Advanced Wet Explosion (AWEx) Pretreatment for making viable biorefineries from lignocellulosic biomass

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Feedstocks – Washington State

Wheat Straw

- *In Washington state, up to 2 million dry tons is produced per year, could add potential value to the state's economy.*
- *More than 25,000 jobs are tied to wheat farming in*

Production Zone	Million Metric Tons (MMT)	Million Bushels
North Central	1.86	68.3
Northeast	1.86	68.3
Central	1.24	45.6
Southeast	0.74	27.3
Southwest	0.47	17.1
Northwest	0.03	1.0
Total	6.20	227.6

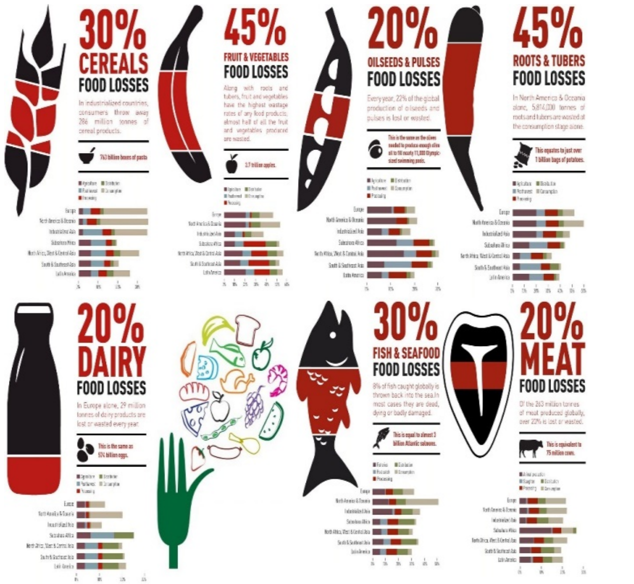
Hardwood (e.g. Poplar)

- *In USA, 368 million tons of woody biomass is produced. Currently, there are nearly 100,000 acres of hybrid poplars growing in the Pacific Northwest.*
- *Can be harvested with short rotations*

Boardman, Oregon

Softwood (e.g. D. Fir)

- *8.1 million tons forest residues biomass produced in WA alone.*
- *On the commercial timberlands of the western region, there are approximately 14 million hectares of Douglas fir managed primarily in natural stands.*



Food Processing Waste

Courtesy: https://makanaka.wordpress.com/tag/food-waste/

Manure

- *USDA estimates more than 335 million tons of "dry matter" waste is produced annually on farms in the United States. More than 1.9 million tons animal waste in WA.*

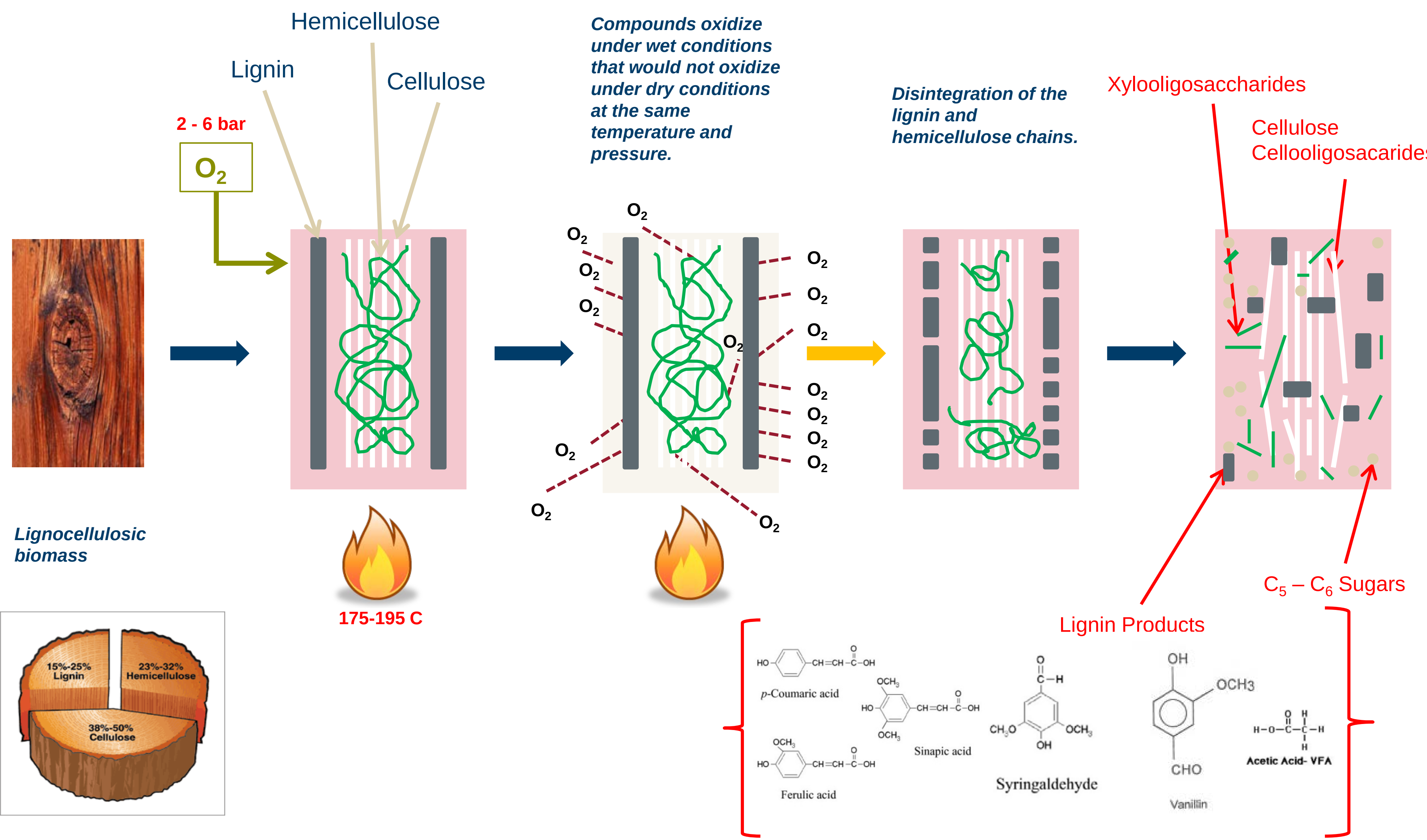
Why is Pretreatment Needed?

- Biomass recalcitrance requires pretreatment
- Pretreatment is the most costly process step: the only process step more expensive than pretreatment is no pretreatment
  - Low yields without pretreatment drive up all other costs more than amount saved
  - Enhancing yields via improved pretreatment would reduce all other unit costs
- Lowering cost of pretreatment makes biorefineries more viable
- Making full use of the biomass raw materials allows for improved economy
- What you add of chemicals during pretreatment will stay around and set limits for the full use of the biomass

Biomass Pretreatment Technologies

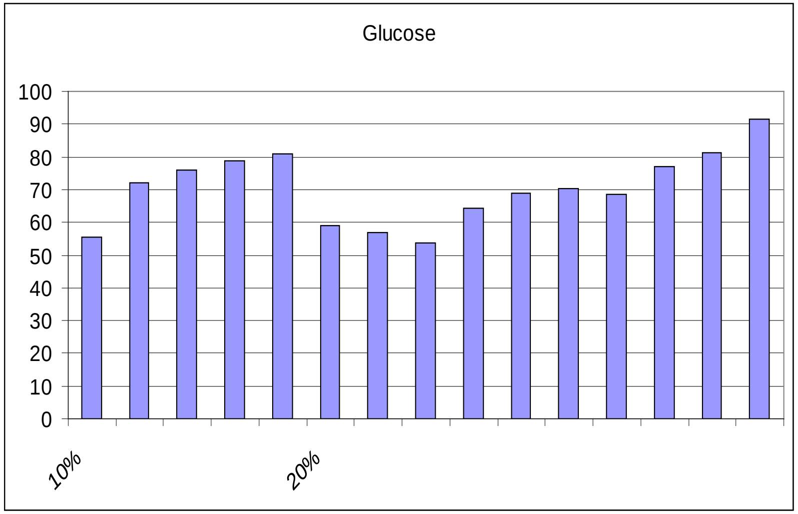
- Size reduction (comminution)
- Low pH (acid)
  - Dilute acid, SO_2, etc.
- Neutral pH (water)
  - Autohydrolysis, controlled pH
- High pH (alkaline)
  - Lime, liquid ammonia soaking, AFEX, etc.
- Organic solvent
  - Organosolv, COSLIF, etc.
- Ionic liquids (ILs)
- Biological

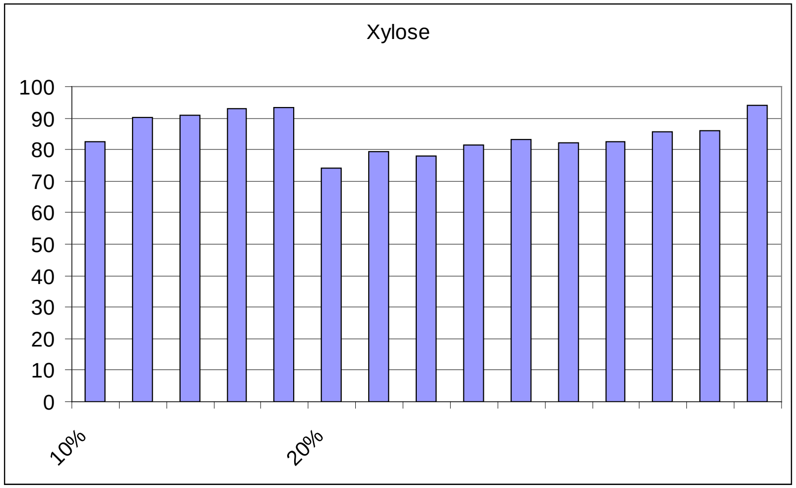
WET OXIDATION



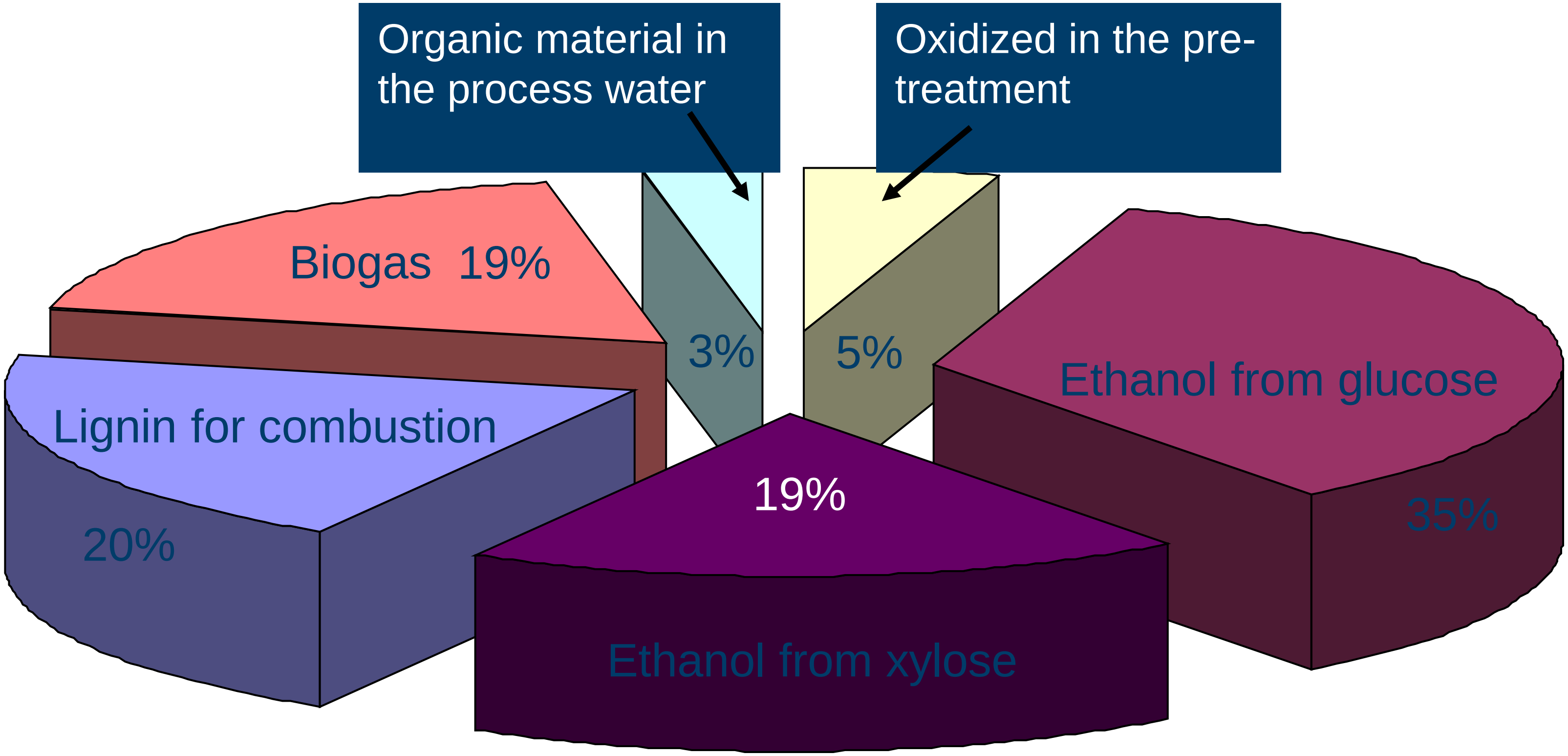
Pretreatment to promote fibrous conversion
Wet Explosion – pilot-scale (CleanVantage LLC IP)

Pilot plant


Glucose
100
90
80
70
60
50
40
30
20
10
0
10%
20%


Xylose
100
90
80
70
60
50
40
30
20
10
0
10%
20%

Optimized use of the biomass

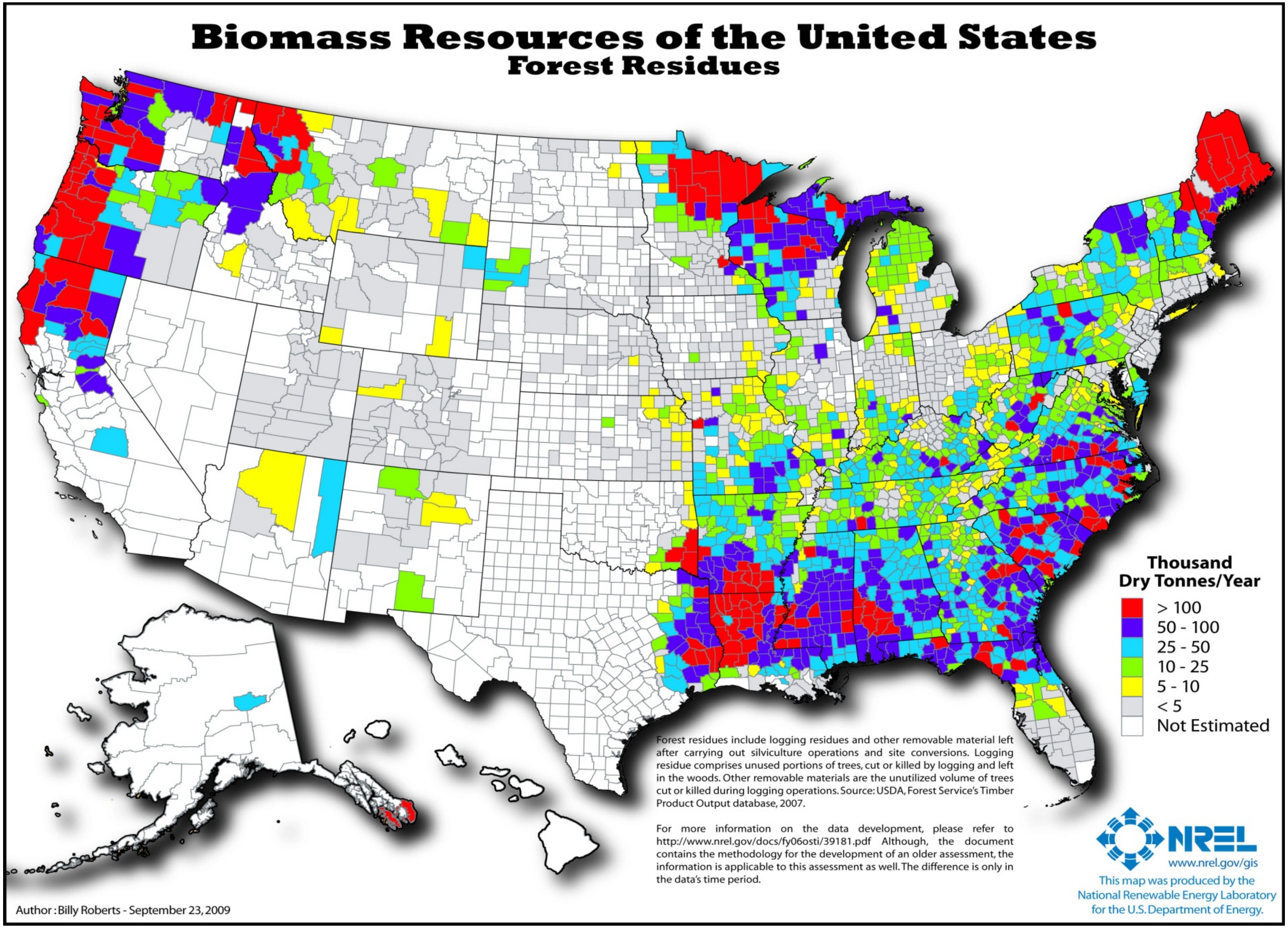


Conclusions Ag Waste

- Wet explosion gave high sugar yields even with high solids loading
- With the newest development of AWEx and cellulosic enzymes we can run the process at 30% DW with over 90% sugar yield
- New results in our lab has shown that on-site produced enzymes can substitute commercial enzymes and result in a significant lowering of enzyme cost

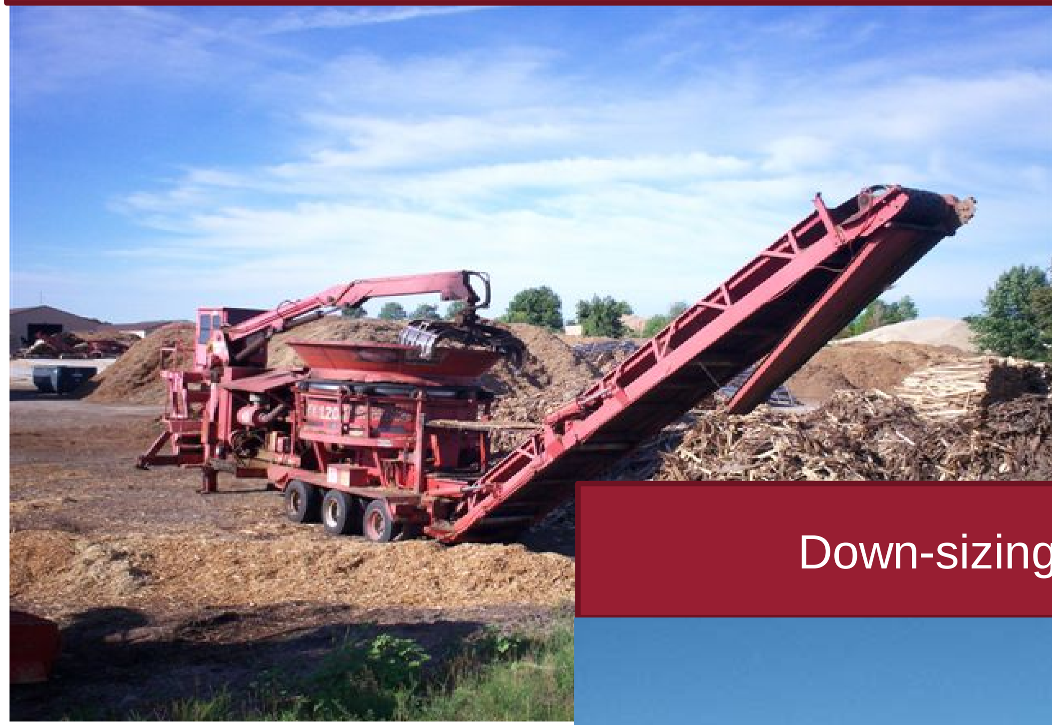
Forest slash: Opportunities and problems for turning Slash to Cash!

- **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.



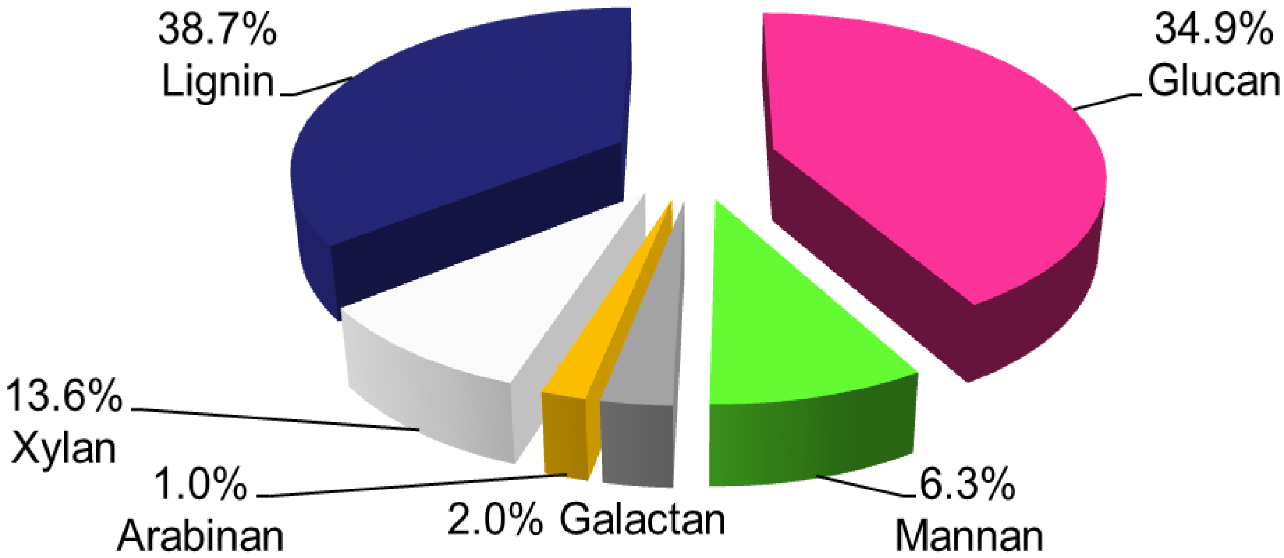
Biomass Resources of the United States
Forest Residues
Thousand Dry Tonnes/Year
> 100
50 - 100
25 - 50
10 - 25
5 - 10
< 5
Not Estimated
Forest residues include logging residues and other removable material left after carrying out silviculture operations and site conversions. Logging residue comprises 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.
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



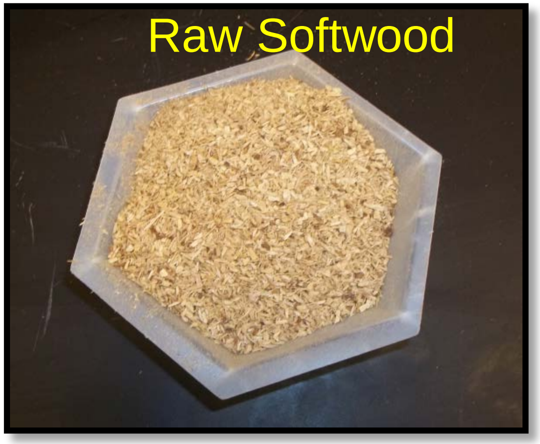
Down-sizing before use for combustion

Douglas fir (FS-03) Composition of washed material



Softwood to Hydrolysate and Sugars

Milling



Pretreatment

Enzymatic Hydrolysis

MASS BALANCE – Douglas fir (FS-03)

20 kg TS /
100 kg slurry

FS-03

Cellulose	7.2
Hemicellulose	4.2
Lignin	7.7

Wet oxidation
185 C, 25 min,
5 bar oxygen

Enzymes

40 mg EP CTec2/g cellulose

Enzymatic Hydrolysis

Solid

Cellulose	0.6
Hemicellulose	0.4
Klason Lignin	7.2

Liquid

Cellulose	6.6
Hemicellulose	3.8
Acid soluble Lignin	0.4

Conversion

Cellulose	**91.8%**
Hemicellulose	**90%**

NARA: Bioprocessing forest residues

- Optimization of process conditions
- Mass balance closure of the cell-wall components

Table 1
Experimental design of the wet explosion pretreatment of Douglas fir FS-10 samples in pilot-scale at 30% dry matter.

Run	Pattern	Temp., °C (T)	O_2, % DM	Time, min. (t)
1	−−−	170	0.5	10
2	−+−	170	7.5	10
3	a00	170	4.0	20
4	−−+	170	0.5	30
5	−++	170	7.5	30
6	00a	180	4.0	10
7	0a0	180	0.5	20
8 (central)	000	180	4.0	20
9 (central)	000	180	4.0	20
10 (central)	000	180	4.0	20
11	0A0	180	7.5	20
12	00A	180	4.0	30
13	+−−	190	0.5	10
14	++−	190	7.5	10
15	A00	190	4.0	20
16	+−+	190	0.5	30
17	+++	190	7.5	30

WASH

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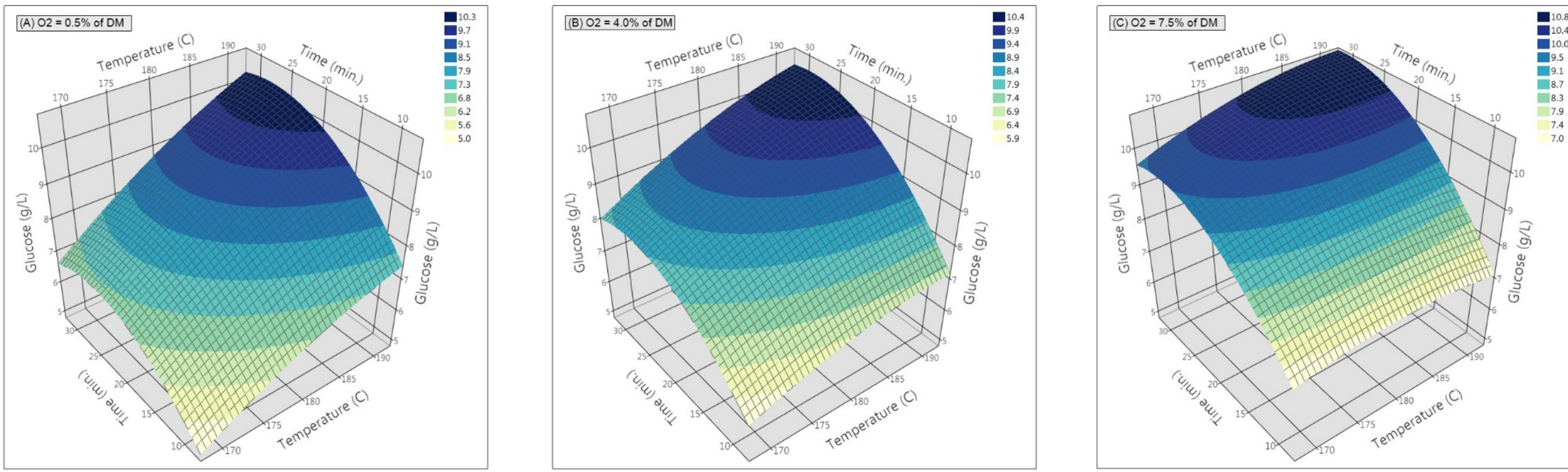
Bioprocessing forest residues



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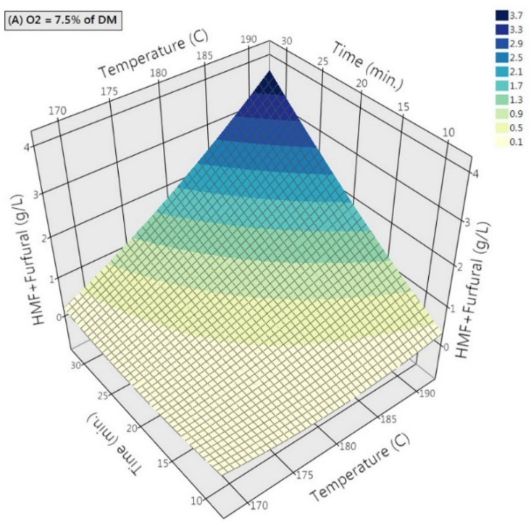
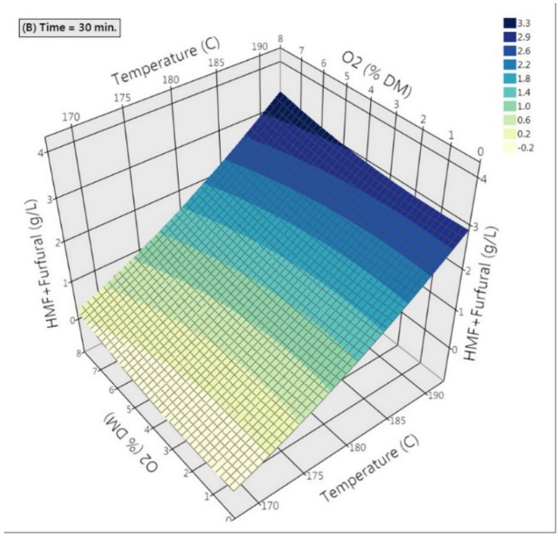
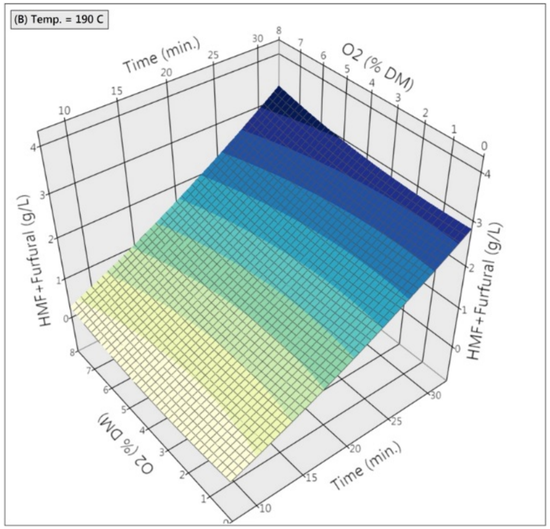
Bioprocessing forest residues







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Bioprocessing forest residues

Enzymes used:

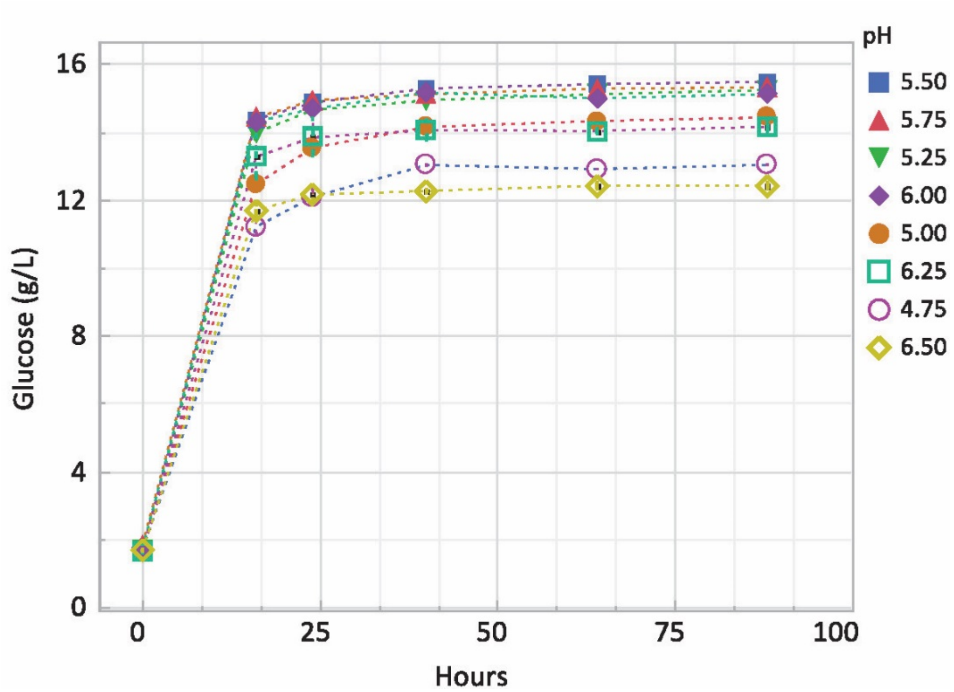
Mixture of Cellic® CTec2 and Cellic® HTec2

Enzyme dosage:

16 mg enzyme proteins (EP)/g PFS-10

(oven dry basis, of which 14 mg EP from CTec2

and 2mg EP from HTec2)



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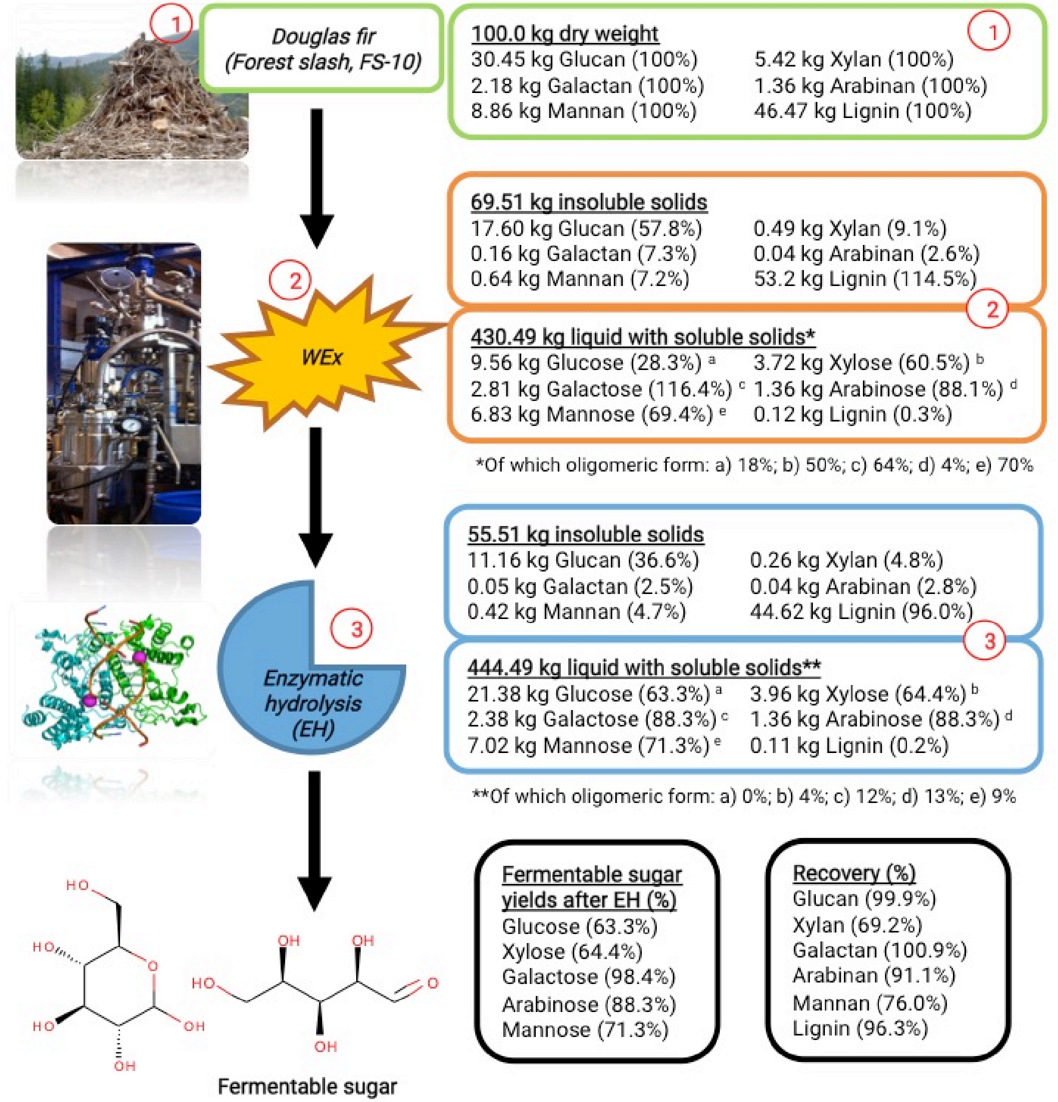
Bioprocessing forest residues

Highlights

- The wet explosion at pilot-scale tested, process conditions were optimized using DOE.
- Maximum digestibility achieved at 190 °C, time 30 min, and oxygen loading of 7.5%.
- Glucose yield at optimal pH of 5.5 was 63.3% of the theoretical maximum.
- A recovery of cellulose and lignin of 99.9% and 96.3%, respectively, was achieved.

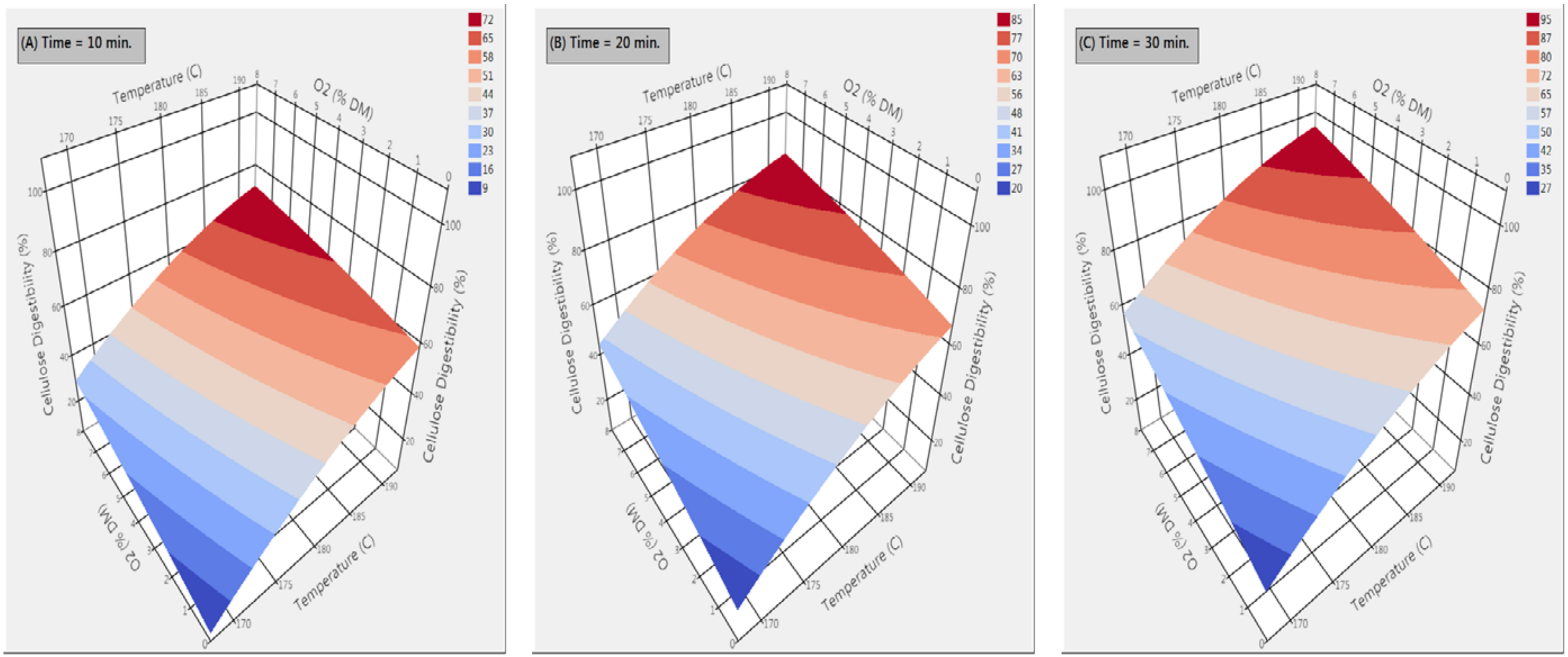


COMPARING SUGAR YIELDS FROM SOFTWOOD

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

Bioprocessing of poplar sawdust

Up to 90% of sugar production as monomers



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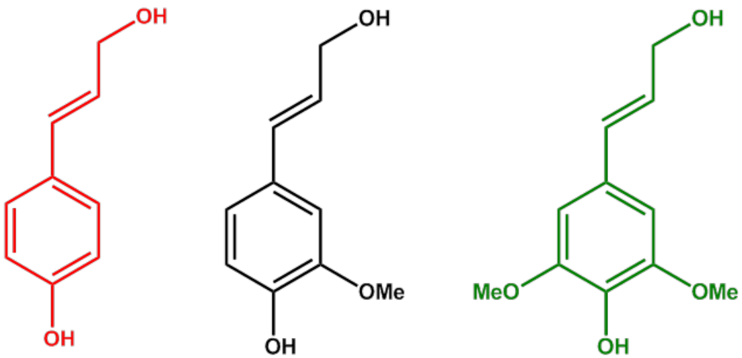
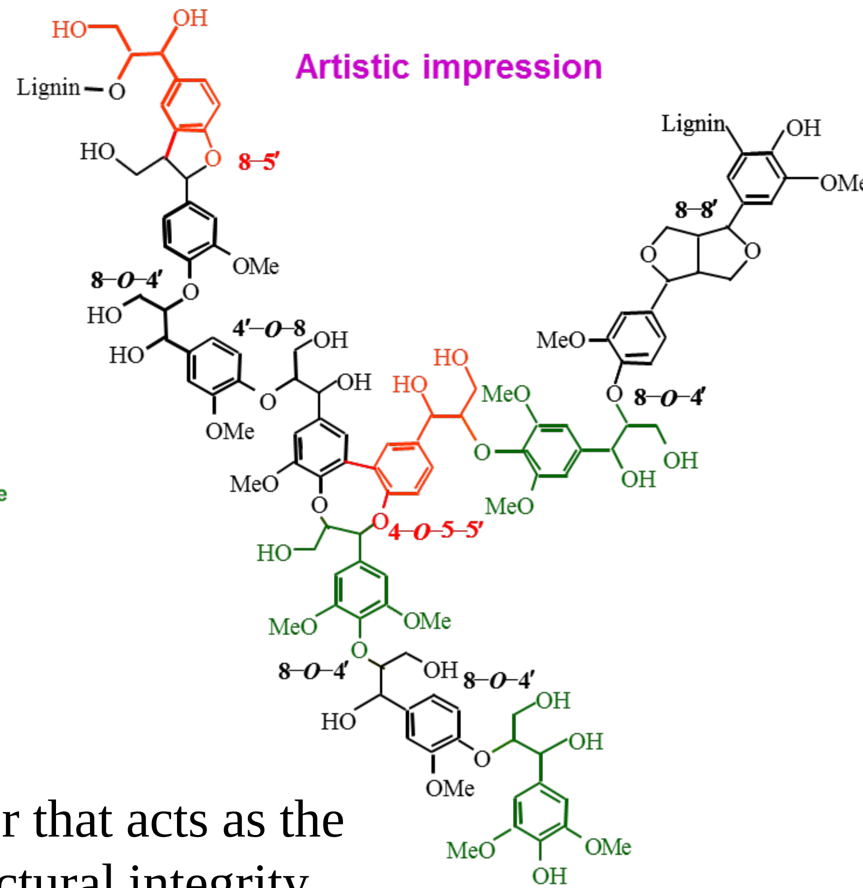
● **Lignins are formed by oxidative radical-radical coupling using three main monolignols.**



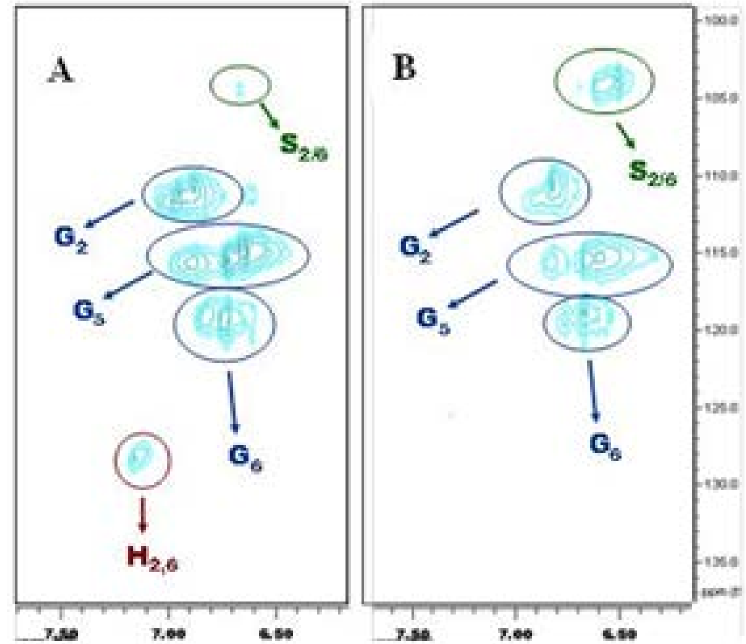
p-coumaryl alcohol	coniferyl alcohol	sinapyl alcohol
H-Unit	G-Unit	S-Unit



● 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.

Wet Exploded Lignin

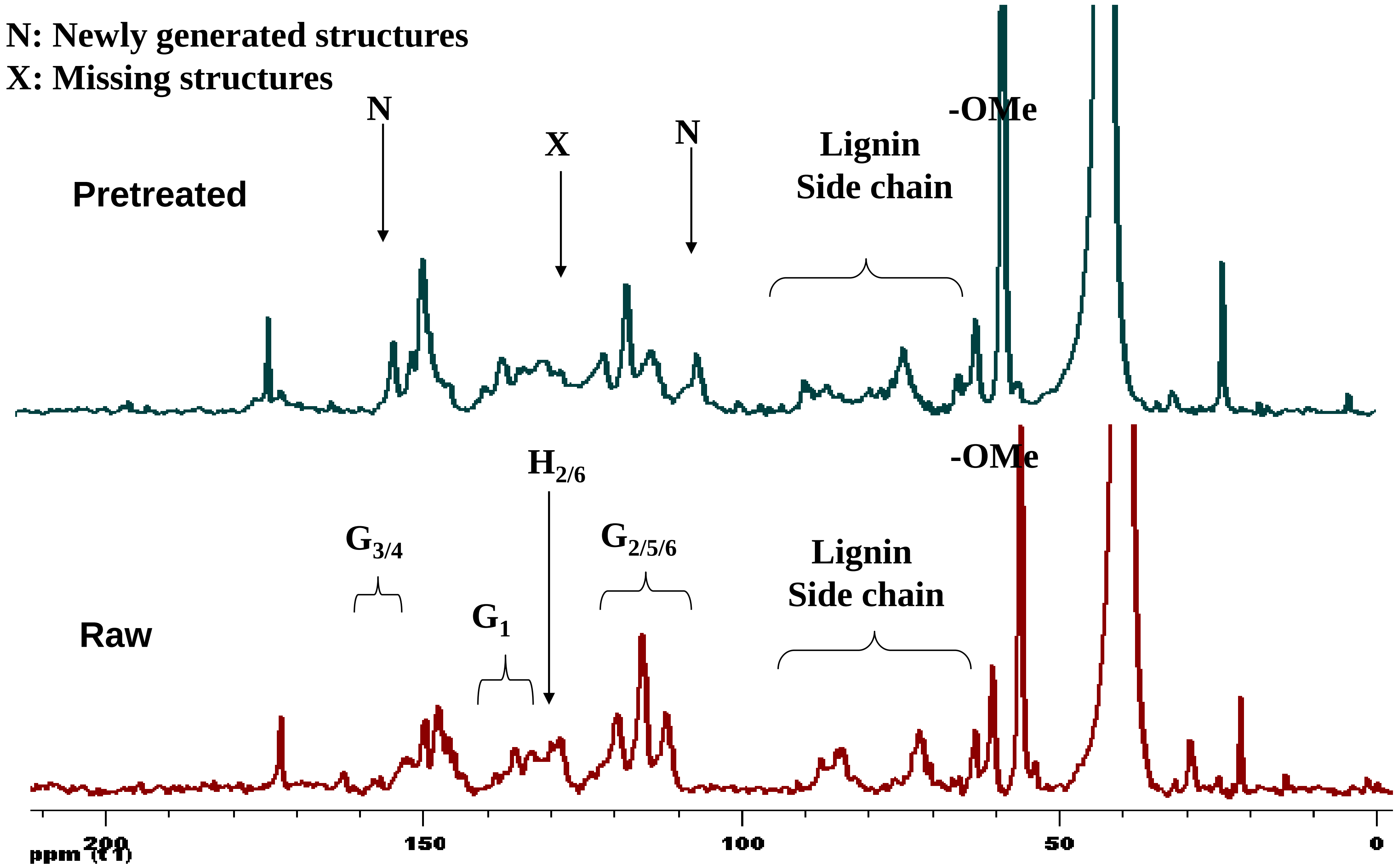
Sample	% C	% H	% N	% O	% S
Forest Residual Lignin	61	6.0	0.07	32.9	0.032
Wet Exploded Lignin	64.9	5.3	0.96	28.7	0.096
Mild Bisulfite Lignosulfonic acid	52.1	4.8	0.36	34.7	8.10



- Initial studies were done on both Douglas Fir and Loblolly Pine lignin after wet explosion pretreatment at optimized conditions for sugar recovery.
- Studies showed that wet explosion pretreatment increased amount of methylated compounds (S- & G- units) which reduced recondensation and repolymerization of lignin after cooling.
- Wet explosion pretreatment also showed higher Carbon concentration when compared to lignosulphonates.

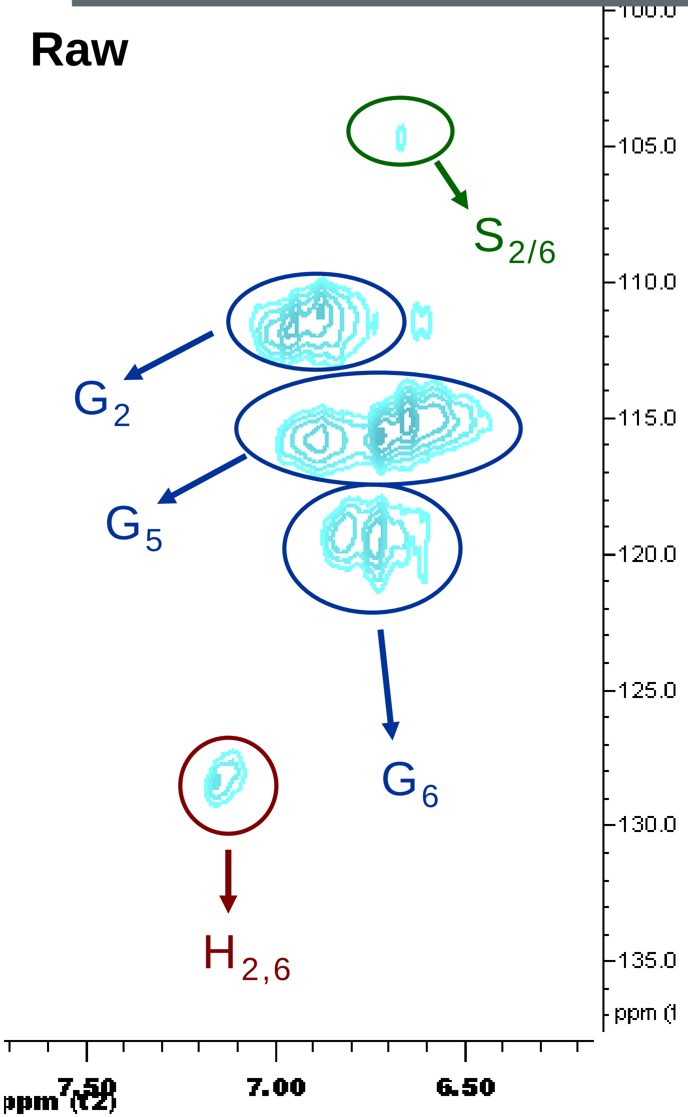
^{13}C NMR of loblolly pine

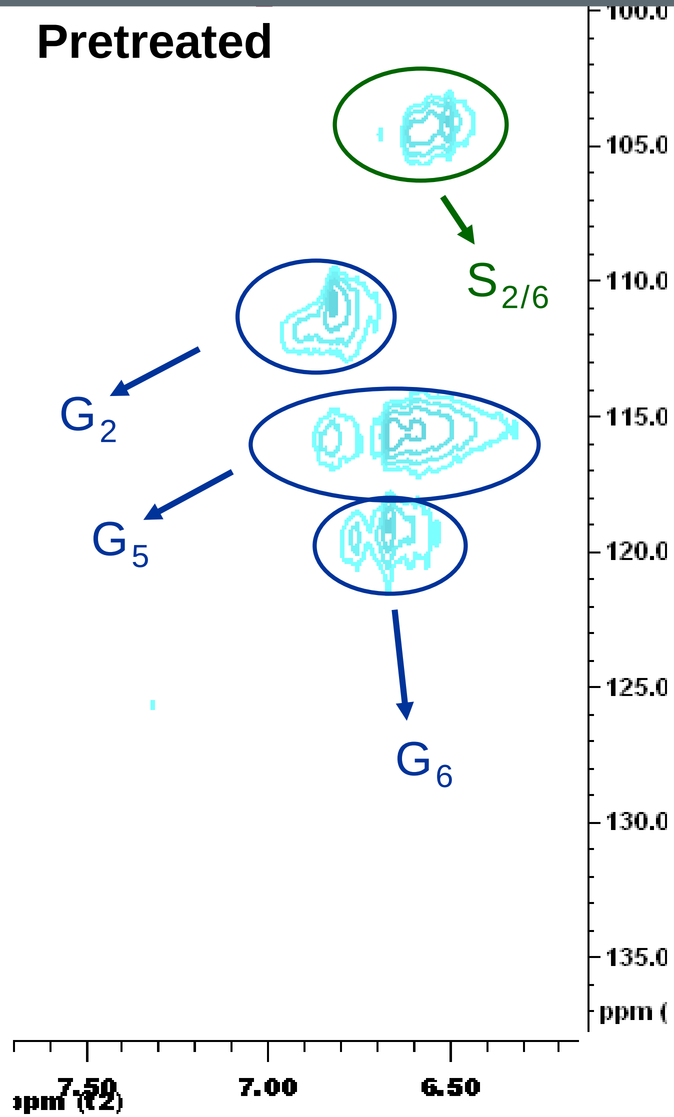
Effect of WEx pretreatment

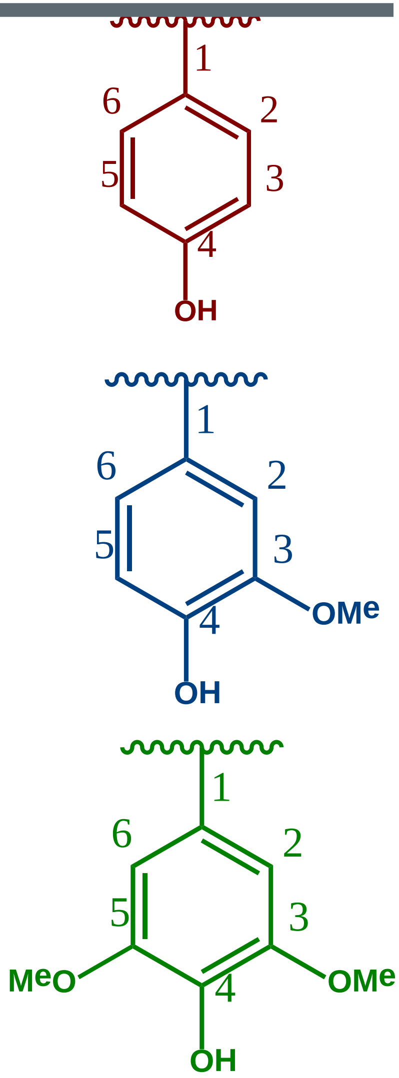


2D Heteronuclear Single Quantum Coherence (HSQC)of loblolly pine

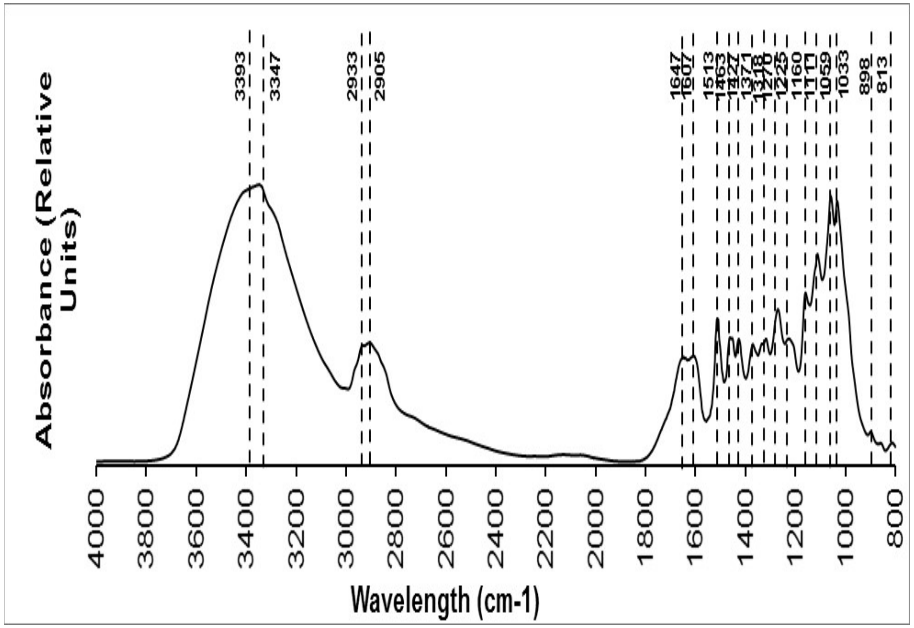
Effect of WEx pretreatment







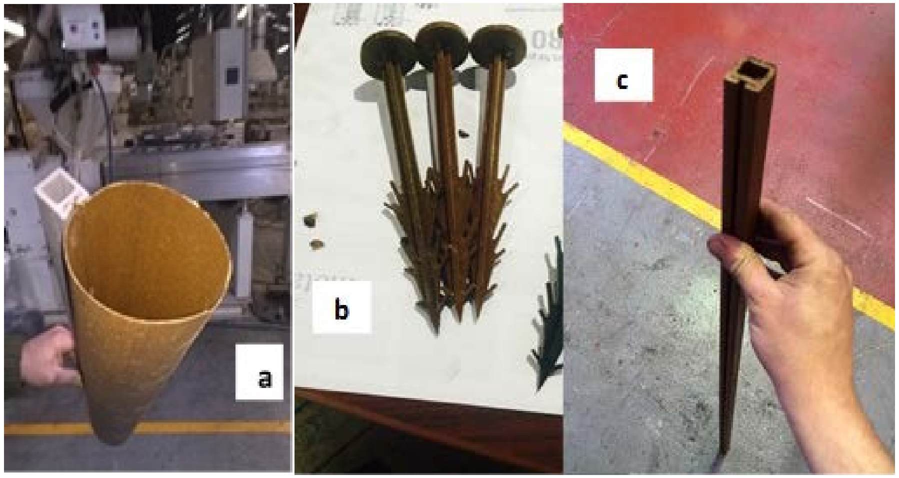
FTIR Analysis of Wet Exploded FS-10 Lignin



Observed Peak Maximum (cm^{-1})	Peak Assignment
3347, 3393	O-H stretch (hydrogen bonded)
2905, 2933	C-H stretching of methyl and methylene groups
1647	Adsorbed O-H, conjugated C=O (cellulosic)
1607	C=C stretching of aromatic ring in lignin
1513	Aromatic skeletal vibrations (guaiacyl>syringyl)
1463	C-H bending of methyl and methylene groups
1427	C-H deformation in lignin
1371	C-H deformation symmetric (cellulosic); Phenolic OH (lignin)
1318	CH_2 wagging (cellulosic)
1270	C-O stretching of guaiacyl unit
1225	C-C, C-O and C=O stretching of guaiacyl unit
1160	C-O-C asymmetric vibration (cellulosic)
1111	Aromatic C-H deformation of syringyl units
1059	C-O stretching of secondary alcohols/cellulosic
1033	C-O stretching of primary alcohols
898	C-H deformation vibration of cellulose
813	C-H bending of syringyl units

- FTIR analysis indicated greater amount of guaiacyl (G-) components in the biorefinery lignin when compared to syringyl (S-) or hydroxyphenyl (H-) components with an S/G ratio of 0.811 (obtained from comparing FTIR absorbance at 1270 cm^{-1} and 1225 cm^{-1}.
- These studies also showed that linkages related to both softwood and hardwood biomass was found in FS-10 (softwood being more prominent)

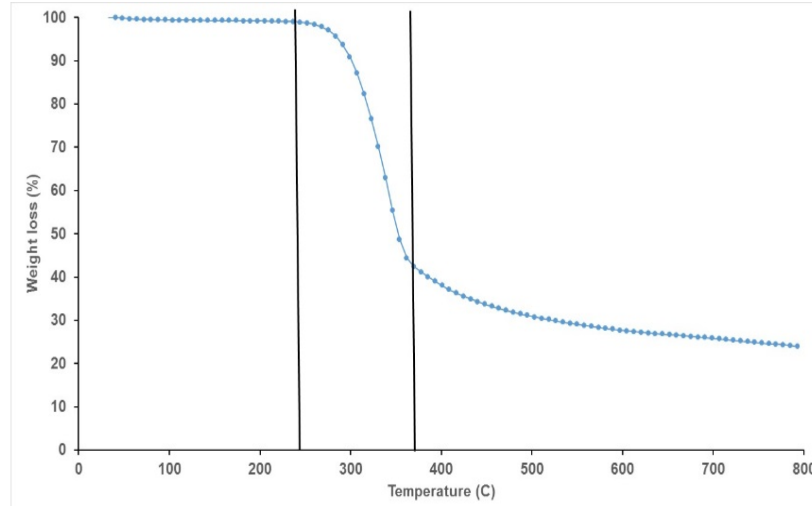
Lignin-Based Products

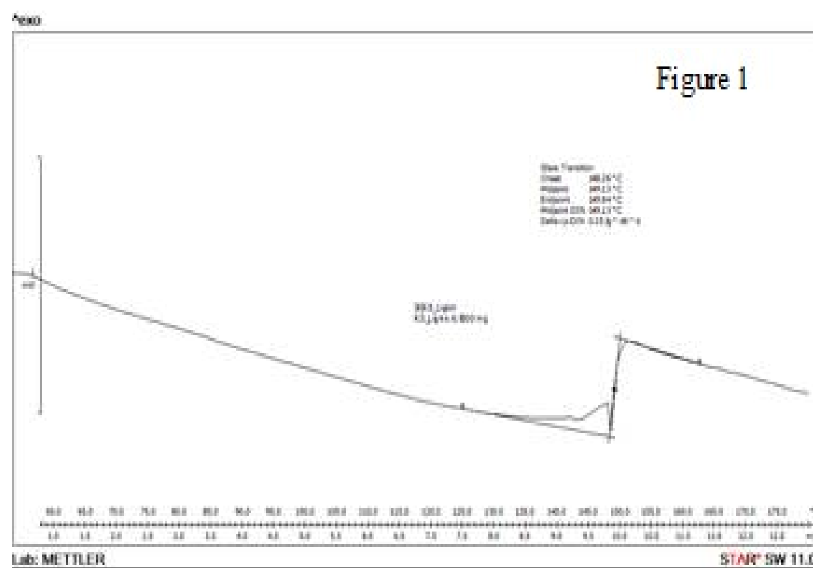


Different reinforced PLA products produced from WEx-treated lignin at 20 wt% loading (a) tree sapling protector attached to a stake; (b) pegs; (c) stake.

- These products were made in collaboration with Greener Polymers LLC for forestry applications.
- Currently, other biodegradable plastics for common household applications such as paper cups, coffee lids, paper plates etc. are being produced using WEx Lignin-reinforced PLA.
- These products were found to have superior mechanical properties compared to natural wood fibers and required less additives due to aromatic nature of the WEx Lignin. 20% Blending with PLA also showed cost savings.

Carbon Fibers from WEx Lignin





- Current work is being done in modifying WEx biomass lignin for carbon fiber production.
- The research is being done in conjunction with companies such as Ford and Hyundai in increasing lignin reinforcement in carbon fibers using different environmentally-benign and low-cost techniques.

Other Products

- Srinivas, K., Oliveira, F. D. C., Teller, P., Gonclaves, A. R. and Ahring, B. K., 2015, Characterization and oxidative degradation of biorefinery lignin obtained from pretreated forest residues of Douglas Fir, Manuscript submitted.

- Srinivas, K., Oliveira, F. D. C., Teller, P., Gonclaves, A. R. and Ahring, B. K., 2015, Characterization and optimization of alkaline wet oxidation of biorefinery lignin obtained from pretreated forest slash, Pacifichem, Honolulu, Hawaii, December 15-20.

- Rana, D., Laskar, D. D., Srinivas, K. and Ahring, B. K. 2015, Wet explosion pretreatment of loblolly pine leads to an increase in methoxylation of the lignin, Bioresour. Bioprocessing, 2, 26, doi: 10.1186/s40643-015-0054-8.

CONCLUSION

- Wet oxidation was found to be a well suited pretreatment method for forest slash (softwood)
- Wet oxidation was further found to produce high sugar yields (both C6 and C5) from both softwood and hardwood
- Fermentation tests showed no inhibition with up to 25% hydrolysate with both bacteria and fungal biocatalysts
- 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
- The pure lignin produced as a result of AWEx makes the material suitable as raw material for high-value bioplastics

AD of manure

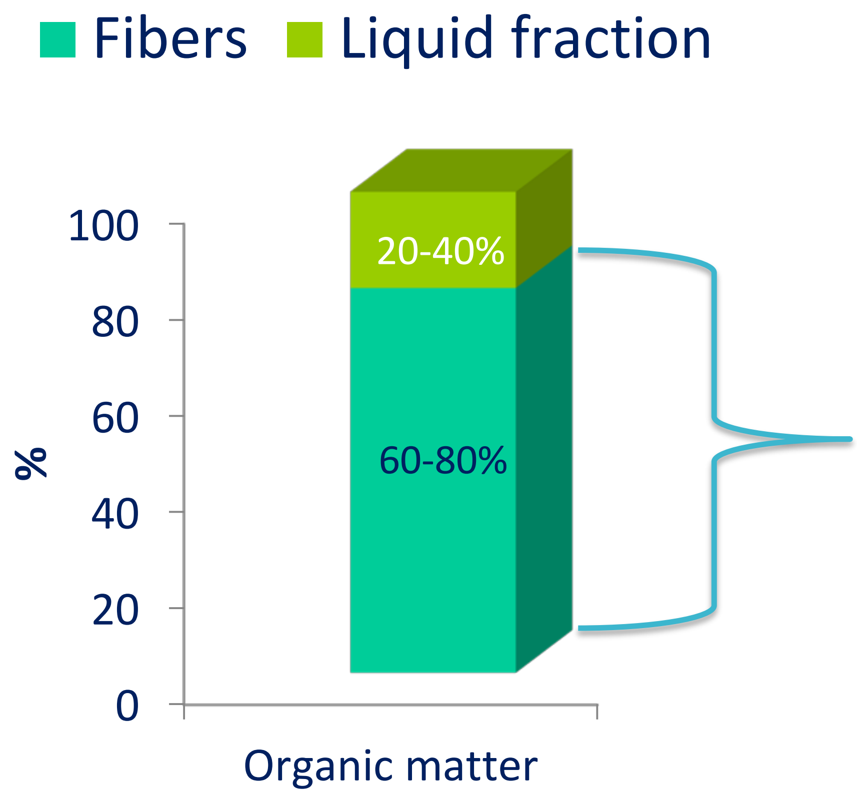
Biogas production from manure has the highest reduction effect on greenhouse gas emissions

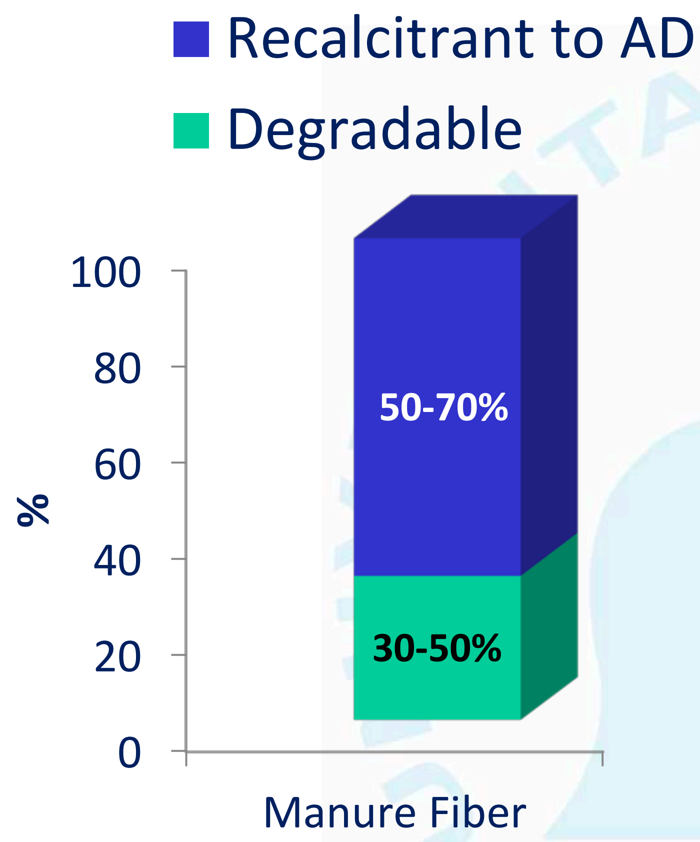
Key Focus Areas:

- Yield, < 25 m^3 biogas/m^3 manure
- Fibers of manure is recalcitrant to AD
- Economic operation, yield > 30 m^3 biogas/m^3 manure required.
- Reduce the dependency on limited amount of high biogas potential industrial organic waste.

*[Thyø and Wenzel, 2007]

AD of manure

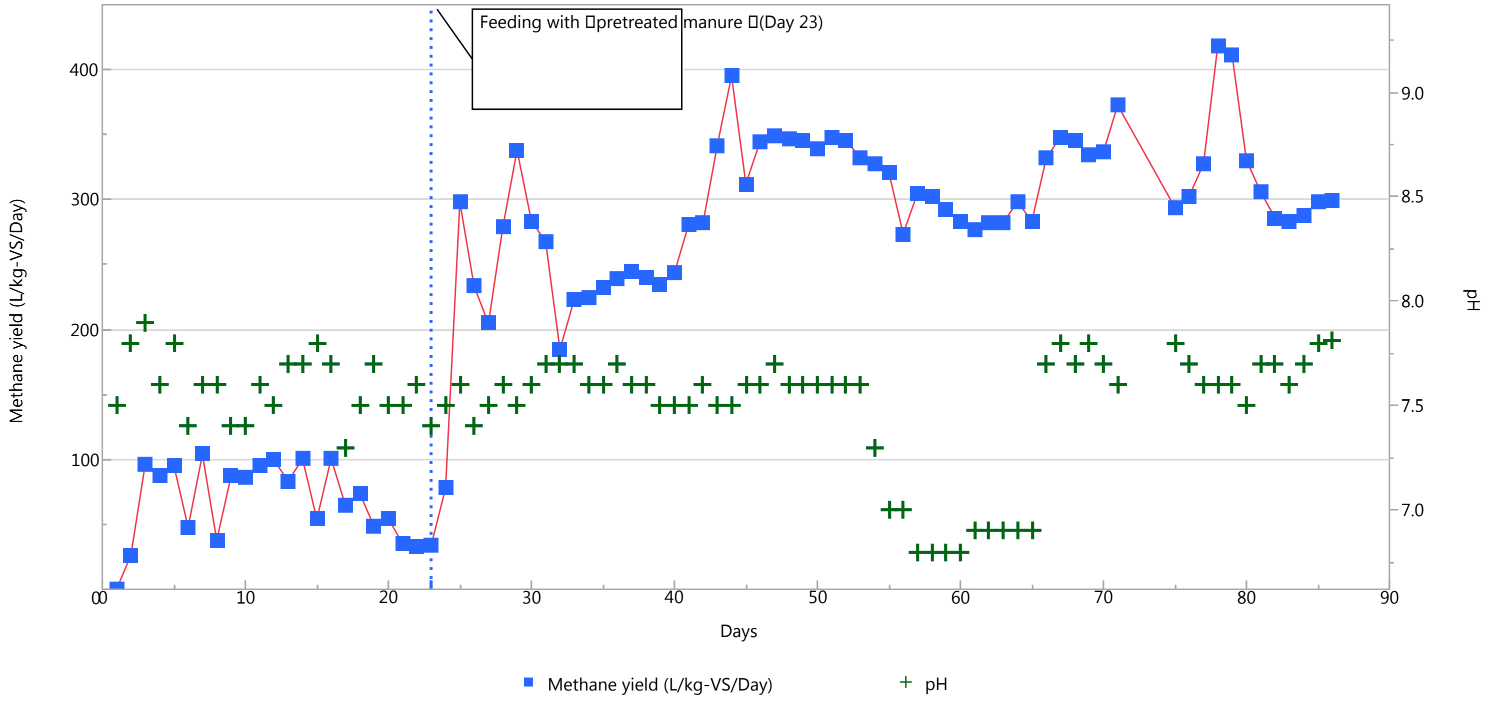




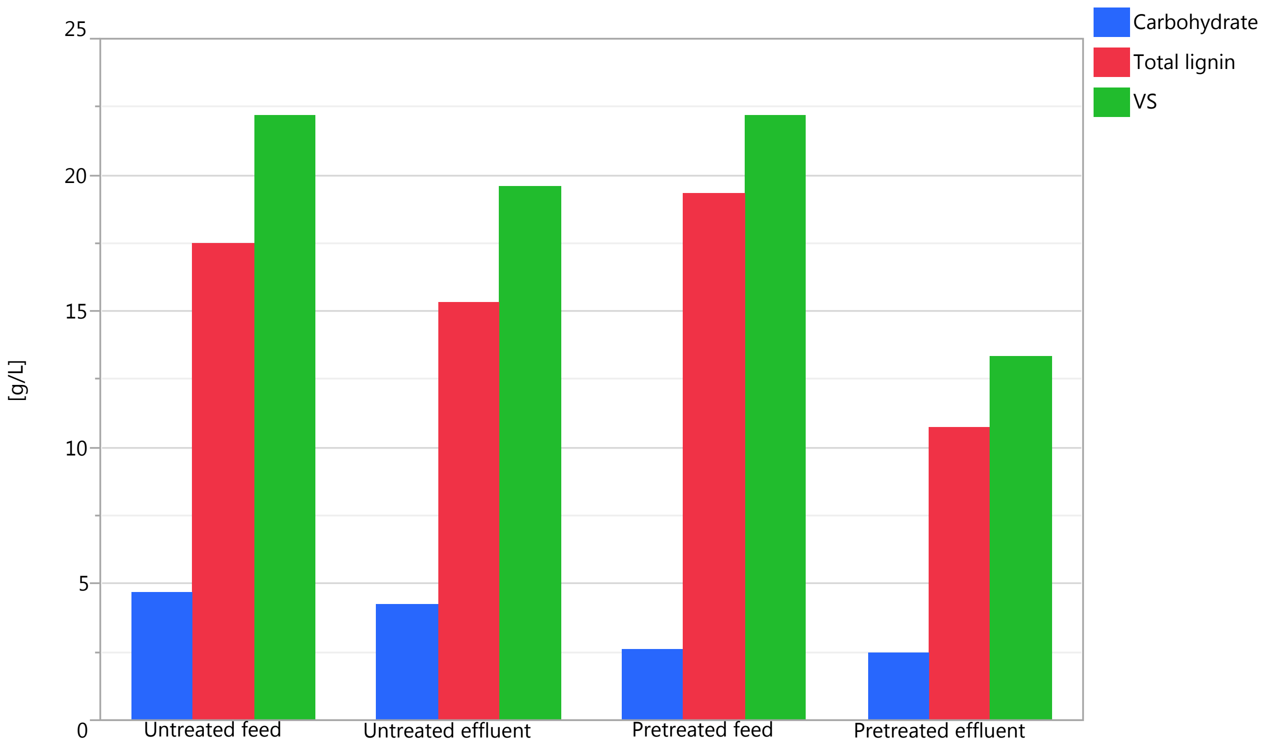
Organic matter distribution in manure slurry

Degradability of manure fiber in traditional AD

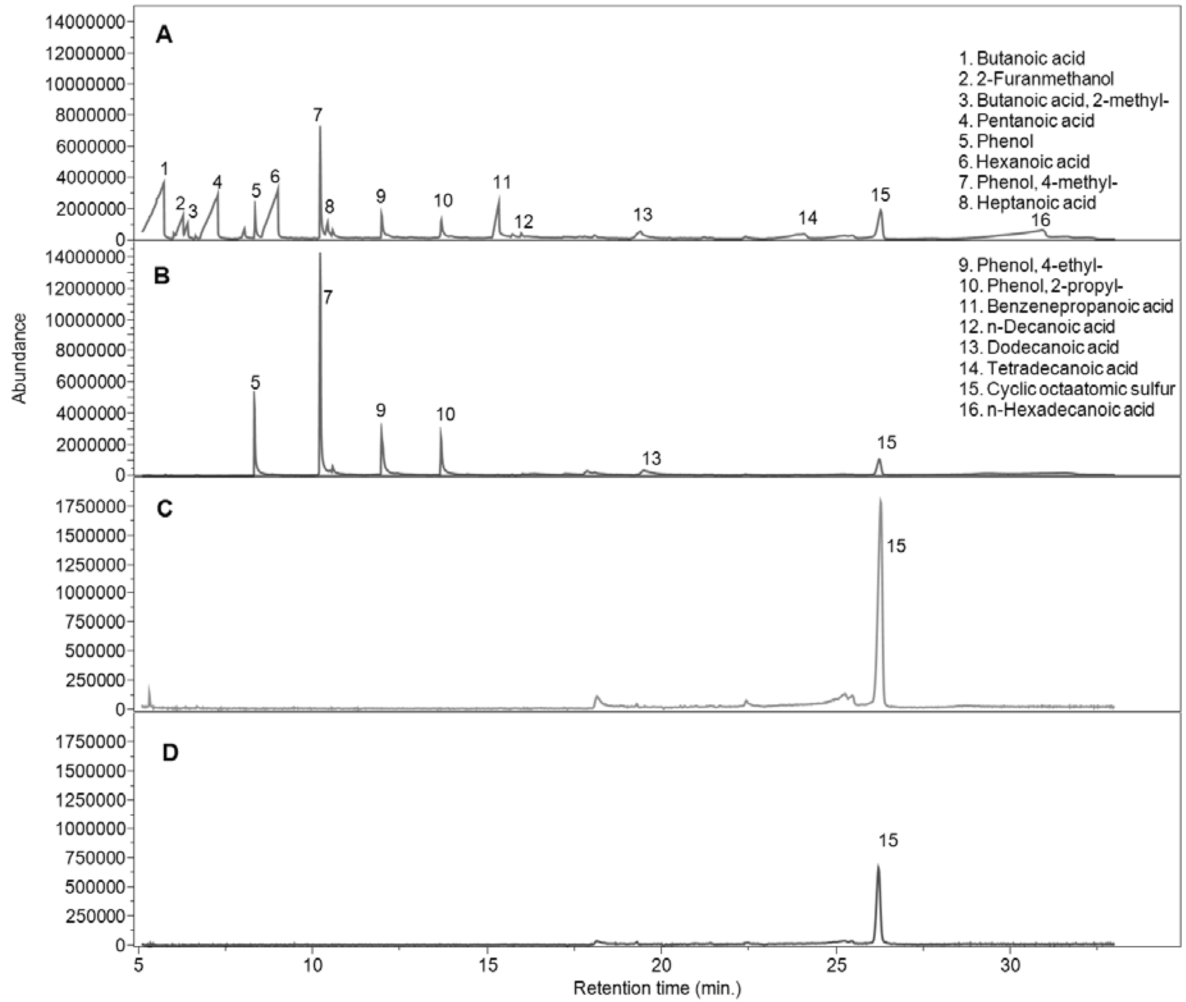
Methane from lignin-enriched manure after AWEx



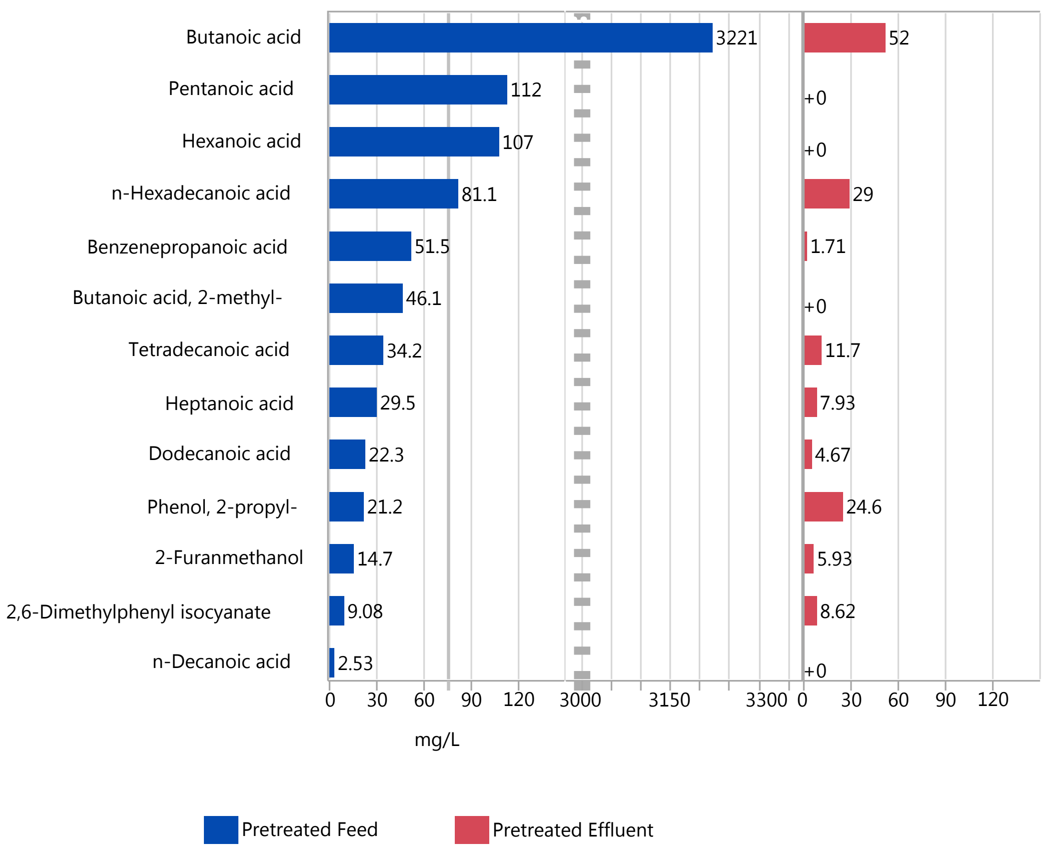
Lignin conversion in AD after AWEx



Wet explosion of feedlot manure



Wet explosion of feedlot manure



Raw Material	Methane Yield (l CH_4/ g VS)	Gas Increase (%)
Woody yard waste	0.35	
Same with AWEx	0.69	97%
Food waste	0.54	
Same with AWEx	0.57	6%
AD-digested Biowaste (yard/food)	0.19	
Same with AWEx	0.37	95%
AD-digested sewage sludge	0.16	
Same with AWex	0.32	100%

Conclusion manure/AD:

- CH_4 yield from manure can be significantly improved using the AD-Booster concept.
- CSTR expt. shows between 50 and 300 % higher CH_4 yield when the fibers are treated by AWEx after AD
- Addition AWEx pretreated lignocellulosic biomass materials could change the economics of biogas production
- The first industrial scale AD-Booster (4 ton per hour) continuous plant is currently being implemented in Europe in connection to a large centralized biogas plant