Effects of Dilute Acid Hydrolyzate Components on Glucose Degradation

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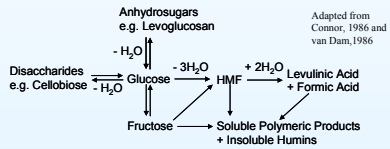
Interaction of Sugars with Components of Biomass Hydrolyzates

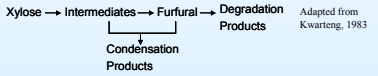
- At NREL we are interested in dilute acid processes for hydrolyzing the hemicellulose and cellulose components of lignocellulosic biomass
- Some pretreatment of biomass is necessary to prepare cellulose for enzymatic hydrolysis.
- Some acid catalyzed pretreatment processes, can convert not only all of the hemicellulose, but significant amounts of the cellulose to glucose.
- I am interested to learn where the unaccounted cellulose goes in low yielding hydrolyses and to increase glucose yields.
- A report by Professor YY Lee (Auburn U.) that glucose degradation was substantially increased by biomass hydrolyzate stimulated this study.

Acid Catalyzed Degradation of Sugars



Adapted from Connor, 1986 and van Dam,1986

- **Glucose degrades under acidic conditions to hydroxymethyl furfural (HMF) and a number of other products**



Adapted from Kwarteng, 1983

- **Similarly xylose degrades to furfural and other products**

What is in Biomass Hydrolyzates

- Biomass hydrolyzate made from Yellow Poplar sawdust treated without acid at 180 °C in a Percolation reactor for 25 min
- Appearance – Light brown cloudy liquid with dark brown particles
- Fractionation
  - Colloidal Fraction - siphoned from the top of the liquid
  - Clear Fraction - centrifugation at 10,000 rpm for 10min + filtering 0.45µm
  - Solid Fraction - centrifugation
- Composition of Whole Hydrolyzate and Liquid Fractions
  - Mostly oligomeric sugars (~7 mg/mL) + monosaccharides (< 1 mg/mL each) + acid-soluble lignin (ASL), acid-insoluble lignin (AIL). Furfurals v. small
- Solid Fraction - 90% lignin, 10% sugars (mostly xylose)
- Table shows Total Sugar Analysis plus the other components

Sample	glucose	xylose	galactose	arabinose	mannose	Total Sugars	ASL	AIL	Furfural	HMF	Total Solids
Concentrations in mg/mL											
Whole hydrolyzate	0.90	8.60	0.97	0.44	1.38	12.29	3.59	4.97	0.12	0.03	20.84
Colloidal Fraction	0.89	8.42	0.95	0.42	1.34	12.02	3.13	0.70	0.12	0.02	15.99
Clear Fraction	0.76	8.15	0.90	0.41	1.26	11.49	2.99	0.00	0.11	0.01	14.47
Solid Fraction is as Wt% of the solid											
Solid Fraction	0.81	6.33	0.84	0.36	1.19	9.47		88.37			

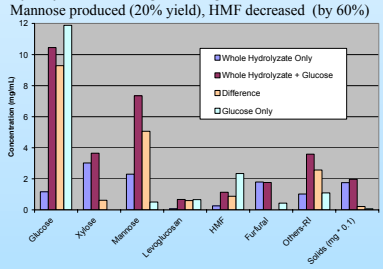
Experimental

- Small Batch Steel (4.5 mL) or Glass (20 mL) reactors
- Fluidized sand bath heating system
- Glucose Concentration 21.5 g/L
- Reaction Conditions 200 °C, 10 min, 0.07% H_2SO_4.
- HPLC Analysis w/ HPX-87H after filtering
- HPLC Analysis w/ HPX-87P neutralize w/$CaCO_3$ and filter
- GC Analysis on DB-5 column

Neutralized and lyophilized samples reacted with NH_4OH in pyridine then acetic anhydride. Aldoses make acetylated aldononitriles and ketoses make acetylated ketoximes. (Seymour 1989)

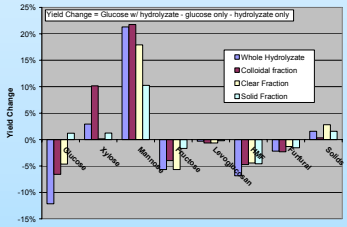
Effect of Whole Hydrolyzate

- If Hydrolyzate had no effect Difference should equal Glucose only
- Hydrolyzate increased glucose degradation from 45% to 54%
  Mannose produced (20% yield), HMF decreased (by 60%)



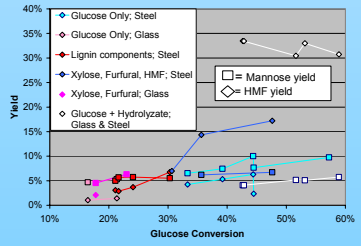
Effect of Fractions on Glucose Degradation

- All fractions catalyze glucose loss, produce mannose, decrease HMF
- Whole hydrolyzate > Colloidal > Clear > Solid Fraction
- What component in the fractions can explain this behavior?



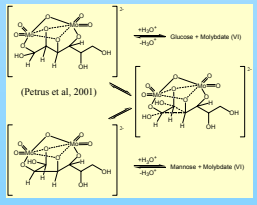
Effect of Reactor Type, Hydrolyzate and Components on Glucose Degradation

- Furfural and xylose behaved most similarly to hydrolyzate
- More glucose degradation seen with steel reactors except with hydrolyzate, and with Lignin components



How is Mannose Formed

- Epimerization of glucose to mannose does not readily occur
- Bilik reaction known for epimerization of C-2 carbon of tetroses and higher aldoses; gives 3:1 ratio of glucose : mannose
- Normal reaction conditions pH 2-4 and molybdate ions Mo(VI)



(Petrus et al, 2001)

- Other transition metals (Ni, Cu, Co, Cd) also catalyze reaction but less selectively also giving isomerization to fructose (Kolaric, 1996)
- Is Molybdate present in the hydrolyzate from reactor corrosion?
- Hydrolyzate made in Hastelloy reactor
  Mo content ~15%

Conclusions

- Degradation of glucose is catalyzed by Yellow Poplar hydrolyzate under the conditions used.
- All fractions of the hydrolyzate catalyze the degradation reaction, even the solid fraction that contains almost no sugars, sugar degradation products, or solubilized lignin.
- Organosolv lignin and the lignin-derived chemicals tested did not catalyze glucose degradation even with steel reactors.
- Furfural and xylose have a similar effect to hydrolyzate but only with the steel reactors not glass.
- Hydrolyzate catalyzes the reaction in glass or steel reactors.
- Is the glucose degradation observed just epimerization of glucose to mannose catalyzed by steel corrosion products, Mo and/or other transition metal ions?

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Acknowledgements

- I wish to thank the US DOE Office of Biomass Programs (Director Doug Kaempf) for funding this work, and NREL and DOE Program managers, Cindy Riley and Gerson Santos-Leon, for their support.
- I would also like to thank several of my colleagues at NREL, including Rick Elander and Bob Torget for their encouragement and advice.
- Finally, I would like to thank Professor Y.Y. Lee , Auburn University whose initial results on glucose degradation with hydrolyzate prompted this work.