Beneficiation of by-products from biofuel plant processes for the production of an eco-friendly polyurethane foam

LC Muller, Sanette Marx, Idan Chiyanzu
Problem statement

- Increase profitability of biodiesel and bioethanol production processes
- Utilize by-products to generate additional revenue
- Minimize waste production.
Cellulosic ethanol - Lignin

- Removal of lignin from biomass improves cellulosic ethanol production yield.¹

<table>
<thead>
<tr>
<th>Agricultural waste</th>
<th>Lignin content (% of dry weight)¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat straw</td>
<td>15</td>
</tr>
<tr>
<td>Corn stover</td>
<td>19</td>
</tr>
</tbody>
</table>

- US estimated 250 million gall. of cellulosic ethanol installed capacity in 2015.³
- This would require approx. 2.2 million tons of corn stover.⁴
- Many pre-treatment processes focus on the removal of lignin and lignin may likely in future be produced in large volumes as by-product.²
Biodiesel – Crude glycerol

• Produce 0.1 kg/1 kg of biodiesel through transesterification.\textsuperscript{5}

• US produced 135.1 million gall. biodiesel in December 2013.\textsuperscript{6}

• Crude glycerol for same period should be approx. 44000 ton.

• EIA estimates refiners receive $0.03/gallon of crude glycerol.\textsuperscript{7}
Polyurethane (PUR)

• Numerous options for beneficiating aforementioned by-products being investigated to generate additional diversified revenue for refiners. Polyurethane amongst these.

• PUR made-up 7.3% of total plastic produced in Europe in 2012.\(^8\)

• U.S. PUR industry's 2010 output totalled $59.9 billion.\(^9\)

• 1.9 million tons.\(^9\)

• 44% used in building & construction, appliances and packaging. A major part in the form of rigid polyurethane foam.
Polyurethane (PUR)

HO \( \text{A} \) OH + OCN \( \text{B} \) NCO \( \rightarrow \) \( \text{A} - \text{O} - \text{C} - \text{N} - \text{B} \)_n

Diol (or polyol) Diisocyanate (or polyisocyanate) Polyurethane

- Polyurethane foam made with polyols to create a structure that is three-dimensionally highly cross-linked. The result is a rigid, light-weight foam.\(^{10}\)
- Polyols are largely petroleum derived.\(^{11}\)
- It is however possible to prepare polyols out of lignocellulose in a range of solvents. Active research into use of agricultural waste as source of lignocellulose.
Renewable polyols

Lignocellulose + Solvent $\rightarrow$ Polyol
Liquefaction / Oxy-propylation

<table>
<thead>
<tr>
<th>Lignocellulose</th>
<th>Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat straw</td>
<td>Polyethylene glycol (PEG) + Glycerol</td>
</tr>
<tr>
<td>Soy straw</td>
<td>Crude glycerol</td>
</tr>
<tr>
<td>Corn stover</td>
<td>Crude glycerol</td>
</tr>
<tr>
<td>Corn stalk</td>
<td>PEG + Glycerol</td>
</tr>
<tr>
<td>Dried distillers grains</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>Waste paper</td>
<td>PEG + Glycerol</td>
</tr>
<tr>
<td>Lignin</td>
<td>PEG + Glycerol</td>
</tr>
<tr>
<td>Lignin</td>
<td>Propylene oxide</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td>Wood</td>
<td>PEG + Glycerol</td>
</tr>
</tbody>
</table>
Lignin

• Proposed model structure for Pine kraft lignin.\textsuperscript{12}

• "$\text{Hydroxyl groups and free positions in the aromatic ring are the most characteristic functions in lignin; they determine its reactivity and constitute the reactive sites to be exploited in macromolecular chemistry.}" \textsuperscript{13}
Crude glycerol components

- **Glycerol:**
  \[
  \begin{align*}
  &\text{HO-} \\
  &\text{HO} \\
  &\text{HO}
  \end{align*}
  \]

- **Glycerides:**
  - Monoglyceride: \[
  \begin{align*}
  \text{CH}_2\text{-O-C-} & \text{R } 1 \\
  \text{CH} & \text{- OH} \\
  \text{CH}_2\text{-OH}
  \end{align*}
  \]
  - Diglyceride: \[
  \begin{align*}
  \text{CH}_2\text{-O-C-} & \text{R } 1 \\
  \text{CH} & \text{- O-C-} \text{R } 2 \\
  \text{CH}_2\text{-OH}
  \end{align*}
  \]
  - Triglyceride: \[
  \begin{align*}
  \text{CH}_2\text{-O-C-} & \text{R } 1 \\
  \text{CH} & \text{- O-C-} \text{R } 2 \\
  \text{CH}_2\text{-O-C-} & \text{R } 3
  \end{align*}
  \]

- **Biodiesel:**
  \[
  \text{R-O-C-R}_{1,2,3}
  \]

- **Minor components:**
  Alcohol, water, catalysts, soap, free fatty acids.
Liquefaction

- Fragments lignocellulose.\textsuperscript{14}

- Fragments rebind and bind to solvent chains.\textsuperscript{15}

- Phenolic hydroxyl content are decreased while aliphatic primary and secondary hydroxyl groups are introduced.\textsuperscript{15}

- Branched liquid polymers are formed\textsuperscript{13}, with accessible hydroxyl groups\textsuperscript{17}, which are suitable for rigid polyurethane formation.
Experimental

- Liquefaction: 160°C, 90min, 9:1 (weight solvent : weight lignin), \( \text{H}_2\text{SO}_4 \) catalyst.

- Technical lignins: Kraft (Softwood)
  - Lignosulfonates (Hardwood)
  - Organosolv lignin (Sugarcane bagasse)

- Crude glycerol: Transesterification of sunflower oil with ethanol.
  - Catalyst: KOH.
# Results: Polyols

## Polyol viscosity

<table>
<thead>
<tr>
<th></th>
<th>Kraft</th>
<th>Lignosulfonate</th>
<th>Organosolv</th>
<th>Crude glycerol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity* (mPa.s)</td>
<td>610</td>
<td>210</td>
<td>80</td>
<td>85</td>
</tr>
</tbody>
</table>

* Determined according to ASTM D4878-08

## Polyol hydroxyl number (OH#)

<table>
<thead>
<tr>
<th></th>
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<th>Organosolv</th>
<th>Crude glycerol</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH#* (mgKOH/g)</td>
<td>410</td>
<td>590</td>
<td>220</td>
<td>770</td>
</tr>
</tbody>
</table>

* Determined according to ASTM D4274-11 Method D

## Liquefaction yield

<table>
<thead>
<tr>
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<th>Lignosulfonate</th>
<th>Organosolv</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biopolyol / Lignin (g/g)</td>
<td>5.6</td>
<td>5.5</td>
<td>6.5</td>
</tr>
<tr>
<td>Solid residue / Lignin (g/g)</td>
<td>1.2</td>
<td>1.3</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Results: Polyurethane foam

<table>
<thead>
<tr>
<th>Foam properties</th>
<th>Kraft</th>
<th>Lignosulfonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive strength* (kPa)</td>
<td>350</td>
<td>220</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>80</td>
<td>160</td>
</tr>
</tbody>
</table>

*Determined according to ASTM D1621-10
Biodegradability

- Depending on PUR application, biodegradability may or may not be desirable.

- Polyether PUR highly resistant to microbial degradation. Polyester PUR is susceptible.\(^{18}\)

- Polyols made from crude glycerol and lignin are plant derived and may therefore show enhanced biodegradability.

- Lignin contains many ether bonds and degrades slowly in the environment.\(^{19}\) Crude glycerol on the other hand contains esters.

- Crude glycerol based PUR shown to have enhanced biodegradability.\(^{20}\)
Overview: Polyurethane preparation

Byproducts
Biodiesel:

Crude glycerol

Cellulosic ethanol: → Liquefaction → Renewable polyol → Polyurethane foam

Lignin

Benefits:
- Crude glycerol and lignin are renewable.
- Crude glycerol is unrefined, minimize waste.
- Different technical lignin types suffice and yield distinctive polyols. Different types of pre-treatments methods may therefore be suitable.
- Polyurethane foam show high compressive strength.
- Potential of increased biodegradability.
References

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