

Opportunities for Kraft Lignin

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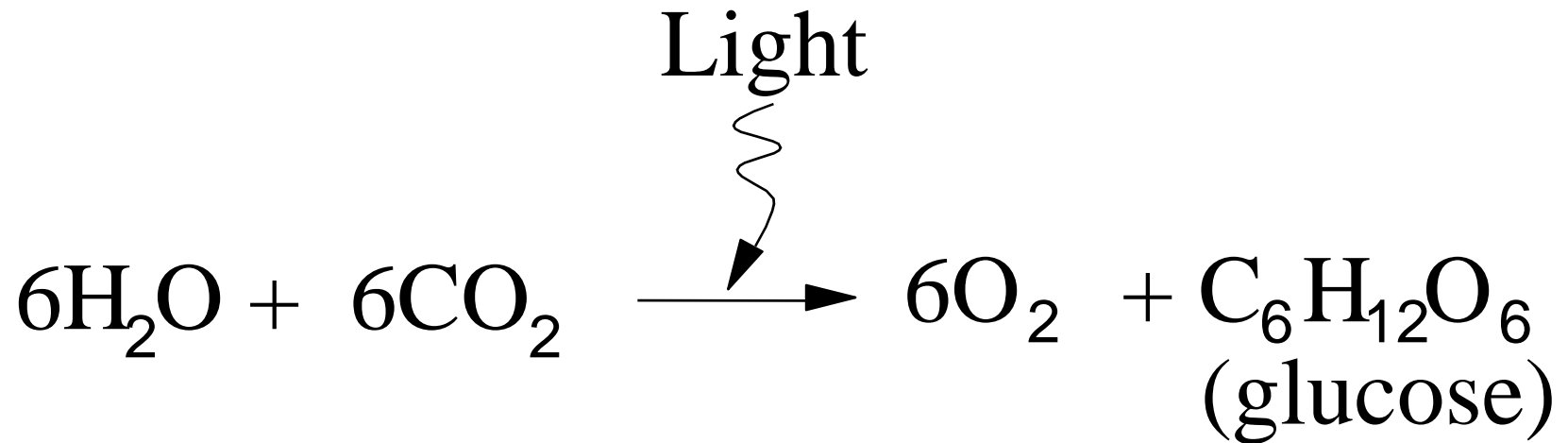
October 10, 2012



The look of a kraft lignin after precipitated from black liquor



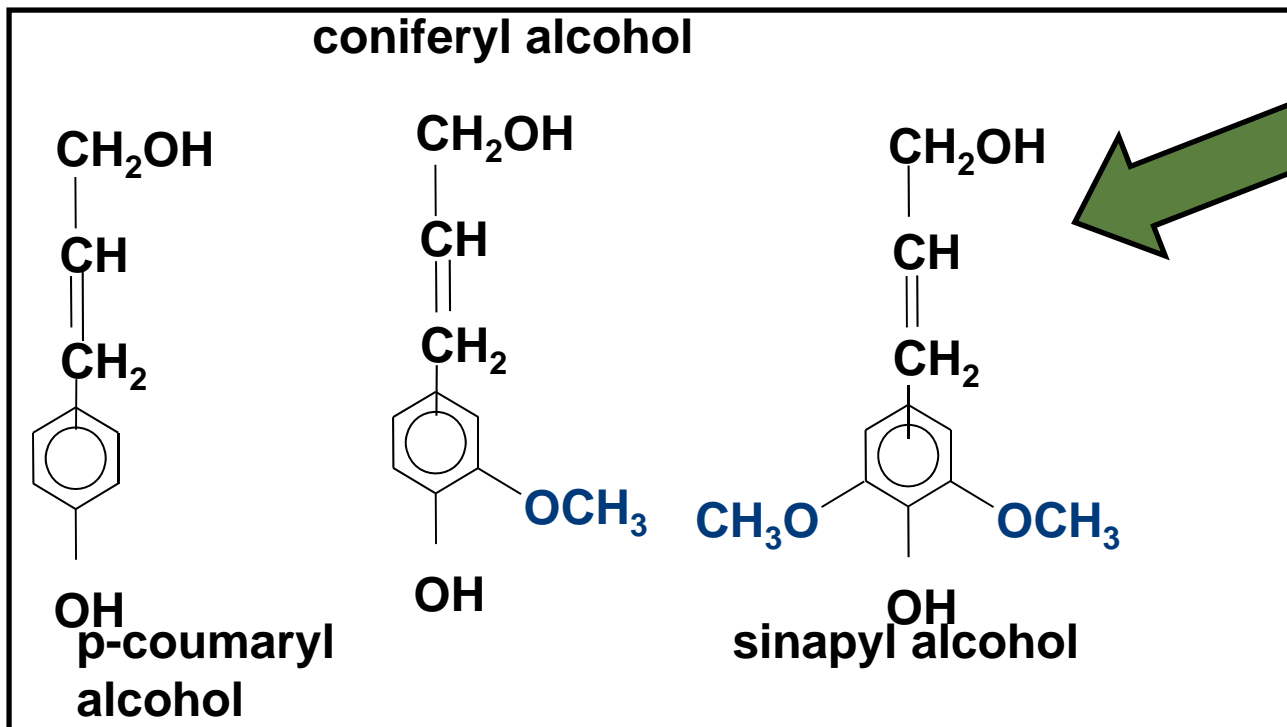
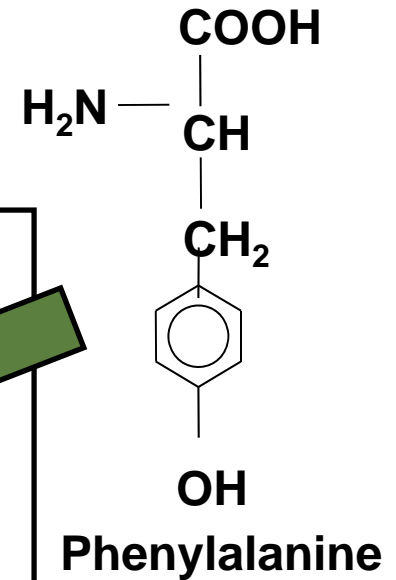
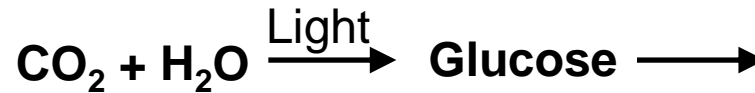
Photosynthesis: the key to life, the key to wood



Cellulose
Hemicelluloses
Lignin

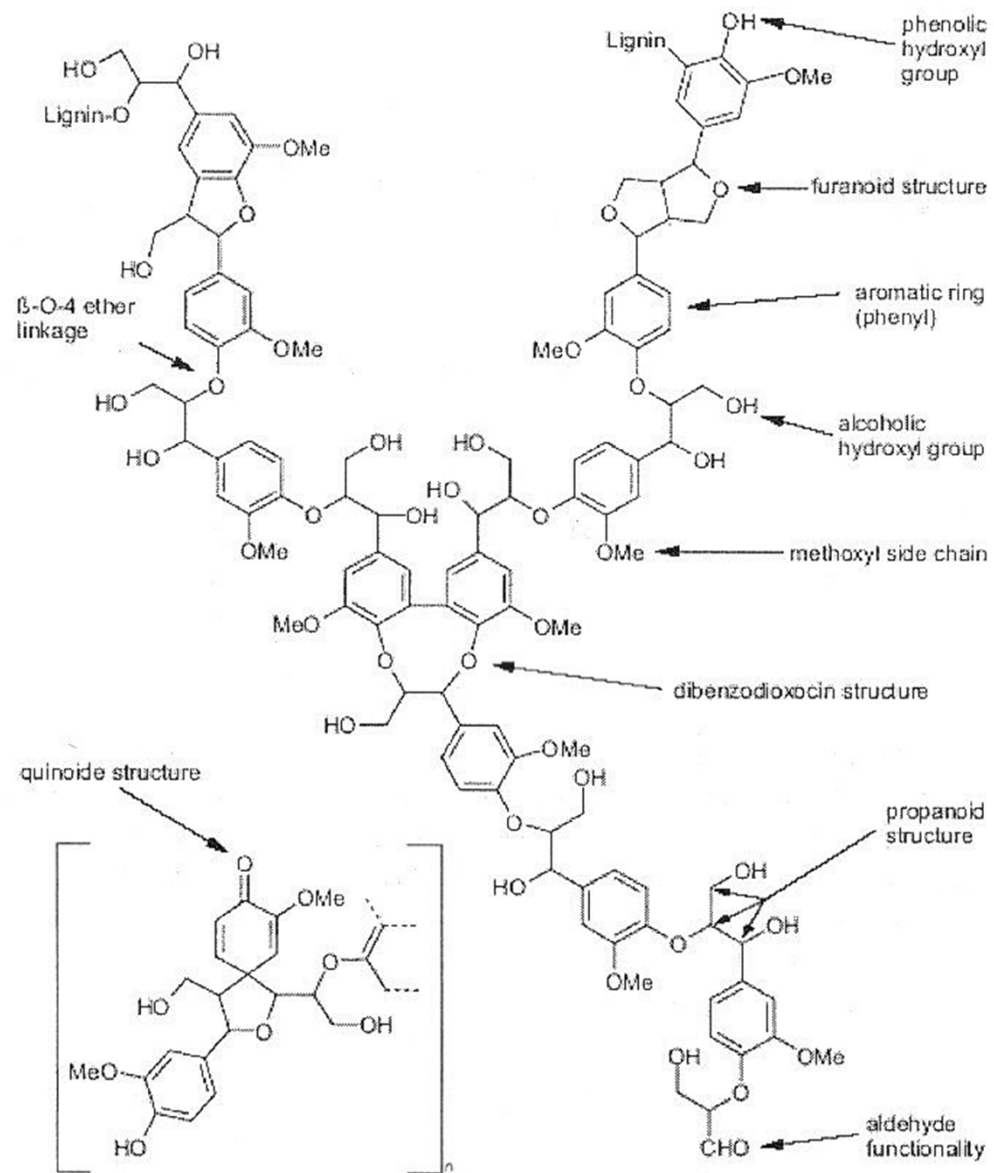


Phenyl propane building units



Lignin is a complex macromolecule:

- amorphous
- heterogeneous
- cross-linked in 3D
- a polyphenol
- a polyol
- free aromatic ring positions

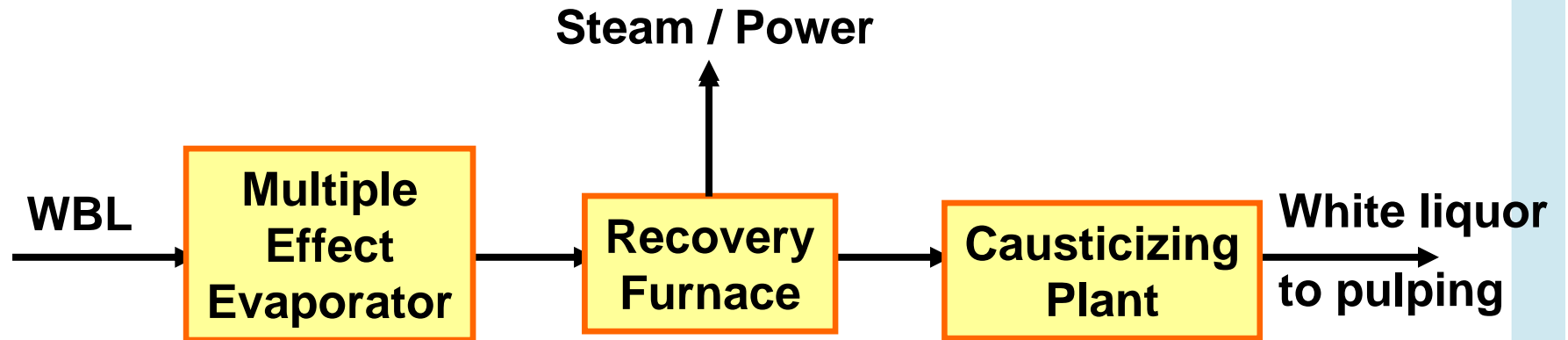


Softwood lignin from Brunow et al., 2001

Principal components of wood (%)

	<u>Softwood</u>	<u>Hardwood</u>
Cellulose	40-50	40-50
Hemicelluloses	15-20	20-35
Lignin	23-33	16-25
Extractives	1-5	1-2
Inorganics (ash)	0.2-0.5%	

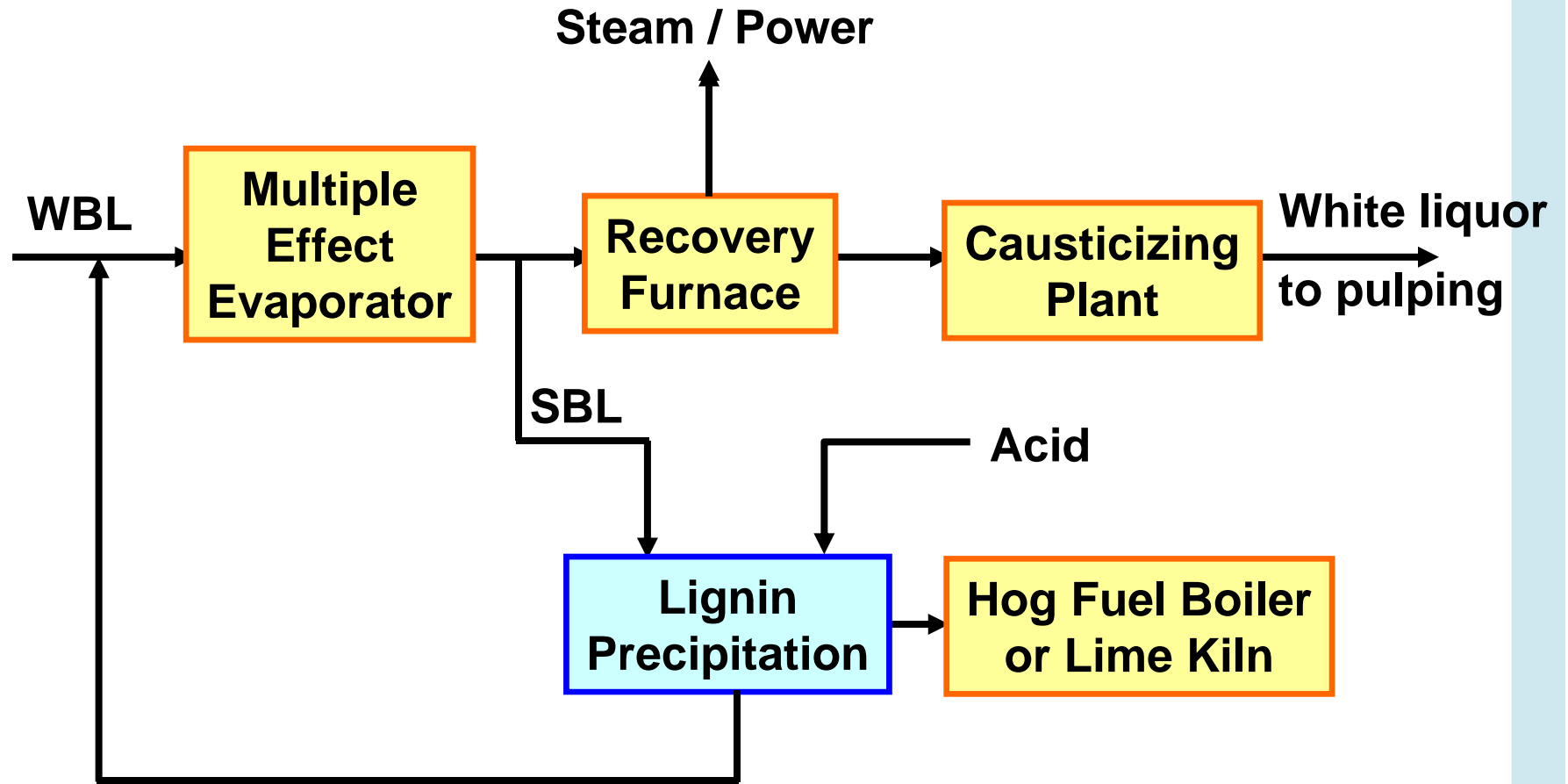
How is lignin used at conventional kraft pulp mills?



Note: 60% of recovery boilers in North America are calorific-load limited

WBL: Weak Black Liquor; SBL: Strong Black Liquor

How can we offload recovery boilers?



WBL: Weak Black Liquor; SBL: Strong Black Liquor

FPIinnovations lignin demo plant in Thunder Bay, Ontario, 12.5 kg/h

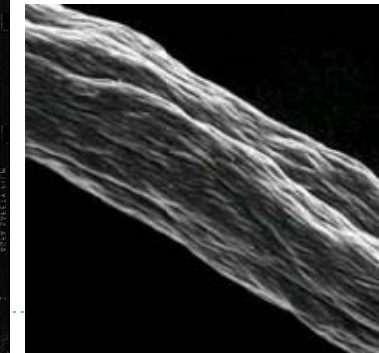
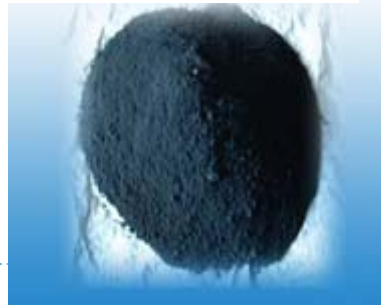
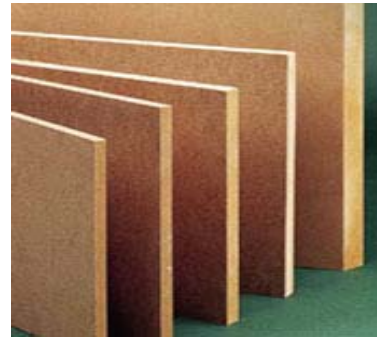


Instead of burning the lignin, can we generate high-value products from it? If so, how?

Answer: by exploiting lignin and lignin product properties of high value in the market place. These include:

- Dispersive properties
- Adsorption/desorption properties
- Thermal stability
- Surface-active properties
- Adhesive (binding) properties
- Hydrophobic properties
- Antioxidant and antiozonant properties
- Antimicrobial properties
- High carbon density
- Low gravimetric density (light)
- Electrical insulation properties
- High chemical derivatization potential

What products can we make from lignin?



Potential lignin products

- Fuels:
Lime kiln fuel, Power boiler fuel, Wood pellets
- Thermoset resins:
Phenol-formaldehyde resins, Foundry resins, Polyurethane foams, Epoxy resins, Rubber
- Thermoplastics (blends or composites):
PE, PP, PVC, PET
- Dispersants & Flocculants:
Sulphonated, carboxylated, aminated lignins
- Carbon products:
Activated carbon, Carbon black, Carbon fiber
- Chemical products:
Vanillin, low MW phenolics, BTX, etc.

Lignin as a fuel in the lime kiln

- Prior work at UBC demonstrated the technical feasibility of burning lignin in a pilot lime kiln.
- Innventia recently conducted trials at a Swedish mill replacing the fossil fuel with dry lignin.
- Market size (100%): enormous
- Lignin value: \$150/tonne at a natural gas price of \$6/GJ and \$300/tonne at oil price of \$100/barrel



Lignin as a fuel in power plants

- Lignin pellets successfully used as a supplementary fuel in a coal-fired power boiler
- Efforts being made to qualify lignin as a fuel for coal-fired power plants in Ontario
- Lignin used as a binder in wood pellets at FPInnovations
- Market size (2%): 240,000 tonne/y
- **Lignin value > \$800/tonne**



Wood pellet preparation



Blender used for wood furnish blending with lignin



- Feeding and collecting wood furnish
- Collecting wood pellets

Heating value and integrity of wood pellets with and without lignin

lignin		Gross heating value			Net heating value		
(type)	(%)	(kcal/kg)	(MJ/kg)	(Btu/lb)	(kcal/kg)	(MJ/kg)	(Btu/lb)
Control	0	4,648	19.50	8,367	4,332	18.10	7,797
FPI innovations Kraft lignin	3	4,837	20.30	8,707	4,530	19.00	8,154
FPI innovations Kraft lignin	6	4,920	20.60	8,857	4,603	19.30	8,286



Durability of wood pellets

Pre-sieving: A sample of pellets to be tested was sieved to remove the fines

lignin		Pre-sieving		improvement
	(%)	% (≥4.75m m)	% (<4.75 mm)	%
Control	0	55.3	44.7	0.0
FPIinnovations Kraft lignin	3	92.3	7.7	66.8
FPIinnovations Kraft lignin	6	95.1	4.9	72.0

Durability testing: Pre-sieved pellets were placed in a tumbling box device. After tumbling for 10 min at 50 RPM in a dust –tight enclosure, the sample was removed, sieved, and the percentage of whole pellets was calculated.

Lignin		Durability	Moisture
	(%)	%	%
Control	0	72.7 (0.5)	2.68
FPIinnovations Kraft lignin	3	93.1 (0.2)	0.87
FPIinnovations Kraft lignin	6	93.7 (0.2)	0.54

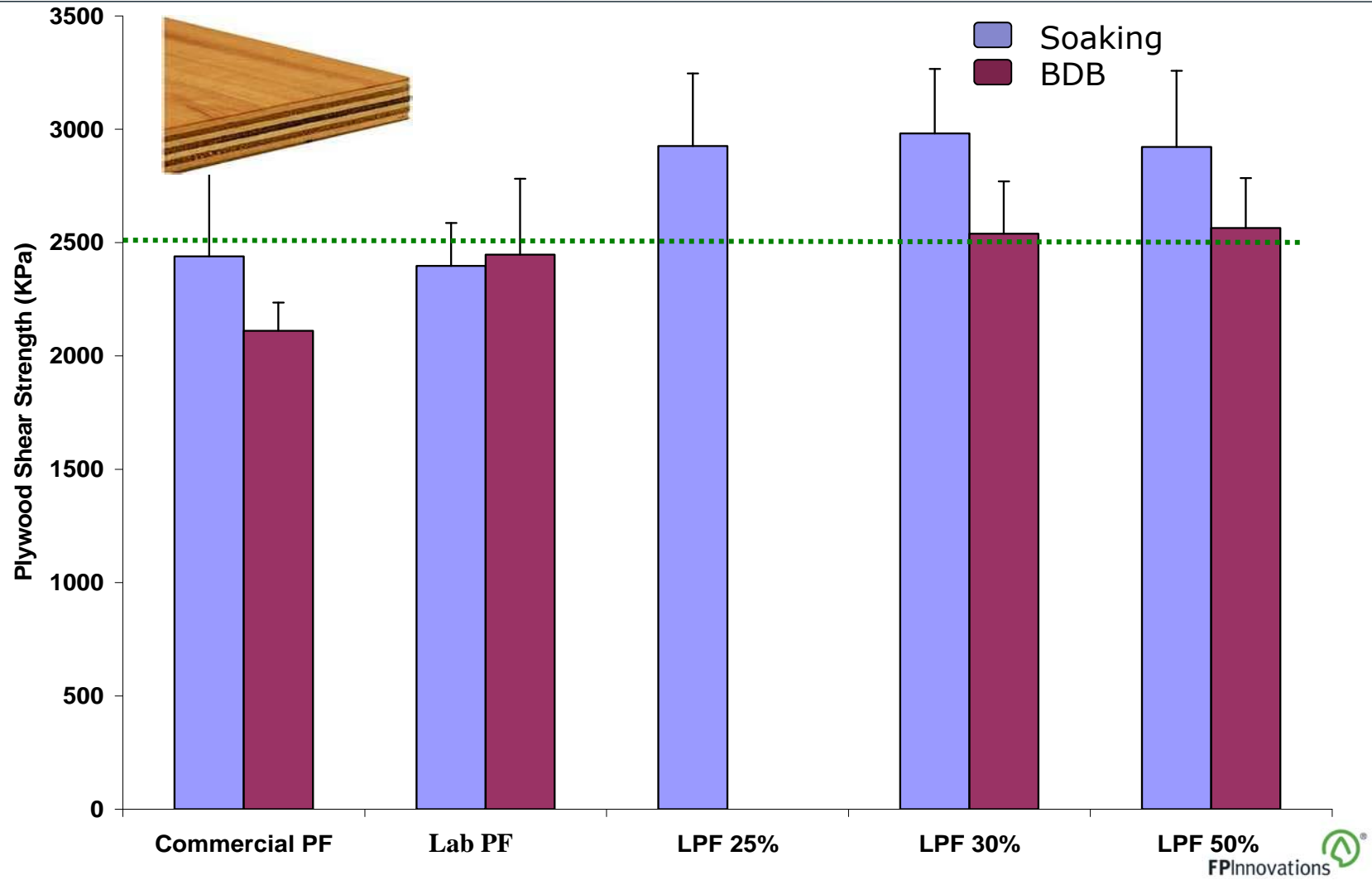
$$durability = \frac{\text{mass of pellets after tumbling}}{\text{mass of pellets before tumbling}} \times 100$$

Lignin as a substitute of phenol in phenolic adhesives for wood products

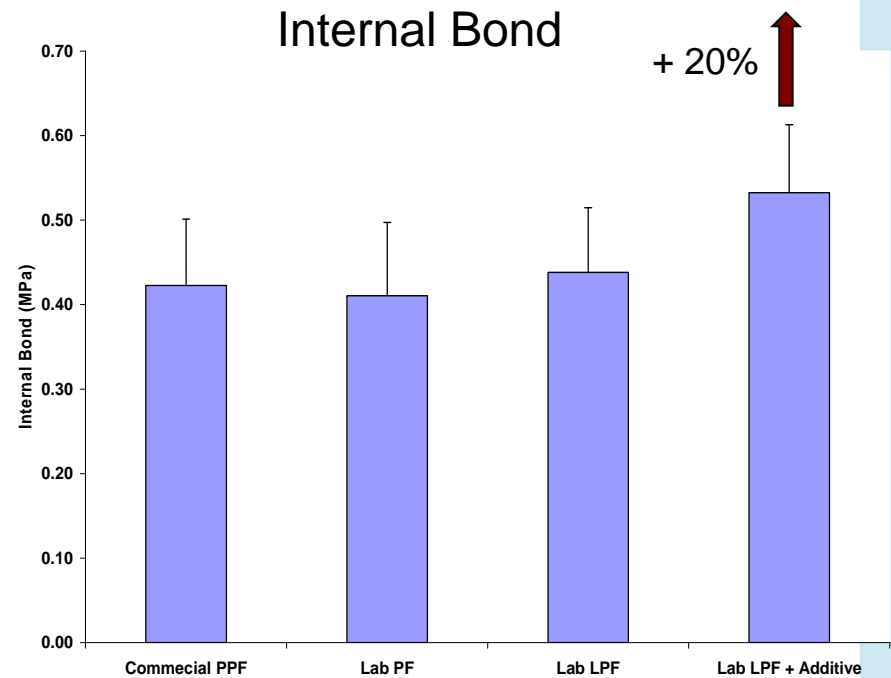
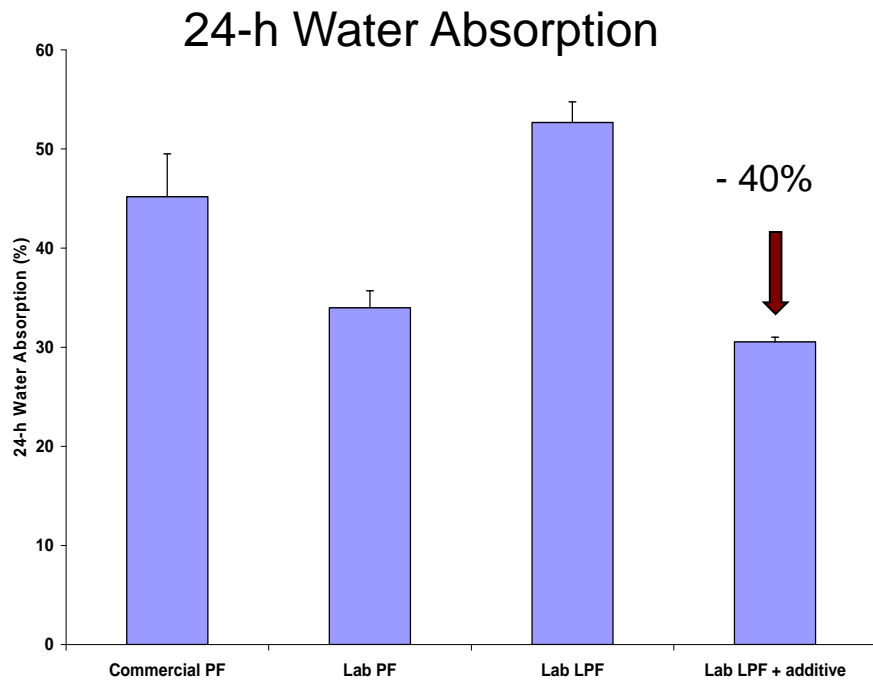
- PF resin form:
 - liquid or dry powder (40% higher price)
- Shelf life:
 - 1 to 3 months (liquid form), longer for dry form
- Feedstocks to PF plants:
 - phenol and methanol
- Advantages of lignin:
 - Rich in phenolic structures
 - Lower cost
- Disadvantages of lignin
 - Slower cure rate at high substitution rate
 - Increased swelling in some wood products
- Market size (30%): 100,000 tonne/y
- **Lignin value: >\$1500/tonne**



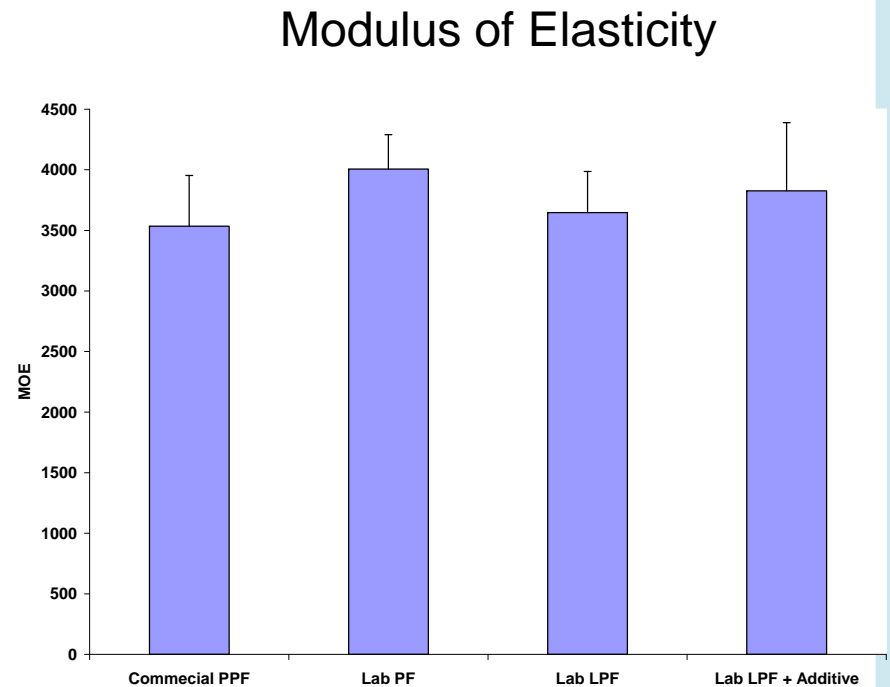
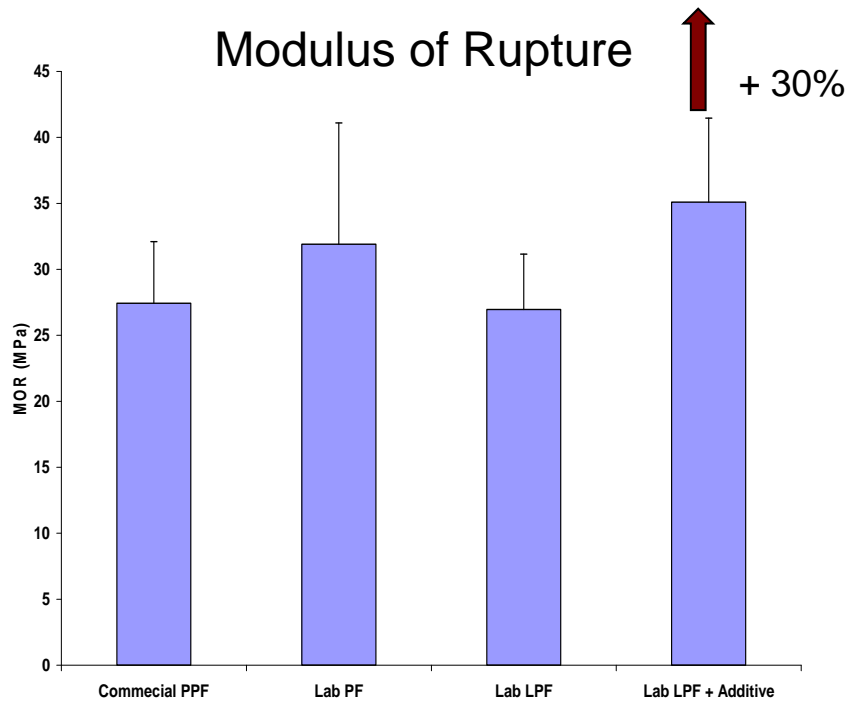
Plywood Shear Strength after vacuum/pressure and Boil-Dry-Boil (BDB) Treatments



OSB 24-h Water Absorption and Internal bond – 33% Substitution of Lignin for Phenol



OSB Modulus of Rupture and Modulus of Elasticity



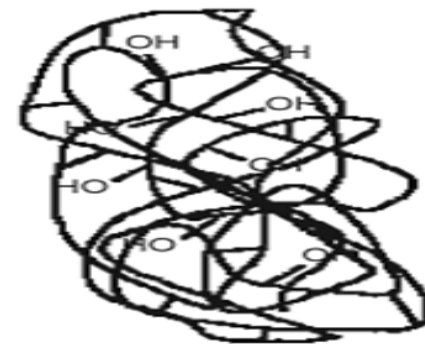
Lignin as an adhesive in foundry resins

- Conducted trial in which 100% of PF resin in foundry resin was replaced by lignin
- Trial approach: Poured stainless steel 304 at approx. 2830° F in 10 kg molds
- Tested mold strength, burn and smoke of lignin-containing binder vs. a standard binder
- Market size (20%): 10,000 tonne/y
- Lignin value: >\$2000/tonne



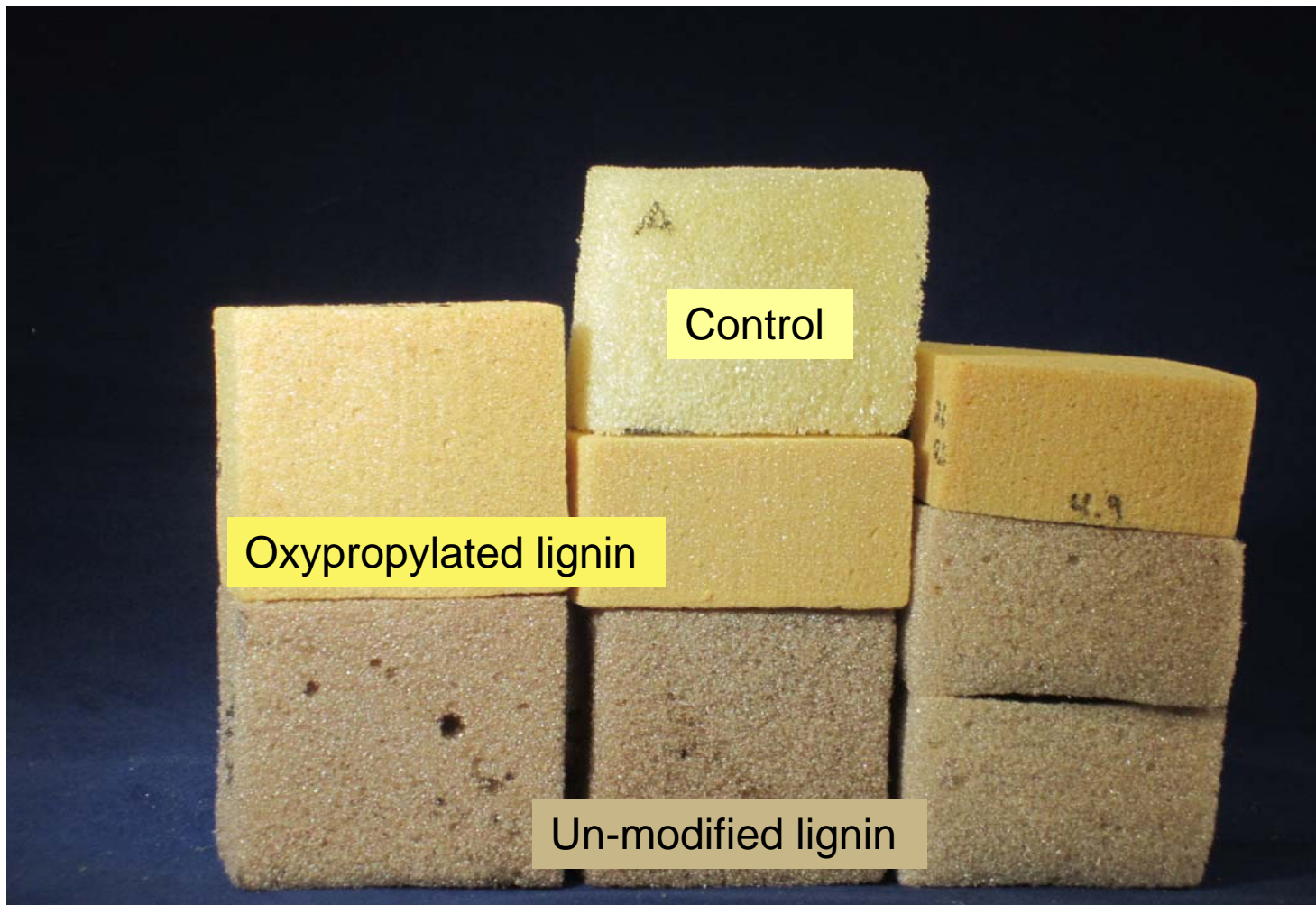
Lignin in rigid polyurethane foams

- To make polyurethane foams isocyanate is reacted with petroleum-based polyols
- Lignin is a natural polyol as a result of its numerous phenolic and aliphatic hydroxyl groups
- These hydroxy groups, however, are too sterically hindered to react easily with isocyanate
- Approaches have been developed to unhinder lignin hydroxy groups
- Lignin-based polyols are viewed as potentially useful for making rigid polyurethane foams with beneficial thermal degradation (fire-resistant) properties
- Market size (20%): 220,000 tonne/y
- Lignin value: >\$2000/tonne



Solid substrate

Rigid polyurethane foams

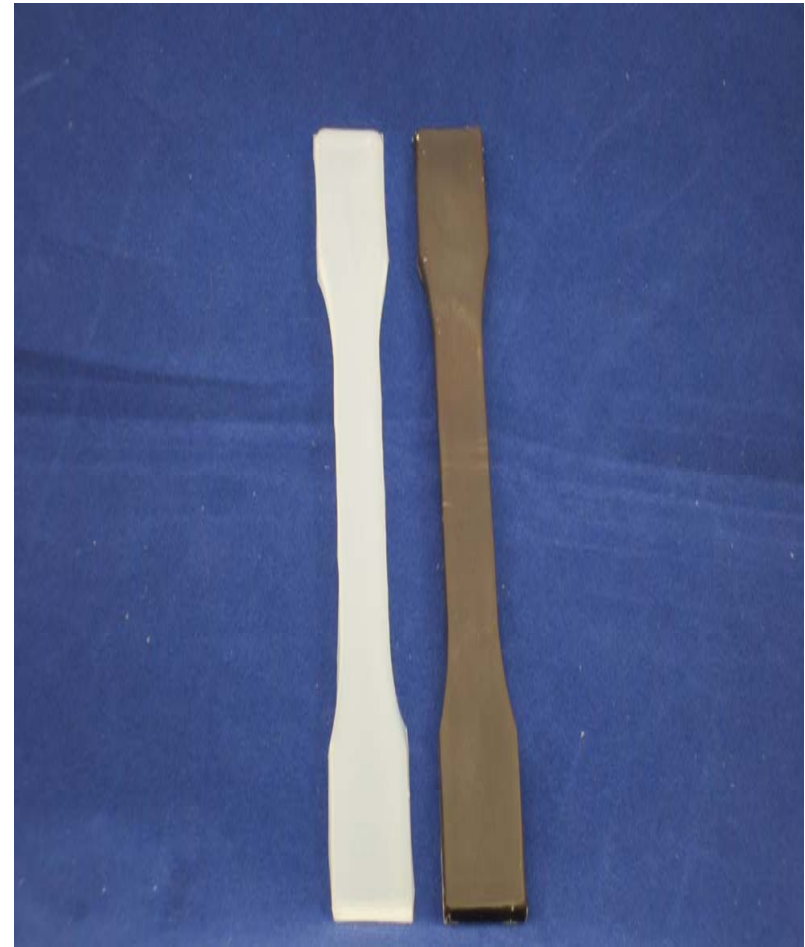
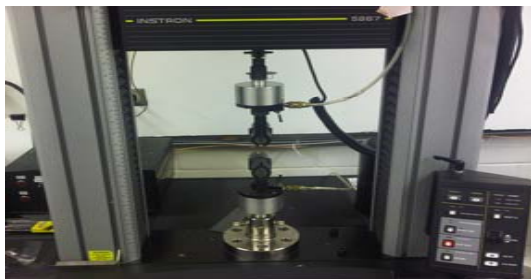


Lignin in thermoplastics and composites

- Incorporation of lignin into thermoplastics represents by far the largest market opportunity
- PP + PE market size: 130 million tonnes/y
- Market size (1%): 1.3 million tonnes - we would need 74 mills producing 50 tonne/d of lignin to meet this demand
- Lignin value: \$1500-2000/tonne



Polypropylene at 20wt% lignin



Lignin product-related challenges and opportunities

- PF resins:
 - lignin reactivity with formaldehyde
 - lignin solubility in pH 9-10 rxn solution
 - Lignin polydispersity
- PU rigid foams:
 - lignin reactivity with isocyanate
 - Lignin solubility/dispersibility in petroleum-based polyols
 - Lignin polydispersity
 - Low abrasion resistance of final product
- Thermoplastics
 - Lignin compatibility with various polymers (chemical & thermal)
 - Lignin polydispersity
 - Odour produced during processing and from final product
 - Colour of final product (depending on application)
 - Multiple and complex polymer formulations (moldings, foams, fibers, films)

The future for lignin is bright !!

Questions & Answers