Levulinic Acid Production From Bagasse

CPD-3271
Bagasse (lignocellulose)

1. Cellulose
   - Hexose
     - HMF
     - Levulinic Acid
2. Hemicellulose
   - Pentose
     - Furfural
3. Lignin
   - Tar
     - Asphalt-like Substance
Mechanism via Pentoses

Scheme 1. Linear\textsuperscript{46} and tentative cyclic pathway of 2-furaldehyde formation from D-xylose, and from D-fructose and D-glucose via a retro-aldol formaldehyde split-off\textsuperscript{49}.
Mechanism via Hexoses

Scheme 2. Linear$^{53}$ and cyclic$^{47}$ pathway of HMF formation from D-glucose and D-fructose, and rehydration of HMF to levulinic acid and formic acid.
Tar Formation

- Glucose $\rightarrow$ Aromatics at longer residence time
- HMF + HMF or HMF + Furfural
- 2\textsuperscript{nd} order reactions
- Process has to minimize tar formation
Preventing Tar Formation

• Short residence time for glucose
• Low concentrations of HMF and furfural
Process Types

- Reactive Extruder
- Two Stage Reactor
- Reactive extruder + CSTR
Reactive extruder

- One Reactor
- Twin Screw Extruder
- Plurality of Temperature zones
- Yield ≥ 70%
- Temp. range: 120-150°C
- Process time 80-100 sec.
- Uses Starch
Two Stage Reactors

- PFR and CSTR
- Yield: minimal 70 %
- Temp. range: 205-220°C
- Process time: several minutes
- Uses all kinds of biomass
Process chosen: Reactive extruder with CSTR

- Reactive Extruder + CSTR
- Yield: minimal 70%
- Temp. range: 195-220°C
- Process time: 25-30 minutes
Process chosen: Reactive extruder with CSTR

• Advantages:
  – Tar production minimized
  – Pump and reactor 1 unit

• Disadvantages:
  – Use of patents, expensive
Bagasse
- 1000 kton wet bagasse needed
- harvesting season 4-6 months
→ At least 500 kton has to be stored

Losses, due to fermentation

Can reach 20-30% in the first three months until the temperature is high enough to stop the micro-organisms.
Avoid loss

1. Increase the moisture to 50%
2. Decrease moisture to 25 %
3. Add chemicals
Drying of bagasse

1. Mechanically with hot flue gases
2. By producing pellets/briquettes or by producing large bales
Bulky stored bagasse with 50% wetness
Bulky stored bagasse with 50% wetness

• Reaches a temperature of 60-65 °C in 6-7 days.
• Until then approximately 10% fibre is lost and 10% water evaporated → still 50% wetness
• With $T=60-65$ °C fermentation continues with 1% per month only
Assumptions

• After elution in the sugar cane plant with water of 90°C, the bagasse pile easily reaches a temperature of 50°C. Losses due to fermentation will be small.

• Temperature of bagasse will rise initially and drop some later. The temperature (50°C) and wetness (50%) are taken constant throughout the year.
Plant Capacity

- Production of 100 kton LA/year
- 8000 hours/year running, continuous
- Running time = 15 years
- Wet bagasse is feedstock
- Furfural, formic acid are by-products
- Gypsum and tar are wastes
Levulinic acid
100,000 t/a (1.00)

Reaction
Section 1
(reactive extruder)
21 Bar
215°C

Reaction
Section 2
(CSTR)
16 Bar
195°C

Make up
Sulfuric acid
600 t/a (0.006)

Bagasse (wet)
912,000 t/a (9.12)

HP Steam generation

HP Steam
182,000 t/a (1.82)

Gypsum 7000
7000 t/a (0.07)

Power plant wastes
241,000 t/a (2.50)

LA purifier
(Reactor and centrifuge)

Asphalt processing plant

Sulfuric acid recovery
104,000 t/a (1.04)

Lignin/ asphalt centrifuge

Acid catalyst decanter

Levulinic acid
100,000 t/a (1.00)

Formic acid
Destillation columns
0.2 – 3 bar
54 – 135 °C

Formic acid
40,000 t/a (0.40)

Waste Water
460,000 t/a (4.6)

Furfural
65,000 t/a (0.65)

Lime
400 t/a (0.004)

Water 182,000 t/a (1.82)

Asphalt, 241,000 t/a (2.50)
Reactive Extruder

- T = 210°C, P = 21 bar
- Residence time = 14 s
- Acid concentration ± 8.5 %$_{\text{mass}}$
CSTR

- $T = 195^\circ C$, $P = 16$ bar
- Residence time $= 1800$ s
- Acid concentration $\pm 8.5\%_{\text{mass}}$
• T = 195°C, P = 16 bar
• Residence time = 239 s
• Separation of LA and sulphuric acid
• ±90% pure LA
Decanter

- Sulfuric acid contains ±10% water
- Sulfuric acid and LA separate to 90% pure
- In decanter LA and Sulfuric acid separate
- LA is 90% pure with 9% sulfuric acid and 1% water (besides other impurities)
Gypsum reactor

- $T = 195^\circ\text{C}$, $P = 16$ bar
- Lime addition 400 t/a
Streams (from bottom of CSTR)

- LA: 100 kton/a
- Gypsum: 7 kton/a
- Sulfuric acid recycle 104 kton/a
- Asphalitic substance 241 kton/a, processed in powerplant (wastes such as CO\textsubscript{x}, Ash, etc.)
Separation of Furfural

- Furfural separated from Formic Acid/Water
- Furfural and Formic Acid form azeotrope with Water
- Furfural leaves at the top, Formic Acid/Water leaves at the bottom
- P = 3 bar, T = 120°C
T-x-y diagram for furfural and water at 3 bar.

Thermodynamic model used: Wilson – Hayden O’Connell
T-x-y diagram for water and formic acid at 3 bar

Thermodynamic model used: Wilson – Hayden O’Connell
T-x-y diagram for water and formic acid at 0.2 bar

Thermodynamic model used: Wilson – Hayden O’Connell
Separation of Formic Acid

Formic Acid and Water form an azeotropic mixture

Possible separation methods:
• azeotropic distillation
• extractive distillation
• pressure shift distillation
Pressure shift distillation

First column:
• Water leaves the top, bottom stream enters second column
• P = 3 bar, T = 125°C

Second column:
• Formic Acid leaves the top, bottom stream is recycled to first column
• P = 0.2 bar, T = 147°C
Wastes

- Waste water ($T = 25^\circ C$): disposed into water outside plant
- Gypsum: could be sold, if not sold it has to be disposed of
- Ashes from tar: has to be disposed of
<table>
<thead>
<tr>
<th>Cost Type</th>
<th>k€/a</th>
<th>%</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Direct</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Variable</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Raw materials</td>
<td>13,682</td>
<td>96%</td>
<td>36%</td>
</tr>
<tr>
<td>2. Miscellaneous materials</td>
<td>552</td>
<td>4%</td>
<td>1%</td>
</tr>
<tr>
<td>3. Utilities</td>
<td>0</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>4. Shipping &amp; packaging</td>
<td></td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td><strong>Sub-total</strong></td>
<td>14,234</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>Fixed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst</td>
<td>34</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>5. Maintenance</td>
<td>5,516</td>
<td>29%</td>
<td>14%</td>
</tr>
<tr>
<td>6. Operating labour</td>
<td>2,350</td>
<td>12%</td>
<td>6%</td>
</tr>
<tr>
<td>7. Laboratory</td>
<td>470</td>
<td>2%</td>
<td>1%</td>
</tr>
<tr>
<td>8. Supervision</td>
<td>470</td>
<td>2%</td>
<td>1%</td>
</tr>
<tr>
<td>9. Plant overhead</td>
<td>1,175</td>
<td>6%</td>
<td>3%</td>
</tr>
<tr>
<td>10. Capital charges</td>
<td>5,516</td>
<td>29%</td>
<td>14%</td>
</tr>
<tr>
<td>11. Insurance</td>
<td>552</td>
<td>3%</td>
<td>1%</td>
</tr>
<tr>
<td>12. Local taxes</td>
<td>1,103</td>
<td>6%</td>
<td>3%</td>
</tr>
<tr>
<td>13. Royalties</td>
<td>1,812</td>
<td>10%</td>
<td>5%</td>
</tr>
<tr>
<td><strong>Sub-total</strong></td>
<td>18,997</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>33,231</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td><strong>Other</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14. Sales expenses</td>
<td></td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>15. General overhead</td>
<td>4,985</td>
<td>13%</td>
<td>(A)+(B): k€ 33.23 15%</td>
</tr>
<tr>
<td>16. Research &amp; Dev.</td>
<td></td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td><strong>Total Production Costs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annual [k€/a]</td>
<td>38,216</td>
<td>100%</td>
<td>(A)+(B)+(C)</td>
</tr>
<tr>
<td>Per ton LA [€/t]</td>
<td>382.16</td>
<td>100000 t/a</td>
<td></td>
</tr>
</tbody>
</table>
## GROSS INCOME, NET CASH FLOW, ECONOMIC CRITERIA

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Value</th>
<th>k€/a</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gross Income</td>
<td></td>
<td></td>
<td>66,391</td>
<td></td>
</tr>
<tr>
<td>Production Costs</td>
<td></td>
<td></td>
<td>38,216</td>
<td></td>
</tr>
<tr>
<td><strong>Net Cash Flow, Before Tax</strong></td>
<td></td>
<td></td>
<td>28,175</td>
<td>= (A)</td>
</tr>
<tr>
<td>Economical Plant Life &amp; Depreciation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Total Investment</td>
<td>k€</td>
<td>61,977</td>
<td>= (B)</td>
<td></td>
</tr>
<tr>
<td>- Econ. Plant Life, years:</td>
<td>Years</td>
<td>10</td>
<td></td>
<td>Incl. 2 yrs Des.&amp; Con.</td>
</tr>
<tr>
<td>- Annual Depreciation over 10 years</td>
<td></td>
<td></td>
<td>6,198</td>
<td></td>
</tr>
<tr>
<td><strong>Net Cash Flow, After Depreciation</strong></td>
<td></td>
<td></td>
<td>21,977</td>
<td></td>
</tr>
<tr>
<td>Pay-Out Time, Before Tax</td>
<td>Years</td>
<td>2.2</td>
<td>= (B) / (A)</td>
<td></td>
</tr>
<tr>
<td>Rate of Return, Before Tax</td>
<td>%</td>
<td>45.5%</td>
<td>= (A) / (B)</td>
<td>DCFRoR, IRR, EP</td>
</tr>
<tr>
<td>DCF Rate of Return, Before Tax</td>
<td>%</td>
<td>18.6%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Net Present Value, Before Tax</td>
<td>%</td>
<td>7.0%</td>
<td>171</td>
<td>From DCF Calc.</td>
</tr>
<tr>
<td>Net Future Value, Before Tax</td>
<td></td>
<td></td>
<td>336</td>
<td>Interest = 0</td>
</tr>
</tbody>
</table>
Profits without formic acid sales
Half Year Production
(fixed costs * 1.5)
Conclusions

• Process profitable because of furfural/formic acid sales
• Plant most profitable at full year production
• Sufficient steam and power generation by burning of tar (plant is self-sufficient)
• Wet bagasse can be used, no need for drying
• Wet bagasse can be stored easily
Conclusions

• Furfural and formic acid can be produced with a purity of 98%

• The production of 100 kton/yr LA from bagasse is achieved
Recommendations

• Sulfuric acid removal from LA has to be sought out in more detail
• Other technologies possible, like chromatographic removal of sulfuric acid
• Better knowledge of kinetics of tar formation will improve reactor design
• Tar processing plant can be more accurate
• Impact of formic acid sales (on world market) can be more accurate
• Consequences of great increase of LA on market has to be investigated