Ethanol Production from the Mixture of Hemicellulose Pre-hydrolysate and Paper Sludge

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Current Kraft pulping process

Black Liquor: 80% of hemicelluloses and lignin
Heating Value: Hemicellulose (13.6 MJ/kg) Lignin (27 MJ/kg).

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Proposed Kraft pulping process

Wood Chips → Pre-extraction → Hemicellulose → Ethanol → Digester → Pulp

Black Liquor → Furnace

White Liquor

Steam
2. Pre-extraction Process

Liquor/wood = 5.8 / 1, 170 °C
The profile of weight, hemicellulose and cellulose loss versus extraction time

Cellulose = Glucose \times \left( \frac{162}{180} \right) - \text{Mannose} \times \left( \frac{162}{180} \right)

Hemicellulose = (Arabinose + Xylose) \times \left( \frac{132}{150} \right) + (Galactose + Glucose + Mannose) \times \left( \frac{162}{180} \right) - \text{Cellulose}
Composition of pre-hydrolysate

Sugars Concentration (g/L)

- Glu, 0.4
- Xyl, 1.1
- Gal, 0.7
- Ara, 1.4
- Man, 9.1

Other Compounds (g/L)

- Acetic acid: 0.8
- Acetyl group: 0.3
- Levulinic acid: 0.1
- HMF: 0.2
- Furfural: 0.4
Three stage pre-extraction process

First Stage
Pre-hydrolysate I

Second Stage
Pre-hydrolysate II

Third Stage
Pre-hydrolysate III

Extracted Wood Chip

Screw Reactor

Fresh Wood Chip

Pre-hydrolysate

Water

Make-up Water

Fresh Wood Chip

Extracted Wood Chip

Extracted Wood Chip

Fresh Wood Chip

Extracted Wood Chip

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Composition of pre-hydrolysate III after three-stage pre-extraction

Sugars Concentration (g/L)

- Glu2, 3.0
- Xyl, 1.1
- Xyl2, 2.7
- Gal, 0.7
- Gal2, 3.9
- Ara, 1.4
- Man2, 15.5
- Man, 0.6
- Ara2, 0.1

Other Compounds (g/L)

- Acetic acid, 2.6
- Acetyl group, 0.5
- Levulinic acid, 0.2
- HMF, 1.0
- Furfural, 1.4

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3. De-toxification of Pre-hydrolysate

Average composition of Woody biomass and main derived hydrolysis products

De-toxification test

Overliming: Pre-hydrolysate III was added CaO to pH=10.0, 25 °C or 60 °C for half hour, centrifuge, then adjust supernatant pH to 5.0 by adding 70% sulfuric acid.

UV-Vis Absorbance Changed During De-toxification Test
Composition change after de-toxification test

<table>
<thead>
<tr>
<th>Component</th>
<th>untreated</th>
<th>25 °C</th>
<th>60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Sugar</td>
<td>90</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>Mannose + Glucose</td>
<td>80</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>100</td>
<td>90</td>
<td>80</td>
</tr>
<tr>
<td>Levulinic Acid</td>
<td>80</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>HMF</td>
<td>70</td>
<td>60</td>
<td>50</td>
</tr>
<tr>
<td>Furfural</td>
<td>60</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>Soluble Phenolic</td>
<td>100</td>
<td>90</td>
<td>80</td>
</tr>
</tbody>
</table>
4. Separate hydrolysis and fermentation (SHF) of pre-hydrolysate

Enzyme Loading: 25mg protein enzymes / g-mannose oligomer

50 °C, pH=4.8
Fermentation of pre-hydrolysate III by *Saccharomyces cerevisiae*

**SHF condition**

- **Enzymatic Hydrolysis**: 25mg protein Pectinase / g-mannose oligomer and 50°C.
- **Fermentation Conditions**: 32°C, *Saccharomyces cerevisiae D5A*
5. Increasing the ethanol concentration

a. concentrated pre-hydrolysate

**Laboratory Scale:** Rotary evaporator.
- Total sugar concentration increased.
- Furfural and acetic acid are removed up to 90%.

**Industry Scale:** Steam-Stripping or Flash Tank and Multiple-effect Evaporator (Kraft mill).

<table>
<thead>
<tr>
<th>Total Sugars (g/L)</th>
<th>Glu+Mann (g/L)</th>
<th>Ethanol Conc. (g/L)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>246</td>
<td>146</td>
<td>III</td>
</tr>
<tr>
<td>94</td>
<td>26</td>
<td>55</td>
<td>IV (2.2 ×)</td>
</tr>
<tr>
<td>11</td>
<td>20</td>
<td>44</td>
<td>V (5.9 ×)</td>
</tr>
<tr>
<td>85</td>
<td>76</td>
<td>63</td>
<td></td>
</tr>
</tbody>
</table>

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Kraft Paper Mill Sludges as a Feedstock

- 4.1 to 5 million tons sludge per year in U.S.
  - Incineration (greenhouse gas emission, low energy efficiency)
  - Landfill (greenhouse gas emission, limited land availability)

- Low/ Negative Cost (0 to 50$ per ton disposal cost)

- High Carbohydrate and Low Lignin Content (Kraft pulping process removes most of lignin and hemicellulose)

- Easily Digested by Cellulase (No need for expensive pretreatment)

b. mixing pre-hydrolysate with paper sludge
Composition of various sludges

Primary Sludge is from Boise paper mill, Jackson, AL.


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Fermentation of pre-hydrolysate III with paper sludge

<table>
<thead>
<tr>
<th></th>
<th>Maximum Ethanol Yield (%)</th>
<th>Maximum Ethanol Conc. (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-hydrolysate III with paper sludge</td>
<td>71.5 (120h)</td>
<td>31.5</td>
</tr>
<tr>
<td>Pre-hydrolysate only</td>
<td>82.6 (48h)</td>
<td>10.3</td>
</tr>
<tr>
<td>Paper sludge only</td>
<td>73.4 (120h)</td>
<td>27.8</td>
</tr>
</tbody>
</table>

Enzyme Loading: Cellulase (15FPU/g glucan) + Cellobiase (30CBU/g glucan) + 25mg protein Pectinase/ g-mannose oligomer
Solid Loading: 15 g total solid /100ml work volume
SSF Conditions: 36°C, *Saccharomyces cerevisiae D5A*
Fermentation of pre-hydrolysate with de-ashed sludge

<table>
<thead>
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<th>Maximum Ethanol Yield (%)</th>
<th>Maximum Ethanol Conc. (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-hydrolysate III with de-ashed sludge</td>
<td>71.3 (120h)</td>
<td>40.1</td>
</tr>
<tr>
<td>De-ashed sludge only</td>
<td>75.2 (120h)</td>
<td>35.0</td>
</tr>
</tbody>
</table>

Enzyme Loading: Cellulase (15FPU/g glucan) + Cellobiase (30CBU/g glucan) + 25mg protein Pectinase/ g-mannose oligomer
Solid Loading: 15 g total solid /100ml work volume
SSF Conditions: 36°C, Saccharomyces cerevisiae D5A
Conclusion

• Combining pre-hydrolysate with sludge can more than double ethanol production

• Hemicellulose pre-hydrolysate can be converted to ethanol through de-toxification, enzymatic hydrolysis and fermentation processes.

• The fermentation of concentrated pre-hydrolysate can increase the ethanol concentration.

• The fermentation performance of the mixture of pre-hydrolysate with sludges has high efficiency and more practical.
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