

Catalytic Solubilization and Conversion of Lignocellulosic Feedstocks

PD042

LANL Team

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LANL Project Overview

Timeline

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

Budget

- Project End Date: FY2008
- Funding:
 - 2008: \$300K
 - 2009: \$0K*
 - 2010: \$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 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).

LANL Project Approach (cont'd, Figure 1)

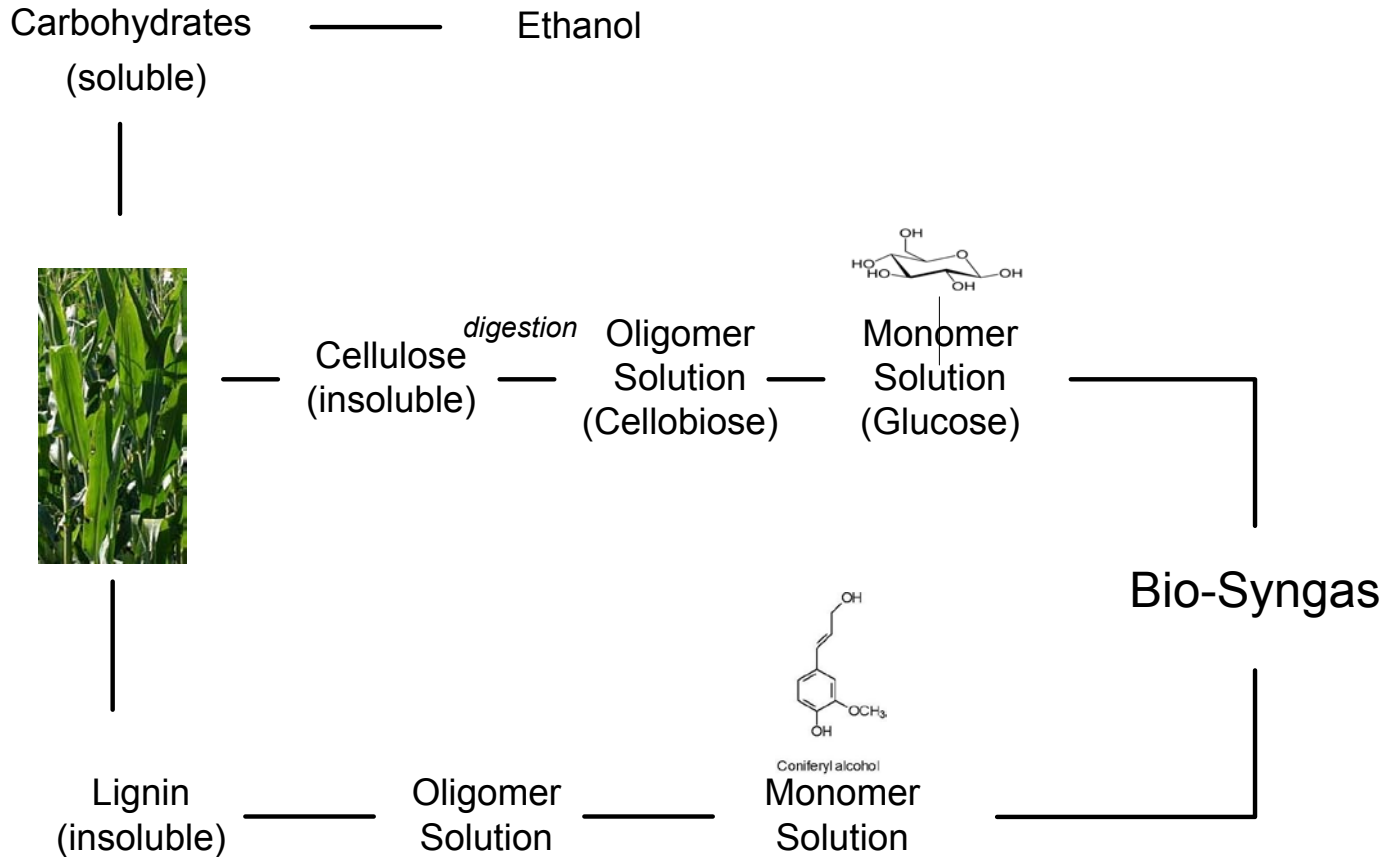


Figure 1. A rudimentary diagram showing LANL's approach to producing bio-syngas (i.e, hydrogen and carbon monoxide) from lignocellulosics

LANL Technical Accomplishments and Progress

Accomplishments for FY2007-2008

Cellulose

- Demonstrated heterogeneous catalyzed hydrolysis of cellobiose to glucose
- Demonstrated the conversion of cellobiose to syngas [albeit at low conversions (~5%)]

Lignin

- 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

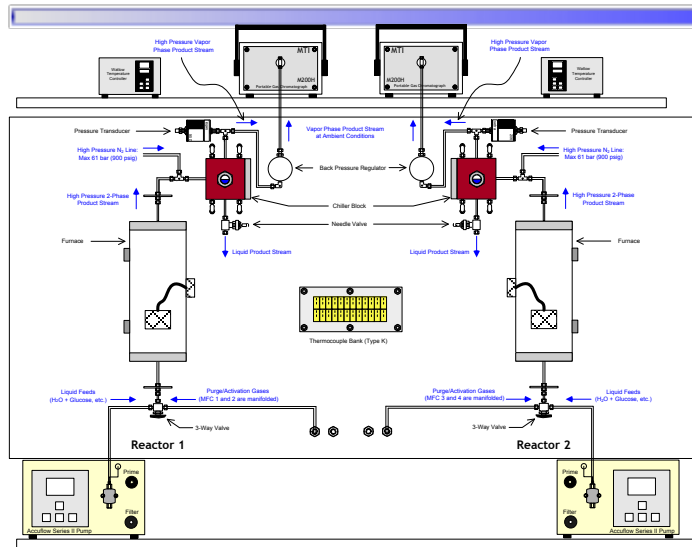
LANL Overview of Scoping Experiments Performed in FY07-08

- 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 Oligomeric Cellulose

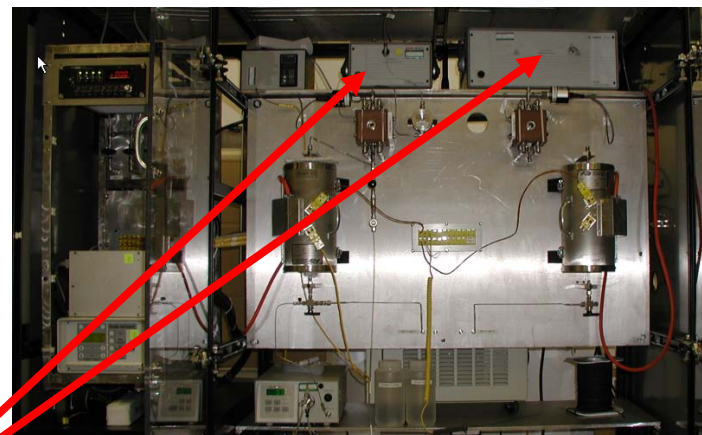
- Heterogeneous catalytic conversion of soluble phase
 - Glucose and Cellobiose to vapor phase products
- Homogeneous catalytic conversion of model cellulose
 - Cellobiose as model compound to demonstrate solubization
- Operation
 - Flow reactor
 - Well defined conditions (control of T, P, flows)
 -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

Analytical Tools Employed for Biomass Research



Multi-phase flow reactor

- T = 20-1000°C
- P = 1-60 atm



Additional Analytical Tools

- Liquid NMR
- Solid-state NMR
- Solid-state DRIFTS

Additional Reactors

- Multi-well batch reactors for rapid screening

Gas Chromatograph (GC)

- Gas analyses

Liquid Chromatograph (LC)

- Liquid analyses

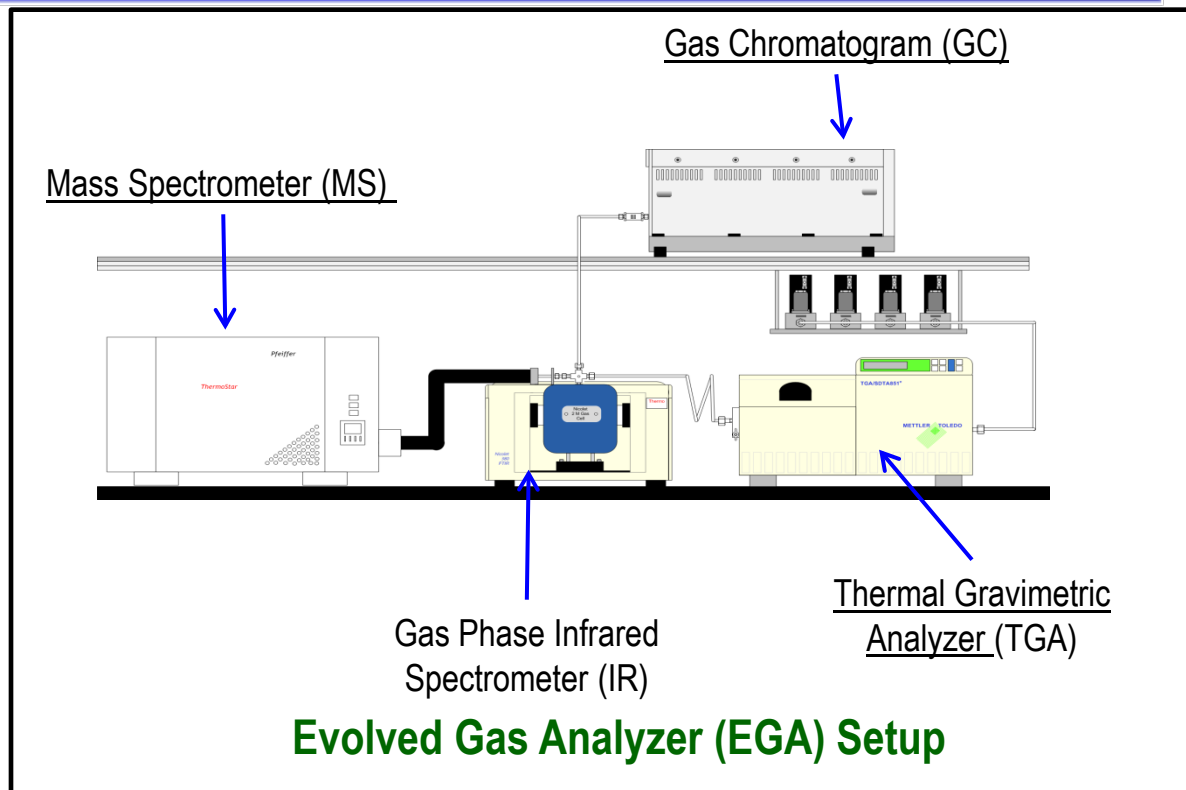


Analytical Tools Employed for Biomass Research

EGA Capabilities

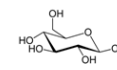
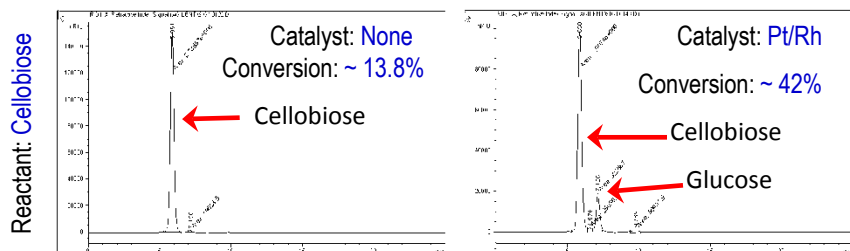
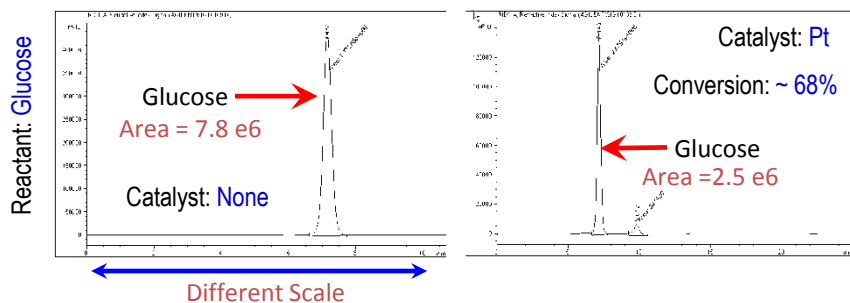
- Measure mass changes as function of temperature
- Correlate mass changes with evolved gas
- Identify evolved gases with IR, MS, and GC

EGA system facilitates a deeper understanding of the reaction rates and chemistry



Our suite of analytical tools allow us to gain insight into the fundamental processes of biomass pretreatment and hydrogen production from biomass, thus allowing for tailor-made, energy efficient, cost-effective processes for biomass utilization

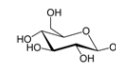
Aqueous Phase Oligomeric-Cellulose Reforming



Monomer
Solution
(Glucose)

→ Biosyngas

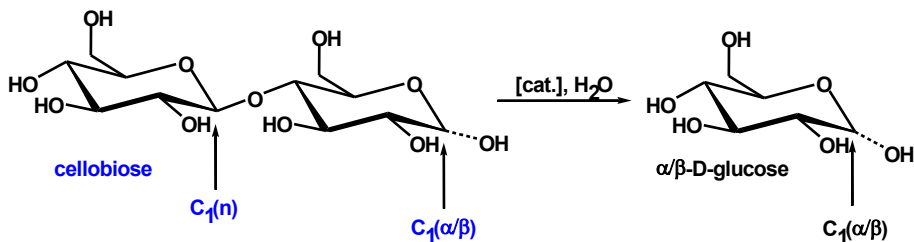
Glucose conversion to vapor phase products and trace liquid phase products




Monomer
Solution
(Glucose)

Cellulose Oligomer → Monomer Solution → Biosyngas

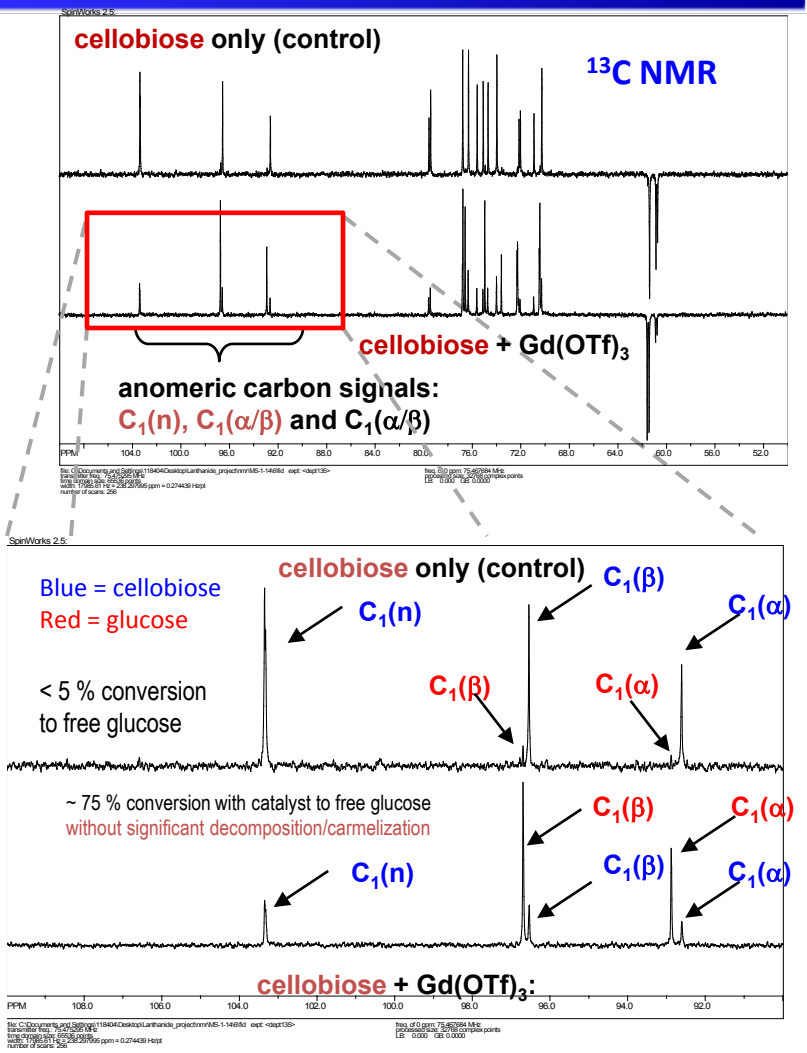
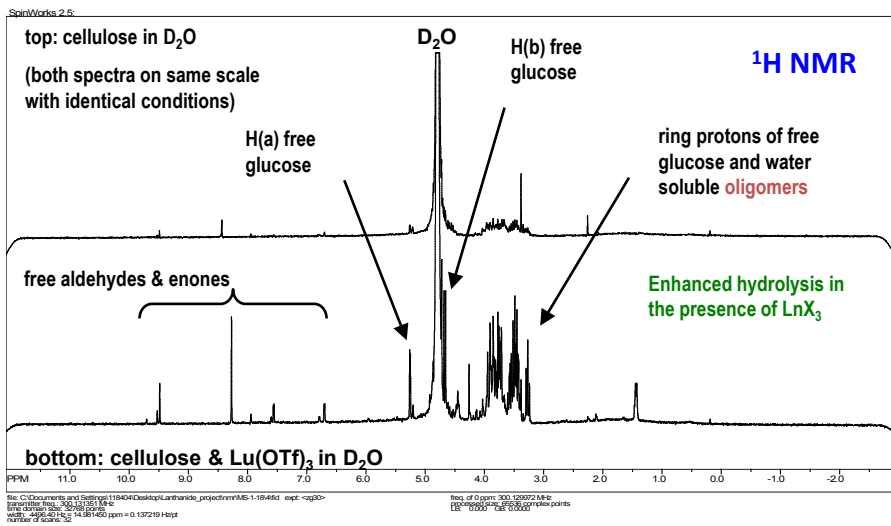
Oligomeric-cellulose conversion to glucose, vapor phase products and trace liquid phase products



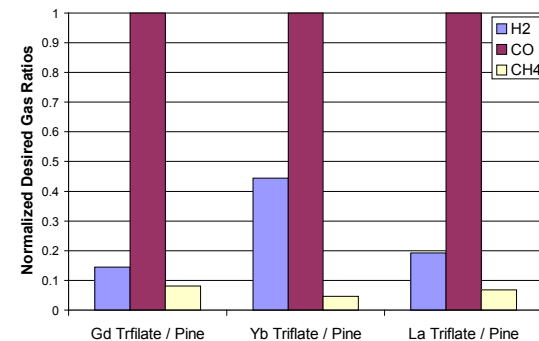
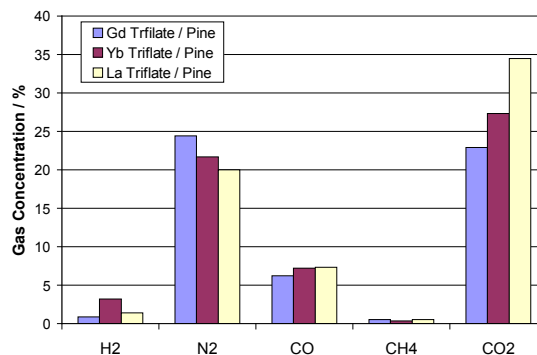
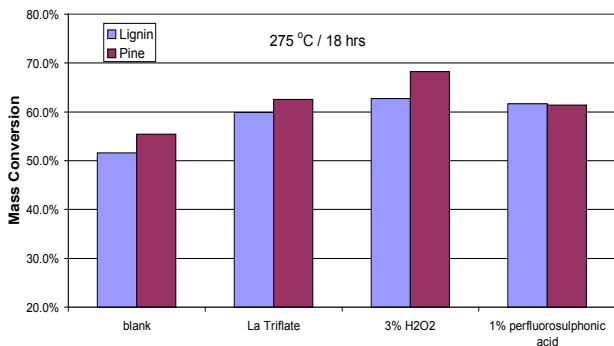
Catalyzed Hydrolysis of Cellobiose to Glucose



Lewis acid catalysis performs hydrolysis of cellulose to glucose

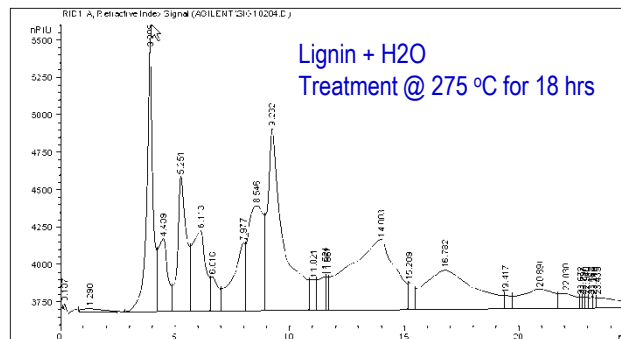
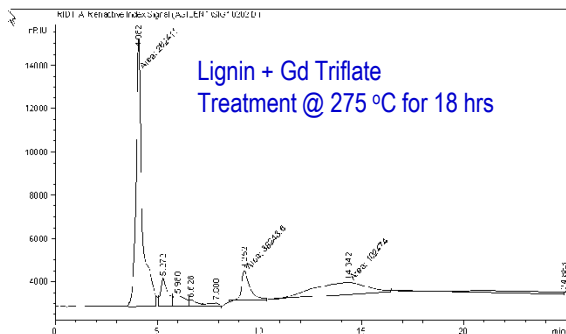


Solid Phase Conversion of Lignin



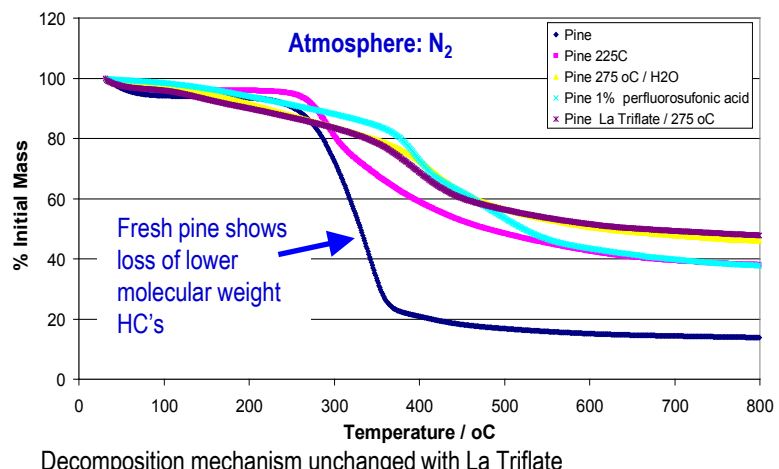
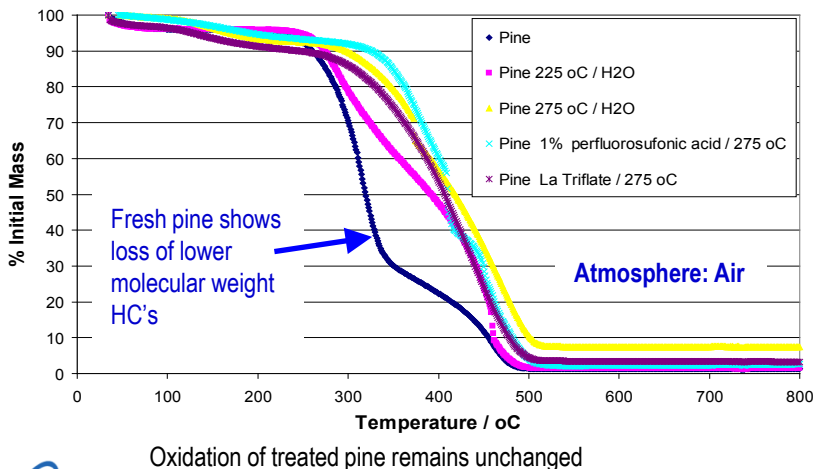
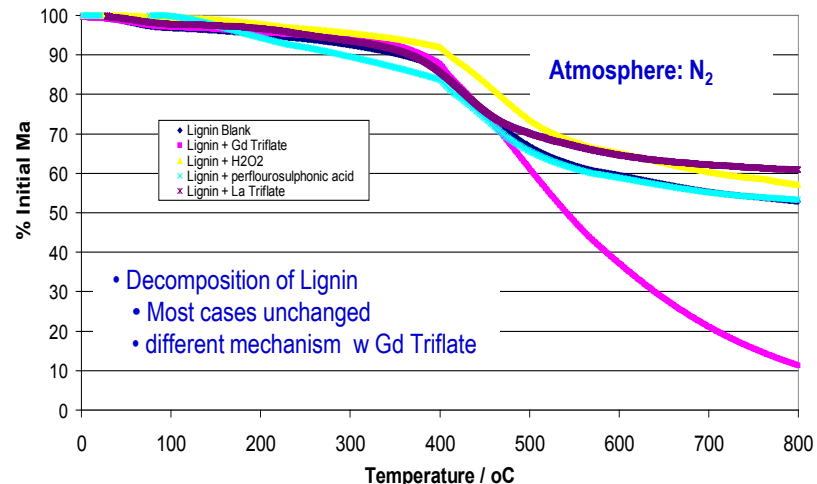
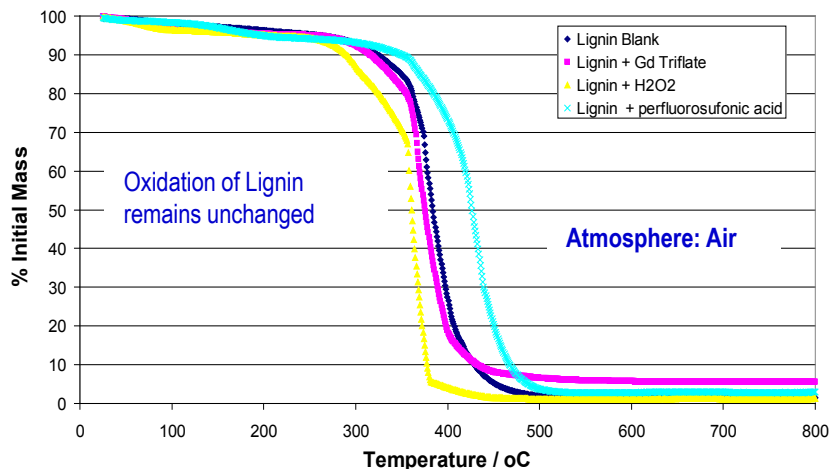
Gas Analysis post batch reactor operation
(N₂ from air in overhead reactor space)

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



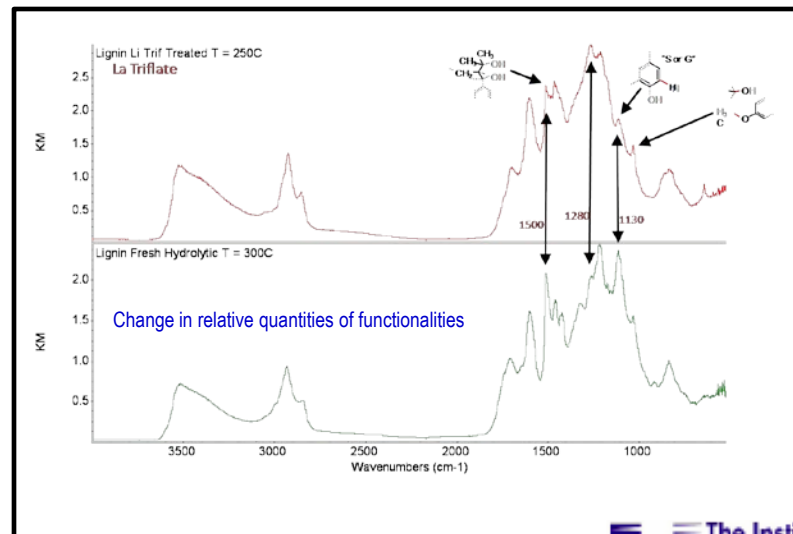
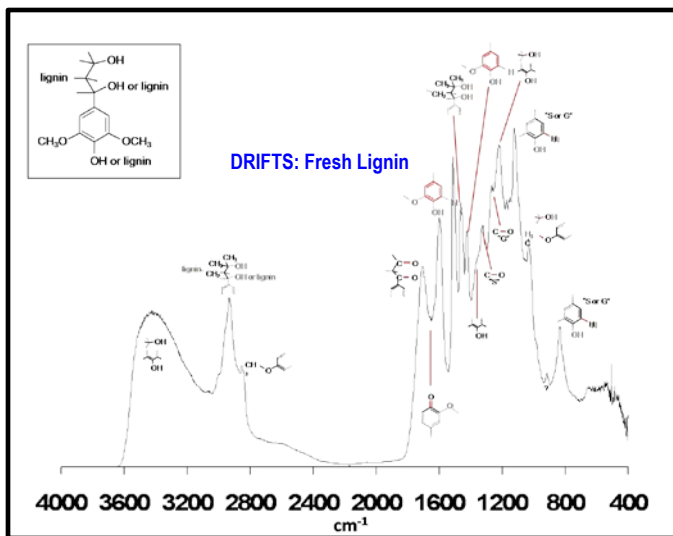
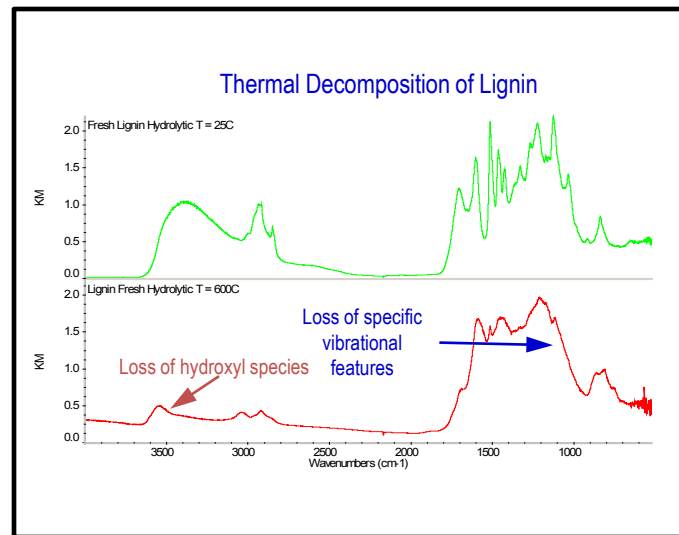
Enhanced catalytic conversion of solids, but rates slow

TGA of Lignin Residue After Various Treatments



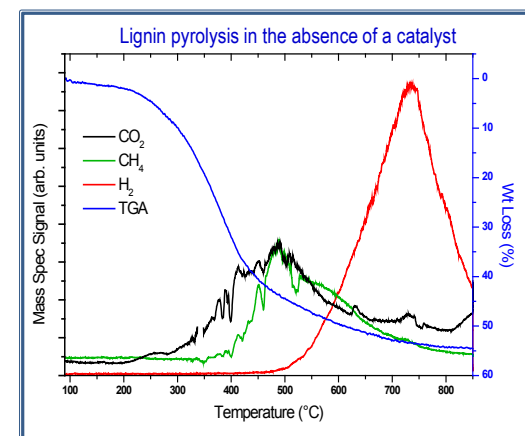
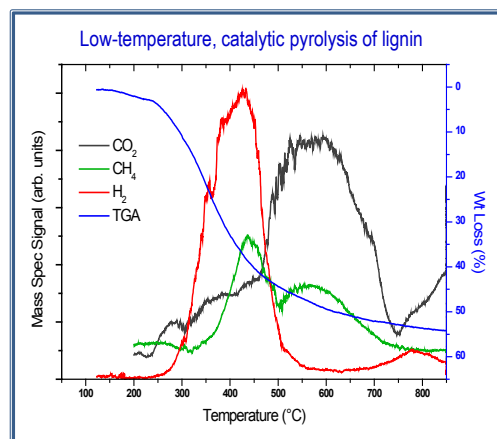
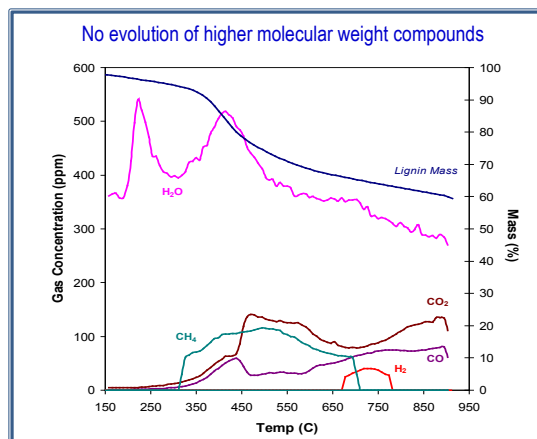
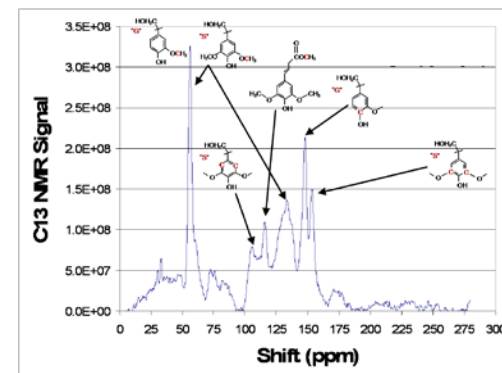
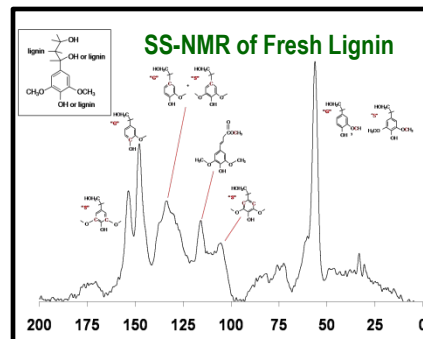
TGA and Evolved Gas Analysis: Lignin Treated with Yb Triflate

Observed changes in lignin DRIFTS spectrum after various pretreatments
 ➔ chemistry is occurring



TGA and Evolved Gas Analysis: Lignin Treated with Yb Triflate

Observed changes in SS-NMR spectrum after various pretreatments
➔ chemistry is occurring



➔ Catalysts show a reduction in temperature required for hydrogen production

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

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 hindrance
- **Conversion chemistry**
 - Reaction mechanisms not understood
- **Innovation in chemistry and catalysis**
- **Innovation in reactor design and reaction engineering**
- Current approaches use highly corrosive bases (>10 molar) requiring costly materials of construction

LANL Future Work (FY10/11)

- Continue screening for novel low-temperature biomass gasification catalysts
- Explore conversion chemistry of oligomeric cellulose in phase transfer media
- Explore lignin solubilization and catalytic conversion chemistry of lignin in phase transfer media (*PRIMARY FOCUS*)

➤ Obstacles addressed:

- 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
- Eliminate highly corrosive solvents and/or reactants
- Reduce process cost
- Increase process efficiency

LANL Future Work: Envisioned Process

➤ Biomass Digestion Tank:

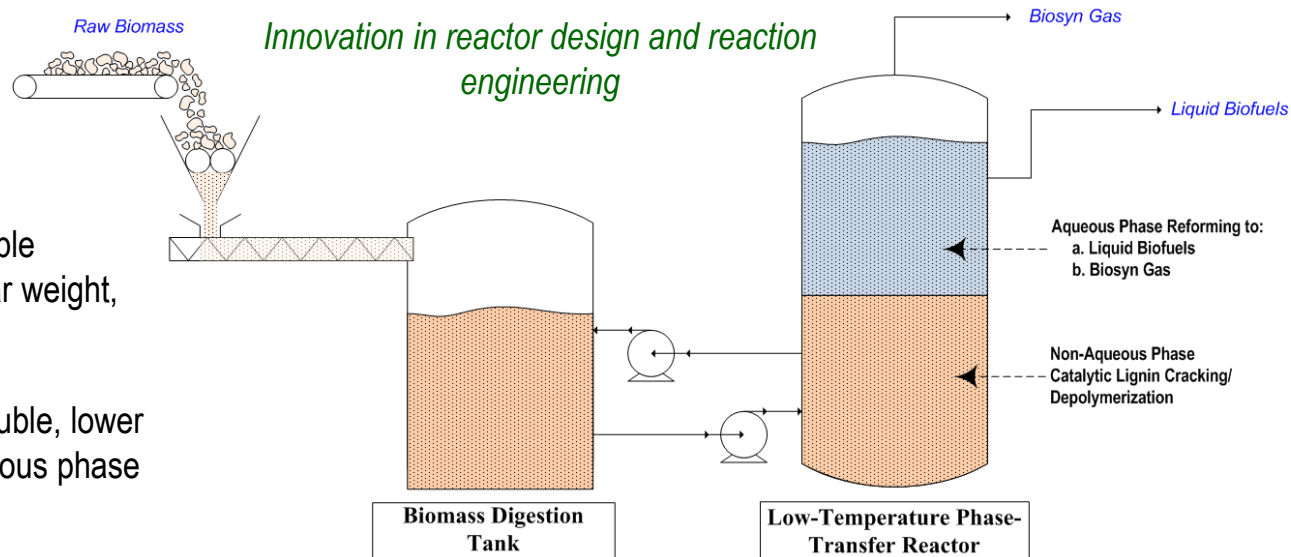
Complete dissolution of raw biomass

➤ Non-Aqueous Phase Reactor:

Soluble biomass is cracked into lower molecular weight, water-soluble species

➤ Aqueous Phase Reactor:

Water-soluble, lower molecular weight species react in aqueous phase producing biosyn gas or liquid biofuels



❖ Requirements for process viability

1. A non-corrosive, cheap solvent required to dissolve/digest raw lignin, making lignin tractable
[Lignin Solubilization, Reduce process cost]
2. An active, durable, cheap water-insoluble catalyst required for cracking lignin into water-soluble oligomers
[Innovation in chemistry and catalysis, Innovation in reactor design and reaction engineering, & Increase process efficiency]
3. Reaction chemistries and mechanisms must be understood to optimize process viability and reduce cost
[Innovation in chemistry and catalysis, Innovation in reactor design and reaction engineering, & Increase process efficiency]

LANL Future Work: Biomass Digestion Tank Chemistry

➤ Biomass digestion tank

- Lignocellulosics are cross-linked by extensive intra- and inter-chain hydrogen bonds
- Solvents that can break up the hydrogen bond network are known to solubilize lignocellulosics
- Ionic liquids are known to have the ability to solubilize lignocellulosics in this way

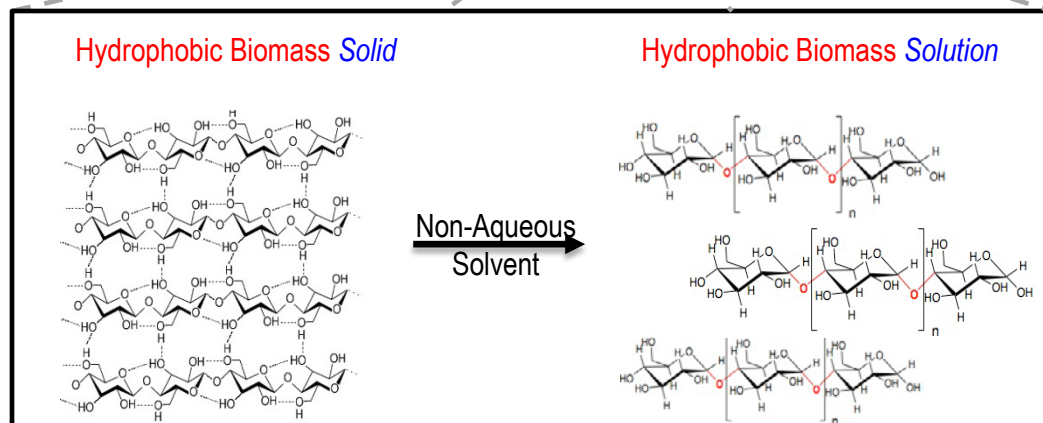
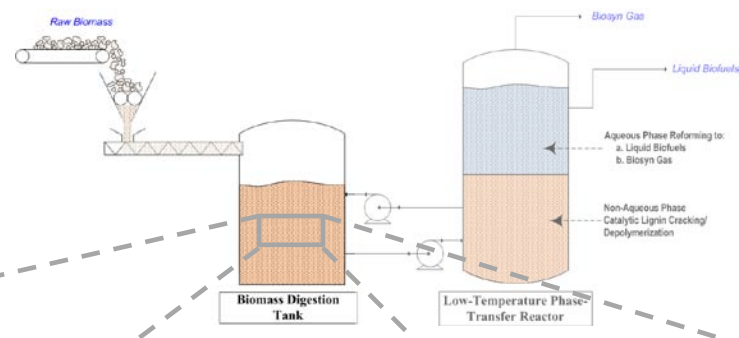
➤ LANL has demonstrated experimentally the dissolution of lignin, keratin, cellulose, and pine dust in various non-aqueous media

➤ Literature precedents



Cellulose film containing entrapped laccase (2.78% w/w) formed using the IL-dissolution and reconstitution treatment, before (left) and after (right)

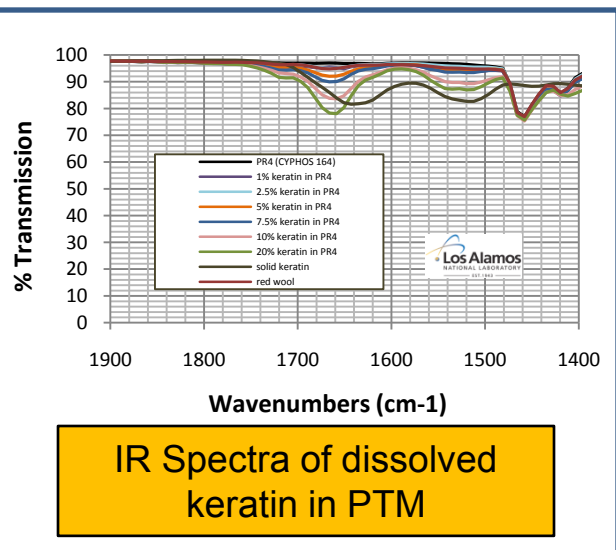
*M. Turner, et al *Biomacromolecules*. Vol: 5, 1379-1384 (2004)



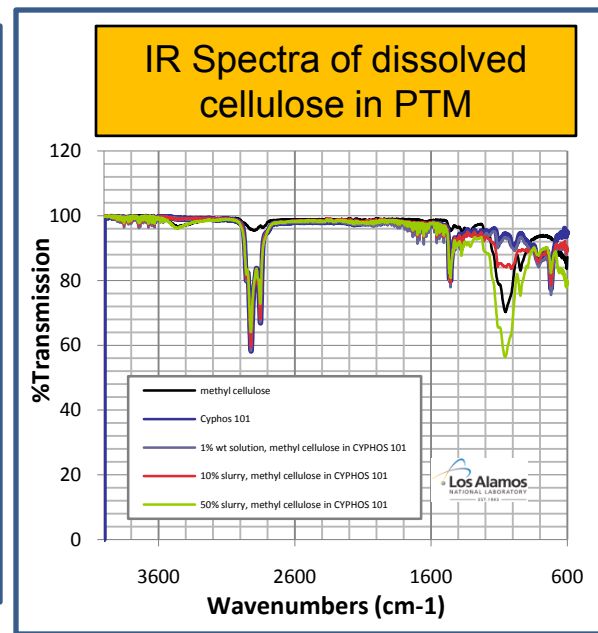
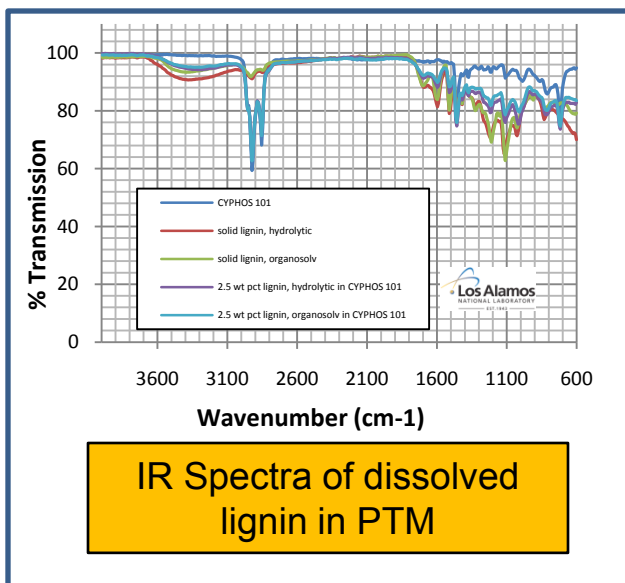
LANL Future Work: Biomass Digestion Tank Chemistry

➤ Biomass digestion tank

- LANL has demonstrated experimentally the dissolution of lignin, keratin, cellulose, and pine dust in various non-aqueous media



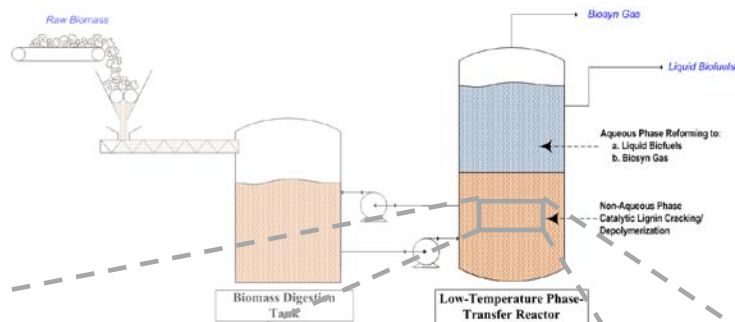
- Liquid phase IR capable of detecting and quantifying extents of dissolution of keratin, lignin, and cellulose
 - ✓ We will also employ this technique to track the cracking of lignin and cellulose into lower MW oligomers



LANL Future Work: LT Phase Transfer Chemistry

➤ LT Phase Transfer Reactor (LT-PTR)

- PTM catalyst in presence of trace water partially hydrolyses cellulose
- Produces water-soluble lower MW oligomers of cellulose and lignin



➤ Water-immiscible ILs

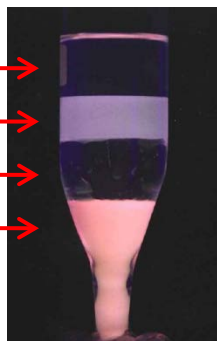
- Known and demonstrated at LANL

PTM Phase 1

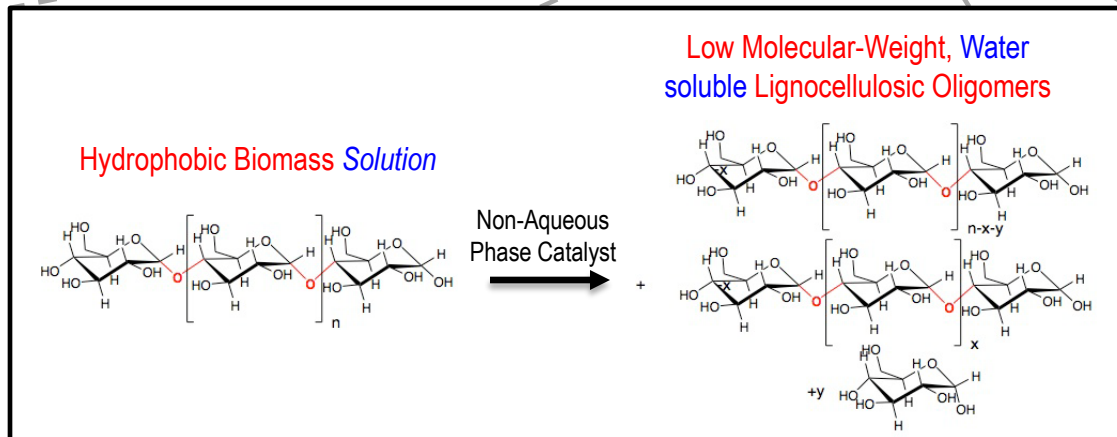
PTM Phase 2

PTM Phase 3

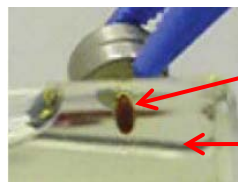
PTM Phase 4



Quaternary PTM immiscible mixture



- Biphasic IL-metal cation/water systems
 - Known and demonstrated at LANL



PTM phase

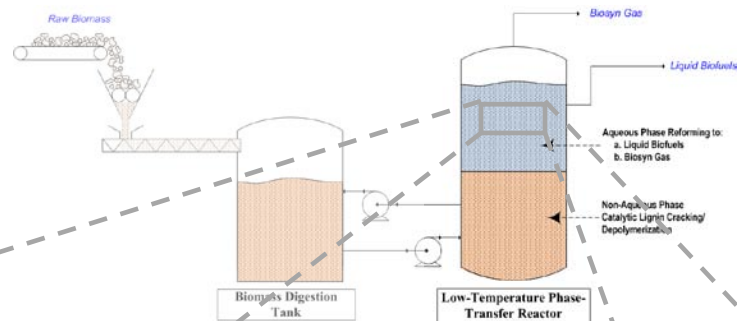
Water phase

Phases have remained immiscible for greater than seven months

LANL Future Work: LT Phase Transfer Chemistry

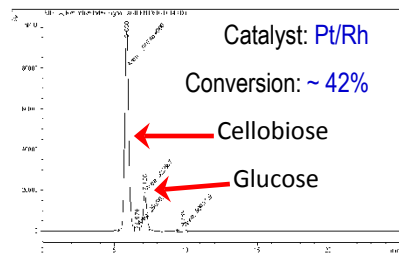
➤ LT Phase Transfer Reactor (LT-PTR)

- Cellulose and lignin oligomers converted to biosyn gas or other engineered products

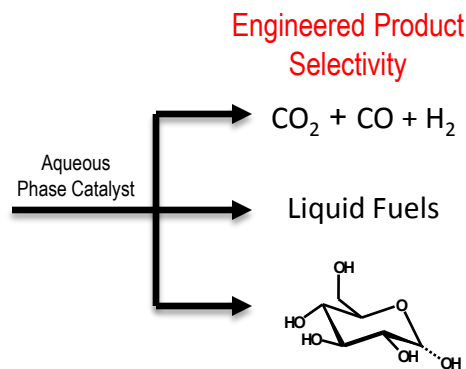
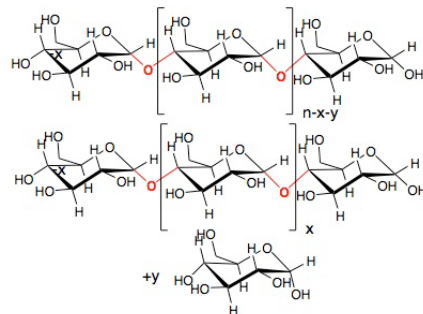


➤ Catalytic hydrolysis of cellulose

- Demonstrated in FY2007-2008 research funded by Hydrogen Production

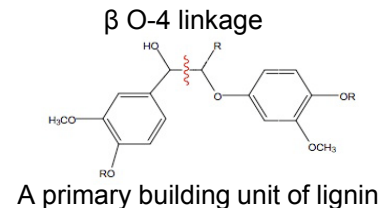
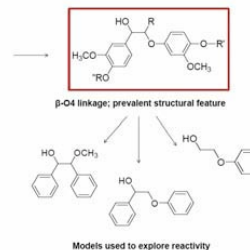


Low Molecular-Weight, Water soluble Lignocellulosic Oligomers



LANL LDRD-funded research* has demonstrated catalytic selective oxidation at the β O-4 linkages of a series of model compounds that generate low molecular weight phenols, benzoic acids, aldehydes, among others

*S.K. Hanson, et al *J. Am. Chem. Soc.* **131**, 428, (2009)



LANL Future Work: Cost Estimates

➤ Cost Estimates using Phase Transfer Media (PTM)

Catalyst assumptions:

- Mass is equal to SMR plant
- Equivalent lifetimes as SMR catalyst
- Pt loading = 0.5%

Sizing assumptions:

- PTM mass/volume based on a solubility of $0.5 \text{ g}_{\text{biomass}}/\text{g}_{\text{PTM}}$
- Equivalent lifetimes as SMR catalyst
- Reactor residence time = 10 min

Catalyst cost includes:

- Precious metal recycling cost
- 10% Pt loss
- Interest

Basis: SMR Plant

- H₂ Production capacity = $2.8 \times 10^5 \text{ kg H}_2/\text{day}$
- Catalyst volume = 20.5 m^3
- Catalyst mass = $1.9 \times 10^4 \text{ kg}$
- Catalyst lifetime = 5 yrs

Catalyst and PTM Costs

- Raw Pt catalyst cost = $\$5.5\text{M}^a$
- Assumed catalyst cost = $\$19\text{M}$
- Phase transfer media (@ $\$45^b/\text{kg}$) = $\$0.32\text{M}$

^a Pt catalyst loading 0.5%, Stock Price = $\$55/\text{g}$

^b PTM quoted price

MAXIMUM COST CONTRIBUTION OF PTM AND CATALYST

$\$ (\text{Solvent and Catalyst}) / \text{kg H}_2 \text{ Produced} = 0.02 - 0.04 \$ / \text{kg H}_2$

Costs reflect worst case scenario

Note: assumed catalyst cost is extremely high compared to current industrial prices; Proposed catalysts do not contain precious metals

LANL Future Work: LT Phase Transfer Chemistry

❖ Issues to be resolved

- Individual steps known independently, but not in one system – need to demonstrate
- If APR of short-chain cellulose oligomers is slow, then we will focus on cracking lignocellulosics all the way to glucose

❖ Advantages/Uniqueness of LANL Project

- One pot reactor capable of solubilizing and catalyzing both lignin and cellulose
 - Phase transfer catalysis
 - Water soluble fractions fed into APR process
- Extremely flexible process capable of producing various chemical feedstocks for further APR processing
- Maximum cost contributions of PTM and catalyst are on the order of \$0.02-0.04 per kg of H₂ produced
- Reactor and plumbing materials can be carbon steel

Acknowledgements



U.S. Department of Energy
**Energy Efficiency
and Renewable Energy**

Bringing you a prosperous future where energy
is clean, abundant, reliable, and affordable

Hydrogen, Fuel Cells & Infrastructure Technologies Program:
Hydrogen Production and Delivery
Program Manager: Richard Farmer