Title: Use of Carbohydrates and Triglycerides for the Production of Fuels and Chemical feedstocks.

Author(s): silks, Louis a

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Biological resources
Reading Room
RCRA

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Use of Carbohydrates and Triglycerides for the Production of Fuels and Chemical feedstocks.


Los Alamos National Laboratory, Bioscience and Chemistry Divisions, MS 529, Los Alamos, New Mexico, 87545, USA.
LANL Bioenergy Catalysis Programs in Bioscience and Chemistry Divisions

- **LDRD DR**
  - Biomass to Fuels
  - new start FY10
  - Gordon PI, Silks Co-PI

- **CRADA**
  - Chemical Feedstocks from Biomass
  - Silks PI

- **EERE**
  - Chemical Feedstocks from Biomass
  - Silks PI

- **LANL-TT**
  - New Biodegradable Chemical Feedstocks from Biomass
  - Ruilian Wu

- **LDRD ER**
  - Lignin Deconstruction
  - New start FY19
  - Silks PI, Hanson Co-PI

- **LDRD ER**
  - Developing a Mild Catalytic Route for the Reduction of $N_2$ to $NH_3$
  - Gordon, PI

- **NABC**
  - Fuels from Biomass via Catalysis
  - Gordon, Silks PI

- **LANL-NAABB**
  - Fuels-Chemical Conversion
  - Silks, Lodwig, Unkefer
Upgrading of Biorenewables into (High Energy Density) Fuels and Feedstocks

Non-food based sources:
agricultural residues (e.g. corn stover), dedicated energy crops, wood residues (paper mill discards), municipal paper waste

~ 200 x 10^9 tons Lignocellulose/yr

Ligno-cellulosic Biomass

Cellulose: 44%
Lignin: 26%
Hemicellulose: 30%
Other (Plentiful) Biomass Derived Molecules..

- Low cost
- Feedstock to valuable intermediates
- Low selectivity

> 1 million tons/year!
Development of effective biomass conversion technologies that integrates with existing fuel production and distribution infrastructure: shift away from our dependence on foreign petroleum imports

M. Schlaf, *Dalton. Trans.* 2006, 4645
BACKGROUND (as to how we stumbled into acetals…)  
Upgrading of Cellulosics into (High Energy Density) Fuels  
Smaller Bioderived Polyols and Lanthanide Catalyzed Dehydrations
Use of Simple Biomass Derived Polyols..?

Also require O-atom removal..

Want to avoid use of Brønsted Acids
(may want stereo - and chemo-selectivity....).

LA catalysis..

Also for dehydration chemistry, need water tolerant catalysts........

Lu(OTf)$_3$ (strongly Lewis Acidic and f$^{14}$ system)
Glycerol + Lu(OTf)$_3$ (in acetone...........)
Glycerol Protection - Acetals/Ketals as Fuel Additives

\[ \text{R}_1 = \text{R}_2 = \text{CH}_3, \text{H} \]

Energy Fuels 2010, 24, 2733

**Acetals/Ketals as Fuel Additives**

- Increased octane number
- Decreased gum formation
Experimental Comparisons

\[
\begin{align*}
\text{HO-CH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{CO}_2\text{H} & \xrightarrow{\text{[cat.]}} \text{HO-CH}_2\text{CH}_2\text{CH}_2\text{OH} \quad \text{a} \\
\text{HO-CH}_2\text{CH}_2\text{OH} \quad + \quad \text{b}
\end{align*}
\]

- Selectivity for 5-membered dioxolane \textit{in all cases}
- Lu(OTf)$_3$: 100% conversion after 1hr. at R.T., 1 mol% !
- Mechanistic explanations needed

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>RT (min.)</th>
<th>%conv</th>
<th>% Selectivity (a)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlyst-36</td>
<td>38.1-40.0</td>
<td>480</td>
<td>88</td>
<td>100</td>
<td>i</td>
</tr>
<tr>
<td>Amberlyst-15</td>
<td>70</td>
<td>15</td>
<td>95</td>
<td>100</td>
<td>ii</td>
</tr>
<tr>
<td>Zeolite beta</td>
<td>35</td>
<td>240</td>
<td>100</td>
<td>100</td>
<td>iii</td>
</tr>
<tr>
<td>[Cp*IrCl$_2$]$_2$</td>
<td>40</td>
<td>60</td>
<td>86</td>
<td>98</td>
<td>iv</td>
</tr>
<tr>
<td>Lu(OTf)$_3$</td>
<td>R.T.</td>
<td>60</td>
<td>100</td>
<td>100</td>
<td>present work</td>
</tr>
</tbody>
</table>

\[\text{Lu(OTf)$_3$: 100% conversion after 1hr. at R.T., 1 mol% !}\]

\[\text{Mechanistic explanations needed}\]

\[\text{i. J. Catal., 2007, 245, 428}\]
\[\text{ii. Green Chem., 2009, 11, 38}\]
\[\text{iv. Green Chem., 2010, 12, 2225}\]
RT Polyol Reactivity with Acetone (Small Selection…)

<table>
<thead>
<tr>
<th>Polyol</th>
<th>Product</th>
<th>Reaction time (hr)</th>
<th>NMR conversion (%)</th>
<th>Isolated Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>glycerol</td>
<td></td>
<td>1</td>
<td>99</td>
<td>83</td>
</tr>
<tr>
<td>erythritol</td>
<td>X-ray</td>
<td>3</td>
<td>94</td>
<td>88</td>
</tr>
<tr>
<td>D-sorbitol</td>
<td></td>
<td>5</td>
<td>99</td>
<td>76</td>
</tr>
</tbody>
</table>

Cyclic

| D-xylose       | X-ray   | 20*                | 90                 | 90                 |

Nucleosides

| uridine        |         | 48                 | 99                 | 81                 |

Typical conditions: 0.01 mmol Lu(OTf)$_3$; 1 mmol polyol; 10mL acetone; RT

(* = 40°C)
# RT Polyol Reactivity Evaluation (Small Selection…)

![Chemical Reaction Diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde ( (R_1=R_2=R_3=H) )</th>
<th>Conditions</th>
<th>Glycerol conversion</th>
<th>1 : 2 (in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzaldehyde ( (R_1=R_2=R_3=H) )</td>
<td>( \text{Lu(OTf)}_3 ) (0.01), ( \text{CH}_3\text{CN} ), rt, 24h</td>
<td>74%</td>
<td>40 : 60</td>
</tr>
<tr>
<td>2</td>
<td>Gd(OTf)_3 (0.01), CH_3CN, rt, 2d</td>
<td>N/A</td>
<td>42 : 58 (27% isolated, combined)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Lu(OTf)_3 (0.01), ( \text{CH}_3\text{CN} ), MS, rt, 24h</td>
<td>40%</td>
<td>83 : 17 (1h), 74 : 26 (6h)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Lu(OTf)_3 (0.01), ( \text{CH}_2\text{Cl}_2 ), reflux (39°C), 6h</td>
<td>75%</td>
<td>48 : 52</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Lu(OTf)_3 (0.01), ( \text{CH}_3\text{CN} ), reflux (81°C), 6h</td>
<td>70%</td>
<td>42 : 58</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Lu(OTf)_3 (0.01), ( \text{CH}_3\text{CN} ), MS, reflux (81°C), 6h</td>
<td>~100%</td>
<td>58 : 42 after cooling/standing</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Tolualdehyde ( (R_1=R_3=H, R_2=\text{CH}_3) )</td>
<td>( \text{Lu(OTf)}_3 ) (0.01), ( \text{CH}_3\text{CN} ), rt, 48h</td>
<td>52%</td>
<td>44 : 56 (36% combined, isolated)</td>
</tr>
<tr>
<td>8</td>
<td>Mesitaldehyde ( (R_1=R_2=R_3=\text{CH}_3) )</td>
<td>( \text{Lu(OTf)}_3 ) (0.01), ( \text{CH}_3\text{CN} ), rt then 80°C, 3d</td>
<td>34%</td>
<td>33 : 67</td>
</tr>
<tr>
<td>9</td>
<td>( \rho )-Anisaldehyde ( (R_1=R_3=H, R_2=\text{OCH}_3) )</td>
<td>( \text{Lu(OTf)}_3 ) (0.01), ( \text{CH}_3\text{CN} ), rt, 4d</td>
<td>23%</td>
<td>38 : 62</td>
</tr>
<tr>
<td>10</td>
<td>( \omega )-Anisaldehyde ( (R_1=R_3=H, R_2=\text{OCH}_3) )</td>
<td>( \text{Lu(OTf)}_3 ) (0.01), ( \text{CH}_3\text{CN} ), rt, 4d</td>
<td>80%</td>
<td>40 : 60</td>
</tr>
<tr>
<td>11</td>
<td>4-Fluorobenzaldehyde ( (R_1=R_3=H, R_2=\text{F}) )</td>
<td>( \text{Lu(OTf)}_3 ) (0.01), ( \text{CH}_3\text{CN} ), rt, 18h</td>
<td>92%</td>
<td>33 : 67</td>
</tr>
<tr>
<td>12</td>
<td>4-Hydroxybenzaldehyde ( (R_1=R_3=H, R_2=\text{OH}) )</td>
<td>( \text{Lu(OTf)}_3 ) (0.01), ( \text{CH}_3\text{CN} ), rt, 18h</td>
<td>23%</td>
<td>41 : 59</td>
</tr>
</tbody>
</table>
RT Polyol Reactivity Evaluation (Small Selection…)

Peak assignment ref: Journal of Catalysis 2007, 245, 428
**Water Sensitivity Evaluation (Small Selection...)**

\[
\text{HO-} \begin{array}{c}
\text{OH} \\
\text{OH} \\
\text{OH}
\end{array} + \quad \begin{array}{c}
\text{O}
\end{array} \\
10.0 \text{ mL}
\]

1.0 mmol

\[\text{Lu(OTf)}_3 \quad (0.01 \text{ mmol})\]

\[\begin{array}{c}
\text{HO-} \\
\text{O} \\
\text{O}
\end{array} \quad \text{?}
\]

<table>
<thead>
<tr>
<th>H\text{O added}/\text{mL}</th>
<th>Time to completion/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1</td>
</tr>
<tr>
<td>0.020</td>
<td>1</td>
</tr>
<tr>
<td>0.050</td>
<td>2</td>
</tr>
</tbody>
</table>

\[1.5 \quad 1.4 \quad \text{ppm}\]
Comparison (Small Selection...)

\[
\text{HO-\text{OH-\text{OH + \text{O}}}} \quad 1 \text{ mol\% cat.} \quad \text{rt} \quad \text{HO-\text{O-\text{O}}}
\]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>time</th>
<th>% conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p\text{-TsOH})</td>
<td>0.5 h</td>
<td>&gt; 99 *</td>
</tr>
<tr>
<td>(\text{Lu(O\text{Tf})}_3)</td>
<td>1.0 h</td>
<td>&gt; 99</td>
</tr>
</tbody>
</table>

* Reverse reaction competes

\[
\text{HO-\text{OH-\text{OH + \text{O}}}} \quad 1 \text{ mol\% cat.} \quad \text{rt} \quad \begin{array}{c}
\text{a} \\
\text{b}
\end{array}
\]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>time</th>
<th>(a : b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p\text{-TsOH})</td>
<td>1.5 h</td>
<td>86 : 14</td>
</tr>
<tr>
<td>(\text{Lu(O\text{Tf})}_3)</td>
<td>3.0 h</td>
<td>&gt; 99 : 0</td>
</tr>
</tbody>
</table>

\[
\text{HO-\text{OH-\text{OH + ^13C-pa}raformaldehyde}} \quad 1 \text{ mol\% Lu(O\text{Tf})}_3 \quad \text{CH}_3\text{CN, 24 h reflux (81 - 82°C)} \quad \text{HO-\text{O-\text{O}} + ^13C-\text{OH}}
\]
Future Work

\[ \text{1 mol\% Lu(OTf)}_3 + 2 \text{ mol} + 2 \text{ H}_2\text{O} \rightarrow \text{5-membered product: 100\% selectivity} \]

\[ \text{R.T., 30 min.} \]

\[ \text{1 mol\% Lu(OTf)}_3 + 2 \text{ mol} + 2 \text{ H}_2\text{O} \rightarrow \text{6-membered product: 100\% selectivity} \]

\[ \text{R.T., 24 hr.} \]

Why is stereoselectivity reversed with benzaldehyde?

MD Simulations

Glycerol/hemiketal/ketal binding modes?

H\textsubscript{2}O/Acetone solvation?

Role of OTf\textsuperscript{−} counterions?
Acknowledgements

Theory
- Aaron W. Pierpont
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Experimental
- Weizhong Chen
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