Overview

Timeline
- Start date: 2005
- End date: 2012
- Percent complete: 75%

Budget
- FY 2005: $100K
- FY 2006: $300K
- FY 2007: $350K
- FY 2008: $700K
- FY 2009: $0K
- FY 2010: $500K

Barriers
Production Barriers
A. Fuel processor capital
C. Operation & maintenance
D. Feedstock issues
F. Control & safety

2012 Targets
- $3.80/gallon gasoline equivalent
- 72% energy efficiency (bio-oil to H₂)

Partners
- Colorado School of Mines – Oxidative cracking; completed.
- University of Minnesota – Catalyst development; ongoing.
- Chevron – Feedstock effects (3-year CRADA); completed.
Relevance

• Biomass can be an important resource for hydrogen production.
  ➢ 1.3 Gt/year biomass available for energy and fuels production represents potential for 100 Mt/year hydrogen that could supply 300 million fuel cell vehicles.
  ➢ Producing hydrogen from domestic resources, such as biomass, can reduce dependence on petroleum and yield virtually zero greenhouse gas emissions.

• This project addresses the challenge of cost reduction of distributed hydrogen production from renewable liquids.
Biomass fast pyrolysis produces high yields of a liquid product, bio-oil, which can be stored and shipped to a site for renewable hydrogen production.

NREL is investigating the partial oxidation and catalytic autothermal reforming of bio-oil for this application.
**Process Chemistry Concept**

**Pyrolysis:**

\[
\text{CH}_{1.46}\text{O}_{0.67} \rightarrow 0.71\text{CH}_{1.98}\text{O}_{0.76} + 0.21\text{CH}_{0.1}\text{O}_{0.15} + 0.08\text{CH}_{0.44}\text{O}_{1.23}
\]

Biomass: Bio-Oil (75%) Char (13%) Gas (12%)

**Catalytic Steam Reforming of Bio-oil:**

Bio-oil - 90 wt% of feed + CH\(_3\)OH - 10 wt% of feed

Elemental formula of the combined feed: CH\(_{2.18}\)O\(_{0.78}\)

H\(_2\)O (steam to carbon molar ratio = 2)

**Overall Reaction:**

\[
\text{CH}_{2.18}\text{O}_{0.78} + 0.51\text{O}_2 + 0.19\text{H}_2\text{O} \rightarrow \text{CO}_2 + 1.28\text{H}_2
\]

*Estimated Practical Yield:* 9.3 wt%

*Estimated Energy Efficiency:* 79% LHV H\(_2\) out/(LHV in + input energy)
Distributed Bio-Oil Reforming Approach

Staged Process Concept and Related Research Areas

Enabling Research:
- Oxidative Cracking Kinetics and Mechanisms
- Low-Temperature Catalytic Oxidation Mechanisms

Process Integration:
- Catalyst Screening
- Process Optimization
- Engineering Testing
- Heat and Mass Balance

Atomization
Bio-Oil (+MEOH)
~400 °C
Oxygen
O₂
~650 °C
Indirect Heat
Oxidative Cracking

Catalytic Auto-Thermal
Separation
H₂O, CO, CH₄, CO₂

H₂
Air

Q
H₂O + CO₂
Objectives

- Overall
  - Develop the necessary understanding of the process chemistry, compositional effects, catalyst chemistry, deactivation, and regeneration strategy as a basis for process definition for automated distributed reforming; demonstrate the technical feasibility of the process

- FY 2010
  - Demonstrate catalytic partial oxidation/steam reforming of bio-oil to syngas at bench scale
  - Demonstrate long-term catalyst performance
  - Provide mass balance data for H2A
  - Go/No Go decision
Technical Accomplishments

- **FY 2006**
  - Bio-oil volatilization method developed
  - Oxidative cracking to CO with minimal CO₂

- **FY 2007**
  - Demonstrated equilibrium catalytic conversion to syngas at low temperature and low H₂O/C

- **FY 2008**
  - Demonstrated catalyst performance
  - Designed and built a bench-scale reactor system

- **FY 2009**
  - Demonstrated operation of a bench-scale reactor system using 90 wt% bio-oil/10 wt% methanol mixture

- **FY 2010**
  - Demonstrated 60 hours of catalyst performance
  - 7.3 g H₂ produced per 100 g bio-oil (9.5 g/100 g bio-oil after water-gas shift)
Continuous flow reactor for producing hydrogen from bio-oil

*(micro steam generator added to the initial system)*
Task 1. Process Performance Demonstration

Syngas Composition at Different T and O/C levels

POX of 90% Bio-oil/10% Methanol
1% Rh, 1% Ce on Al₂O₃

High temperature and low O/C favor higher yields of syngas (CO + H₂)
Task 1. Process Performance Demonstration

Yields of CO and H$_2$ by POX of Bio-oil

POX of 90% Bio-oil/10% Methanol

3.5 g H$_2$/100 g bio-oil (7.5 g H$_2$/100 g after WGS complete)

Yield significantly less than stoichiometric potential
Task 1. Process Performance Demonstration

UMN 1% Rh, 1% Ce cat.; 850°C; O/C=1.5; S/C= 1.6; GHSV=4200 h⁻¹

7.25 g H₂/100 g bio-oil (9.6 g H₂/100 g after WGS complete)
Addition of steam significantly increased the hydrogen yield.
Task 1. Process Performance Demonstration

BASF 0.5% Rh cat.; 850ºC; O/C=1.5; S/C= 1.6; GHSV=4100 h⁻¹

POX/SR Bio-oil/Methanol
Gas Composition

7.4 g H₂/100 g bio-oil (10.3 g H₂/100 g after WGS complete)
Very good performance of catalyst from a commercial manufacturer
Task 2. Catalyst Development

1. University of Minnesota synthesized a series of noble and transition metal catalysts and tested in their POX reactor.

2. Best performing catalyst (1% Rh, 1% Ce on Al$_2$O$_3$) was provided for tests in the NREL POX/steam reforming system.

3. Ni-based catalyst performed much less efficiently, producing less hydrogen (4.75 g/100 g bio-oil; 7.7 g after water-gas shift) and more coke.

4. Rh catalyst provided by a commercial company (BASF) performed as well as the UMN catalyst during the tests at NREL.
Task 3. Process Analysis

Conceptual Process Diagram

NOMINALLY

- Steam / Carbon = 3.0
- \( O_2 / \text{Carbon} = 0.7 \)
- Methanol / Bio Oil = 10 wt%

- NREL- lead design
- Industry - available subsystems

W.G. SHIFT

NREL- lead design

Industry - available subsystems
Task 3. Process Analysis

Hydrogen Cost \( (2005\$, \text{ } n^{th} \text{ plant}) \)

1500 kg/day station used for H2A analysis

(Current projected high volume cost based on 2008 performance)

• Capital costs $1,660,000

• Bio-oil cost – $6/GJ  (cost of methanol not included)

• Total cost of delivered hydrogen $4.48/gge
  
  ➢ $2.59/gge for production
  
  ➢ $1.89/gge for compression, distribution, and dispensing
Collaborations

• Colorado School of Mines
  - POX of bio-oil
  - POX modeling

• Chevron
  - Feedstock variability

• University of Minnesota
  - Catalyst development
Summary

- Bench-scale reactor system tests of catalytic partial oxidation and autothermal reforming of bio-oil were performed using 90 wt% bio-oil/10 wt% methanol mixtures.

- The catalysts:
  - 1% Rh, 1% Ce on Al₂O₃ prepared at University of Minnesota
  - 1% Ni, 1% Ce on Al₂O₃ prepared at University of Minnesota
  - 0.5% Rh on Al₂O₃ provided by BASF.

- Carbon-to-gas conversion was 91%–93%.

- During 60 hours on stream, the UMN catalyst showed a steady performance; 7.3 g hydrogen was produced per 100 g bio-oil. This yield could increase to 9.6 g after completing water-gas shift.

- The estimated cost of hydrogen production: $2.59/gge.
Proposed Future Work

- **FY 2010**: Using the bench-scale system, obtain process performance data for bio-oil produced from two different biomass feedstocks
  - Long-term catalyst performance tests (less expensive catalysts)
  - Assess the impact of the bench-scale results on the process design and on hydrogen production cost
  - “Go/No Go” on conceptual design

- **FY 2011**: Prototype system

- **FY 2012**: Long duration runs to validate the process
Supplemental Slides
Responses to Previous Year Reviewers’ Comments

In 2009 the project received an overall score of 3.2 and most of the reviewers’ comments were very positive. Below we respond to some concerns:

- A reviewer suggested feeding the produced hydrogen to a fuel cell. At this stage of the project, we are not ready to do it yet. We need to install a hydrogen separation module and buy a fuel cell, which are planned in the future.
- Within this project we are not involved in the production of pyrolysis oil, assuming that this is already in an early stage of commercialization. Storage and distribution of bio-oils are also being developed by technology providers.
- We agree that it would be beneficial to use a lower-cost catalyst. However, our tests with a Ni-based catalyst showed significantly lower yields of hydrogen, less effective bio-oil to gas conversion, and more coke formation.
- We obtained a Rh catalyst from a commercial manufacturer (BASF) and started testing its performance in our reactor system. The results are as good as those obtained using the University of Minnesota catalyst.
- We are working on a different reactor design that will include bio-oil volatilization and catalytic reforming stages separated by a char collecting filter. This will allow us to avoid catalyst poisoning by volatile inorganic contaminants that are more abundant in bio-oils generated from herbaceous biomass and agri-residues.

