Sugars and Phenolic Oil from Autothermal Pyrolysis of Biomass

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IEA Bioenergy Task 34 Webinar

Production of Chemicals and Materials from Direct Thermochemical Liquefaction

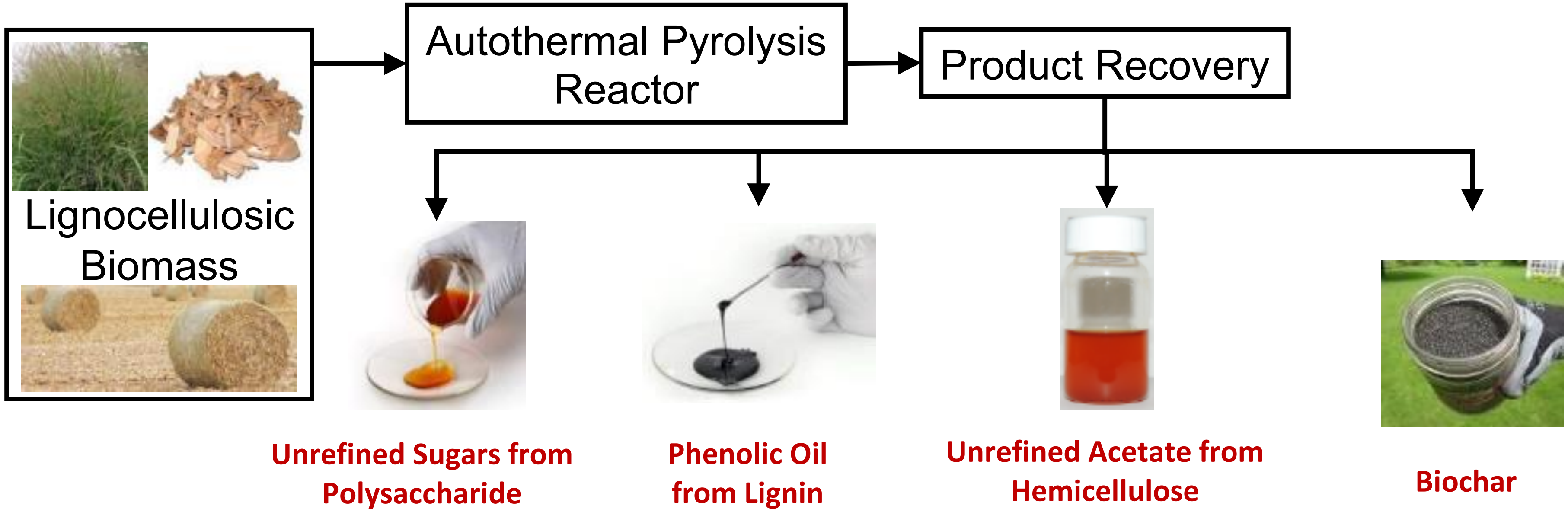
April 9, 2024

Outline

- Modular chemical process intensification in pyrolysis
- Autothermal pyrolysis
- Biomass pretreatments to enhance sugar yields
- Fractionating recovery of bio-oil
- Refining pyrolytic sugars
- Stabilization of phenolic oil
- Future directions

*Brown, R. C., Heterodoxy in fast pyrolysis of biomass, Energy & Fuels 2021, 35, 987-1010

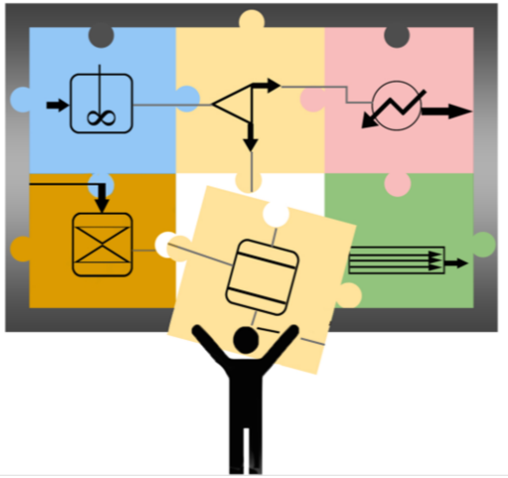
Concept for Pyrolysis Biorefinery

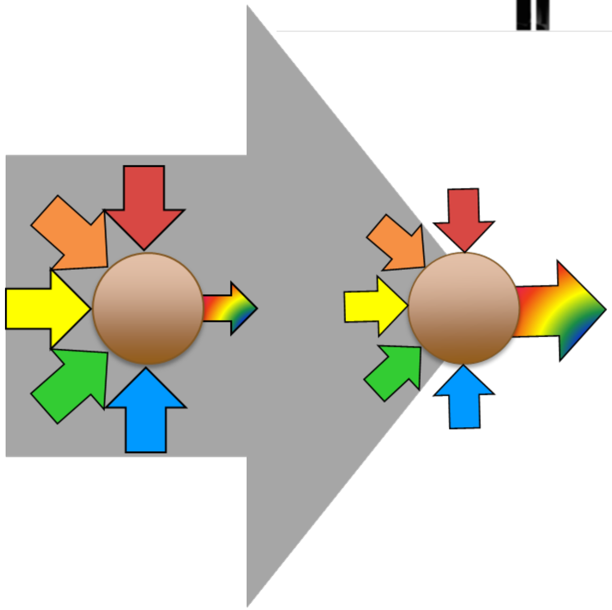


First Generation Products	Ethanol 	Bio-asphalt and marine fuel  	In-plant thermal energy 	Soil enrichment & sequestration of carbon 
Potential Future Products	-Pharmaceuticals -Polymers -Alcohol-to-jet fuel 	-Renewable diesel -Octane enhancers -Biobased chemicals	-Acetone -Acetic Acid -Bio-cement 	-Slow release fertilizer 

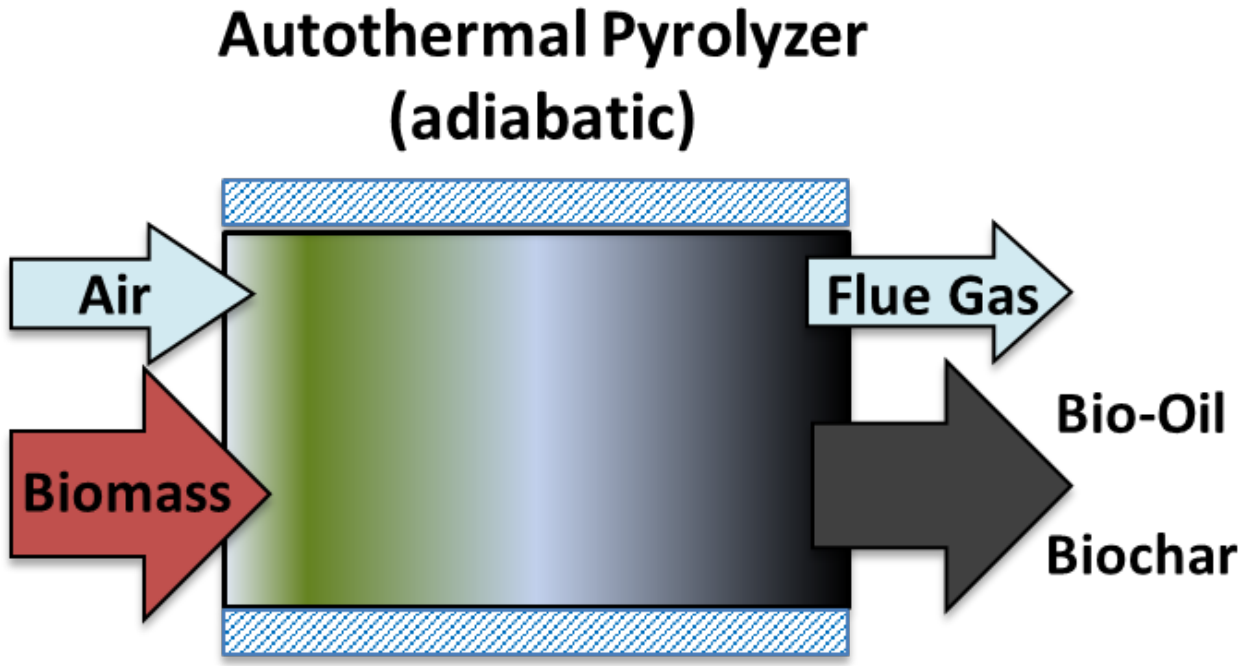
Modular Chemical Process Intensification (MCPI) Enables Distributed Processing

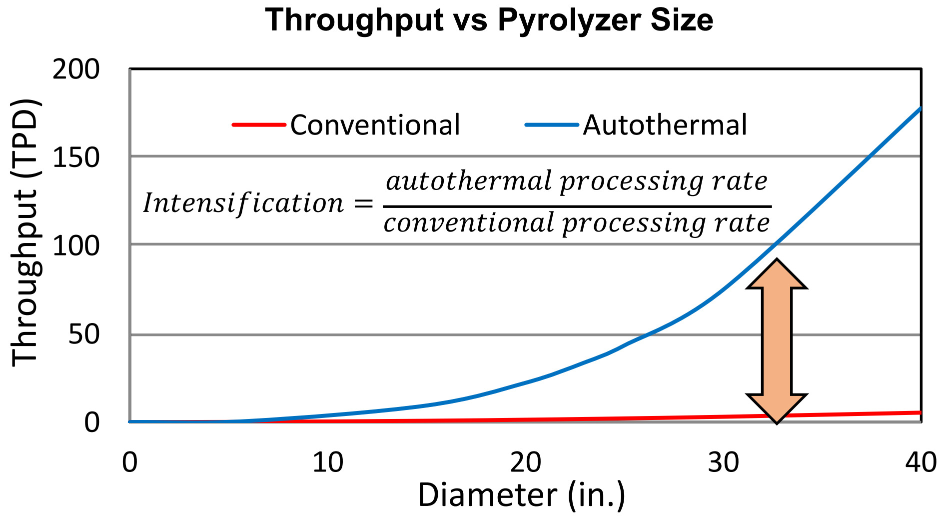
- Modular manufacturing: subdivides system into subunits (modules) that can be factory built and field assembled
  - Replaces economies of scale with economies of number
  - Enables distributed processing
- Intensification: Increasing desired outputs while decreasing inputs of feedstock, energy, water, capital, and labor.
  - Also reduce pollution emissions
  - Enables modular manufacturing

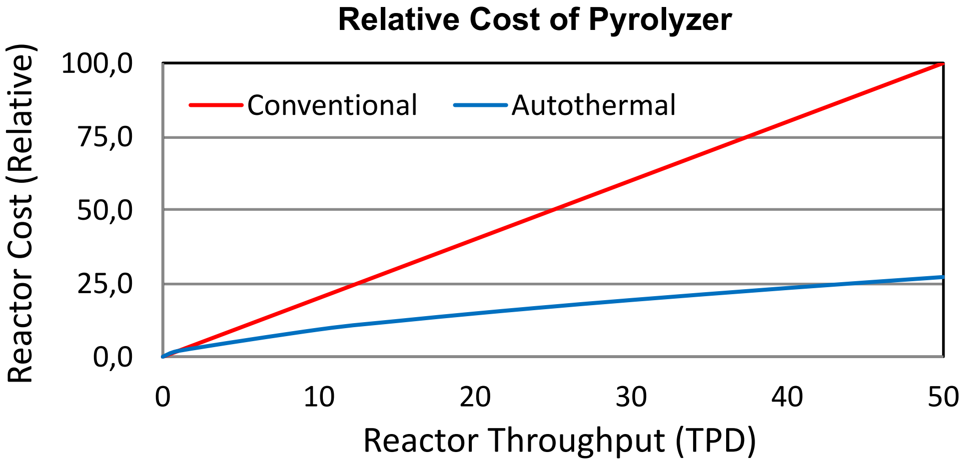




Autothermal pyrolysis: Prospects







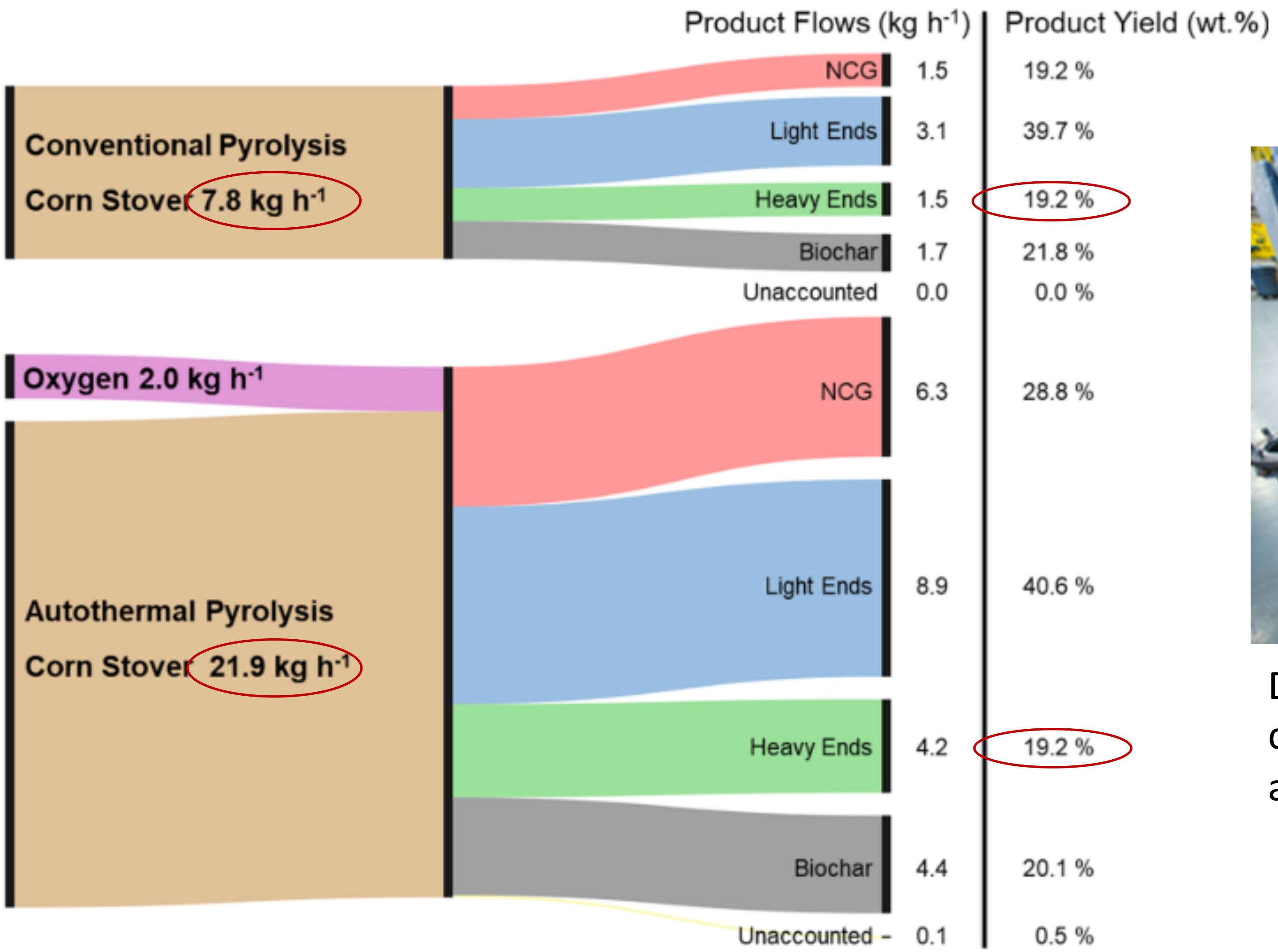
Autothermal Pyrolysis
$0.06 \leq \phi \leq 0.12$

Gasification
$0.20 \leq \phi \leq 0.35$

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

Brown (2020) Joule 4:2268-2289

Autothermal pyrolysis: Process intensification



Downsizing pyrolysis vessel (3.5 in vs 6 in dia.) to accommodate higher throughputs achieved with autothermal pyrolysis

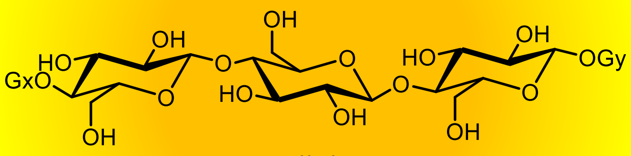
Polin et al. (2019) J. Anal. Appl. Pyrolysis 143, 104679

Biomass Pretreatments: Passivation of alkali and alkaline earth metals to increase pyrolytic sugar yields

Biomass pretreatment with sulfuric acid or ferrous sulfate in proportion to AAEM in biomass

Alkali and alkaline earth metals (AAEM) in fertilizer

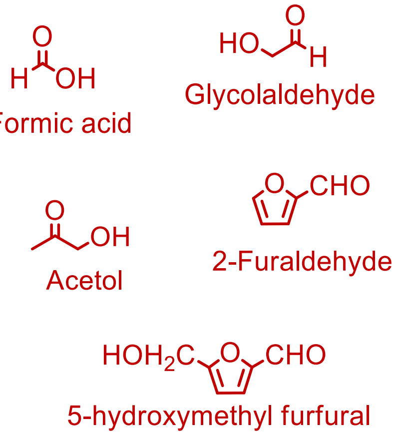
Thermally stable AAEM salts



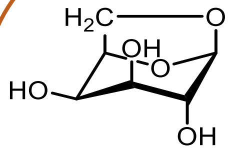
Cellulose

Pyrolysis

Alkali and alkaline earth catalyzed pyranose ring fragmentation



Dominant reaction when biomass pretreated



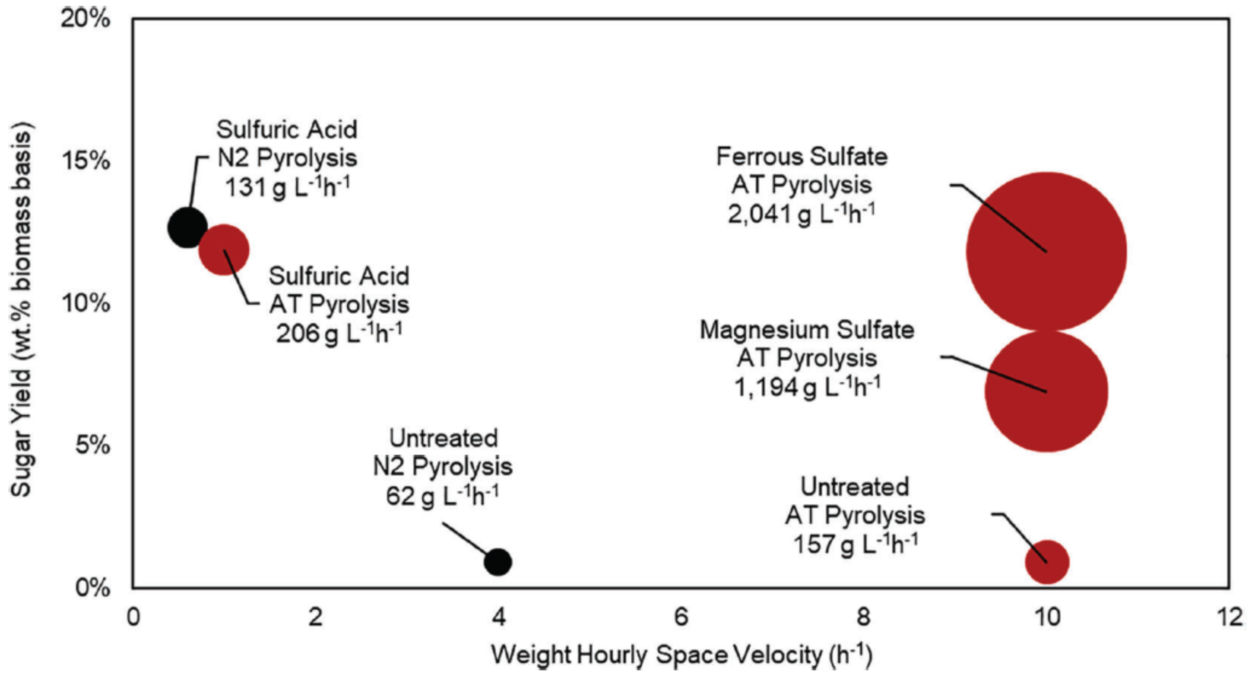
Levoglucosan

Similar principal applies to both cellulose and hemicellulose

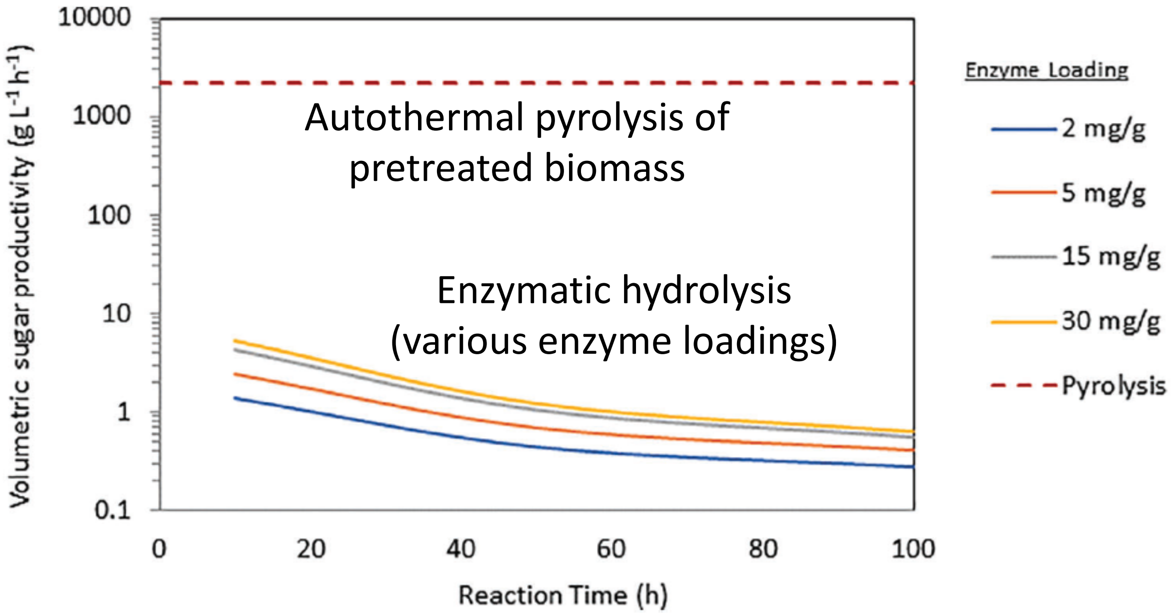
Cellulose depolymerization

Biomass pretreatments: Process intensification of sugar production

Sugar yield and volumetric sugar productivity gains from biomass pretreatments



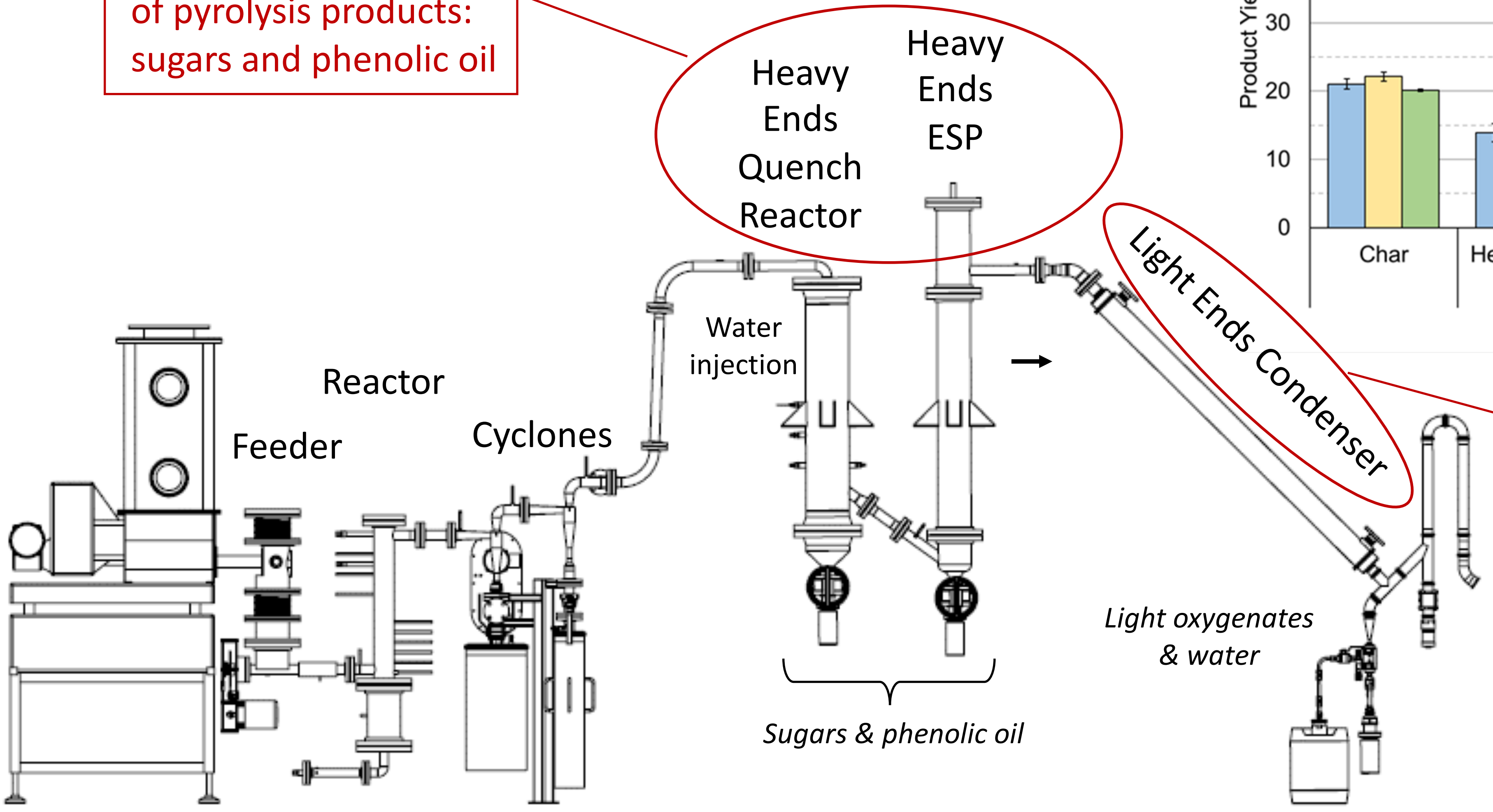
Comparing volumetric sugar productivity of pyrolysis vs enzymatic hydrolysis

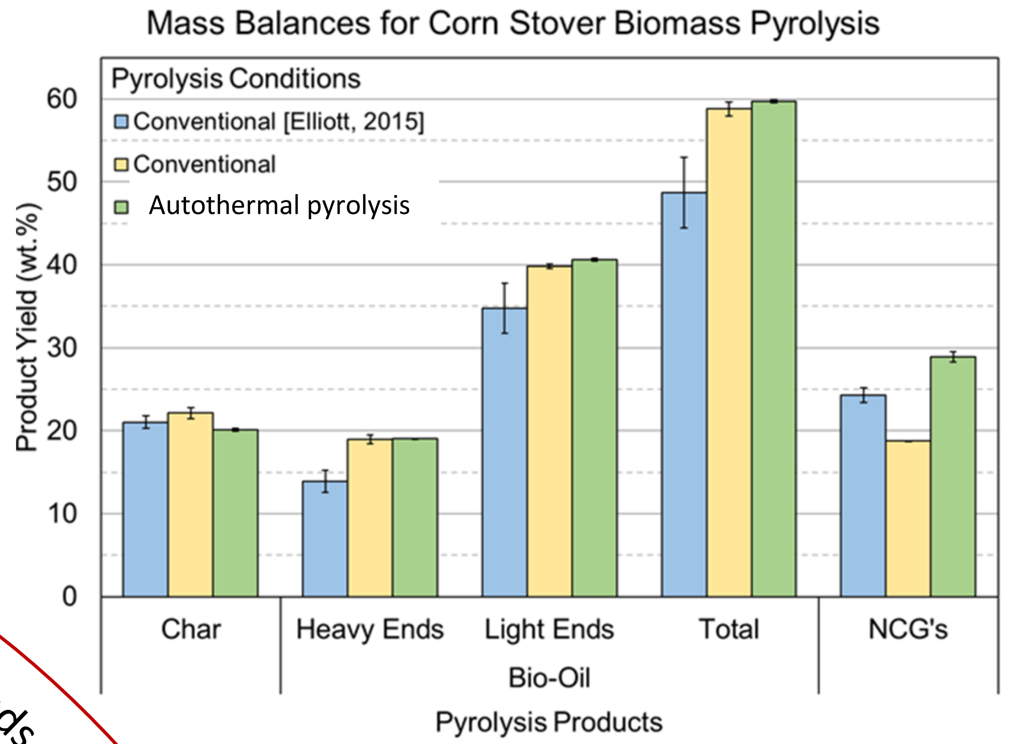


Rollag et al. (2020) Chemical Engineering Journal 385, 123889

Fractionating Recovery of bio-oil

Most valuable fraction of pyrolysis products: sugars and phenolic oil





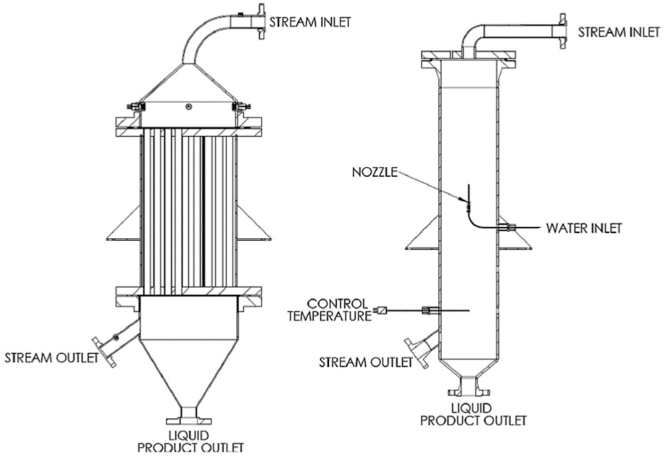
Significant carbon but so dilute in water to be of questionable value in recovering

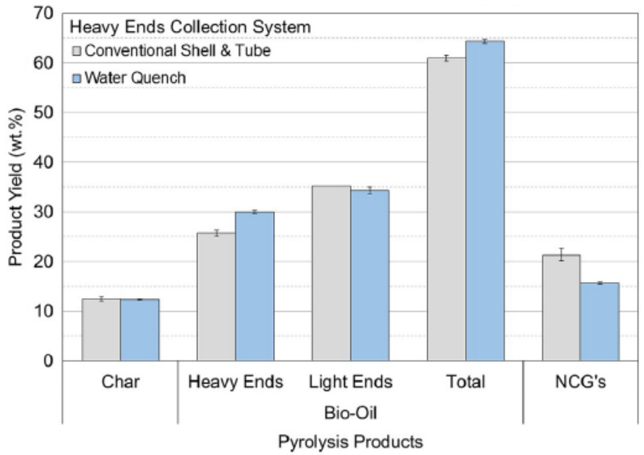
Pollard et al. (2012) Journal of Analytical and Applied Pyrolysis 93, 129-138
Polin et al. (2019) Journal of Analytical and Applied Pyrolysis 143, 104679

Other innovations in product recovery

Direct contact water quench

Indirect contact — Direct contact

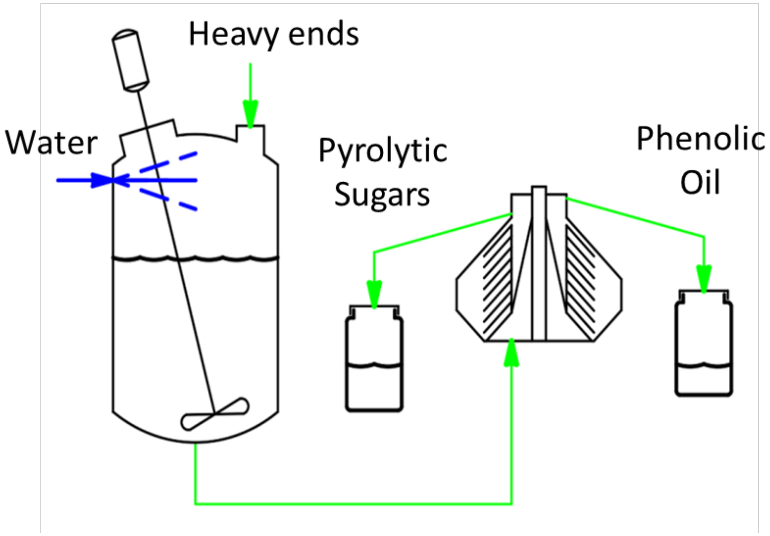




Direct contact quench reactor increased heavy ends yield by 15% and reduced fouling

Dalluge et al. (2019) Applied Energy 251, 113346

Continuous liquid-liquid extraction of sugars



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. (2014) ChemSusChem 7, 1662-1668

Refining pyrolytic sugars

Pyrolytic Syrup

Contaminant Removal
(phenolic compounds)

Pyrolytic Sugars

Purified Levoglucosan

Phenolic Monomers

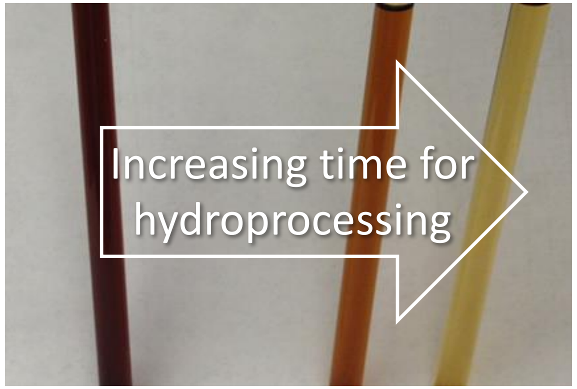
Rover et al. (2019) Green Chemistry 21, 5980

Stabilization of phenolic oil

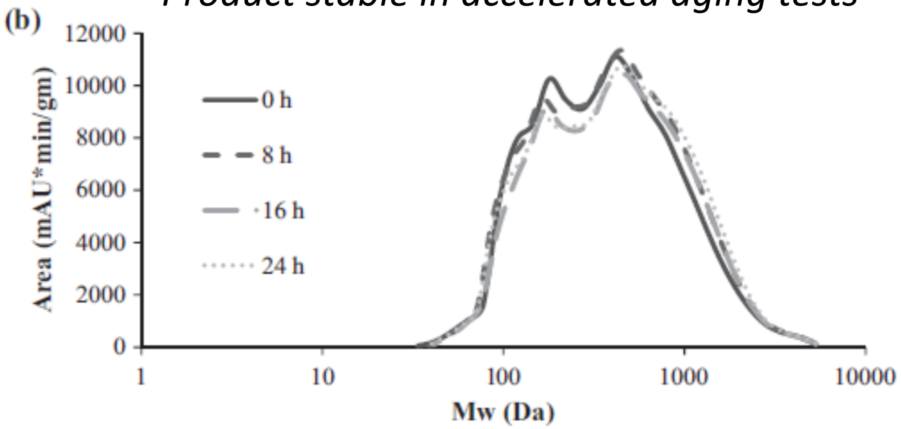
- Distributed stabilization of bio-oil for shipping and process and centralized refinery
- Fuel oils suitable for dispatchable renewable power, marine fuels, and heating oil

Low temperature, low pressure(LTLP) hydrogenation

Rover et al. (2015)
Fuel 153, 224-230

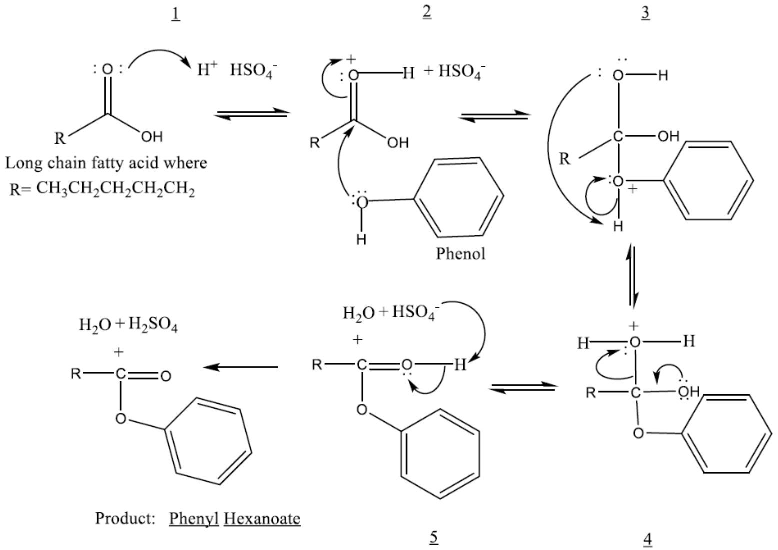


Product stable in accelerated aging tests



Esterification of phenolic oil with volatile fatty acids

Bakshi et al. (2022)
Energy and Fuels
36, 6317-6328



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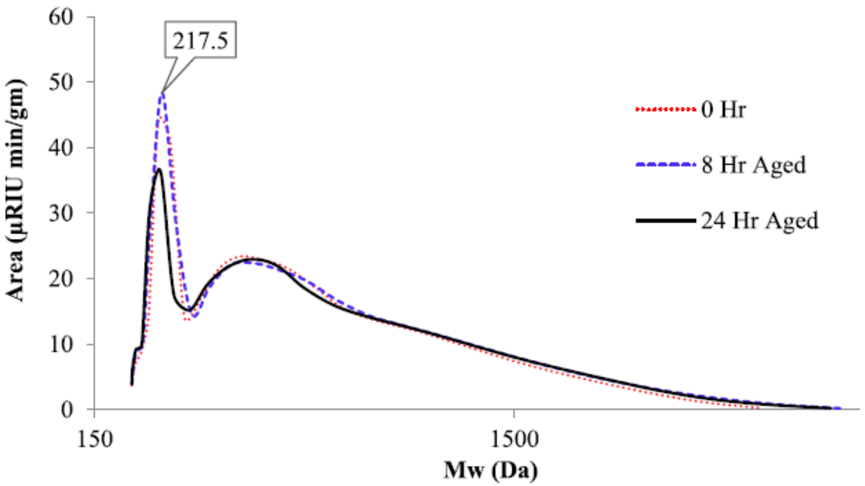
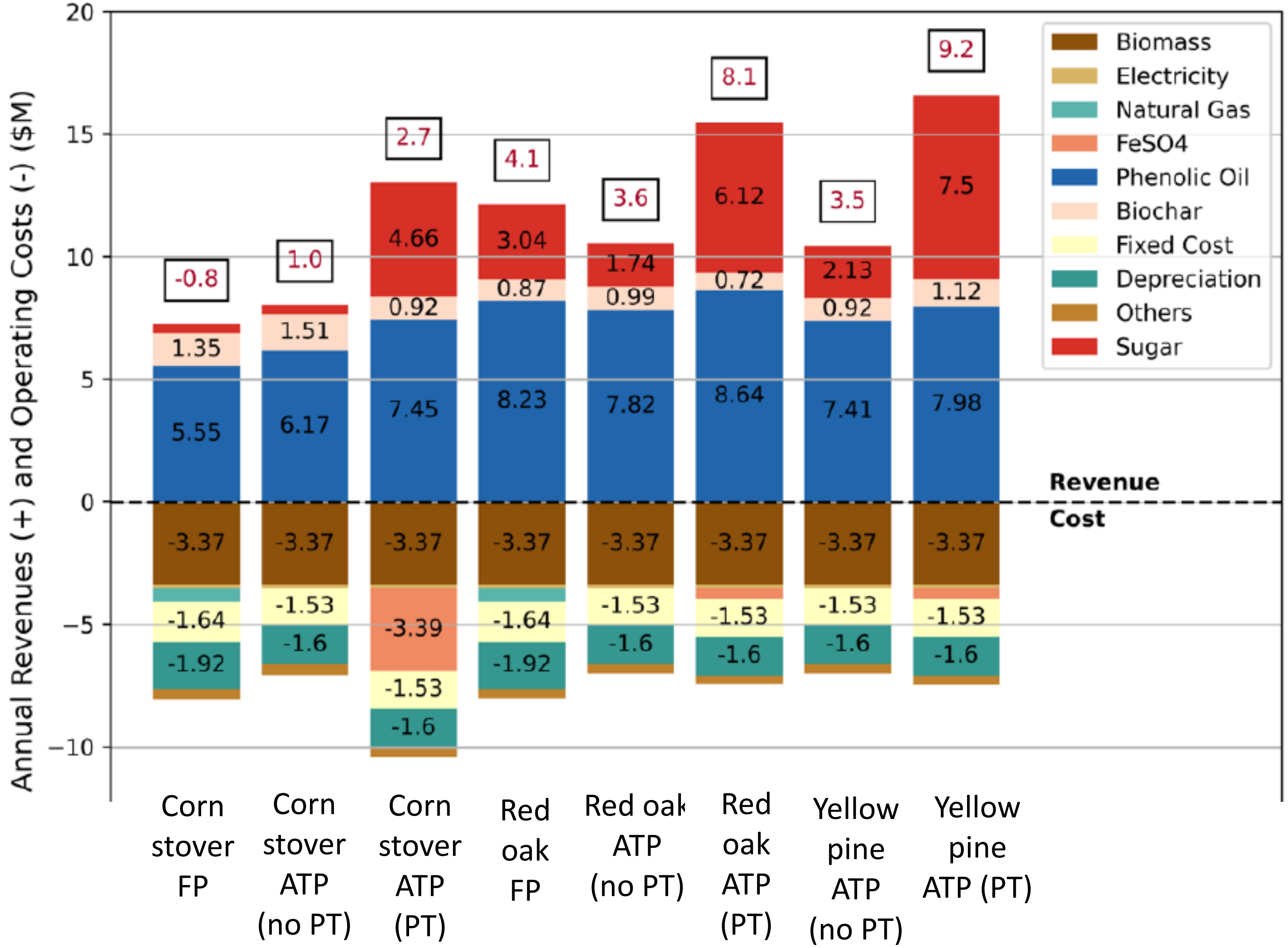


Favorable economics for a 250 TPD Pyrolysis Biorefinery

Total Project Investment: $16 million



NG – non-condensable gas
PO – phenolic oil
BC – biochar
EM – emission
Seq – sequestered

PT – pretreated
No PT – not pretreated

Ganguly et al. (2022) Green Chemistry 24, 9290

First Demonstration Project

- Partners: Stine Seed Company, Frontline Bioenergy, Rise Energy and Iowa State University
- Technology: ISU pyrolysis technologies incorporated into modular system
- Approach: Pilot scale research to guide design of 50 tpd demonstration plant using corn stover as major biomass feedstock

Pilot plant (15-20 kg/h) used to design demonstration plant

Py Refinery demonstration plant (50 tpd)

https://www.youtube.com/watch?v=VvnnHIGP7h4

Pyrolysis Products

Phenolic oil

Biochar

Future Directions

- Further enhance sugar yields via hot water extraction of hemicellulose and AAEM prior to fast pyrolysis
- Demonstrate upgrading of stabilized phenolic oil to renewable diesel and sustainable aviation fuel
- Tunable pyrolysis for apportioning product yield between sugars/phenolic oil and biochar
- Design and construction of integrated pilot plant producing sugars, phenolic oil, and biochar at scale greater than 10 TPD