Combining Bio- and Chemo-catalysis for the Conversion of Bio-Renewable Alcohols

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Andrew C. Marr, Queen’s University Belfast

3rd ISGC, La Rochelle, France, May 2015.
Biomass and Bio-Renewables

- Renewables industries must be sustainable businesses and able to operate competitively without subsidy.
- **Biomass** is ubiquitous, as human’s need to grow food.
- Promising substrates are food and agricultural wastes.
- Similar to oil, biomass is a potential source of energy and chemicals.
- The economics of biomass utilisation depend upon the extent to which value added products are produced.
- In EU FP7 project GRAIL we are looking at utilising biodiesel waste for further energy and chemicals.
GRAIL FP7: Valorising Biodiesel Waste

Energy and chemicals from waste: recycled cooking oil

Fats & Oils  →  Liquid Fuel

• **Biodiesel** is produced in large volume in the EU.
• In some cases the input is *used vegetable oil*.
• Energy from waste.
• 160,000 tons/anum (per plant).
• Reducing pollution.
• Recycling chemical energy.
• Not atom-efficient...

[http://www.grail-project.eu](http://www.grail-project.eu)
9 countries, 15 partners
The Problem with Biodiesel

Glycerol is formed as the by-product

\[
\begin{align*}
\text{CH}_2\text{OCOR} + 3\text{CH}_3\text{OH} & \xrightarrow{\text{catalyst}} 3\text{CH}_3\text{OCOR} + \text{HO}-\text{C}-\text{CH}_2\text{OH} \\
\end{align*}
\]

- Approx. 10% is **crude** glycerol.
- Crude glycerol is of low value [in 2010 about 20 times less than purified glycerol].
- Glycerol has potential uses in chemicals and energy.
- **But** purification is expensive.
- Much of the glycerol could go unused (become waste).
- **Crude** glycerol **must** be used.
- Whole cell biocatalysis.
Using Whole Cell Biocatalysis.

- Crude biomass is a difficult substrate.
- Bio-renewable substrates are often:
  - Impure
  - Oxygenated
  - Aqueous
- Petrochemical catalysts tend to convert crude biomass unselectively and become poisoned.
- One solution is whole cell biocatalysis.
- Micro-organisms live on biomass and enrich the aqueous growth medium in a chemical.
- Chemicals produced depend on metabolic pathways
- Coupling whole cell biocatalysis to chemocatalysis provides routes to many other chemicals.
Combining Bio and Chemo-Catalysis

The Biorefinery Concept:

Fuels and chemical products from biomass.

We are combining whole cell biocatalysis with chemocatalysis in order to transform waste into value-added chemicals

Whole cell biocatalytic fermentation + Chemocatalysis

– minimizing intermediate separations – intensification
– minimizing hazards
**Biocatalysis: Whole Cell Fermentation of Glycerol**

Dr Martin Rebros and Prof Gillian Stephens

![Chem. Commun. 2009, 2308 – 2310.](image)

Further studies for GRAIL, Martin Rebros

---

**Anaerobic Fermentation**

<table>
<thead>
<tr>
<th>Performance</th>
<th>Purified glycerol</th>
<th>Bio-diesel glycerol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial glycerol /g.dm(^{-3})</td>
<td>18.8</td>
<td>19.1</td>
</tr>
<tr>
<td>Final 1,3-propanediol /g.dm(^{-3})</td>
<td>9.7</td>
<td>10.2</td>
</tr>
<tr>
<td>Duration of fermentation /h</td>
<td>9.25</td>
<td>5.5</td>
</tr>
<tr>
<td>Productivity /g.dm(^{-3}).h(^{-1})</td>
<td>0.97</td>
<td>1.71</td>
</tr>
<tr>
<td>Productivity /Mol.dm(^{-3}).h(^{-1})</td>
<td>0.0064</td>
<td>0.0225</td>
</tr>
</tbody>
</table>

**Clostridium butyricum**

1,3-Propanediol
Strategy to Utilize Crude Biomass Combining Bio- and Chemo-catalysis

Aqueous solution of a chemical intermediate.

Extract using Ionic liquid containing a Catalyst.

Fermentation of crude biomass. Cells in an aqueous growth medium.

Impure Biomass

Renewable Platform Chemical (Intermediate)

Value-added Product

Trends Biotech. 2011, 29, 199–204
Ionic Liquids

- A salt that is liquid under reasonable temperatures
- Behaves as an *involatile polar solvent*
- Can change the cation and anion to tune properties.

Cations + anions

\[
\begin{align*}
\text{Cations} & \quad \text{+ anions} \\
\text{Cl}^-, \text{Br}^-, \text{I}^- & \\
\text{CH}_3\text{CO}_2^-, \text{CF}_3\text{CO}_2^-, \text{CF}_3\text{SO}_3^- & \\
\end{align*}
\]
Ionic Liquids in Bio-Alcohol Processes

Ionic liquids have the potential to extract and transform bio-alcohols.

- Non-volatile, very high boiling solvents (comparable with sulfolane).
- Toxicity, biocompatibility, biodegradation can be varied.
- IL can be functionalized to suit a purpose e.g. hydrophobicity.
- Act like high polarity solvents, high affinity for alcohols.
Chemo-Catalysis on Bio-Alcohols
Hydrogen Transfer Reactions

- Aliphatic alcohols like 1,3-PDO are not highly activated for reaction
- Addition of a homogeneous catalyst can reversibly remove hydrogen
- Hydrogen transfer or hydrogen borrowing reactions enable transformation of bio-renewable alcohols under mild conditions
- Examples include amination, hydrogenation and dehydrogenation.

Our catalysts

Hydrogen Transfer literature: Bäckvall, Beller, Blum, Cole-Hamilton, Crabtree, de Vries, Grigg, Milstein, Morris, Peris, Vogt, Watanabe, Williams, Wills, Yamaguchi and others.

Alcohol Amination in Ionic Liquid vs. Toluene

Sealed tube, 1 mol% catalyst, 24h

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp. / °C</th>
<th>Conversion /%</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>115</td>
<td>&gt;99</td>
<td>ND</td>
<td>65</td>
<td>35</td>
</tr>
<tr>
<td>N₁₈₈₈NTf₂</td>
<td>115</td>
<td>&gt;99</td>
<td>14</td>
<td>43</td>
<td>43</td>
</tr>
<tr>
<td>Toluene</td>
<td>60</td>
<td>16</td>
<td>100</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>N₁₈₈₈NTf₂</td>
<td>60</td>
<td>&gt;99</td>
<td>20</td>
<td>15</td>
<td>65</td>
</tr>
<tr>
<td>None</td>
<td>60</td>
<td>51</td>
<td>83</td>
<td>17</td>
<td>ND</td>
</tr>
</tbody>
</table>

- N₁₈₈₈NTf₂ is a good solvent for amination
- High tendency to form the amination + dehydration product (5)
- Supports **lower temperature activity**  
  *Chem. Commun. 2009, 2308 – 2310*
Product Formation

- Dehydration occurred readily in the presence of catalyst 1
- The ionic liquid promoted this pathway.
Conducting the amination in N\textsubscript{1,8,8,8}NTf\textsubscript{2} 3 is rarely observed. Selectivity could be controlled to yield 4 or 5.

<table>
<thead>
<tr>
<th>Temp /°C</th>
<th>1,3-PDO: aniline</th>
<th>Conv. /%</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>1:2</td>
<td>&gt;99</td>
<td>ND</td>
<td>trace</td>
<td>&gt;99</td>
</tr>
<tr>
<td>115</td>
<td>1:10</td>
<td>&gt;99</td>
<td>ND</td>
<td>&gt;99</td>
<td>ND</td>
</tr>
</tbody>
</table>

Prepared at concentration 0.2 moldm\textsuperscript{-3}, 48h


Sophie Lacroix
Combined Bio and Chemo-catalysis

- To the aqueous solution resulting from biocatalysis on crude waste glycerol we added:
  - Solvent $N_{1,8,8,8}NTf_2$ (or toluene)
  - Aniline
  - A hydrogen transfer catalyst
  - The base $K_2CO_3$
- and performed amination

<table>
<thead>
<tr>
<th>Temp /°C</th>
<th>Time /h</th>
<th>Solvent</th>
<th>Convers. /%</th>
<th>Av. rate / Moldm$^{-3}$h$^{-1}$</th>
<th>Fermentation Broth</th>
<th>Extraction solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>24</td>
<td>Toluene</td>
<td>20</td>
<td>0.008</td>
<td>82</td>
<td>18</td>
</tr>
<tr>
<td>60</td>
<td>48</td>
<td>$N_{1,8,8,8}NTf_2$</td>
<td>12</td>
<td>0.003</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>42</td>
<td>48</td>
<td>$N_{1,8,8,8}NTf_2$</td>
<td>10</td>
<td>0.002</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>


Shifang Liu
Observations from Proof of Concept

1. Coupled extraction and chemical conversion from fermentation broth is achievable with a catalyst in an ionic liquid.
2. Dehydration occurs readily in the presence of water in hydrophobic ionic liquids.
3. Low conversions as the extraction from aqueous solution with $N_{1,8,8,8}NTf_2$ was poor.

Action points

- Can we tune the ionic liquid and improve extraction?
- Can we run dehydration of bio-alcohols in an IL?

ILs, Extraction of Diols from Water

Testing hydrophobic ILs for the extraction of polyols from water.

Extraction can be greatly improved by tuning the ionic liquid.

Xiaohan Liu
Hydrogen Transfer Initiated Dehydration: HTID

• Under hydrogen transfer conditions and employing catalysts 1 or 2 dehydration occurs, particularly in IL solvents.
• Can dehydration be carried out under mild conditions in the absence of an amine? Yes.

![Chemical reaction diagram]

• Products are the result of coupled hydrogen transfer and dehydration reactions.
• The dehydration chemistry is initiated by metal catalyzed dehydrogenation.
• Aldehydes are required for a wide range of chemical applications


Thomas Eisenhart, Yueming Wang
In NTf$_2^-$ ionic liquids dehydration was found to be facile.
Dehydrogenation forms an *aldol*.
The aldol readily *dehydrates*.
The catalysts operate in air and in the presence of water.
The *Ionic liquid* also boosts propanal selectivity and aids separation.
HTID in ILs, aldehyde isolation

- The *involatile* nature of ionic liquids can be exploited
- Products are *more volatile* and can be distilled out.

![Diagram of IL, substrate, catalyst, and products](image)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp / °C</th>
<th>Time / h</th>
<th>Conv. / %</th>
<th>( \text{CH}_2=\text{CH}_2 )</th>
<th>( \text{HO-CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH} )</th>
<th>( \text{CH}_3-\text{C}=(\text{CH}_3) )</th>
<th>( \text{CH}_3-\text{CH}=(\text{CH}_3) )</th>
<th>( \text{CH}_3-\text{CH}_2-\text{OH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene(^a)</td>
<td>110</td>
<td>48</td>
<td>92</td>
<td>15</td>
<td>9</td>
<td>39</td>
<td>10</td>
<td>26</td>
</tr>
<tr>
<td>(\text{N}_1,8,8,8\text{NTf}_2)(^b)</td>
<td>110</td>
<td>30</td>
<td>100</td>
<td>80</td>
<td>6</td>
<td>8</td>
<td>3</td>
<td>trace(^d)</td>
</tr>
<tr>
<td>(\text{N}_1,8,8,8\text{NTf}_2)(^c)</td>
<td>140</td>
<td>24</td>
<td>100(^\ast)</td>
<td>87</td>
<td>3</td>
<td>3</td>
<td>trace(^d)</td>
<td>trace(^d)</td>
</tr>
</tbody>
</table>

\(^a\) Sealed tube, catalyst 1 mol%, a+b: 0.35 bar; b. Catalyst 1 mol%;
\(^b\) Catalyst 0.5 mol%; a+b+c: products expressed as mol %.
\(^d\) Balance was acetaldehyde.

YueMing Wang
Optimising & Catalyst Recycling

\[
\text{HO-CH}_2\text{-OH} \quad \xrightarrow{\text{Catalyst, } \text{K}_2\text{CO}_3, 150^\circ\text{C, IL}} \quad \text{O=C=CH}_2
\]

Poster 994

Run

% Yield

Crude propanal

Catalyst precursor

YueMing Wang and Fabio Lorenzini
Summary

• Combining Bio- and Chemo-catalysis to valorise bio-renewable waste streams.
  – Combining biocatalysis and chemocatalysis enables the valorisation of crude biomass waste
  – Whole cell biocatalysis converts crude biomass to diols
  – Ionic liquids can be tuned to extract bio-renewable alcohols from fermentation broth
  – Hydrogen transfer activates aliphatic alcohols
  – Addition of amine leads to amination (N-alkylation)
  – Operating in ionic liquid promotes dehydration to aldehydes
  – Ionic liquids enable facile removal of volatile products and catalyst recycling.
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Xiaohan Liu
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Prof Pete Licence, Nottingham, UK

Gels
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