Optimization of Lignin Conversion Processes into Value-added Fuels and Chemicals

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PSU Co-workers

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  - Dr. John Larsen, Professor Emeritus at Lehigh University

Biomass Utilization for Fuels

- Advantages to using biomass
  - Availability within US
  - Incorporation into liquid fuel infrastructure
  - Lower greenhouse gas emissions
- Disadvantage
  - Need to develop economic processes to produce fuels and chemicals to effectively reduce market of petroleum

Challenges

- Wide variety of biomasses for conversion technologies
- Biomass sources are natural biopolymers, so structural characteristics of the biopolymer will determine type of chemistry

Why focus on lignin?

- Renewable
- Cellulosic ethanol production:
  - Identified as having great economic potential due to low cost of feedstocks, and generally favorable chemistry
  - Major by-product is lignin – second most abundant biomass source next to cellulose.
- Often used as low-value heat source

Research Goal

- To develop economic process for lignin conversion
- Evaluating various processes of lignin conversion to determine the best option
- Focus on fuel and chemical products of greater value (e.g., aromatic compounds, phenolic compounds, DME, methanol)

Project Motivation

- General goal of lignin conversion: depolymerization into liquid and gas products
- Unresolved problems reported in literature
  - Incomplete conversion or condensation of lignin occurs forming solids
  - Specific interests in producing one type of product ignoring other phases or types of products generated particularly residual solids
- Focus: Complete characterization of lignin and products after reaction should contribute to better understanding of its partial or complete reaction, basis for optimization of reactions.

Background on Wood and Lignin[1,2]

- Wood is composed of organic polymers: cellulose, hemicellulose and lignin
- All consist of primarily carbon, hydrogen and oxygen
- Low inorganic matter makes wood ideal for industrial utilization
- Cellulose and hemicellulose are uniform chain structures of repeating sugar monomers
- Lignin is comprised of crosslinked, branched aromatic monomers

1. Fengel, D. and Wegener, G., 1984. Wood : chemistry, ultrastructure, reactions W. de Gruyter, New York, 613 pp.
2. Sarkanen, K.V. and Ludwig, C.H., 1971. Lignins: Occurrence, formation, structure and reactions. Wiley-Interscience, New York, 916 pp.

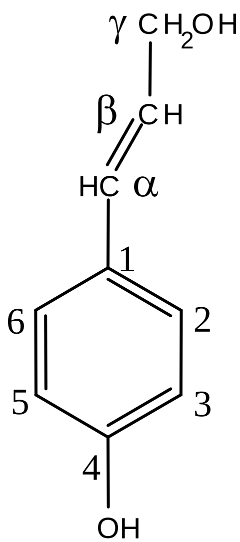
General Conversion Process of Biomass-to-Ethanol[3,4]

1. Woody biomass handling and pretreatment to separate cellulose from lignin and hemicellulose
2. Conversion of the cellulose and hemicellulose into bioethanol via fermentation and enzymatic processes
3. Utilization of lignin and other by-products
   a. Low value waste heat during conversion process
   b. Conversion into chemicals and fuels

3. Huber, G.W., Iborra, S. and Corma, A., 2006. Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. Chemical Reviews, 106: 4044-4098.
4. US DOE Energy Efficiency and Renewable Energy. *Biomass Program*. 2006 [cited 2007 Feb. 20]; Available from: http://www1.eere.energy.gov/biomass/.

Basic Monomer Structures of Lignin[1,5]

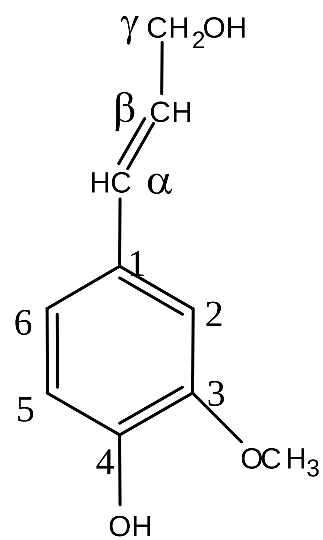
_p_-coumaryl alcohol



_p_-hydroxyphenol derivative

Grasses

coniferyl alcohol



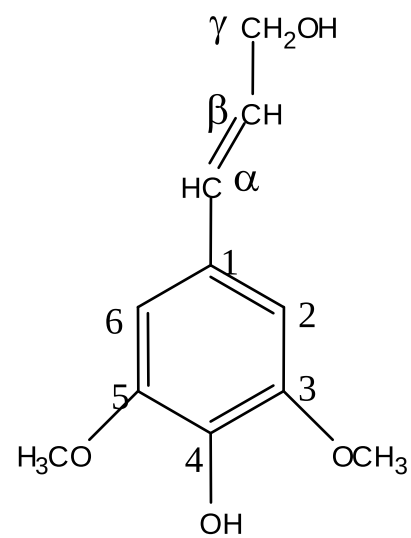
guaiacyl derivative

Grasses

Softwoods

Hardwoods

sinapyl alcohol



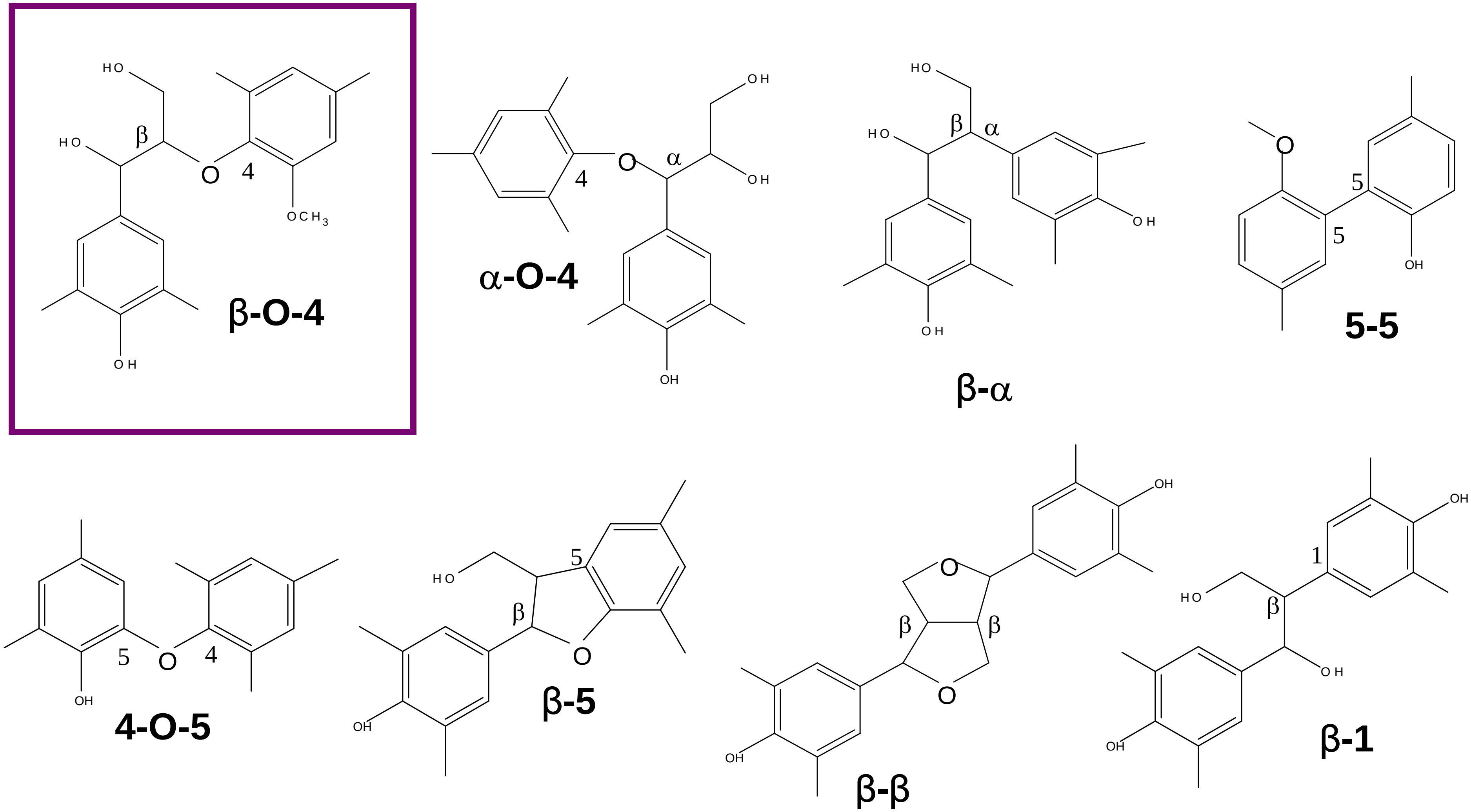
syringyl derivative

Grasses

Hardwoods

1. Fengel, D. and Wegener, G., 1984. Wood : chemistry, ultrastructure, reactions W. de Gruyter, New York, 613 pp.
5. Boerjan, W., Ralph, J. and Baucher, M., 2003. Lignin biosynthesis. Annual Reviews of Plant Biology, 54: 519-516.

Examples of Major Linkages[3]



3. Huber, G.W., Iborra, S. and Corma, A., 2006. Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. Chemical Reviews, 106: 4044-4098.

Reaction Emphasis

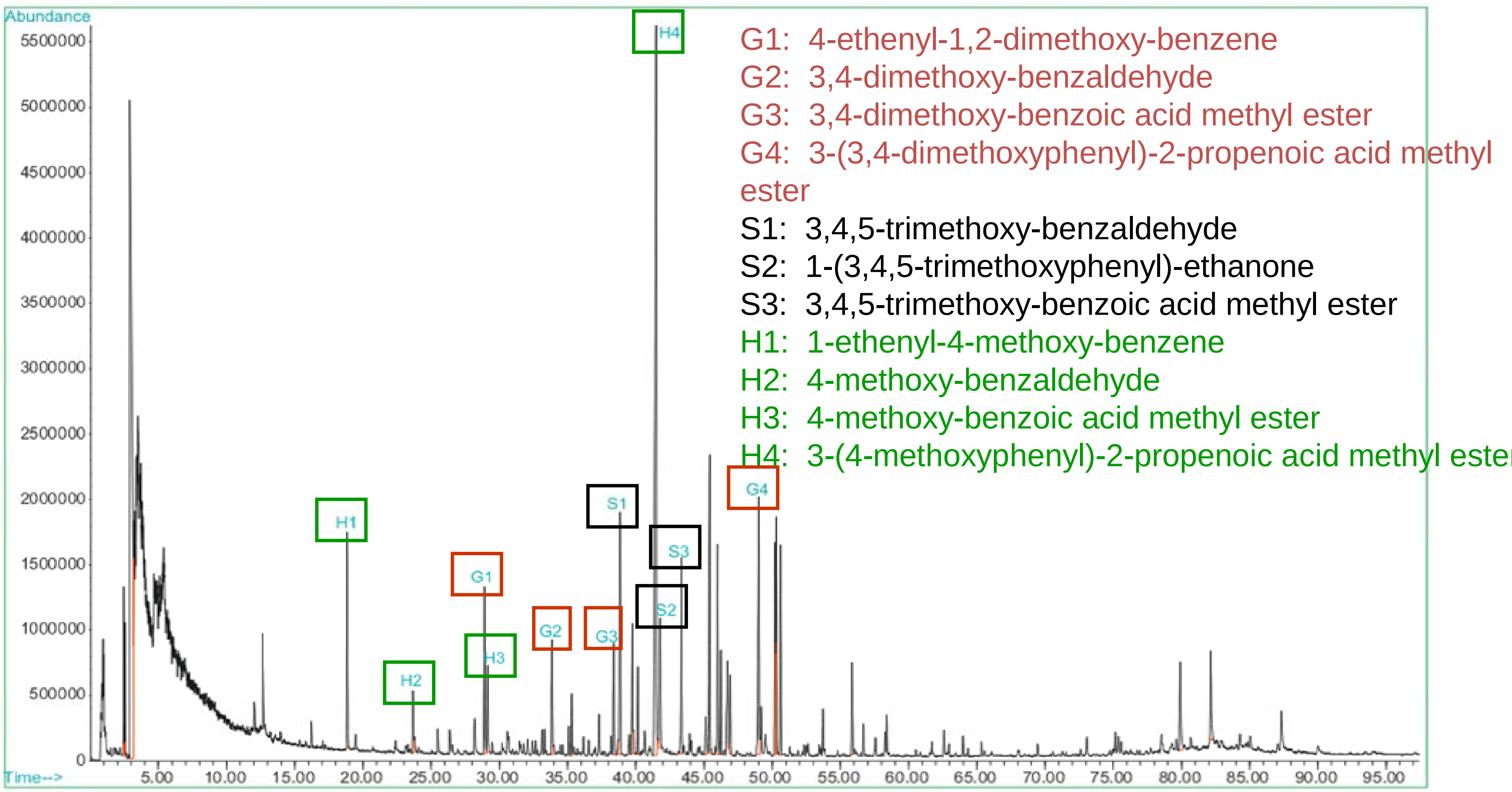
- Compare various lignin degradation methods:
  - Base hydrolysis in methanol and water
  - Oxidation/decarboxylation of lignin to produce phenolic mixture
  - Flash/fast pyrolysis
  - Reactions in subcritical and supercritical water
- Continue with emphasis on complete characterization and optimization of reactions
  - Assess the reactions occurring to help understand how and why particular products are formed
  - Identify value-added products, emphasize

Characterization Methods

- **Solids (Before and After Reaction)**:
  1. Thermochemolysis with tetramethylammonium hydroxide (TMAH) and analysis using pyrolysis-GC/MS (py-GC/MS)[6]
  2. Solid State ^{13}C NMR
- **Liquids**: GC/MS and HPLC
- **Gases**: GC/MS

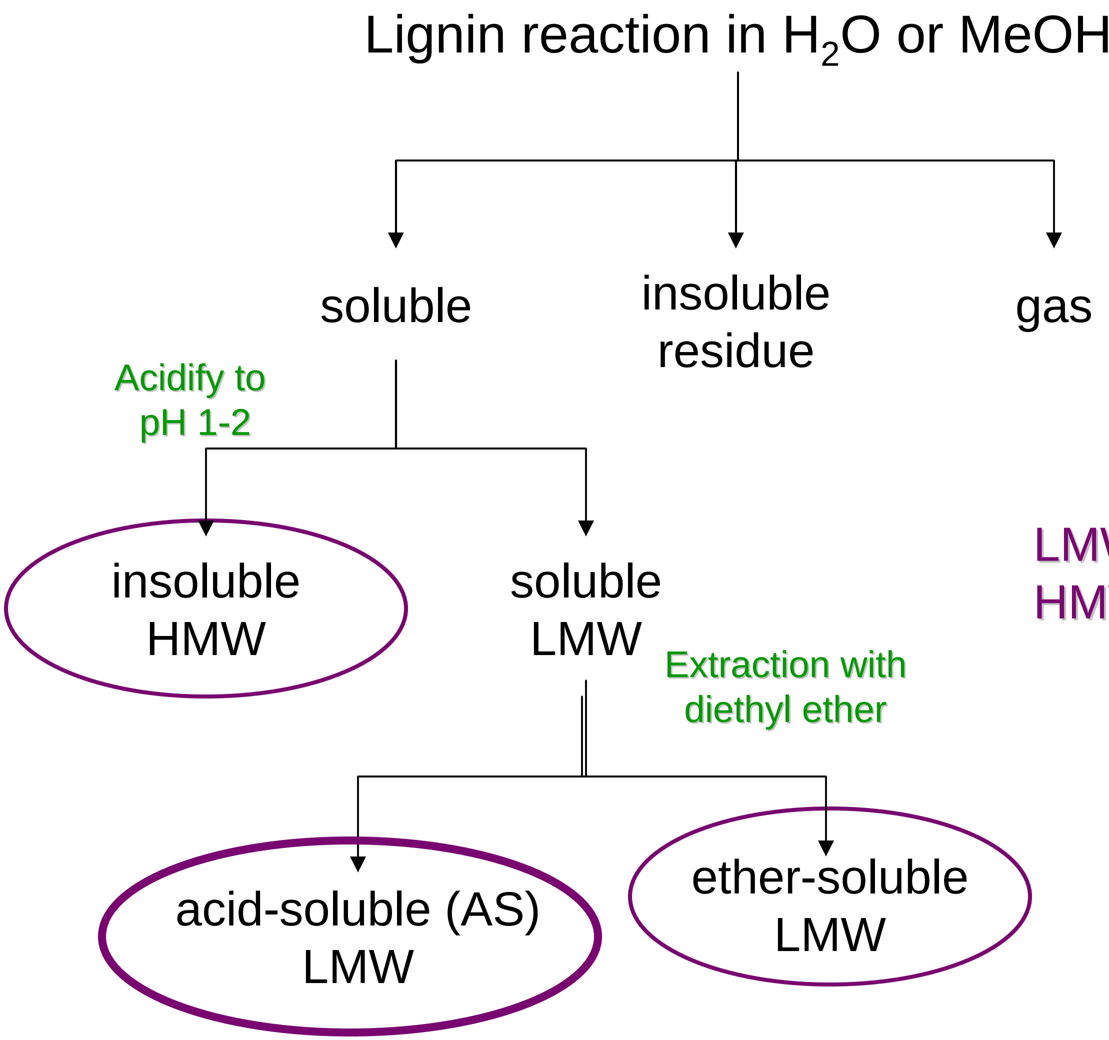
6. Clifford, D.J., Carson, D.M., McKinney, D.E., Bortiatynski, J.M., and Hatcher, P.G., 1995. A new rapid technique for the characterization of lignin in vascular plants: Thermochemolysis with tetramethylammonium hydroxide (TMAH). Organic Geochemistry, 23(2): 169-175

Lignin Characterization - Thermochemolysis



- Source: Hydrolytic lignin from Aldrich: Mainly composed of grasses based on the mixture of guaiacyl, syringyl, and *p*-hydroxyphenol derivatives present in analysis

Product Separation



LMW: low molecular weight
HMW: high molecular weight

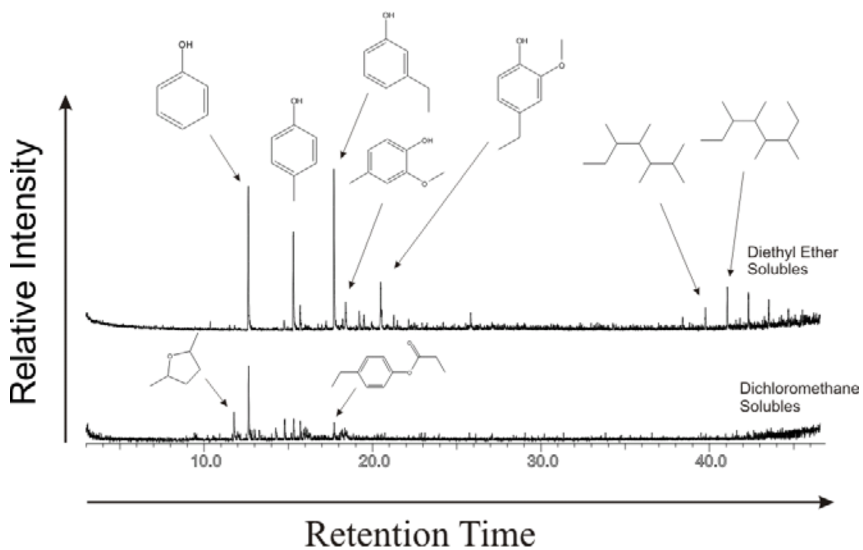
Preliminary Data from Current Research – Base Hydrolysis of Hydrolytic Lignin (from Grass) in Methanol at 290°C

			Gases		Liquids		Solids		
Run	**Time (min.)**	**Initial Lignin Wt. (g)**	**Wt. (g)**	**%**	**Wt. (g)**	**%**	**Wt. (g)**	**%**	**Total Recovery**
A	30	0.435	0.21	48	0.040	9	0.188	43	101
B	30	0.435	0.22	51	0.049	11	0.181	42	103
C*	45	0.436	0.02	5	0.030	7	0.246	56	68
D	45	0.433	0.12	28	0.048	11	0.168	39	77

*Reactor Leakage Suspected

Products of Reaction

Diethyl ether fraction – Analysis with GC/MS



- Gases
  - Primarily DME, with small amounts of CO, and CO_2
- Solids
  - Work in progress using Py-GC/MS and ^{13}C NMR
- Acid Soluble Fraction
  - Still working on getting accurate information from organic fraction remaining in water (low pH)

Summary and Future Focus

- Our group's research is in the early stages…
- Characterization capabilities will augment our group's primary goals emphasizing complete characterization to help understand how and why particular products are formed, dependent on reaction chemistry
- Future work
  - Continue with methodology development
  - Incorporate representative model compounds
  - Focus on economics and optimization of processes that show the most promise

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