Hydrothermal Liquefaction of Biorefinery Lignin-rich Streams: Carbon Recovery from Residual Aqueous Phase

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Summary

• Introduction

• Hydrothermal liquefaction of Lignin-rich streams

• Residual aqueous phase collection and characterization

• Aqueous phase valorization: Liquid-Liquid Extraction

• Conclusion and further developments
**Ethanol biorefinery: Lignin-rich streams**

Lignocellulosic biomass → Pretreatment (e.g. steam explosion) → Enzymatic hydrolysis → Fermentation → Ethanol distillation and separation → Ethanol

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total lignin</td>
<td>57.8</td>
<td>wt.% daf</td>
</tr>
<tr>
<td>Structural sugars</td>
<td>35.5</td>
<td>wt.% daf</td>
</tr>
<tr>
<td>Moisture</td>
<td>69.7</td>
<td>wt.% wb</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>71.0</td>
<td>wt.% db</td>
</tr>
<tr>
<td>Ash</td>
<td>2.6</td>
<td>wt.% db</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>26.4</td>
<td>wt.% db</td>
</tr>
<tr>
<td>C</td>
<td>54.2</td>
<td>wt.% db</td>
</tr>
<tr>
<td>H</td>
<td>5.9</td>
<td>wt.% db</td>
</tr>
<tr>
<td>N</td>
<td>1.0</td>
<td>wt.% db</td>
</tr>
<tr>
<td>S</td>
<td>0.2</td>
<td>wt.% db</td>
</tr>
<tr>
<td>O*</td>
<td>36.1</td>
<td>wt.% db</td>
</tr>
<tr>
<td>Slurry pH</td>
<td>5</td>
<td>-</td>
</tr>
</tbody>
</table>
Hydrothermal Liquefaction of LRS

Micro-reactors test bench:
- Tubular batch reactor, OD 3/4”
- Fluidized sand bath
- Fast water bath cooling

HTL reaction conditions:
- Temperature = 350° C
- Residence time = 10 min
- Lignin to water ratio = 10 wt.%
**LRS-HTL aqueous phase characterization**

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td>9.73 ± 0.780</td>
<td>g/l</td>
</tr>
<tr>
<td>Water content KF Titration</td>
<td>97.7 ± 1.09</td>
<td>wt.%</td>
</tr>
<tr>
<td>ICP – Inorganic elements*</td>
<td>0.114</td>
<td>wt.%</td>
</tr>
<tr>
<td>pH</td>
<td>4.27</td>
<td>-</td>
</tr>
</tbody>
</table>

*Na, K, Ca, Fe, Al, Mg, Zn

- **Total detected organics** → **1.93 wt.%** → **GC-MS, HPLC**
- **Organic mass balance closure** → **83-86 %** → **KF, TOC**
  - **Acids** (34 wt.%) and **Alcohols** (30 wt.%) → **HPLC**
  - **Phenolics** (20 wt.%) and **Carbonyls** (3.0 wt.%) → **GC-MS**
Liquid-Liquid Extraction HTL integration

- Liquid-Liquid Extraction (LLE) → Selective separation of phenolics compounds
- Potential valorization pathways:
  - Biocrude yield enhancement for **Fuel** production
  - Precursors for **Chemicals and Bioproducts**
## Solvent selection

<table>
<thead>
<tr>
<th>ID</th>
<th>Name</th>
<th>DH_vap [kJ mol⁻¹]</th>
<th>T_boil [°C]</th>
<th>Flash Point [°C]</th>
<th>Solubility in H₂O [g/l]</th>
<th>Price* [$ kg⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEE</td>
<td>Diethyl ether</td>
<td>28</td>
<td>34.5</td>
<td>-45</td>
<td>60.5</td>
<td>2.0</td>
</tr>
<tr>
<td>EtAc</td>
<td>Ethyl Acetate</td>
<td>33</td>
<td>77</td>
<td>-4</td>
<td>83</td>
<td>0.8</td>
</tr>
<tr>
<td>BuAc</td>
<td>Butyl Acetate</td>
<td>41</td>
<td>126</td>
<td>22</td>
<td>6.8</td>
<td>1.7</td>
</tr>
<tr>
<td>MIBK</td>
<td>Methyl Isobutyl ketone</td>
<td>40.5</td>
<td>117</td>
<td>13</td>
<td>19.1</td>
<td>1.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ID</th>
<th>Safety score</th>
<th>Healthy score</th>
<th>Env. Score</th>
<th>Ranking</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEE</td>
<td>10</td>
<td>3</td>
<td>7</td>
<td>Highly Hazardous</td>
</tr>
<tr>
<td>EtAc</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>Recommended</td>
</tr>
<tr>
<td>BuAc</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>Recommended</td>
</tr>
<tr>
<td>MIBK</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>Recommended</td>
</tr>
</tbody>
</table>

*Updated using producer price index to adjust values

Lab scale solvents screening tests

Experimental conditions
- Constant AP feed pH
- Temperature 25°C
- Extraction time 5 min
- Phase separation after 5 min of centrifugation
- Solvent to AP ratio = 1

Analytical methods
- AP feed: GC-MS and HPLC
- Extract: GC-MS
- Raffinate: HPLC
Liquid-Liquid Extraction: Extract recovery

Fraction Extracted \( F_i \) → \( F_i = \frac{m_{i,org}}{m_{i,feed}} \)

- Alcohols
- Acids
- Phenol
- Other Carbonyls
- Methoxyphenols
- Methoxycatechols
- Cyclopentenones
- Catechols

Fraction extracted [wt.%]
Liquid-Liquid Extraction: $K_d$ and Selectivity

**Distribution ratio**

- $K_{d,i} = \frac{c_{\text{extr},i}}{c_{\text{raff},i}}$

**Selectivity**

- $\alpha_{P,A} = \frac{K_{d,P}}{K_{d,A}}$

**Highest phenolics $K_d$ and selectivity compared to acids and alcohols with Ethyl acetate and Butyl acetate**
Liquid-Liquid Extraction Carbon Balance

- Biocrude, C = 52 wt.%
- Aqueous phase, C = 12 wt.%
- Extract C, = 3 wt.%
- Raffinate, C = 9 wt.%
- Solids, C = 16 wt.%
- CO₂, C = 3 wt.%
- Losses, C = 17 wt.%

HTL of LRS

- 83% phenolics
- 16% acids

Butyl Acetate extraction

LLE

- 13% phenolics
- 46% acids
- 41% alcohols
LLE integration for biocrude enhancement

HTL → AP → LLE → Extract → Biocrude → Fuel

Overall Process Yield Recovery

<table>
<thead>
<tr>
<th>Yield on feed [wt. %]</th>
<th>DEE</th>
<th>EtAc*</th>
<th>BuAc</th>
<th>MIBK</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- About 8% of increment in **Biocrude yield**
- No differences in extract yields changing the solvent
- DEE and MIBK extracts higher fractions of acids

*estimated acetic, propionic acids and methanol content from BuAc data
**Lignocellulosic Ethanol Biorefinery**

- Estimated lignin amount produced in EU: from **49 kTA (2017)** to **4340 kTA (2030)**

* Data estimated from ethanol data: C. Chudziak, G. Alberts, A. Bauen, Ramp up of lignocellulosic ethanol in Europe to 2030 Final Report, 2017, E4tech

<table>
<thead>
<tr>
<th>Compound</th>
<th>Kd</th>
<th>Fraction extracted [wt.%]</th>
<th>Yield on feed * [wt.%]</th>
<th>Production 2017 [kTA]</th>
<th>Production 2030 [kTA]</th>
<th>Market size [kTA]</th>
<th>Price [$ kg⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Benzenediol</td>
<td>2.5</td>
<td>71%</td>
<td>0.02%</td>
<td>0.01</td>
<td>0.9</td>
<td>44a</td>
<td>4.0b</td>
</tr>
<tr>
<td>1,2-Benzenediol, 3-methoxy-</td>
<td>2.3</td>
<td>64%</td>
<td>0.05%</td>
<td>0.02</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Phenol, 2,6-dimethoxy-</td>
<td>3.6</td>
<td>78%</td>
<td>0.06%</td>
<td>0.03</td>
<td>2.4</td>
<td>40c</td>
<td>2.0c</td>
</tr>
<tr>
<td>Phenol, 2-methoxy-</td>
<td>1.5</td>
<td>61%</td>
<td>0.03%</td>
<td>0.01</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>2.2</td>
<td>69%</td>
<td>0.05%</td>
<td>0.03</td>
<td>2.4</td>
<td>11400b</td>
<td>1.1b</td>
</tr>
</tbody>
</table>

* Estimation of compound purification efficiency of 10%

a https://www.gep.com/mind/blog/catechol-faces-supply-crunch-while-prices-rise


Conclusions

➢ AP from LRS-HTL still contains 2-3 wt.% of organic matters
  • 12 wt.% of C trapped in AP

➢ Liquid-liquid extraction (LLE) was evaluated as possible pathway for selective organics recovery

➢ DEE, EtAc, BuAc and MIBK were tested as extraction solvent
  • EtAc and BuAc → highest selectivity for phenolics extraction
  • 3 wt.% of C recovered in extract

➢ LLE-Integration for biocrude yield enhancement
  • Potential biocrude yield increment of 8 %

➢ LLE-Integration for bio-based chemicals precursors
  • Targeted molecules: 1,2 benzenediol, 1,4-Benzenediol, 2-methoxy-, Phenol, 2,6-dimethoxy-, Phenol, 2-methoxy-.
Thanks for the attention!

**Stefano Dell’Orco** ¹,², Edoardo Miliotti ², Nolan Wilson ³, Andrea Maria Rizzo ², Kimberly A. Magrini ³ and David Chiaramonti ¹,²

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