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LignoForce™ Kraft Lignin Extraction: Process Scale-Up, and Product Development

Kraft Lignin Innovation Forum – Oct. 12, 2017

Iron Mountain, Michigan

Kirsten Maki, Michael Paleologou, Yaolin Zhang, Martin Feng and Pedram Fatehi

Outline

- FPI & BETC Introduction
- Biorefinery & Lignin Basics
- Process Development
  - Kraft Lignin Extraction process
  - LignoForce Pilot Plant
  - LignoForce Commercial Scale-Up
- Product Development
  - Lignin properties and applications

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- Canadian not-for-profit Forest Research Organization
  - 90 years of history
  - 500 employees
  - 175 Member companies
  - Links with academia, government labs, industrial R&D, research networks
- Major facilities in Montreal, Vancouver and Quebec City; offices across Canada
- Covering the entire value chain from Forests to Markets
  - Forest Operations
  - Wood Products
  - Pulp, Paper, Packaging & Consumer Products
  - Bioproducts & Bioenergy

Bio-Economy Technology Centre (BETC)

- Regional R&D centre operated by FPInnovations
  - Located in the Resolute Forest Products mill in Thunder Bay, Ontario
  - 6 staff (1 group leader, 2 operators, 2 chemists, 1 PDF)
- Centre Focus:
  - Forest based bio-product R&D, process scale up
  - Pilot plant and pre-commercial demonstrations (bio-methanol, lignin)
- Resources:
  - On-site lab, offices, pilot plant equipment
  - Off-site research & analytical support – FPInnovations, Universities
  - Noram Engineering

The Forest Biorefinery

- As petroleum becomes less sustainable, alternatives are more attractive - particularly non-food, plant based
- New products will strengthen the Forest Sector – wood derived biofuels and biochemicals hold promise
- Existing forest sector assets and infrastructure are well suited to further utilization
- Many pulp mills are already biorefineries – tall oil and turpentine
- There are further opportunities

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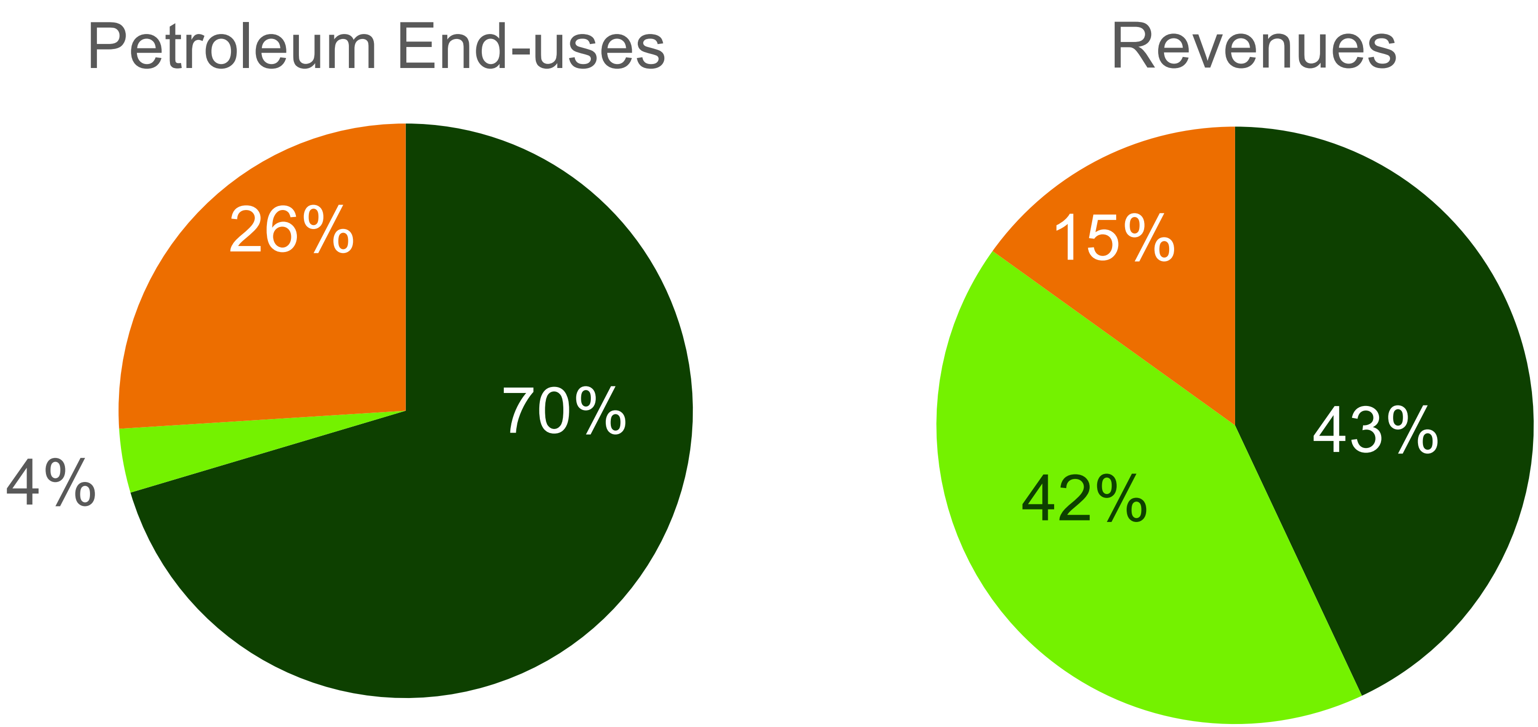
Biorefinery Considerations

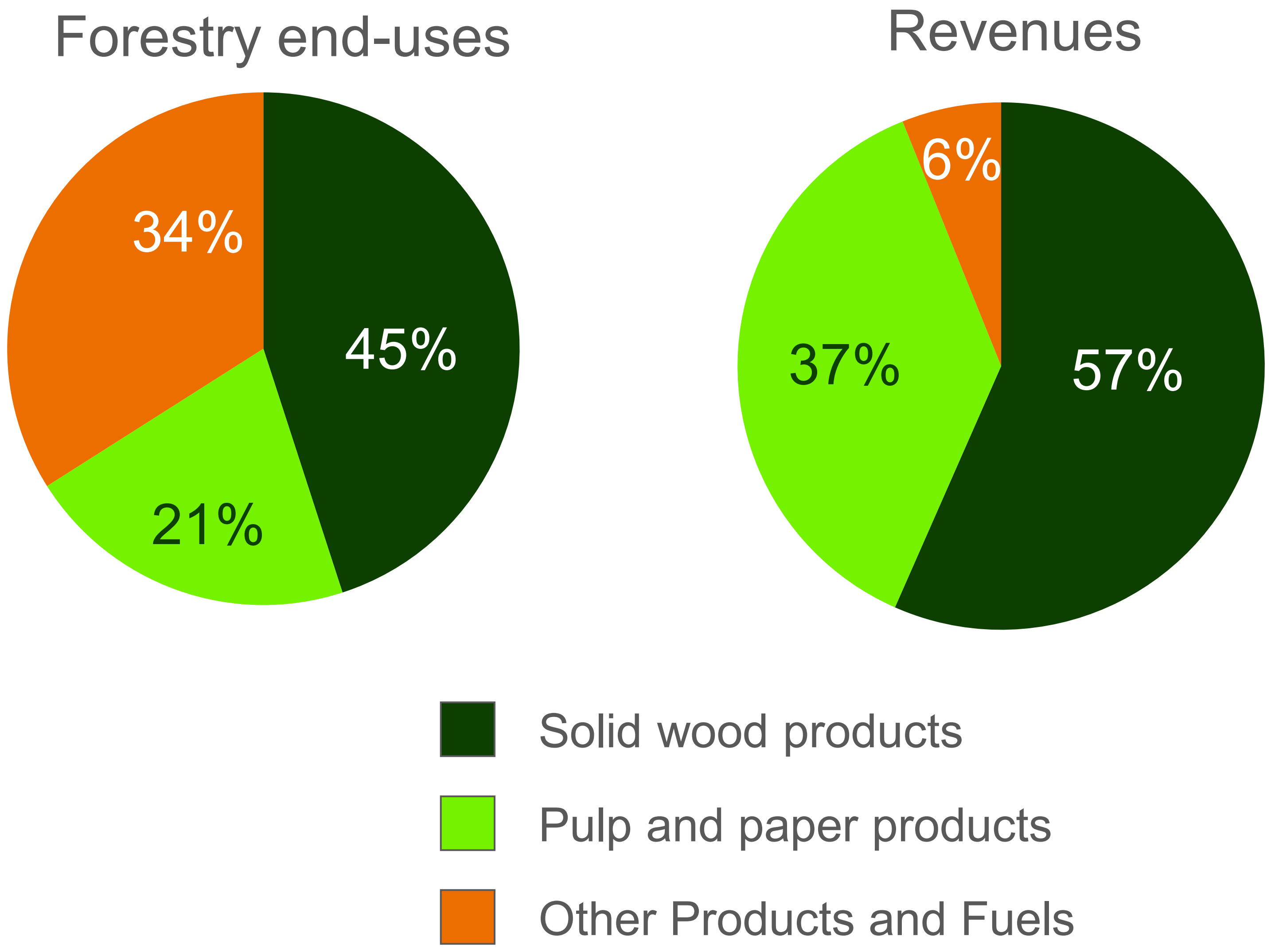
- Biomass is bulky, wet and distributed; Petroleum is cheap, dense, and comes out of a pipe
  - Economics site specific
- Focus on value added chemicals first, then energy from residues
- Build relationships with customers
  - Ensure product meets customer's needs, integrate with end user's infrastructure
- Co-locate with an existing mill – 'bolt-on' addition, or repurpose existing/idle capacity
  - Improve economics of existing infrastructure and raw material supply logistics

A Lesson from Petroleum Refineries



Source: T. Werpy,
2009 BioWorld Conference

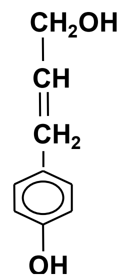
Today's Forest 'Bio-refinery'



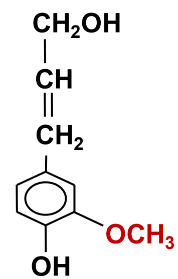
What is lignin?

Lignin is a complex macromolecule

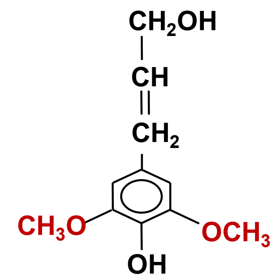
- Aromatic
- Heterogeneous
- Amorphous
- Cross-linked in 3D



p-coumaryl alcohol



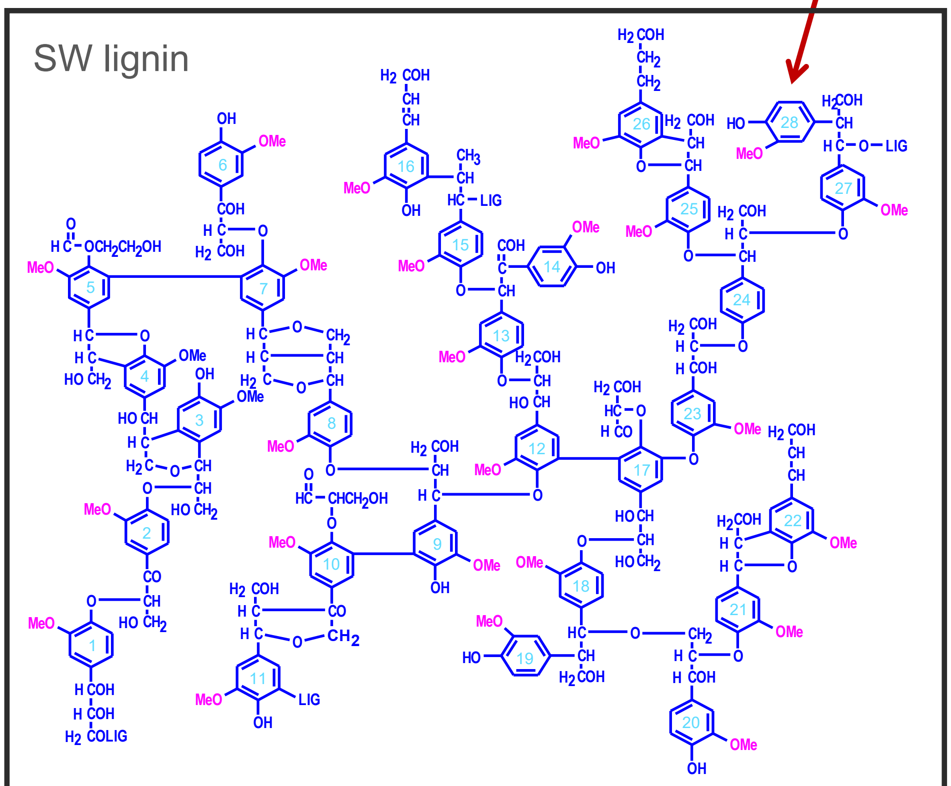
coniferyl alcohol

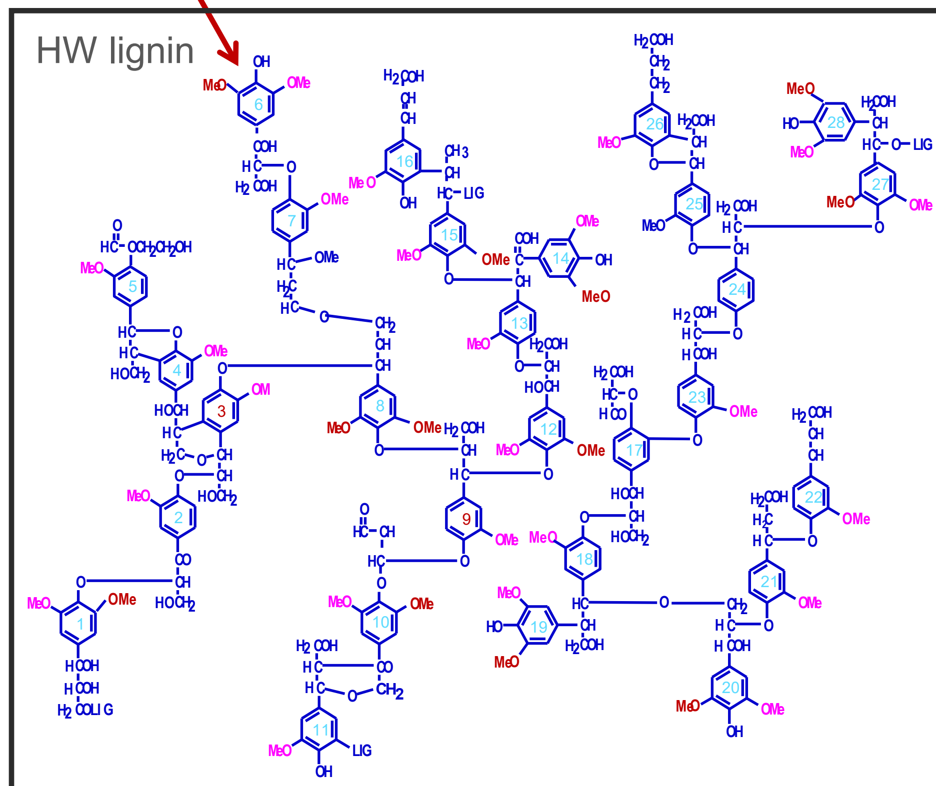


sinapyl alcohol

Contains high no. of:

- Phenolic hydroxyl groups
- Aliphatic hydroxyl groups
- Carboxylic acid groups
- Free aromatic ring positions





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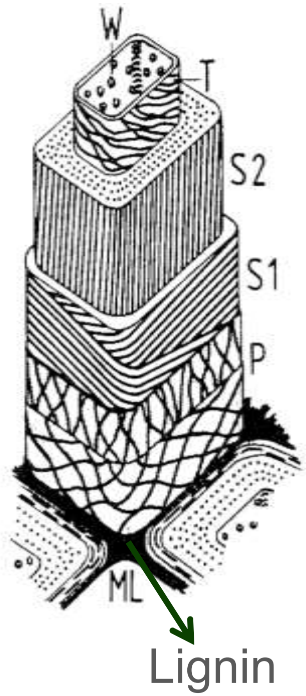
Types of Lignin

- Not all lignin is the same, even from the same feedstock!
  - some inherent building block differences between hardwood vs. softwood vs. agricultural products / residue, but more to it
- Depending on extraction process, lignin will have different properties
  - Process options
    - Extract with organic solvents
    - Hydrolysis byproduct (acid or enzymatic process)
    - From soda process
    - From sulfite pulping process
    - From Kraft pulping process (black liquor)
- Lignin can be modified to achieve desired properties

How much lignin is there?

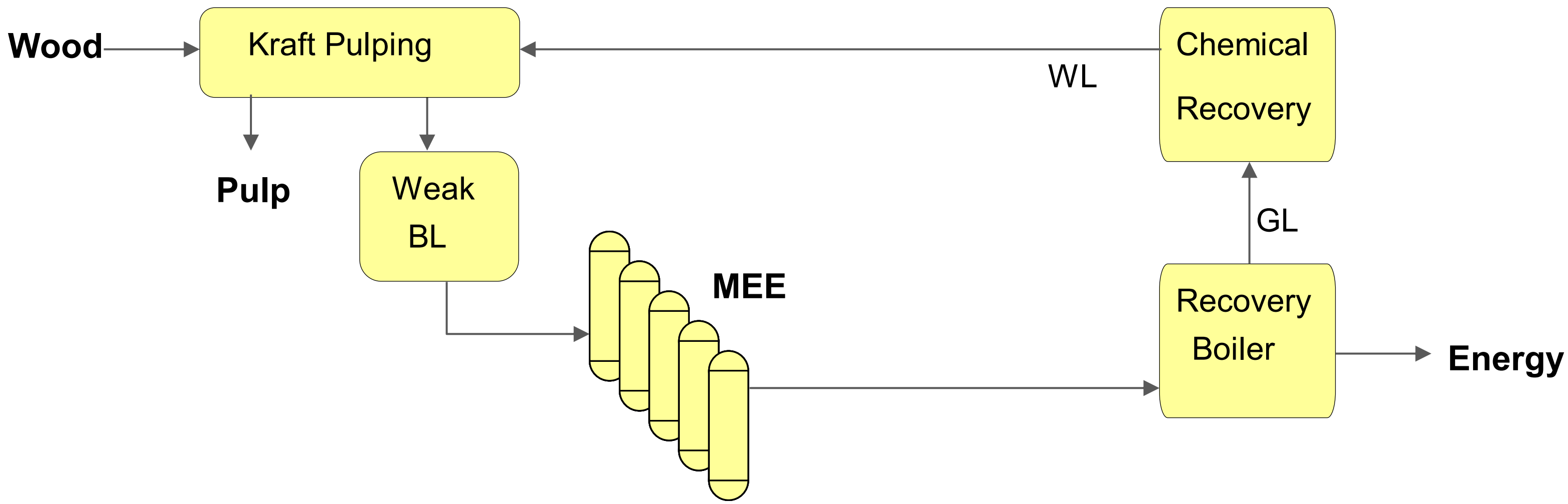
- The most abundant natural aromatic polymer
- One of the principal components of woods and non-woods

	Softwoods	Hardwoods	Non-woods
Cellulose	40-50%	40-50%	30-40%
Hemicelluloses	15-20%	20-35%	20-30%
Lignin	**25-35%**	**15-25%**	**15-20%**
Extractives	1-5%	1-2%	2-10%
Inorganics	0.2-0.5%	0.2-0.5%	2-12%



- e.g. a 1000 TPD kraft mill processes ~500 TPD lignin (of which ~10% can be recovered without negative process impact); can easily extract 50 TPD

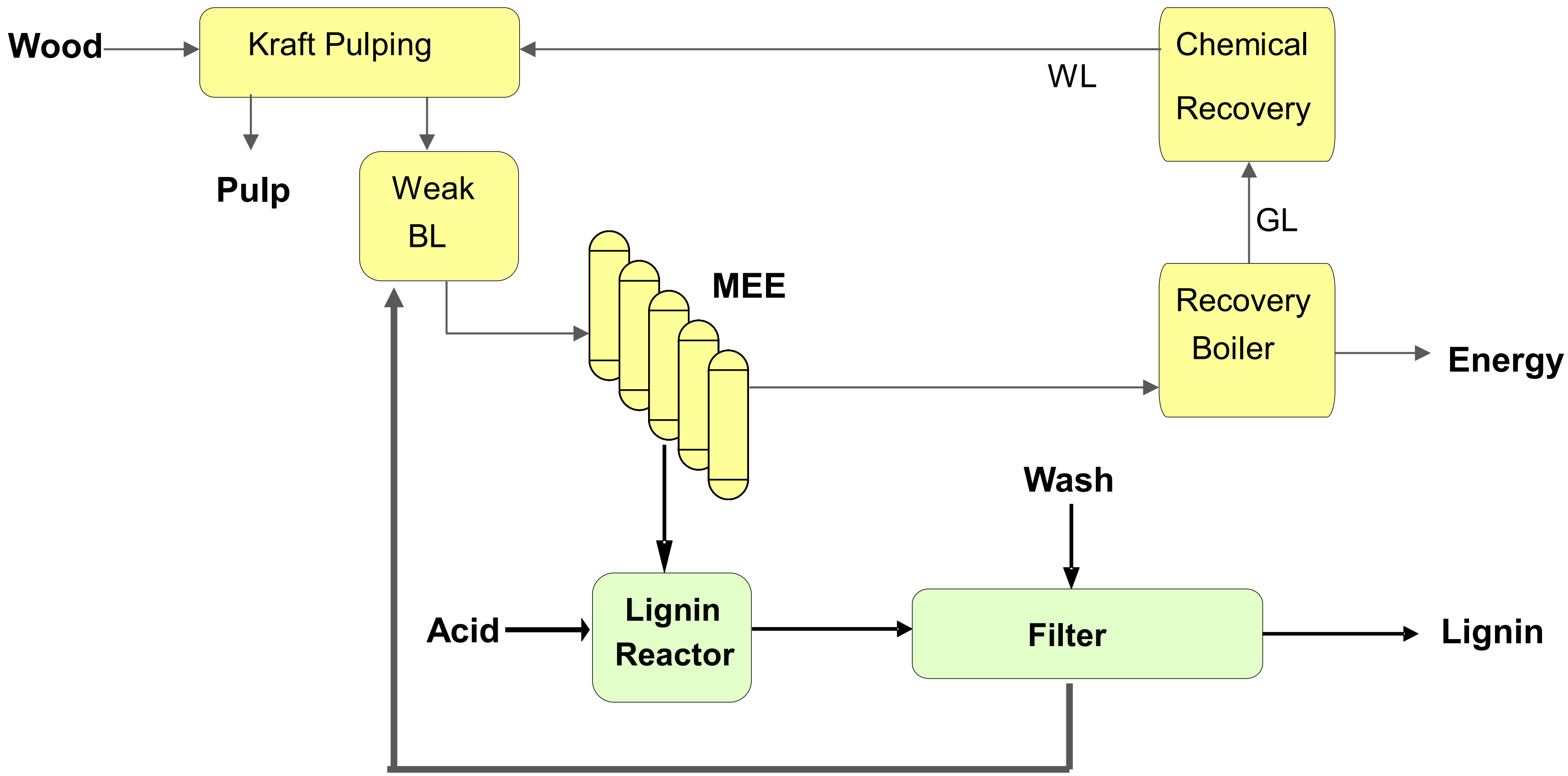
How is lignin used at conventional chemical pulp mills?



Basic Kraft Process (Liquor Cycle)

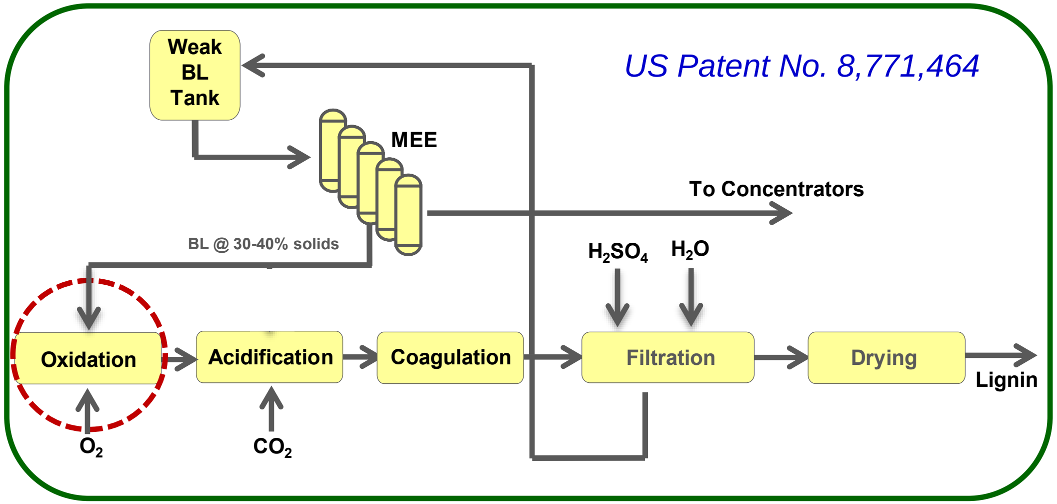
Lignin value ~ $150/tonne

Basic Kraft Process with Lignin Extraction



How can we produce pure lignin cost-effectively?

The LignoForce System™



Advantages of the LignoForce System™	Consequences
Patented oxidation step results in low sulphur compound emissions from process and product	less odour, less health and safety concerns
Reduced chemical consumption	reduced operating costs
Higher filtration rates	reduced capital costs
Higher lignin purity	wider range of applications
Simplified equipment – single press	reduced capital costs

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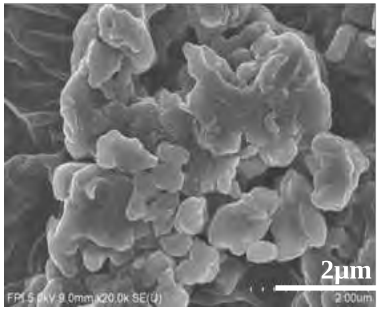
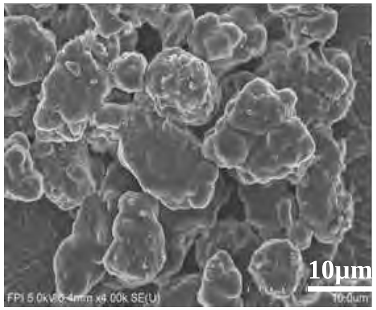
LignoForce System™ vs Conventional process

Chemical requirements	Conventional process	LignoForce System™
CO_2 consumption (kg/kg of lignin)	0.50 – 0.60	0.2 – 0.4
H_2SO_4 consumption (kg/kg of lignin)	0.30 – 0.40	0.1 – 0.2
Water usage (L/kg of lignin)	10-15	4 - 5
Sulphur gas emissions (g/kg of lignin)*	75.2	2.2

Lignin characteristics	Conventional process	LignoForce System™
Lignin particle size (µm)	0.2 - 1	5 - 10



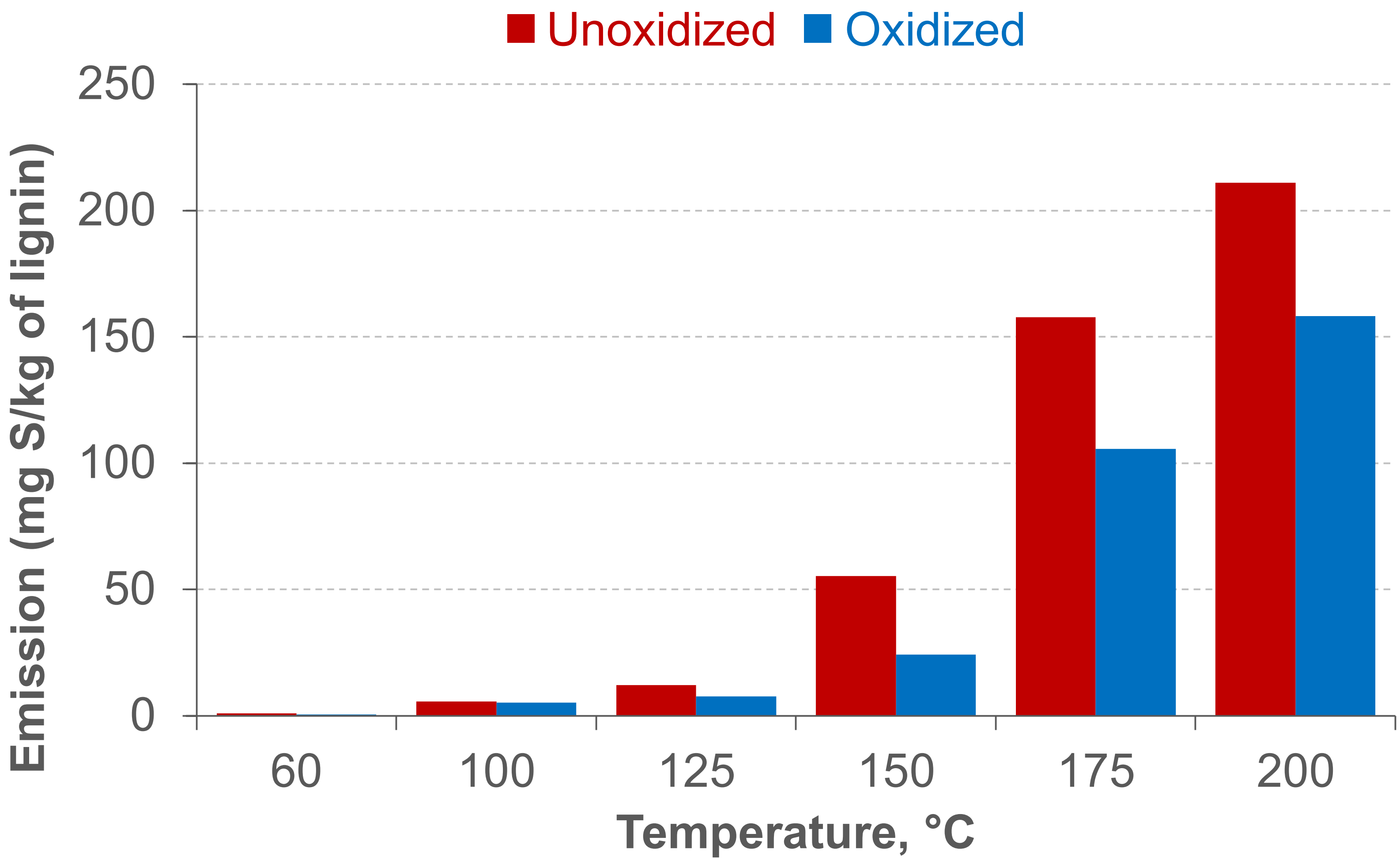
SEM image of lignin product recovered from **conventional process**



SEM image of lignin product recovered from **LignoForce System™**

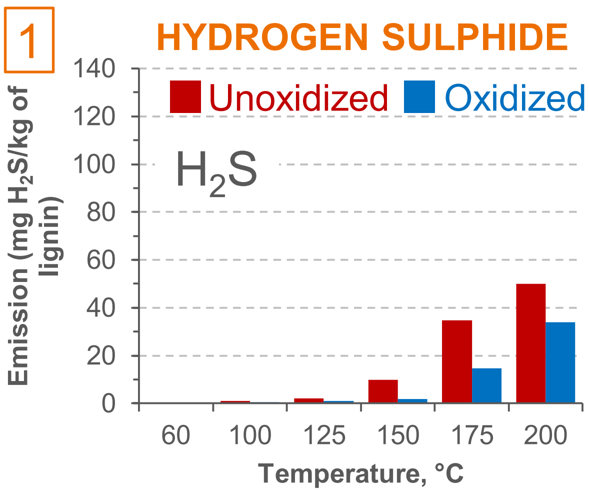
*Kouisni et al., Sustainable Chemistry & Engineering, 4(10), 5152-5159 (2016)

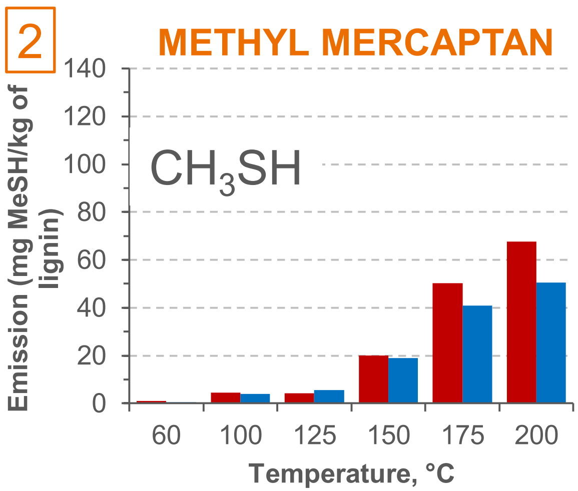
Sulphur compound emissions from SW lignin derived from unoxidized and oxidized black liquor

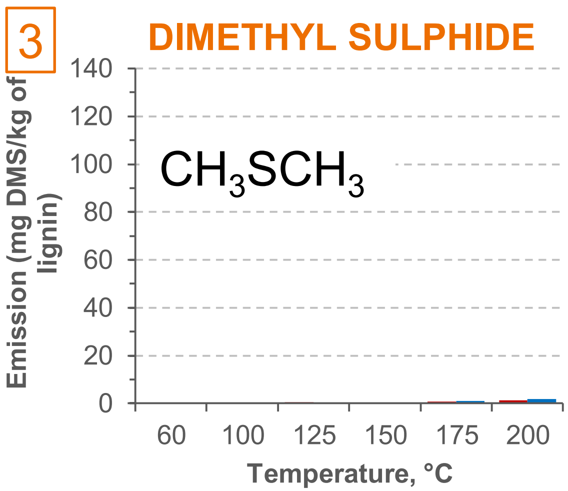


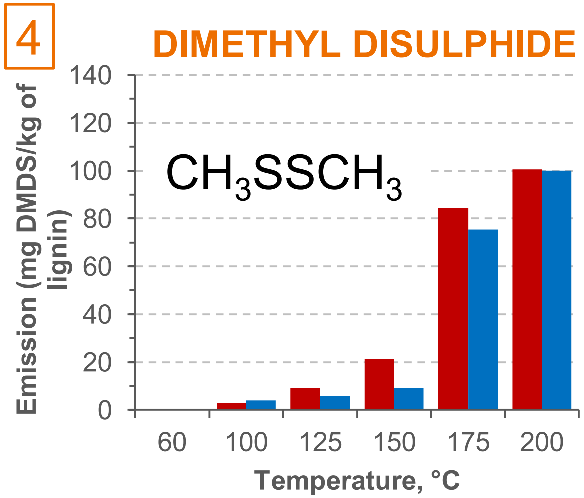
30 minutes of heating in sealed vials followed by Headspace GC-FPD analysis

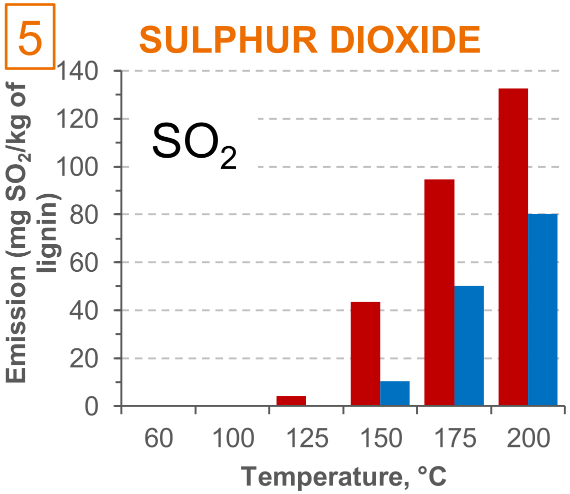
Sulphur compounds detected using headspace analysis











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Pilot Plant Objectives

- Identify engineering challenges and key economic factors
- Optimize process conditions
- Make sufficient quantities of product for research and commercial scale trials
- Operate process under industrially realistic conditions > better commercial scale plant design

Risk reduction!

Kraft Lignin Pilot Plant

Footprint: ~ 7 meters by 15 meters
Capacity: ~15 kg/hr lignin

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Kraft Lignin Pilot Plant

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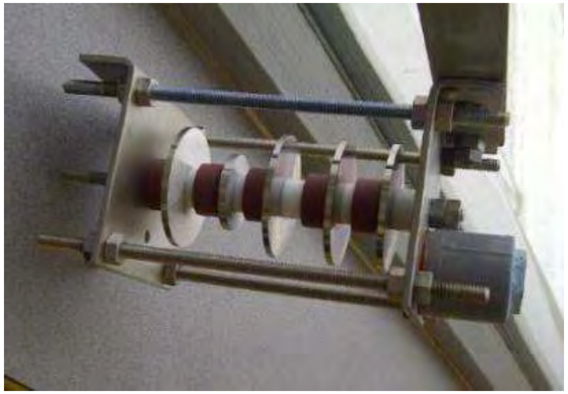
Pilot vs. Commercial Scale

- Pilot plant experience applied to commercial plant design (material selection, equipment selection, design/configuration, etc.)
- Coupons tested in the pilot plant and commercial plant (longer term study)
- Learning what not to do is as important as learning what to do…

Before>



After>

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Lignin Scale-Up Team

- West Fraser Hinton Pulp
  - Plant owners and host site
- Noram Engineering
  - Engineering and equipment supply
- Engineering & Trades contractors
  - Civil, electrical, BOP Engineering
  - Mechanical installation, piping, electrical
- FPInnovations
  - Assist with equipment and material selection based on pilot plant experience (e.g. press cloths, sensors, etc.); process modeling
  - fundamental R&D for product development, support end user trials

Implementation at Hinton

- Re-purposing of an existing mill area
  - some challenges - working within an operating plant e.g. construction near running equipment; demolition of obsolete equipment; isolation issues (water, steam and air lines)
- Mill interface points: black liquor feed, lean liquor return
  - Modelling showed minimal impact to evaporators
- Hot water produced → steam savings
- New CO_2 tank required
- Oxygen was available from an existing system
- Vent collection from all tanks, tied to mill system
- Sewers – segregate acidic waste

Plant Layout and Equipment

- Layout largely determined by existing structure
- Idled pulp machine area > 2 floors
  - Some equipment is 2 floors high, used existing floor openings where possible
- Convenient location, good foundation, close to most utilities
- Crane in area + hoistways

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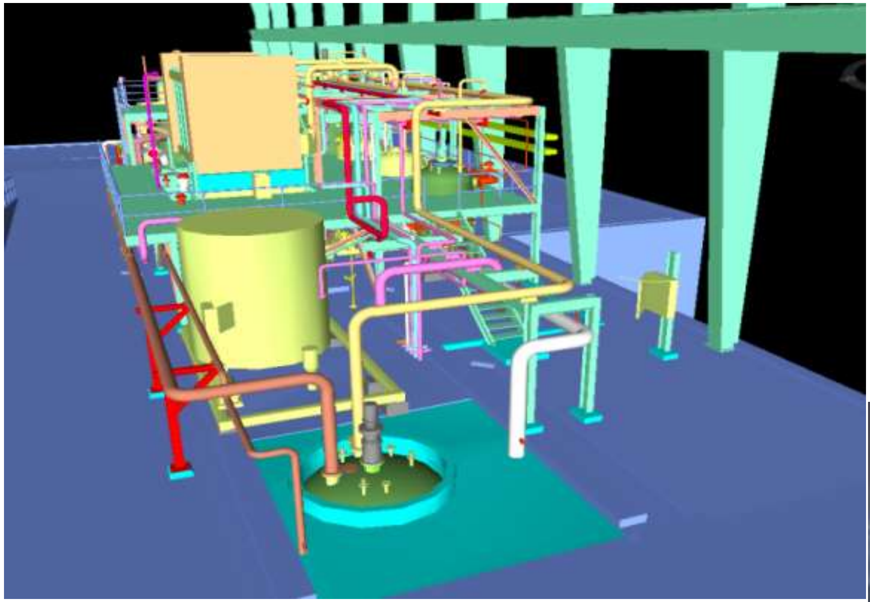
Equipment Installation

- Tricky access for equipment
  - Existing plant layout led to maximum size for incoming equipment skids
- Equipment delivered as modular skids
  - Complete with valves, instrumentation, wiring
  - Minimize site installation time
- Equipment delivery staged in specific order

LRP Commissioning

- Performed in phases
- First Phase Focus: interface with operating plant, startup of liquor filters and reactors to make quality slurry
- Second Phase Focus: pressing, washing and packaging
- Third Phase: Validate continuous and stable operation of all components

Hinton LRP –
Design → Completion!



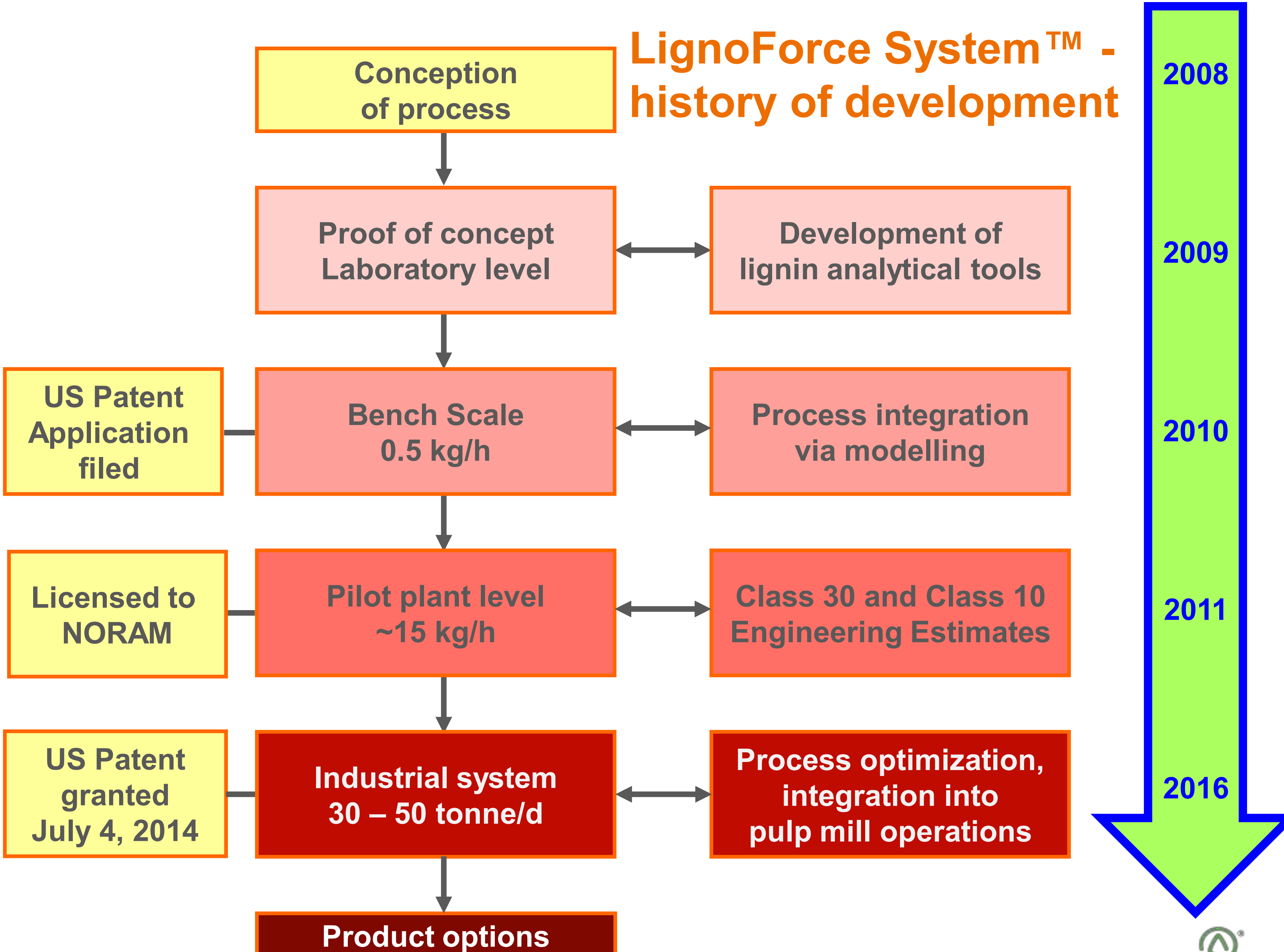
First commercial scale LignoForce plant

Production Capacity: 30 tonnes/day

LRP Commissioning Summary

- Precipitation, coagulation worked as expected
  - Chemical consumption mirrored pilot plant results
- Lignin quality on spec
  - Low ash content; good solids content from press
- No injuries or safety issues during installation and startup
- A few challenges
  - mainly peripheral (mechanical issues- e.g. pump seals etc.; sensors, calibration)

LignoForce System™ - history of development



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Kraft Lignin – Product Development

- Developing a robust lignin-making process is important; using the lignin in commercial quantities is equally important!
- Product development began early for launch market (wood based panels – a good fit)
  - Must expand beyond launch market – the more applications the better
- Modifying lignins to expand their functionality is a natural extension to the work of extracting lignin
  - Copolymerization, depolymerization and/or derivatization expand potential lignin applications or boost efficacy
- Other lignin sources
  - Worth comparing different lignins alongside kraft

How can we use the unique attributes of lignin to make high value products?

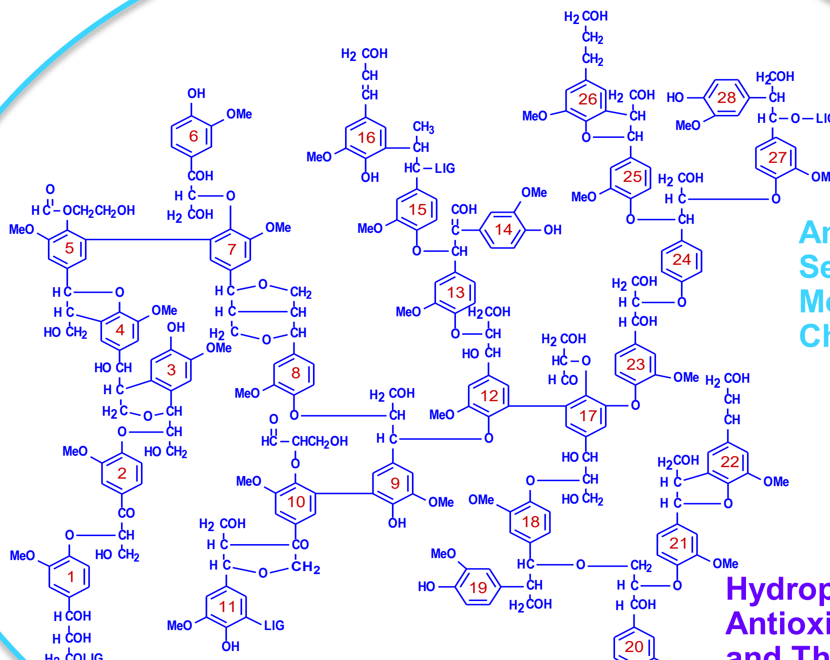
Adhesive in Wood Products

Adhesive in Pellets

Polyol in Polyurethane Foams

Adhesive in Foundry Resins

Binding Properties

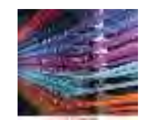


Chemicals

Epoxy Resins

Amenability to Several Modification Chemistries

Dispersants Flocculants



Activated Carbon

Hydrophobic, Antioxidant, and Thermal Properties

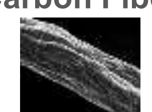
Thermoplastics and Composites

Carbon Black

High Carbon Density

Packaging

Carbon Fiber



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Kraft Lignin – typical properties

Lignin type/chemical composition	SW Lignin	HW lignin	Eucalyptus lignin
Wet lignin solids, wt%	45-65	45-68	45-66
pH @ 15wt% solids	1.7-5.9	1.9-3.8	1.8-3.9
Ash, wt%	0.10-1.5	0.04-1.2	0.3-0.8
Na, wt%	0.05-0.60	0.01-0.30	0.03-0.1
S, wt%	1.3-2.1	1.7-2.6	1.7-2.1
UV-lignin, wt%	92-98	96-97	95-97
Carbohydrates, wt%	1.2-2.4	0.26-1.8	0.25-1.1

Kraft Lignin - main functional groups

Lignin type/functional groups	SW lignin	HW lignin	Eucalyptus lignin
Carboxylic hydroxyl, mmol/g	0.20-0.50	0.11-0.40	0.28-0.30
Aliphatic OH, mmol/g	1.4-2.1	1.3-1.6	1.1-1.2
Phenolic OH, mmol/g	1.3-1.8	2.2-3.2	3.1-3.3
Condensed unit OH, mmol/g	1.1-1.6	0.31-0.50	0.33-0.38
Total OH groups, mmol/g	4.3-5.7	4.1-5.6	4.7-5.2

Kraft Lignin - MW and thermal properties

Lignin type/MW and thermal properties	SW lignin	HW lignin	Eucalyptus lignin
Molecular weight (Mw) using the UV detector, Dalton	6000- 12500	2635-6249	2100-2700
Polydispersity index	3.0-4.6	2.4-4.1	1.9-2.9
Glass transition temp., °C	162-185	133-152	118-128
Initial decomposition temp., °C	212-358	220-260	255-266
Calorific Value, BTU/lb	11200- 11800	10200- 11200	10800- 11200

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Lignin as a fuel in the lime kiln

- The lime kiln is the main consumer of fossil fuels at kraft pulp mills
- Prior FPInnovations work at UBC, demonstrated the technical feasibility of burning lignin in a pilot lime kiln
- Stora Enso is currently replacing the fossil fuel with dry lignin in the lime kiln
- Market size: enormous
- Lignin value: $150/tonne at a natural gas price of $6/GJ and $200/tonne at an oil price of $50/barrel

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Lignin in phenol formaldehyde (PF) resins for wood products

- **Commercial PF resin forms:**
  - liquid
  - dry solids (40% higher price)
- **Advantages of lignin:**
  - Rich in phenolic structures
  - Lower cost
  - Reduced formaldehyde emissions
- **Disadvantages of lignin:**
  - Slower cure rate at high substitution rates
  - Increased swelling in some wood products at high substitution rates
- **Market size (20%):** 200,000 tonne/y
- Lignin value: $1500-2000/tonne

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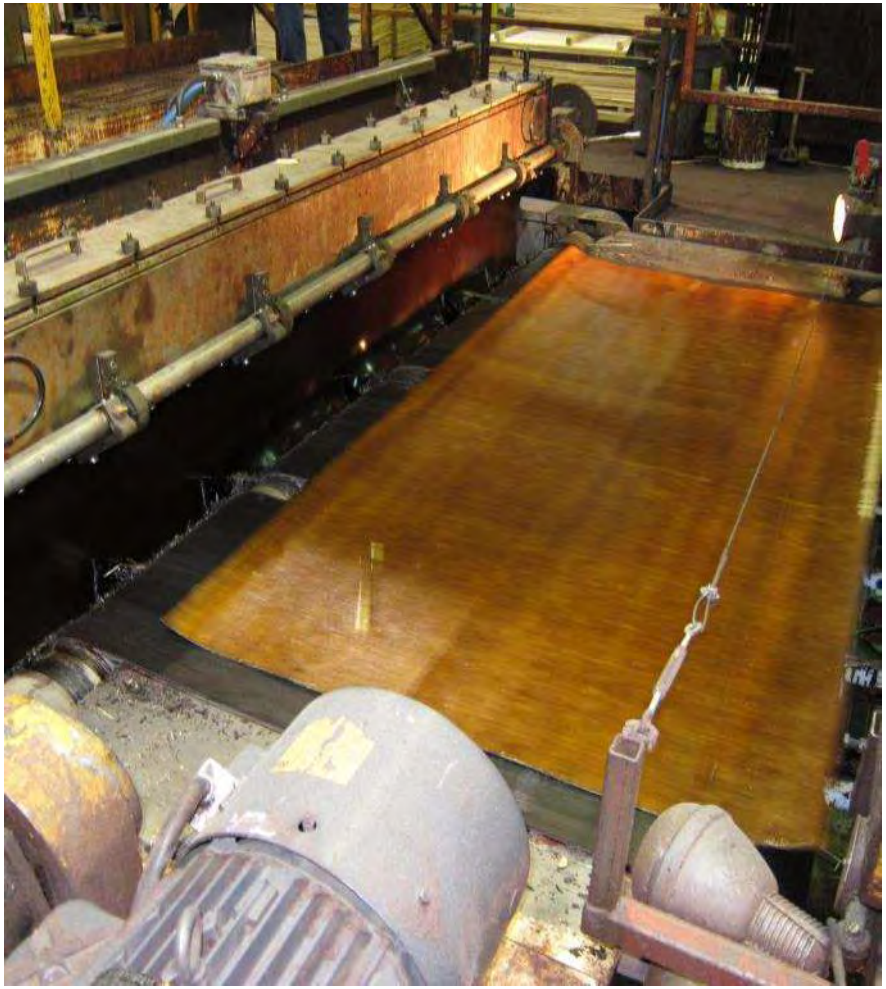
Successful mill trials incorporating lignin in PF resins for wood products

1. Replacement of 50wt% of fillers with lignin in plywood glue (Mill A)
2. Replacement of 10wt% of PF resin with lignin in plywood glue (Mill B)
3. Replacement of 15wt% of PF resin with lignin in plywood glue (Mill B)
4. Replacement of 20wt% of solids (fillers & PF resin) in plywood glue (Mill B)
5. Replacement of 33wt% of phenol with lignin in liquid PF resin for OSB (Mill C)
6. Replacement of 36wt% of phenol with lignin in powder PF resin for OSB (Mill D)



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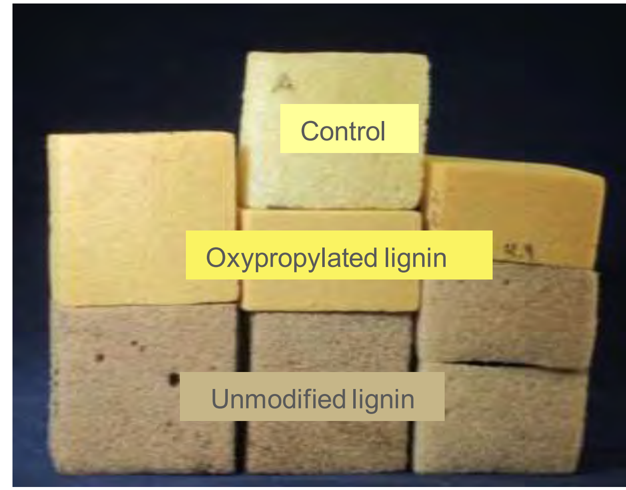
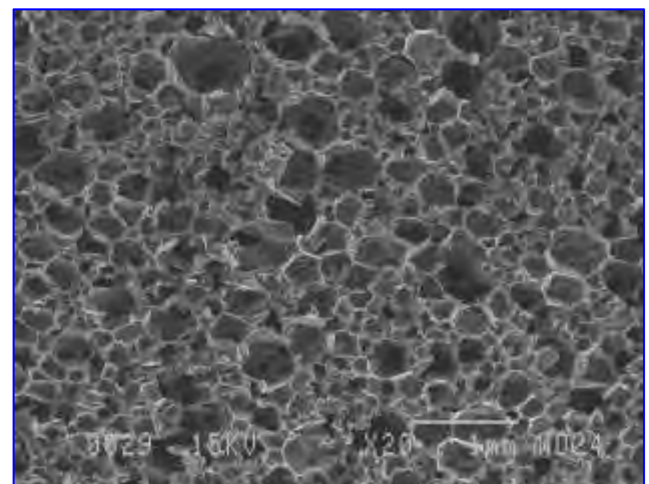
Lignin in rigid polyurethane (PU) foams

- To make PU foams isocyanate is reacted with petroleum-based polyols
- Lignin is a natural polyol as a result of its numerous phenolic and aliphatic hydroxyl groups
- Lignin-based polyols are potentially useful for making rigid PU foams with good thermal degradation (fire-resistant) properties
- FPInnovations prepared PU foams in which as much as 20wt% of polyol was replaced with lignin
- The properties of these foams (e.g. density, compressive strength, water absorption and thermal conductivity) were comparable to the control
- Market size (20%): 280,000 tonne/y
- Lignin value: >$2000/tonne





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Properties of lignin-based PU foams

	Foam density (kg/m^3)	R-value by inch	Water absorption (%, v/v)
Polyol (control)	39.4	4.38	2.4
SW kraft lignin	42.7	5.04	0.7
HW kraft lignin	39.2	4.38	1.8

Lignin in thermoplastics

- Incorporation of lignin into thermoplastics represents by far the largest market opportunity
- Lignin market size (1% of PP, PET and PS): 1.1 million tonnes
- Growth rate: 5%
- Lignin value: $1500-2000/tonne
- A very segmented industry with diverse needs with respect to raw materials, mechanical and other properties
- So far, two successful commercial products are emerging from our collaboration with an industrial partner:
  - Compostable bags (30% lignin)
  - Utensils of high renewable content (40% lignin)

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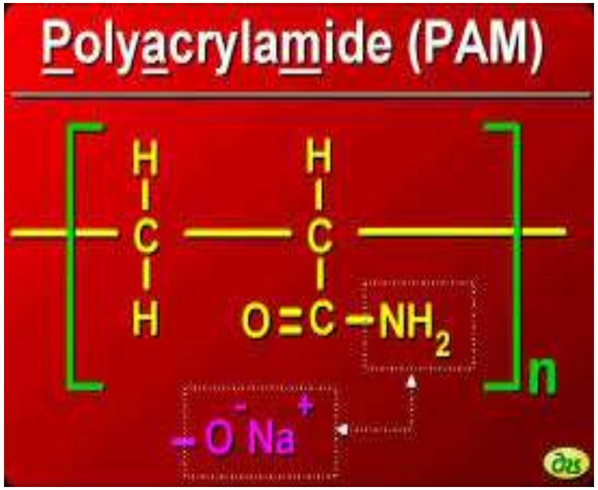
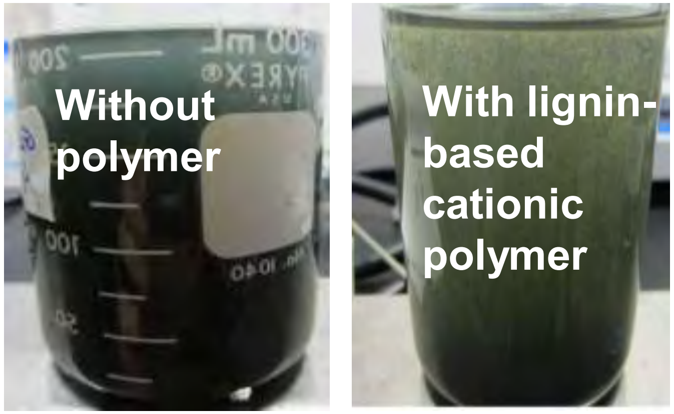
Lignin in water-soluble polymer applications

- Water-soluble polymers are organic substances that dissolve, disperse or swell in water thus modifying the physical properties of aqueous systems
- These polymers usually contain hydrophilic groups which may be anionic, cationic, amphoteric or nonionic
- Examples include: polyacrylamide, polyacrylic acid, polyvinyl alcohol, polyethylene glycol, polyamines and nonionic polyurethanes
- Large markets in: mining, oil, paint, cement admixture, wastewater treatment and pulp & paper industries
- Market size (20%): 600,000 tonne/y
- Growth rate: 4.1%
- Lignin value: >$2000-3500/tonne





Unclarified green liquor

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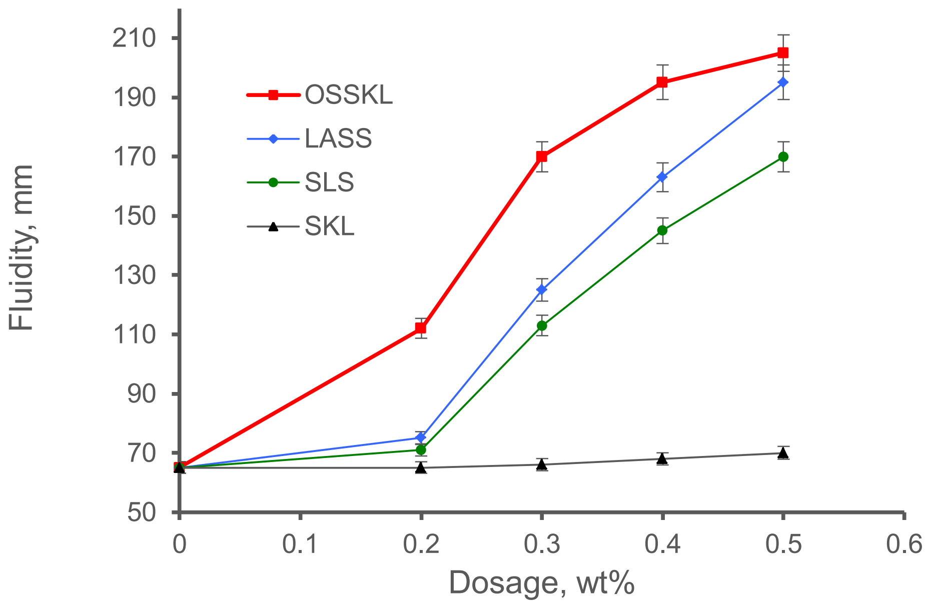
Using sulphonated LignoForce lignin as a dispersant/water reducer for concrete (Prof. Pedram Fatehi's Group, Lakehead University)



SKL: softwood kraft lignin (LignoForce)
SLS: sodium lignosulphonate (commercial)
LASS: sodium lignosulphonate (commercial)
OSSKL: sulphonated softwood kraft lignin (LignoForce)

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Summary

- Developing and scaling up a new process is a long journey requiring a committed, multidisciplinary team and good partners
- Pilot plants are a key step in moving from the lab to commercial scale
  - Large samples (100's of kilos to tonne scale) are required to convince producers and users to invest
- The first LignoForce™ commercial plant is now running in Hinton, Alberta (West Fraser), supplying high-quality kraft lignin
- Important to consider Product Development in parallel with Process Development; need multiple applications to support and develop the lignin market
- Lignin of various types and in various forms has great potential in high-value applications

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Acknowledgements

- Funding agencies
  - Natural Resources Canada (NRCan)
  - CRIBE (Ontario)
- Licensee
  - NORAM Engineering
- FPInnovations Member Companies
  - West Fraser
  - Resolute
- Academic partners
  - Prof. Charles Xu, Western University
  - Prof. Pedram Fatehi, Lakehead University

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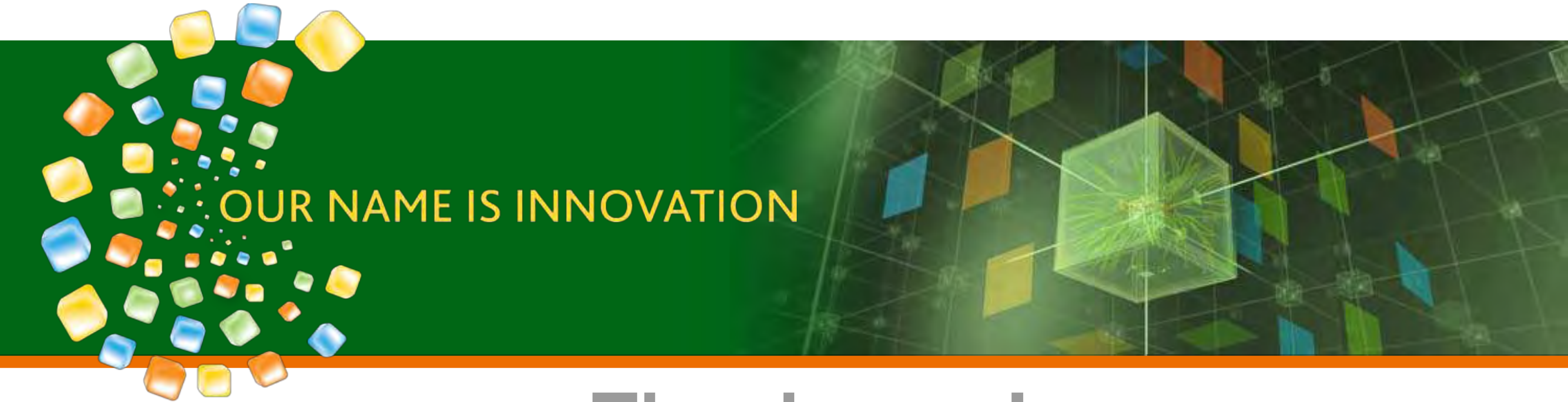

Thank you !

For more information contact:

Kirsten Maki

Bio-economy Technology Centre, Thunder Bay

kirsten.maki@fpinnovations.ca

807-475-2685

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