Electronic Supplementary Material (ESI) for RSC Advances.

Supplemental Information

The Impact of Lignin Source on its Self-Assembly in Solution

Dilru R. Ratnaweera[1], Dipendu Saha[2], Sai Venkatesh Pingali[3], Nicole Labbé[5], Amit K. Naskar[2], Mark Dadmun[1,4]

[1]Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA

[2]Material Science & Technology Division, [3]Biology and Soft Matter Division and [4]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

[5]Center for Renewable Carbon, The University of Tennessee Institute of Agriculture, Knoxville, TN 37996

Advantages and limitations of neutron scattering:

Neutron scattering is a very powerful tool to determine the structure and dynamics of polymers, primarily because of the ability to tune the contrast between components by selectively deuterating the polymer, portions of polymers, or the surrounding media. Additionally, neutrons can readily penetrate matter because the neutrons interact with the nucleus of an atom. This means that the sample holder of a neutron scattering experiment can be quite large and complex. It is therefore common to complete neutron-scattering experiments in a broad range of sample environments

However, there are some drawbacks to using neutron scattering. These include the fact that completion of the experiment usually requires travel to a national facility, and the flux of neutrons available is much lower than in similar light or X-ray experiments. This limitation on the flux of neutrons requires significant sample size (usually, ~0.1–1.0 g), with larger sizes needed for unusual sample environments, such as a shear cell. This may be a particular problem for biological and exotic samples, where it is difficult to create more than a few milligrams of a given material.

Even given these limitations, neutron scattering is a unique and very powerful technique distinctively characterizes the microscopic structure and dynamics of polymers, colloids, and other soft materials. For instance, no other method provides a direct measure of the size of a polymer chain in the melt. Similarly, the structure and thermodynamic interactions of polymers in concentrated solutions and blends are most effectively monitored by carefully designed neutron-scattering experiments.

Pyrolysis Gas Chromatography Mass Spectrometry (PyGC/MS)

This technique has been used to assess lignocellulosic biomass and their isolated components. S/G and impurity (carbohydrates) levels can be calculated from the pyrograms. Figure 1 show representative pyrogram for the three lignins and Table 1 summarizes the major fragments that are usually found in biomass and lignin.

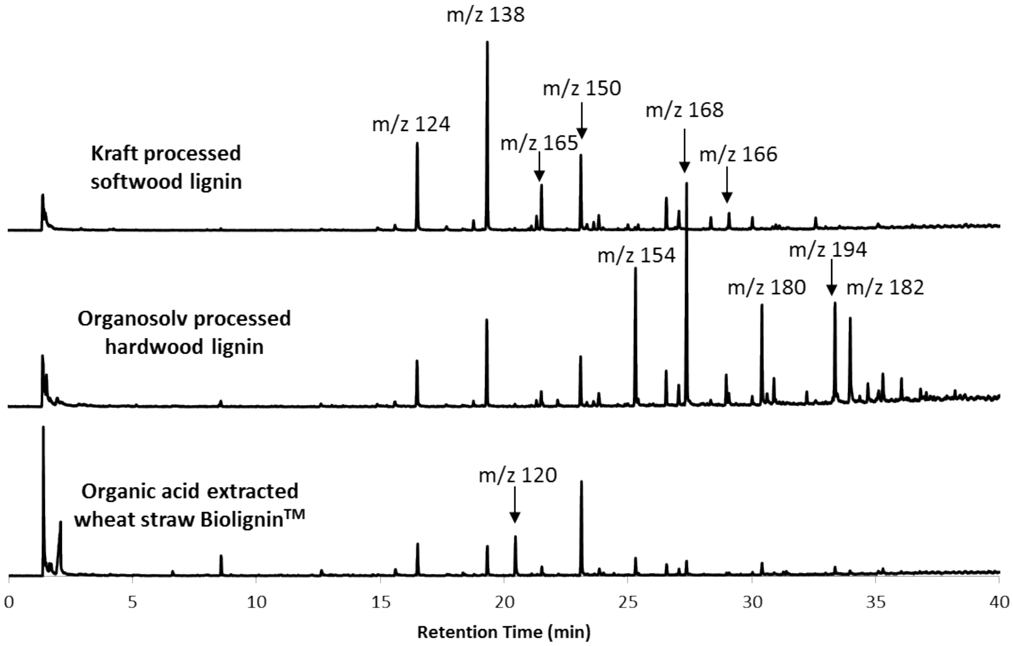

Table 1: Mass spectrum peak assignments associated with PyGC/MS lignin samples. Abbreviation: *m/z* = mass:charge ratio of fragments extracted, major lignin peaks assignments: syringyl (S), guaiacyl (G), *p*-hydroxyphenyl (H) (adapted from References 1 and 2.)

m/z	***Assignment***	***S,G,H precursor***
57, 73, 85, 96, 114	C5 sugars	
57, 60, 73, 98, 126, 144	C6 sugars	
94	Phenol	H, S, G
109	Guaiacol	G
120	Vinylphenol	H, S, G
123	4-Methyl guaiacol	G
124	Guaiacol	G
137	Fragment ions of ethylguaiacol, homovanillin, coniferyl alcohol	G
138	4-Methyl guaiacol	G
150	4-Vinylguaiacol	G
151	Fragment ion of vanillin and 4-ethylguaiacol	G
152	Vanillin , 4-ethylguaiacol	G
153	2,6-Dimethoxy-4-methylvinylphenol	S
154	Syringol	S
164	Eugenol, (iso)eugenol,	G
165	Sinapaldehyde, 2,6-dimethoxy-4-vinylphenol	S
167	Fragment ions of 4-ethylsyringol, syringylacetone, 4-propylsyringol	S
168	2,6-dimethoxy-4-methylvinylphenol	S
178	Coniferyl aldehyde	G
180	2,6-dimethoxy-4-vinylphenol, coniferyl alcohol	S, G
182	Syringaldehyde	S
194	4-Propenylsyringol	S
208	Sinapyl aldehyde	S
210	Sinapyl alcohol	S

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[1] Sykes, R.; Kodrzycki, B.; Tuskan, G.; Foutz, K.; Davis, M. Within tree variability of lignin composition in Populus. *Wood Sci Technol*. **2008**, 42, 649-661.

[2] Izumi, A.; Kurada, K. Pyrolysis-mass spectrometry analysis of dehydrogenation lignin polymers with various syringly/guaiacyl ratios. Rapid Communication in Mass Spectrometry 11: 1709-1715, 1997.