Catalytic Solubilization and Conversion of Lignocellulosic Feedstocks

**LANL Team**
T.A. Semelsberger (P.I.), Kevin C. Ott (Co-PI), Rod L. Borup, & Roshan Shrestha

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LANL Project Overview

**Timeline**
- Project Start Date: FY07
- Project End Date: FY08
- Percent Complete: 100%

**Budget**
- Total Project Funding: 500K
- Project End Date: FY2008
- Funding:
  - 2007: $200K
  - 2008: $300K
  - 2009: $0K*

**Barriers**
- Barriers Addressed
  - *Feedstock Cost and Availability*
  - *Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology*

**Partners**
- None

*EERE Hydrogen Production and Delivery Budget Zeroed Out*
LANL Project Objectives

Project Objective

Develop novel low temperature chemical routes and catalysts to produce hydrogen/syngas from lignocellulosic feedstocks

Target: By 2012, reduce the cost of hydrogen produced from biomass gasification to $1.60/gge at the plant gate (<$3.30/gge delivered). By 2017, reduce the cost of hydrogen produced from biomass gasification to $1.10/gge at the plant gate ($2.10/gge delivered).

The most abundant constituent of biomass is lignocellulosic (~80%). Discovering new chemistries and catalysts that can convert lignocellulosic into hydrogen/syngas will be critical if biomass is to be used as a feedstock for hydrogen or other alternative fuels.

Lignocellulosic depolymerization/decomposition is the most process intensive (and most challenging) constituent of biomass to convert to hydrogen/syngas.
## LANL Project Milestones

### Milestones: Catalytic Solubilization and Conversion of Lignocellulosic Feedstocks

<table>
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<tr>
<th>Milestone</th>
<th>FY07 (200K)</th>
<th>FY08 (300K)</th>
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<td>Cellulosics conversion to syngas mechanism</td>
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<td>Lignin solubilization and conversion</td>
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<tr>
<td>Cellulose solubilization/depolymerization</td>
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<td>Preliminary study of reduced intensity lignin gasification</td>
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LANL Project Approach

In general terms, LANL is in search of novel hydrogen/syngas production routes from lignocellulosics. Two approaches will be explored:

• Catalytic solubilization of lignocellulosics to generate a sugar feedstock stream for downstream APR, and
• Solubilization of lignocellulosics followed by APRxn of oligomeric, soluble cellulose.

LANL will conduct screening experiments for evidence of direct aqueous-phase low-temperature reforming of lignocellulosics to hydrogen/syngas through the use of catalysts designed to cleave carbon-carbon bonds of the cellulose backbone. Tandem catalysis approaches, where two catalysts or processes are linked together in a single reaction vessel, will be explored to demonstrate “one-pot” cellulose solubilization followed by aqueous phase catalytic reforming to generate hydrogen. This is important in that if catalysts can be found that will generate hydrogen directly from soluble cellulose oligomers, this provides a ‘one-pot’ approach and offers increased utilization of residual biomass, increased efficiency and the potential for cost reductions both in feedstock and in capital equipment. LANL’s approach to producing hydrogen from lignocellulosics (i.e., middle and bottom routes) is represented by the chemical routes shown in Figure 1 (next slide).
Figure 1. A rudimentary diagram showing LANL’s approach to producing bio-syngas (i.e., hydrogen and carbon monoxide) from lignocellulosics.
LANL Technical Accomplishments and Progress

Accomplishments

• Demonstrated heterogeneous catalyzed hydrolysis of cellobiose to glucose.

• Demonstrated the conversion of cellobiose to syngas [albeit at low conversions (~5%)]

• Demonstrated catalytically enhanced decarboxylation of lignin.

• Performed baseline characterization studies on model compounds (i.e., lignin and cellobiose)

• Demonstrated low temperature catalyzed gasification of lignin
LANL Overview of Scoping Experiments

- Flow reactor system for liquid conversion (bench-scale)
- Batch reactors for liquid/solid conversion (bench-scale)

- Scoping experimental results
  - Liquid phase conversion
    • (Glucose, Cellobiose)
  - Solid phase mass conversion
    • (Lignin, Pine)
  - Residual solids analysis
    • TGA (thermal gravimetric analysis)
    • NMR
    • FTIR (molecular vibrational frequencies)
  - Product analysis
    • LC (liquid chromatograph)
    • Gas Analysis
Conversion of Liquid Phase

- Heterogeneous catalytic conversion of soluble phase
  - Glucose and Cellobiose to vapor phase products
- Homogeneous catalytic conversion of model cellulose
  - Cellobiose as model compound to demonstrate solubization
- Operation
  - Flow reactor
    - Well defined conditions (control of T, P, flows)
    - Gas analysis
  - Batch reactors – closed system
    - Reactants loaded, put in oven
      - $T = 100 – 275 \degree C; 4 – 18$ hrs
    - Post analysis
  - Catalysts
    - Base metals, noble metals with Lewis acid supports ($Al_2O_3, \text{ zeolites}$)
    - Ln Triflates, perfluorosulphonic acid as homogeneous Lewis acids
Liquid Chromatography Analysis

Observations:
• Unidentified liquid phase products (trace)
• Products primarily in vapor phase

Reactant: Glucose  Catalyst: Pt
Batch Reactor Conditions:
\[ T_{rxn} = 100 \, ^{\circ}\text{C}, t_{rxn} = 18 \, \text{hrs} \]
Conversion: \(~68\%\)

**Glucose**

Area = 7.8 e6

(standard)

**Glucose**

Area = 2.5 e6
Liquid Chromatography Analysis (cont’d)

Reactant: Cellobiose  Catalyst: None
Batch Reactor Conditions:
$T_{rxn} = 100 \, ^\circ C$, $t_{rxn} = 18 \, hrs$
Conversion: $\sim 13.8\%$

Reactant: Cellobiose  Catalyst: Pt/Rh
Batch Reactor Conditions:
$T_{rxn} = 100 \, ^\circ C$, $t_{rxn} = 18 \, hrs$
Conversion: $\sim 42\%$
Observations:
• Unidentified liquid phase products (trace)
• Products primarily in vapor phase
Liquid analysis indicates heterogeneous conversion of Glucose and Cellobiose
Digestion of Cellulose with LnX₃

Can Lanthanide Salts LnX₃ (X = OTf, Cl) act as hydrolysis catalyst?

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Cellobiose as a Model for Cellulose

**NMR Analysis**
- Anomeric carbons $C_1$ and their associated protons give distinct and easily tracked resonances in the $^{13}$C and $^1$H NMR.
- Expect 3 signals for cellobiose: $n$, $\alpha$ & $\beta$
- Expect 2 slightly shifted signals for glucose: $\alpha$ & $\beta$
Catalyzed Hydrolysis of Celllobiose to Glucose

**13C NMR**

- **Celllobiose only (control)**
- **Celllobiose + Gd(OTf)₃**

Anomeric carbon signals:
- $C_1(n)$, $C_1(α/β)$ and $C_1(α/β)$

Gd(OTf)₃ (1 mol%)
Celllobiose (0.33 mol/L in water)
(120 °C for 13 h)

Next Slide: Compare anomeric carbon signals
Catalyzed Hydrolysis of Cellobiose to Glucose

\[ \text{Cellobiose only (control)} \]

- Blue = cellobiose
- Red = glucose

\[ \text{Cellobiose + Gd(OTf)}_3: \]

\[ \text{Gd(OTf)}_3 \text{ (1 mol\%)} \]

Cellobiose (0.33 mol/L in water)

(120 °C for 13 h)

\[ \text{~ 75 \% conversion to free glucose without significant decomposition} \]

\[ \text{< 5 \% conversion to free glucose} \]
Catalyzed Hydrolysis of Cellulose (Aqueous Suspension)

- Lewis acid catalysis shows substantially enhanced hydrolysis in the presence of LnX₃.
- Cellobiose is a good model compound.

**Top:** Cellulose in D₂O (both spectra on same scale with identical conditions)
- H(α) free glucose
- H(β) free glucose
- Ring protons of free glucose and water soluble oligomers
- Free aldehydes & enones

**Bottom:** Cellulose & Lu(OTf)₃ in D₂O
- Lu(OTf)₃ (~1 mol%)
- (150 °C for 20 h)
Solid Phase Conversion of Lignin

Enhanced catalytic conversion of solids, But rates too slow
Lignin Gasification Product Distribution

Batch Operation: Pine Treatment @ 225°C for 18 hrs

Gas Analysis post batch reactor operation

$N_2$ from air in overhead reactor space
Lignin Gas Phase Product Ratios

Desired products:
CO > H2 > CH4
Major products are not alkanes

Should have ~
equilibrium via W.G.S.
reaction between H₂, CO, CO₂, H₂O
Likely losing H₂ via reactor septum
Liquid Analysis of Lignin products

Lignin + H2O
Treatment @275 °C for 18 hrs

Lignin + Gd Triflate
Treatment @275 °C for 18 hrs

Significant reduction in higher residence time species when catalyzed by Gd Triflate
TGA of Lignin Residue After Various Treatments

- Lignin Blank
- Lignin + Gd Triflate
- Lignin + H2O2
- Lignin + perfluorosulfonic acid

Oxidation of Lignin remains unchanged

Atmosphere: Air
TGA of Lignin Residue after Various Treatments

- Decomposition of Lignin
  - Most cases unchanged
  - via a different mechanism for Lignin + Gd Triflate

Atmosphere: N₂
TGA of pine in an Oxidizing Atmosphere (Air)

Fresh pine shows loss of lower molecular weight HC’s

Oxidation of treated pine remains unchanged
TGA of Pine in inert atmosphere ($\text{N}_2$)

Fresh pine shows loss of lower molecular weight HC’s

Decomposition mechanism unchanged with La Triflate
TGA and Evolved Gas Analysis: Lignin Treated with Yb Triflate

Batch Operation: Pine Treatment @ 275°C for 18 hrs

No evolution of higher molecular weight compounds
DRIFTS: Fresh Lignin

DRIFTS: Diffuse Reflectance Infrared Fourier Transform Spectroscopy
DRIFTS of Lignin with Decomposition

Decomposition of Lignin

Loss of hydroxyl species

Loss of specific vibrational features

Fresh Lignin Hydrolytic $T = 25^\circ C$

Lignin Fresh Hydrolytic $T = 600^\circ C$
Comparison of Fresh and Treated Lignin (300 °C)

Fresh and treated lignin (300 °C)

Change in relative quantities of functionalities
DRIFTS of Fresh Pine and Thermally Treated

- Fresh Pine T=21.4°C
- Fresh Pine after Thermal Treatment at 600°C

Loss of hydroxyl species
SS-NMR of Fresh Lignin
C$^{13}$ SS-NMR of Fresh Lignin

Shift (ppm)

C$^{13}$ NMR Signal

- H$_3$CO
- OH
- OCH$_3$
- HOH$_2$C
- “S”
- OCH$_3$
- OH
- HOH$_2$C
- “G”
- O
- OH
- OH
- CH$_3$
- COCH$_3$
- O
- H$_3$C
Low Temperature Catalytic Pyrolysis/Gasification of Lignin

Catalysts show a reduction in temperature required for hydrogen production (reduce the activation energy for the reaction)

(Unclassified)

Tramp rate = 5°C/min, N₂ purge rate = 30 ml/min
LANL Project Summary

• Conversion of cellobiose to glucose is feasible, but rates currently too low
• Lignin hydrophobicity is a critical challenge for APRxn processes
• Recent results of low temperature catalyzed pyrolysis of lignin shows potential
  ➢ Mechanism of the low temperature catalyzed pyrolysis of lignin currently unknown
• Heterogeneous catalysis of glucose and cellobiose
  ➢ Relatively high conversions during batch reaction (~60 – 90%)
  ➢ Major products appear to be gas phase for heterogeneous catalysis
• Homogeneous catalysis of cellobiose hydrolysis to glucose without significant decomposition and/or caramelization
  ➢ Aqueous cellulose suspension marginally hydrolyzed to free glucose
• Solid conversion of Lignin & Pine increased by Lewis Acid catalysis
  ➢ Gas phase products tend to syngas rather than alkanes
  ➢ Minimal structural change of remaining Lignin (TGA, NMR, DRIFTS)
    — Some change in vibrational structure with La Triflate
  ➢ Lignin/Gd Triflate demonstrates different decomposition mechanism
LANL Proposed Future Work* (FY09)

• Continue screening for novel hydrogen production catalysts
• Explore conversion chemistry of model monolignols
  ➢ Develop heterogeneous catalyst for aqueous phase reactions
• Continue to explore lignin solubilization and pyrolysis
  ➢ Investigate hydrophobic/hydrophilic effects on reaction chemistry of lignin
  ➢ Improve homogeneous catalyst formulations

*Due to EERE Hydrogen Production and Delivery’s budget being zeroed out, LANL is not currently funded for FY09
Obstacles to Lignocellulosic Conversion

- Conversion of solubilized hydrocarbons to vapor phase
- Conversion of model compounds simulating solubilization
- Unknown reactivity as a function of lignin pretreatment
- Lignin Solubilization
  - Interactions with catalysts limited
  - Hydrophobicity
  - Steric hinderance
- Conversion chemistry
  - Reaction mechanisms not understood
- Innovation in chemistry and catalysis
- Innovation in reactor design and reaction engineering
Hydrogen, Fuel Cells & Infrastructure Technologies Program: Hydrogen Production and Delivery
Program Manager: Richard Farmer