University of Maine Forest Biorefining Concept

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Forest Biomass Potential

- Cellulose is the most abundant organic chemical on earth at an annual terrestrial production of 90 billion tonnes/year
- On energy basis, carbon synthesis by plants is equivalent to ~10 times world consumption
- Forest biomass is carbon neutral

➔ Managed forests have enormous potential to reduce "green-house gas" emissions by generating liquid fuels and bioproducts

Forest Products Challenge

- Due to global competition, prices for forest products decrease by about 1% per year.
- Wood/biomass cost is correlated with energy cost, so feed stock price is increasing
- Profitability is “squeezed” from both sides

➔NA forest products industry desperately needs more revenue from higher value-added products besides wood, pulp and paper products

US Market (2004) of Products in Million Metric Tons per Year

Market	Pulp	Corn	Gasoline	Ethanol	Unsat. Poly-esters	Poly-urethanes	Carbon Fibers
10^6 metric tons	50	260	390	10	0.8	3	0.01

- Ethanol market to replace gasoline is "unlimited"
- In petroleum refinery only 5% goes to chemical products
- Markets for polymers and materials in structural materials are significant, but need to grow

Prices (2005) of Feedstocks and Products

Price	Pulp Wood	Corn Kernels	Glucose	Ethanol	Hardwood Kraft Pulp
US$/MT	75	100	250	840	500
Details	Oven Dry	US$2.5/ Bushel	15ct/lb	US$2.50/ Gallon	Market Price

- Corn is highly competitive
- Hardwood pulp has a lower value than ethanol!

Fuel Costs in Forest Biorefinery

Fuel	Heating Value (GJ/MT)	Fuel Cost (US$/MT)	Energy Cost (US$/GJ)
Oil	43.5	512 (US$60/barrel)	11.8
Biomass (20% moisture)	15	55	3.7
Black Liquor (20% moisture)	12.6	75 x 3/4 = 56 (org/inorg = 3/1)	4.4
Lignin	26.9	75	2.8
Carbohydrates	13.6	75	5.5

- Do not use oil!
- Obtain energy from biomass and/or black liquor!
- Minimize use of carbohydrates for energy purposes

Value of Cellulose Pulp Fibers

- Maximum theoretical yield of ethanol from cellulose pulp on weight basis is ~ 50%
- Ethanol price must be > $1000/MT ($3.00/gallon) for economical conversion of pulp into ethanol
- Cellulose has high crystallinity, is durable and has unique structural properties

→Use cellulose pulp directly in a final product

Value of Hemicelluloses

Hemicelluloses: - have low fuel value
- are valuable in pulp
- degrade during pulping

→**Extract hemicelluloses before pulping**

→**Use extract for production of biofuels and bioproducts**

→**Benefits of hemicellulose extraction on pulp production:**

– Decreased alkali consumption
– Reduced organic + inorganic load to recovery
– Increased delignification rate

Principles for Forest Biorefinery

- Alkaline pulping process is proven and most economical ligno-cellulosic separation process.
- Pulp mills have infrastructure and permits for wood conversion.
- Extract hemicelluloses before pulping or wood processing, and use hemicelluloses for ethanol, chemicals or polymer production.
- Convert lignin in black liquor in transportation fuel, chemicals and structural materials
- Use extra biomass to replace black liquor energy.
- Biorefinery is highly energy integrated, and does not use fossil fuel
- Pulp remains important product.

Hemicellulose Conversion Strategy

- Produce oxygen containing products to increase yield, shorten conversion path and competitiveness relative to petroleum-based
- Produce alcohols, carboxylic acids, lactones, and esters
- Fermentation may provide stereo-specificity
- Catalytic reactions in aqueous systems are also of interest
- Should work for both C5 and C6 sugars

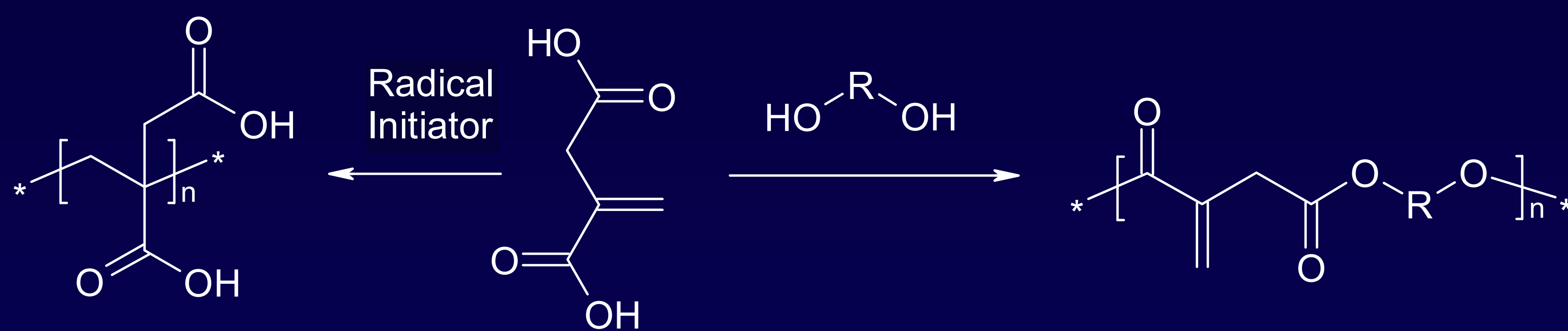
Examples of Hemicellulose-Derived Chemicals

- **Ethyl levulinate**, a diesel additive. Made from esterification of levulinic acid with ethanol
- **1,3 propane diol**, the monomer for Dupont polyester Sonomo® made from this diol and phtalic anhydride. Diol is made from HPA.
- **Poly-itaconic acid.** Made from sugar monomers by fermentation and then polymerization.
- **Engineered wood products**. Use of the new unsaturated polymers in wood composites (for example polypropylene fumarate?)
- **1,2 propylene glycol.** Non toxic anti freeze

Polymerization of Itaconic acid

Radical homopolymerization to polyitaconic acid

Copolymerization to polyester

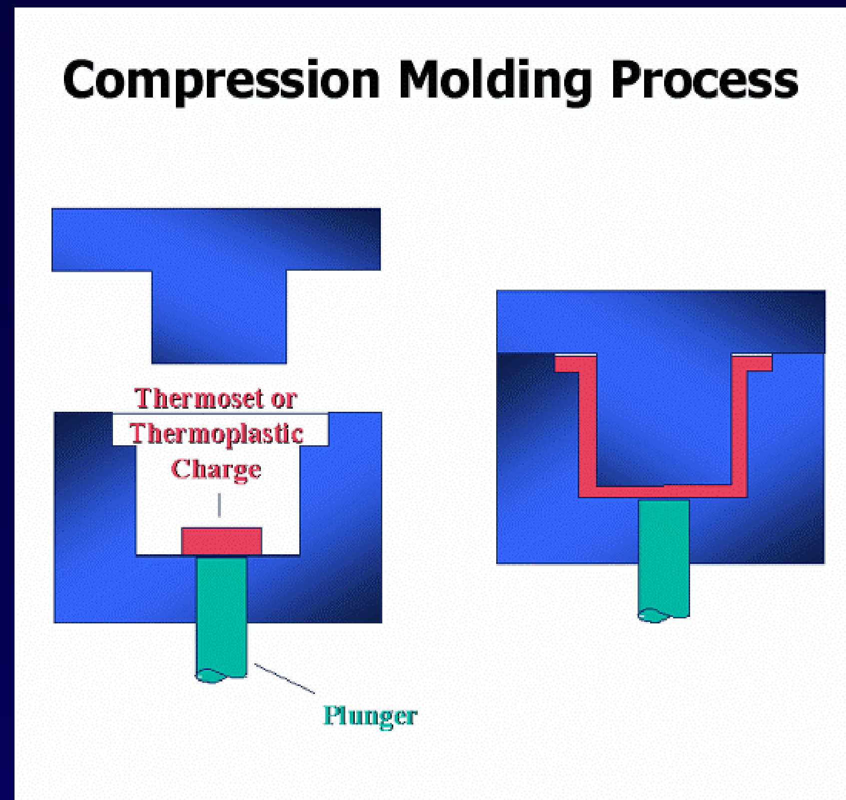


Dispersion chemical in paper coating

Unsaturated resin for cross linking in wood composites and SMC

Sheet Molding Compound (SMC)

- Compression SMC replaces metal because it is lighter at the same strength and does not rust
- Uses polymers which may be sugar based.
- Uses glass fibers, but could also use cellulosic fibers



Separation and Purification Research and Development Issues

- Important because it represents 60-80% of cost of mature chemical processes
- Concentration of aqueous extract by recirculation and multiple effect evaporation
- Selective cleavage of lignin-carbohydrate bonds needed
- Separation of sugars, lignin, acetic acid, etc. by extraction, membranes, chromatography?
- Separation of product by pervaporation?

Lignin Precipitation

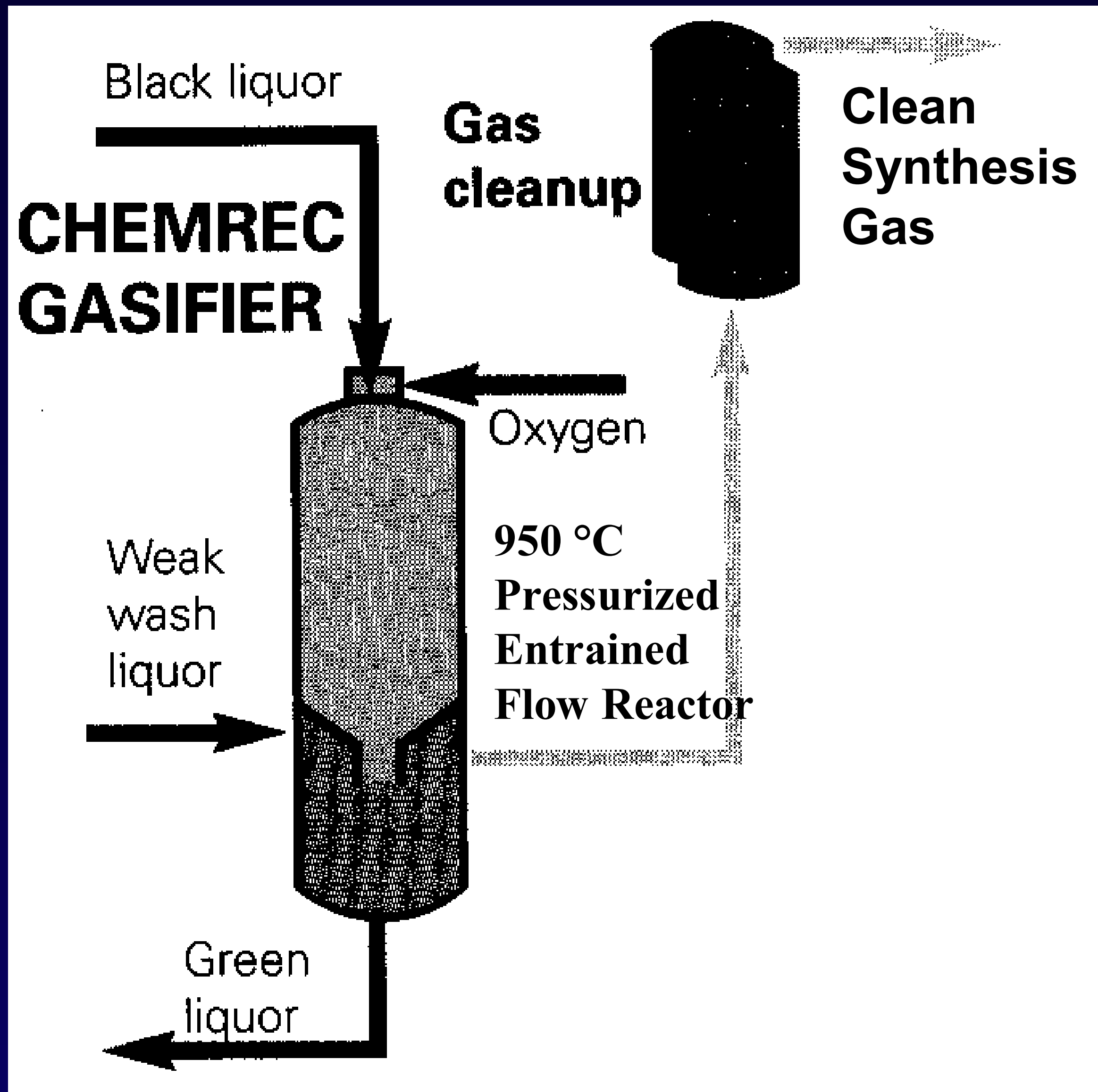
- Lignin precipitation from black liquor by acidification with CO_2 to pH = 10
- Acid wash of filtered lignin to remove sodium
- Low sulfur content when using soda-AQ pulping
- Carbohydrate content of precipitated lignin?

Lignin-Reinforced Polyurethanes

(adapted from Shaw Hsu)

	Modulus (MPa)	Tensile Strength At 100% Strain (MPa)	Elongation (%)
6-50 Sample	108	9.7	388
6-50, 5% Hwdlgn Direct Mix	65	5.8	182
6-50, 5% Hwdlgn Heat	160	12.1	373

Black Liquor Gasification



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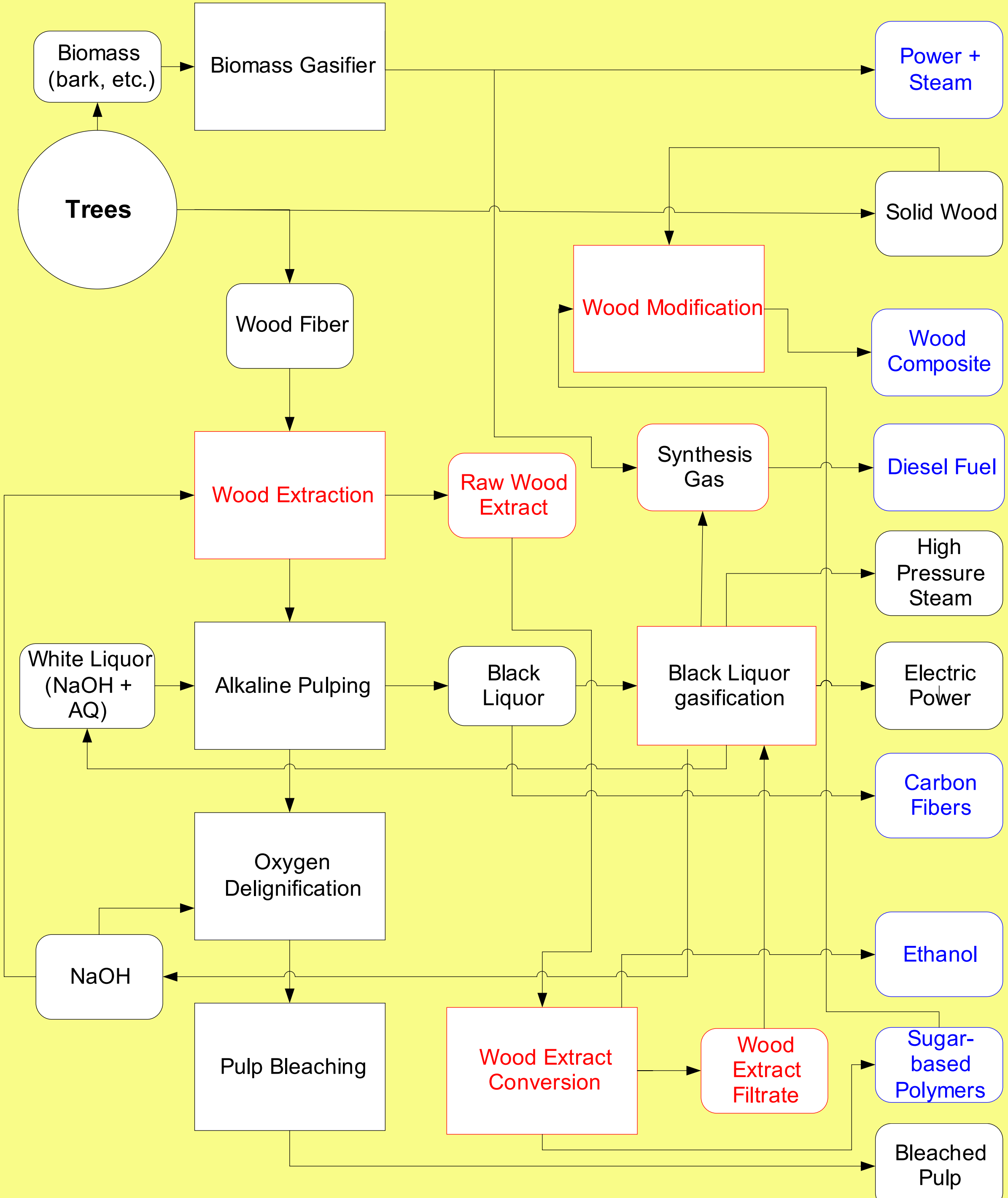
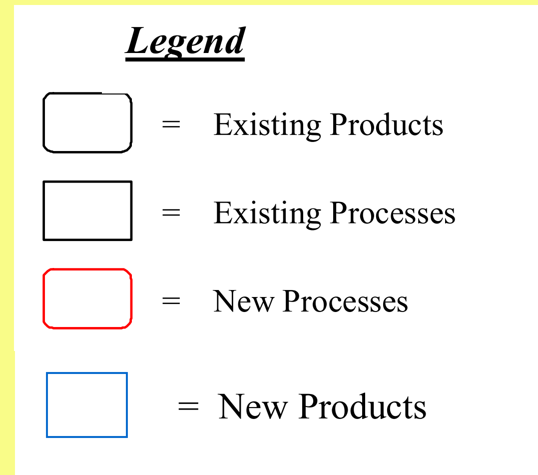


Biomass (bark, etc.)
Biomass Gasifier
Trees
Wood Fiber
Wood Extraction
Raw Wood Extract
Synthesis Gas
Wood Modification
Alkaline Pulping
White Liquor (NaOH + AQ)
Black Liquor
Black Liquor gasification
Oxygen Delignification
NaOH
Pulp Bleaching
Wood Extract Conversion
Wood Extract Filtrate
Power + Steam
Solid Wood
Wood Composite
Diesel Fuel
High Pressure Steam
Electric Power
Carbon Fibers
Ethanol
Sugar-based Polymers
Bleached Pulp



Legend
= Existing Products
= Existing Processes
= New Processes
= New Products

Coproducts Pulp + Transportation Fluids

Pulp Production

Product	Price ($/ODMT)	Yield (%)	Value (US$/ODMT wood)
Kraft pulp	500	45	225
Wood fuel	55	55	30
Total		**100**	**255**

Value-Added: 255 – 75 = 180 US$/ODMT wood

Pulp and Transportation Fluids Coproduction

Product	Price	Wood Yield (%)	Conversion (%)	Value(US$/ODMTwood)
Pulp	$500/ODMT	45	100	225
Ethanol from hemi	$840/ODMT $2.50/gallon	10	43	36
Diesel	$630/ODMT $2.00/gallon	45	40	113
Total		**100**		**374**

Value-Added: 374 – 75 = 299 US$/ODMT wood

Maximizing Value

Present situation

Product	Price ($/ODMT)	Yield (%)	Value (US$/ODMT wood)
Kraft pulp	500	45	225
Wood as fuel	55	55	30
Total		**100**	**255**

Value-Added: 255 – 75 = 180 US$/ODMT wood

Future Situation

Product	Price	Wood Yield (%)	Conversion (%)	Value (US$/ODMT wood)
Kraft pulp	$500/ODMT	45	100	225
Polymer	$3000/MT	10	50	150
PU	$3000/MT	10	45	135
Diesel	$630/MT $2.00/gallon	35	40	88
Total		**100**		**598**

Value-Added: 598 – 75 = 523 US$/ODMT wood

http://www.forestbioproducts.umaine.edu/

Forest Biorefinery NSF-EPSCOR Grant at U Maine

$10 Million Investment in Research Infrastructure

April 1st, 2005 – March 31st, 2008

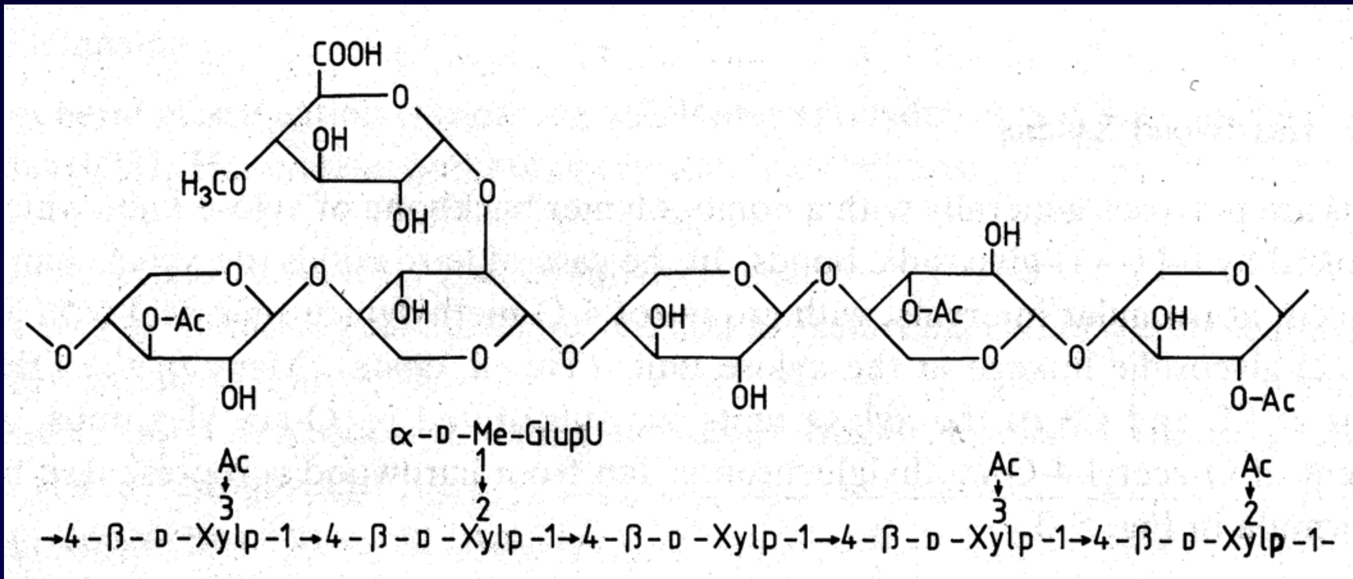
E-mail: forestbioproducts@maine.edu

Conclusions

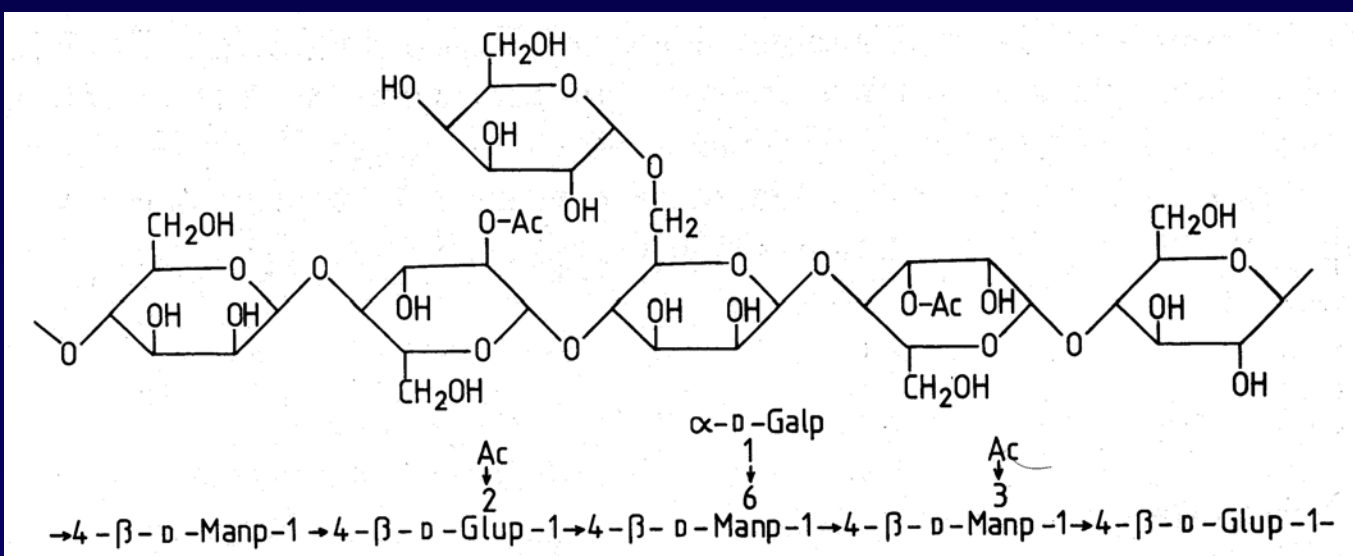
Benefits of Forest Biorefinery:

- **Protects the Core**: Increases the profits in support of traditional forest products production
- **Ecofriendly**: Transportation fuels, power, and bioproducts from a carbon-neutral, renewable resource
- **Lower Capital**: Use existing pulping equipment and infrastructure for production of new, high value-added products besides traditional wood and paper products
- **Synergy**: Full integration of the traditional forest products and new bioproducts will lead to synergies
- **Self-Sufficiency**: Replacement of imported fossil fuels by domestic renewable fuel
- **Employment**: Preserves and creates jobs in rural forest-based communities

Hemicellulose Feed Stock



Hardwood
Arabino-methy glucorono-xylan



Softwood
Acetyl galacto -glucomannan

Top 12 Chemical Building Blocks from Sugars according to DOE

1,4 diacids (succinic, fumaric and malic)
2,5 furan dicarboxylic acid
3 hydroxy propionic acid
aspartic acid
glucaric acid
glutamic acid
itaconic acid
levulinic acid
3-hydroxybutyrolactone
glycerol
sorbitol
xylitol/arabinitol

From Pulp to Transportation Fluids

Pulp Production

Product	Price ($/ODMT)	Yield (%)	Value (US$/ODMT wood)
Kraft pulp	500	45	225
Wood fuel	55	55	30
Total		**100**	**255**

Value-Added: 255 – 75 = 180 US$/ODMT wood

Transportation Fluids Production

Product	Price	Wood Yield (%)	Conversion(%)	Value ($/ODMT wood)
Ethanol from cellulose	$840/ODMT $2,50/gallon	40	47	158
Ethanol from hemi	$840/ODMT $2.50/gallon	25	43	90
Diesel	$630/ODMT $2.00/gallon	35	40	88
Total		**100**		**336**

Value-Added: 336 – 55 = 281 US$/ODMT wood