Ultra-low cost ionic liquids for biorefining of waste wood

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Why use ionic liquids for lignocellulosic biofuels?

- Increase enzyme activity at minimal cost
  - Several options (kraft, ammonia, organosolv, etc.)
  - Ionic liquids provide highest activity
  - Ionic liquids are generally very expensive

- Ionic liquids are just organic salts
  - Have advantages over organic solvents
    • Can be designed for a specific function
  - Have disadvantages also

- The application must be logical
  - Rational choices must be made
**ionoSolv lignin extraction**

- Most ILs are not good solvents for cellulose
  - Biocatalytic conversion of cellulose to fuels
  - Want de-lignified cellulose
- **ionoSolv**: Dissolve lignin not cellulose
  - Highly pure cellulose easily recovered
  - Lignin solution for chemical conversion
  - Water helps the process
  - *Do salts have to be expensive?*

Process economics – IL cost are critical

- Other important factors
  - Recycling rate
  - Biomass loading

Klein-Maruschamer et al., *Biofuels, Biproducts, Biorefining*, 5, 562 (2011)
Can Ionic Liquids be Cheap?

- $[C_4C_1im][NTf_2]$ (Sigma-Aldrich):
  - $2500/kg (250g)$
- Ethaline (Scionix):
  - $60/kg (50kg)$
- $[(C_8)_3C_1N][Br]$ (Solvent Innov.):
  - $40/kg (100t)$
- $[C_2C_1im][acetate]$
  - $60/kg (bulk guesstimate)$
- $[C_1Him][HSO_4]$
  - $2.60/kg (bulk estimate)$
- $[(C_2)_3NH][HSO_4]$
  - $0.84/kg (bulk estimate)$
- $[(C_4)(C_1)_2NH][HSO_4]$
  - $0.44/kg (bulk estimate)$
- Acetone: $1.30/kg$

Chen et al., Green Chem., 16, 3098 (2014)
How NOT to make a Green solvent

Waste in every step!

Cost = $2500/kg; E-factor > 100

How to make a Green solvent

Cost = €1/kg; E-factor < 0.1
Fewer steps = lower cost = less waste

Chen et al., Green Chem., 16, 3098 (2014)
Material flow diagram

Lignocellulose → Ionic liquid Treatment → Cellulose → Filtration washing → Precipitation & filtration → Volatiles (Furfural, acetic acid) → Distillation

Cellulose in an IL stream

Lignin → Decanting → Tall oil

Extractives → Monomeric hemicellulose → Furfural

Fun facts about the cellulose

- We typically get ca. 96% glucan recovery (relative to native biomass)
  - 5% of the glucan is in the hemicellulose
- Max saccharification yields (rel. to native)
  - Miscanthus: 96%
  - Willow: 90%
  - Pine: 100%
- Most ‘pure’ cellulose pulp ca. 94% glucan
  - 1 h, 150 °C, 20% solids

Gschwend et al., *Green Chem.*, 20, (2018), accepted
Results – Particle size

Coarse | Medium | Fine

Chambon et al., (2018), under review
Results – Scale up

- Max sacch. yields at 20% (50%) solids
  - Miscanthus: 96% (78%)
  - Willow: 90% (??)
  - Pine: 100% (82%)
Comparison of economics with other technologies

<table>
<thead>
<tr>
<th>Virgin wood/ton</th>
<th>£/ton feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Plant size</strong></td>
<td>100,000 tpa</td>
</tr>
<tr>
<td>Solvent</td>
<td>£11</td>
</tr>
<tr>
<td>Biomass</td>
<td>£52</td>
</tr>
<tr>
<td>Water</td>
<td>£4</td>
</tr>
<tr>
<td>Capital</td>
<td>£25</td>
</tr>
<tr>
<td>Energy</td>
<td>£51</td>
</tr>
<tr>
<td><strong>COST</strong></td>
<td>£142</td>
</tr>
<tr>
<td>Cellulose</td>
<td>£84</td>
</tr>
<tr>
<td>Lignin</td>
<td>£88</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>£36</td>
</tr>
<tr>
<td><strong>VALUE</strong></td>
<td>£207</td>
</tr>
<tr>
<td><strong>NET</strong></td>
<td>£65</td>
</tr>
<tr>
<td><strong>MARGIN</strong></td>
<td>46%</td>
</tr>
</tbody>
</table>

Glucose can be sold at €0.16/kg
Also lower energy costs per ton of sugar than steam explosion
• Higher solids loading possible
  • (based here on 20%)
  • 100% sugar release from grasses or softwoods at 10% solids loading
  • 80% sugar release from softwoods at 50% solids loading
• Less phase change = less cost

• Compared to (dilute acid pretreatment)
  • 30% lower capital costs
  • 40% higher product value
  • 100% larger profit margin

Brandt et al., Green Chem. 2017, 19, 3078-3102.
Process Flow Scheme

Brandt et al., Green Chem. 2017, 19, 3078-3102
IL recovery and recycling:

- Very high IL stability (>330 C)
- 99.5 +/- 1% IL recovery
- ca. 100% lignin recovery
- No inorganic salt buildup

<table>
<thead>
<tr>
<th>Use</th>
<th>IL Recovery (%)</th>
<th>±</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st use</td>
<td>99.0</td>
<td>±3.7</td>
</tr>
<tr>
<td>2nd use</td>
<td>97.9</td>
<td>±1.7</td>
</tr>
<tr>
<td>3rd use</td>
<td>99.4</td>
<td>±8.4*</td>
</tr>
<tr>
<td>4th use</td>
<td>99.3</td>
<td>±0.9</td>
</tr>
</tbody>
</table>

* error due to mixing two replicates during pulp washing

**Figures**: Fresh IL, After 1st use, After 4th use

**Graphs**: % of lignin content, Yield (% of max), Enzymatic saccharification (h)

Feedstock doesn’t matter?

Glucose yield (% of theoretical max) vs. Saccharification time (hours)

- Miscanthus
- Untreated Miscanthes
- Pine
- Untreated Pine

High Biomass loadings

Saccharification yield

<table>
<thead>
<tr>
<th>Loading</th>
<th>with air drying</th>
<th>without air drying</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>64.8±3.5%</td>
<td>99.2±1.9%</td>
<td>✓ Higher yields if pulp drying is avoided</td>
</tr>
<tr>
<td>50%</td>
<td>34.4±3.2%</td>
<td>74.9±2.9%</td>
<td>✓ Larger impact at high loadings</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>✓ Multiple feedstocks combined</td>
</tr>
</tbody>
</table>
Metal-containing waste wood

- Extraction of Cu, Cr and As
- Recovery of the metals through electro-plating
- High sugar yields

- 60 Mt/y US; 70 Mt/y EU
- Cannot be incinerated for biopower
- UK: £130/t for landfilling
OK, So It Works

Pretreatment of CCA wood with recycled IL (170°C - 30 mins - [HMIM][Cl])

Cycle 1 Cycle 2 Cycle 3 Cycle 4 Cycle 5 Cycle 6
- Chromium Extraction - Copper Extraction - Arsenic Extraction - Glucose Yield

Cyclic Voltammetry of [HMIM][HSO4] saturated with Cu ions and containing 20wt% water:

Oxidation: Cu(II) → Cu(III) + 2e
Reduction: Cu(III) + 2e → Cu(II)
Any Waste Wood?

You don’t get to choose what is in waste!
Waste wood to fuels & materials

**Contributing to circular economy**

- Use post-consumer waste wood as very cheap (negative) feedstock for biorefinery
- Use low-cost ionic liquid process to:
  - *Save environment*: divert from landfill and remove heavy and toxic metals
  - *Make fuels & chemicals*: fractionate decontaminated waste wood to cellulose & lignin
Waste wood to fuels & materials

Contributing to circular economy

- Use waste wood as very cheap (negative) feedstock for biorefinery
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Ionic liquid processing

Pretreatment of contaminated waste wood with using [H1Cim]Cl

![Graph showing metal removal with different biomass loadings](image)

Aida Rafat
### Feedstock-controlled economics?

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<thead>
<tr>
<th></th>
<th>Waste wood/ton</th>
<th>Virgin wood/ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant size</td>
<td>20,000 tpa</td>
<td>100,000 tpa</td>
</tr>
<tr>
<td>Cellulose</td>
<td>£ 90</td>
<td>£ 90</td>
</tr>
<tr>
<td>Lignin</td>
<td>£ 94</td>
<td>£ 94</td>
</tr>
<tr>
<td>Hemic/Furfural</td>
<td>£ 38</td>
<td>£ 38</td>
</tr>
<tr>
<td>Gate fee</td>
<td>£ 54</td>
<td>-</td>
</tr>
<tr>
<td><strong>REVENUE</strong></td>
<td>£ 276</td>
<td>£ 222</td>
</tr>
<tr>
<td>Solvent</td>
<td>£ 11</td>
<td>£ 11</td>
</tr>
<tr>
<td>Biomass</td>
<td>-</td>
<td>£ 56</td>
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<tr>
<td>Water</td>
<td>£ 4</td>
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<tr>
<td>Capital</td>
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<tr>
<td>Energy</td>
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<td>£ 55</td>
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<tr>
<td><strong>COST</strong></td>
<td>£ 113</td>
<td>£ 152</td>
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<td><strong>PROFIT</strong></td>
<td>£ 163</td>
<td>£ 70</td>
</tr>
<tr>
<td><strong>GROSS MARGIN</strong></td>
<td>59%</td>
<td>32%</td>
</tr>
</tbody>
</table>
Onward to bioderived plastics!
Conclusions

• Ionic liquids do not have to be expensive
  – Targeted applications still possible
  – Use common sense when designing
• Delignification of biomass
  – Simple process
  – Stable, recoverable, recyclable solvents
  – High solids loadings possible
• Recycling improves performance
• Economics-driven approach to solvent design
  – Can be application specific