Processing of Lignin and the Removal of Detrimentals with Deep Eutectic Solvents

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Deep Eutectic Solvents (DESs) are low transition temperature mixtures (LTTMs) consisting of at least one hydrogen bond donor (HBD) and one hydrogen bond acceptor (HBA) counterparts that result on a liquid mixture showing unusual low freezing point.

Freezing point of Choline Chloride / Urea mixtures as a function of composition.

Visual representation of Choline Chloride / Urea mixtures as a function of composition.

Due to the high hydrogen bonding interaction, some of the promising characteristics of ionic liquids as solvents are shared by DESs:

- Wide liquid range
- Low or negligible vapor pressure
- Good solvation properties
- Ability to customize properties as a function of:
  - DES constituents nature
  - DES constituents ratio
  - Water content
  - Temperature
- Easy recovery using a non H-bonding anti-solvent
About Deep Eutectic Solvents (DESs)

Additionally:

- Easy preparation
- Readily available and cheap starting materials
- No need of purification
- Water-compatibility
- Non-flammability
- Non-toxicity
- Biocompatible
- Biodegradable
- Can be considered as environmentally benign solvents
Why for paper industry?

Why for paper industry?

Lignin Dissolving for 3 hours at 60°C
## Superscreening DESs

| DES         | Lactose | Fructose | Glucose | Inosine | Hesperidin | Phytic Acid | Citric Acid | Citric Acid (Dihydrate) | Terephthalic Acid | Trans-stilbene | Sulfamic Acid | Sulfonamide | Sucrose | Fructose | Malic Acid | Succinic Acid | Glutaric Acid | Adipic Acid | Glycolic Acid | Malic Acid | Tartaric Acid | Citric Acid | Urea | Thioammon | Chlorine | Glucose | Fructose |
|-------------|---------|----------|---------|---------|-----------|-------------|-------------|--------------------------|-------------------|----------------|--------------|-------------|-------------|------------|---------|----------|-----------|-------------|--------------|-----------|-------------|-----------|-----------|----------|--------|----------|---------|--------|---------|
# DESs screening

## Lignin solubility

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Lignin solubility [ w%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCC</td>
<td>15%</td>
</tr>
<tr>
<td>XCC</td>
<td>14%</td>
</tr>
<tr>
<td>OCC</td>
<td>2%</td>
</tr>
<tr>
<td>GCC</td>
<td>7%</td>
</tr>
<tr>
<td>OG</td>
<td>32%</td>
</tr>
<tr>
<td>GG</td>
<td>30%</td>
</tr>
<tr>
<td>OEG</td>
<td>35%</td>
</tr>
<tr>
<td>SEG</td>
<td>33%</td>
</tr>
<tr>
<td>GEG</td>
<td><strong>37%</strong></td>
</tr>
<tr>
<td>AEG</td>
<td>31%</td>
</tr>
</tbody>
</table>
Simple procedure

Mix  Stir  Centrifuge

Antisolvent  Filtrate

Washing  Filtrate
### Lignin extractability

<table>
<thead>
<tr>
<th>pKa HBD</th>
<th>DES</th>
<th>Kappa Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td></td>
<td>25.5</td>
</tr>
<tr>
<td>1,25</td>
<td>OEG</td>
<td>8.1</td>
</tr>
<tr>
<td>4,16</td>
<td>SEG</td>
<td>13.2</td>
</tr>
<tr>
<td>4,31</td>
<td>GEG</td>
<td>15.7</td>
</tr>
<tr>
<td>4,43</td>
<td>AEG</td>
<td>18.4</td>
</tr>
</tbody>
</table>
## Effect of DESs on the fibers

<table>
<thead>
<tr>
<th></th>
<th>Sulphite</th>
<th>Extracted Sulphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kappa number</td>
<td>25,5</td>
<td>18,1</td>
</tr>
<tr>
<td>Mean fibre length</td>
<td>1,555</td>
<td>0,825</td>
</tr>
<tr>
<td>Mean fibre width</td>
<td>29,1</td>
<td>29,8</td>
</tr>
</tbody>
</table>
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Until recently, only hydrophilic DESs were produced. The constituents of the currently produced DESs all promote the preparation of hydrophilic DESs. This is due to the high amount of hydrogen bonding donating and hydrogen bonding accepting groups.

**Hydrogen Bond Donors (HBDs)**
- Oxalic acid
- Malic acid
- Lactic acid
- Urea
- Glycolic acid

**Hydrogen Bond Acceptors (HBA)**
- Choline chloride
- Tetrabutylammonium bromide
- Proline
- Betaine
- Glycine
Hydrophobic DESs
Hydrophobic DESs

Introduction

- Produced with a fatty acid, decanoic acid, and quaternary ammonium salts

![Diagram showing molecular structures of hydrophobic DESs]
## Hydrophobic DESs

### Results

- Physicochemical properties of the developed DESs

<table>
<thead>
<tr>
<th>DESs</th>
<th>$\rho$ [kg·m$^{-3}$]</th>
<th>$\eta$ [mPa·s]</th>
<th>$W_{\text{before,H}_2\text{O}}$ [ppm]</th>
<th>$W_{\text{after,H}_2\text{O}}$ [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DecA:N$_{4444}$-Cl (2:1)</td>
<td>916.8</td>
<td>265.26</td>
<td>8140</td>
<td>69380</td>
</tr>
<tr>
<td>DecA:N$_{8881}$-Cl (2:1)</td>
<td>896.4</td>
<td>783.41</td>
<td>2580</td>
<td>62220</td>
</tr>
<tr>
<td>DecA:N$_{7777}$-Cl (2:1)</td>
<td>890.7</td>
<td>172.87</td>
<td>7740</td>
<td>23387</td>
</tr>
<tr>
<td>DecA:N$_{8888}$-Cl (2:1)</td>
<td>888.9</td>
<td>472.58</td>
<td>4640</td>
<td>17849</td>
</tr>
<tr>
<td>DecA:N$_{8881}$-Br (2:1)</td>
<td>942.2</td>
<td>576.53</td>
<td>3225</td>
<td>42433</td>
</tr>
<tr>
<td>DecA:N$_{8888}$-Br (2:1)</td>
<td>929.8</td>
<td>636.36</td>
<td>920</td>
<td>20049</td>
</tr>
</tbody>
</table>
### Hydrophobic DESs

#### Results

- **Leaching of the quaternary ammonium salt**

<table>
<thead>
<tr>
<th>DESs</th>
<th>(C_{\text{salt}}) [mg\text{salt}/g\text{water}]</th>
<th>(m_{\text{salt,leached}}/m_{\text{salt,DES}}) [g·g(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DecA:N(_{4444})-Cl (2:1)</td>
<td>155.21</td>
<td>0.3475</td>
</tr>
<tr>
<td>DecA:N(_{8881})-Cl (2:1)</td>
<td>16.19</td>
<td>0.0300</td>
</tr>
<tr>
<td>DecA:N(_{7777})-Cl (2:1)</td>
<td>13.09</td>
<td>0.0232</td>
</tr>
<tr>
<td>DecA:N(_{8888})-Cl (2:1)</td>
<td>11.44</td>
<td>0.0193</td>
</tr>
<tr>
<td>DecA:N(_{8881})-Br (2:1)</td>
<td>13.08</td>
<td>0.0231</td>
</tr>
<tr>
<td>DecA:N(_{8888})-Br (2:1)</td>
<td>14.23</td>
<td>0.0523</td>
</tr>
</tbody>
</table>
# Hydrophobic DESs

## Results

- **Extraction of volatile fatty acids**

<table>
<thead>
<tr>
<th>DESs</th>
<th>Acetic Acid</th>
<th>Propionic Acid</th>
<th>Butyric Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>DecA:N\textsubscript{8881}-Cl (2:1)</td>
<td>38.0</td>
<td>70.5</td>
<td>89.8</td>
</tr>
<tr>
<td>DecA:N\textsubscript{7777}-Cl (2:1)</td>
<td>32.0</td>
<td>76.5</td>
<td>91.5</td>
</tr>
<tr>
<td>DecA:N\textsubscript{8888}-Cl (2:1)</td>
<td>25.0</td>
<td>52.7</td>
<td>81.3</td>
</tr>
<tr>
<td>DecA:N\textsubscript{8881}-Br (2:1)</td>
<td>29.7</td>
<td>63.4</td>
<td>83.1</td>
</tr>
<tr>
<td>DecA:N\textsubscript{8888}-Br (2:1)</td>
<td>30.6</td>
<td>65.9</td>
<td>87.4</td>
</tr>
<tr>
<td>TOA</td>
<td>18.6</td>
<td>45.9</td>
<td>73.5</td>
</tr>
</tbody>
</table>
Hydrophobic DESs

Future

• The development of these hydrophobic DESs allows for the removal of all kind of detrimentals from an aquatic environment

• Disadvantage of the hydrophobic DESs that have to be resolved:
  • High price of the quaternary ammonium salts
  • Relative high leaching of the quaternary ammonium salts

• We are just at the verge of a new class of DESs!
  • A vast amount of research still has to be conducted

• For more information
  • Download the article ‘Hydrophobic deep eutectic solvents as water-immiscible extractants’ (see also reference below)

Recovery Protocols for DES based pulping processes

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19-11-2015
Regeneration of DESs

Techno-economical feasible process

DES pulping

DES recovery
Regeneration of DESs

Different methods for DES separation and recycling after pulping with lignin-dissolving DES

- Removal of contained water
- Ultra-filtration / Nano-filtration
- Precipitation with anti-solvents
Regeneration of DESs

Anti-solvent addition to Malic Acid:Glycine
2 mL/ 1.5 gram (left) 9 mL/1.5 gram (right)
Recycle Process

- **Biomass**
  - **Pulping**
  - **Mild T**

- **DES**

- **Pulping mixture**
  - **Refining**

- **Filtrate**
  - **Filtrate**
    - **DES**
    - **Water**
    - **Extractives**

- **Cellulose fibers**
  - **Reuse**
  - **Recycle**
  - **Valorize**
Participants
Acknowledgement

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