A review of opportunities for lignocellulosic biorefineries: Maximizing value by minimizing waste

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Leveraging from what we have learned

Utilizing and finding value from all parts of the feedstock has been the cornerstone of the petroleum industry and first generation ethanol facilities.

**First Generation Ethanol**
- Fuel: Ethanol + Corn Oil
- Value-added Co-Product: DDGS
- Cost of waste treatment ~ a few cents/gallon

**Petroleum Refining**
- Fuel: Gasoline, Diesel, Jet, Fuel Oil, Bunker…
- Value-added Co-Product: Numerous chemicals
- Cost of waste treatment ~ a few cents at most
Opportunities in thermochemical processes

Opportunities for waste valorization via lost carbon to aqueous streams in thermochemical pyrolysis processes

Waste valorization could add economic benefit to TC biorefineries
- Currently around $0.10 to 0.16/gge attributed to wastewater treatment for targeted TC cases
- Overall capital costs is ~$20MM for waste treatment
- Waste streams can contain up to 3%–10% of biomass-derived carbon

Challenge: Analyzing the carbon available for upgrading and a tractable approach for upgrading
Fast pyrolysis and catalytic fast pyrolysis characterization

Develop consistent methodologies for characterizing aqueous streams

<table>
<thead>
<tr>
<th>Fast Pyrolysis</th>
<th>Catalytic Fast Pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP\textsubscript{NREL}</td>
<td>CFP\textsubscript{NREL}\textsubscript{ex-situ}</td>
</tr>
<tr>
<td>81%</td>
<td>99%</td>
</tr>
</tbody>
</table>

75 – 100% Mass Closure

- \( \geq 75\% \) mass closure (100+ compounds quantified, 200+ identified)
- Wide range of carbon in aqueous streams depending on upstream technology
- Thorough characterization can guide development of selective valorization strategies
- Multiple methods developed or optimized to characterize TC aqueous streams.


Work led by Gregg Beckham and team (NREL)
Developing strategies for upgrading dilute carbon aqueous streams to value added products

Conversion of aromatics to value-added co-products

*P. putida* can convert aromatics in DCR streams to PHAs

<table>
<thead>
<tr>
<th>Compound</th>
<th>ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>6.35 ✔</td>
</tr>
<tr>
<td>Formic acid</td>
<td>3.78 ✔</td>
</tr>
<tr>
<td>Propanoic acid</td>
<td>0.13 ✔</td>
</tr>
<tr>
<td>2-Hydroxyacetic acid</td>
<td>0.00 +</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.77 +</td>
</tr>
<tr>
<td>2-Hydroxyacetaldehyde</td>
<td>0.00 +</td>
</tr>
<tr>
<td>Phenol</td>
<td>2.38 +</td>
</tr>
<tr>
<td>2-Methylphenol</td>
<td>1.05 +</td>
</tr>
<tr>
<td>3-Methylphenol</td>
<td>2.25 +</td>
</tr>
<tr>
<td>4-Methylphenol</td>
<td>0.76 +</td>
</tr>
<tr>
<td>2,5-Dimethylphenol</td>
<td>0.74 +</td>
</tr>
<tr>
<td>2-Ethylphenol</td>
<td>0.27 +</td>
</tr>
<tr>
<td>Benzene-1,2-diol</td>
<td>0.05 ✔</td>
</tr>
<tr>
<td>Benzene-1,4-diol</td>
<td>0.20 +</td>
</tr>
<tr>
<td>3-Methylbenzene-1,2-diol</td>
<td>0.12 +</td>
</tr>
<tr>
<td>4-Methylbenzene-1,2-diol</td>
<td>0.09 +</td>
</tr>
<tr>
<td>4-Ethylbenzene-1,2-diol</td>
<td>0.10 +</td>
</tr>
<tr>
<td>4-Ethylbenzene-1,3-diol</td>
<td>0.11 +</td>
</tr>
<tr>
<td>Methanol</td>
<td>3.57 +</td>
</tr>
</tbody>
</table>

✔ = Native pathway

+ = Known pathway

- Currently can use ~50% of C
- Theoretically can utilize 100% of C

Work led by Gregg Beckham and team (NREL)
Opportunities in biochemical processes

Opportunities for waste valorization via lost carbon to aqueous streams in biochemical processes

Waste valorization could add economic benefit to BC biorefineries

- Currently around $0.60/gge attributed to wastewater treatment for targeted BC cases
- Overall capital costs is ~$70MM for waste treatment
- Utilize CH$_4$/CO$_2$ produced via WWT for production of value-added co-products

Challenge: Impurities in off-gas streams and a tractable approach for upgrading
Evaluate opportunities and risk for conversion of waste streams to value-added co-products

Range of potential pathways for upgrading

- Analysis of alternative waste stream feedstocks (methane and CO2) to fuels and chemicals using biological, thermochemical, or hybrid concepts.
- Initial study focused on:
  - Availability of waste feedstocks considering impurity.
  - Potential pathways for upgrading with current SOT and R&D needs.

Work led by Ling Tao (NREL)
Integrated analysis approach

Linking economic, market, and technology assessments to evaluate upgrading opportunities

Market value of each waste biogas-to-product versus estimated TRLs

NREL TEA Model Database for Waste Biogas to Products

Overall objective of this initial scoping work is to provide

- Insights to gain understanding for the potential of the pathways of interests
- A clear path forward to research directions to achieve cost targets as well as to effectively ways to utilize waste feedstocks

Work led by Ling Tao (NREL)
Summary

• Integrated approach to maximize carbon utilization/minimize waste has supported the economics of petroleum and first generation ethanol for decades

• Clear opportunity to improve economics of a biorefinery by utilizing “lost” carbon to value-added coproducts

• On-going R&D and analyses are working to develop pathways towards waste minimization/value creation from these streams
Acknowledgments

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- NREL technology platform researchers

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