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Process Technologies – Wood to Wing

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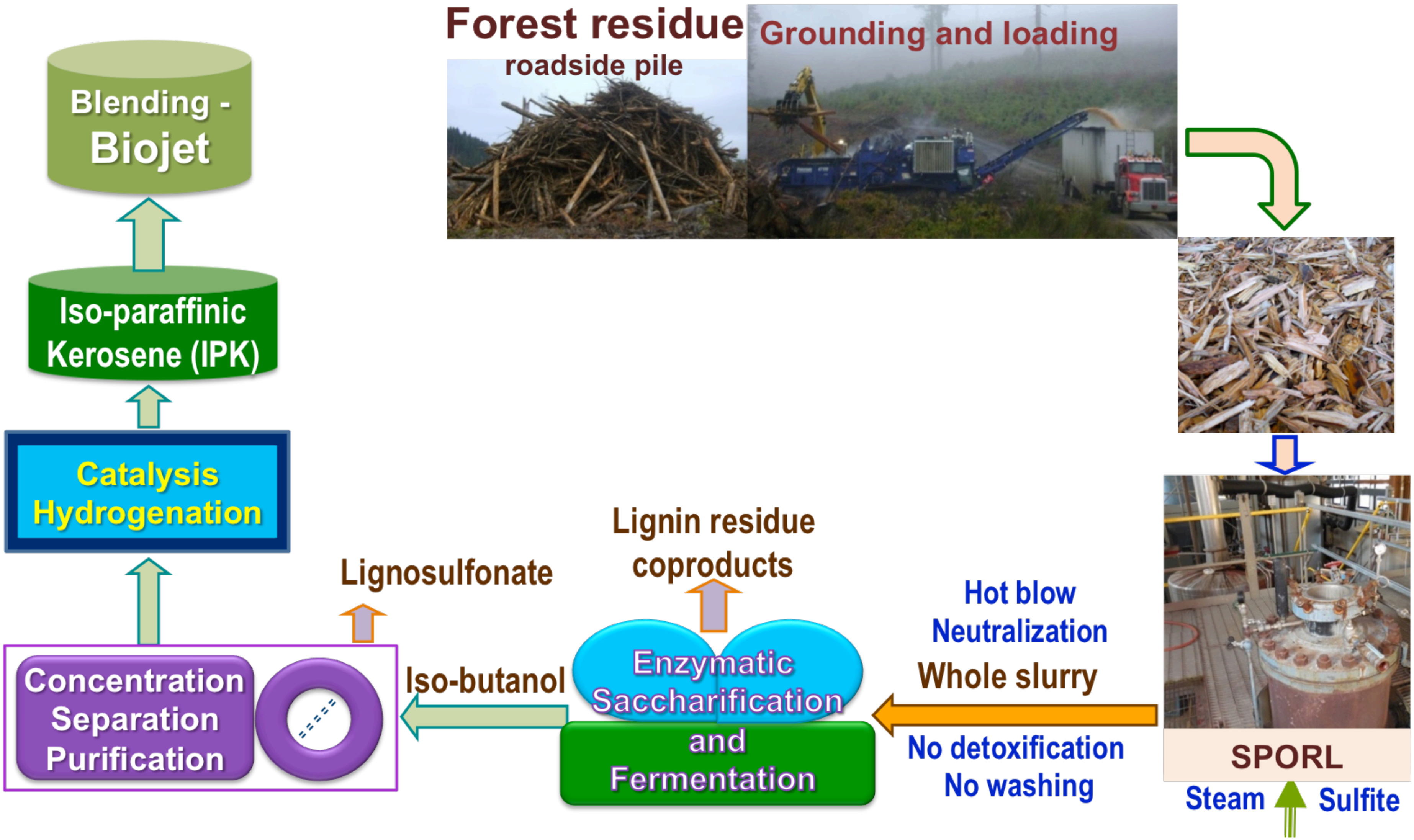
USDA-Forest Products Laboratory

Northwest Advanced Renewables Alliance

USDA

Process Technologies-Wood to Wing



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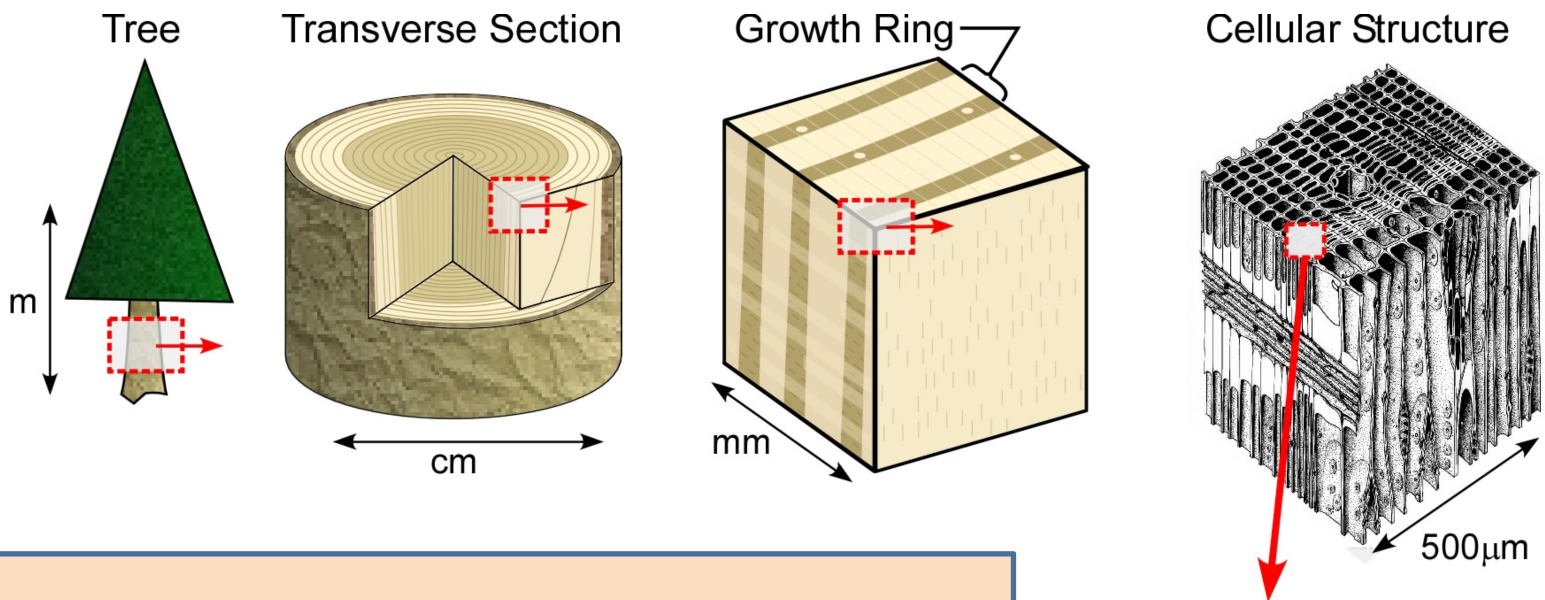
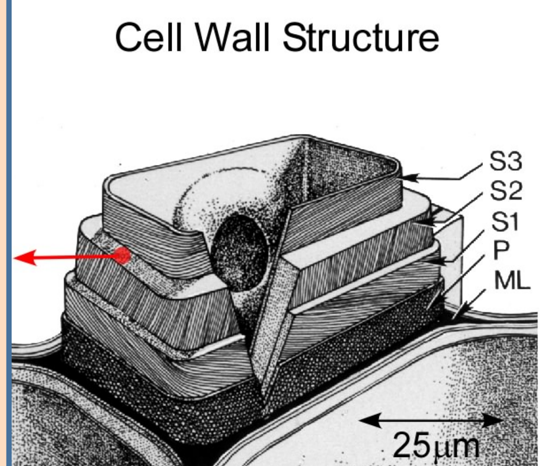
1000 gallon IPK – Conversion Supply Chain

Wood Tracheid Structure



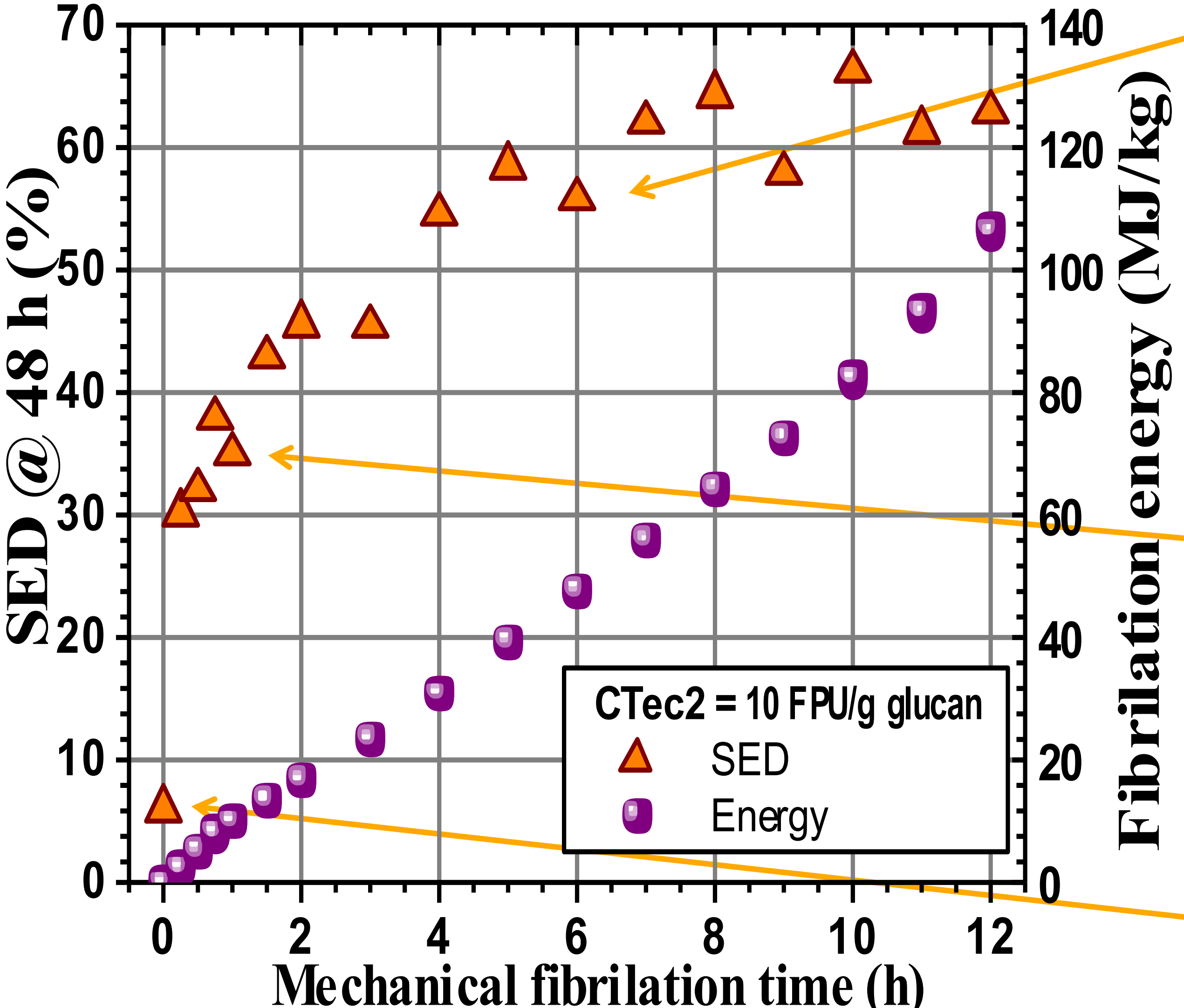


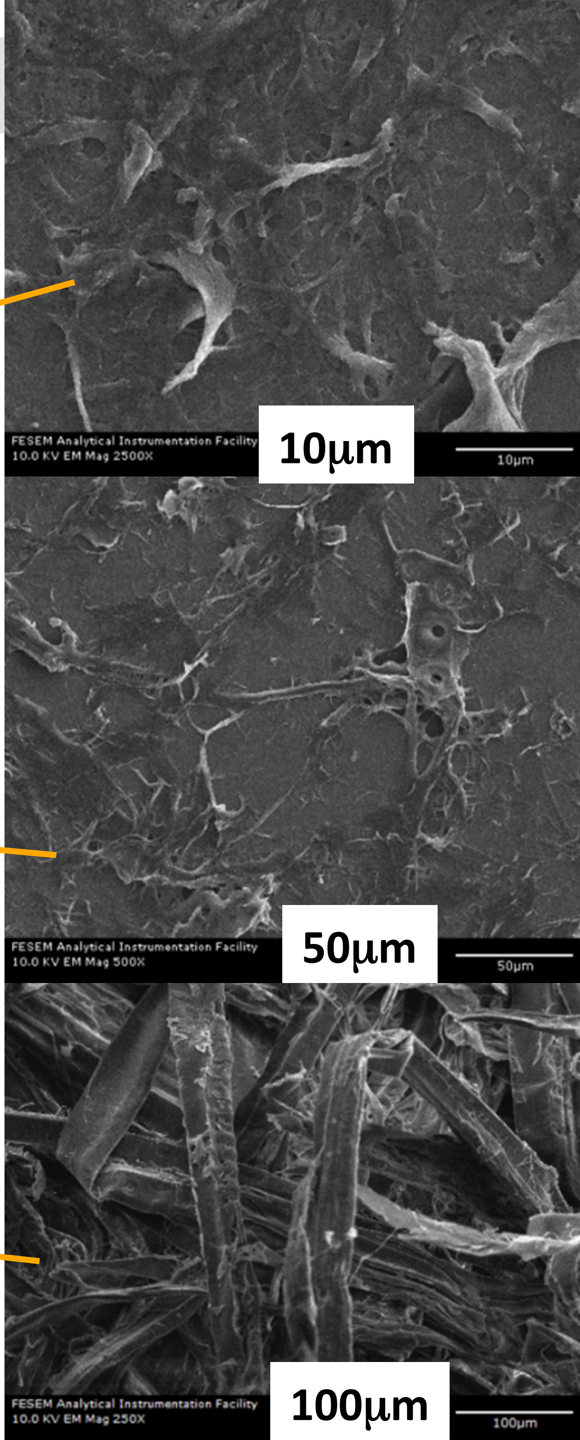
Fermentable sugars
Lignin co-products

Mechanical Disk Milling

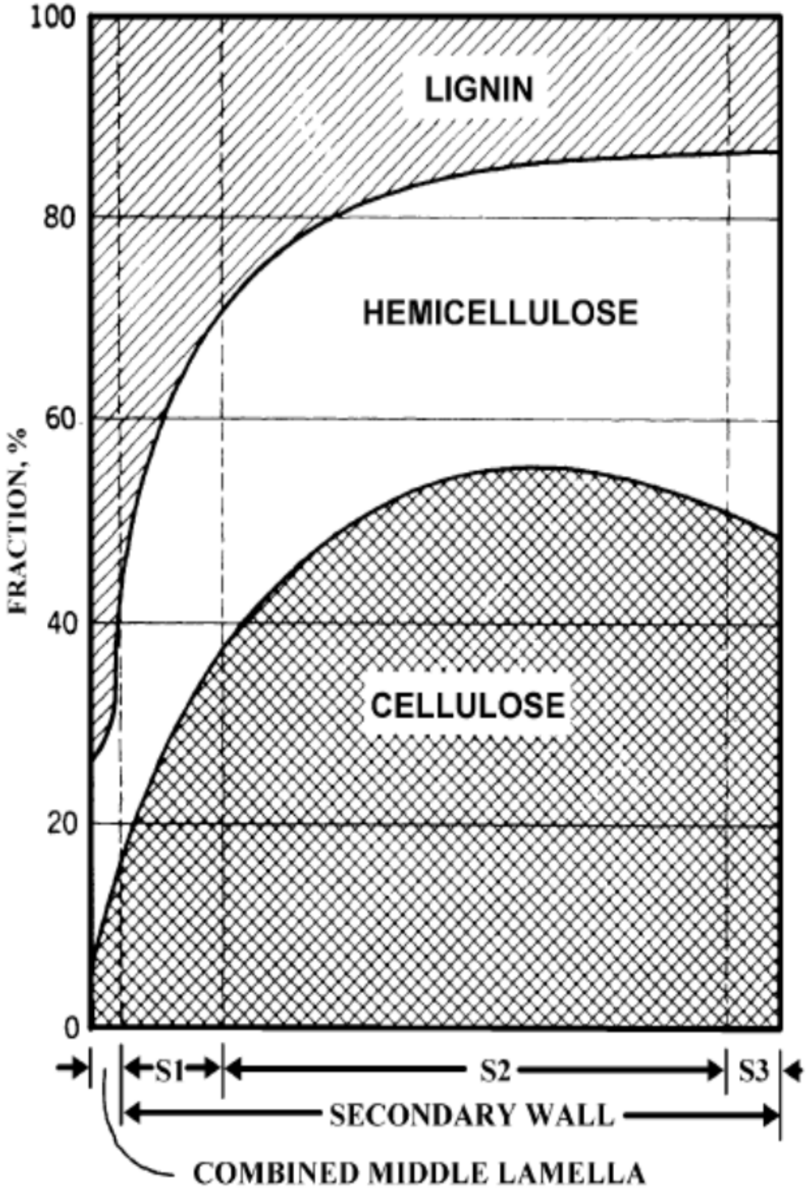
Hoeger et al, *Cellulose*, 20:807, 2013

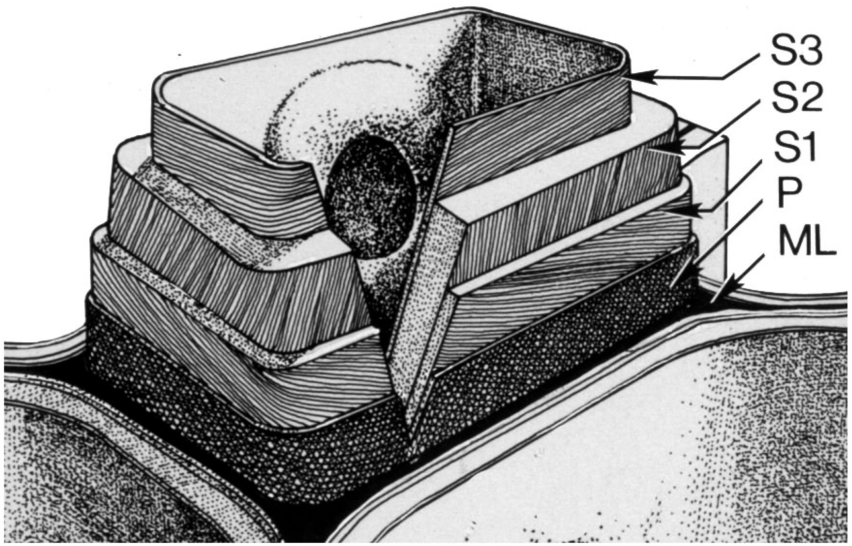
20 MJ/kg ~ 6 kWh/kg ~ 5-6 times of TMP energy cost





Cell Wall Composition Spatial Distribution



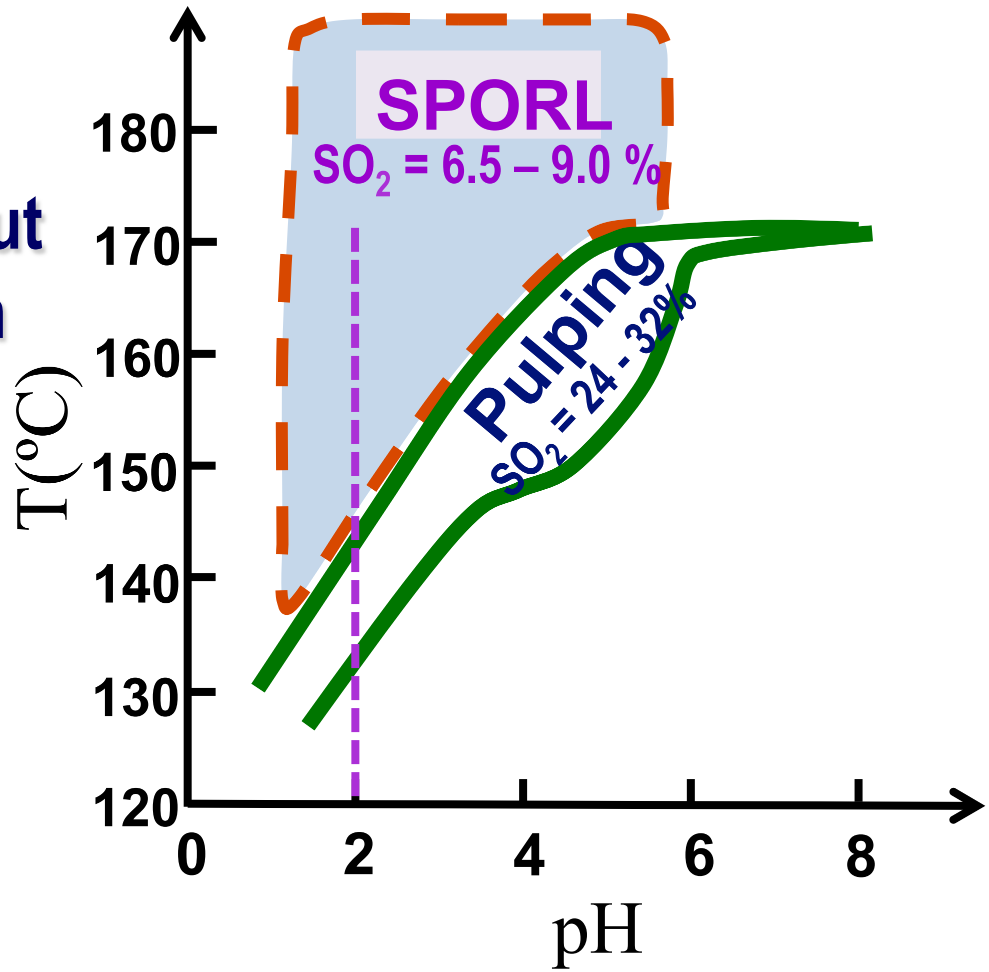


Panshin & de Zeeuw, Text book of Wood technology, 1980, p107

The SPORL Process (Softwood)

SPORL Effects:

- Partial delignification without excessive lignin condensation
- Lignin sulfonation
- Hemicellulose degradation
- Cellulose depolymerization



Patent Nos. ***9,090,915 B2 (2015);***
9,074,231 B2 (2015);
9,243,364 B2 (2016)

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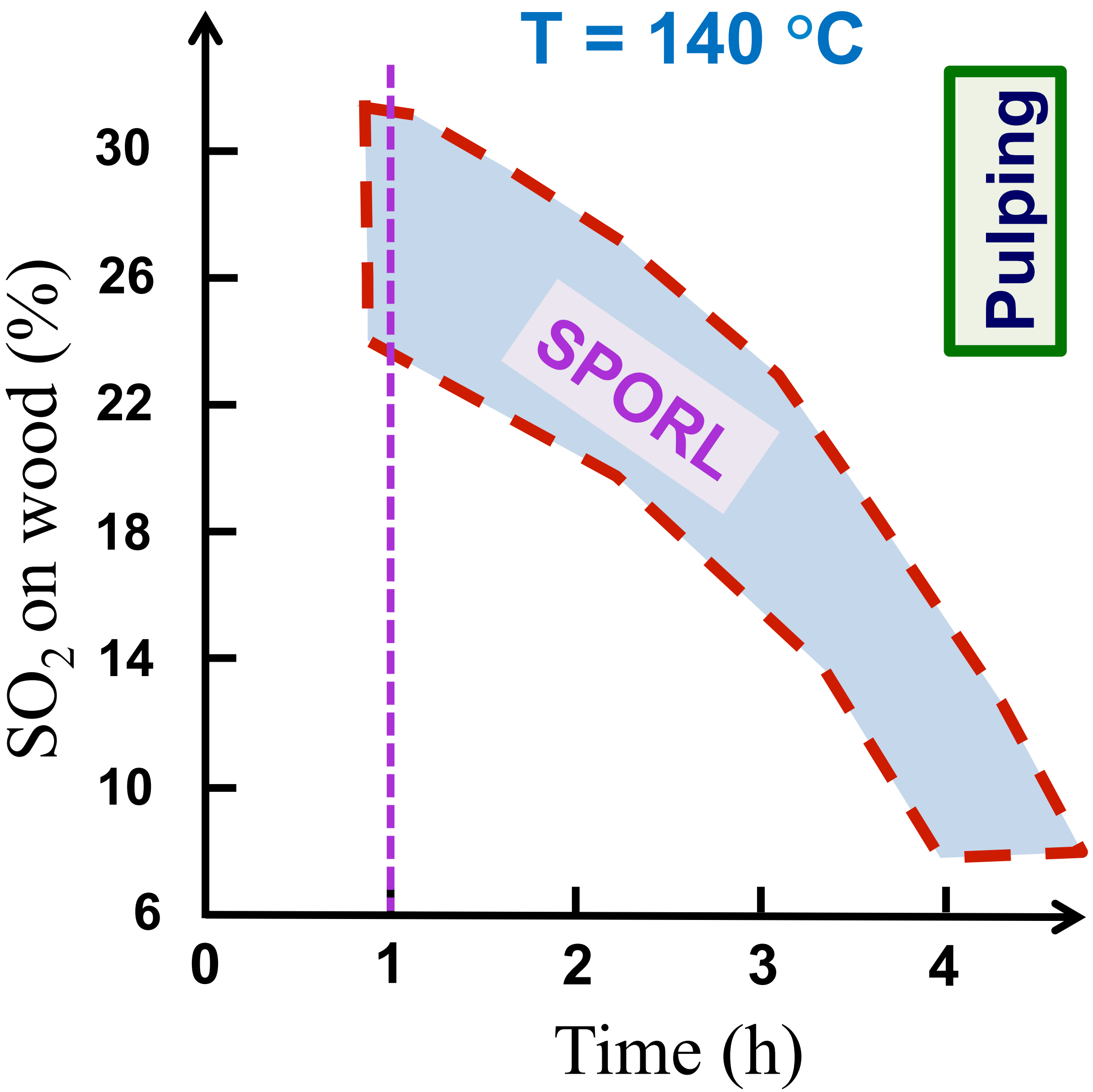
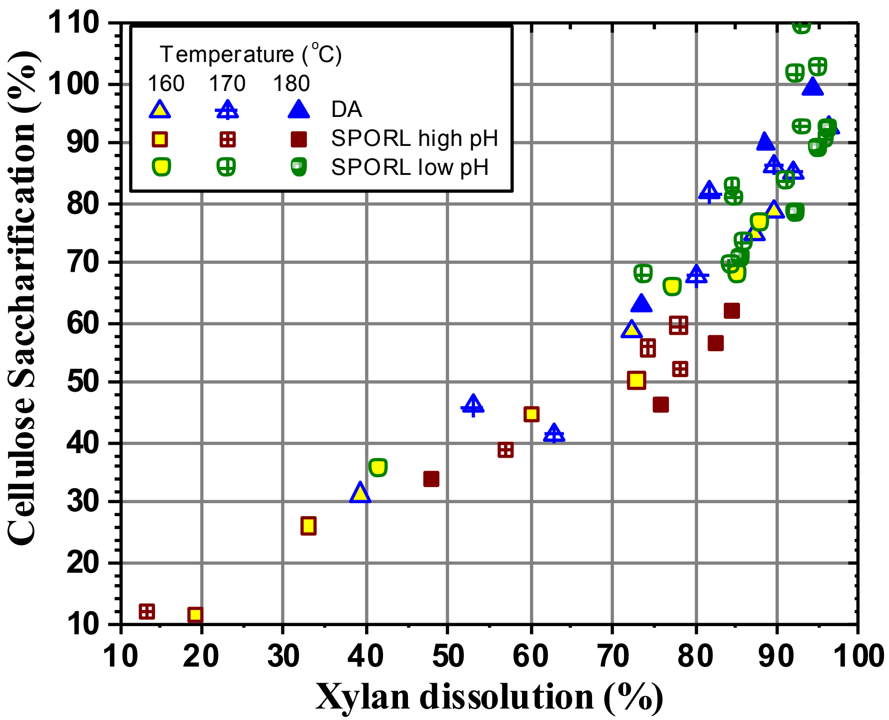
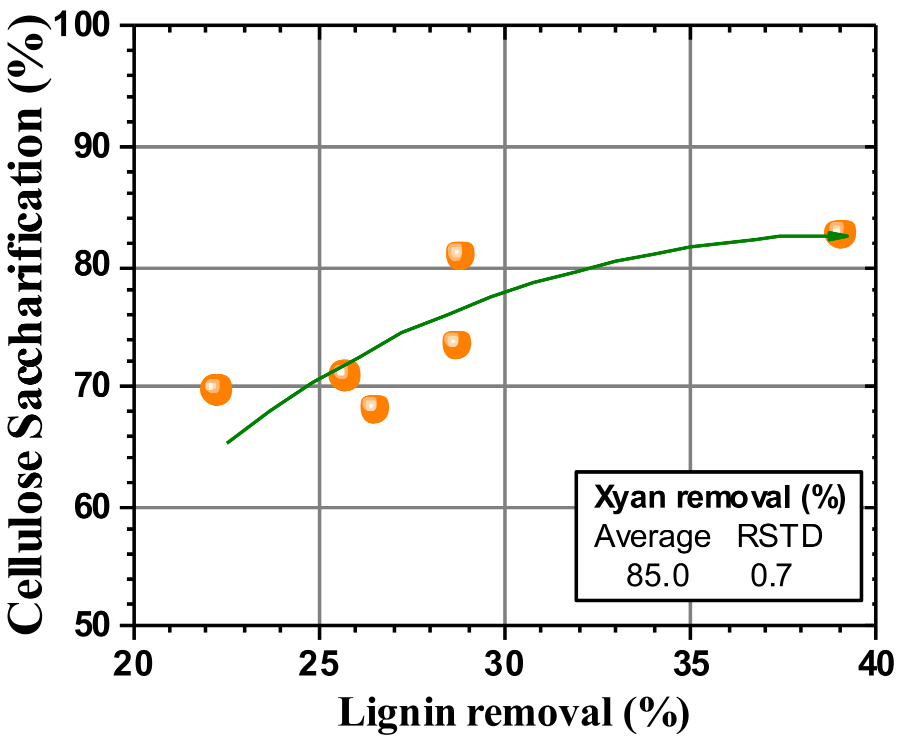
The SPORL Process (Softwood)

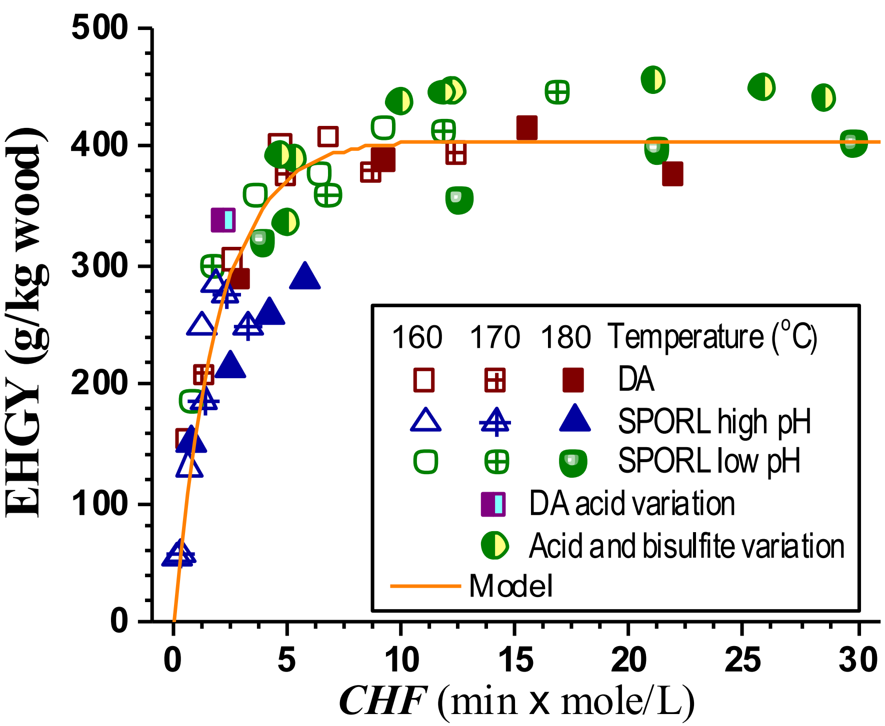


Effect of Pretreatment

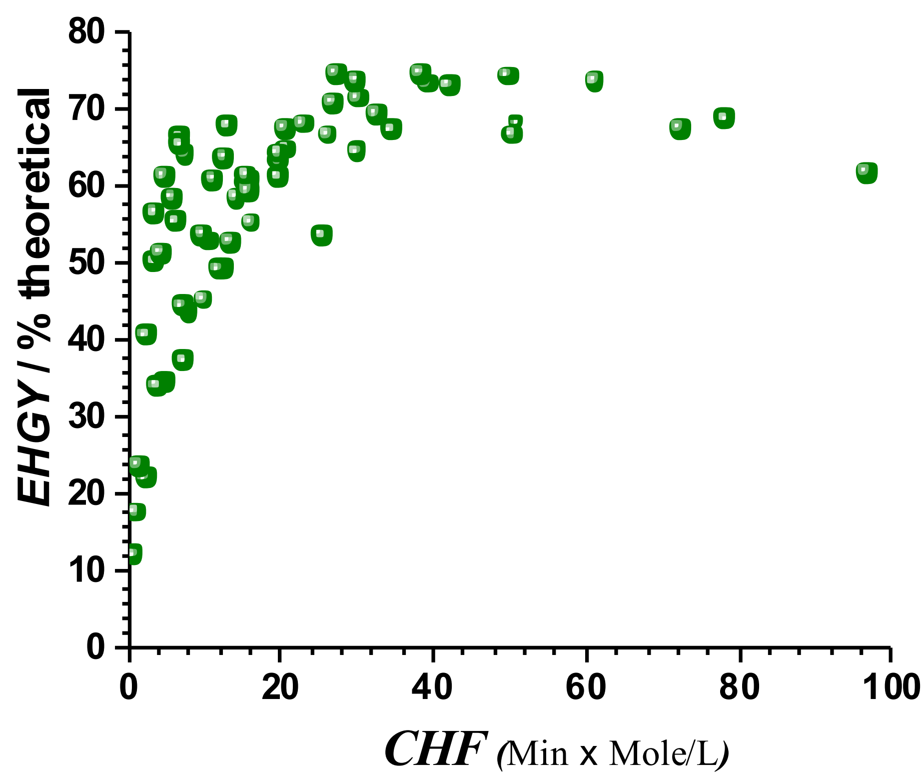




Enzymatic Glucose Yield – Combined Hydrolysis Factor (CHF)



Zhu et al., *Proc. Biochem*, 47:785. 2012



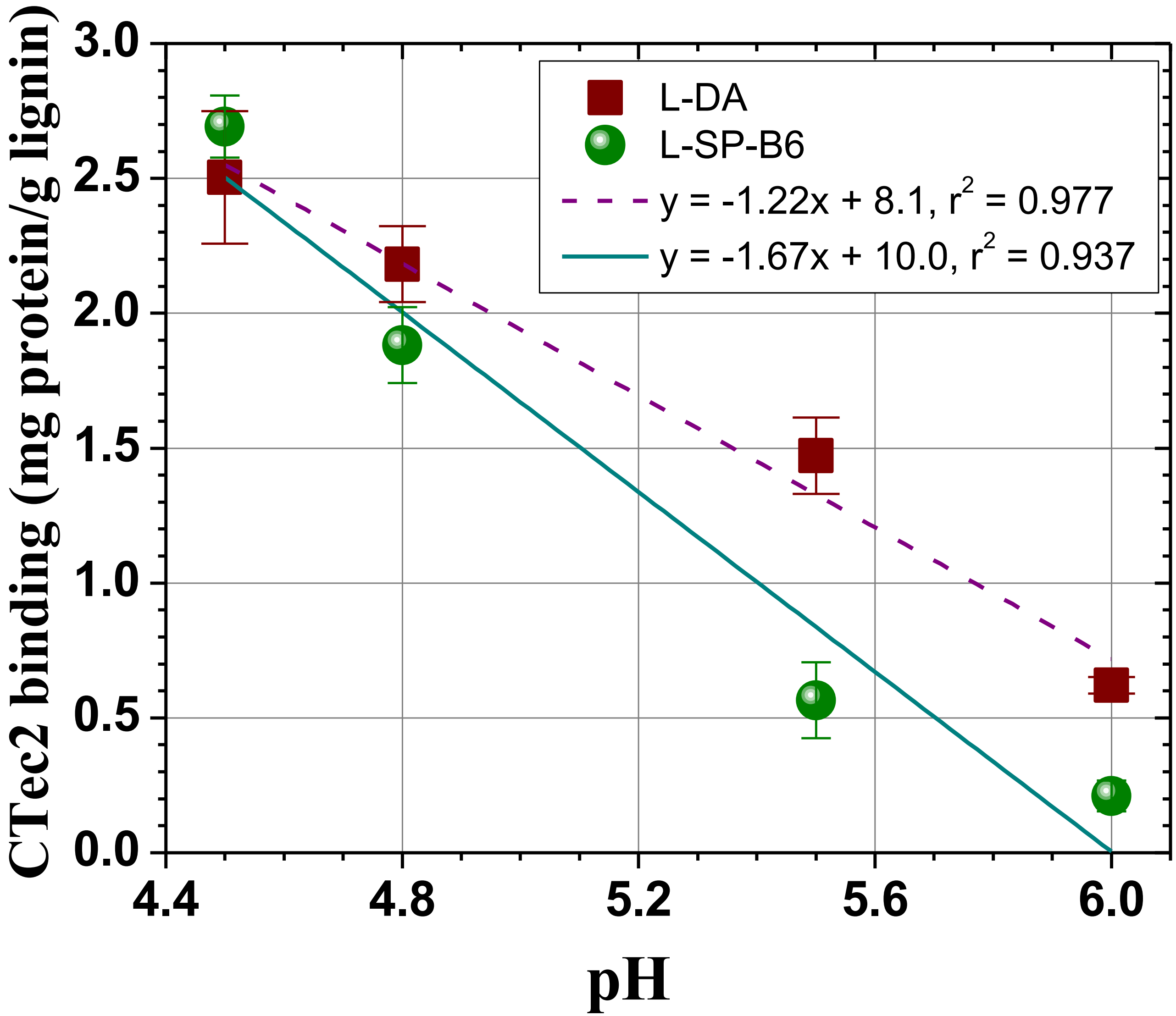
Zhou et al., *Ind Eng Chem Res*, 52:8464. 2013

Process Scale up design and Inhibitor Formation

T (°C)	Time (min)	Inhibitor
180	26	1.000
173	39	0.776
170	47	0.694
165	75	0.575
155	123	0.389
145	240	0.258

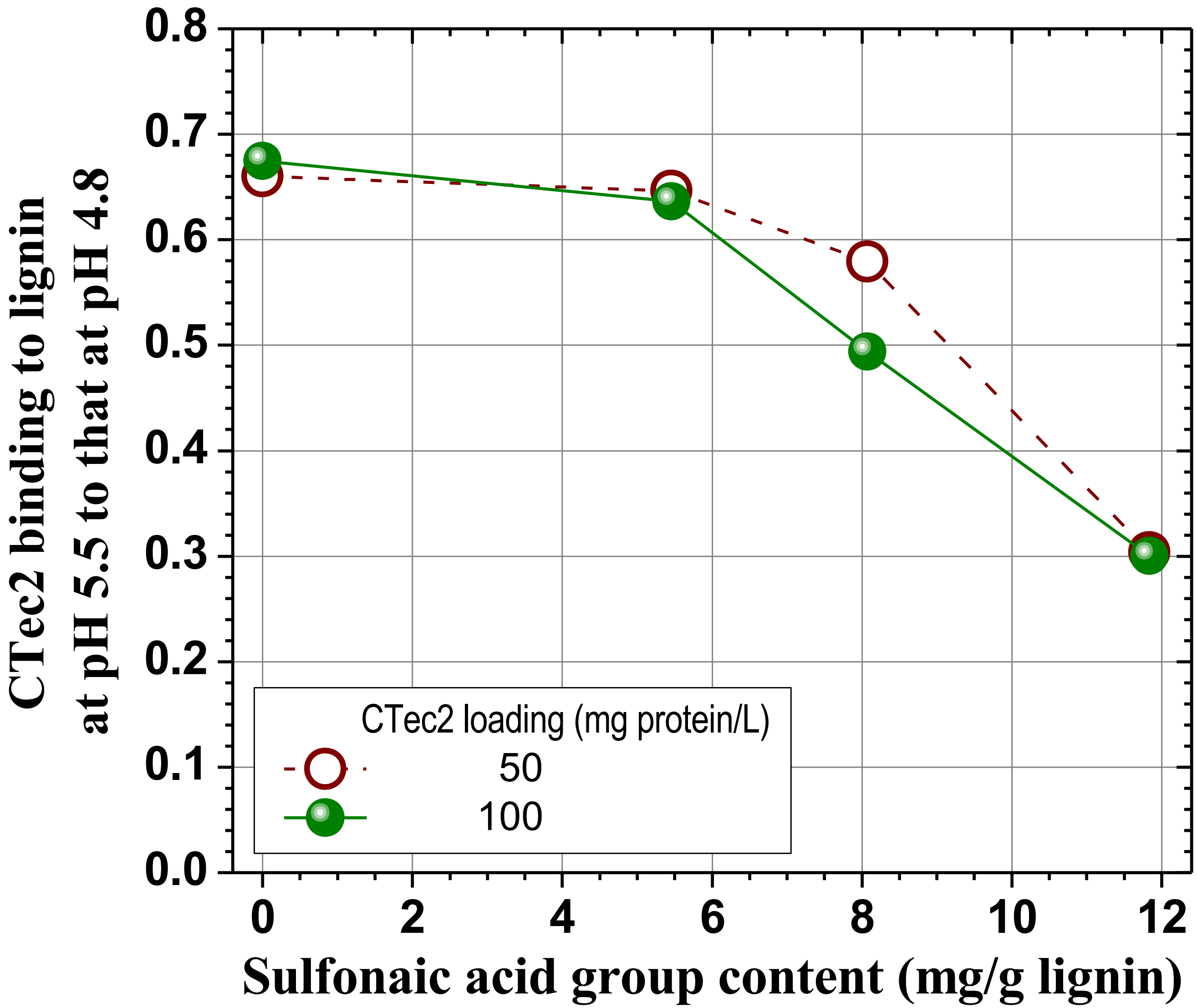
Zhang et al., *Process Biochemistry*, 49:466, 2014

Reduce Non-productive Cellulase Binding



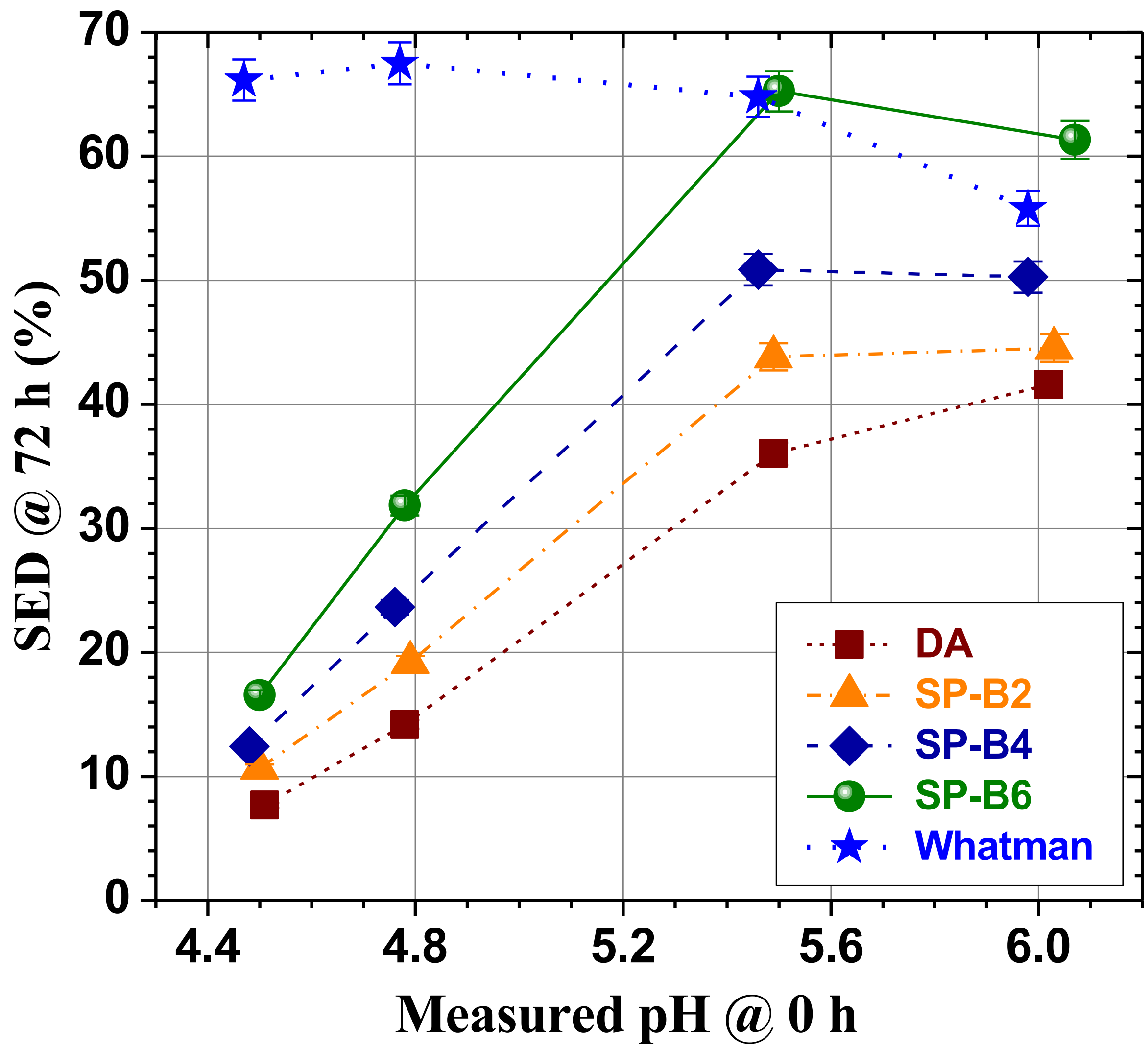
Lou et al., *ChemSumChem*, 6:919-927, 2013

Reduce Non-productive Cellulase Binding



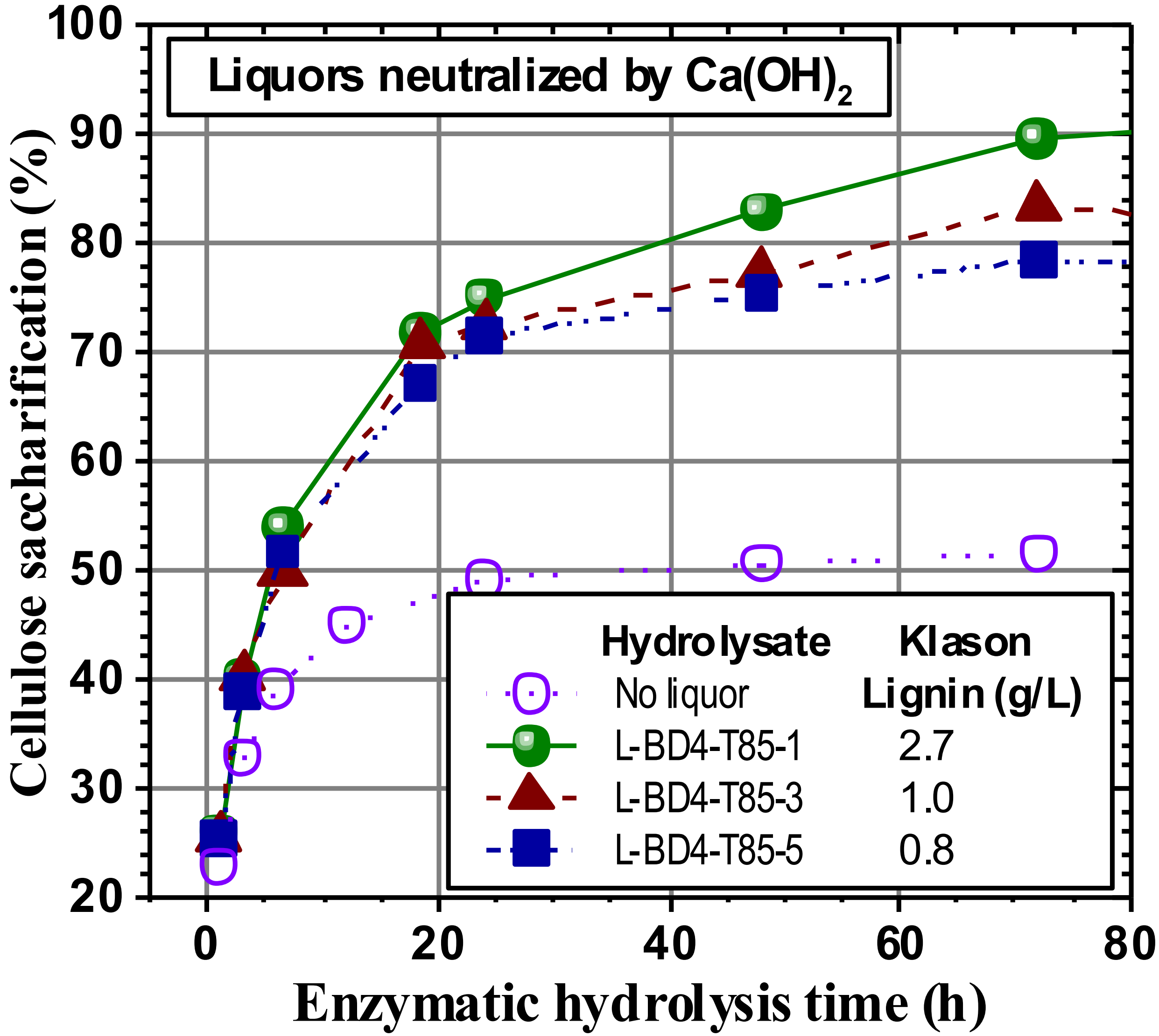
Lou et al., *ChemSumChem*, 6:919-927, 2013

Enzymatic Saccharification- pH of Effect



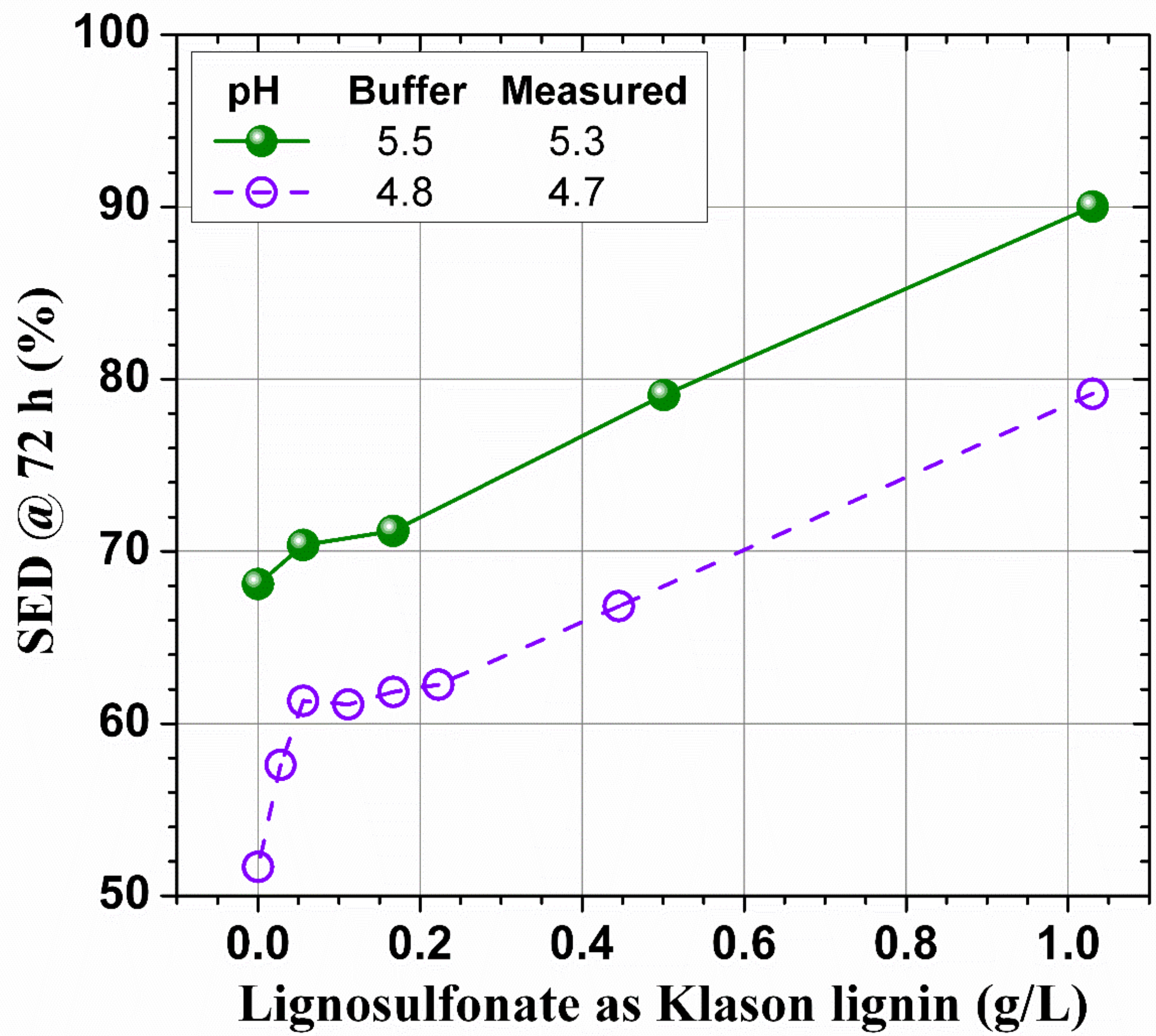
Lou et al. (2013), ***ChemSumChem***, 6(5):919-927

Lignosulfonate (LS) on
Enzymatic Hydrolysis – Lignocelluloses



Wang et al., ***Biotechnology for Biofuels***, 2013, 6,9

Lignosulfonate (LS) on Enzymatic Hydrolysis – Lignocelluloses



Wang et al., *Biotechnology for Biofuels*, 2013, 6,9

SPORL: High SO_2 Loading at 140°C

Douglas-fir Forest Residue

	R-t50	C-t60	C-t120	R-t240-$SO_2$6
Terminal maximal ethanol				
Time to reach maxima (h)	48	72	48	72
Ethanol concentration (g/L)	**54.6±0.6**	**56.3±0.5**	**54.5±2.0**	**41.9±0.3**
Ethanol yield (g/g sugar)	0.487±0.005	0.504±0.004	0.460±0.017	0.412±0.003
Ethanol yield (L/tonne wood)	**315.5±3.5**	**321.6±2.9**	**289.0±10.6**	**284±2.0**
Ethanol yield (% theoretical)	**77.6±0.9**	**79.1±0.7**	**71.1±2.6**	**70.0±0.5**

Gu et al. (2016), *Ind. Biotechnol.* 12(3):168-175

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Lignosulfonate

Ultrafiltration experiment

Sample	LS-Ca (%)	Sugar (%)	Mass (%)	Lignin Purity (%)
Original	100	100	100	44.5
> 200 kDa	3.9	n/a	2.4	89.1
4-200 kDa[a]	69.6	7.6	43.2	86.8
< 4 kDa	24.9	84.3	41.5	19.3

GPC (MALS) analysis

Sample	Mw[b]	Mn[c]	Mw/Mn[d]
4-200 kDa	23430	12910	1.8
D748	24660	14190	1.7

GPC (UV) analysis

4-200 kDa	2704	1092	2.5
D-748	13113	3293	4.0

Zhu et al., *Bioresource Technology*, 179:390-397, 2015

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Summary

- SPORL pretreatment is effective to remove the strong recalcitrance of softwood forest residue.
- The success of the technology substantially change the landscape of feedstock supply and technology platform.
- Co-products from lignin or sugar are the key to economical biofuel production
- Sustained funding of government lab will pay off in long term.

Acknowledgements

- **Funding Sources**
  - USDA NIFA 2011-68005-30416 through Northwest Advanced Renewables Alliance (NARA)
  - USDA Forest Service

- **NARA Feedstock Team**
- **Prof. X.J. Pan of University of Wisconsin**
- **Other collaborators and visitors**


WARRIORS
FUN IN THE SUN
WILD WAVES
OPEN

Thank you for attention

Feed Stock Cost Estimate (T4-1):

NAS Renewable Fuel Standard - 2011

Feedstock	WTA ($/ton)	WTP ($/ton)	Price Gap ($/ton)	Price Gap ($/gallon EtOH)
Corn Stover	92	25	67	0.96
Alfalfa	118	26	92	1.31
Switchgrass – MW	133	26	107	1.51
Switchgrass – SC	98	26	72	1.03
Miscanthus – App	105	27	79	1.13
Short Rotation Woody	89	24	65	0.93
Forest Residues	78	24	54	0.77
Wheat Straw	75	27	49	0.70

SPORL: High SO_2 Loading at 140°C

Douglas-fir Forest Residue

Gu et al. (2016), *Ind. Biotechnol.* (In Press)

Run Labels	R-t50	C-t60	C-t120	R-t240-$SO_2$6
Pretreatment conditions				
T (°C)	140	140	140	145
Heat-up time to T (min)	40	32	36	37
Time at T (min)	50	60	120	240
Metal base	Mg	Mg	Mg	Ca
Total SO_2 on wood (wt%)	32; 27.4 (measured)	**32**; 28.6 (measured)	32; 26.3 (measured)	**6.6**; 6.6 (measured)
Combined SO_2 on wood (wt%) [a]	4.4; 3.2 (measured)	4.4; 4.8 (measured)	4.4; 3.6 (measured)	4.1; 4.1 (measured)
Liquor to wood (L/kg)	4.0	4.0	4.0	3.55
Mixing mechanism	rotation	circulation	circulation	rotation
Carbohydrate dissolution and inhibitor formation - Concentration in spent liquor (g/L)				
Glucose	7.29	6.72	9.93	9.40
Mannose	20.70	17.66	18.39	20.64
Xylose	10.36	8.29	9.91	8.54
Acetic acid	4.73	4.15	5.43	3.18
Levulinic acid	0.12	0.09	0.24	ND
HMF	0.04	**0.08**	0.32	**0.26**
Furfural	0.16	**0.33**	1.00	**0.69**

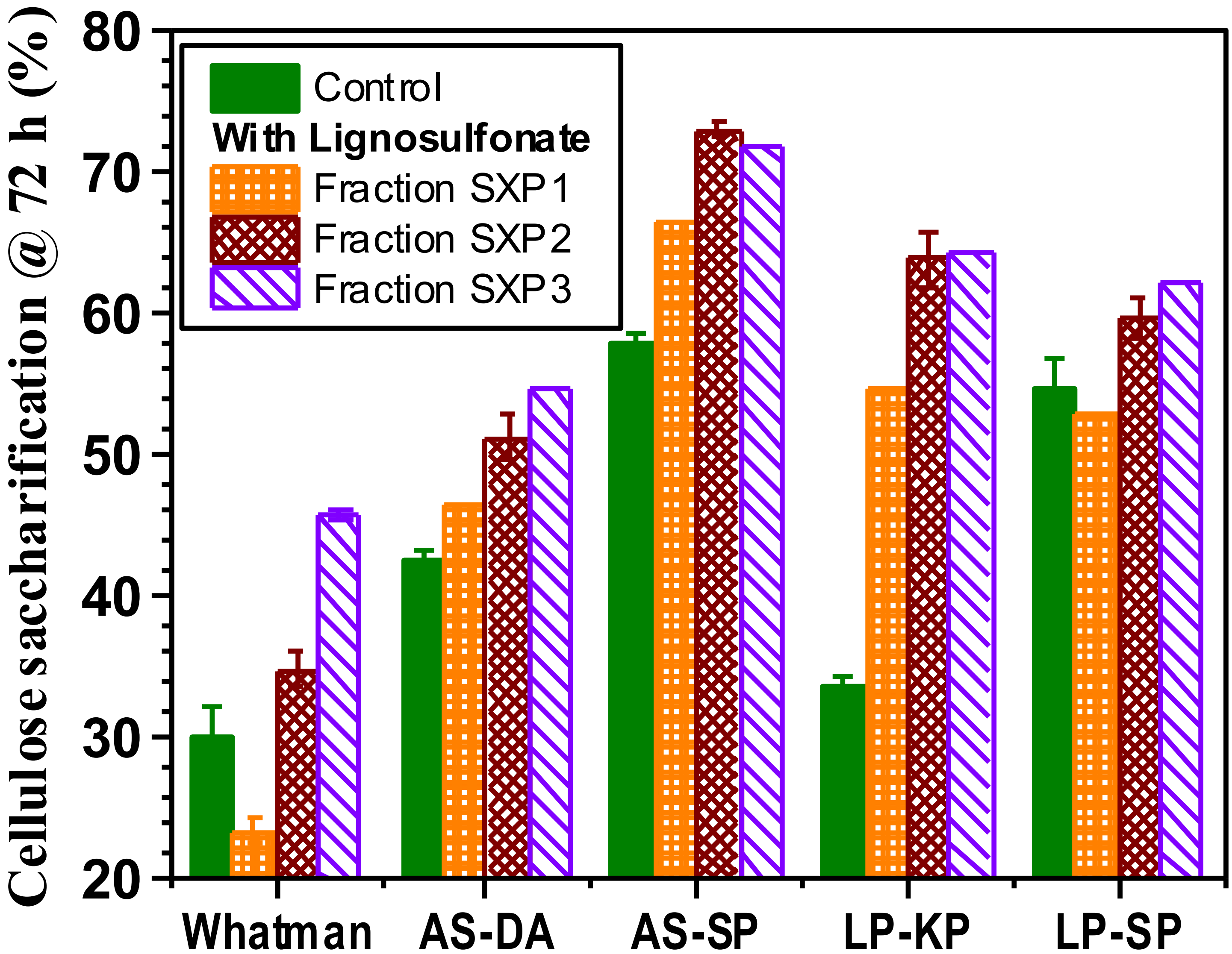
SPORL Solubilized Lignin - Lignosulfonate

Functional group contents and molecular weights of three LSs

Sample	Functional group content (mmol/g)			Molecular weight		
	Sulfonic	Phenolic hydroxyl	Carboxyl	M_w	M_n	M_w/M_n
Ca-LS-DF	1.35	1.75	0.84	10650	3730	2.86
Na-LS-LP	1.47	1.76	0.73	8870	3120	2.84
Reax-85A	1.23	1.75	0.90	8020	3240	2.47

Qin et al., (2016), *ACS-Sustainable Chem. Eng.,* (under re-review)

LS MW on
Enzymatic Hydrolysis – Lignocelluloses



Zhou et al., *Ind Eng Chem Res*, 2013, 52:8464

Scale-up Pretreatment

- Maintain same pretreatment severity (CHF):

$$CHF = e^{(\alpha - E/RT + \beta C_A + \gamma C_B)} (C_A + C_B) t$$

- Reaction time at low T can be determined

$$t^{Tup} = \exp[-E/R(1/T^{up} - 1/T^{lab})] t^{Tlab}$$

R = 8.314 J/mole/K, E = 100,000 J/mole

Zhang et al., *Process Biochemistry*, 49:466, 2014

Sugar Degradation

$$dD/dt = k\downarrow d\ (1 - X\downarrow R\ )k\downarrow d = e\uparrow(\alpha\downarrow d - E\downarrow d\ /RT\ )$$

$$X\downarrow R = (1-\theta)e\uparrow - CHF + \theta e\uparrow - f\ CHF$$

$$D = k\downarrow d \cdot t[1 - 1 - \theta/CHF\ (1 - e\uparrow - CHF\ ) - \theta/f \cdot CHF\ (1 - e\uparrow - f \cdot CHF\ )]$$

$$\frac{D_{T1}}{D_{T2}} = \frac{k_d^{T1}}{k_d^{T2}}\frac{t^{T1}}{t^{T2}} = exp\left[\frac{E - E_d}{R}\left(\frac{1}{T1} - \frac{1}{T2}\right)\right]$$

Zhang et al., *Process Biochemistry*, 49:466, 2014

Project Status

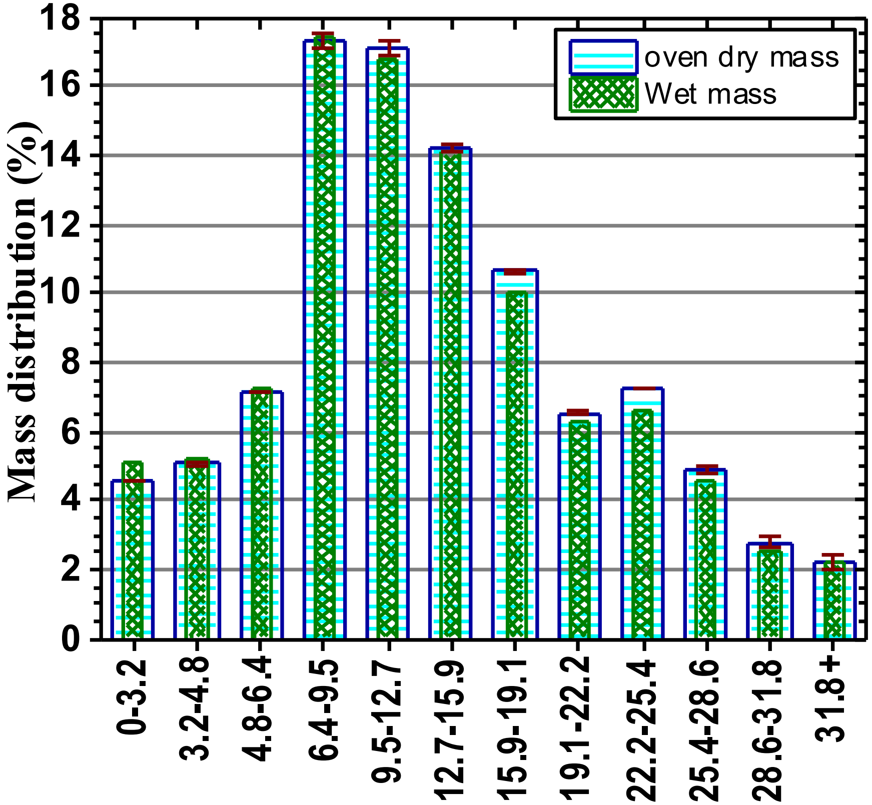
- Pretreated 60 tonnes Forest Residue using SPORL – ZeaChem, OR – Aug - Sep., 2015

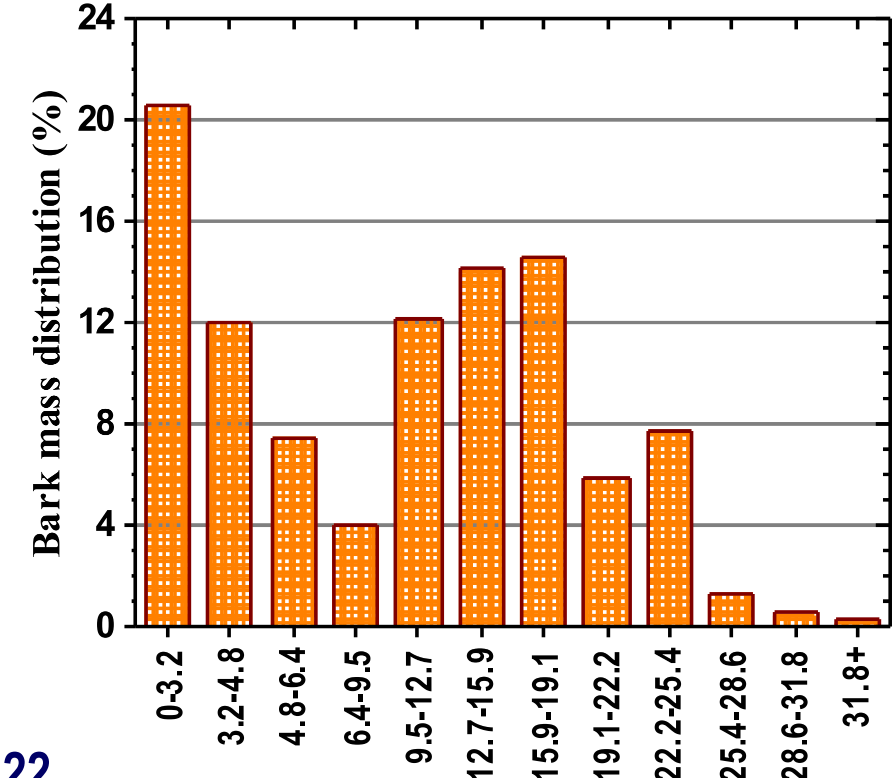
- Enzymatic Saccharification and Fermentation at ICM, MO – Nov.-Dec., 2015
- IPK conversion at South Hampton, TX – June, 2016
- Biojet-blending and certification – August. 2016
- Commercial flight by Alaska Airlines – 2016

Douglas-fir Forest Residue - FS-17

Ground Douglas-fir Residue Fractions

Mass Distribution and Selectivity





Cheng et al. (2015), *Biotechnol. Biofuels* 8:22

Zhang and Zhu (2013), *BioEnergy Research* 5(4):978-988

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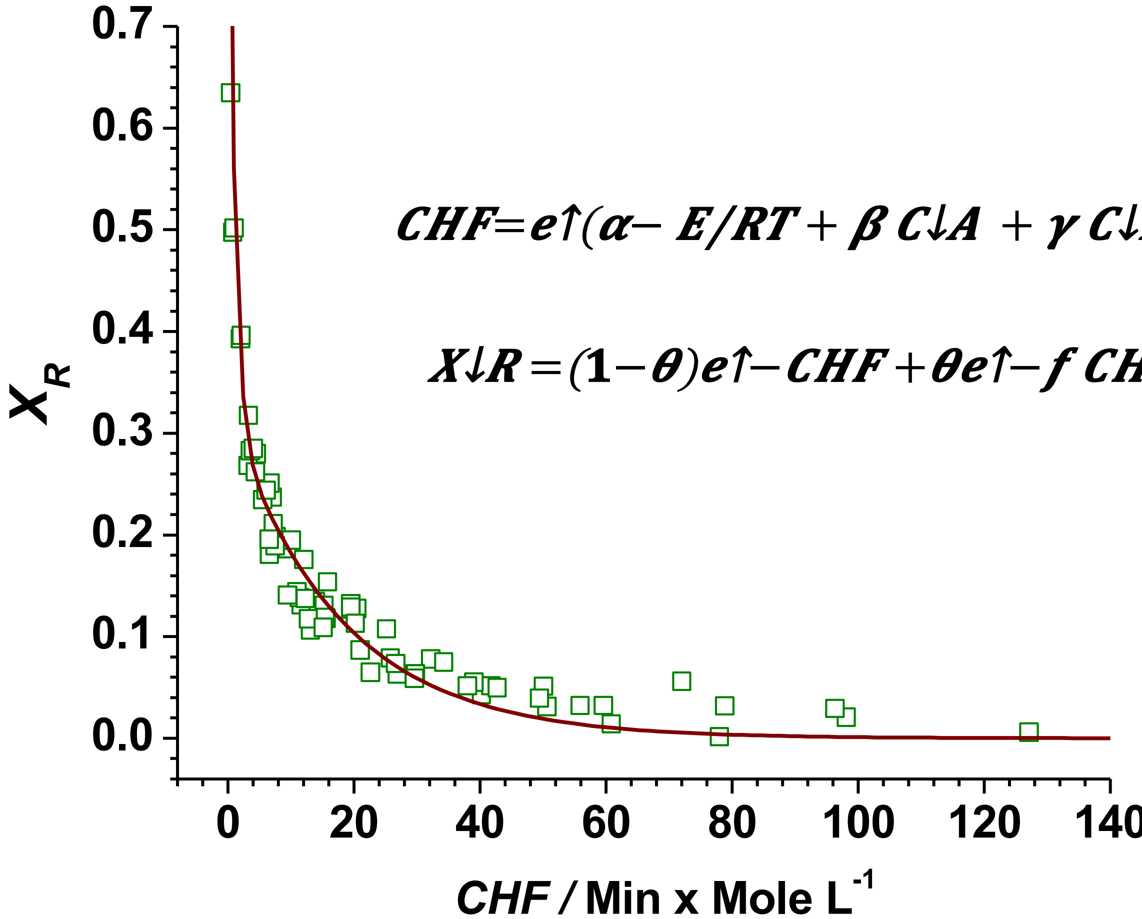
FPL – Pilot Scale Results

FS – 10 Chemical Compositions

Sample	Bark	Klason Lignin	Glucan	Xylan	Mannan	G+X+M
As harvested	5.9	30.5	38.4	4.4	7.5	50.3
FS-10 screened out fraction I	3.4	29.3	41.0	5.7	9.7	56.4

Hemicellulose Dissolution vs Combined (hemicelluloses) Hydrolysis Factor (CHF) – Lodgepole Pine



$$CHF = e^{(\alpha - E/RT + \beta C_A + \gamma C_B)} (C_A + C_B) t$$

$$X_R = (1-\theta) e^{-CHF} + \theta e^{-f\,CHF}$$

Zhou et al., *Ind Eng Chem Res*, 52:8464. 2013

Scale-up Pretreatment

- **Maintain same pretreatment severity (CHF):**

$$CHF = e^{\left(\alpha - E/RT + \beta C_{A} + \gamma C_{B}\right)} \left(C_{A} + C_{B}\right) t$$

- **Reaction time at low T can be determined**

$$t^{T_{up}} = \exp\left[-E/R\left(1/T^{up} - 1/T^{lab}\right)\right] t^{T_{lab}}$$

R = 8.314 J/mole/K, E = 100,000 J/mole

Zhang et al., *Process Biochemistry*, 49:466, 2014

Sugar Degradation

$$dD/dt = k_d(1 - X_R) \qquad k_d = e^{(\alpha_d - E_d/RT)}$$

$$X_R = (1-\theta)e^{-CHF} + \theta e^{-f\,CHF}$$

$$D = k_d \cdot t[1 - 1 - \theta/CHF\,(1 - e^{-CHF}) - \theta/f \cdot CHF\,(1 - e^{-f \cdot CHF})]$$

$$X_R = (1-\theta)e^{-CHF} + \theta e^{-f\,CHF}$$

Zhang et al., *Process Biochemistry*, 49:466, 2014