PRETREATMENT METHODS FOR BIOETHANOL PRODUCTION

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ETHANOL PRODUCTION

- Ethanol can be produced from lignocellulose feedstocks
  - Agricultural and forest residues, dedicated crops

- Four steps of ethanol production

  1) Pretreating
  2) Hydrolyzing
  3) Fermenting
  4) Separation

Pretreatment overcomes cell wall recalcitrance
Pretreatment process is the most costly process

M. Balat et al. (2008)
What is Pretreatment?
Types of Pretreatment

- 4 types of pretreatment methods

- Physical
- Chemical
- Physiochemical
- Biological
PHYSICAL PRETREATMENT METHOD

- Chipping, milling, grinding
  - Increases surface area
- High power consumption
  - Could surpass theoretical biomass energy content

CHEMICAL PRETREATMENT METHOD

- Alkaline pretreatment
  - Ie. NaOH
- Dilute acid treatment
  - Cannot be too strong or too weak
- Organic/aqueous-organic solvent mixture
  - Organosolv processes
PHYSIOCHEMICAL PRETREATMENT METHOD

- **Steam pretreatment (steam explosion)**
  - Can be improved using acid catalyst
  - Closest to commercialization

- **Liquid hot-water (LHW)**
  - Lower temperature than steam pretreatment
  - Can also use acid catalyst
  - Causes downstream processes to be more energy demanding

- **Wet oxidation pretreatment**
  - Suited for materials with low lignin content

- **Ammonia fibre explosion (AFEX)**
  - Treated with liquid ammonia at moderate temperatures

BIOPHYSICAL PRETREATMENT METHOD

- Applying microorganisms
  - White and soft-rot fungi
- Environmentally friendly
- Energy saving
- Rate is far too low for industrial use
- Some material is lost
- Could be followed by other pretreatment methods

RESEARCH ON PRETREATMENT METHODS

- Pretreatment of soft-wood based lignocellulosic wastes
  - Kim et al. Auburn U
- Various mixtures of ammonia and peroxide
  - Two delignifying treatments that were environmentally benign
- Determined successive treatment yielded the best results
- Improved digestibility 41% -> 71%

Kim et al. (2000)
yorkshiretimbermerchants.co.uk
RESEARCH ON PRETREATMENT METHODS

- Pretreatment of sugar cane bagasse
  - Laser et al. Dartmouth College
- Compared liquid hot water and steam pretreatment
- Optimized process by varying:
  - Temperature, pH, time
- Liquid hot water yielded higher bioethanol conversion
- Results were comparable to convention dilute acid pretreatment

Laser et al. (2002)
vivbizclub.com
RESEARCH ON PRETREATMENT METHODS

- Pretreatment of sunflower stalks
  - Viathanomsat et al.
- Pretreated with steam explosion
- May be useful in Thailand

Viathanomsat et al. 2009

eurotherm.com

transitioncityallotment.blogspot.com
### Wasted Crop Available for Ethanol

Quantities of wasted crop and lignocellulosic biomass potentially available for bioethanol

<table>
<thead>
<tr>
<th></th>
<th>Africa</th>
<th>Asia</th>
<th>Europe</th>
<th>North America</th>
<th>Central America</th>
<th>Oceania</th>
<th>South America</th>
<th>Subtotal</th>
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<tbody>
<tr>
<td><strong>Wasted crop (Tg)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Corn</td>
<td>3.12</td>
<td>9.82</td>
<td>1.57</td>
<td>0.30</td>
<td>1.74</td>
<td>0.01</td>
<td>4.13</td>
<td>20.70</td>
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<tr>
<td>Barley</td>
<td>0.17</td>
<td>1.23</td>
<td>2.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.19</td>
<td>0.04</td>
<td>3.66</td>
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<tr>
<td>Oat</td>
<td>0.004</td>
<td>0.06</td>
<td>0.43</td>
<td>0.01</td>
<td>0.001</td>
<td>0.001</td>
<td>0.05</td>
<td>0.55</td>
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<tr>
<td>Rice</td>
<td>1.08</td>
<td>21.86</td>
<td>0.02</td>
<td>0.96</td>
<td>0.08</td>
<td>0.02</td>
<td>1.41</td>
<td>25.44</td>
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<tr>
<td>Wheat</td>
<td>0.83</td>
<td>10.28</td>
<td>4.09</td>
<td>0.02</td>
<td>0.24</td>
<td>0.82</td>
<td>0.91</td>
<td>17.20</td>
</tr>
<tr>
<td>Sorghum</td>
<td>2.27</td>
<td>0.54</td>
<td>0.004</td>
<td>0.00</td>
<td>0.13</td>
<td>0.001</td>
<td>0.18</td>
<td>3.12</td>
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<tr>
<td>Sugar cane</td>
<td>0.46</td>
<td>1.64</td>
<td>0.00</td>
<td>0.00</td>
<td>0.36</td>
<td>0.00</td>
<td>0.74</td>
<td>3.20</td>
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<tr>
<td>Subtotal</td>
<td>7.94</td>
<td>45.43</td>
<td>8.13</td>
<td>1.30</td>
<td>2.56</td>
<td>1.05</td>
<td>7.45</td>
<td>73.86</td>
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</tbody>
</table>

|                      |        |       |        |               |                |         |               |         |
| **Lignocellulosic biomass (Tg)** |        |       |        |               |                |         |               |         |
| Corn stover          | 0.00   | 33.90 | 28.61  | 133.66        | 0.00           | 0.24    | 7.20          | 203.62  |
| Barley straw         | 0.00   | 1.97  | 44.24  | 9.85          | 0.16           | 1.93    | 0.29          | 58.45   |
| Oat straw            | 0.00   | 0.27  | 6.83   | 2.80          | 0.03           | 0.47    | 0.21          | 10.62   |
| Rice straw           | 20.93  | 667.59| 3.92   | 10.95         | 2.77           | 1.68    | 23.51         | 731.34  |
| Wheat straw          | 5.34   | 145.20| 132.59 | 50.05         | 2.79           | 8.57    | 9.80          | 354.35  |
| Sorghum straw        | 0.00   | 0.00  | 0.35   | 6.97          | 1.16           | 0.32    | 1.52          | 10.32   |
| Bagasse              | 11.73  | 74.88 | 0.01   | 4.62          | 19.23          | 6.49    | 63.77         | 180.73  |
| Subtotal             | 38.00  | 923.82| 216.56 | 218.90        | 26.14          | 19.70   | 106.30        | 1549.42 |

COST COMPARISONS

<table>
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<tr>
<th>Pretreatment</th>
<th>Pretreatment</th>
<th>Total fixed capital, $MM</th>
<th>Ethanol production, MM gal/year</th>
<th>Total fixed capital, $/gal annual capacity</th>
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<tbody>
<tr>
<td>direct capital</td>
<td>breakdown</td>
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<tr>
<td>corn stover</td>
<td>25.0</td>
<td>64/36</td>
<td>208.6</td>
<td>56.1</td>
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<td>Hot water</td>
<td>4.5</td>
<td>100/0</td>
<td>200.6</td>
<td>44.0</td>
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<td>AFEX</td>
<td>25.7</td>
<td>26/74</td>
<td>211.5</td>
<td>56.8</td>
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<td>ARP</td>
<td>28.3</td>
<td>25/75</td>
<td>210.9</td>
<td>46.3</td>
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<tr>
<td>Lime</td>
<td>22.3</td>
<td>19/18</td>
<td>163.6</td>
<td>48.9</td>
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<tr>
<td>Non-pretreatment</td>
<td>0</td>
<td>–</td>
<td>200.3</td>
<td>9.0</td>
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<tr>
<td>Pretreatment</td>
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<td></td>
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<tr>
<td>Ideal</td>
<td>0</td>
<td>–</td>
<td>162.5</td>
<td>64.7</td>
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</tbody>
</table>

- Corn stover
- Low cost pretreatment processes were counterbalanced by higher cost catalyst recovery

P. Alvira et al. (2010)
CONCLUSIONS

- Pretreatment methods are still being researched and optimized
- Pretreatment methods are usually combined in processes
- Improved pretreatment methods can facilitate the conversion of waste crop to bioethanol
ARE BIOFUELS WORTH IT?

No

- Extremely inefficient land use
- Conversion of Brazilian Amazon to a source of bioethanol

Michel (2012)
ALTERNATIVES?

- Biofuels should be produced from waste plant material
- Improve pretreatment methods