Lignin valorization to chemicals

Gregg T. Beckham
Bioeconomy 2017
July 12, 2017

National Renewable Energy Laboratory
National Bioenergy Center
Lignin from 2G biorefineries will be quite abundant.

At a high capacity factor, each plant could process up to 400 tons/day of lignin.
Lignin can offer economic and sustainability value to biorefineries

Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbons: Dilute-Acid and Enzymatic Deconstruction of Biomass to Sugars and Biological Conversion of Sugars to Hydrocarbons

R. Davis, M.J. Biddy, et al., 2013

Vardon et al., EES 2015
Lignin valorization is essential for biochemical conversion.

![Graph showing minimum fuel selling price and cost metrics for different processes.]

### Metric

<table>
<thead>
<tr>
<th></th>
<th>Lipids</th>
<th>Fatty Alcohols</th>
<th>Organic Acids</th>
<th>BDO + EtOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFSP ($/GGE, 2014$) — Prior to coproducts</td>
<td>$7.80</td>
<td>$7.43</td>
<td>$5.48</td>
<td>$5.60</td>
</tr>
<tr>
<td>Fuel C efficiency from biomass (%)</td>
<td>20%</td>
<td>21%</td>
<td>25%</td>
<td>27%</td>
</tr>
<tr>
<td>Fuel yield (GGE/ton)</td>
<td>34.2</td>
<td>35.7</td>
<td>43.5</td>
<td>46.5</td>
</tr>
<tr>
<td>TCI ($MM) — Prior to coproducts</td>
<td>$640</td>
<td>$628</td>
<td>$520</td>
<td>$527</td>
</tr>
<tr>
<td>Fuel-carbon chain length</td>
<td>~9–20</td>
<td>~16–20</td>
<td>11</td>
<td>~8–18</td>
</tr>
<tr>
<td>Carbon efficiency through lignin-to-coproduct train required to achieve $3/GGE (C in adipic acid vs C available in residual biomass)</td>
<td>59%</td>
<td>56%</td>
<td>40%</td>
<td>45%</td>
</tr>
</tbody>
</table>

*R. Davis, M.J. Biddy, et al., 2013*
Native lignin structure (monocot)

- Common polysaccharide-centric treatments break labile C-O linkages and form more recalcitrant C-C linked structures
- More than a century of research in lignin depolymerization
Heterogeneity is the main barrier for lignin upgrading to chemicals

Lignin’s Alkyl Aromatic Structure

Deconstruction

Thermal, catalytic, enzymatic

Depolymerization Product Slate

There is a world of difference between a valuable mixture of chemicals and a mixture of valuable chemicals (Art Power)

- Overcoming lignin heterogeneity is the key problem in lignin valorization to chemicals
Emerging routes to overcome lignin heterogeneity: Engineering plants

Lignin biosynthesis is plastic and can be successfully manipulated
- The C-lignin discovery highlights that native lignin polymers remain to be discovered
- Work in model systems can be transitioned to energy crops via emerging genome editing
Lignin in many species can be quite diverse
Emerging routes to overcome lignin heterogeneity: Biological funneling

Microbial degradation of aromatic compounds — from one strategy to four

*Georg Fuchs*, *Matthias Boll* and *Johann Heider*

*NATURE REVIEWS MICROBIOLOGY*
Biological funneling enables metabolism of heterogeneous aromatics

Microbes can funnel lignin-derived aromatics to central metabolism

Significant body of work going into process development around this concept to optimize biocatalysts, biological cultivation processes, separations, and chemical catalysis
Biopolymer production from lignin

Lignocellulosic Biomass

Alkaline Pretreatment
Black Liquor

Lignin Liquor Stream

Biological Funneling

Upper Pathways

β-KA Pathway

β-ketoadipic acid

PHA Valorization

Depolymerization
Depoly-Deoxy

Renewable Chemicals, Materials, & Fuels

Hydroxy acids

Composition (wt.%)

MW<sub>w</sub> 124 kDa
PDI 1.93
T<sub>g</sub> -47°C
T<sub>m</sub> 50°C
T<sub>d</sub> 259°C

Atom-efficient intermediates from lignin

Titer ~ 30-48 g/L
Rate ~ 0.4-0.6 g/L/hr
Yield ~ 100%
Towards selective lignin valorization

Biological funneling (along with other emerging techniques) may enable a solution to overcome lignin heterogeneity

- Significant opportunity in co-designing in planta lignin with biological and catalytic conversion
- Emerging 2G biorefineries offer space for new lignin valorization processes
Conference announcement!

For your calendars!

The inaugural Lignin Gordon Research Conference will be held in the August 5-10, 2018

The goal of this proposed GRC on lignin is to bring together leading researchers, postdocs, and students involved in multiple aspects of lignin including its characterization, in planta engineering, depolymerization and upgrading, and material science.

Interaction and discussion between plant researchers, chemists, engineers, and material scientists working on this recalcitrant polymer is critical to move the field forward.
Acknowledgements

Thank you for your attention!

Collaborators:
- John McGeehan, Portsmouth
- Linda Broadbelt, Keith Tyo, Northwestern
- Ellen Neidle, UGA
- Adam Guss, ORNL
- Yuriy Román-Leshkov, MIT
- Lindsay Eltis, Bill Mohn, UBC
- John Dorgan, MSU
- Rick Dixon, Fang Chen, UNT
- Sam Purvine, Erika Zink, EMSL
- M. Sandgren, Jerry Ståhlberg, SLU
- Jen DuBois, Montana State