Recycling of Dilute Deacetylation Black Liquor to Enable Efficient Recovery and Reuse of Spent Chemicals and Biomass Pretreatment Waste

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Background

Deacetylation and Mechanical Refining Process (DMR)

*EH of dilute acid pretreated solids severely inhibited above 17%
Motivation of Black Liquor Recycling

• Recycle of black liquor needed:
  o Recover pretreatment chemicals
    – Key to success!
  o Reduce water/energy/chemical usage
  o Valorize value-added components from biomass
    – Acetate, carbohydrate
    – Lignin and aromatics
    – Potentially potassium and phosphorous

• Current deacetylation is conducted at 8-10% solids
  – Titers are too dilute to be economically valorized
  – Direct evaporation of the black liquor is very energy intensive and may lead to undesired condensation and degradation of valuable chemicals!
Counter-Current Reverse Batchwise Black Liquor Recycling

Positive outcomes
- Lower water/chemical usages
- Higher concentration streams

Possible negative impacts
- Black liquor gets too viscous
- Reduced deacetylation effect
- Inhibitors may accumulate in solids that will end up in fermentation

<table>
<thead>
<tr>
<th>Number of Recycles</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass Loaded (kg)</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Dry Biomass (kg)</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>NaOH (kg)</td>
<td>0.165</td>
<td>0.165</td>
<td>0.165</td>
<td>0.165</td>
<td>0.165</td>
<td>0.165</td>
</tr>
<tr>
<td>Initial Water Added (kg)</td>
<td>29.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Makeup Water Added in Black Liquor (kg)</td>
<td>-</td>
<td>6.3</td>
<td>6</td>
<td>7.1</td>
<td>5.1</td>
<td>5.6</td>
</tr>
<tr>
<td>Initial Wash Water (kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Makeup Wash Water (kg)</td>
<td>-</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>-</td>
</tr>
</tbody>
</table>

MWW – Make-up Wash Water
MWL - Makeup White Liquor (NaOH)
WBL - Weak Black Liquor
Solids Accumulation in Black Liquor and Wash Liquor

Total solids and soluble solids in the recycled black liquors

Total soluble solids in the wash liquors
Accumulation of Inorganics and Spent Sodium in Black Liquor

\[ y = 0.3579x + 0.396 \]
\[ R^2 = 0.9844 \]

\[ y = 1.6349x + 2.0747 \]
\[ R^2 = 0.9799 \]

Concentration (g/L) vs. Number of Recycles

- Calcium (g/L)
- Potassium (g/L)
- Sodium (g/L)

pH vs. Number of Recycles
Lignin and acetate removal is not affected by black liquor recycling and the number of recycles.

Xylan dissolution is reduced possibly due to adsorption onto solids or oligomer solubility limitations.
Batch 2-6 (where washing is available) show a reversed trend between sugar yield and lignin concentration.

Batch 1 does not have washing and do not follow the trend.

Sugar yield is lower compared to previous study due to refining issues (more to read in publication).

### Enzymatic Hydrolysis

**Graph:**

- **X-axis:** Number of Recycles
- **Y-axis (left):** Sugar yield (%)
- **Y-axis (right):** Lignin in liquor phase surrounding DMR biomass slurry prior to EH (g/L)

**Legend:**

- Blue line: glucose yield (%)
- Red line: xylose yield (%)
- Green line: Lignin (g/L)

**Note:**

With wash
Ethanol Fermentation

- Fermentation is performed using *rZymomonas*
- Final ethanol titer approximately 60g/L
Key properties of black liquor for conventional Kraft recovery process (combustion to produce energy)

- Viscosity and boiling point rise (BPR)
- Normally combusted at 65% solids

Black liquor concentrated to 65% solids

- Viscosity at room temperature - 2000 cP
- Viscosity at 100°C – 154 cP

Compared to 65% Kraft black liquor in literature

- Viscosity at 100°C – approximately 100 cP
## Techno Economic Analysis

With black liquor recycling, we can reduce water usage by ~50% and energy usage by ~75%, thus lowering MESP by 4 to 15 cents per gallon.

<table>
<thead>
<tr>
<th></th>
<th>Without Recycle</th>
<th>With Recycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deacetylation (total solids %)</td>
<td>10% 30% 30%</td>
<td>10%</td>
</tr>
<tr>
<td>Water for deacetylation (kg/hr)</td>
<td>666,667 166,667</td>
<td>166,667</td>
</tr>
<tr>
<td>Wash water after deacetylation (kg/hr)</td>
<td>0 563,117 0</td>
<td>67,620</td>
</tr>
<tr>
<td>Steam for A200 (kg/hr)</td>
<td>58,764 17,266 17,266</td>
<td>14,870</td>
</tr>
<tr>
<td>Total water used for A200 (kg/hr)</td>
<td>728,107 748,949 358,054</td>
<td>404,178</td>
</tr>
<tr>
<td>MESP ($/gal)</td>
<td>$2.32 $2.27 $2.21</td>
<td>$2.17</td>
</tr>
</tbody>
</table>
Valorizing Black Liquor (joint effort with Greg Beckham’s group at NREL)

- Converting p-coumaric acid and ferulic acid in the black liquor to muconic acid (Lignin Biological Funneling process)

- By recycling black liquor, we could achieve approximately 6g/L p-coumaric acid and 1.5 g/L ferulic acid after 6 recycles
Microbial Electrochemical Technology to Recover Pretreatment Chemicals, Water and Lignin (Joint work with Princeton University)

**Challenges:**
- DMR black liquor
  - Too dilute
  - Valuable and underutilized lignin, organic acids and sodium
- Conventional Kraft process
  - Expensive recovery boiler/lime kiln
  - Burns lignin and other organics
  - GHG, air pollution and LCA issues

**Solutions:**
- MET degrades low conc. waste organics
  - Chemical energy -> Electrical potential
  - Salt migration and recovery
- MET precipitates lignin with no added acids

**Results:**
- Lignin and salt recoveries of $\sim61.2 \pm 2.7\%$ and $92.2 \pm 1.6\%$, respectively.
Near theoretical yields of hydrocarbons were produced from lignin model compounds. Products mostly alkyl-dicyclohexanes (30%) from lignin in DMR Black Liquor. They are high energy and high density.

**Challenges:**
- Lignin’s intrinsic heterogeneous robust structure
  - Upgrade/Recovery to single product is very difficult
  - Condensation/Repolymerization
- HDO with acid combined metal as bifunctional catalytic system
  - Most Brønsted acids: less selective
  - Most Lewis acids: water sensitive

**Solutions:**
- Super Lewis acid- Metal Triflates
  - Widely used in organic synthesis
  - Water tolerant and thermal stable

**Results:**
- Hydrocarbon yields from DMR lignin in HDO conversion under different conditions. Reaction conditions: lignin (50 mg), n-octane (1 mL), T=250 °C, t=4 h, P Hydrogen =4 MPa, in 1 mL n-octane containing 10 wt % water as solvent.

*Wang, Yang and Tucker et al., ChemSusChem, 2018, 11(1)*
Future work – from batch to continuous reactor

Continuous Counter Current Inclined Shaftless Screw Reactor
• Xiaowen Chen
Email: Xiaowen.chen@nrel.gov
Thank you

www.nrel.gov

NREL/PR-5100-74639