IOWA STATE UNIVERSITY
Bioeconomy Institute






Heterodoxy in fast pyrolysis: Air-blown reactors and sugar production

Robert C. Brown
Director, Bioeconomy Institute
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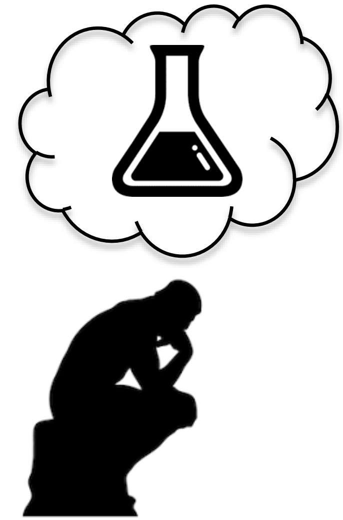
Orthodoxy in fast pyrolysis

- **Definition of pyrolysis:** "Thermal decomposition of organic compounds in the absence of oxygen."
  - – *Biorenewable Resources: Engineering New Products from Agriculture*
- **Products of pyrolysis:** "Bio-oil, biochar, non-condensable gases."
  - – *Biorenewable Resources: Engineering New Products from Agriculture*
- **Bio-oil: "**Bio-oil is an emulsion of lignin-derived oligomers in an aqueous phase composed primarily of carbohydrate-derived compounds."
  - – *Biorenewable Resources: Engineering New Products from Agriculture*

Heterodoxy in fast pyrolysis

- **Definition of pyrolysis:** "Thermal decomposition of organic compounds – and a little oxygen is just fine."
- **Products of pyrolysis:** "Let's add sugar among the major products."
- **Bio-oil: "**Why would you even want to produce an unstable emulsion?"

A scientist and engineer walk into a bar…



- Scientist: Asks questions.

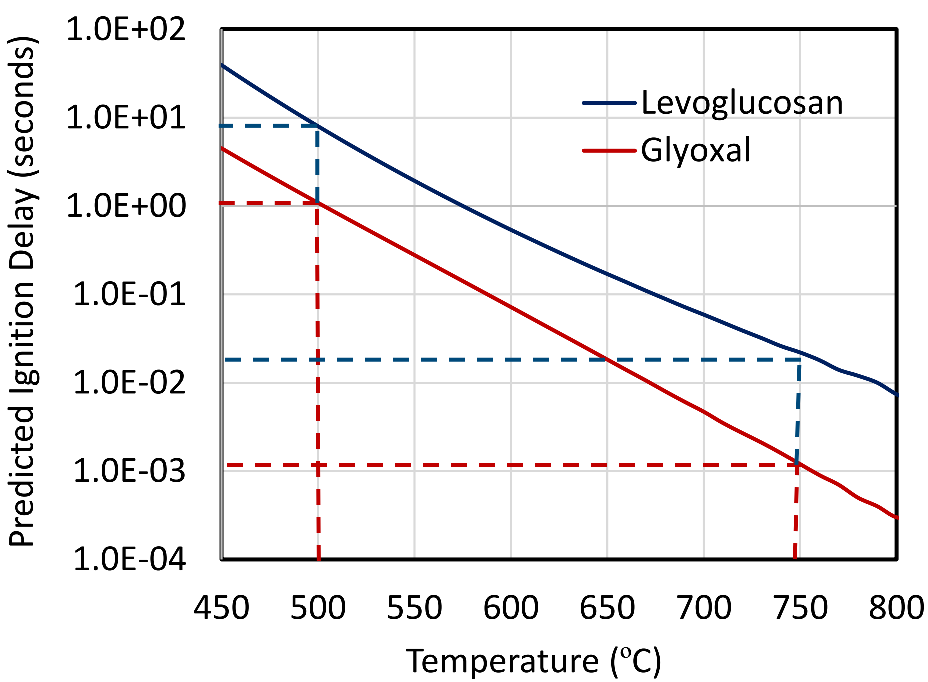
- Engineer: Solves problems.

Why do we exclude oxygen from pyrolysis?

- Combustion happens:

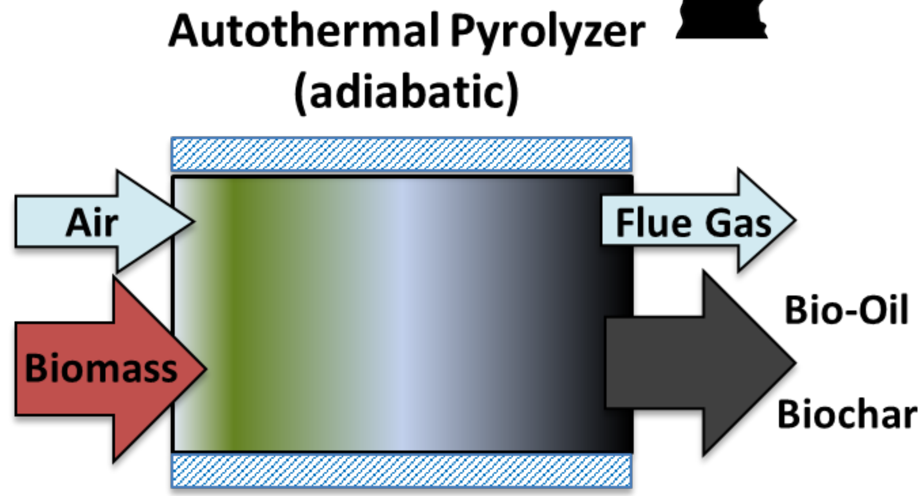
  $C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O$

- Mitigating factors:
  - Operation at low equivalence ratios
  - Operation at temperatures lower than traditional combustion
  - Variations in reaction rates among pyrolysis products

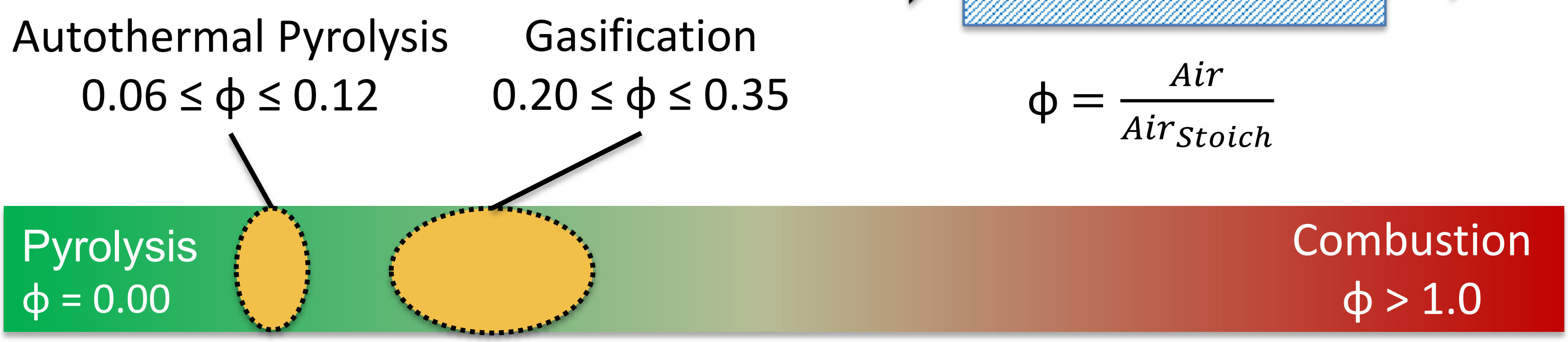


What is the upside of adding oxygen (as air)?

- Eliminates tail gas recycle
- Exothermic energy release of oxidation can provide enthalpy for pyrolysis
- Heat transfer bottleneck to process intensification can be removed!

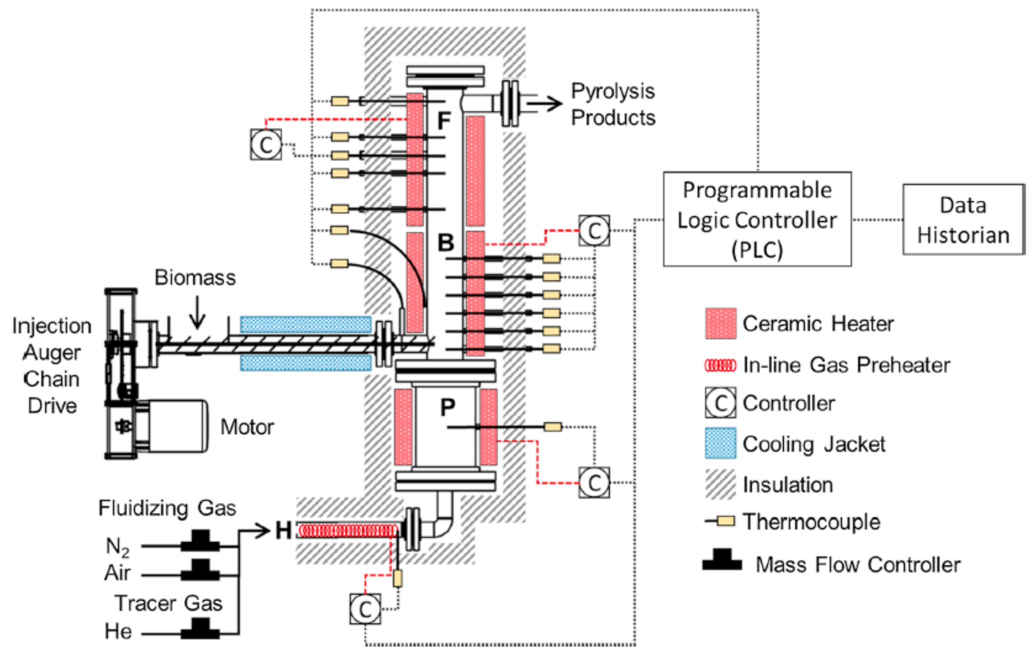


$$\phi = \frac{Air}{Air_{Stoich}}$$



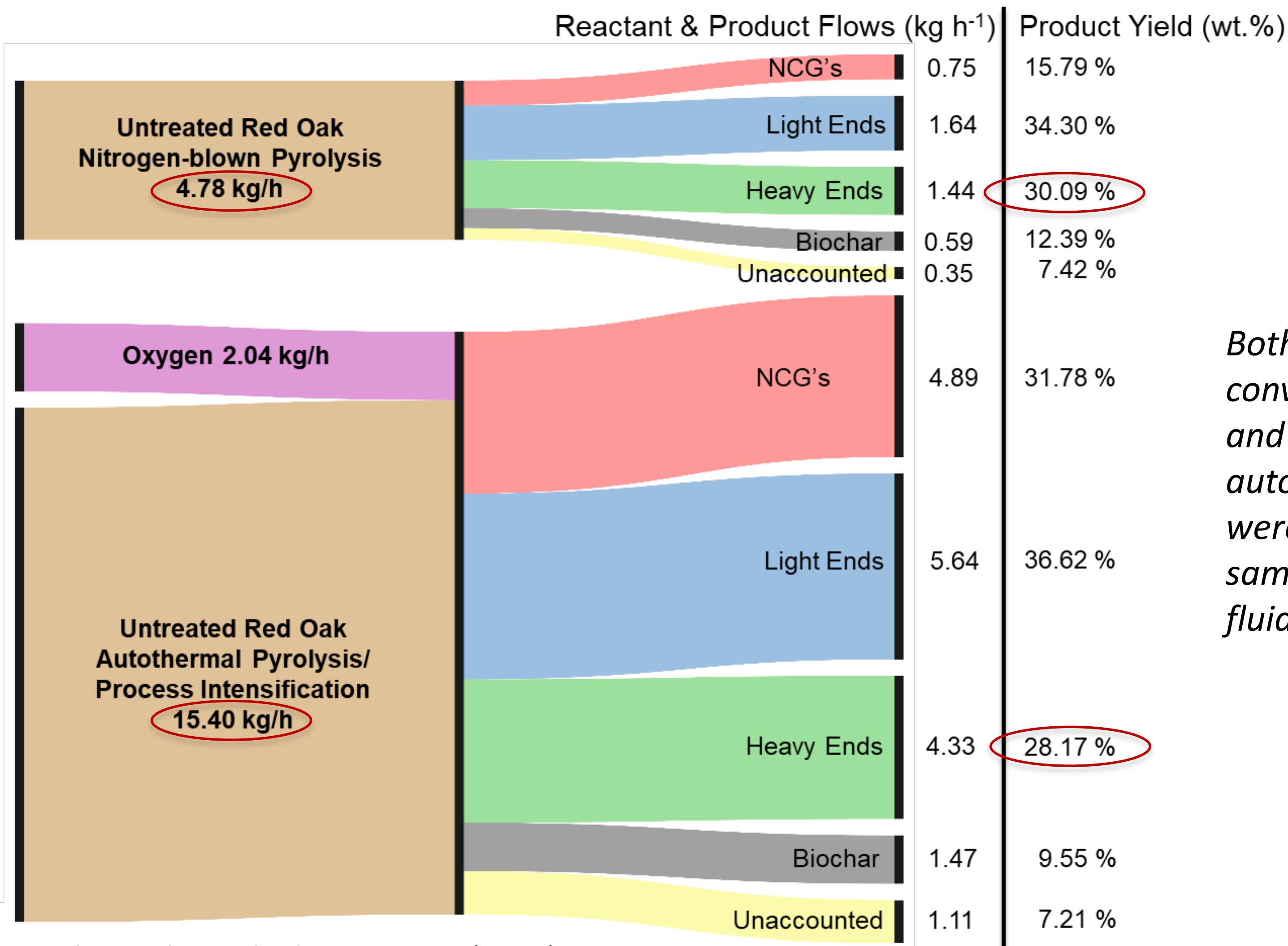
Design considerations for a lab-scale autothermal pyrolyzer

- Simulate adiabatic operation
  - Use of guard heaters to overcome parasitic heat losses at small scale
- Mitigate hot spots that promote undesired oxidation reactions
  - Use of fluidized bed for good internal heat and mass transfer
- Operate at minimum equivalence ratio that provides enthalpy for pyrolysis



Polin et al., Applied Energy 249 (2019) 276-285

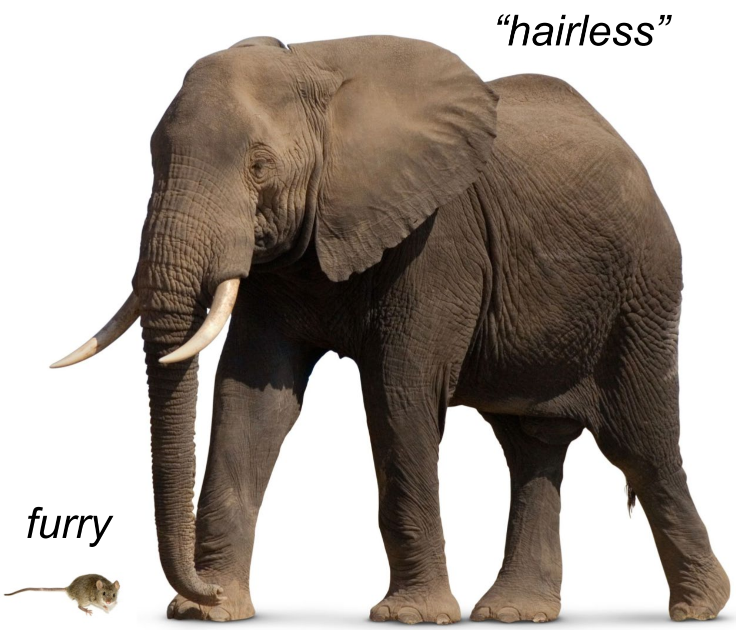
Process intensification through autothermal pyrolysis

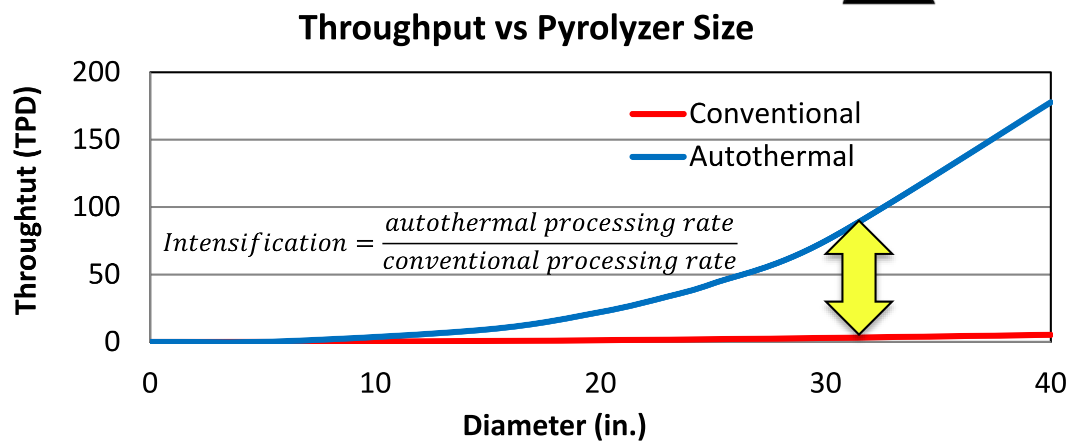


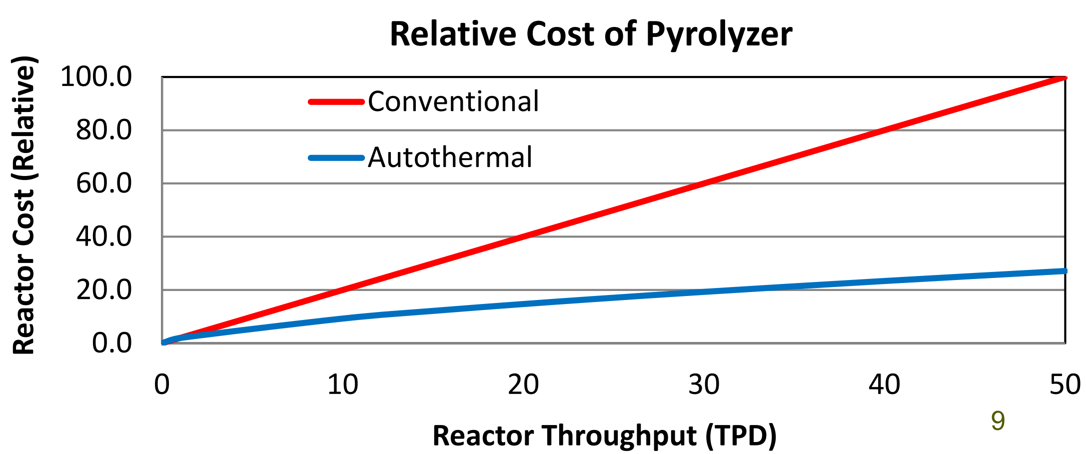
Both nitrogen-blown, conventional pyrolysis and air-blown (φ=0.11), autothermal pyrolysis were performed in the same 8.9 cm diameter fluidized bed reactor.

Polin et al., Applied Energy 249 (2019) 276-285

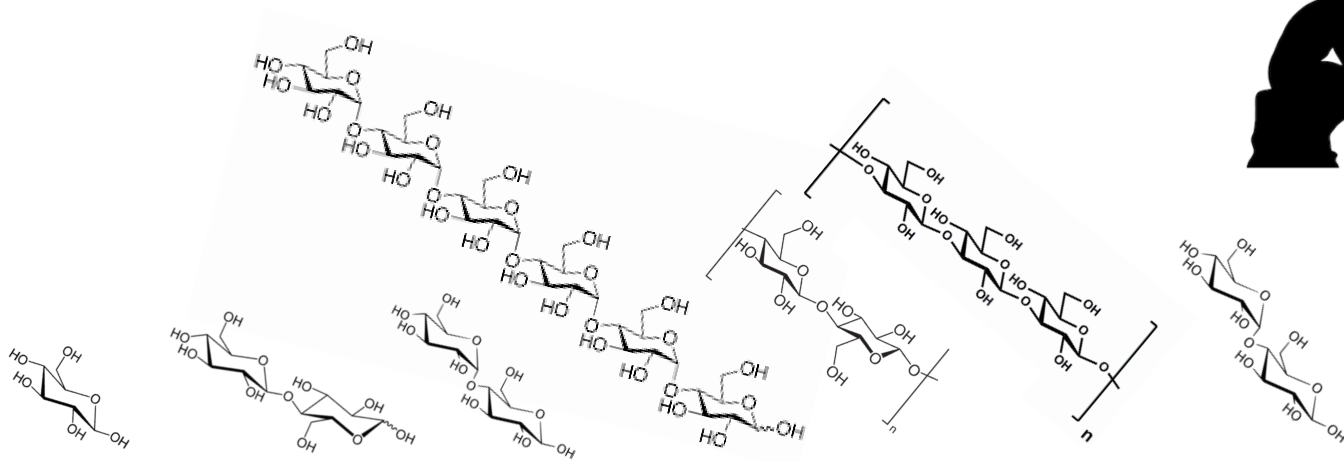
What is the impact of heat transfer on scaling up processes?







How much sugar can be produced via fast pyrolysis?



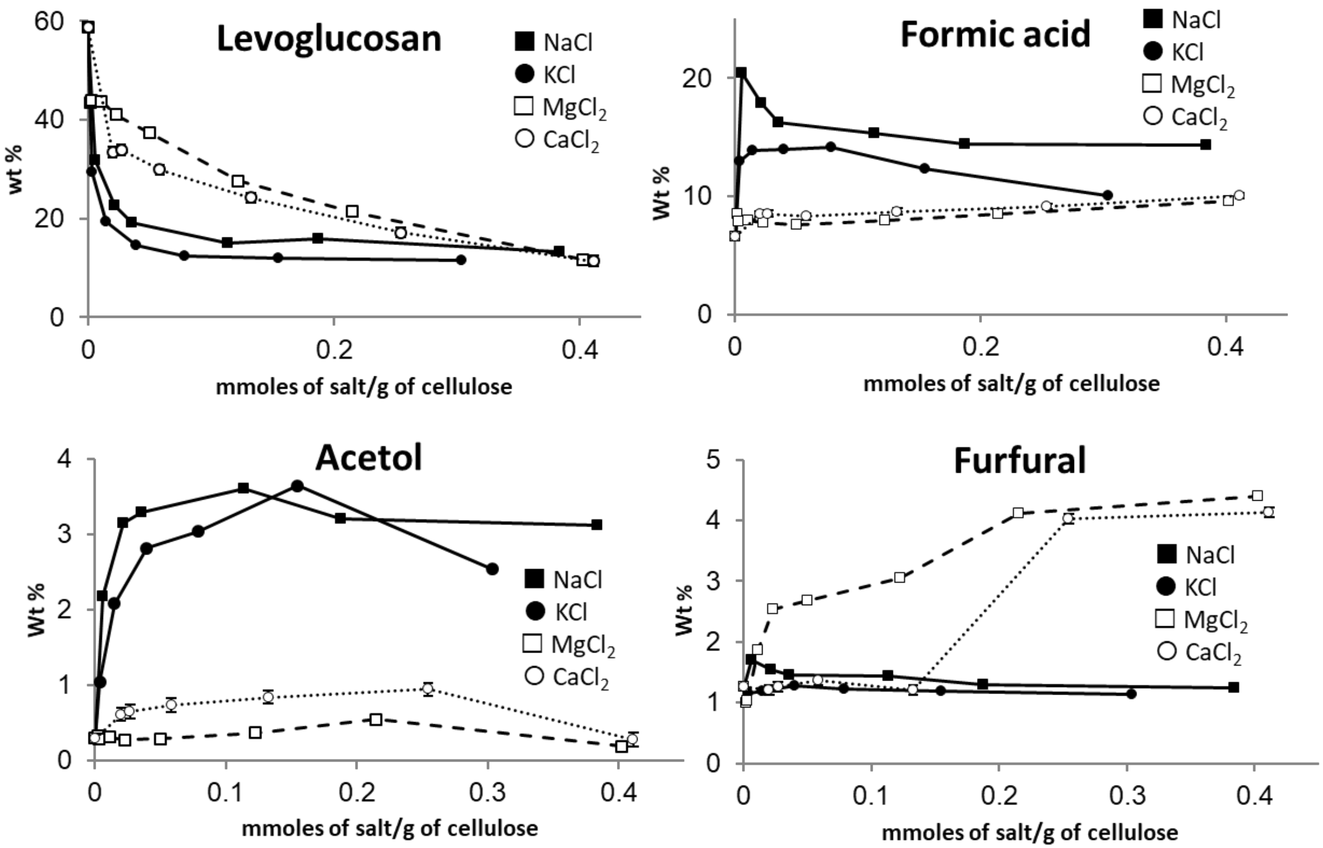
Compound	Glucose (wt%)	Cellobiose (wt%)	Maltose (wt%)	Malto-hexaose (wt%)	Cellulose (wt%)	Curdlan (wt%)	Waxy maize starch (wt%)
Levoglucosan	7.00	24.4	20.5	33.1	58.8	44.2	48.5
Unidentified*	40.8	23.6	32.4	20.5	7.1	18.1	13.2

*Includes gases, water and some unidentified organic compounds

Patwardhan et al., J. Anal. Appl. Pyrolysis 86 (2009) 323-330

Why don't we find much sugar in bio-oil?

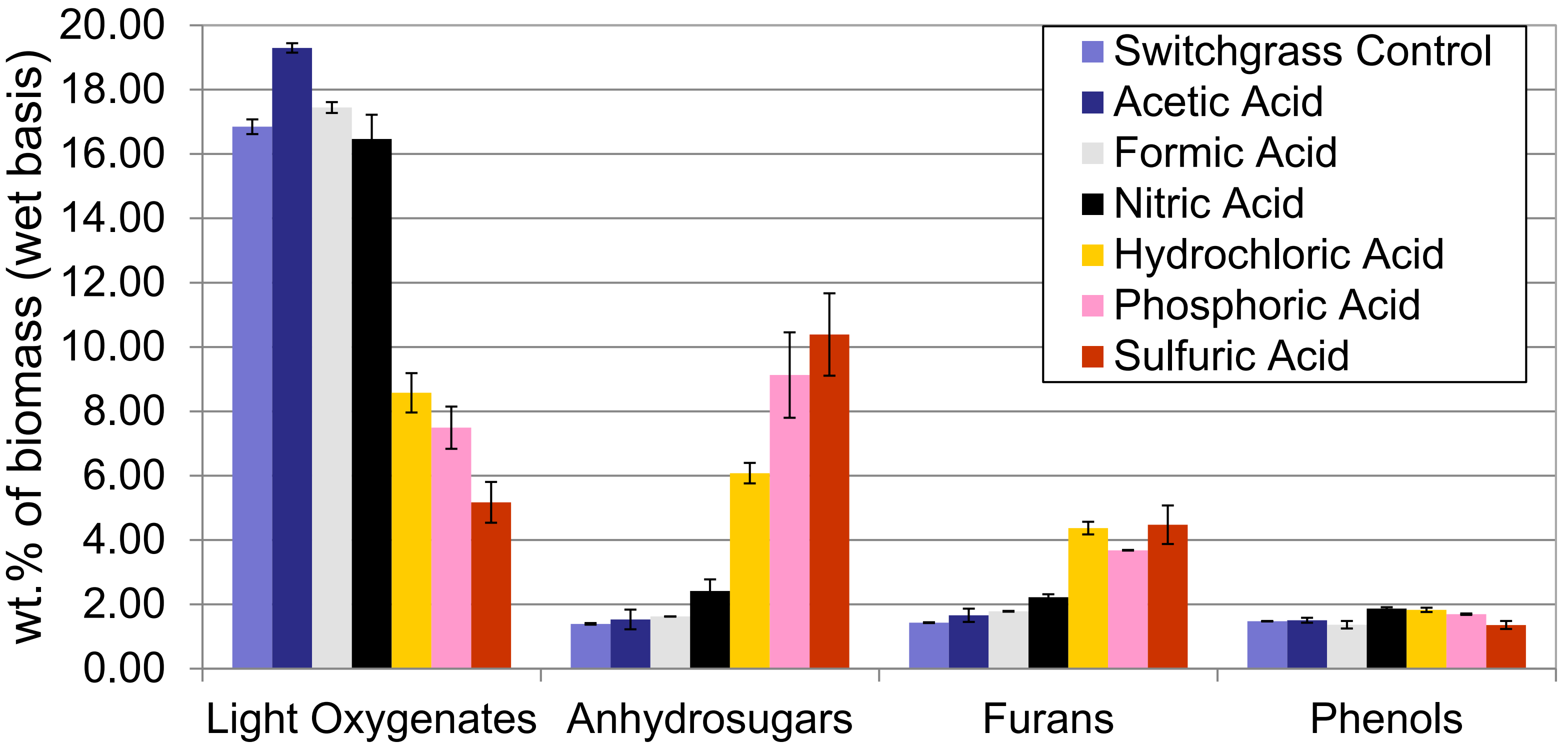
Alkali and alkaline earth metals (AAEM) catalyze pyranose (and furanose) ring fragmentation during pyrolysis



Patwardhan et al., Bioresource Technology 101 (2010) 4646-4655

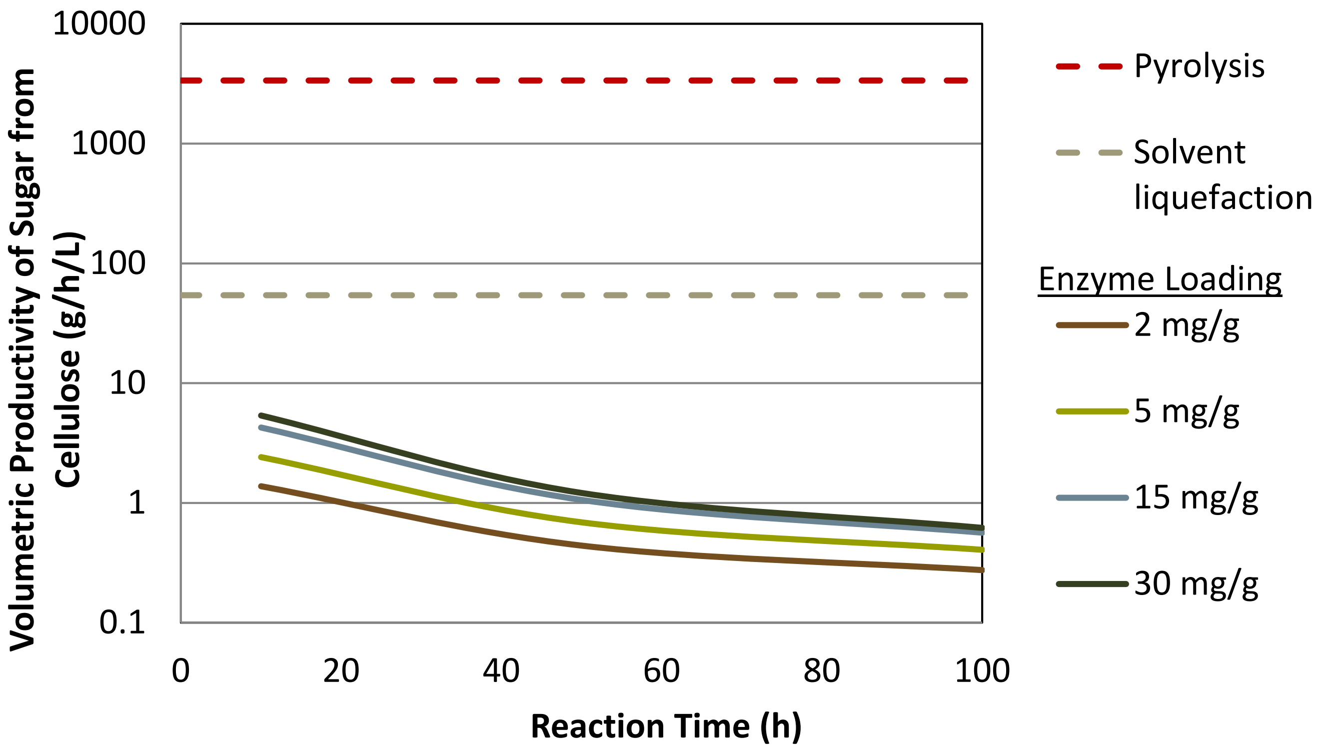
Overcoming the deleterious effect of AAEM on sugar yields

Mineral acid pretreatments convert AAEM into thermally stable salts that passivate catalytic activity of the metals



Kuzhiyil et al, ChemSusChem 5 (2012) 2228-2236

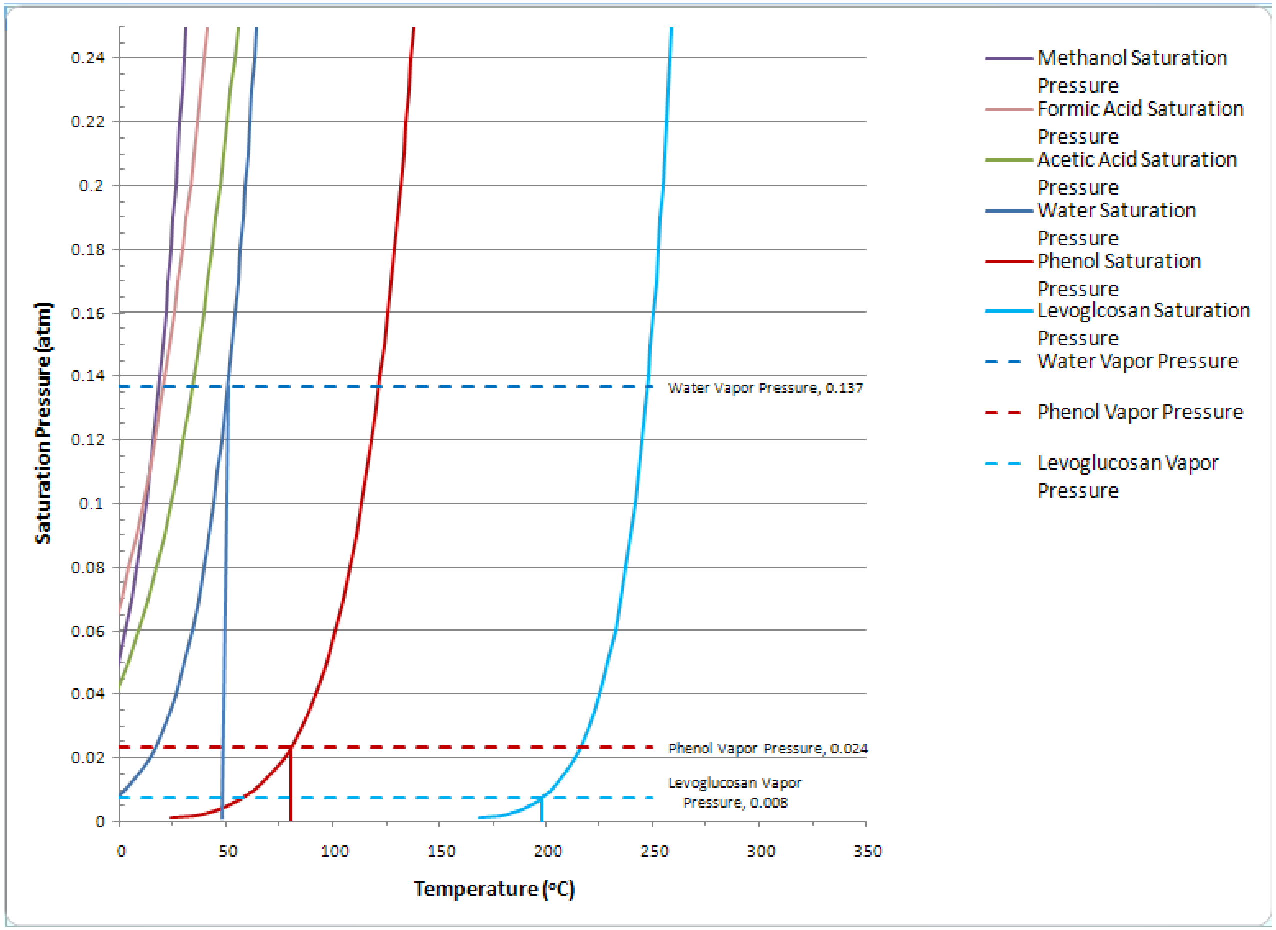
Process intensification through py sugar production



Sugar production for pyrolysis and solvent liquefaction based on sugar yields and processing rates experimentally observed at ISU. Enzymatic hydrolysis data from Nguyen et al., 2015.

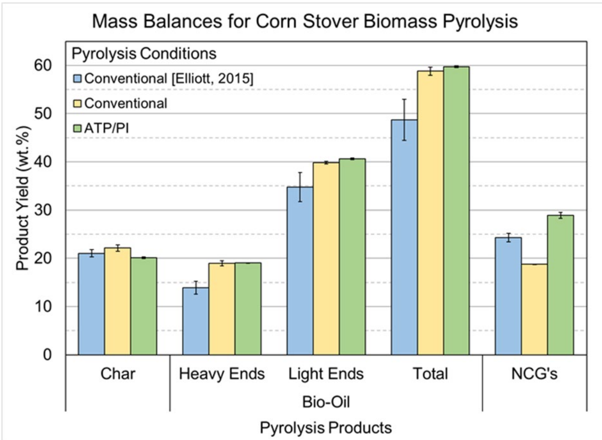
How can we separate organic components of pyrolysis vapors?

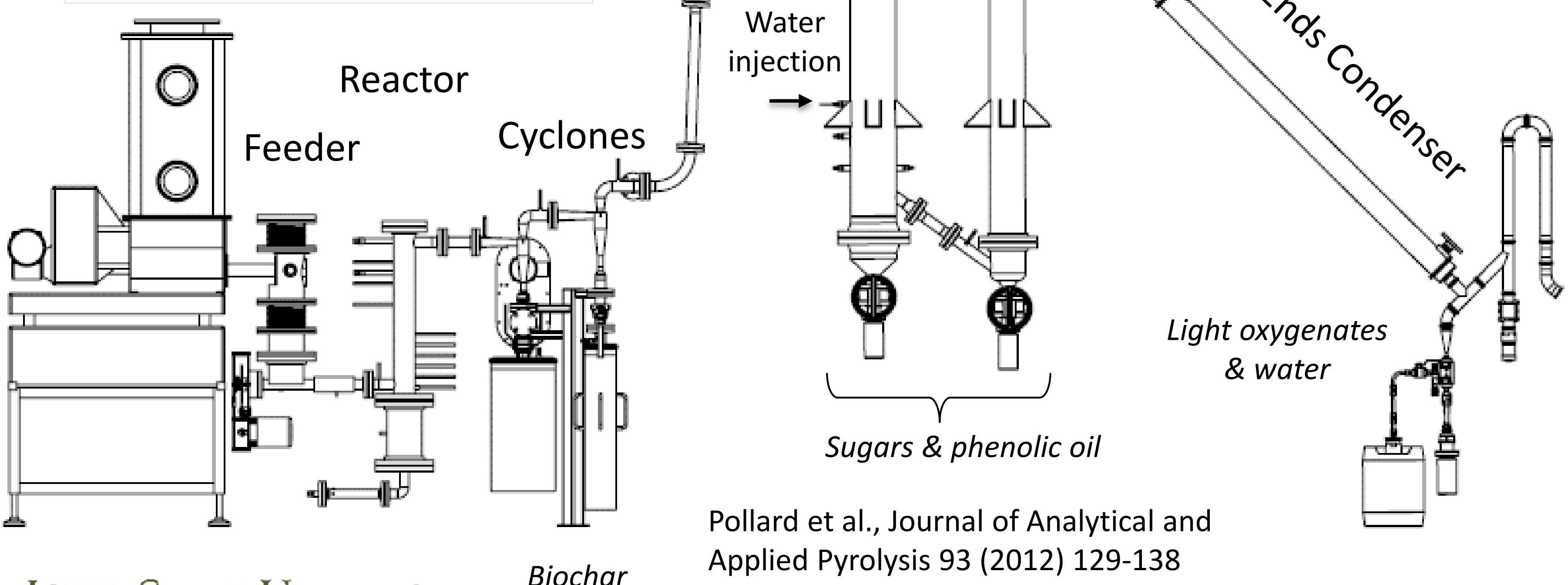
Selective condensation of pyrolysis vapors



Pollard et al., Journal of Analytical and Applied Pyrolysis 93 (2012) 129-138

Fractionating Bio-oil Recovery

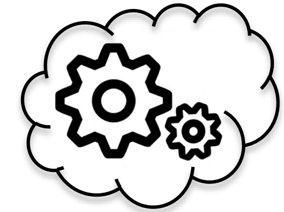


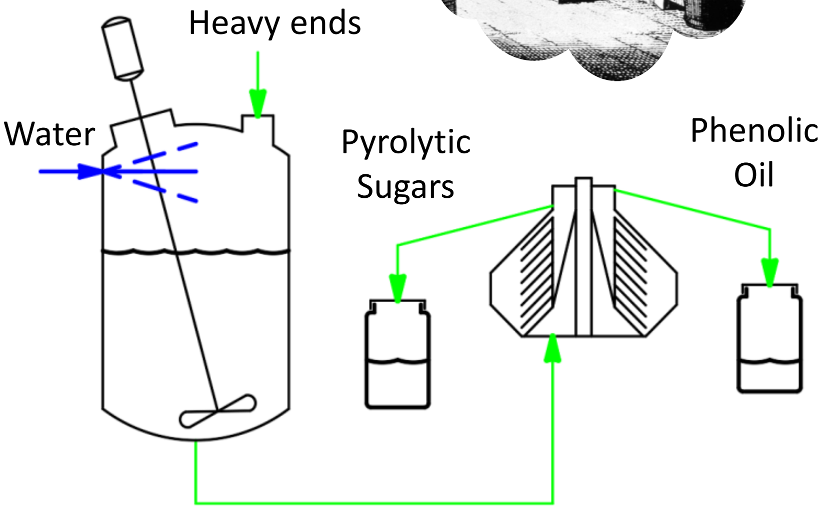


Pollard et al., Journal of Analytical and Applied Pyrolysis 93 (2012) 129-138

Polin et al., Journal of Analytical and Applied Pyrolysis 143 (2019) 104679

Separating heavy ends into sugars and phenolic oil





Extraction of corn stover-derived heavy ends

Component	Heavy ends (wt% d.b.)	Extracted sugar fraction (wt% d.b.)
Sugars	29.2	61.1
Phenols	61.9	22.4
Acids	3.0	3.8
Other	5.87	12.7

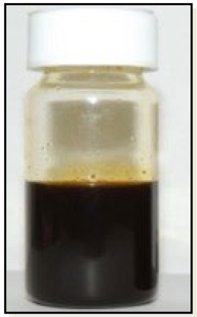
Rover et al., ChemSusChem 7 (2014) 1662-1668

Cleaning py sugars

Pyrolytic Syrup

Contaminant Removal
(phenolic compounds)

Pyrolytic Sugars
(99.5% pure)



Phenolic Monomers

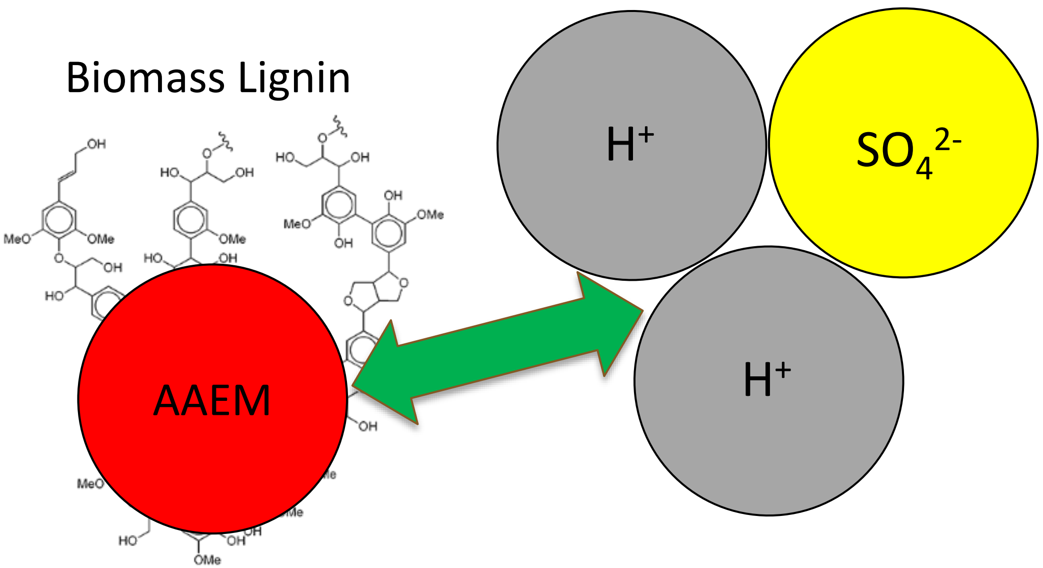
Levoglucosan (99.4% pure)

Stanford et al., Separation & Purification Technology 194 (2018) 170-180

Rover et al., Green Chemistry (2019) DOI: 10.1039/C9GC02461A

Why does acid pretreated biomass agglomerate?

- Alkali and alkaline earth metals in biomass catalyze both pyranose/ furanose ring fragmentation and lignin depolymerization
- Lignin melts and agglomerates rather than depolymerizes and volatilizes in the absence of suitable metal catalyst



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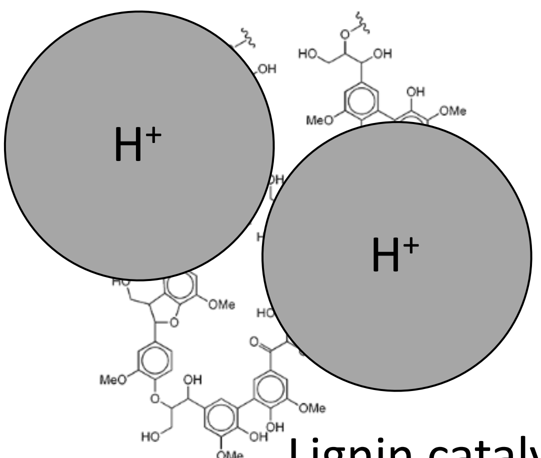
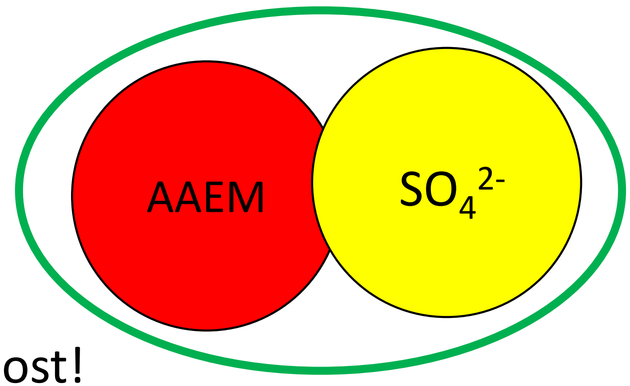
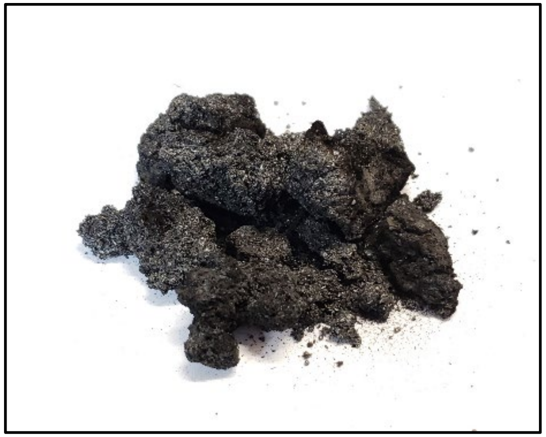
Biomass Lignin



Lignin catalyst lost!

Stable salt



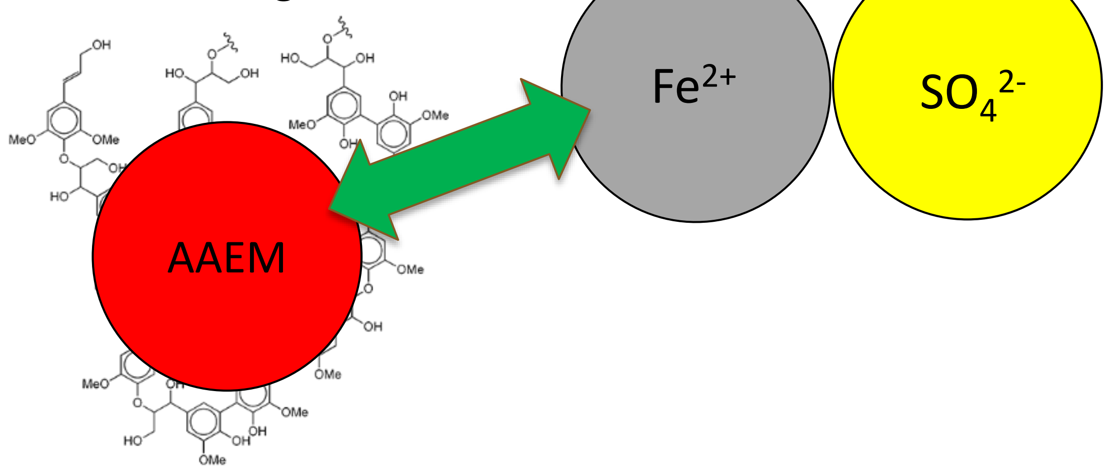


Agglomerated char from acid pretreated biomass

Preventing char agglomeration

- Find an ionic compound for which:
  - Anion passivates AAEM
  - Cation selectively catalyzes lignin depolymerization
- Compound must be water soluble to assure its diffusion into the plant cell walls
- Ferrous sulfate provides these functions

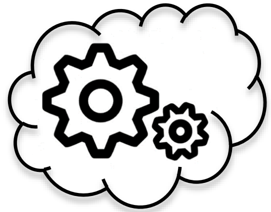
Biomass Lignin



Lignin catalyst replaced!

Rollag et al., manuscript in preparation (2019)

Preventing char agglomeration



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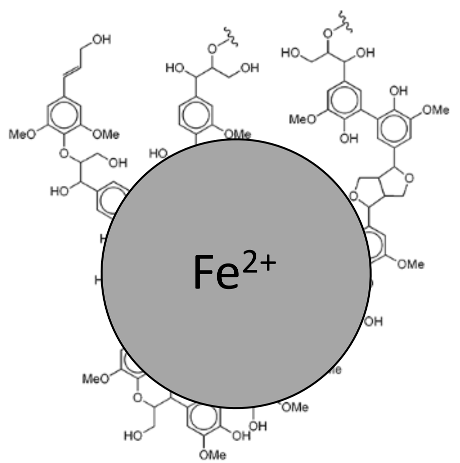
Biomass Lignin



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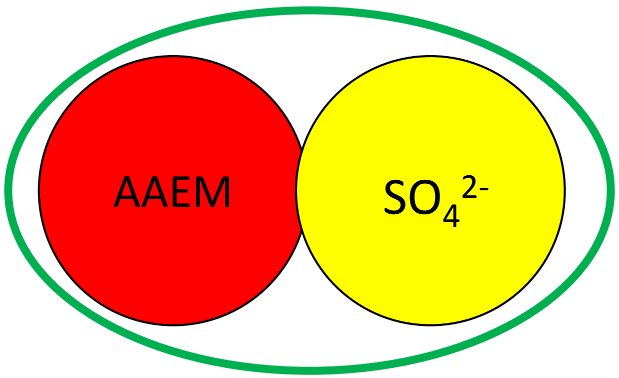
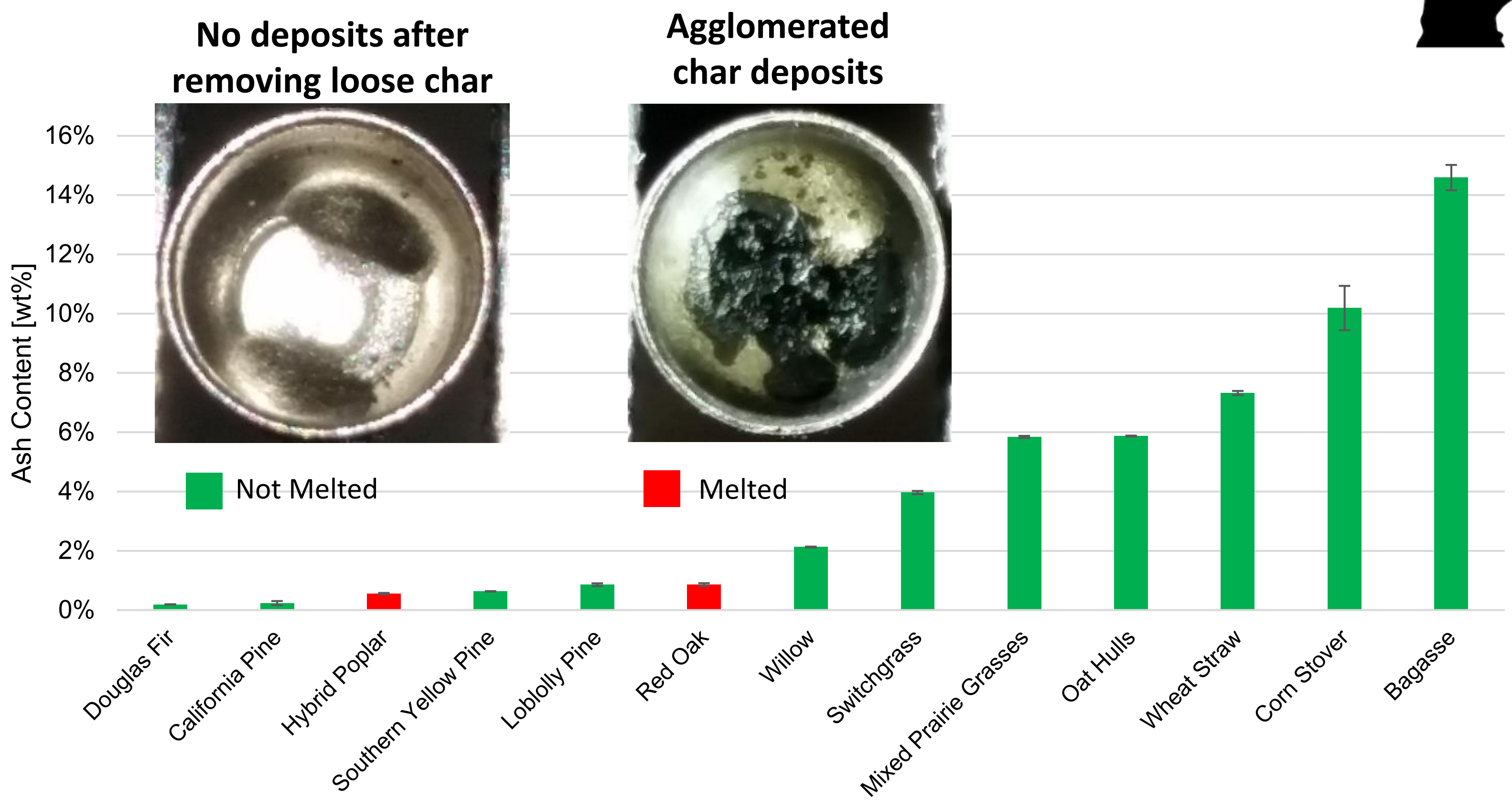


Powdered char from ferrous sulfate pretreated biomass

Rollag et al., manuscript in preparation (2019)

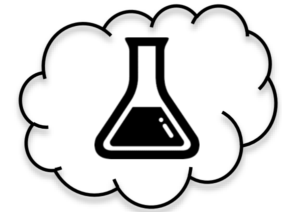
Preventing char agglomeration

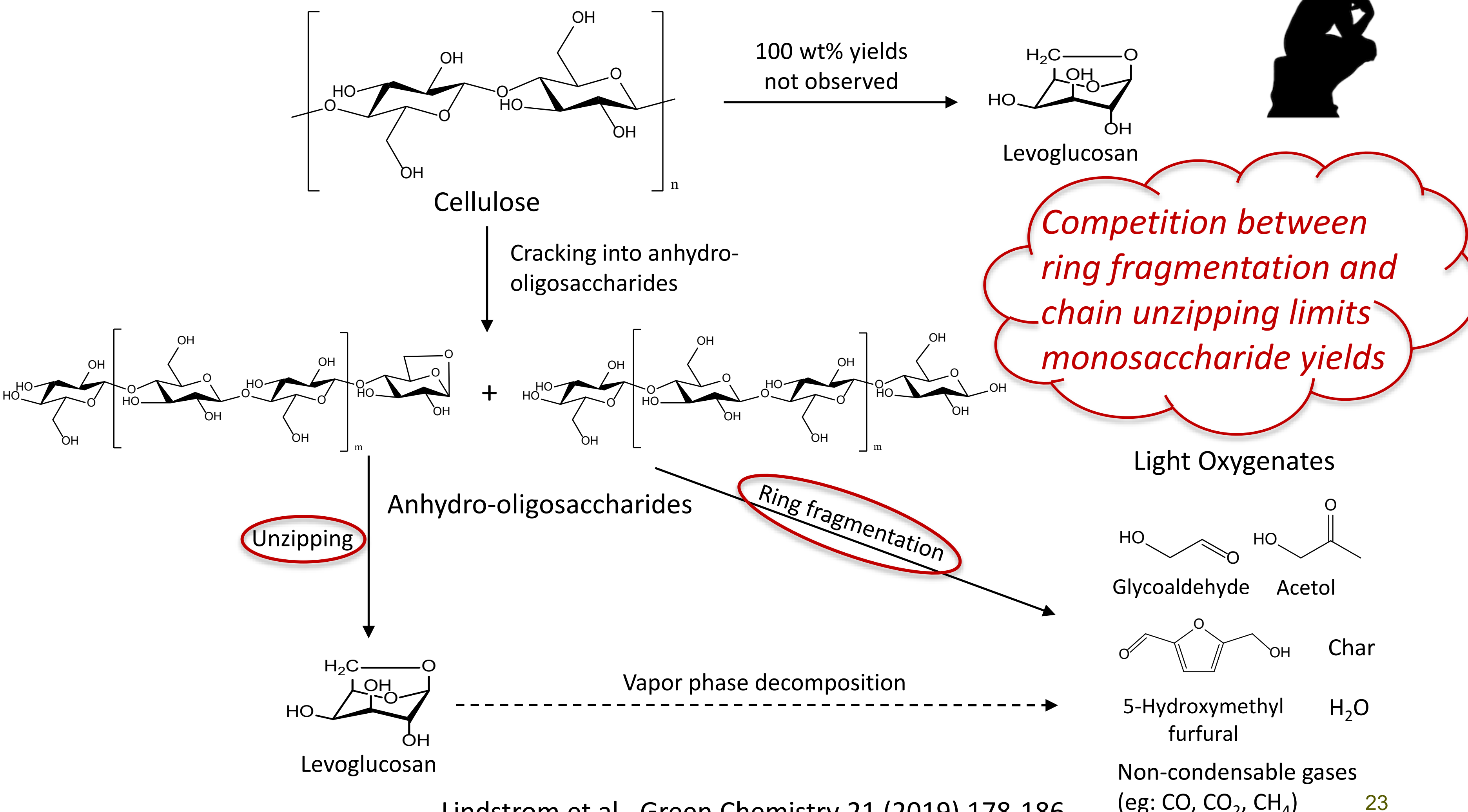
Ferrous sulfate pretreatment eliminated char agglomeration for most kinds of biomass tested



Rollag et al., manuscript in preparation (2019)

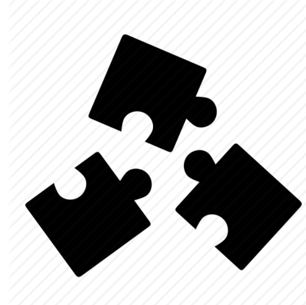
Why don’t we get more than 60% yield of sugars from cellulose?





Lindstrom et al., Green Chemistry 21 (2019) 178-186

Putting it all together: Py refinery




Lignocellulosic Biomass

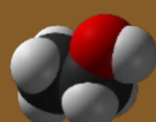
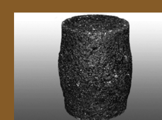
→ Autothermal Pyrolysis → Product Recovery

Unrefined Sugars from Polysaccharide

Phenolic Oil from Lignin

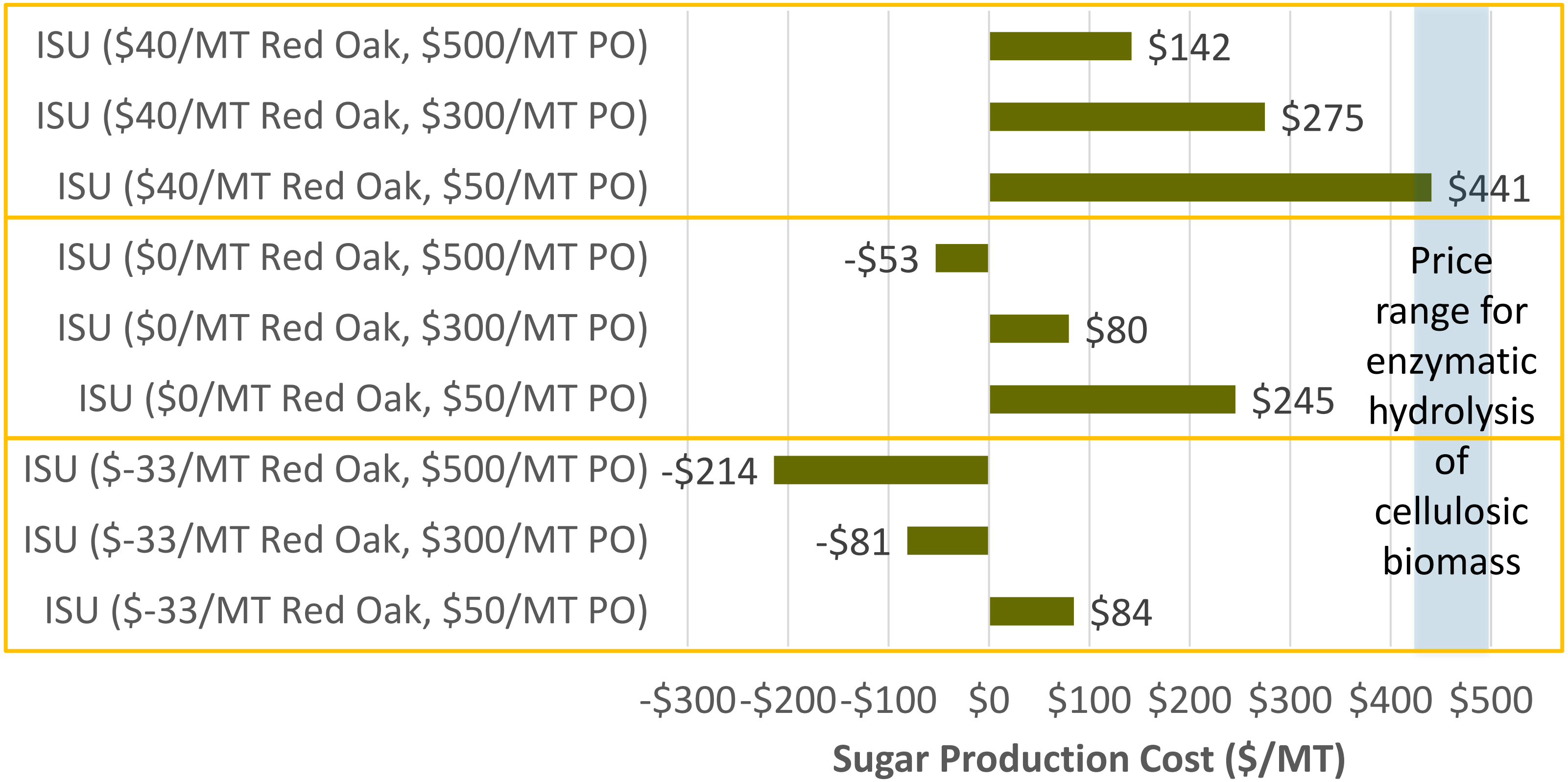
Unrefined Acetate from Hemicellulose

Biochar

	Unrefined Sugars from Polysaccharide	Phenolic Oil from Lignin	Unrefined Acetate from Hemicellulose	Biochar
First Generation Products	Ethanol 	Bio-asphalt and marine fuel  	In-plant thermal energy 	Soil Amendment 
Potential Future Products	-Pharmaceuticals -Polymers 	-Octane enhancers -Drop-in Fuels -Biobased Chemicals	-Acetone -Acetic Acid -Bio-cement -Alcohols 	-Activated Carbon 

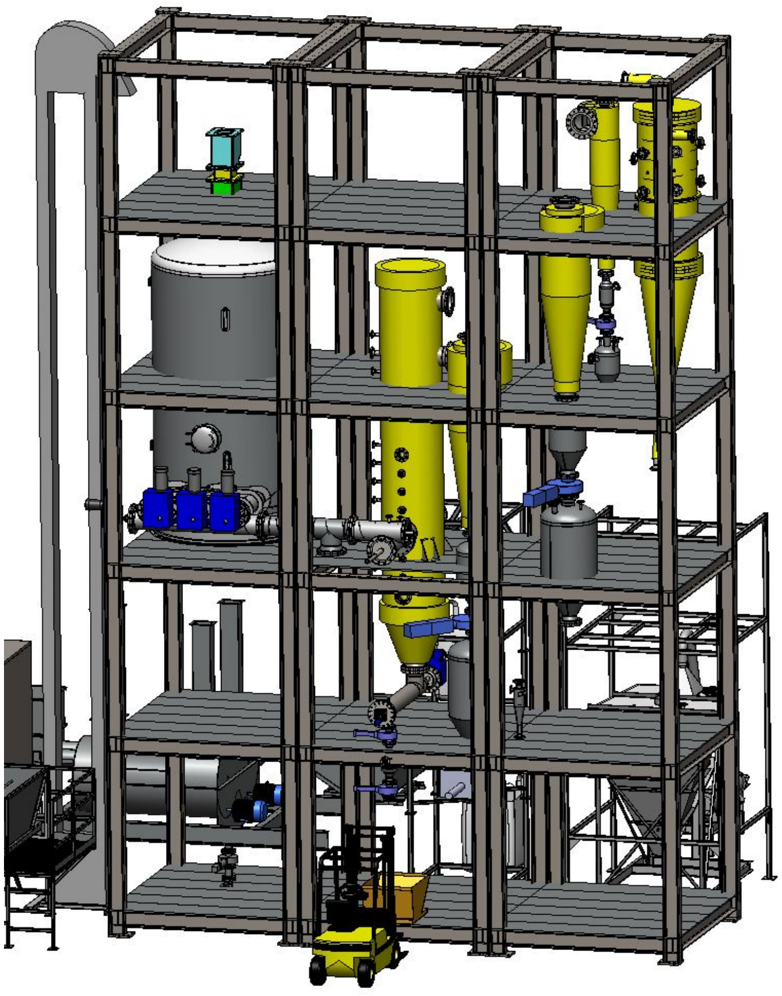
Economics of Py Refinery

- Low cost cellulosic sugars from woody biomass across a wide range of assumptions
- Feedstock cost and phenolic oil (PO) value are key cost drivers



Next Step: Demonstrate autothermal pyrolysis at 50 tons per day scale

- Iowa project (Redfield, IA)
  - Privately financed by Stine Seed Farms
  - Engineering, Procurement and Construction provided by Frontline Bioenergy
  - Conversion of corn stover into sugars, phenolic oil and biochar
- California project (El Dorado Hills)
  - Funded by CA Energy Commission
  - Partnership with Lawrence Livermore National Laboratory and Frontline Bioenergy
  - Feasibility of converting wood waste into drop-in biofuels



Acknowledgments

I appreciate the creativity and dedicated efforts of a long line of graduate students and staff scientists and engineers who made possible the discoveries and innovations described in my talk.

Heterodoxy in pyrolysis has been made possible through funding from several sources in the last decade including the U.S. DOE, the USDA, the NSF, Conoco-Phillips, Phillips 66, and ExxonMobil. Our work is currently being supported by the U.S. DOE AMO sponsored RAPID Institute as part of an effort to develop modular chemical process intensification (MCPI) in pyrolysis. We are indebted to Stine Seed Company for financing the construction of the first demonstration-scale autothermal pyrolysis plant.

Questions?