Pretreatment of Forest Slash using Wet Oxidation

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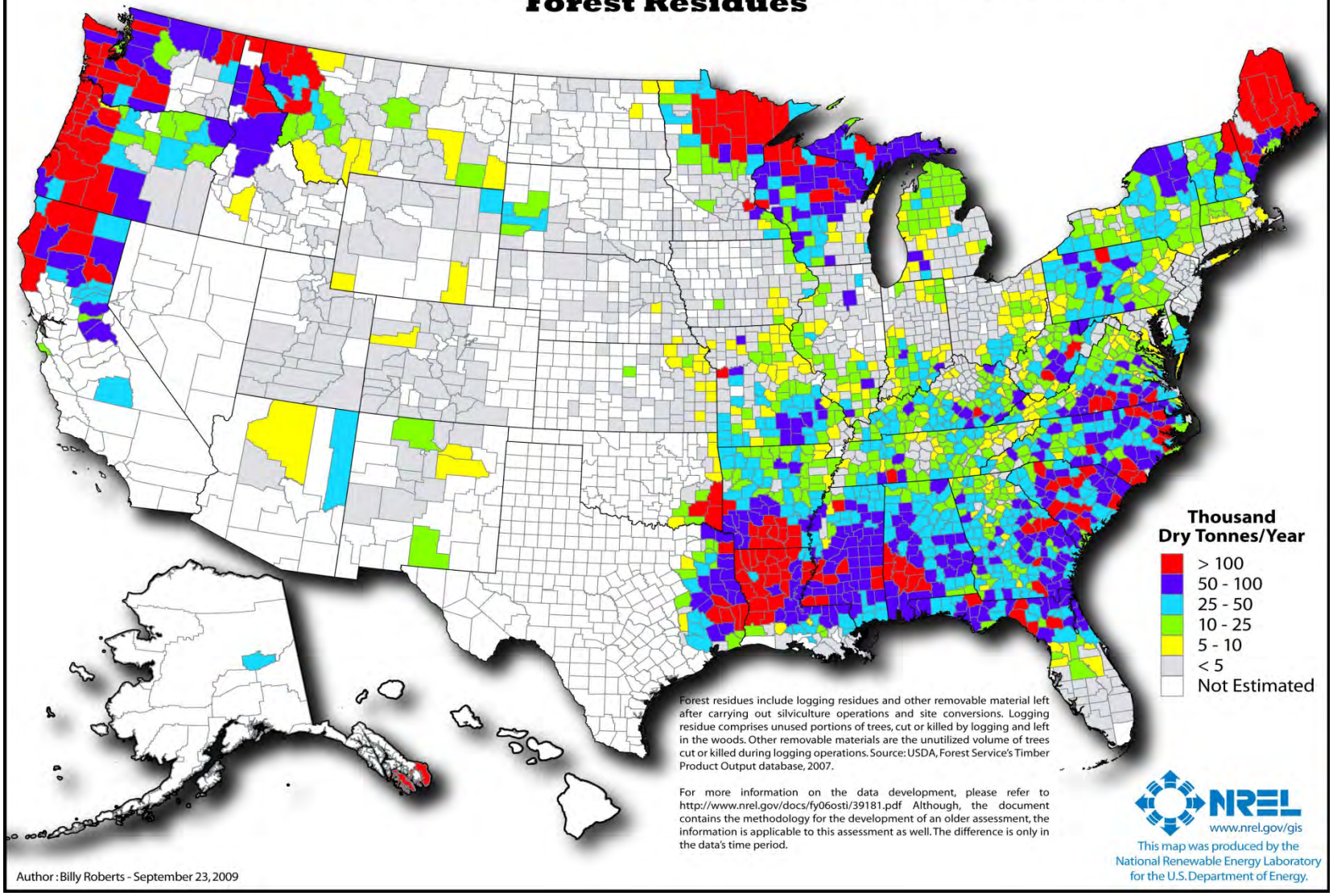
Forest slash: Opportunities and problems for turning Slash to Cash!

- **What is it**: Tops, stumps, leaves and needles that are removed during trunk stripping.
- **What is the opportunity**: Slash tallies 16% of logging activities in the USA resulting in 49 million tons in 2004, according to the U.S. Department of Energy.
- Current slash management includes on site burning, chipping and/or collection at the sides of roads for later pickup and combustion.
- **What is the problem**: Forest slash is bulky, low-density material, usually located in remote logging areas. This abundant, essentially free feedstock can be too expensive to collect and transport.

Biomass Resources of the United States

Forest Residues



Forest residues include logging residues and other removable material left after carrying out silviculture operations and site conversions. Logging residue comprises unused portions of trees, cut or killed by logging and left in the woods. Other removable materials are the unutilized volume of trees cut or killed during logging operations. Source: USDA, Forest Service's Timber Product Output database, 2007.

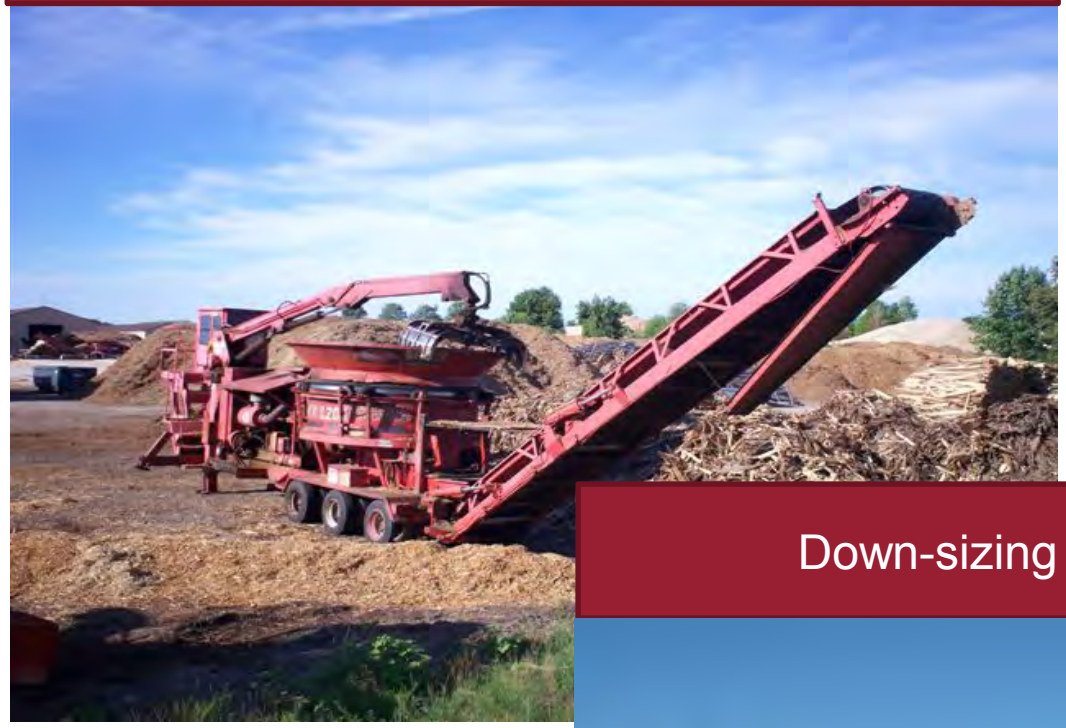
For more information on the data development, please refer to http://www.nrel.gov/docs/fy06osti/39181.pdf Although, the document contains the methodology for the development of an older assessment, the information is applicable to this assessment as well. The difference is only in the data's time period.

NREL
www.nrel.gov/gis

This map was produced by the National Renewable Energy Laboratory for the U.S. Department of Energy.

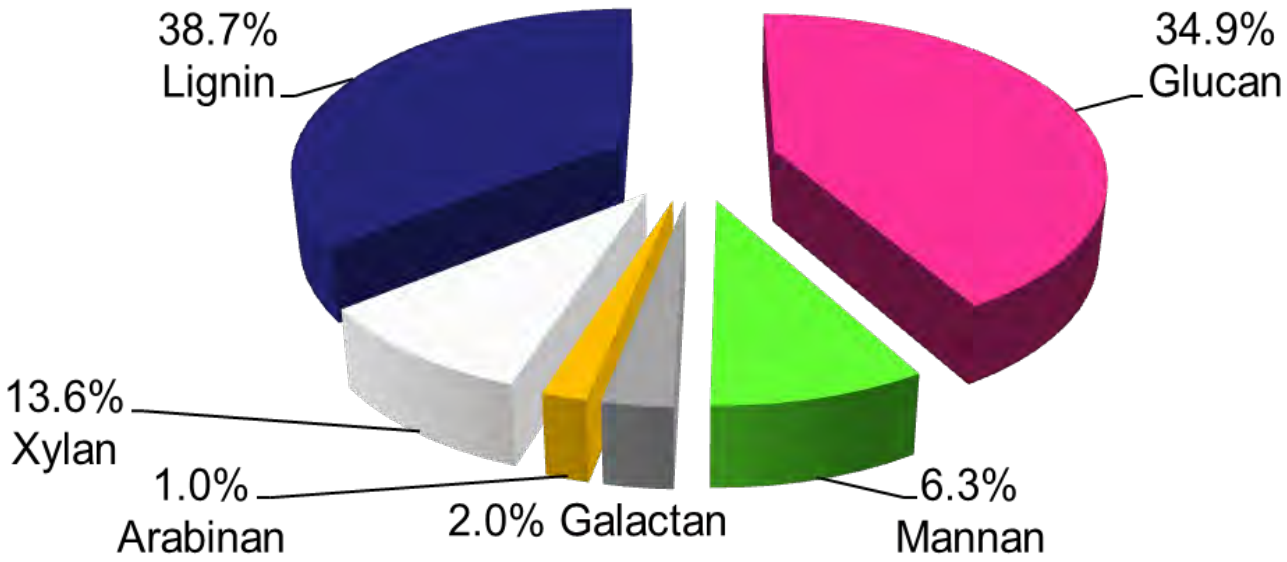
Author : Billy Roberts - September 23, 2009

Downsizing on the logging spot



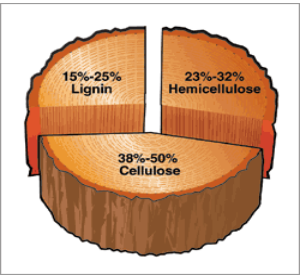
Down-sizing before use for combustion

Douglas fir (FS-03) Composition of washed material



WET OXIDATION

Lignocellulosic biomass



Hemicellulose

Lignin

Cellulose

2 - 6 bar

O_2

175-195 C

Compounds oxidize under wet conditions that would not oxidize under dry conditions at the same temperature and pressure.

O_2

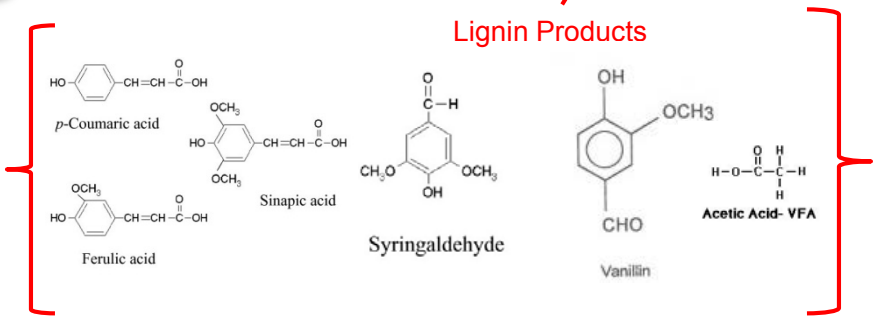
Disintegration of the lignin and hemicellulose chains.

Xylooligosaccharides

Cellulose Cellooligosacarides

C_5 – C_6 Sugars

Lignin Products



WSU PILOT PLANT FACILITY

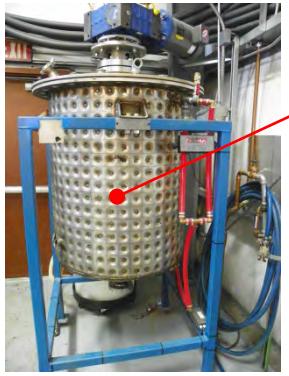
Biomass Preprocessing

Liquid/Solid separation

10L Pretreatment

100L Pretreatment

2x400L Fermentation / SSF



500L Flash and Hydrolysis

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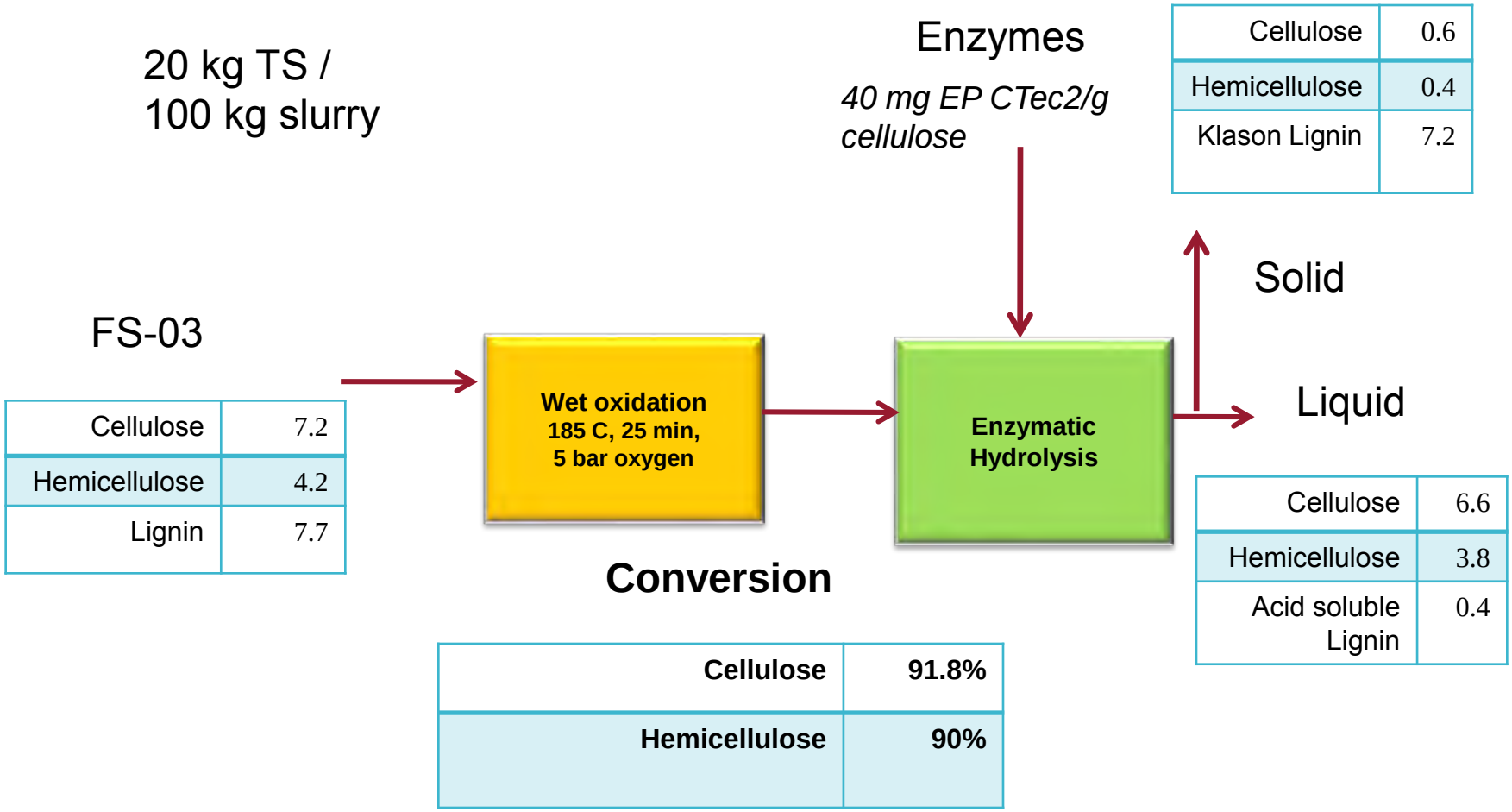
Softwood to Hydrolysate and Sugars

Milling

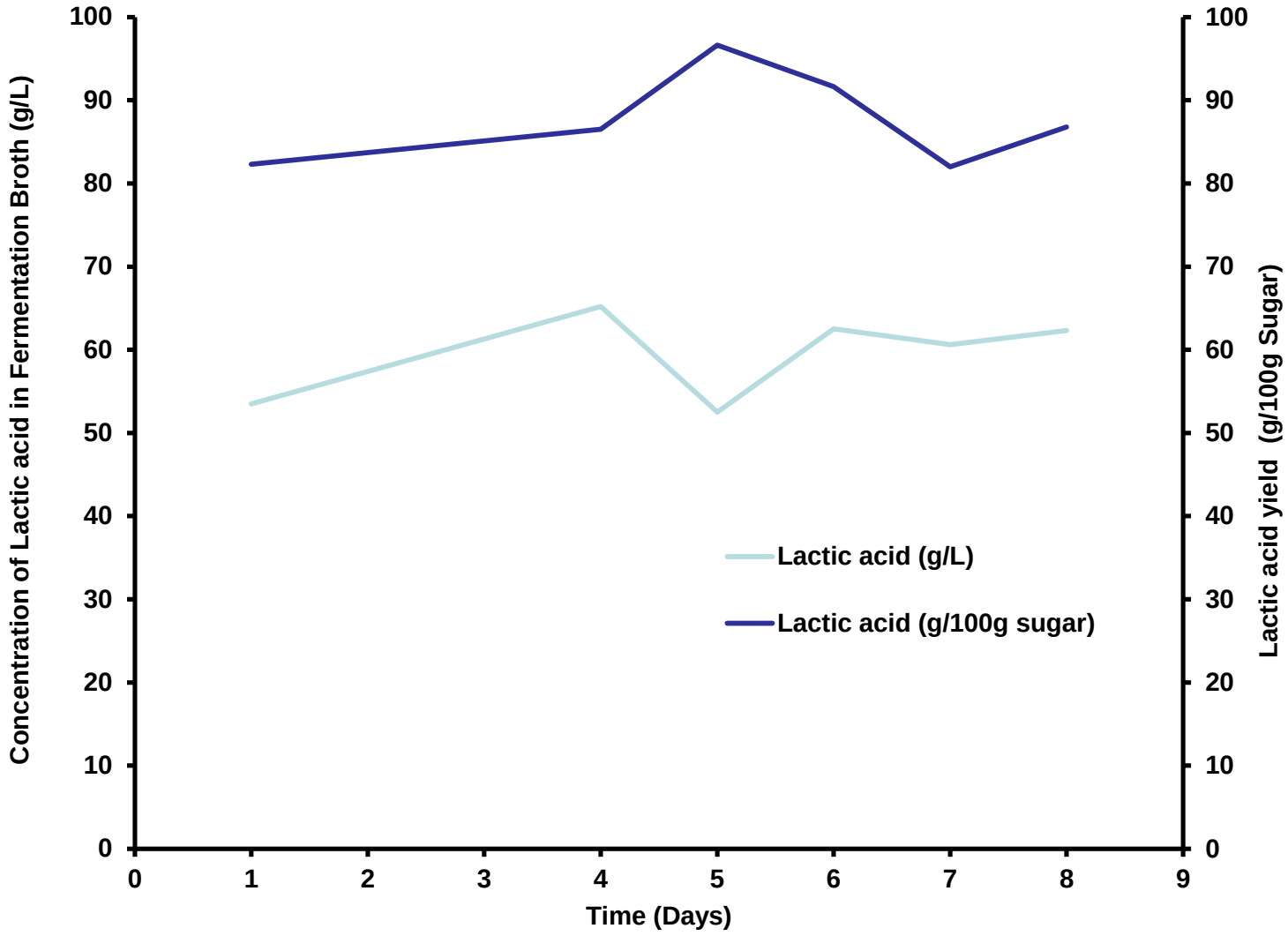
Pretreatment

Enzymatic Hydrolysis

MASS BALANCE – Douglas fir (FS-03)



FERMENTATION OF FS-03:
No inhibition



INITIAL RESULTS

- Wet oxidation pretreatment performed well on forest slash (softwood)
- Preprocessing (washing) was beneficial
- High sugar yields were obtained 91.8% of cellulose and 90% of hemicellulose
- Fermentation tests show no inhibition of microbial performance with up to 20% hydrolysate

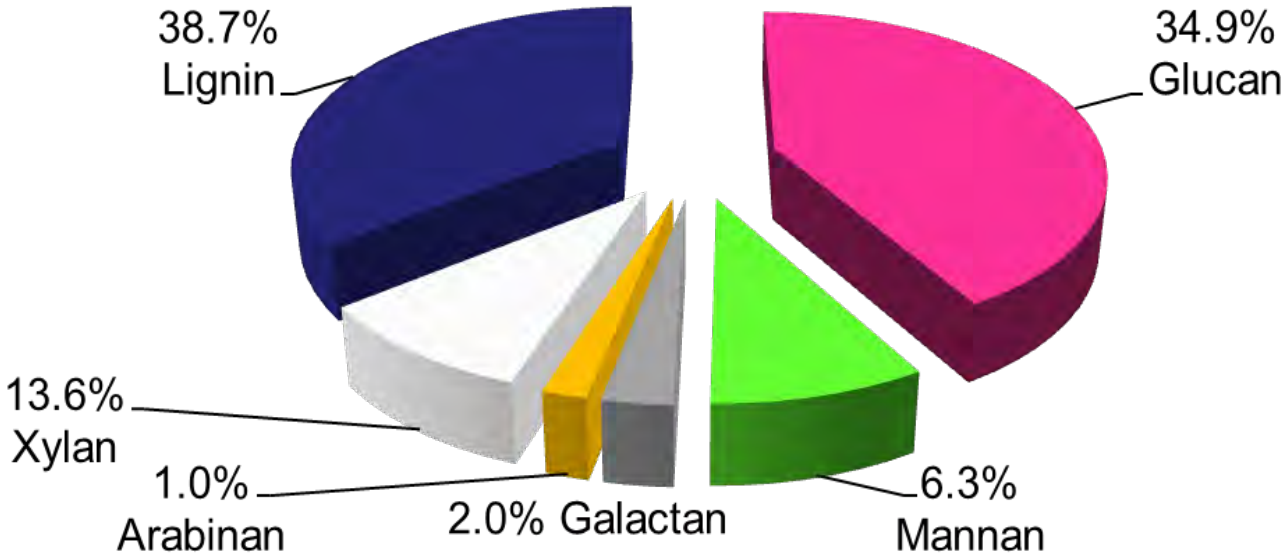
COMPARING SUGAR YIELDS FROM SOFTWOOD

Type of Biomass	Type of Pretreatment	Pretreatment Temperature (^{0}C)-Time (min)	Enzymatic Hydrolysis	Theoretical Yield (Total Sugars)	Reference
Softwood	Two- step Steam Pretreatment	Stage 1: 190-2, 3% **SO_2** Stage 2: 220-5, 3% **SO_2**	2% DM	80%	Söderström J. et al. (2002)
Pinus rigida	Organosolv	210-10, 1% **$MgCl_2$**	1% DM	75.88%	Park N. et al. (2010)
Bettle Killed Lodgepole	One step Steam Pretreatment	200-5, 4% **SO_2**	2% DM	75%	Ewanick S. et al. (2007)
DF (FS-03)	Wet oxidation	185-25, 5 bar **O_2**	20% DM	**90-92%**	This study

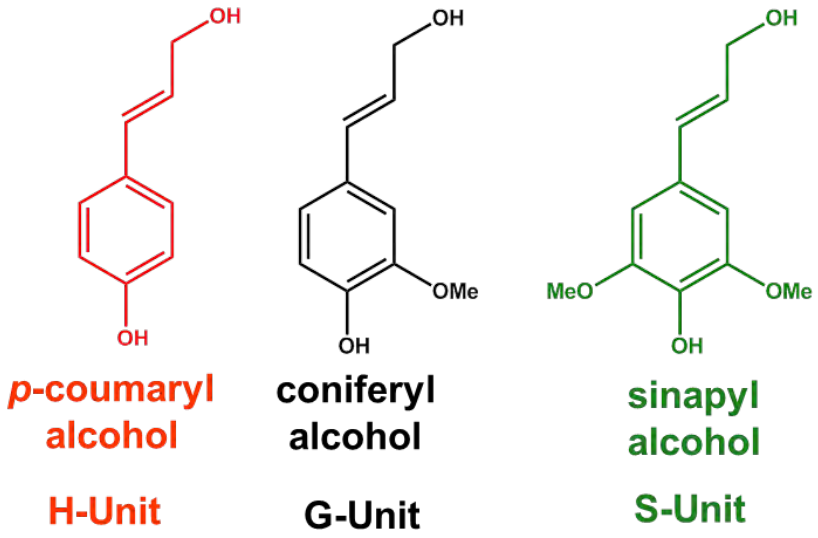
FS-03 Composition of washed material

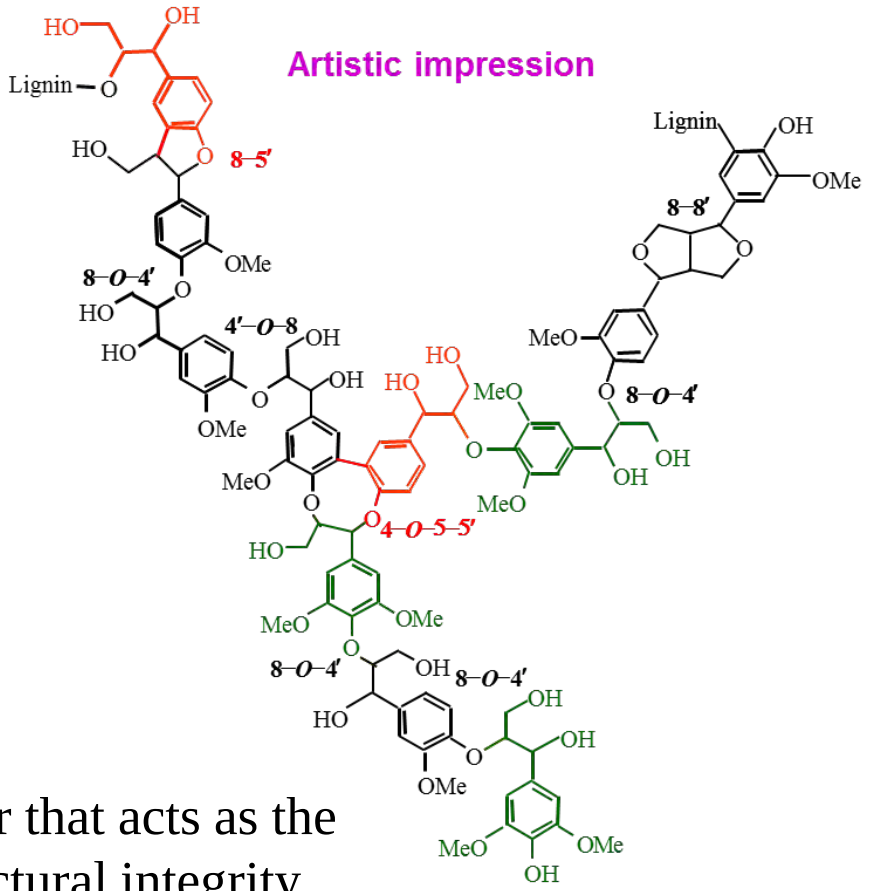
Lignin most abundant polymer!

Loblolly Pine



● Lignins are formed by oxidative radical-radical coupling using three main monolignols.

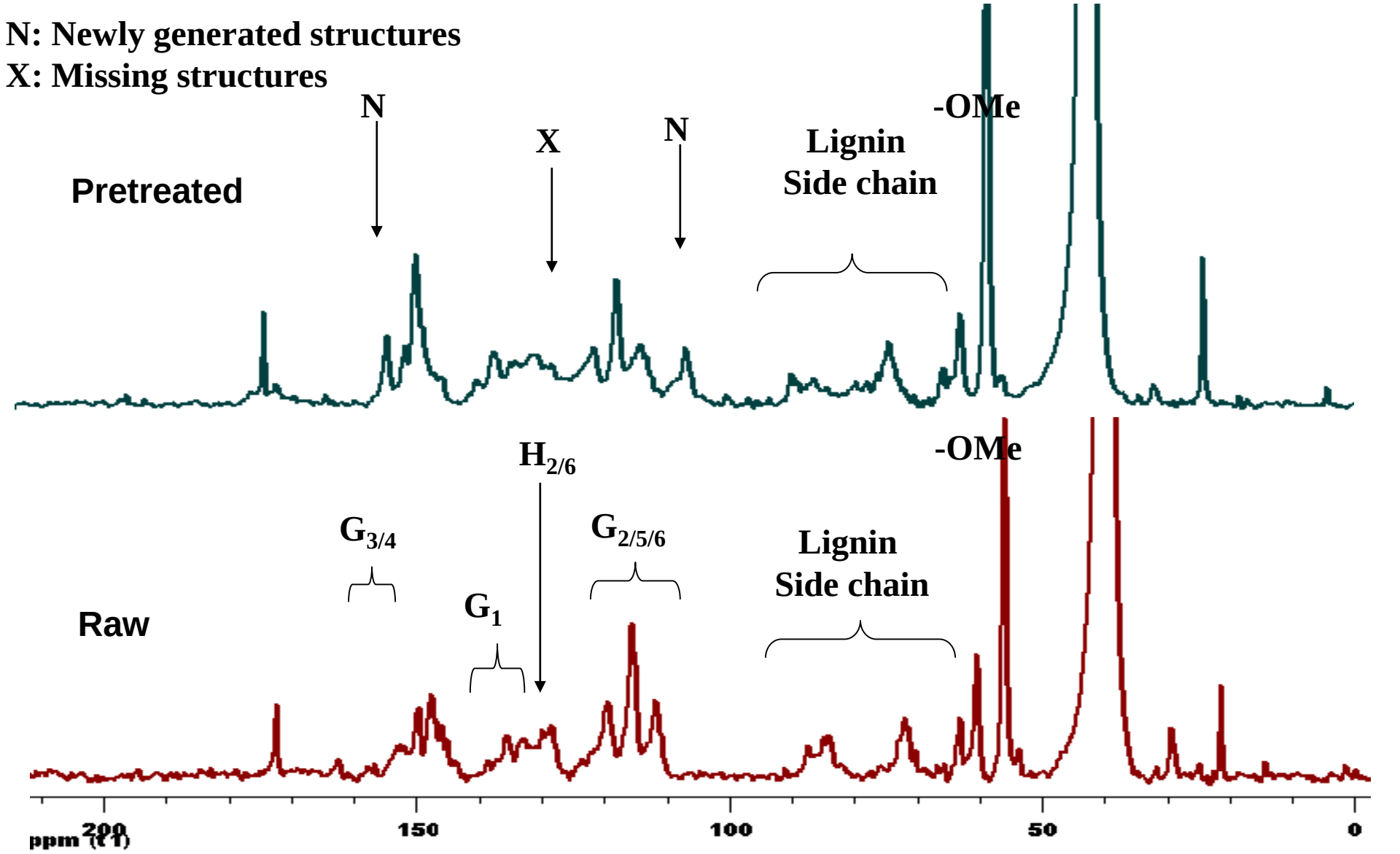




● Lignin is a natural amorphous polymer that acts as the essential glue that gives plants their structural integrity. The current vision undervalues lignin's potential to address production of high value and commodity products. An attractive alternative is valorization of lignin for conversion to value added products.

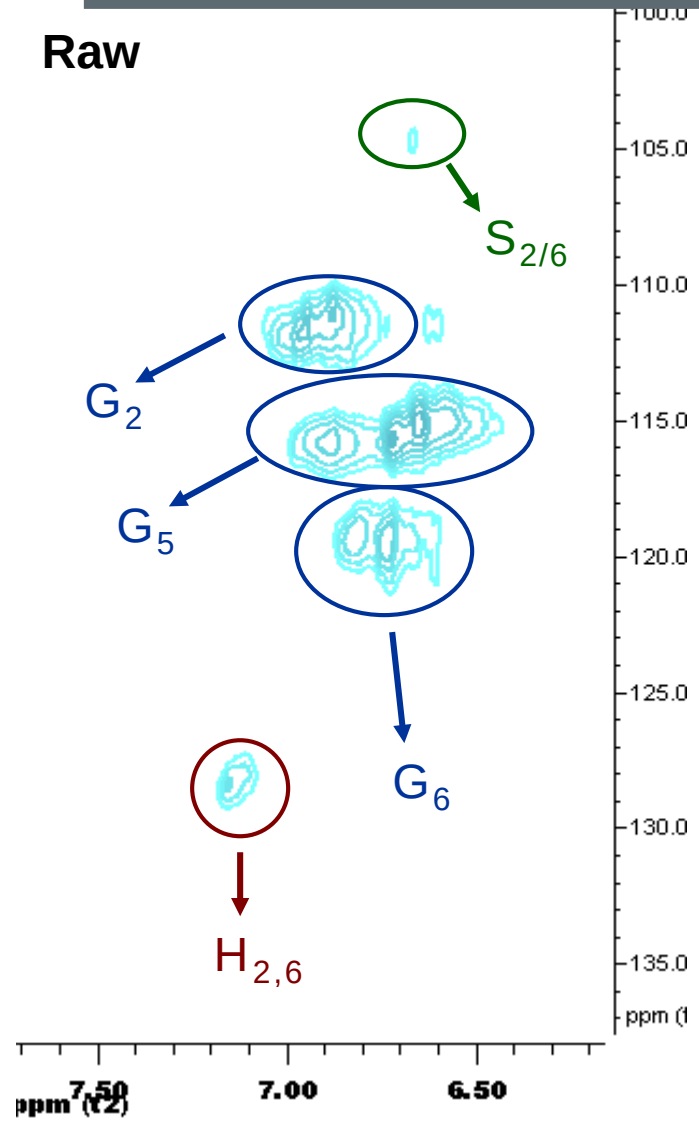
^{13}C NMR of loblolly pine

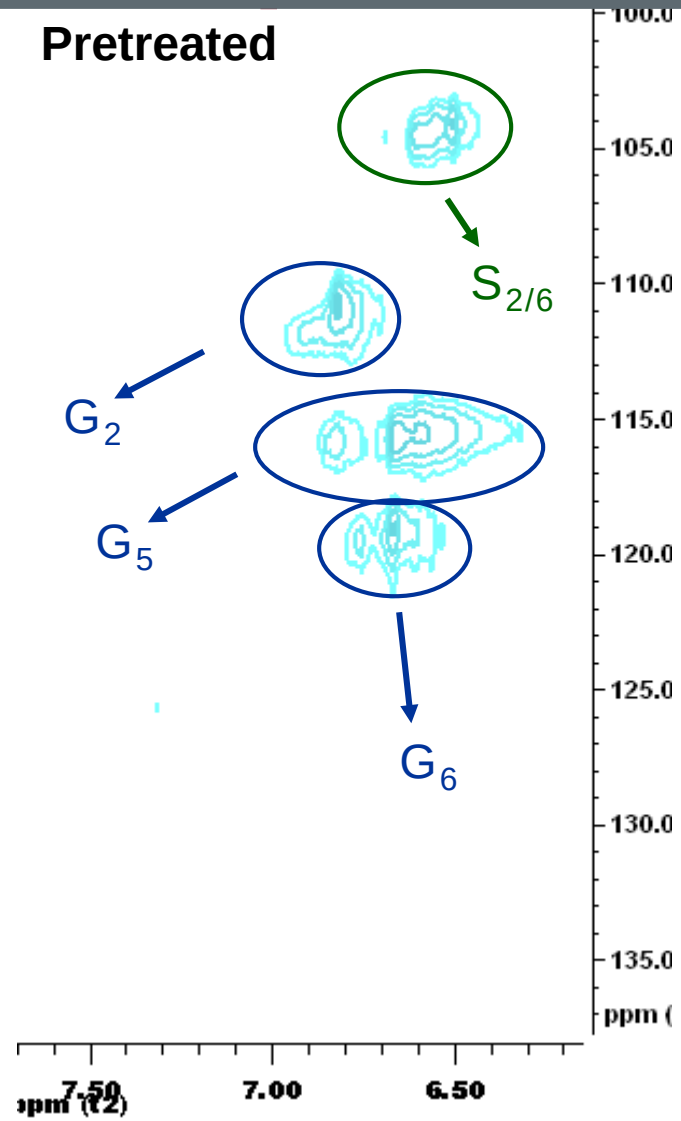
Effect of WEx pretreatment

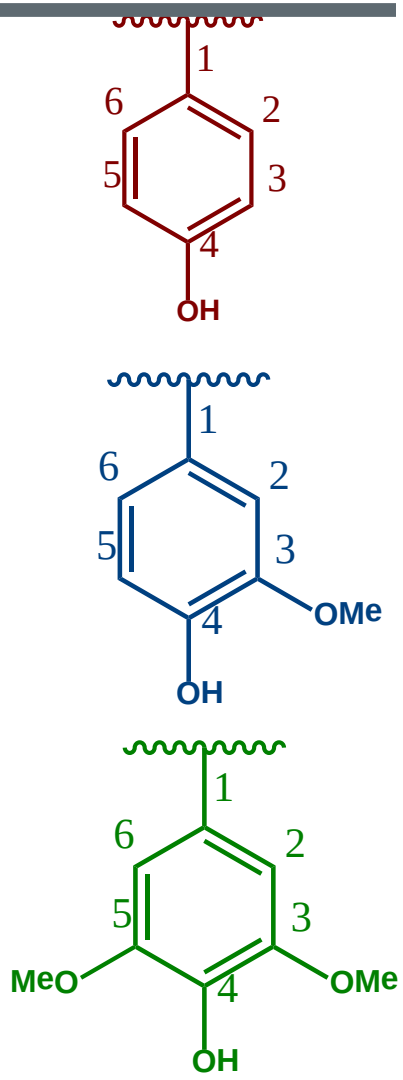


2D Heteronuclear Single Quantum Coherence (HSQC)of loblolly pine

Effect of WEx pretreatment







RESULTS

- Structural modification within the lignin assembly while retaining its core framework
- Modification of highly condensed H-lignin via *in situ* methoxylation reactions
- Methoxylation occurred at the aromatic ring of corresponding H and/or G units, possibly resulting in generation of S-like structures within the lignin assembly
- Generation of S-like units suggests a possible usage of modified lignin for high value products

CONCLUSION

- Wet oxidation was found to be a well suited pretreatment method for forest slash (softwood)
- Preprocessing of the material before pretreatment showed to be necessary
- Wet oxidation was further found to produce high sugar yields (both C6 and C5) from softwood
- Fermentation tests show no inhibition with up to 20% hydrolysate
- Investigation of the lignin modification during wet oxidation pretreatment show that the pretreatment results in significant changes to the lignin structure
- The decrease in highly condensed lignin structure resulting from wet oxidaton might increase the cellulose accessability, thus decrease the need for enzymes and further increase the value of the lignin for producing high-value lignin products.

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Thank you for your attention and Questions
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