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

Robert C. Brown
Director, Bioeconomy Institute
tcbiomassplus2019
Rosemont, IL
October 7-9, 2019
Orthodoxy in fast pyrolysis

• **Definition of pyrolysis:** “Thermal decomposition of organic compounds in the absence of oxygen.”
  
  – *Bioresnewable Resources: Engineering New Products from Agriculture*

• **Products of pyrolysis:** “Bio-oil, biochar, non-condensable gases.”
  
  – *Bioresnewable 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.”
  
  – *Bioresnewable 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

![Graph showing predicted ignition delay vs. temperature](image)
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!

Autothermal Pyrolysis: $0.06 \leq \phi \leq 0.12$
Gasification: $0.20 \leq \phi \leq 0.35$

$\phi = \frac{\text{Air}}{\text{Air}_{\text{Stoich}}}$

Pyrolysis: $\phi = 0.00$
Combustion: $\phi > 1.0$
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
Process intensification through autothermal pyrolysis

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

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

Throughput vs Pyrolyzer Size

Relative Cost of Pyrolyzer

Throughput (TPD)

Reactor Cost (Relative)

Intensification = \frac{\text{autothermal processing rate}}{\text{conventional processing rate}}
How much sugar can be produced via fast pyrolysis?

![Chemical structures of sugars](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Glucose (wt%)</th>
<th>Celllobiose (wt%)</th>
<th>Maltose (wt%)</th>
<th>Malto-hexaose (wt%)</th>
<th>Cellulose (wt%)</th>
<th>Curdlan (wt%)</th>
<th>Waxy maize starch (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levoglucosan</td>
<td>7.00</td>
<td>24.4</td>
<td>20.5</td>
<td>33.1</td>
<td>58.8</td>
<td>44.2</td>
<td>48.5</td>
</tr>
<tr>
<td>Unidentified*</td>
<td>40.8</td>
<td>23.6</td>
<td>32.4</td>
<td>20.5</td>
<td>7.1</td>
<td>18.1</td>
<td>13.2</td>
</tr>
</tbody>
</table>

*Includes gases, water and some unidentified organic compounds

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

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

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

Fractionating Bio-oil Recovery

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

<table>
<thead>
<tr>
<th>Component</th>
<th>Heavy ends (wt% d.b.)</th>
<th>Extracted sugar fraction (wt% d.b.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugars</td>
<td>29.2</td>
<td>61.1</td>
</tr>
<tr>
<td>Phenols</td>
<td>61.9</td>
<td>22.4</td>
</tr>
<tr>
<td>Acids</td>
<td>3.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Other</td>
<td>5.87</td>
<td>12.7</td>
</tr>
</tbody>
</table>

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)

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.
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.

![Diagram showing biomass lignin and the process of agglomeration with ions and salts.](image)
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

AAEM

Fe^{2+}

SO_4^{2-}

Lignin catalyst replaced!

Rollag et al., manuscript in preparation (2019)
Preventing char agglomeration

• Find an ionic compound for which:
  – Anion passivates AAEM
  – Cation selectively catalyzes lignin depolymerization
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Biomass Lignin

Fe$^{2+}$

Lignin catalyst replaced!

Stable salt

AAEM

SO$_4^{2-}$

Rollag et al., manuscript in preparation (2019)
Preventing char agglomeration

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

Iowa State University
Bioeconomy Institute

Rollag et al., manuscript in preparation (2019)
Why don’t we get more than 60% yield of sugars from cellulose?

Cellulose

Cracking into anhydro-oligosaccharides

Anhydro-oligosaccharides

Unzipping

Vapor phase decomposition

100 wt% yields not observed

Levoglucosan

Competition between ring fragmentation and chain unzipping limits monosaccharide yields

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

Light Oxygenates

Glycoaldehyde

Acetol

5-Hydroxymethyl furfural

Char

Non-condensable gases (eg: CO, CO₂, CH₄)

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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

<table>
<thead>
<tr>
<th>First Generation Products</th>
<th>Ethanol</th>
<th>Bio-asphalt and marine fuel</th>
<th>In-plant thermal energy</th>
<th>Soil Amendment</th>
</tr>
</thead>
</table>
**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

<table>
<thead>
<tr>
<th>ISU ($40/MT Red Oak, $500/MT PO)</th>
<th>ISU ($40/MT Red Oak, $300/MT PO)</th>
<th>ISU ($40/MT Red Oak, $50/MT PO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$142</td>
<td>$275</td>
<td>$441</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ISU ($0/MT Red Oak, $500/MT PO)</th>
<th>ISU ($0/MT Red Oak, $300/MT PO)</th>
<th>ISU ($0/MT Red Oak, $50/MT PO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-$53</td>
<td>$80</td>
<td>$245</td>
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<thead>
<tr>
<th>ISU ($-33/MT Red Oak, $500/MT PO)</th>
<th>ISU ($-33/MT Red Oak, $300/MT PO)</th>
<th>ISU ($-33/MT Red Oak, $50/MT PO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-$214</td>
<td>-$81</td>
<td>$84</td>
</tr>
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</table>

**Price range for enzymatic hydrolysis of cellulosic biomass**

Sugar Production Cost ($/MT)

- $300-$200-$100 $0 $100 $200 $300 $400 $500
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?