

Study of Sunflower Hulls as a Potential Feedstock for Biofuel and Chemical Production

By

Srinivas Reddy Kamireddy

Department of Chemical Engineering

University of North Dakota

Advisor

Dr. Yun Ji



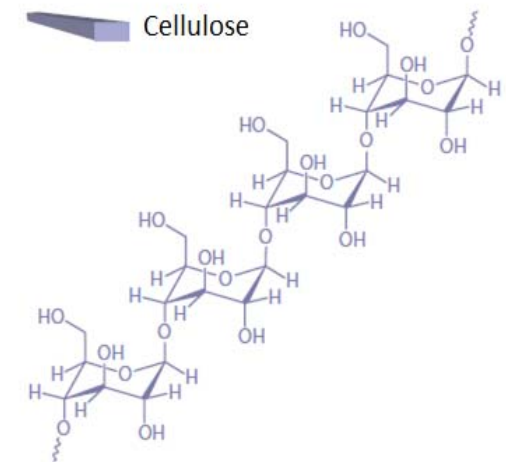
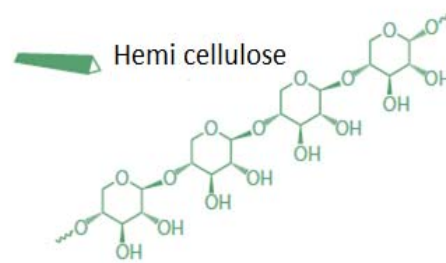
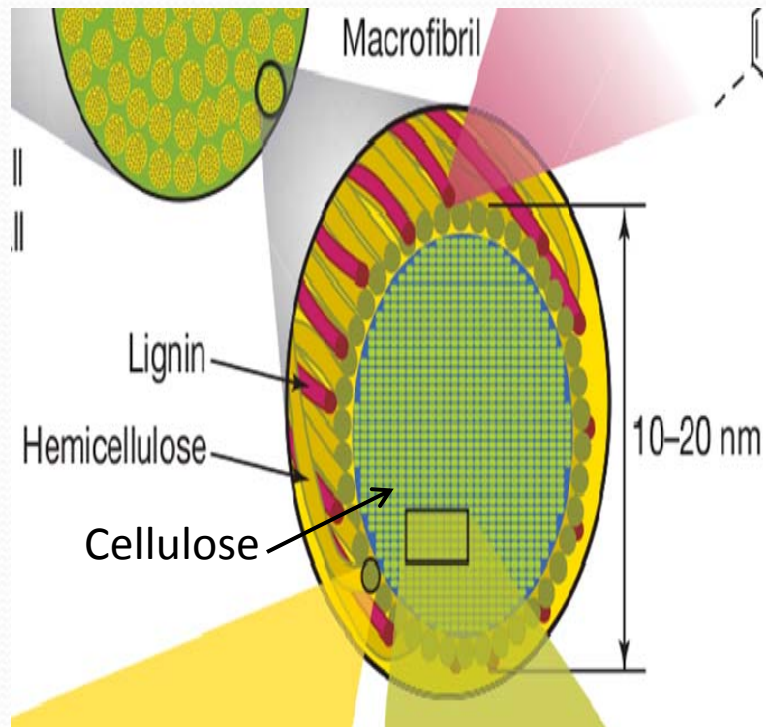
Outline

- Introduction
- Background
- Experimental procedure
- Results and Discussion
- Conclusion
- Acknowledgements
- Questions

Lignocellulosic Biomass

- Lignocellulosic material provides structural support to plants and it is found in plant stalks, roots, leaves
- It is most abundant renewable material available on the planet
- According to USDA Annually around 1.3 billion tons of agricultural biomass is available in USA
- It consists of cellulose, hemicellulose and lignin
- Cellulose and hemicellulose can be converted into fermentable sugars
- Lignin can be used as a solid fuel, manufacture organic polymers, liquid fuels

Structure of Lignocellulosic Biomass



Edward M. Rubin, "Genomics of cellulosic biofuels," Nature 454, no. 7206 (print 2008): 841-845.

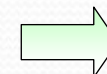
Background

- According USDA report in 2010 around 1.5 MMT of sunflower seeds were produced
- Sunflower seeds have a good commercial value since 80% of them are used to produce edible oil and 20% of them consumed as snack
- However, sunflower hulls are obtained as a waste product from de-hulling process. They have little commercial value and become a disposable problem owing to their low bulk density
- The sunflower hulls were obtained from Dahlgren Company Inc in Crookston, MN

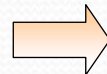
Process of Conversion to Biofuels



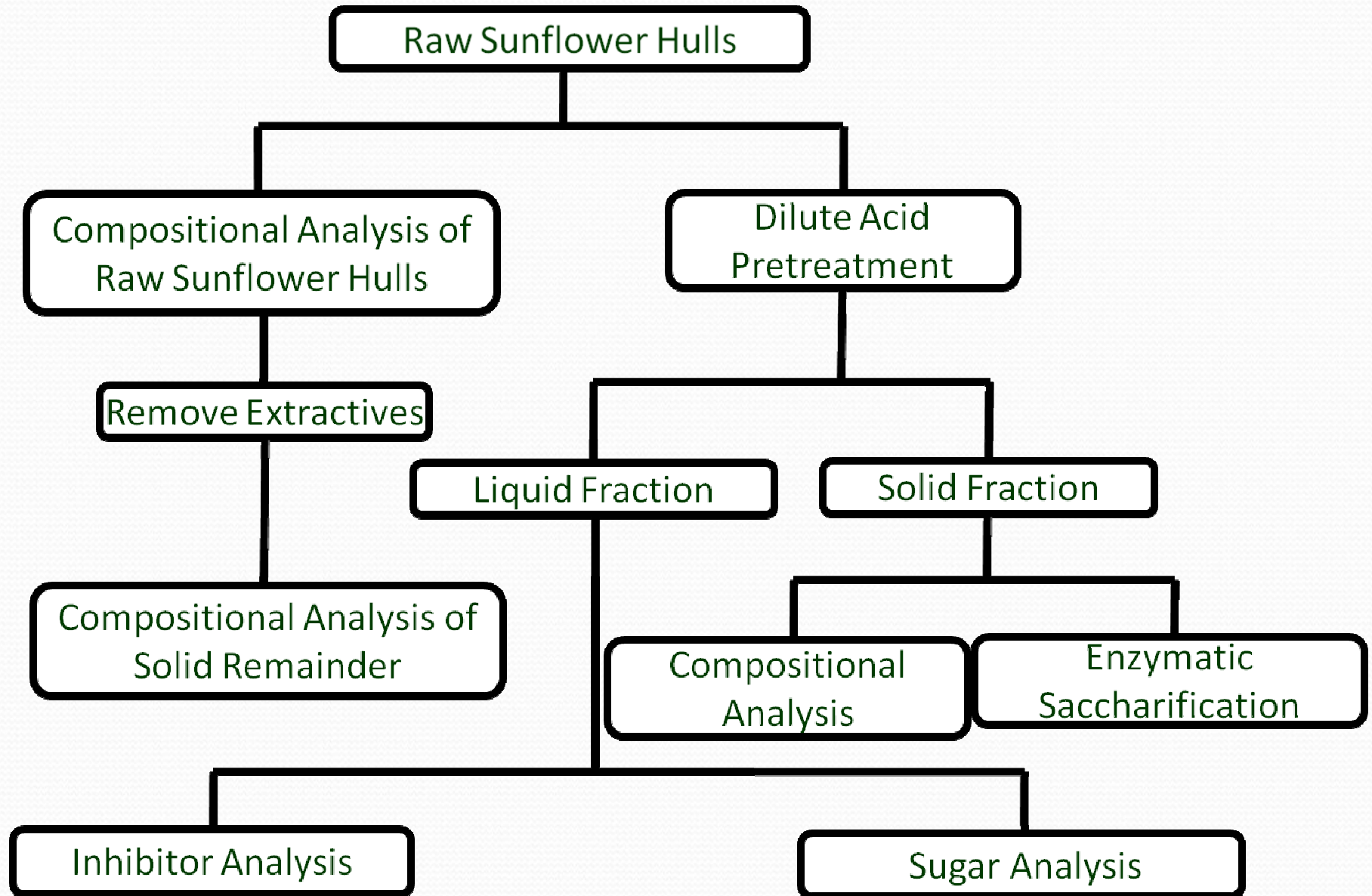
**Biochemical Process:
(Sugars then Fermentation to
Alcohol Fuels)**



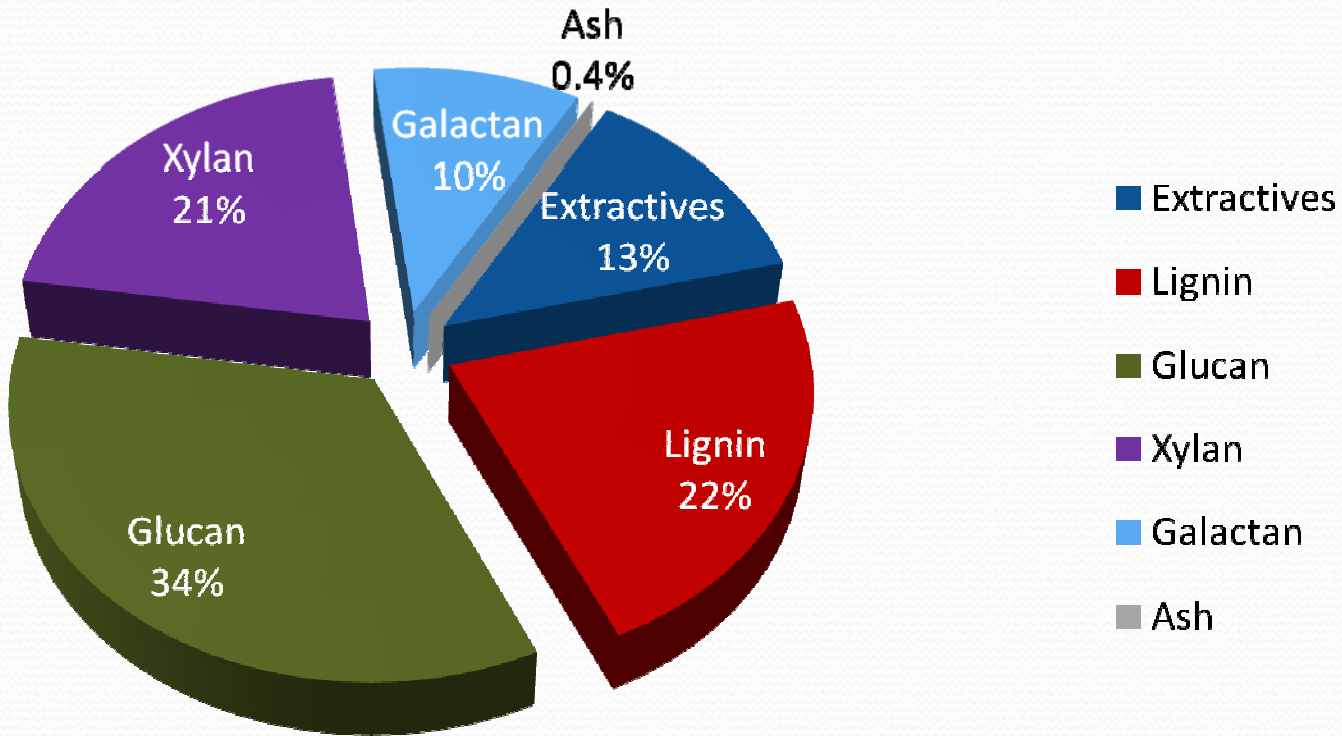
**Thermochemical Process:
(Syngas or BioOil to Gasoline &
Diesel)**



Experimental Procedure



Compositional Analysis of Sunflower Hulls



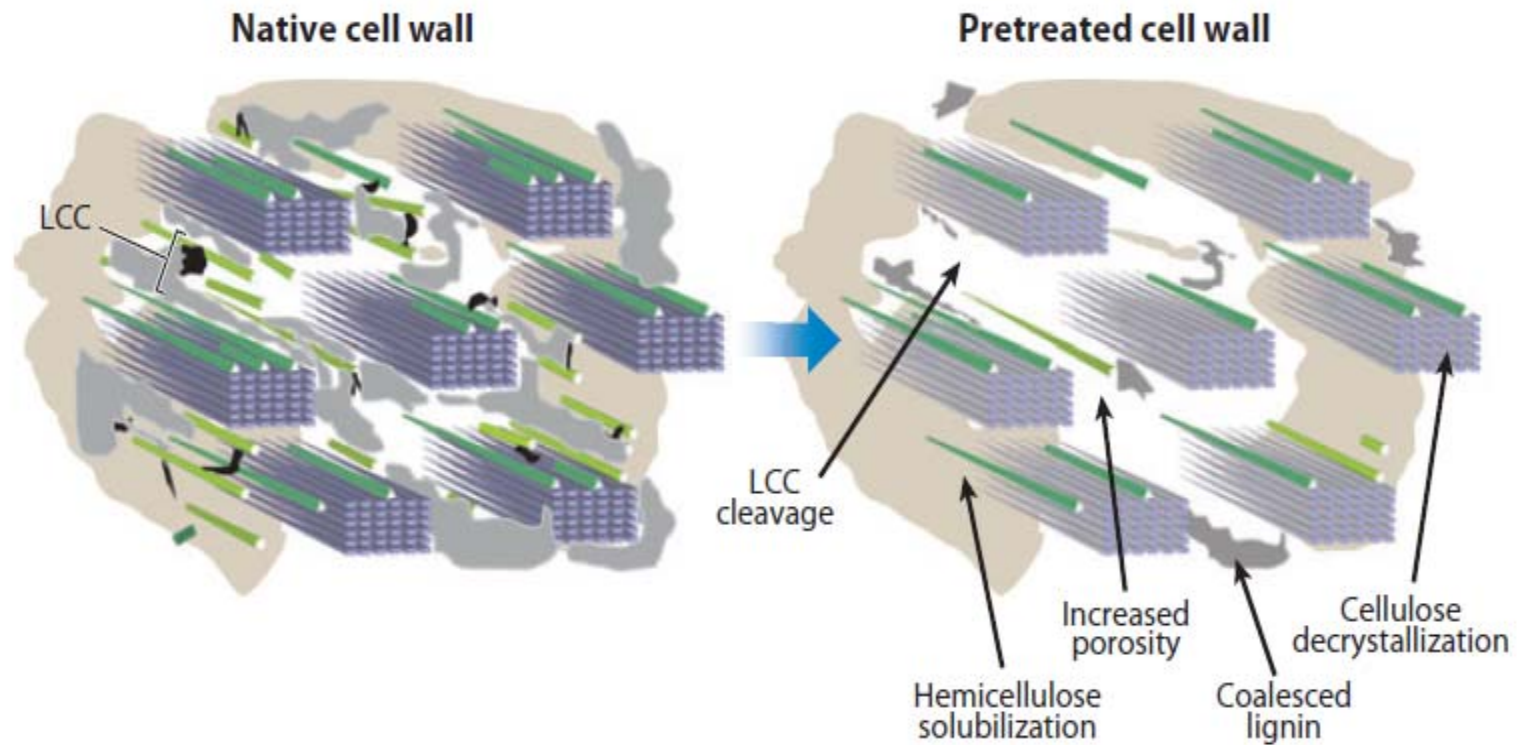
Compositional Analysis of Different Feedstocks

Feedstock	Cellulose	Hemicellulose	Lignin	Extractives	Ash	References
Sunflower hulls	34	31	22	13	0.4	
Corn stover	37	25	19	7.6	8.5	Hames et al., 2003;
Switch grass	37	29	21	17	5.8	Wiselogel et al., 1996;
Miscanthus	48	19	24	6.4	2.4	Velasquez et al., 2003;
Kenaf	43	16	17	21	0.33	

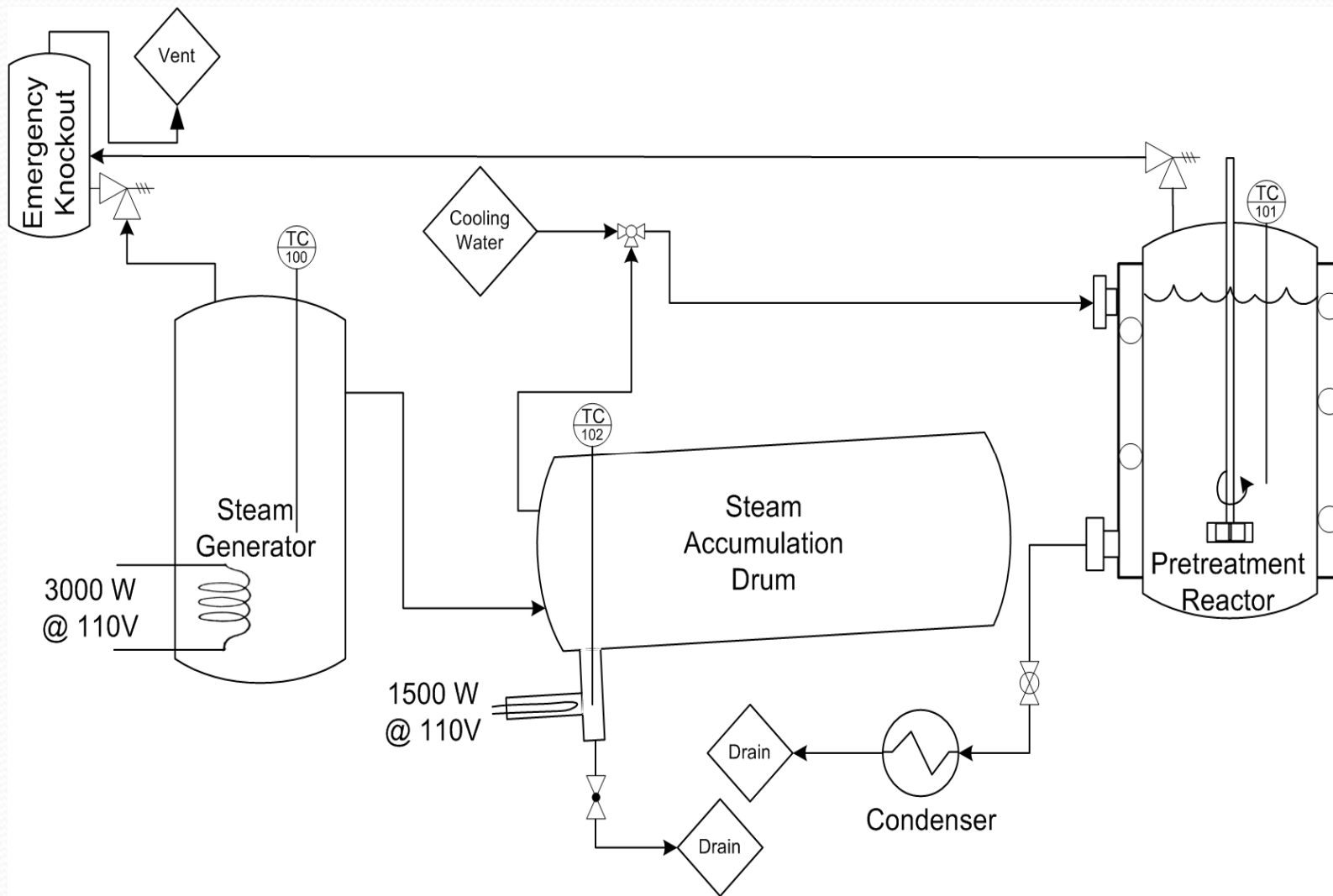
Response Surface Methodology

Pretreatment Conditions		Run Order	Reaction Temperature °C	Reaction Time Min	Acid Concentration % (w/w)
		Sulfuric acid Concentration	0.5 %, 1.25%, 2% (w/w)	7	140
Reaction Temperature	140, 150, 160 °C	3	160	10	0.5
Reaction Time	10, 20, 30 min	9	140	10	2
		18	140	30	0.5
		16	150	20	0.5
		6	140	20	1.25
		20	150	10	1.25
		2	160	30	0.5
		5	150	20	1.25
		1	150	20	1.25
		14	150	20	1.25
		13	150	20	1.25
		19	140	30	2
		17	150	20	1.25
		11	150	20	1.25
		8	150	30	1.25
		15	160	10	2
		12	150	20	2
		10	160	20	1.25
		4	160	30	2

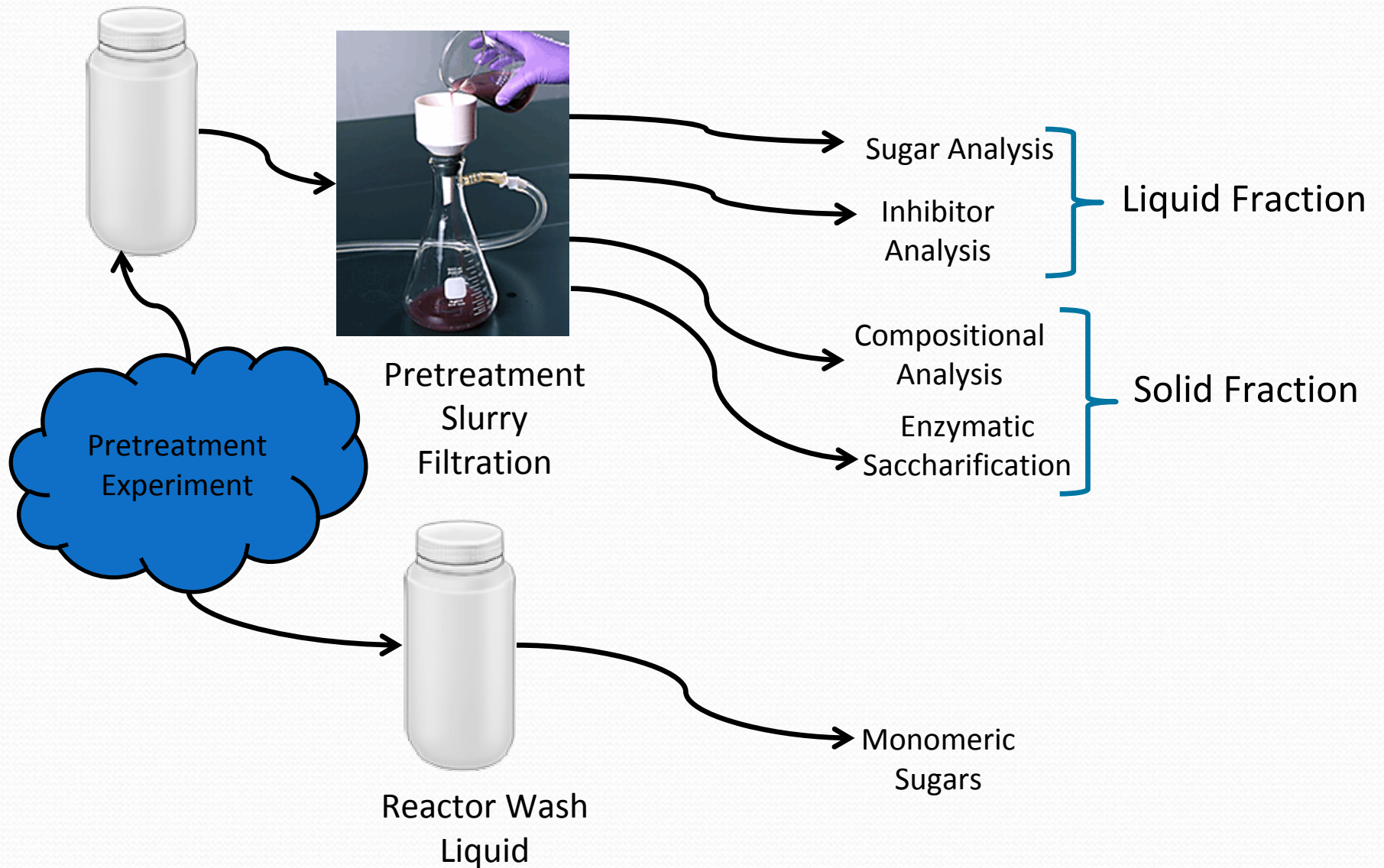
Why Pretreatment is Necessary?



Pretreatment in Batch Reactor



Analysis of Pretreated Sample



Combined Severity Factor

- The Combined Severity Factor (CSF)

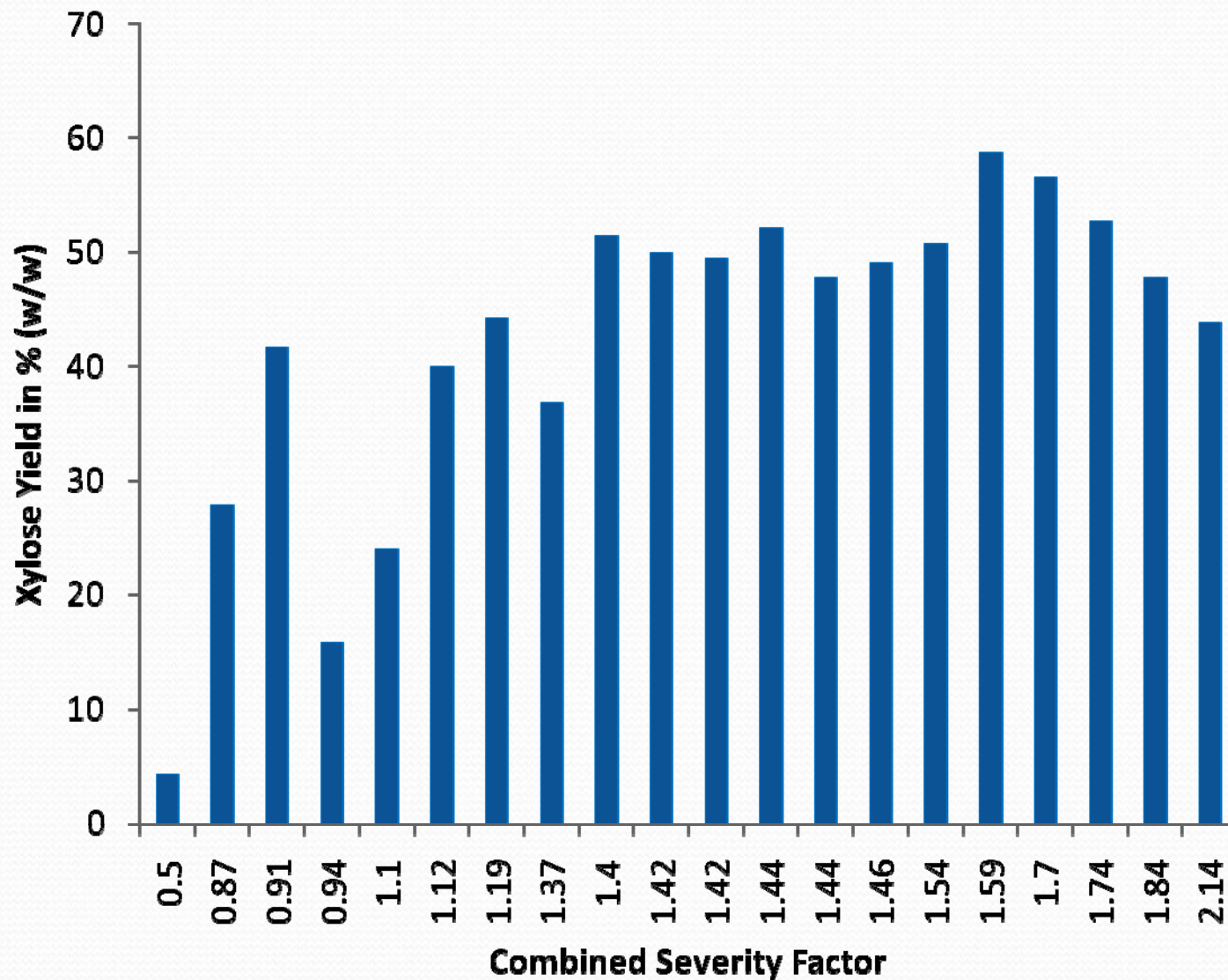
The CSF is an empirical equation combines three factors reaction time, reaction temperature and acid concentration

$$CSF = \text{Log}_{10} \left[t * \exp \left(\frac{T - 100}{14.75} \right) \right] - pH$$

t = Reaction time (Min)

T = Reaction temperature (°C)

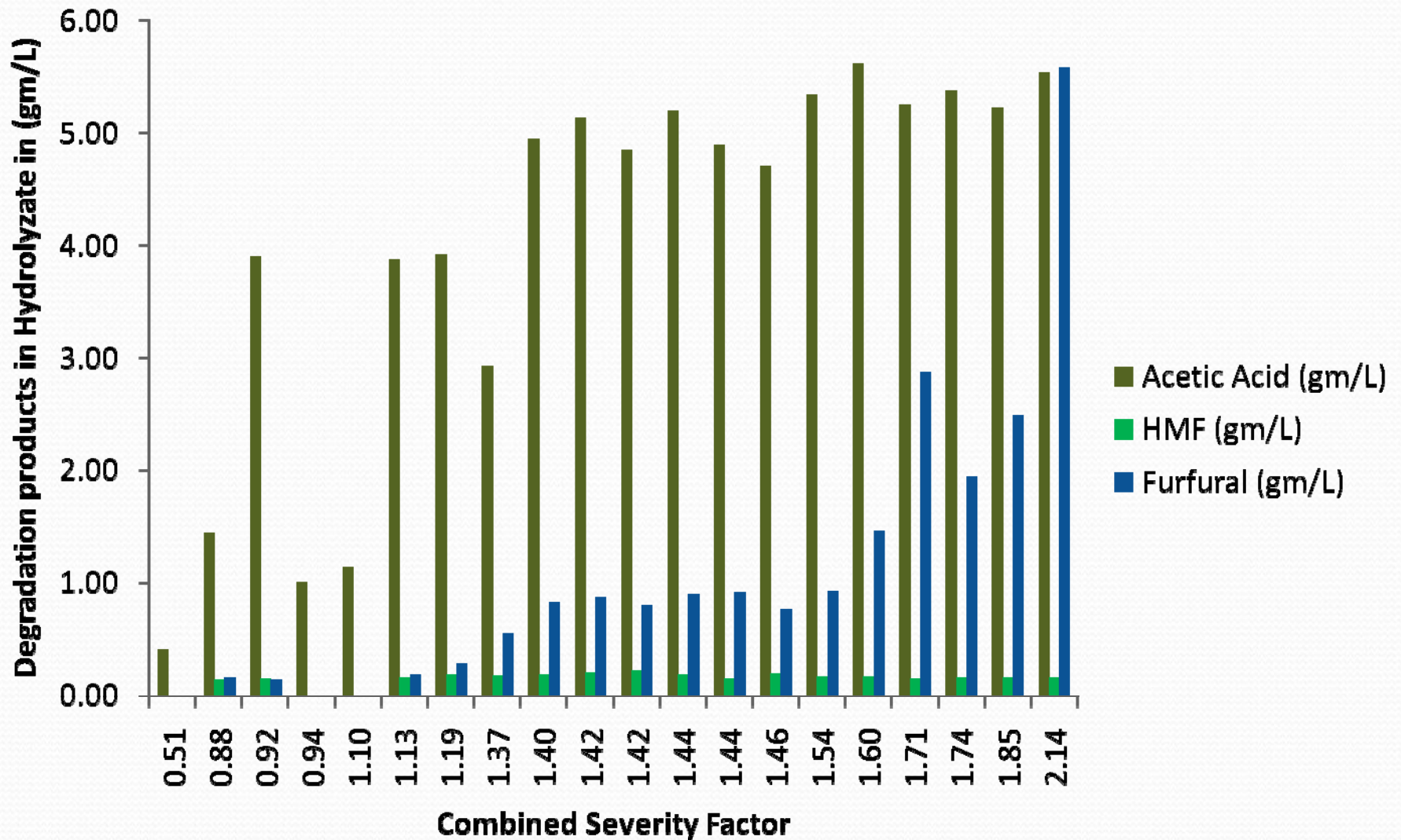
Xylose Yield in Liquid Fraction



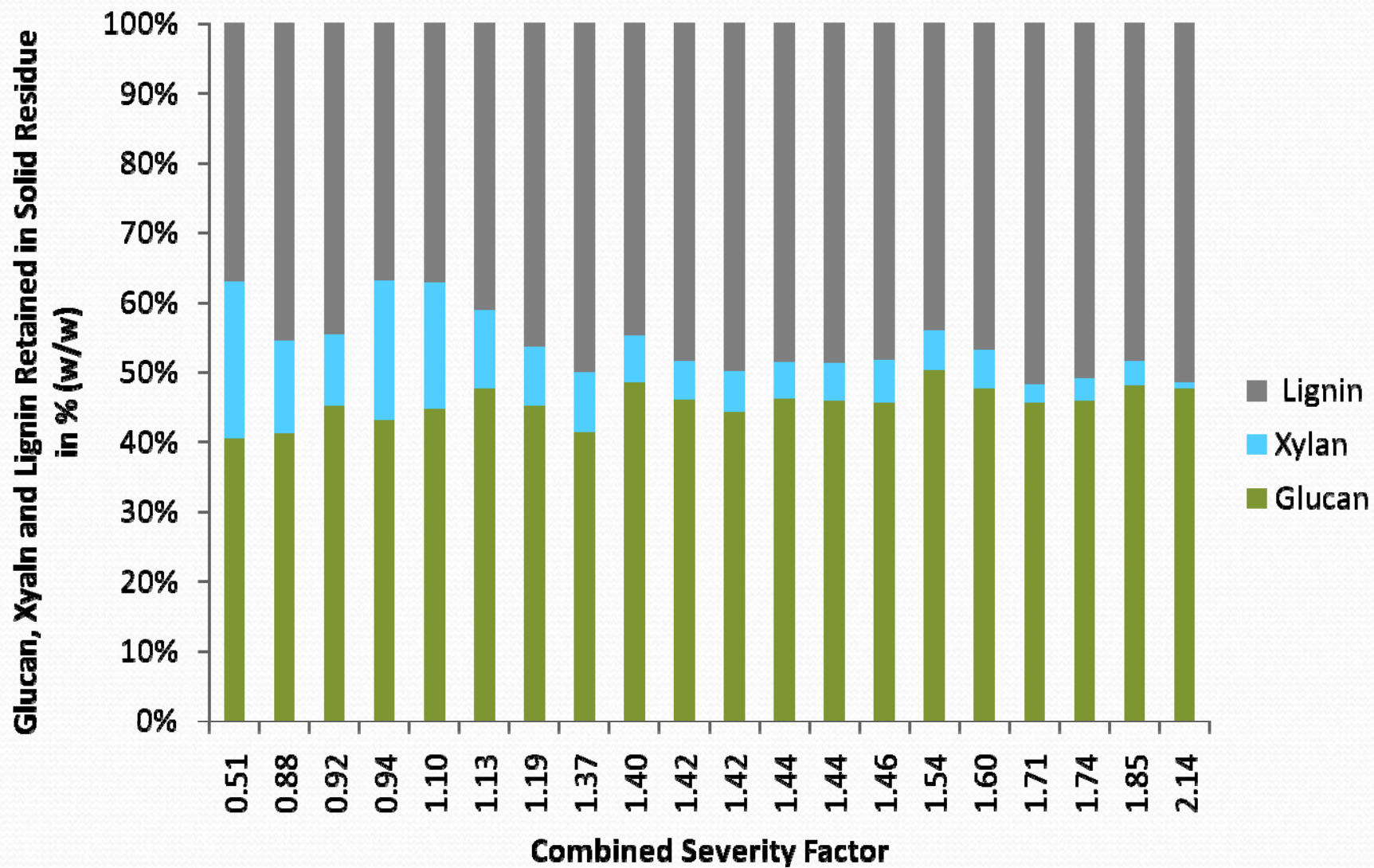
Inhibitor Products

- There are some inhibitor by products formed during pretreatment such as acetic acid, furfural, HMF
- The ether bonds between lignin and xylan leads to acetic acid
- The degradation of xylose leads to furfural
- The degradation of glucose leads to HMF

Degradation Products



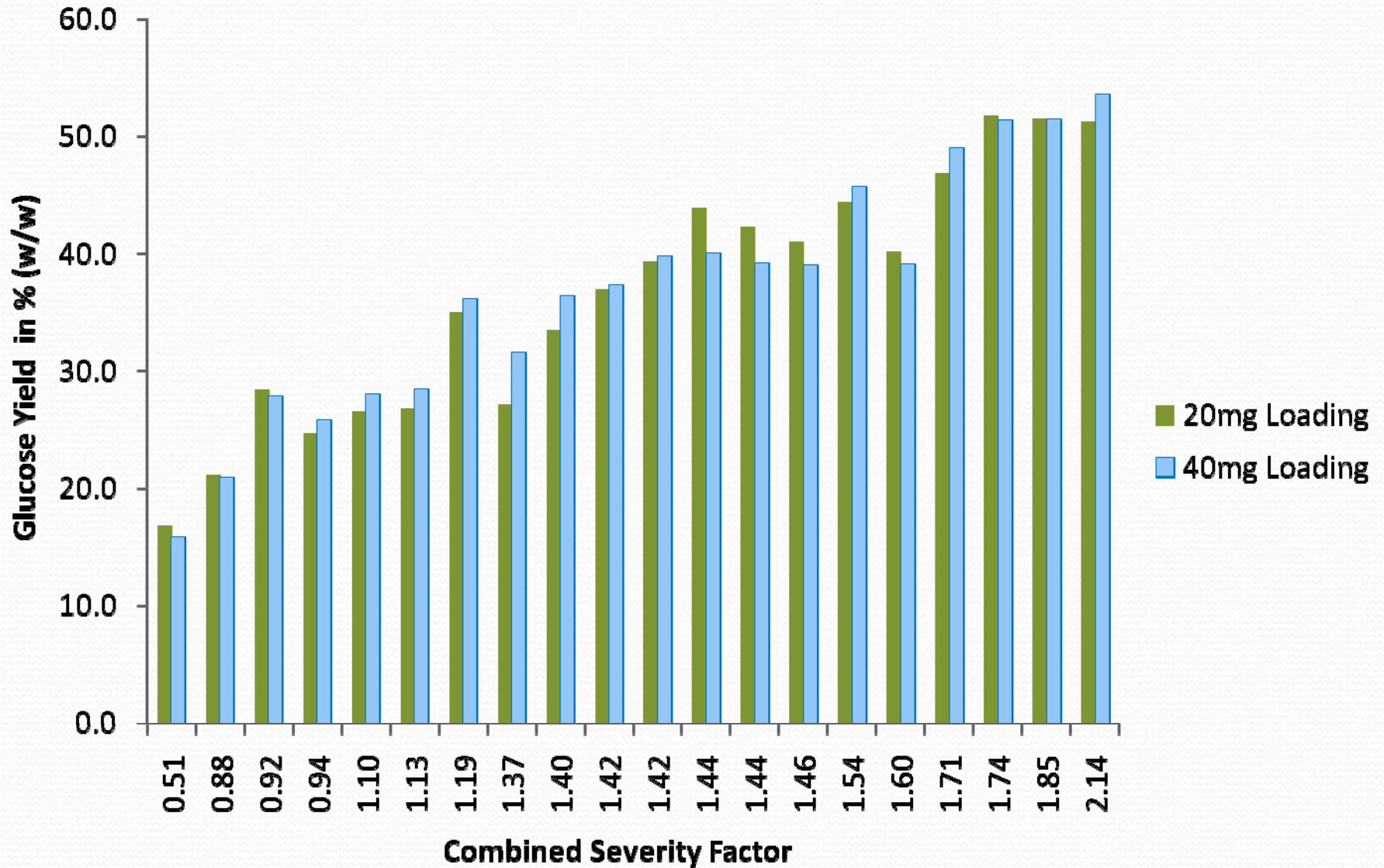
Solid Fraction Analysis



Enzymatic Hydrolysis Conditions

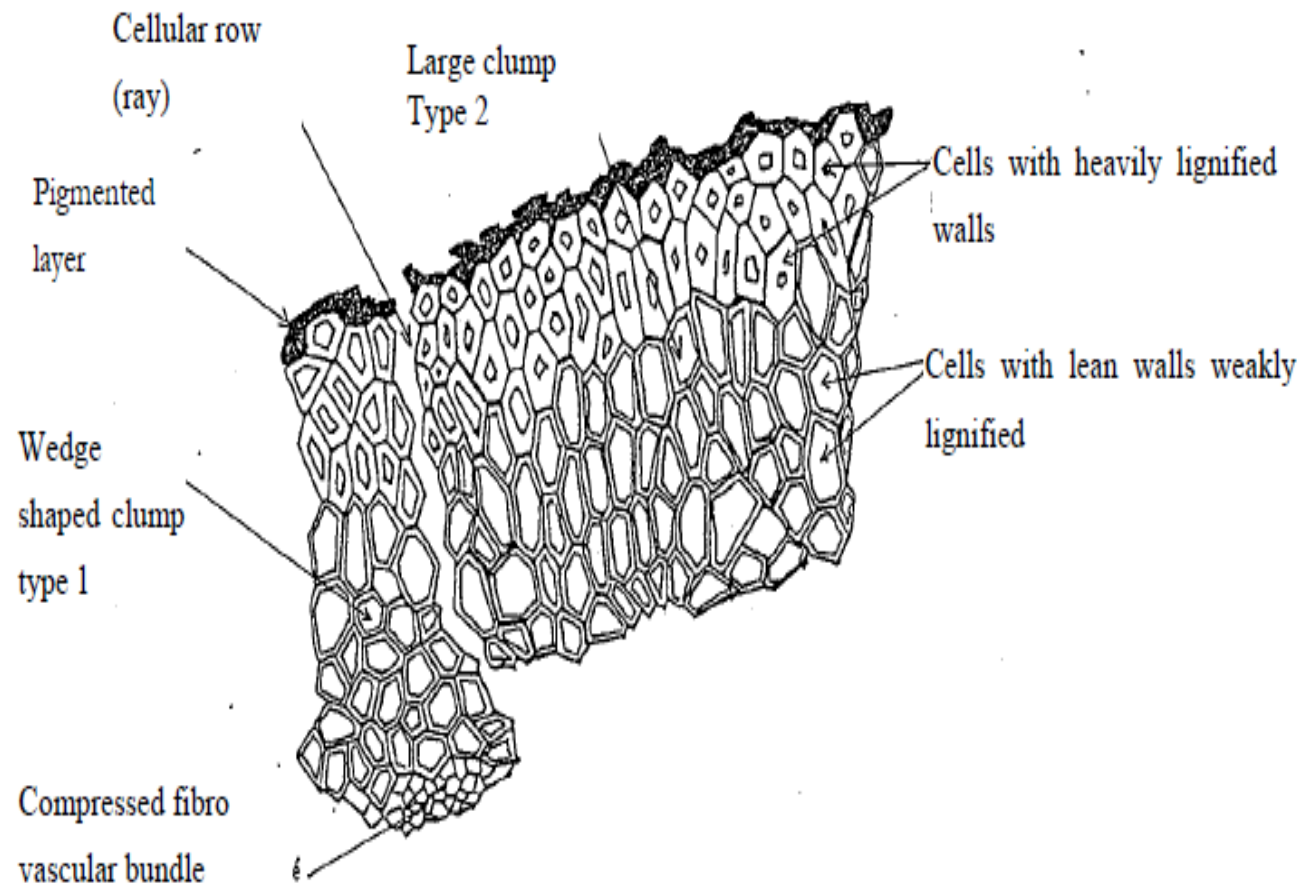
Compounds and Conditions	Amount
Biomass	0.1 g of glucan
Sodium citrate buffer of 4.8 pH	5 ml
Sodium Azide	20 mg/ml
Accellerase 1500 (Enzyme)	20, 40 mg of protein/g of cellulose
Reaction Temperature	50 °C
Shaker rpm	250
Reaction Time	72 h

Enzymatic Hydrolysis



Reason Behind Low Glucose Yields

Structure of the sunflower hulls



Conclusion

- As the severity factor increased the amount of xylose liberated in to the liquid fraction. However, at higher severity factor yield of xylose reduced since xylose was degrading into furfural
- The concentration of glucose increased with severity factor after enzymatic hydrolysis. Nevertheless, there was not much difference between 20mg and 40mg enzyme loadings
- The degradation products (acetic acid) increased relatively with increase in severity factor. However, copious amounts were furfural was formed at high severity factor

References

- Lloyd, T.A., Wyman, C.E., 2005. Combined sugar yields for dilute sulfuric acid pretreatment of corn stover followed by enzymatic hydrolysis of the remaining solids. *Bioresource Technology*. 96, 1967–1977
- Harmsen, P., Huijgen, W., Bermudez, L., Bakker, R. 2010. Literature review of physical and chemical pretreatment processes for lignocellulosic biomass. *Biosynergy Report Number 1184*, 1-53
- Hsu, T. C., Guo, G. L., Chen, W. H., Hwang, W. S. 2009. Effect of dilute acid pretreatment of rice straw on structural properties and enzymatic hydrolysis. *Bioresource Technology*. 101, 4907-4913
- Wei, Q., Su-Ping, Z., Li, X-Q., Wi, R.Z., Jie, Y.Y., 2008. Degradation kinetics of xylose and glucose in hydrolyzate containing dilute sulfuric acid. *Chinese J. Process Engineering*. 8, 1132-1137
- Hames, B. R., Thomas, S. R., Sluiter, A. D., Roth C.J., 2003. Templeton, Rapid biomass analysis new tools for compositional analysis of corn stover feed stocks and process intermediates for ethanol production. *Applied Biochemistry and Biotechnology*. 105, 5-16.
- Velasquez, J. A., Ferrando, F., Farriol X., Salvado, J., 2003. Binder less fiberboard from steam exploded *Miscanthussinensis*. *Wood Science Technology*. 37, 269–278.
- Wiselogel, A.E., Agblevor, F.A., Johnson, D.K., Deutch, S., Fennell, J.A., Sanderson, M.A., 1996. Compositional changes during storage of large round switchgrass bales. *Bioresource Technology*. 56, 103– 109.
- Sharma, S.K., Krishan L., Kalra, Gurvinder, Kocher, S., 2004. Fermentation of enzymatic hydrolysate of sun flower hulls for ethanol production and its scale-up. *Biomass and Bioenergy*, 27, 399-402.

Acknowledgements

- I would like thank Dr. Yun Ji for her insightful guidance
- I would like thank Christopher Schaefer and Matt Defrese for helping me with the pretreatment and analysis
- I would like thank ND EPSCoR for funding the project





Thank You for your Time

QUESTIONS ?