

II.B.2 Catalytic Solubilization and Conversion of Lignocellulosic Feedstocks to Hydrogen

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Objectives

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

Technical Barriers

Feedstock Cost and Availability

Feedstock costs are high. Improved feedstock/agriculture technology (higher yields per acre, etc.), lower cost feedstock collection, and improved feedstock preparation are needed. Because biomass feedstocks are seasonal in nature, feedstock-flexible processes and cost-effective feedstock storage are needed.

Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology

The capital cost for biomass gasification/pyrolysis needs to be reduced. Process intensification by combining unit operations can significantly reduce capital costs. This could range from combining the current two step water-gas shift and pressure swing adsorption separation to a one step water-gas shift with integrated separation, to integrating gasification, reforming, water-gas shift and separation all in one unit operation. Improved process efficiency and higher hydrogen yields and selectivities through catalyst research, better heat integration, and alternative gas clean-up approaches are needed. Improved catalysts or engineering approaches for tar cracking are also needed.

This project addresses the following technical barriers from the Biomass Gasification/Pyrolysis Hydrogen Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(T) Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology

Technical Targets

LANL is conducting applied research that will increase the research knowledge base on biomass solubilization/depolymerization and hydrogen producing reaction pathways from biomass. LANL's research is anticipated to provide alternative routes to hydrogen production from biomass that are aimed at meeting or exceeding the DOE targets (Table 1).

TABLE 1. DOE Technical Targets for Hydrogen Production via Biomass Gasification/Pyrolysis

Characteristics	Units	2005 Status	2012 Target	2017 Target
H ₂ Cost (Plant Gate)	\$/gge	<\$2.00	\$1.60	\$1.10
Total Capital Investment	\$M	<\$194	\$150	\$1
Energy Efficiency	%	>35%	>43%	>60%

gge – gasoline gallon equivalent; M - million

Accomplishments

- Conversion of cellobiose to glucose is feasible, but rates currently too low.
- Recent results of low-temperature catalyzed pyrolysis of lignin shows potential.
- Demonstrated heterogeneous catalysis of glucose and cellobiose:
 - Relatively high conversions during batch reaction (~60–90%).
 - Major products appear to be gas phase for heterogeneous catalysis.
- Demonstrated 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 and pine increased by Lewis Acid catalysis:

- Gas phase products tend to syngas rather than alkanes.
 - Minimal structural change of remaining lignin:
 - Some change in vibrational structure with La Triflate.
 - Lignin/Gd Triflate demonstrates different decomposition mechanism
- Demonstrated catalytically enhanced decarboxylation of lignin.



Introduction

Aqueous-phase reforming (APR) at low temperature has been successfully demonstrated for simple sugars, sugar alcohols, and glycols. In these instances, the simple sugars are derived from cellulosic feedstocks via acid or base hydrolysis via batch processing followed by neutralization of the sugar solutions to near-neutral pH. Successful approaches to the direct utilization of lignocellulosic feedstocks using APR to convert the carbon-hydrogen bonds of polymeric or oligomeric cellulose into hydrogen directly have not been demonstrated. We propose to seek out direct or tandem routes from lignocellulosic feedstocks to hydrogen, gaining a significant advantage in feedstock cost reduction while maintaining the low-pressure, low-temperature capital cost advantages of aqueous phase reforming that have been demonstrated by others.

Utilization of lignocellulosic biomass to generate CO₂-neutral, renewable hydrogen is an attractive pathway to meet the DOE goal of producing hydrogen at a cost of \$2-3/gge. Existing technology based on glucose or sorbitol results in approximately twice the target cost given current estimates. In addition, utilization of more of the biomass by being able to process lignin, which represents up to 30% of many sources of biomass, is anticipated to yield additional hydrogen per unit of biomass. Catalytic approaches to solubilization and depolymerization of lignocellulose also offer the advantage that they eliminate the use of stoichiometric dilute acid or base to hydrolyze the cellulose to sugars, and obviate the need to deal with the large mass of salt that results from eventual neutralization of the acid or base solutions.

Approach

In general terms, LANL is in search of novel hydrogen production routes from lignocellulosics. Two approaches will be explored: 1) catalytic solubilization of cellulose to generate a sugar feedstock stream for downstream APR, and 2) solubilization of lignocellulosics followed by aqueous phase reaction (APRx_n) of oligomeric, soluble cellulose.

LANL will conduct screening experiments for evidence of direct APR_g of cellulose to hydrogen 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 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.

Results: Hydrolysis of Cellobiose to Glucose

For a complete summary of our research, please refer to our 2009 DOE Annual Merit Review presentation (project ID: pdp_12_semelsberger). LANL has investigated catalytic routes of glucose production (which then can be reformed to bio-syngas) from cellobiose (i.e., oligomers of glucose). Depicted in Figure 2 is the reaction of cellobiose to glucose reaction that is being investigated.

LANL has demonstrated the feasibility of converting cellobiose to glucose via catalytic hydrolysis routes. Figure 3 shows the nuclear magnetic resonance results of the uncatalyzed thermal treatment of cellobiose and the results of a catalyzed treatment of cellobiose (the carbon color coding correlate to those in Figure 2). The uncatalyzed reaction of cellobiose does produce trace amounts of glucose. In contrast, the catalyzed reaction of cellobiose produces greater quantities of glucose as compared to the control experiment. These results are promising in that the low temperature catalyzed

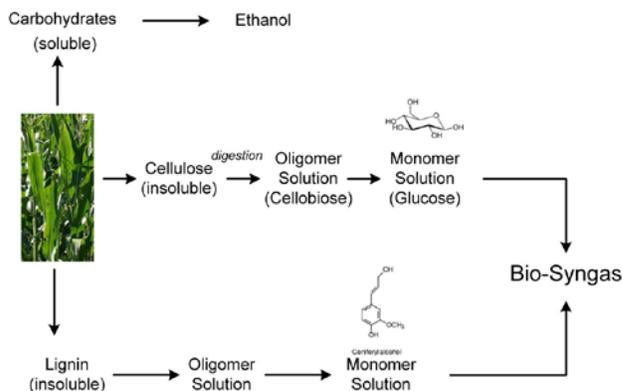


FIGURE 1. A Rudimentary Diagram Showing LANL’s Approach to Producing Bio-Syngas (i.e, Hydrogen and Carbon Monoxide) from Lignocellulosics

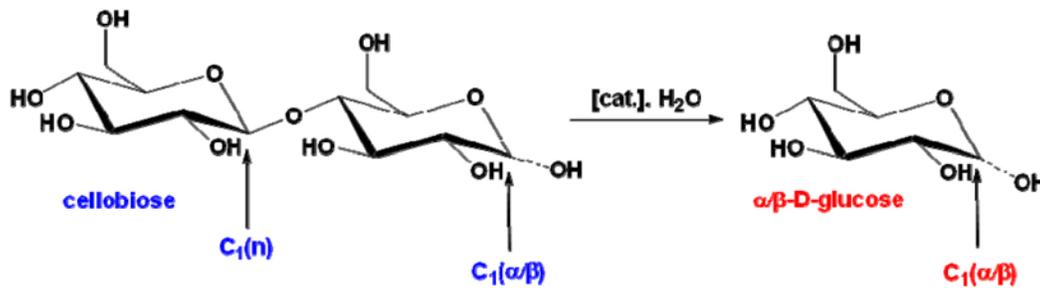
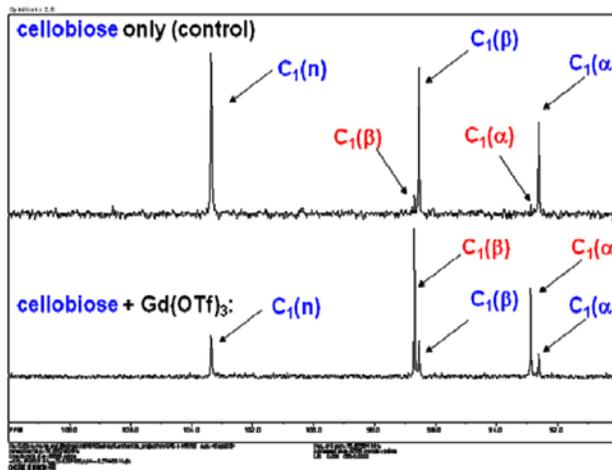


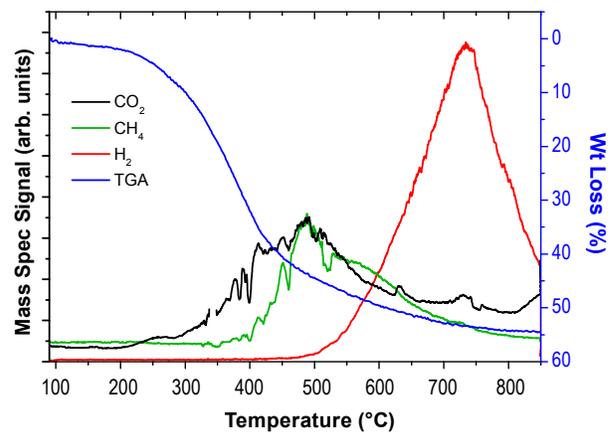
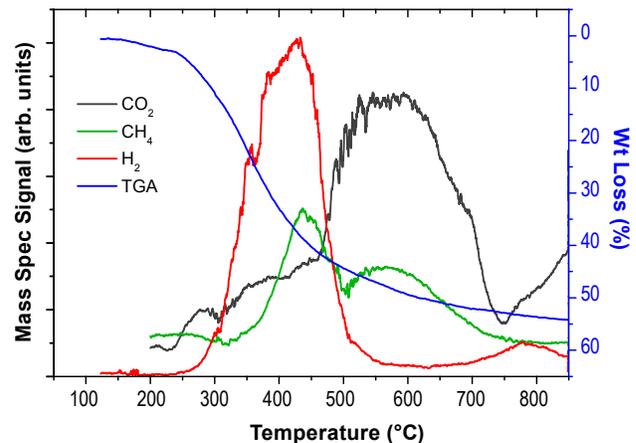
FIGURE 2. Schematic of Cellulose to Glucose Reaction

FIGURE 3. Catalyzed Hydrolysis of Cellobiose to Glucose (1 mol% Gd(OTf)₃, 0.33 mol cellobiose/L H₂O, 120°C for 13 hrs)

hydrolysis of cellobiose is feasible. Although the results are feasible, the rates are still too low. Further research on improving catalyst performance (i.e., rates) is necessary.

Results: Low-Temperature, Catalytic Pyrolysis of Lignin

Recent LANL results has shown the low temperature catalytic pyrolysis of lignin (Aldrich). Shown in Figure 4 and Figure 5 are the thermogravimetric mass spectrometry results of the uncatalyzed and catalyzed pyrolysis of lignin. In the uncatalyzed pyrolysis of lignin, lignin was the only reactant. In the catalyzed reaction, lignin was physically mixed with a catalyst forming a solid-phase homogeneous mixture. On the industrial scale, the solid-phase catalytic reaction of lignin is not most likely an unviable process, but the primary objective is to uncover the reaction mechanism. Understanding the reaction mechanism allows for catalyst optimization and novel industrial-scale catalytic processes.

FIGURE 4. Lignin Pyrolysis in the Absence of a Catalyst ($T_{\text{ramp rate}} = 5^\circ\text{C}/\text{min}$, N₂ purge rate = 30 ml/min)FIGURE 5. Low-Temperature, Catalytic Pyrolysis of Lignin ($T_{\text{ramp rate}} = 5^\circ\text{C}/\text{min}$, N₂ purge rate = 30 ml/min)

The pyrolysis products for both cases (catalyzed and uncatalyzed) are carbon dioxide, methane, and hydrogen. The uncatalyzed pyrolysis of lignin produces hydrogen around 700°C, while the catalyzed pyrolysis of lignin produces hydrogen around 400°C. In both

cases, the observed weight loss percentage is the same. The observation of similar weight loss percentages are a coincidence because the added mass of the catalyst is also included in the weight loss percentage. The result of the catalyzed pyrolysis of lignin are encouraging because not only is hydrogen produced at a lower temperature, but the selectivity has also changed.

Conclusions

- 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 and pine increased by Lewis Acid catalysis:
 - Gas phase products tend to syngas rather than alkanes.
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Future Directions

- Continue screening for novel hydrogen production catalysts.
- Explore conversion chemistry of model monolignols:
 - Develop heterogeneous catalyst for aqueous phase reactions.
- Focus on chemistry and catalyst development for cellulosic conversion.