscopy (1H, 13C, 13C/1H HSQC)	Interlinkage structures

Lignin Samples:

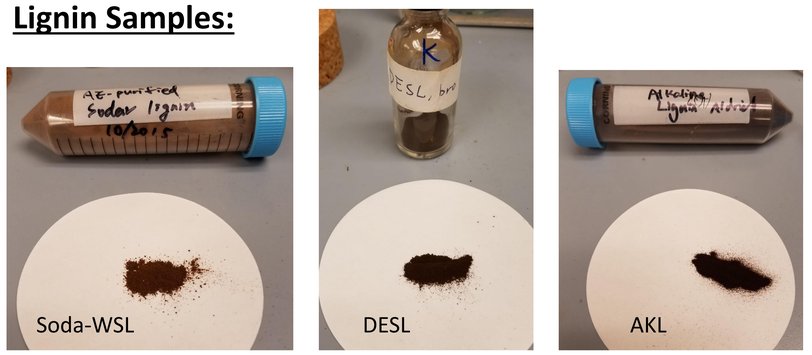

Figure 2: Image of Soda, deep eutectic solvent, and alkaline lignin samples.

Results:

Nitrobenzene oxidation and thioacidolysis show the relative abundance of the three lignin subunits. For most samples, the results from both methods clearly align.

	Alkaline Nitrobenzene Oxidation				Thioacidolysis			
	H	G	S	Yield	H	G	S	Yield
AKL	2	98	-	5.6	8	92	-	5.8
DACSL	25	31	43	34.1	23	31	46	22.4
SESPL	2	98	-	12.6	4	96	-	11.2
MWL	1	99	-	17.3	5	92	3	12.1
SPORL	-	96	4	22	2	85	13	3.4
DESL	15	85	-	6.4	100	-	-	0.9
Soda-WSL	7	50	43	13.7	9	45	46	10.6

Table 1. Comparative analysis of GSH ratio of representative biorefinery lignins determined by alkaline nitrobenzene oxidation and thioacidolysis.

13C NMR can identify minor structures not detectable by other methods. The abundance of these interlinkages is shown below.

Spectral Region	Chemical Shift (ppm)	Numbers of moieties per aromatic rings				
		MWL	DESL	DACSL	SESPL	Soda-WSL
Methoxyl content	57-54	0.97	0.90	1.19	0.97	1.25
Car-H	125-103	2.75	3.09	2.45	2.46	2.67
Car-C	141-125	1.66	1.69	1.93	2.12	1.80
Car-O	160-141	1.59	1.22	1.62	1.42	1.53
Phenolic hydroxyl	174-171	0.05	0.49	0.22	0.30	0.01
Aliphatic hydroxyl	171-168.5	1.62	1.54	0.95	1.03	1.30
Saturated CH2 or CH3 on aliphatic side chain	40-20	1.83	1.97	2.33	2.41	1.93
C-γ in β-5 and β-O-4 with C=O	64-62	0.65	ND	0.26	0.29	0.36
Cα in β-O-4	71-73	0.57	ND	0.21	0.28	0.51
Cβ in β-O-4	84.5-80	0.42	0.16	0.36	0.20	0.21

Table 2: Quantitative 13C analysis of five representative biorefinery lignins.

Results Continued:

The comparative FT-IR spectrums are presented in four wavenumber segment as shown below, including 3050-2750 cm^{-1}, 1830-1550 cm^{-1}, 1550-1175 cm^{-1}, and 1175-800 cm^{-1}. These four segments of wavenumbers represent the regions reflecting the functionality of C-H stretch in methyl and methylene groups, C=O stretch, aromatic skeletal vibration, and C-H deformation, respectively.

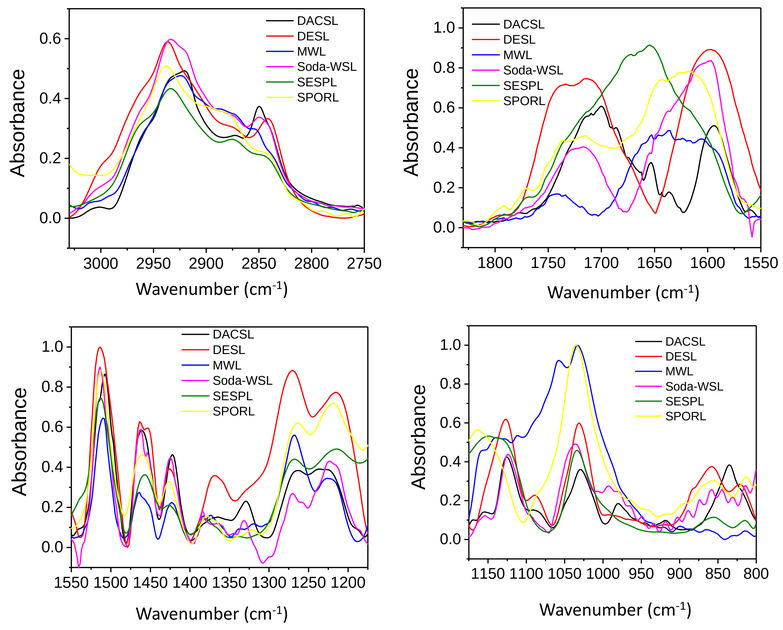

Figure 3: FT-IR spectrums for representative biorefinery lignins.

Conclusion:

This study has provided a detailed comparison of seven representative biorefinery lignins with regards to the molecular structure, interlinkage network, and side chain functionalities. Nitrobenzene oxidation and thioacidolysis showed the relative abundance of molecular subunits (GSH ratio), FTIR showed the presence of specific side chain functional groups, and 13C NMR allowed for an analysis of the interlinkage structures present in the lignins.

Future Application:

We believe that this study will provide new insight and methodology in biorefinery research, especially in lignin valorization. Furthermore, the assembled data can serve as a reference for future studies in lignin chemistry, as it presents a complete comparison of structural and interlinkage patterns between seven different lignin sources.

Acknowledgements:

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