Lignin-derived Monomers for Use in High-Performance Bio-based Resins

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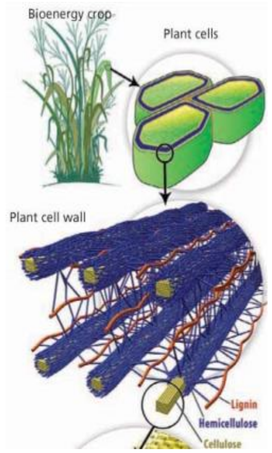
Introduction(1)

- Composite materials with high strength and high thermal resistant resins utilized in a wide-variety of industrial and governmental applications are derived primarily from petrochemical feedstocks:
  - i.e. epoxy resins and vinyl ester resins
  - i.e. carbon and aramid reinforcing fibers
- Cost and supply of these materials are extremely volatile
- Recent developments of bio-based resins include:
  - Maleinized/acrylated/epoxidized soybean oil
  - methacrylated lauric acid
- Hurdles bio-based resins have yet to overcome:
  - have lower T_g's relative to commercial petroleum-based epoxy and vinyl ester resins
  - require the addition of petroleum-based, low viscous monomers and/or diluents to reduce liquid molding resin viscosities (i.e. styrene)
  - utilize major human and animal food sources (i.e. soybeans)
- **Need exists to develop high performance resins and fibers from biological sources to effectively replace petroleum-derived resins/fibers**

Lignin as an Alternative Bio-based Feedstock(2)

- Structural polymer present in woody plants
- Plant stem stiffener
- Microorganism protective barrier
- 18 – 25% content in hardwoods
- 25 – 35% content in softwoods
- 3 x 10^{11} tons exist in biosphere
- 2 x 10^{10} tons generated annually
- Copious paper pulping waste product
- Primarily burned for energy recovery
- High aromatic content
- High polymer-functionalizable substituents



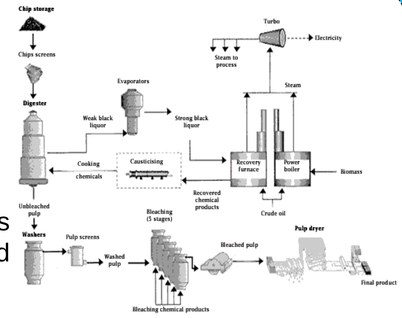
Lignocellulose schematic.(2)

Motivation

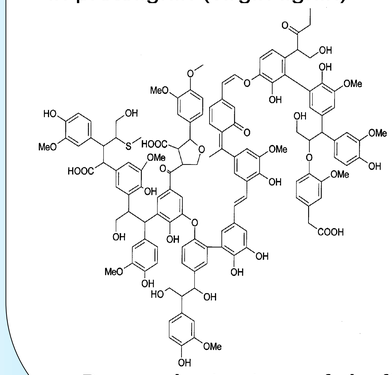
The goal of this research is to use **lignin** in the development of high strength and high thermally resistant thermosetting matrix resins by reducing its MW and/or by chemically modifying it to produce resins with viscosities of <2000 cP.

Lignin Extraction, Structure, and Uses(3)

- Extraction methods include:
  - steam explosion cracking
  - organosolv delignification
  - alkaline or kraft pulping
- 3-D aromatic structure
- Kraft pulped lignin contains hydroxyl groups not found in protolignin (virgin lignin)



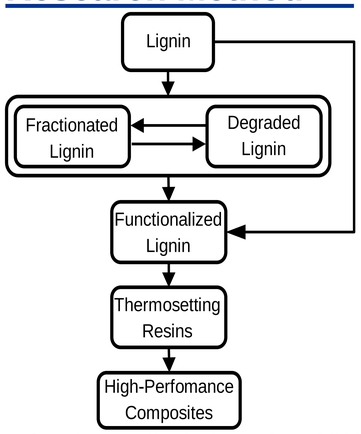
Traditional kraft pulping process (http://www.sfk.ca/EN/Mill_Saint-Felicien/KraftProcess.php).



Proposed structure of kraft pine lignin by Marton.(3)

- Current uses include:
  - H_2O reducer in concrete
  - binding agent in animal feed
  - dust control agent
  - filler in composites, plastics, and thermosets
  - accounts for only 1% of total annual lignin production

Research Method(4-6)



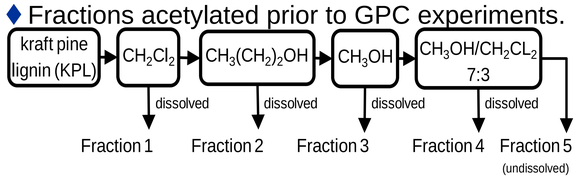
- Hope to fractionate lignin based on MW and # of hydroxyl groups for better reaction/property control
- Hope to degrade lignin in order to obtain lower viscosity fractions
- Hope to functionalize lignin in order to chemically incorporate lignin into bio-based resins

Kraft Pine Lignin Characterization

- Supplied by MeadWestVaco:
  - origin - Charleston, S.C.
  - Indulin® AT (January 2010 batch)
  - brown granules
  - composition = $C_9H_{7.9}O_{2.1}S_{0.1}(OCH_3)_{0.82}$
  - phenyl-propane unit MW = 178 g/mol

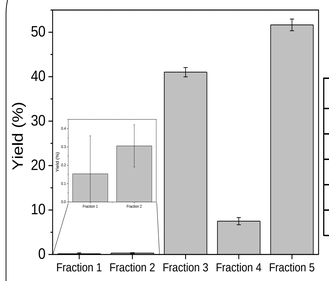
Fractionation Technique

- Followed fractionation technique of Mörck, *et al.*(4)
- Fractions acetylated prior to GPC experiments.



Fractionation scheme for KPL with organic solvents; undissolved lignin was dried before subjection to next solvent (horizontal arrows).(4)

Fractionation Results



GPC results of fractionated KPL.

Fraction #	M_n (Da)	M_w (Da)	PDI
1	309	436	1.41
2	1018	1382	1.45
3	1402	2170	1.55
4	1749	2828	1.64
5*	–	–	–

* Unable to dissolve in THF

- Average % lignin recovery = 93.5 ± 1.2
- Most of the lignin insoluble in utilized solvents
- Lignin dissolved the most in methanol (fraction 3)
- Fraction 4 results contradict those of Mörck, *et al.* (still investigating)(4)
- Overall, as fraction # ↑, M_n ↑ and PDI ↑ (exact correlation between polarity and fractionation results still being investigated)

Ongoing & Future Work

- Degradation of KPL in air and in high purity O_2 using singlet oxidation
- Functionalization via esterification of various forms of KPL
- Degradation of KPL via an olefin metathesis reaction
- Apply the early stages of the research method to hardwood kraft lignin
- Determine optimum methodologies to achieve desired rheological properties.

References

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Acknowledgements

This work is supported by the SERDP WP-1758 and the Army Research Laboratory through the Cooperative Agreement W911NF-06-2-0011.