Production of furfural from corn residue through catalytic fast pyrolysis using \( \text{ZnCl}_2 \) in a fluidized bed reactor

2014.02.14

Univ. of Seoul
Dept. of Energy & Environmental System Eng.
Joo-Sik Kim
Paths from Biomass to Bioenergy

- Thermal (or thermochemical) conversion:
  - Direct combustion ⇒ heat
  - Pyrolysis (slow- or fast pyrolysis) ⇒ bio-oil, biochar
  - Gasification (air, O$_2$, H$_2$O) ⇒ syngas

- Biochemical conversion:
  - Alcoholic fermentation ⇒ bioethanol
  - Anaerobic digestion ⇒ biogas

- Physicochemical conversion:
  - Organic oils ⇒ biodiesel
Pyrolysis

Definition: A thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen

**Pyrolysis of biomass**

- **Slow pyrolysis**
  - a.k.a. carbonization
  - used for producing charcoal (or biochar)
- **Fast pyrolysis**
  - high heating rates
  - low retention times in reactors
  - greater liquid, i.e. ‘bio-oil’ yield
  - coproducts
    - biochar
    - combustible gas
# Bio-oil Properties

<table>
<thead>
<tr>
<th></th>
<th>bio-oil</th>
<th>heavy fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>vol. energy density</td>
<td>21</td>
<td>39</td>
</tr>
<tr>
<td>density</td>
<td>1220</td>
<td>963</td>
</tr>
<tr>
<td>viscosity at 50 °C</td>
<td>13</td>
<td>351</td>
</tr>
<tr>
<td>acidity</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>water content</td>
<td>20</td>
<td>0.1</td>
</tr>
<tr>
<td>ash content</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>C</td>
<td>52</td>
<td>86</td>
</tr>
<tr>
<td>H</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>O</td>
<td>40</td>
<td>0.5</td>
</tr>
<tr>
<td>N</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>S</td>
<td>&lt; 0.1</td>
<td>2</td>
</tr>
</tbody>
</table>
Applications of Bio-oil

- Bio-oil applications
  - Extraction
    - Specific compounds
  - Whole fractions, i.e. sugar
  - Fermentation (hybrid processing)
  - Bio-oil
    - Turbine or diesel engine fuel
    - Co-feeding in boilers
    - Gasification
      - Syngas platform
        - Upgrading, refinery co-feed
        - Drop-in biofuels
Bio-oil Upgrading

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Problem</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low pH</td>
<td>Corrosion</td>
<td>Adequate Materials</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Neutralization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydroprocessing</td>
</tr>
<tr>
<td>High viscosity</td>
<td>Handling, pumping</td>
<td>Add water or solvent</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydroprocessing</td>
</tr>
<tr>
<td>Instability</td>
<td>Storage, phase separation, polymerization, viscosity increase</td>
<td>Avoid heat</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Catalytic Stabilization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Add Water or Diluents</td>
</tr>
<tr>
<td>Solids content</td>
<td>Combustion problems, equipment blockage, erosion</td>
<td>Liquid filtration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hot gas filtration</td>
</tr>
<tr>
<td>Alkali metals</td>
<td>Deposition of solids in boilers, engines, and turbines</td>
<td>Biomass pretreatment</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hot gas filtration</td>
</tr>
<tr>
<td>Water content</td>
<td>Complex effect on heating value, viscosity, pH, homogeneity, etc.</td>
<td>Optimization of water content</td>
</tr>
<tr>
<td></td>
<td></td>
<td>according to application</td>
</tr>
</tbody>
</table>

- Physical upgrading
  - Solvent addition
  - Filtration
  - Separation
- Chemical/catalytic upgrading
  - Esterification/Transesterification
  - Zeolite or
    Hydrodeoxygenation (HDO)
Catalytic Upgrading of Bio-oil: Zeolite

- Bio-oil: 100 wt%
- CO, CO₂, H₂O: 50 wt%
- Coke on Cat.: 20-30 wt%
- Hydrocarbons: 15-30 wt%

Zeolite
Catalytic Upgrading of Bio-oil: HDO

- Hydrodeoxygenation (HDO): commercial sulfided CoMo and NiMo and new catalysts like Ru/C and CuNi/δ-Al₂O₃

Pyrolysis oil + H₂ → HDO
Final T: 230-340 °C
P: 290 bar

Oil Phase
dry yield: 47-50 wt.%
Energy yield: 55-68 %
(MJ HDO oil / MJ PO+H₂)

Aqueous Phase
dry yield: 39-14 wt.%

Gas Phase
dry yield: 3-9 wt.%

Produced water
dry yield: 9-19 wt.%

Biomaterials and Biochemicals from Bio-oil

Biomass residues

- Char
  - Biochar
  - Activated carbon
  - Carbon black
  - Meet browning agent
  - Smoke flavors
  - Acid / Road deicers
  - Bioline
  - Slow-release fertilizer
  - Wood preservatives
  - Boiler/engine/gasifier fuel
  - Adhesives

- Water sol. fraction
  - Acid / Road deicers
  - Bioline
  - Slow-release fertilizer
  - Wood preservatives

- Water insol. fraction
  - Hydroxyacetaldehyde (glycolaldehyde)
  - Levoglucosan
  - Phenols (from lignin)
  - Furfural (from xylose)
  - Levulinic acid (from glucose)

- Gas
Chemical Structure of Lignocellulosic Biomass

**Lignin**

**Cellulose**

**Hemicelluloses**

- p-coumaryl alcohol
- coniferyl alcohol
- sinapyl alcohol
Products of Cellulose Pyrolysis

D-glucose

levoglucosenone

cellulose

hydroxymethylfurfural

levoglucosan
Products of Hemicellulose Pyrolysis

- acetic acid
- 1,5-anhydrofuranoses
- arabinoxylan
- 2-furfural
Products of Lignin Pyrolysis
Maximal Contents of Chemicals in Bio-oil (Reported)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Maximal Contents</th>
<th>Market price: 250$/100g</th>
</tr>
</thead>
<tbody>
<tr>
<td>levoglucosan</td>
<td>30.4 wt%</td>
<td></td>
</tr>
<tr>
<td>hydroxyacetaldehyde</td>
<td>15.4</td>
<td></td>
</tr>
<tr>
<td>acetic acid</td>
<td>10.1</td>
<td></td>
</tr>
<tr>
<td>formic acid</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>acetaldehyde</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td>furfuryl alcohol</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>catechol</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>methyl glyoxal</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>ethanol</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>celllobiosan</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>1,6-anhydroglucofuranose</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>furfural</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>formaldehyde</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>phenol</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>propionic acid</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>acetone</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>methylcyclopentene-ol-one</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>methyl formate</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>hydroquinone</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>acetol</td>
<td>1.7</td>
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</tr>
<tr>
<td>angelica lactone</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>syringaldehyde</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>methanol</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>
Levoglucosan

Coordination bonding of cations on cellulose induces homolytic fission of glucose rings

Market applications: glucose, polymers, antibiotics

Biomass-derived Phenolic Resin

Most phenol is produced from petroleum-derived benzene by the cumene process.

Cleavage of the weak β-O-4 ether bonds in lignin yields phenols and derivatives.

Used mainly as adhesives for plywood and oriented strand board (OSB), circuit boards, molded products, and fire proof/retarding materials.
Application of Furfural

Worldwide Furfural Market: 3,000,000 ton/a
Commercial Production of Furfural

- Acid hydrolysis followed by dehydration
- Huge amount of wastewater
- Batch process

### Main Production Sources 

<table>
<thead>
<tr>
<th>Nation</th>
<th>Main source</th>
<th>Furfural and furfural intermediate [MT/year]</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>Corn cobs</td>
<td>200,000</td>
</tr>
<tr>
<td>India</td>
<td>-</td>
<td>10,000</td>
</tr>
<tr>
<td>Thailand</td>
<td>Corn cobs</td>
<td>8,500</td>
</tr>
<tr>
<td>Republica Dominicana</td>
<td>Bagasse</td>
<td>32,000</td>
</tr>
<tr>
<td>Republic of South Africa</td>
<td>Bagasse</td>
<td>20,000</td>
</tr>
<tr>
<td>Spain</td>
<td>Corn cobs</td>
<td>6,000</td>
</tr>
<tr>
<td>Others</td>
<td>Corn cobs/Bagasse</td>
<td>15,000</td>
</tr>
<tr>
<td>Russia</td>
<td>Corn cobs</td>
<td>5,000</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>296,500</strong></td>
</tr>
</tbody>
</table>

### Price Data (Year 2001)

- **2011-2012년 약 $1.5/Kg**

### Production Trends

- **2001 Year Price Chart**
  - 1994: $600
  - 1996: $800
  - 1998: $1,000
  - 2000: $1,200
  - 2002: $1,400
Furfural from Hemicelluloses (ex. Xylan)

Furfural formation by non-catalytic pyrolysis
Characteristics of corncob

Proximate analysis

<table>
<thead>
<tr>
<th>Corncob</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile matter</td>
<td>88.1</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>1.1</td>
</tr>
<tr>
<td>Ash</td>
<td>8</td>
</tr>
<tr>
<td>Moisture</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Ultimate analysis

<table>
<thead>
<tr>
<th>Corncob</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>43.3</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.5</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.9</td>
</tr>
<tr>
<td>Sulfur</td>
<td>-</td>
</tr>
<tr>
<td>Oxygen</td>
<td>50.3</td>
</tr>
</tbody>
</table>

Chemical composition

<table>
<thead>
<tr>
<th>Corncob</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>27.5</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>33.6</td>
</tr>
<tr>
<td>Lignin</td>
<td>19.6</td>
</tr>
</tbody>
</table>

Thermogravimetric analysis

Thermal degradation range

- Cellulose: 240 – 350 °C
- Hemicelluloses: 200 – 260 °C
- Lignin: 280 – 500 °C

Feed size (mm): 0.250-0.425, 0.425-1
Characteristics of corn stover

**Proximate analysis**

<table>
<thead>
<tr>
<th></th>
<th>Corn stover wt %</th>
<th>wt %b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile matter</td>
<td>75.7</td>
<td>82.9</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>12.2</td>
<td>12.9</td>
</tr>
<tr>
<td>Ash</td>
<td>6.7</td>
<td>3.6</td>
</tr>
<tr>
<td>Moisture</td>
<td>5.4</td>
<td>0.6</td>
</tr>
</tbody>
</table>

a: before soaking, b: after soaking

**Ultimate analysis**

<table>
<thead>
<tr>
<th></th>
<th>Corn stover wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>44.3</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.28</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.8</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.23</td>
</tr>
<tr>
<td>Oxygen</td>
<td>41.8</td>
</tr>
</tbody>
</table>

**Chemical composition**

<table>
<thead>
<tr>
<th></th>
<th>Corn stover wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>38.8</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>29.6</td>
</tr>
<tr>
<td>Lignin</td>
<td>22.1</td>
</tr>
</tbody>
</table>

**Thermogravimetric analysis**

**Thermal degradation range**

- Cellulose: 240 – 350 °C
- Hemicelluloses: 200 – 260 °C
- Lignin: 280 – 500 °C
Experimental-Corn stover Pretreatment

Soaking
80 °C, 3hr

Washing

Drying
75 °C, 24hr

Corn stover
0.425-1 mm
400-600 g

Distilled water (~6 L)
Experimental-Fluidized bed Reactor
## Experimental-Reaction conditions (Corncob)

Flow rate (NL/min): 38-46  
Feed amount (g): 100

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 4</th>
<th>Run 5</th>
<th>Run 6</th>
<th>Run 7</th>
<th>Run 8</th>
<th>Run 9</th>
<th>Run 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction temperature (°C)</td>
<td>311</td>
<td>357</td>
<td>411</td>
<td>356</td>
<td>358</td>
<td>355</td>
<td>353</td>
<td>347</td>
<td>345</td>
<td>351</td>
</tr>
<tr>
<td>Feed rate (g/min)</td>
<td></td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed size (mm)</td>
<td>0.425-1</td>
<td></td>
<td>0.250-0.425</td>
<td>0.425-1</td>
<td></td>
<td>0.250-0.425</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnCl₂ content (wt%)</td>
<td>0</td>
<td>10 a</td>
<td>20 a</td>
<td>20 a</td>
<td>0</td>
<td>10 b</td>
<td>20 b</td>
<td>20 a</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a* : Mechanical mixing, *b* : Impregnation
# Experimental-Reaction conditions (Corn stover)

Flow rate (NL/min): 38-46  
Feed rate (g/min): 5  
Feed size (mm): 0.425-1  
Feed amount (g): 300

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 4</th>
<th>Run 5</th>
<th>Run 6</th>
<th>Run 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction temperature (°C)</td>
<td>343</td>
<td>370</td>
<td>430</td>
<td>337</td>
<td>346</td>
<td>337</td>
<td>335</td>
</tr>
<tr>
<td>Pretreatment</td>
<td>No</td>
<td></td>
<td></td>
<td></td>
<td>Washing</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>ZnCl₂ content (wt%)</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td>7.6</td>
<td>18.5</td>
<td>18.5</td>
</tr>
</tbody>
</table>
# Results - Mass balances (Corncob)

<table>
<thead>
<tr>
<th>Products (wt %)</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 4</th>
<th>Run 5</th>
<th>Run 6</th>
<th>Run 7</th>
<th>Run 8</th>
<th>Run 9</th>
<th>Run 10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>311 °C</td>
<td>357 °C</td>
<td>411 °C</td>
<td>356 °C</td>
<td>358 °C</td>
<td>353 °C</td>
<td>355 °C</td>
<td>347 °C</td>
<td>345 °C</td>
<td>351 °C</td>
</tr>
<tr>
<td>Oil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>48.2</td>
<td>52.7</td>
<td>58.3</td>
<td>46.3</td>
<td>29.8</td>
<td>46.6</td>
<td>59.0</td>
<td>60.0</td>
<td>48.1</td>
<td>47.8</td>
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<tr>
<td>Gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.7</td>
<td>21.5</td>
<td>24.3</td>
<td>16.8</td>
<td>14.9</td>
<td>15.3</td>
<td>17.7</td>
<td>10.0</td>
<td>10.1</td>
<td>11.4</td>
</tr>
<tr>
<td>Char</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.1</td>
<td>25.8</td>
<td>17.4</td>
<td>36.9</td>
<td>55.3</td>
<td>38.1</td>
<td>23.3</td>
<td>30.0</td>
<td>41.8</td>
<td>40.8</td>
</tr>
</tbody>
</table>

Run 4, 5, 6 and 10: Mechanical mixing
Run 8 and 9: Impregnation
Results-Furfural yield (Corncob)

<table>
<thead>
<tr>
<th></th>
<th>Run1</th>
<th>Run2</th>
<th>Run3</th>
<th>Run4</th>
<th>Run5</th>
<th>Run6</th>
<th>Run7</th>
<th>Run8</th>
<th>Run9</th>
<th>Run10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>0.2</td>
<td>0.8</td>
<td>0.6</td>
<td>1.4</td>
<td>2</td>
<td>2.6</td>
<td>0.6</td>
<td>3.4</td>
<td>8.2</td>
<td>4</td>
</tr>
</tbody>
</table>
# Results - Mass balance (Corn stover)

<table>
<thead>
<tr>
<th>Products (wt %)</th>
<th>Run 1 343 °C</th>
<th>Run 2 370 °C</th>
<th>Run 3 430 °C</th>
<th>Run 4 337 °C</th>
<th>Run 5 333 °C</th>
<th>Run 6 346 °C</th>
<th>Run 7 335 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>46.84</td>
<td>46.27</td>
<td>48.21</td>
<td>53.08</td>
<td>49.44</td>
<td>42.34</td>
<td>36.2</td>
</tr>
<tr>
<td>Gas</td>
<td>20.58</td>
<td>20.25</td>
<td>23.56</td>
<td>18.79</td>
<td>11.54</td>
<td>10.9</td>
<td>14.6</td>
</tr>
<tr>
<td>Char</td>
<td>36.77</td>
<td>34.34</td>
<td>31.43</td>
<td>28.13</td>
<td>39.03</td>
<td>46.76</td>
<td>49.2</td>
</tr>
</tbody>
</table>

Run 4, 5, and 6: Soaking  
Run 5, 6, and 7: ZnCl₂ impregnation
Results-Furfural yield (Corn stover)

<table>
<thead>
<tr>
<th></th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 4</th>
<th>Run 5</th>
<th>Run 6</th>
<th>Run 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>0.6</td>
<td>0.1</td>
<td>0.2</td>
<td>1.9</td>
<td>7.6</td>
<td><strong>11.5</strong></td>
<td>6.5</td>
</tr>
</tbody>
</table>
Results - Furfural from cellulose and hemicellulose via ZnCl$_2$

Cellulose $\xrightarrow{\text{ZnCl}_2}$ Fast pyrolysis $\xrightarrow{}$ LGO, DGP, LAC, FF

Xylan $\xrightarrow{\text{ZnCl}_2}$ Fast pyrolysis $\xrightarrow{}$ FF
Results-Furfural from cellulose via ZnCl₂
Conclusion

1. Maximum bio-oil yield: about 60 wt%
2. Maximal furfural yield: 11.5 wt%
3. ZnCl$_2$ was effective for the production of furfural
4. Washing led to the increase in bio-oil and furfural yields
5. Economical separation method for furfural should be found (ex. Extraction).
Thank you for your attention