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Chemicals and Fuels from Lignocellulosic Materials

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Two Broad Themes….

- Cellulosic ethanol from agricultural biomass (Serge Laberge, AAFC, laberges@agr.gc.ca, 418-210-5028)
- Chemicals from pulp and paper biomass (John Schmidt, FPInnovations, john.schmidt@fpinnovations.ca, 514-630-4101 x2370)

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Cellulosic Ethanol

- Sustainable ethanol production requires:
  - Growth of biomass
  - “Deconstruction” of biomass to release cellulose
  - Conversion to simple sugars
  - Bacterial or yeast fermentation
- Agricultural Bioproducts Innovation Program (ABIP)
  - AAFC initiative on agricultural biomass
  - NBP project will be complementary

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Cellulosic Ethanol – Objective 1

- Pretreatment of biomass extract cellulose
  - Microwave
  - Ultrasound
  - Chemical catalysts
  - Cell wall “loosening” enzymes e.g. feruloyl esterase, cutinase, to allow access to cellulose
  - Cell wall degrading enzymes, e.g. cellulase, the break cellulose down into digestible sugars
  - Biotechnology Research Institute (BRI), Insititute for Biological Sciences (IBS)

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Cellulosic Ethanol – Objective 2

- Lower cost of enzymes by producing them in oil-seed plants
  - Plant oils are main product
  - Enzymes can be extracted from the leftover meal
  - Alternatively, enzymes can be allowed to breakdown carbohydrates left in the meal to digestible fragments for animal feed, e.g., pigs
  - Plant Biotechnology Institute (PBI)

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Cellulosic Ethanol – Objective 3

- Yeast and/or bacteria that
  - ferment arabinose more efficiently
  - tolerate inhibitors better
  - can ferment 5-carbon sugars
  - produce enzymes to break down fibre and digest cellulose
  - BRI

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Cellulosic Ethanol – Interested?

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Chemicals from Forestry Biomass via Chemical Pulp Mills

- Wood chemistry
- Ethanol economics in a pulp mill
- Chemical streams available from North American pulp mills
  - Lignin, hemicellulose
  - Paprican biorefinery activities
- Projects in NBP

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Chemical Composition of Wood

Cellulose	Hemicellulose	Lignin
45 – 50%	20 – 25%	20 – 25%

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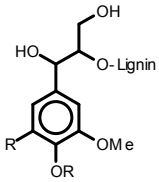
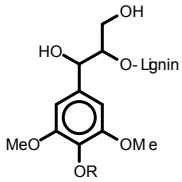
Lignin

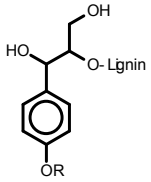
A branched, phenyl propane polymer



Guaiacyl
softwoods
hardwoods



Syringyl
hardwoods
only



Ferulate
grasses

R = H or interunit link

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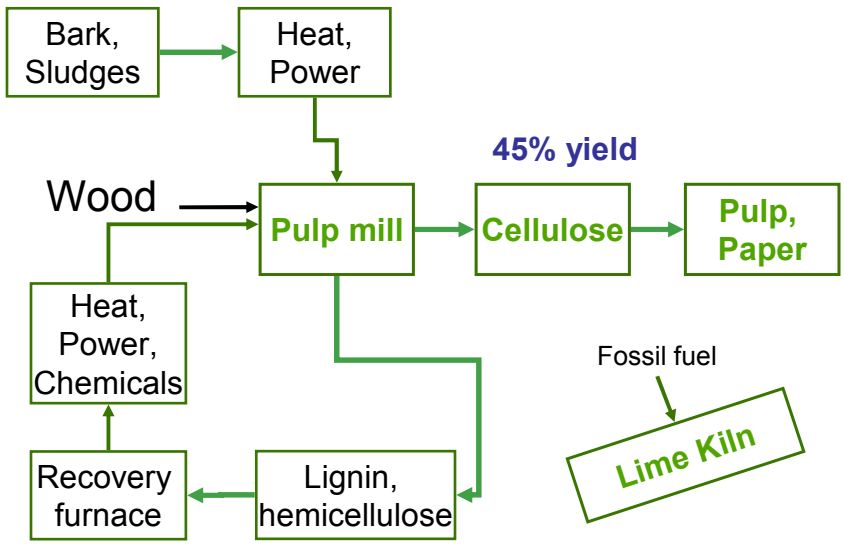
Chemical Pulp Mills



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Ethanol Economics in a Chemical Pulp Mill

- Black liquor @ 15 GJ/t, $10/GJ = $150/t
- Lignin @ 20 GJ/t = $200/t
- Hemis @ 10 GJ/t = $100/t
- Pulp sells for $800/t
- Ethanol at the mill gate earns $0.50 per litre
- Wood costs $80/t delivered

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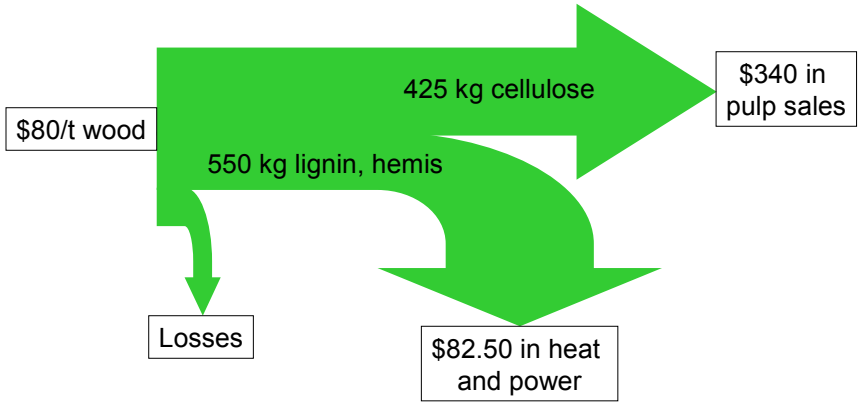
Pulp Only – The Status Quo



Total sales: $340
Net benefit: $260

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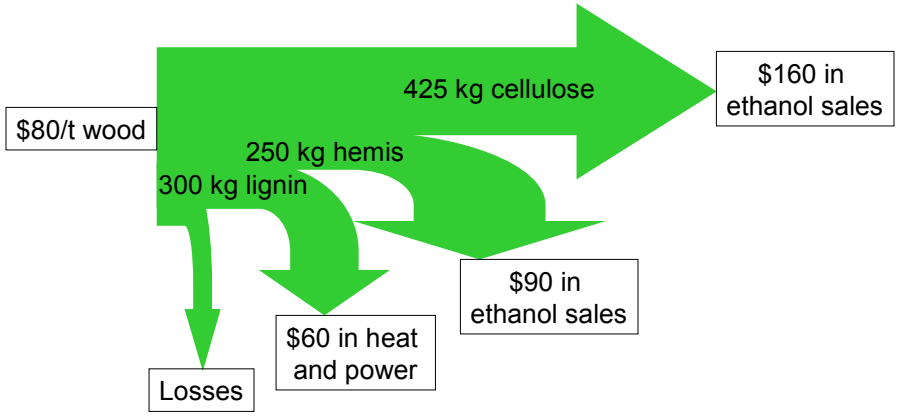
Cellulose to Ethanol



Total sales: $250
New fuel purchases: $22.50
Net benefit $147.50

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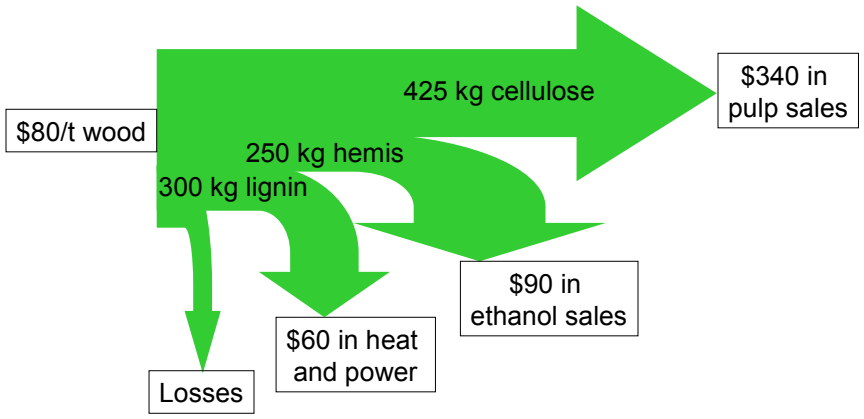
Cellulose + Ethanol



Total sales: $430
New fuel purchases: $22.50
Net benefit $327.50

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Economics Tell Us That We Should:

- Keep making pulp …
  - … unless we can get more than $800/t for the cellulose
- Identify new products for non-cellulose portion
  - Value must exceed value of the fuel we will need to buy, or the steam savings we will need to find in the process
  - Value must also pay for capital modifications

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Chemical Pulp Plants in Canada

- About 15 million tonnes of pulp annually
- Another 19 million tonnes of lignin and hemicellulose are burned annually
  - Not all is recoverable
- Typical Canadian pulp mill produces:
  - 1000 t/d pulp
  - 1300 t/d lignin, hemicellulose

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Lignin Precipitation and Use

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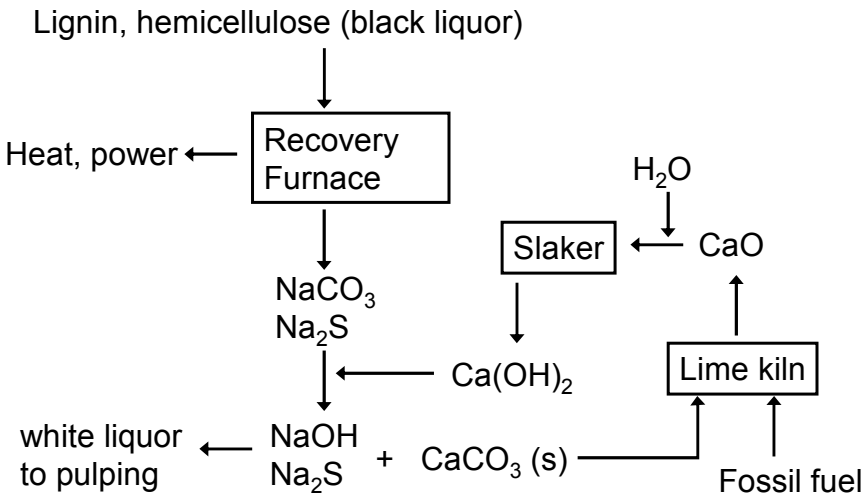
Kraft Recovery and Recausticization



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Lignin Precipitation and Use

- 60-70% of North American kraft mills are recovery boiler limited
- Boiler expansion is $$$$ capital
- Offload boiler by precipitating lignin
  - Immediate benefit of incremental capacity increase
- Typical mill will off-load 35-50 ton/day
  - 1.5M ton/yr potential estimated for North America
- What to do with the lignin?

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Lignin Precipitation and Use

- Scenario 1: lignin as fuel in lime kiln
  - Analysis for a western mill
  - @$190/t fuel value, $2.3M/yr net savings
  - Payback is 4.3 yrs
- Scenario 2: $1,000/t for lignin as a feedstock
  - Net savings $10.8M/yr
  - Payback reduced to 0.9 yrs

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Lignin Products Opportunity Analysis

- MBA co-op student conducted a detailed market study of four potential lignin products
- Replace carbon black in tires ($2000/tonne)
  - Lakehead University with support from FPInnovations and Goodyear, NSERC proposal approved, $400,000 over 3 yrs
- Replace phenol in PF resins ($2000/tonne)
  - Collaboration with FPInnovations Forintek
- Replace polyacrylonitrile (PAN) ($3000/tonne) in carbon fiber manufacture

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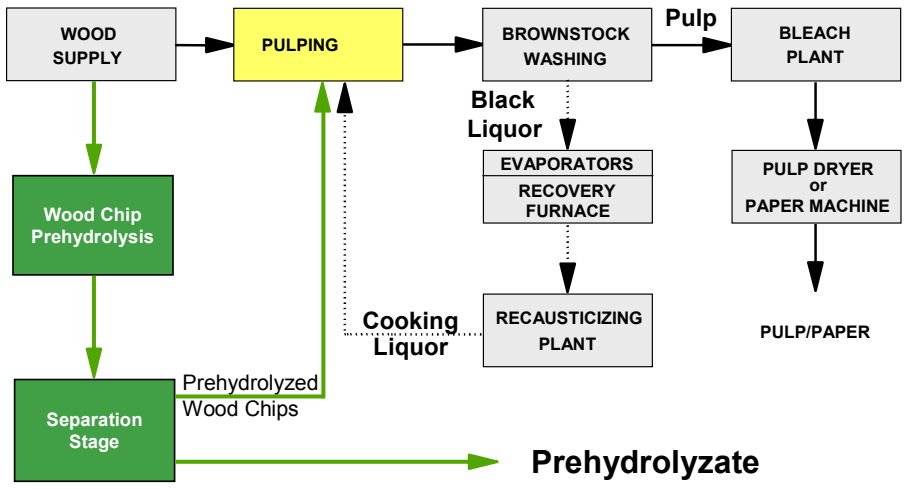
Hemicellulose Extraction in a Kraft Mill



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Prehydrolyzate – What's in it, What to do with it ?

Softwoods: hexoses

Hardwoods: xyloses

Acetic acid

Phenols

Fuels

Fermentation to alcohols

Aqueous reforming to hydrocarbons

Chemicals

Sorbitol

Xylitol/Arabinitol

Furfural

Glycerol

1,4 diacids

Others from "DOE dozen"

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Chemicals - Objective 1

- Single-walled carbon nanotubes (SWCNT) from lignin
  - substitute or modifier for carbon fibre, large demand from aerospace and automotive industries
  - Can be metallic or semiconducting
  - Currently made from carbon black
- Steacie Institute for Molecular Sciences (SIMS): strong research program, 1 kg/day pilot plant
- FPInnovations Paprican to supply kraft lignin, expertise from its biorefinery program
- Lignin available from waste wood-to-ethanol processes: Lignol, Biovision
- Biotechnology Research Institute (BRI): lignin characterization, analysis, pretreatment by microwave, ultrasound, bioconversion

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Chemicals – Objective 2

- Lignin as a substitute for phenol in phenol-formaldehyde resins
- Existing program at FPInnovations in Paprican and Forintek Divisions
- BRI expertise microwave, ultrasound, bioconversion for lignin modification
- Possible connection to SWCNT – nanocomposite PF resin where both nanofibre and resin are derived from biomass?

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Chemicals – Objective 3

- Substitution of kraft lignin for carbon black in tires
  - Prof. Aicheng Chen, Lakehead University with support of NSERC, FPInnovations Paprican, Goodyear
  - Exploring connection with SWCNT

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Chemicals – Objective 4

- Feruloyl esterase – breaks down plant cell walls to liberate cellulose, ferulic acid is also potential source of industrial chemicals
- Bioconversion processes to break down lignin (wood and non-wood) to useful aromatic chemicals
- Expertise at BRI

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Chemicals – Objective 5

- Furfural from hardwood hemicellulose fractions
  - Continuing FPInnovations Paprican interest
  - BRI nanocatalytic technology to enhance furfural yields from xylose
- Hydroxymethyl furfural from softwood hemicellulose
  - BRI nanocatalysts that can convert this to 2,4 furan dicarboxylic acid – a potential replacement for terephthalic acid (component of PET plastic)

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Summary - Chemicals

- Links between FPInnovations, BRI, SIMS, Lakehead U. on
  - SWCNTs from lignin
  - Lignin for carbon black in tires
  - Lignin in PF resins and composite materials
  - Other value-added chemicals from lignin
  - Furfurals from hemicellulose
- Can we make links with chemical industry?

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