

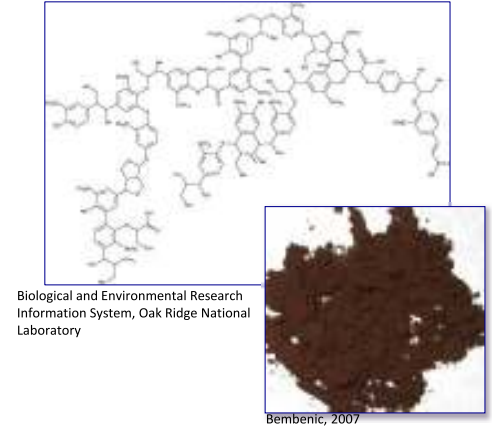
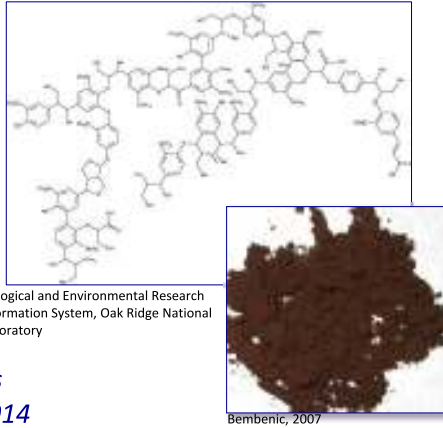
Opportunities for Lignin-Based Byproducts

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May 21, 2014
New Markets for Bioenergy Crops
Bioenergy Short Course Series, 2014



Plant biomass is one of the best alternative and renewable hydrocarbon sources – e.g., forest wastes, agricultural wastes, energy crops, aquatic plants.



Bevill, 2011



Parabel, 2013



ISTOCKPHOTO.COM



Dennis Pennington, MSU, 2014

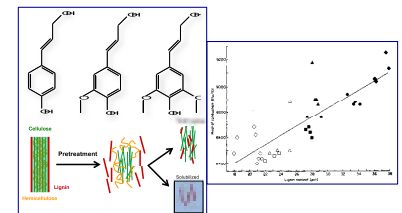


Fiber Fuels, 2010

- Common compositional and structural features
- Favorable post-conversion potential

This talk focuses on the opportunities for producing value-added products from lignin-based byproducts.

Basic Lignin Chemistry



Lignin-Based Products and Applications

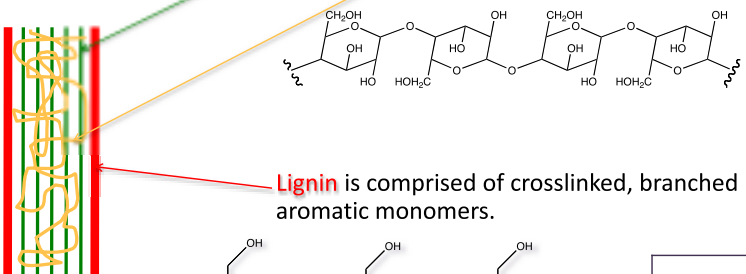


Geographic Distribution of Biomass Crops

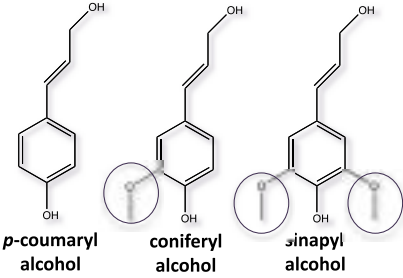
<http://genomicscience.energy.gov/biofuels/>

Lignocellulosic biomass is mostly composed of organic polymers containing primarily carbon, hydrogen and oxygen.

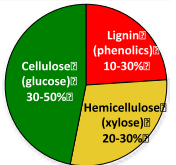
Cellulose and hemicellulose are uniform chain structures of repeating sugar monomers.



Lignin is comprised of crosslinked, branched aromatic monomers.



Woody Biomass	Lignin (wt. %)
Grasses	6-12
Softwood	25-35
Hardwood	18-25



Huber, G.W., Iborra, S. and Corma, A., 2006. Chemical Reviews, 106: 4044-4098.
Fengel, D. and Wegener, G., 1984. W. de Gruyter, New York, 613 pp.
Sarkanen, K.V. and Ludwig, C.H., 1971. Wiley-Interscience, New York, 916 pp.

Properties of lignin...

...why do land plants bother to make it?

It is thought that vascular land plants lignify in order to solve several problems that arise due to terrestrial lifestyles...

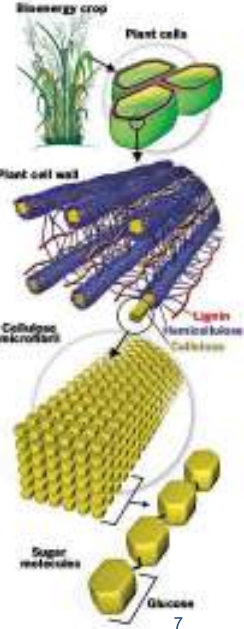
- 1) Water conduction – Lignin helps to keep water from permeating the cell wall.
- 2) Structural support – Lignin may help ‘weld’ cells together and act as a stiffener to provide resistance against bending forces, such as wind.
- 3) Protection against pathogens – Lignin is recalcitrant to degradation, which helps protect against fungal and bacterial pathogens.

Adapted from Brett Diehl

Properties of lignin...

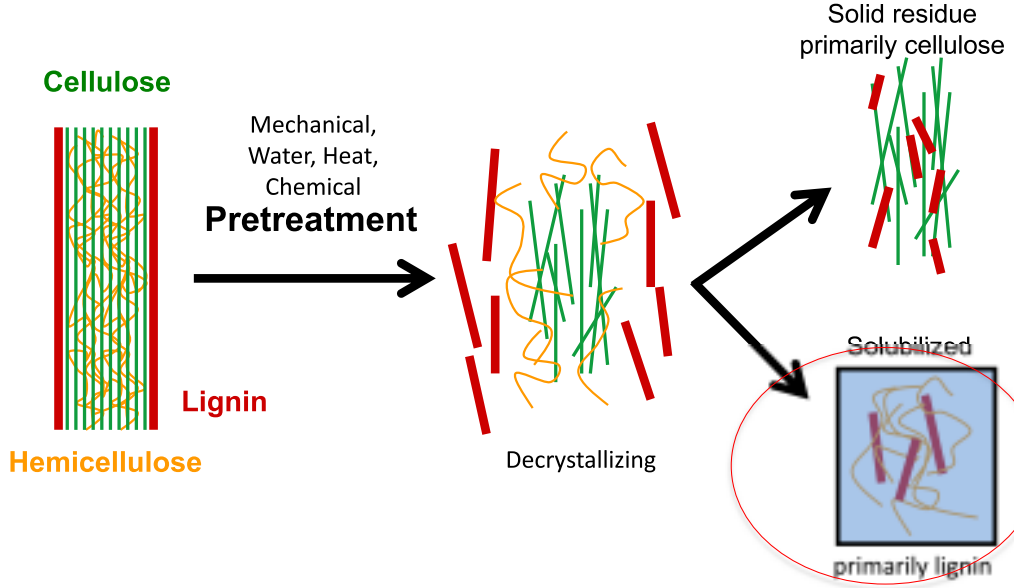
...why do land plants bother to make it?

- Recalcitrance caused by arrangement and makeup of plant cell wall
 - Lignin interlinks with cellulose and hemicellulose
 - Protects cellulose from enzyme digestion



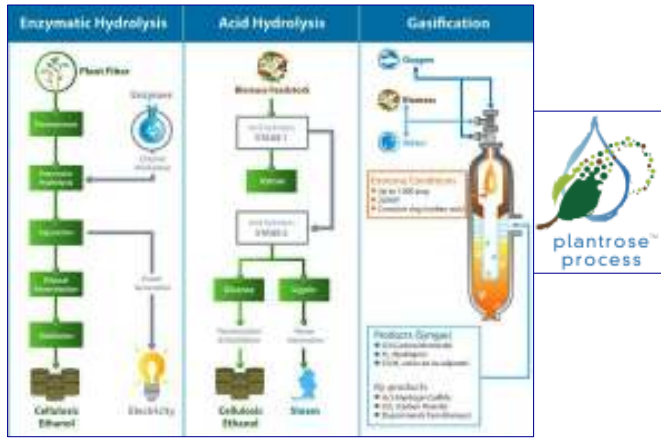
Source: Himmel et al., 2007. Science, 315: 804-807

In some applications (e.g., cellulosic ethanol generation), lignin must be removed from the wood.



Adapted and modified from Dr. Scott Pryor (unpublished materials) and Hsu, 1980. Chem. Technol., 10: 315-319

Renmatix is developing a commercial scale process to convert cellulosic biomass into a variety of chemicals and fuels with a lignin byproduct.



Renmatix Plantrose™ process

In the pulp and paper industry, lignin must be removed so the cellulose can be used to make paper.



Kraft process - NaS and NaOH to depolymerize and remove lignin

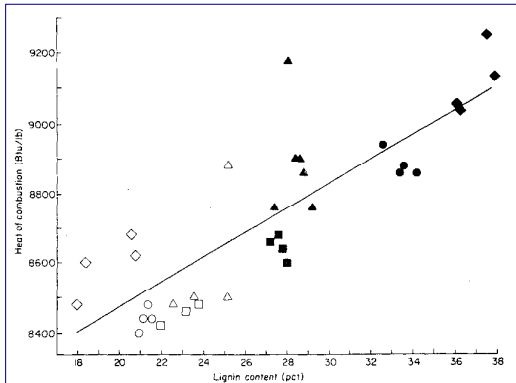
Some information adapted from Brett Diehl

Lignin-based byproducts can be used for heat and energy generation.

- Lignin has a favorable energy density
- Precursor to coal
- Lignin has low sulfur and nitrogen contents, so the release of NOx and SOx is minimized

Lignin-based byproducts can be used for heat and energy generation.

- Burned in boilers of pulp and paper mills
- Co-fired with coal in power plants
- Pelletized and burned to heat homes



Approximate Energy Densities
 Peat: 4500 BTU/lb
 Wood Chips/Shavings: 5000 BTU/lb
 Lignite Coal: 7000 BTU/lb
 Corn: 7000 BTU/lb
 Natural Gas: >23,000 BTU/lb

Bruce Miller, EMS Energy Institute

Fig. 1. Higher heating values of virgin wood versus percent lignin content. ■ = Engelmann spruce, ● = western redcedar, ▲ = southern pine; ◆ = redwood, □ = maple, ○ = yellow-poplar, △ = red oak, and ◇ = basswood. Line is based on linear regression of the data. (ML86 5389)

Robert White, US Forest Service Products Lab, 1986



Lignin-based residue
 EMS Energy Institute



pellets

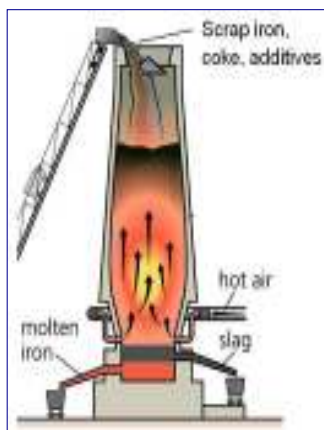
Some information adapted from Brett Diehl

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Lignin-based byproducts can be used as a replacement for bituminous coke in iron foundries.

Lignin can be converted to a “coke-like” byproduct after treatment under high temperatures for short amounts of time.

The carbon content of the lignin is increased, which ensures the “coke-like” byproduct burns slow and yet hot.



Matt Lumadue, PSU

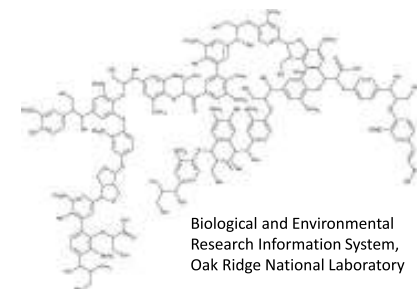
Adapted from Brett Diehl

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Lignin-based byproducts can be used for bulk, platform, and specialty chemicals.

- The U.S. has a LOT of biomass...almost enough to provide raw material for the entire chemical industry
- By 2025, the U.S. has mandated that 20% of transportation fuels and 25% of the commodity chemicals must be derived from renewable sources

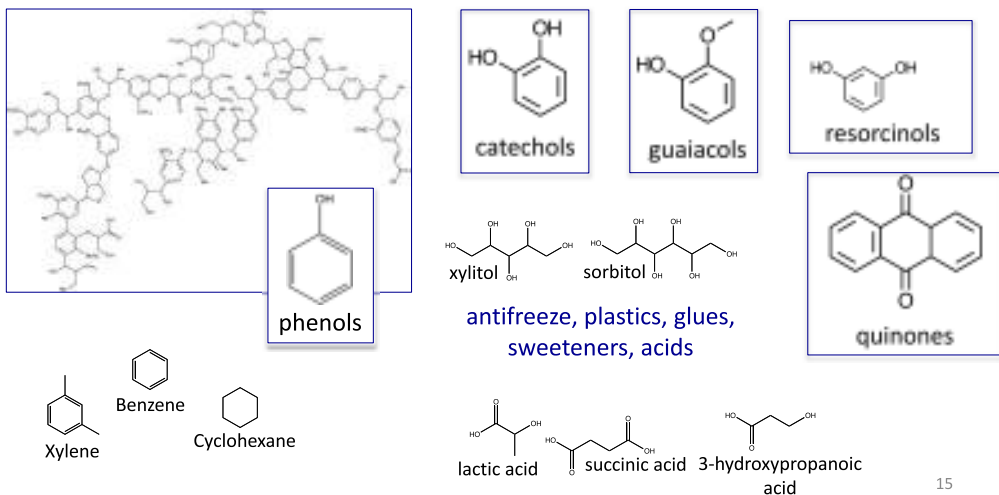
New ways to utilize lignin as a chemical feedstock are being investigated



Adapted from Brett Diehl

Lignin-based byproducts can be used for bulk, platform, and specialty chemicals.

Depolymerization of lignin-based materials can yield a variety of aromatic (phenolic), short chain hydrocarbons and alcohols.

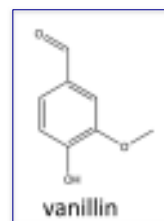


Some information adapted from Brett Diehl

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Lignin-based byproducts can be used for bulk, platform, and specialty chemicals.

Most vanillin (primary component of imitation vanilla) is currently produced from waste lignin in spent pulping liquors.



pacificaperfume.com

Some information adapted from Brett Diehl

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Lignin-based byproducts can be used for bulk, platform, and specialty chemicals.

Some of these chemicals could be used to produce liquid oxygenated fuel additives

- Enhance liquid fuel combustion and reduce emissions of soot and carbon monoxide
- Octane booster



<http://epa.gov/otaq/fuels/gasolinefuels/index.htm>



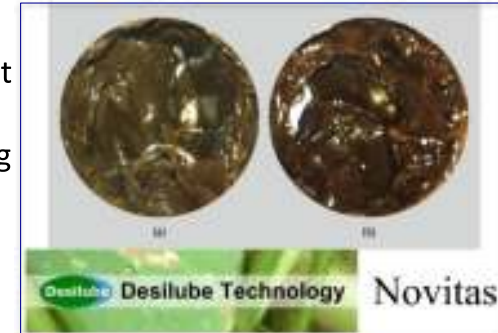
Methanol, E46Fanatics

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Lignin-based byproducts can be used for bulk, platform, and specialty chemicals.

Greases

- Ensure that machinery does not suffer friction, wear and damage under severe operating conditions (i.e., high temperatures and pressures)
- Corrosion protection



Tribology and Lubrication Technology, 2011

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Lignin-based byproducts can be used for plastics and polymers.

- Tailor the mechanical properties
- Entirely renewable and biodegradable unlike petroleum-based plastics



Coca-Cola PlantBottle™ fully recyclable PET plastic bottle made partially from plants



Pepsico PET plastic bottle made entirely from plants

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Lignin-based byproducts can be used for plastics and polymers.

- Tailor the mechanical properties
- Entirely renewable and biodegradable unlike petroleum-based plastics



TECNARO's Arboform, Arboblend, Arboblend products use lignin (and other materials) to make "liquid wood" - renewable plastic that has wood-like qualities but can be cast by a machine

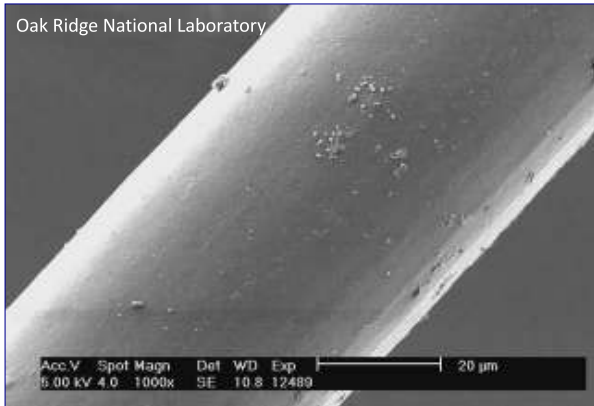


Domtar's BioChoice™ lignin with wide ranging applications in energy, materials and chemicals

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Lignin-based byproducts can be used for carbon fibers.

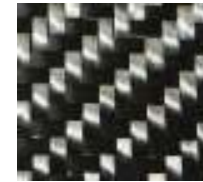
Carbon fibers are extremely strong and lightweight, but generally expensive, and made from non-renewable resources



Photomicrograph of a carbon fiber precursor produced from lignin dissolved from wood

Some information adapted from Brett Diehl

Lignin-based byproducts can be used for carbon fibers.



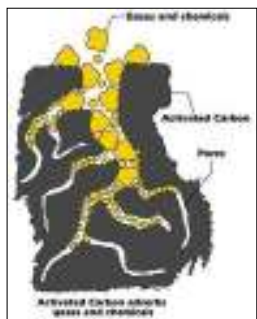
Woven carbon is light and strong

=



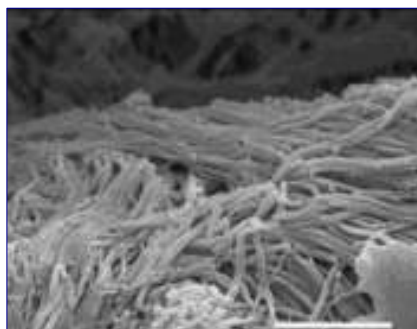
Blackbraided Carbon Fiber Bicycle

Lignin-based byproducts can be used for carbon fibers.



Activated carbon
www.wellwater.bse.vt.edu

Contains small pores for adsorption of contaminants to bind to carbon



Synthesized lignin nanotubes
IFAS at University of Florida, 2012

Targeted delivery of medicine throughout the body

Lignin-based byproducts can be used as dispersants to prevent clumping and settling of undissolved particles in suspensions.

- Lignin-based byproduct attaches to particle surface
- Keeps the particle from being attracted to other particles
- Reduces the amount of water needed to use the product effectively



Oil Drilling Mud, OSHA



Insecticide and Pesticide

Lignin-based byproducts can be used as stabilizing agents for emulsions making them highly resistant to breaking.

The lignin-based byproduct (containing silica) of corn stover ethanol production has been used for making concrete.

When the high-lignin ash byproduct was added to cement, the ash reacted chemically with the cement to make it stronger.



Lignin-based byproducts can be used for binders and adhesives.

- Dandruff shampoo
- Adds firm texture to product
- Gives hair strength and luster



Flax seed, iStock photo



Replace coal tar
Flax lignin

<http://purelignin.com/lignin>
<http://www.biomassmagazine.com/articles/8756/scientists-build-stronger-greener-concrete-with-lignin>

Lignin-based byproducts can act as a binding agent or “glue” in pellets or compressed materials.

- Provide supplemental nutrition to post-fresh cows
- Composite and textile materials
- Wood briquettes



Hooper Feeds
Gordonville, PA



SEKAB, 2014

Lignin-based byproducts can be used for dust control.

- Controlling dust movement in coal mines, coal transportation, stock yards, etc



Zinkan, Sealing storage stockpiles



Eco Dust Control

<http://purelignin.com/lignin>

Lignin-based byproducts can be used for battery applications.

- Researchers have synthesized battery cathode from lignin derivatives
- Lignin forms thin layer on graphite powder surface
- Prevents graphite powder from decreasing overvoltage

There are a number of applications for lignin-based byproducts.

- Lignocellulosic biomass sources have common compositional and structural features.
- The structure needs to be processed to separate the different fractions for further product generation.
- Cellulose can be made into a number of products – paper and ethanol – but a lignin-based byproduct will be generated
- Discussed a broad survey of value-added products from lignin
- Continuing research to improve the economic viability

Acknowledgments

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- Dept of Energy and Mineral Engineering

Penn State Extension



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