Bio Fuels, Chemicals and Materials
A Walk on the Green Side of Sustainability

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Georgia Institute of Technology
Top Global Challenges

GT Chem 2312 Students

- ENERGY
- WATER
- FOOD
- CHEM 2312
- ENVIRONMENT
- TERRORISM & WAR
Global Challenges
Energy/Sustainability

Historical Perspective
Billions of Oil-Equivalent Barrels
Research Opportunities: New Industrial Economy

David Morris - early 1980s

- Coined the term "carbohydrate economy"
- Envisaged that by shifting society's engine toward renewable, environmentally benign materials from agro/forestry-based materials

Defining a Biobased Economy

An economy based on renewable raw materials to produce products and energy in a sustainable manner
Biofuels – Biomaterial Future

Biomass Resources

Cellulose
Polymer of \( \beta-(1,4) \)-glucan
DP: ~300 – 15,000

Content: ~35 – 50%

Major Global Biopolymers

Hemicellulose
Short chain branched, substituted polymer of sugars
DP: ~70 – 200

Content: ~15 – 30%

No Competition with Food Demand

Lower Cost

Higher Availability

BioResource | % | ~ Lignin | Hemicellulose | Cellulose
--- | --- | --- | --- | ---
Softwood | 27 | 28 | 39
Hardwood | 25 | 30 | 40
Corn Stover | 18 | 22 | 38
Wheat Straw | 23 | 21 | 38
Fine Paper | - | 20 | 80
Switch Grass | 18 | 20 | 31
Biofuels – Biomaterials Future

Integrated Biorefinery

The biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. It fully utilizes all components of biomass to make a range of foods, fuels, chemicals, feeds, materials, heat and power in proportions that maximizes sustainable economic sustainability.

The Path Forward for Biofuels and Biomaterials. Ragauskas, A.J.; Williams, C.K.; Davison, B.H.; Britovsek, G.; Cairney, J.; Eckert, C.A.; Frederick, W.J., Jr.; Hallett, J.P.; Leak, D.J.; Liotta, C. L.; Mielenz, J.R.; Murphy, R.; Templer, R.; Tschaplinski, T.
Science (2006), 311(5760), 484-489
Biofuels – Biomass Research
Research Challenges and Opportunities

Biomass Productivity/Processability: Plant Science

Biomaterials
- Biomass Characterization
- New Separations
- New Biopolymers
- New Chemical Conversions
- Biocomposites

Biofuels
- Biomass Depolymerization
- Fermentation C5/C6
- New Catalyst Chemistry
  - Decarboxylation/decarbonylation
  - Dehydration/reductive

BioPower: Gasification – Fischer/Troph
Biofuels: Novel Oxidative Chemistry in Ionic Liquids

Need New Green Chemistry
Catalytic Oxidative System
Preferably in Ionic Liquid

- Inert solvent
- Tailor solubility of lignin
- Almost no vapor pressure
- Facilitate isolation of oxidized fragments

$C_{810} - C_{900}$
Model Compound Studies

<table>
<thead>
<tr>
<th>Solvent</th>
<th>TEMPO (R)</th>
<th>Conversion/Selectivity (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. EtOAc as solvent</td>
<td>H</td>
<td>36/97</td>
<td>31</td>
</tr>
<tr>
<td>2. CHCl₃</td>
<td>H</td>
<td>38/99</td>
<td>36</td>
</tr>
<tr>
<td>3. I₂ replace HBr</td>
<td>H</td>
<td>6/99</td>
<td>--</td>
</tr>
<tr>
<td>4. [bmin]PF₆</td>
<td>H</td>
<td>98/99</td>
<td>90</td>
</tr>
</tbody>
</table>

Yield Grand

But non-recyclable!
**Biofuels: Novel Oxidative Chemistry Ionic Liquids**

![Chemical reaction diagram](image)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>TEMPO (R)</th>
<th>% Conversion - % Selectivity</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. [bmin]PF₆</td>
<td>H</td>
<td>98/99</td>
<td>90</td>
</tr>
<tr>
<td>2. [bmin]PF₆</td>
<td>NH-Ac</td>
<td>98/98</td>
<td>92</td>
</tr>
<tr>
<td>Extracted - Reused</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. [bmin]PF₆</td>
<td>NH-Ac</td>
<td>98/98</td>
<td>90</td>
</tr>
<tr>
<td>Repeated Three Additional Times</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. [bmin]PF₆</td>
<td>NH-Ac</td>
<td>98/96</td>
<td>91</td>
</tr>
</tbody>
</table>

*First example of TEMPO ‘locked’ in an ionic liquid, can not be extracted with Et₂O, n-Hexane*

*Easy and viable alternative to TEMPO-polymer agents*
Biofuels: Novel Oxidative Chemistry
Ionic Liquids

**Strengths**
- Acetamido TEMPO/HBr completely recyclable
- High yield for electron poor, slightly electron rich benzylic alcohols
- No over oxidation

**Concerns**
- Need an expensive oxidant
- Limited range of benzylic alcohols
  - *HBr*

**TEMPO-catalyzed oxidation of benzylic alcohols to aldehydes with the H$_2$O$_2$/HBr/ionic liquid [bmim]PF$_6$ system.**

<table>
<thead>
<tr>
<th>Benzylic alcohols</th>
<th>Conditions</th>
<th>Products</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph-CH$_2$OH</td>
<td>2 eq. H$_2$O$_2$, 2 h</td>
<td>Ph-CHO</td>
<td>92</td>
</tr>
<tr>
<td>Ph-CH$_2$OH</td>
<td>2 eq. H$_2$O$_2$, 3 h</td>
<td>Ph-CHO</td>
<td>83</td>
</tr>
<tr>
<td>Ph-CH$_2$OH</td>
<td>2 eq. H$_2$O$_2$, 3 h</td>
<td>Ph-CHO</td>
<td>81</td>
</tr>
<tr>
<td>Ph-CH$_2$OH</td>
<td>2 eq. H$_2$O$_2$, 2 h</td>
<td>Ph-CHO</td>
<td>87</td>
</tr>
<tr>
<td>Ph-CH$_2$OH</td>
<td>3 eq. H$_2$O$_2$, 4 h</td>
<td>Ph-CHO</td>
<td>93</td>
</tr>
<tr>
<td>Ph-CH$_2$OH</td>
<td>5 eq. H$_2$O$_2$, 4 h</td>
<td>Ph-CHO</td>
<td>72</td>
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<tr>
<td>Ph-CH$_2$OH</td>
<td>3 eq. H$_2$O$_2$, 4 h</td>
<td>Ph-CHO</td>
<td>91</td>
</tr>
<tr>
<td>Ph-CH$_2$OH</td>
<td>4 eq. H$_2$O$_2$, 4 h</td>
<td>Ph-CHO</td>
<td>83</td>
</tr>
<tr>
<td>MeO-CH$_2$OH</td>
<td>2 eq. H$_2$O$_2$, 2 h</td>
<td>MeO-CHO</td>
<td>-</td>
</tr>
</tbody>
</table>
**Biofuels: Novel Oxidative Chemistry**

**Ionic Liquids**

Literature

- TEMPO/Copper Catalyzed Oxidation of Primary Alcohols to Aldehydes Using Oxygen as Stoichiometric Oxidant by *D. GeiBlmeir et al. Montashefte fur Chemie* 136, 1591 (2005)

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**Reaction Scheme**

\[
\text{MeO-CH}_2\text{OH} \xrightarrow{0.05 \text{ equiv. Cu(II), } 0.10 \text{ equiv. DMAP, } 0.05 \text{ equiv. acetamido-TEMPO}} \text{MeO-CHO}
\]

ILs, O₂ (1 atm), RT, 5 h

<table>
<thead>
<tr>
<th>Run</th>
<th>Copper salt</th>
<th>Ionic Liquid</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuCl₂</td>
<td>[bmim]PF₆</td>
<td>52</td>
<td>43</td>
</tr>
<tr>
<td>2</td>
<td>CuCl₂</td>
<td>[bmim]BF₄</td>
<td>47</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>CuCl₂</td>
<td>[mmim]OSO₃Me</td>
<td>44</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>CuCl₂</td>
<td>[bmpy]PF₆</td>
<td>87</td>
<td>81</td>
</tr>
</tbody>
</table>
### Biofuels: Novel Oxidative Chemistry

**Ionic Liquids**

**Exp.** | **Copper salt** | **Ionic Liquid** | **Conversion (%)** | **Yield (%)**
--- | --- | --- | --- | ---
4 | CuCl₂ | [bmpy]PF₆ | 87 | 81
5 | Cu(OAc)₂ | [bmpy]PF₆ | 66 | 59
6 | CuBr₂ | [bmpy]PF₆ | 91 | 88
7 | Cu(ClO₄)₂ | [bmpy]PF₆ | 99 | 91
8⁹ | Cu(ClO₄)₂ | [bmpy]PF₆ | 4 | -
9⁹ | Cu(ClO₄)₂ | [bmpy]PF₆ | 0 | -
10⁹ | - | [bmpy]PF₆ | 0 | -

⁹ No DMAP was added. ⁹ No acetamido-TEMPO was added. ⁹ No copper salt was added.
Biofuels: Novel Oxidative Chemistry
Ionic Liquids

0.05 equiv. Cu(ClO₄)₂, 0.10 equiv DMAP
ArCH₂OH → ArCHO
0.05 equiv. acetamido-TEMPO
[bmpy]PF₆, O₂ (1 atm), RT, 5 h

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alcohols</th>
<th>Time (h)</th>
<th>Product</th>
<th>Convn/yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[ArCH₂OH]</td>
<td>5</td>
<td>[ArCHO]</td>
<td>99/92</td>
</tr>
<tr>
<td>2</td>
<td>[ArCH₂OH]</td>
<td>5</td>
<td>[ArCHO]</td>
<td>98/90</td>
</tr>
<tr>
<td>3</td>
<td>[ArCH₂OH] Cl</td>
<td>5</td>
<td>[ArCHO] Cl</td>
<td>100/90</td>
</tr>
<tr>
<td>4</td>
<td>MeO-[ArCH₂OH]</td>
<td>5</td>
<td>MeO-[ArCHO]</td>
<td>99/91</td>
</tr>
<tr>
<td>5</td>
<td>Br-[ArCH₂OH]</td>
<td>5</td>
<td>Br-[ArCHO]</td>
<td>99/84</td>
</tr>
<tr>
<td>6</td>
<td>[ArCH₂OH]</td>
<td>5</td>
<td>[ArCHO]</td>
<td>98/92</td>
</tr>
<tr>
<td>7</td>
<td>O₂N-[ArCH₂OH]</td>
<td>5</td>
<td>O₂N-[ArCHO]</td>
<td>100/81</td>
</tr>
<tr>
<td>8</td>
<td>MeO-[ArCH₂OH] MeO</td>
<td>5</td>
<td>MeO-[ArCHO] MeO</td>
<td>96/89</td>
</tr>
</tbody>
</table>
Biofuels: Novel Oxidative Chemistry
Ionic Liquids

The reaction was carried out at 40 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alcohols</th>
<th>Time (h)</th>
<th>Product</th>
<th>Convn/yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td><img src="image1" alt="Structure" /></td>
<td>5</td>
<td><img src="image2" alt="Structure" /></td>
<td>99/88</td>
</tr>
<tr>
<td>10</td>
<td><img src="image3" alt="Structure" /></td>
<td>5</td>
<td><img src="image4" alt="Structure" /></td>
<td>97/79</td>
</tr>
<tr>
<td>11</td>
<td><img src="image5" alt="Structure" /></td>
<td>5</td>
<td><img src="image6" alt="Structure" /></td>
<td>100/89</td>
</tr>
<tr>
<td>12</td>
<td><img src="image7" alt="Structure" /></td>
<td>5</td>
<td><img src="image8" alt="Structure" /></td>
<td>100/77</td>
</tr>
<tr>
<td>13</td>
<td><img src="image9" alt="Structure" /></td>
<td>24</td>
<td><img src="image10" alt="Structure" /></td>
<td>94/61</td>
</tr>
<tr>
<td>13d</td>
<td><img src="image9" alt="Structure" /></td>
<td>24</td>
<td><img src="image10" alt="Structure" /></td>
<td>100/54</td>
</tr>
<tr>
<td>14</td>
<td><img src="image11" alt="Structure" /></td>
<td>24</td>
<td><img src="image12" alt="Structure" /></td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td><img src="image13" alt="Structure" /></td>
<td>24</td>
<td><img src="image14" alt="Structure" /></td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td><img src="image15" alt="Structure" /></td>
<td>24</td>
<td><img src="image16" alt="Structure" /></td>
<td>-</td>
</tr>
<tr>
<td>17</td>
<td><img src="image17" alt="Structure" /></td>
<td>4</td>
<td><img src="image18" alt="Structure" /></td>
<td>97/75</td>
</tr>
<tr>
<td>12d</td>
<td><img src="image19" alt="Structure" /></td>
<td>24</td>
<td><img src="image20" alt="Structure" /></td>
<td>12/ -</td>
</tr>
</tbody>
</table>

The reaction was carried out at 40 °C.

![Structure](image1) ![Structure](image2) ![Structure](image3) ![Structure](image4) ![Structure](image5) ![Structure](image6) ![Structure](image7) ![Structure](image8) ![Structure](image9) ![Structure](image10) ![Structure](image11) ![Structure](image12) ![Structure](image13) ![Structure](image14) ![Structure](image15) ![Structure](image16) ![Structure](image17) ![Structure](image18)
Biofuels: Novel Oxidative Chemistry
Ionic Liquids

Strength

• Acetamido-TEMPO ‘locked’ in ionic liquid(s) and easily recycled and reused for five runs without significant loss of catalytic activity
• A mild and efficient aerobic oxidation of primary alcohols in [bmpy]PF₆
• High selectivity to aldehydes and no over-oxidized product observed
• Good tolerance toward heteroatom (S and N) containing compounds
• Electron rich benzylic alcohols oxidized

Concerns

• Will not oxidize secondary alcohols

Biofuels: Novel Oxidative Chemistry
Ionic Liquids

Vanadium Oxyacetylacetonate: VO(acac)$_2$

ILs, O$_2$
**Biofuels: Novel Oxidative Chemistry**

**Ionic Liquids**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ionic Liquid</th>
<th>Additive</th>
<th>Convn/sel</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[bmim]BF₄</td>
<td>Et₃N</td>
<td>37/&gt;99</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>[bm₂im]BF₄</td>
<td>Et₃N</td>
<td>31/&gt;99</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>[hmim]OTf</td>
<td>Et₃N</td>
<td>52/&gt;.99</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>[bmpy]PF₆</td>
<td>Et₃N</td>
<td>59/&gt;99</td>
<td>51</td>
</tr>
<tr>
<td>5</td>
<td>[bmpyr]NTf₂</td>
<td>Et₃N</td>
<td>62/&gt;99</td>
<td>49</td>
</tr>
<tr>
<td>6</td>
<td>[bmim]PF₆</td>
<td>Et₃N</td>
<td>64/&gt;99</td>
<td>58</td>
</tr>
<tr>
<td>7</td>
<td>[bmim]PF₆</td>
<td>Pyridine</td>
<td>28/&gt;99</td>
<td>17</td>
</tr>
<tr>
<td>8</td>
<td>[bmim]PF₆</td>
<td>DMAP</td>
<td>51/&gt;99</td>
<td>40</td>
</tr>
<tr>
<td>9</td>
<td>[bmim]PF₆</td>
<td>DBU</td>
<td>90/45</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>[bmim]PF₆</td>
<td>DABCO</td>
<td>98/&gt;99</td>
<td>91</td>
</tr>
</tbody>
</table>

**Chemical Reaction**

```
0.05 equiv. VO(acac)₂
ILs, O₂, 80 °C, 6h
```

**Ionic Liquids**

- [bmim]BF₄
- [bmim]PF₆
- [bm2im]BF₄
- [hmim]OTf
- [bmpy]PF₆
- [bmim]PF₆

**Additives**

- Et₃N
- Pyridine
- DMAP
- DBU
- DABCO
**Biofuels: Novel Oxidative Chemistry Ionic Liquids**

RCH₂OH $\xrightarrow{0.05 \text{ equiv. VO(acac)}_2, 0.10 \text{ equiv. DABCO}}$ RCHO

0.10 equiv. [bmin]PF₆, O₂, 80-100 °C

Recycling of VO(acac)₂ aerobic catalytic system for 4-methoxybenzyl alcohol into aldehyde

<table>
<thead>
<tr>
<th>Run</th>
<th>Time (h)</th>
<th>% Conversion</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>98</td>
<td>91</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>93</td>
<td>87</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>97</td>
<td>92</td>
</tr>
</tbody>
</table>

**Strengths:**
- Aerobic catalytic
- Tolerant for hetero-atoms
- Electron rich/poor benzylic hydroxyl groups
- Oxidizes 1° and 2° benzylic hydroxyl groups
- First oxovanadium oxidation system in IL

**Concerns**
- none

*Submitted Tetrahedron Lett.*
Novel Oxidative Green Chemistry

- Better to prevent waste than treat it
- Raw materials should be renewable
- Catalytic reagents are superior to stoichiometric reagents
Novel Oxidative Green Chemistry

Question: Can Aerobic Acetamido-TEMPO oxidation occur in other solvents?

Optimization of Aerobic Oxidation of 4-Methoxybenzyl Alcohol with Acetamido-TEMPO in DMSO,a,b

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Additive</th>
<th>Conversion (%)c</th>
<th>Yield (%)d</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>DMAP</td>
<td>none</td>
<td>56</td>
<td>41</td>
</tr>
<tr>
<td>2</td>
<td>Bipy</td>
<td>none</td>
<td>53</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>Phen</td>
<td>none</td>
<td>45</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>TMDP</td>
<td>none</td>
<td>76</td>
<td>66</td>
</tr>
<tr>
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<td>TMDP</td>
<td>KOH</td>
<td>21</td>
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<tr>
<td>6</td>
<td>TMDP</td>
<td>K$_2$CO$_3$</td>
<td>85</td>
<td>70</td>
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<td>TMDP</td>
<td>pyridine</td>
<td>90</td>
<td>84</td>
</tr>
<tr>
<td>8</td>
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<td>90</td>
</tr>
<tr>
<td>9</td>
<td>TMDP</td>
<td>DABCO</td>
<td>100</td>
<td>96</td>
</tr>
<tr>
<td>10e</td>
<td>TMDP</td>
<td>DABCO</td>
<td>100</td>
<td>92</td>
</tr>
<tr>
<td>11</td>
<td>TMDP</td>
<td>Et$_3$N</td>
<td>99</td>
<td>91</td>
</tr>
<tr>
<td>12e,f</td>
<td>TMDP</td>
<td>DABCO</td>
<td>100</td>
<td>94</td>
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<td>13e,g</td>
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<tr>
<td>14e,h</td>
<td>none</td>
<td>DABCO</td>
<td>0</td>
<td>-</td>
</tr>
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</table>

Recycling of the Catalytic System for Aerobic Oxidation of Benzylic and Allylic Alcohols

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Cycle #</th>
<th>% Conversion</th>
<th>% Yield</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>4-MeOPh</td>
<td>1</td>
<td>100/90</td>
<td>94/89</td>
</tr>
<tr>
<td>2</td>
<td>Ph</td>
<td>2</td>
<td>100/85</td>
<td>93/92</td>
</tr>
<tr>
<td>3</td>
<td>3-ClPh</td>
<td>3</td>
<td>99/93</td>
<td>95/85</td>
</tr>
<tr>
<td>4</td>
<td>4-MePh</td>
<td>4</td>
<td>100/92</td>
<td>96/91</td>
</tr>
<tr>
<td>5</td>
<td>trans-PhCH=CH</td>
<td>5</td>
<td>99/93</td>
<td>93/84</td>
</tr>
<tr>
<td>6</td>
<td>Ph</td>
<td>6</td>
<td>98/88</td>
<td>90/85</td>
</tr>
</tbody>
</table>

---

aReaction condition, 0.06 mol equiv. acetamido-TEMPO, 0.04 mol equiv. Cu(ClO$_4$)$_2$·6H$_2$O, 0.04 mol equiv. %. bReaction was run for 2h. cWater (0.1 mL) was added. dNo acetamido-TEMPO was added. eNo TMDP was added.
Novel Oxidative Green Chemistry

Aerobic Catalytic Oxidation of Alcohols in DMSO with Cu$^{2+}$/Acetamido-TEMPO

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alcohols</th>
<th>Product</th>
<th>Time (h)</th>
<th>% Conversion</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{Ph} - \text{CH}_2\text{OH} )</td>
<td>( \text{Ph} - \text{CHO} )</td>
<td>2</td>
<td>100</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>( \text{Ph} - \text{CH}_2\text{OH} )</td>
<td>( \text{Ph} - \text{CHO} )</td>
<td>2</td>
<td>98</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>( \text{Cl} - \text{CH}_2\text{OH} )</td>
<td>( \text{Cl} - \text{CHO} )</td>
<td>2</td>
<td>99</td>
<td>93</td>
</tr>
<tr>
<td>4</td>
<td>( \text{MeO-} - \text{CH}_2\text{OH} )</td>
<td>( \text{MeO-} - \text{CHO} )</td>
<td>2</td>
<td>100</td>
<td>92</td>
</tr>
<tr>
<td>5</td>
<td>( \text{Ph} - \text{CH}_2\text{OH} )</td>
<td>( \text{Ph} - \text{CHO} )</td>
<td>2</td>
<td>100</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td>( \text{Ph} - \text{OH} )</td>
<td>( \text{Ph} - \text{CHO} )</td>
<td>2</td>
<td>99</td>
<td>93</td>
</tr>
<tr>
<td>7</td>
<td>( \text{Ph} - \text{OH} )</td>
<td>( \text{Ph} - \text{CHO} )</td>
<td>24</td>
<td>19</td>
<td>11</td>
</tr>
<tr>
<td>8</td>
<td>( \text{Ph} - \text{OH} )</td>
<td>( \text{Ph} - \text{CHO} )</td>
<td>24 (40 °C)</td>
<td>71</td>
<td>40</td>
</tr>
<tr>
<td>9</td>
<td>( \text{OH} )</td>
<td>( \text{CHO} )</td>
<td>24 (40 °C)</td>
<td>58</td>
<td>33</td>
</tr>
<tr>
<td>10</td>
<td>( \text{N} - \text{CH}_2\text{OH} )</td>
<td>( \text{N} - \text{CHO} )</td>
<td>2</td>
<td>98</td>
<td>71</td>
</tr>
<tr>
<td>11</td>
<td>( \text{S} - \text{CH}_2\text{OH} )</td>
<td>( \text{S} - \text{CHO} )</td>
<td>2</td>
<td>99</td>
<td>92</td>
</tr>
</tbody>
</table>

For Compounds 1 – 7
Turn-over Frequency (TOF) of 12.5/h were achieved, which for a RT reaction is very good.
Novel Oxidative Green Chemistry

Conclusions

- Acetamido-TEMPO is ‘locked’ in DMSO
- No over oxidation
- Amendable to hetero atoms
- Recyclable


<table>
<thead>
<tr>
<th>Entry</th>
<th>Alcohols</th>
<th>Product</th>
<th>Time (h)</th>
<th>% Conversion</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>( \text{PhOH} )</td>
<td>( \text{PhO} )</td>
<td>24 (40 °C)</td>
<td>98</td>
<td>90</td>
</tr>
<tr>
<td>13</td>
<td>( \text{MeOH} )</td>
<td>( \text{MeO} )</td>
<td>24 (40 °C)</td>
<td>87</td>
<td>74</td>
</tr>
<tr>
<td>14</td>
<td>( \text{PhOH} )</td>
<td>( \text{Ph} )</td>
<td>24 (RT/40 °C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>( \text{Ph} ) ( \text{CH}_2 ) ( \text{OH} )</td>
<td>( \text{Ph} ) ( \text{CHO} )</td>
<td>24 (RT/40 °C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>( \text{MeO} ) ( \text{Ph} ) ( \text{CH}_2 ) ( \text{OH} )</td>
<td>( \text{MeO} ) ( \text{Ph} ) ( \text{CHO} )</td>
<td>1.5</td>
<td>97</td>
<td>75</td>
</tr>
<tr>
<td>17</td>
<td>( \text{Ph} ) ( \text{CH}_2 ) ( \text{OH} )</td>
<td>( \text{Ph} ) ( \text{CHO} )</td>
<td>1.5</td>
<td>98</td>
<td>85</td>
</tr>
<tr>
<td>18</td>
<td>( \text{Ph} ) ( \text{CH}_2 ) ( \text{OH} )</td>
<td>( \text{Ph} ) ( \text{CHO} )</td>
<td>24 (40 °C)</td>
<td>95</td>
<td>84</td>
</tr>
</tbody>
</table>
**Novel Oxidative Green Chemistry**

**Solvent Re-use at ‘End-of-Life’**

\[
\text{Piperylene Sulfone (PS)} \quad \text{SO}_2 \quad \text{CHO} \quad \text{Cl} \quad \text{CHO} \quad \text{CHO}
\]

**Table:**

<table>
<thead>
<tr>
<th>run</th>
<th>conversion (%)</th>
<th>yield (%)</th>
<th>TOF (h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>96</td>
<td>33.3</td>
</tr>
<tr>
<td>2</td>
<td>95</td>
<td>88</td>
<td>31.7</td>
</tr>
<tr>
<td>3</td>
<td>85</td>
<td>82</td>
<td>28.3</td>
</tr>
</tbody>
</table>

**Additional collaborative studies ongoing ...**

---

**Piperylene Sulfone: A “Labile” and Recyclable DMSO Substitute**


*Concerted cheletropic reaction of trans-1,3-pentadiene (trans-piperylene) & SO\(_2\)*
Novel Oxidative Green Chemistry

Laccase
Novel Oxidative Green Chemistry

Laccase: Overview

Laccase

- Oxidoreductase enzyme
- Reduces $O_2$ to $H_2O$
- Concomitantly oxidizes
- MW varies 65,000-140,000.
- Carbohydrate content ~10-45 (% wt).
- Active sites near surface

Laccase employed as a novel green oxidation agent for:
- Phenols
- Allylic, benzylic alcohols
- Carbohydrates

Catalysis occurs due to 4 copper atoms/ active site

Potential for Novel Laccase Initiated Cascade Chemistry
Novel Oxidative Green Chemistry
Laccase Initiated Cascade Chemistry

The Effect of Laccase Dose on the Formation of Compound 3

The Effect of Laccase Dose on the Formation of Compound 4
Novel Oxidative Green Chemistry
Laccase Initiated Cascade Chemistry

\[
\begin{align*}
\text{MeO} & \quad \text{OH} & \quad \text{OH} & \quad \text{Laccase, O}_2 & \quad 50 \, ^\circ\text{C}, 24 \, \text{hrs} & \quad \text{MeO} & \quad \text{O} \\
1 & \quad 2 & \quad 3 & \quad 4
\end{align*}
\]

The Effect of Temperature on the Formation of Compound 3

The Effect of Temperature on the Formation of Compound 4

NR > 100 °C
Novel Oxidative Green Chemistry
Laccase Initiated Cascade Chemistry

\[
\text{MeO-}\begin{array}{c}
\text{OH} \\
\end{array} + \begin{array}{c}
\text{MeO-} \\
\end{array} \xrightarrow{\text{Laccase, } O_2} \begin{array}{c}
\text{MeO-} \\
\end{array} + \begin{array}{c}
\text{MeO-} \\
\end{array}
\]

50 °C, 24 hrs

\[
\begin{array}{c}
\text{MeO-} \\
\end{array} \xrightarrow{\text{Diels-Alder}} \begin{array}{c}
\text{MeO-} \\
\end{array}
\]

\[
\begin{array}{c}
\text{MeO-} \\
\end{array} \xrightarrow{[\text{Ox}]} \begin{array}{c}
\text{MeO-} \\
\end{array}
\]

Compound 4

\[
\begin{array}{c}
\text{MeO-} \\
\end{array} \xrightarrow{[\text{Ox}]} \begin{array}{c}
\text{MeO-} \\
\end{array}
\]

Compound 3
New green chemistry 1-pot synthesis of 1,4-naphthoquinones and related structures in water!
New green chemistry synthesis of 1,4-, 1,2-naphthoquinones and related structures employing a nonhazardous oxidizing agent, laccase, and a environmentally benign solvent, water.
Biofuel Research Challenges

SYSTEMS BIOLOGY TO OVERCOME BARRIERS TO CELLULOSIC ETHANOL

- More Available Polysaccharides
- Reduced Lignin
- In planta Enzyme Digestion

- Feedstock Engineering
- Fermentation Microbe (Ethanologen) Development
- Optimal Plant Sugars
- Reduced Toxins
- Reduced Feedstock Costs

Crosscutting Science

- Elements Analysis
- Protein Engineering
- Advanced Imaging
- Protein Machines
- Plant Science
- Soil Science
- High Sugar Yields
- Low Capital Costs
- Low Enzyme Costs
- Microbial Science
- Systems Biology
- Community Modeling
- Cellular Modeling
- Biomolecular Modeling
Biofuel

Enzymatic Hydrolysis of Cellulosics
Biofuels: Enzymatic Hydrolysis of Cellulosics

Background

I – IV Polymorphs
Amorphous
Paracrystalline

Cellulose II:

Native
Cellulose Iα and Iβ

Chains are parallel; Differences due to orientation of Cellulose sheets

Question: What role, if any, does cellulose ultra structure have on enzymatic hydrolysis?
Biofuels: Enzymatic Hydrolysis of Cellulosics

Cellulose: $I_\alpha$ is more abundant in lower plants/bacteria
$I_\beta$ is more abundant in higher plants

Analysis of Cellulose Crystallinity: X-ray, NMR, FT-IR

Assignments Chemical shift (ppm)

- Cellulose I($\alpha$) 89.5
- Cellulose I($\alpha+\beta$) 88.8
- Para-crystalline cellulose 88.3
- Cellulose I ($\beta$) 87.8
- Accessible fibril surface 84.3
- Inaccessible fibril surfaces and hemicellulose 83.7
- Accessible fibril surface 83.3
Biofuels: Enzymatic Hydrolysis of Cellulosics

Cellulase from *Trichoderma reesei*

- Cellulolytic filamentous fungus
- β-glucosidases

![Graphs showing glucose yield vs. hydrolysis time for Pulp and Avicel](image)

![Graphs showing relative intensity vs. hydrolysis time for Cellulose: I_α and I_β](image)
Biofuels: Enzymatic Hydrolysis of Cellulosics

- First study quantifying change in paracrystalline phase
- First to quantify changes in ultrastructure of kraft cellulose after cellulase treatment
- Compliments recent study by Hayashi on cellulase changes on $I_{\alpha}/I_{\beta}$

Cellulosic NMR Studies
• Provide a diagnostic analysis of reactive and resistance cellulose ultrastructure towards enzymatic hydrolysis
• Provides fundamental information for rational design of pretreatments to enhance cellulose reactivity

DARPA: Anaerobic Fermentation of Cellulosics

Cellulose Fermentation

Samples F1 and F3 were fermented with different populations of Bacteroides and Prevotella for 8 weeks
Nanolignin
Nanocellulose
Nanohemicellulose

Structures – Materials - Composites

Defining the Opportunities, Challenges, and Research Needs for NanoBiomaterials Derived from Lignocellulosics
Nanocellulose

Surface Area
Fully Exfoliated Clay ~ Cellulose Whiskers > Fumed Silica > Graphite >> Paper Fiber > E-glass Fibers

Tensile
Carbon Fibers > Cellulose Whiskers >> S-Glass > Aramid
# Nanocellulose

## Pine Cellulosic Fiber

1. **Mechanical Milling**
   - 40 mesh
2. **H^+**, 45 °C

### Crystallinity index

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Fibers – Cellulose I</td>
<td>0.61</td>
</tr>
<tr>
<td>300 – 500 nm Nanocellulose Balls - Cellulose II</td>
<td>0.65</td>
</tr>
<tr>
<td>50 – 100 nm Nanocellulose Balls - Cellulose II</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Cellulose Whiskers
- 100-250 nm length
- 5-15 nm width
Nanocellulose - Composites

Cellulose Whiskers
Cellulose 80 nm Nanoball
Acacia Fibers (0.66 mm)

Polystyrene
PLA

Acrylic Latex

Same benefits observed for Tensile and Strain Properties

Investigation into Nanocellulosics versus Acacia Reinforced Acrylic Films - Accepted in Composites Part B (Biocomposites)
Nanocellulose - Composites

- **Cellulose Whiskers**
  - Composites
    - Biodegradable, Conventional Polymers
    - Crosslinked Whiskers for Film/Barrier Properties
  - Oxidized
    - Hydrophilic Materials
  - Surface Functionalized Whiskers

- **Cellulose Balls**
  - Drug delivery
  - Templating
  - Oxidized/Sulfonated
    - Viscosity modifiers

- **Self Assembly on Paper**
  - ‘Lotus Effect’ hydrophobic coatings
Exploring The Fundamental Chemistry of Bio-Renewable Polymers

2003 – Current

Research Vision

Leader in Sustainable Polysaccharide/Lignin Chemistry

Polysaccharide/Lignin Modification

New Materials

Oligo - Polysaccharide Synthesis

New Biological Tools

Polysaccharide/Lignin Depolymerization

New Resources for Biofuels and Biopolymer
Thank You!