Lignin: Moving Toward Renewable Biobased Adhesives

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Why Lignin?

- Lignin is the second most abundant natural polymer after cellulose on earth (Sustainable)
- Isolated through byproduct of pulp and paper and bioethanol industry
- More than 70 million tons/year lignin are produced every year, but only 2% is used in value-added products.

- **Domtar:** Kraft Lignin 25,000 tons/year
- **POET:** Steam explosion 20,000 tons/year
- **Lignol:** Organosolv 20,000 tons/year

Sustainability

Founded in 2011,

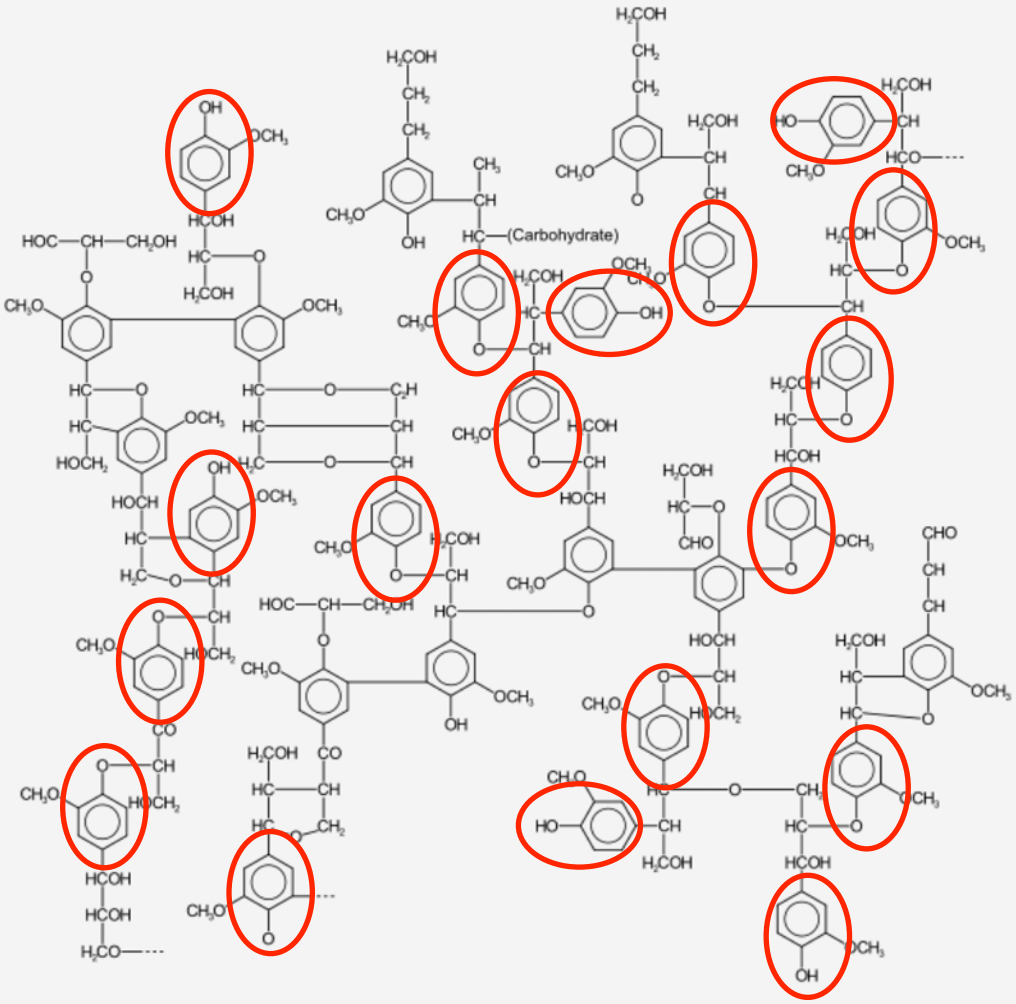
The purpose is to develop and implement a global audit program to assess and improve sustainability practices within the supply chains of the chemical industry.

www.tfs-initiative.com

Members of the Sustainability Initiative

BASF, Bayer, Evonik , Henkel, AkzoNobel, Eastman, Merck, Lanxess, Solvay, Syngenta , Clariant, Covestro, IFF, Wacker, Arkema and DSM

Lignin: Natural Polyphenolic Compound



Glazer, A. W., and Nikaido, H. (1995)

Lignin Variations

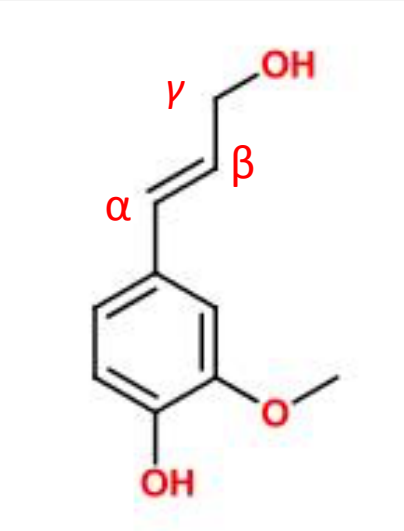
Lignin is heterogeneous and varies based on the source and isolation processes (Kraft, Organosolv, Lignosulfonate and Steam-explosion).

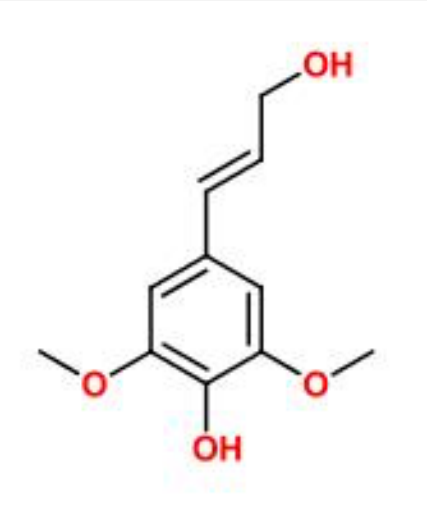
Softwood

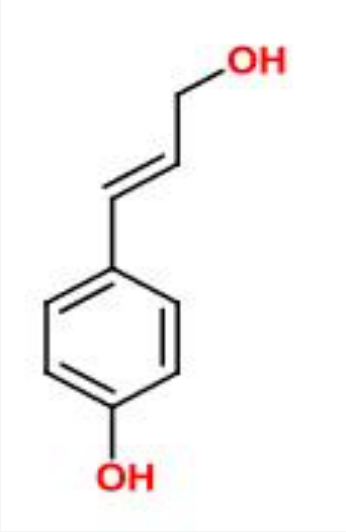
Hardwood

Crops

Lignin Structural Units







Coniferyl **(Guaiacyl)**	**Sinapyl** **(Syringyl)**	**Coumaryl** **(p-Hydroxyphenyl)**
Softwood		
Hardwood	Hardwood	
Agricultural-Plants	Agricultural-Plants	Agricultural-Plants

Lignin-Based PF Adhesive

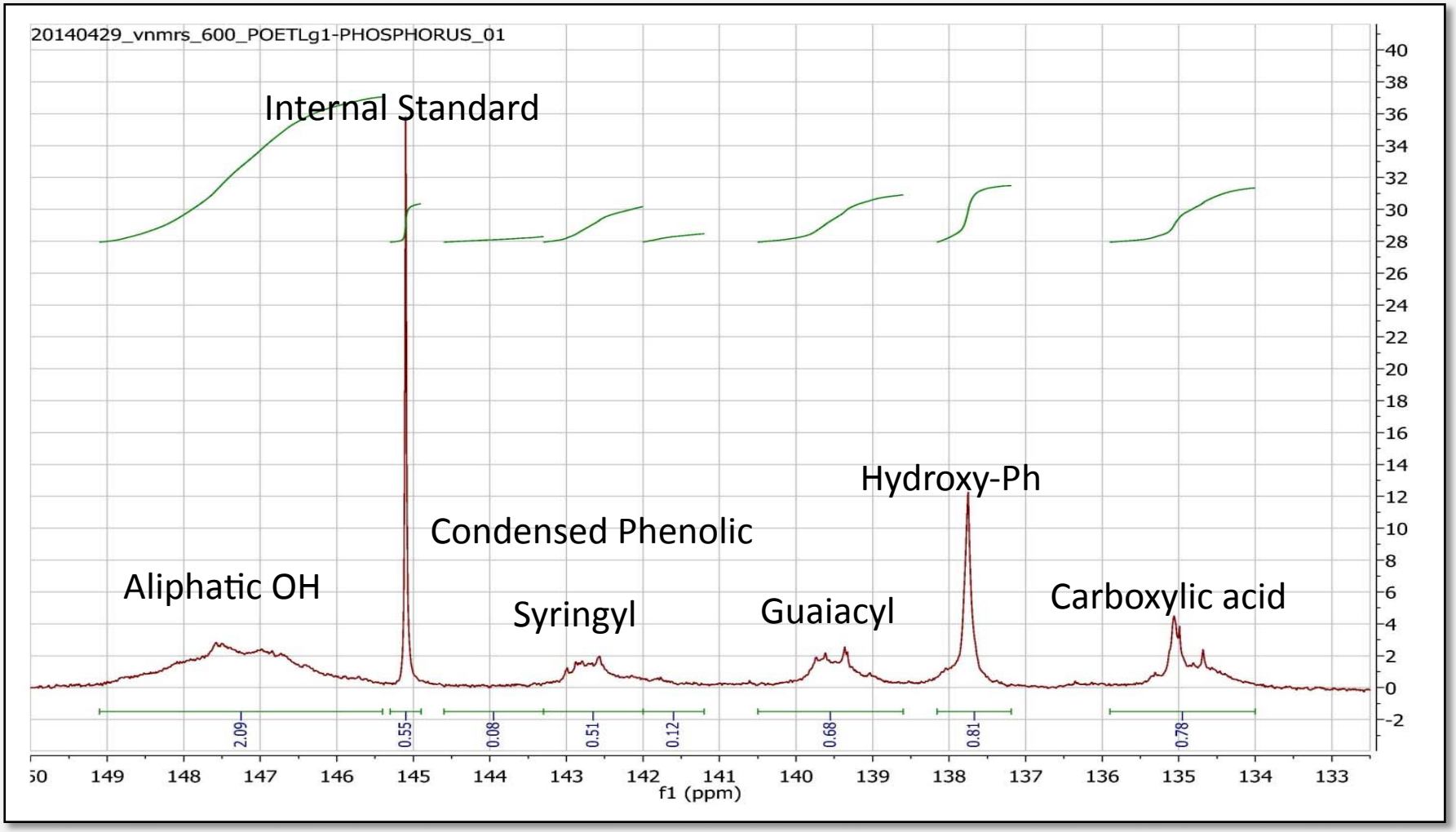
Lignin Characterization

- Chemical analysis using FTIR, ^{31}P NMR, ^{13}C NMR, ^{1}H NMR
- Thermal analysis: Tg using (DSC), degradation (TGA)
- Molecular weight (Mw), number (Mn) and PDI (SEC)
- Moisture content (IR balance, gravimetrically, TGA)
- Ash content (Furnace and TGA)
- Elemental analysis

Properties of Different Lignins

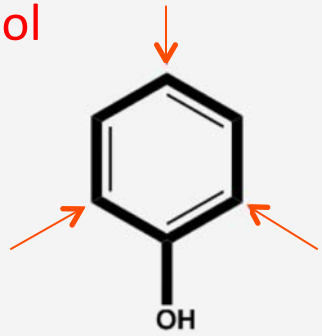
Lignin Samples	S	G	H	Total OH mmol/g	Molecular Number	Molecular Weight	PDI
Oraganosolv-HW	1.5	0.8	0.1	4.8	725	1920	2.7
Organosolv-SW	0	1.6	0.1	4.1	750	2100	2.8
Kraft-SW	0	2.3	0.2	6.7	1170	4500	3.8
Steam Explosion Corn Stover	0.6	0.6	**0.9**	5.3	**542**	**1150**	**2.1**

^{31}P NMR Results (Hydroxyl Content)



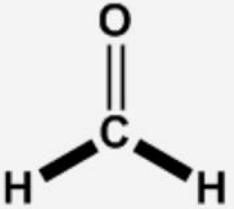
Substituting Phenol in PF Resins

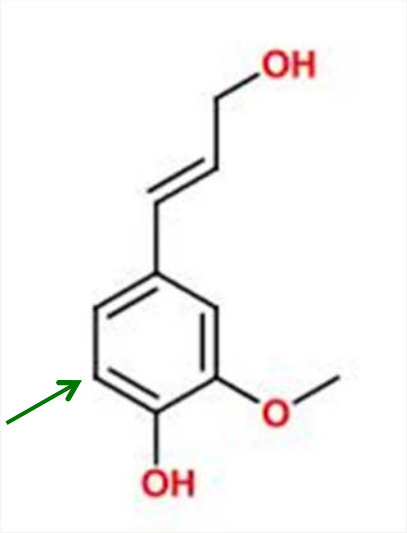
Phenol

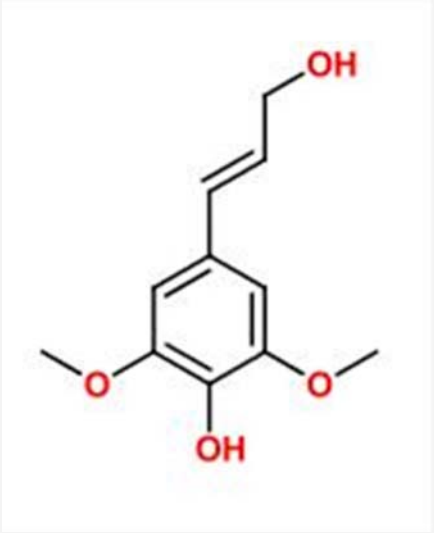


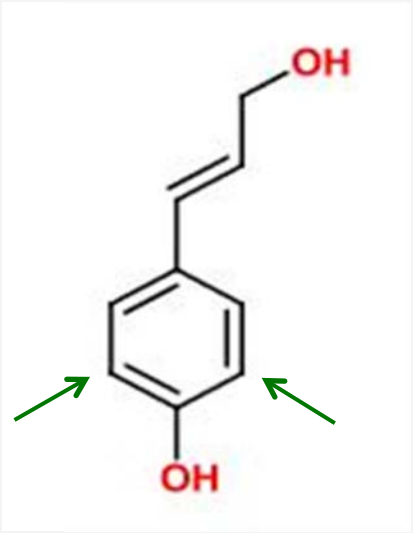
+

Formaldehyde

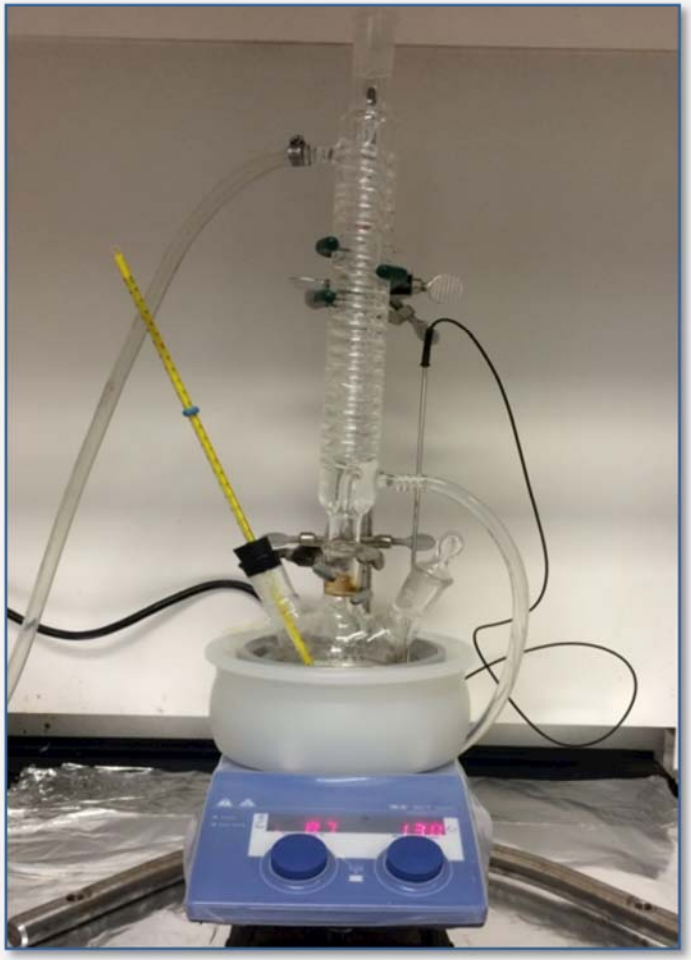


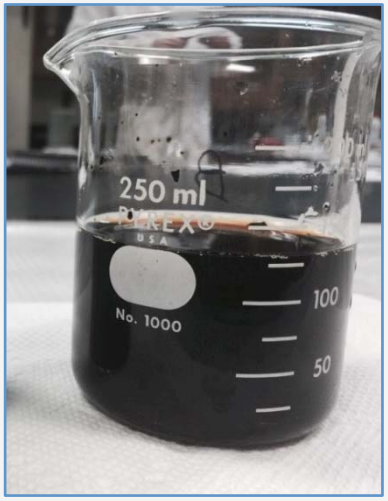




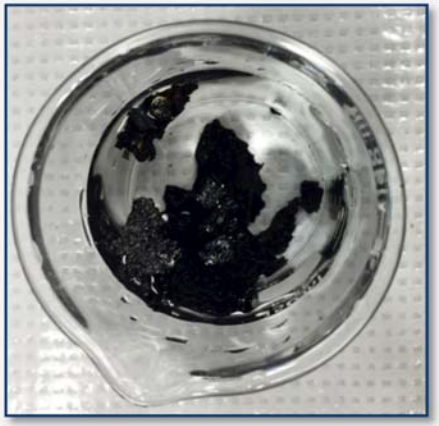


Resin Formulation (with 100% lignin)





SW lignin-based adhesive dissolved right away



Corn-Stover Lignin-based adhesive after 1-week

Adhesive Formulation

Used a digital high speed mixer to prepare the adhesive (plywood mix).

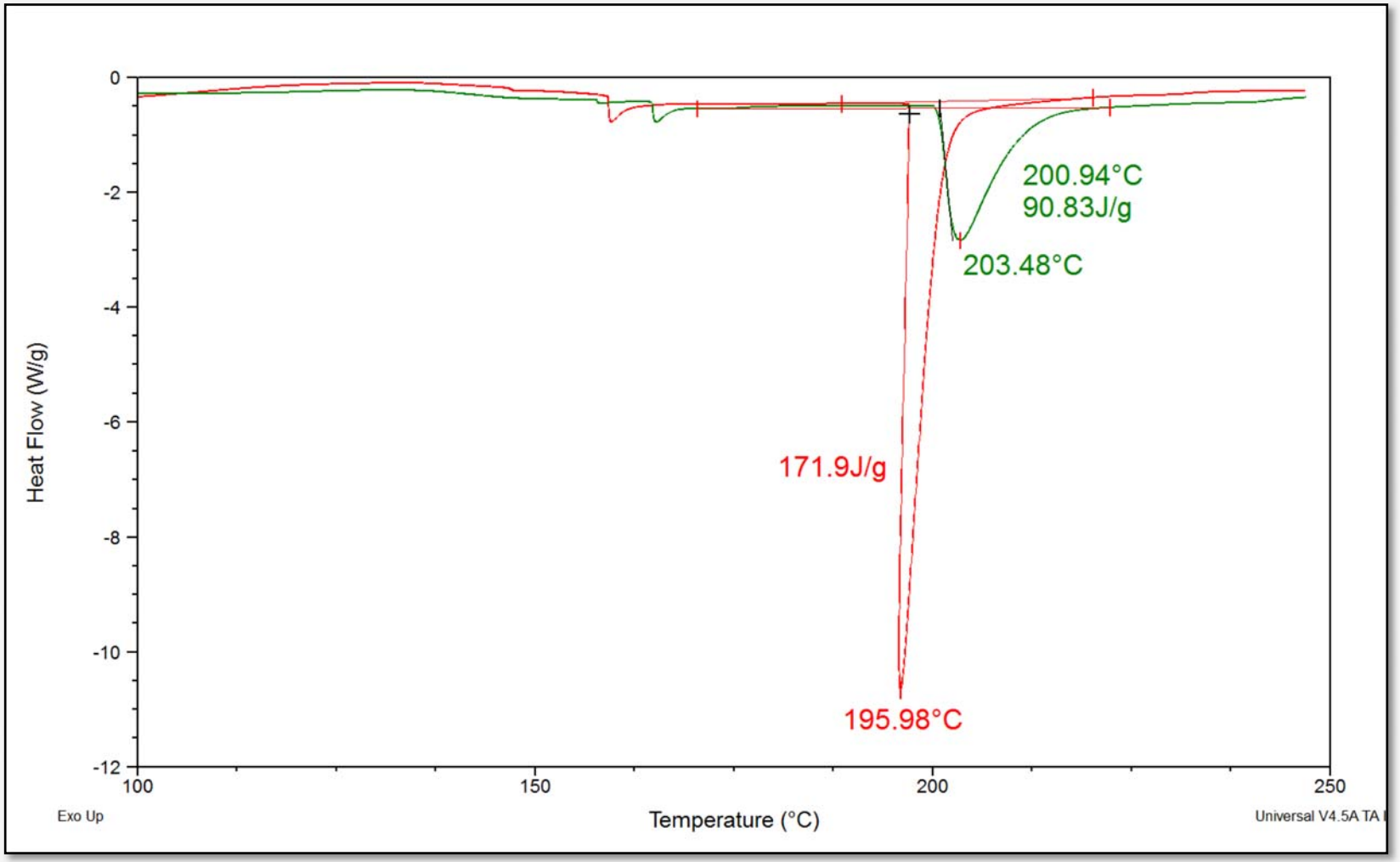
Viscosity = 2500-3500 cps

1. Resin
2. Caustic
3. Water
4. Wheat flour
5. Extender/Filler

Adhesive Properties

Measured Properties	100% Lignin-based Adhesive	PRF Commercial Adhesive
% Solid content	25 (0.1)	33(0.2)
pH	12.7	11.8
% Free Formaldehyde (Titration)	7.5% (resin)	6% (resin)
Curing Temperature (°C)	165, 203	159, 195

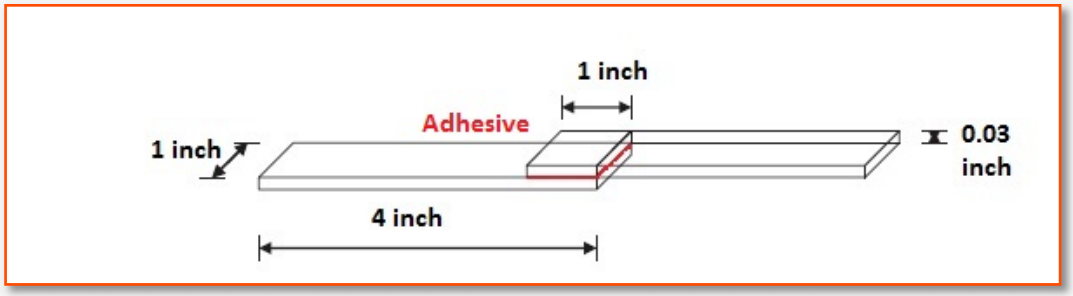
Curing of Adhesives (DSC analysis)



Plywood Preparation

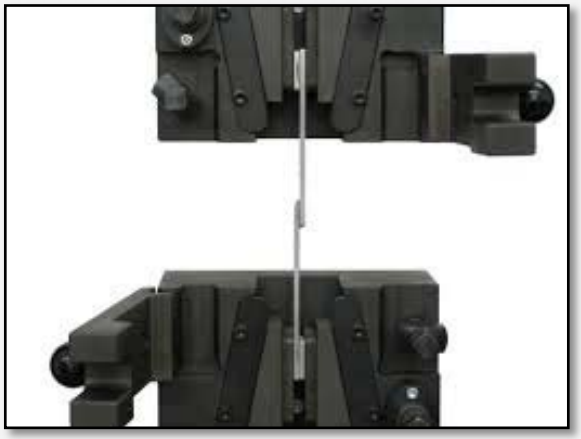
Press Parameters (Curing):

- Temperature: 350°F
- Pressure: 175-200 psi
- Time: 3 – 3.5 minutes
- Spread rate: 0.12 g/ sample (spread rate about 16 grams on a 12in x 12in panel)



Adhesive Lap Joint Shear Test

ASTM D1037 : Evaluating Properties of Wood-Base Fiber and Particle Panel Materials



Lap Shear Strength Test Results

Sample ID	% Lignin Content	Adhesive Amount (g)	Shear Stress (Psi)	Failure Mode
PRF Commercial Adhesive	0	0.11(0.03)	**540 (48)**	Wood
100% lignin-based Resin	100	0.10(0.01)	126(42)	Adhesive
100% Lignin-based Adhesive	100	0.10(0.01)	**507(55)**	Wood

Summary

- Lignin properties differ significantly based on the source and isolation processes
- We were able to formulate a 100% lignin-based adhesive that had excellent water resistancy and similar curing and mechanical strength as of commercial PRF adhesive.

Acknowledgements

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