Distributed Bio-Oil Reforming

S. Czernik¹, R. French¹, M. M. Penev¹, J. Marda², A. M. Dean²

¹National Renewable Energy Laboratory
²Colorado School of Mines

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Overview

**TIMELINE**
- **Start date:** 2005
- **End date:** 2012
- **Percent complete:** 60%

**BUDGET**
- **FY 2005:** $100K
- **FY 2006:** $300K
- **FY 2007:** $350K
- **FY 2008:** $700K
- **FY 2009:** $0K

**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**
- **University of Minnesota - Catalyst Development**
- **Chevron – Feedstock Effects (3 year CRADA)**
Biomass fast pyrolysis produces high yields of liquid product, bio-oil, which can be stored and shipped to a site for renewable hydrogen production.

NREL is investigating the low-temperature, partial oxidation, and catalytic autothermal reforming of bio-oil for this application.
**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 (74 wt% \(\text{CH}_{1.28}\text{O}_{0.41}\), 26 wt % \(\text{H}_2\text{O}\)) - 90 wt% of feed

\(\text{CH}_3\text{OH}\) - 10 wt% of feed

\(\text{H}_2\text{O}\) (2 mole ratio steam to carbon)

**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 %

Energy Efficiency Estimates are in Progress based on Aspen Modeling
Distributed Bio-Oil Reforming Approach

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

Atomization

Bio-Oil (+MEOH) → Oxidative Cracking

Oxygen (O₂)

~400 °C → ~650 °C

Oxidative Cracking

Catalytic Auto-Thermal

H₂O + CO₂ → Separation

H₂O, CO, CH₄, CO₂

H₂ → Engineering Testing

H₂O + CO₂ → Catalyst Screening

Process Integration:
- Process Optimization
- Heat and Mass Balance

Indirect Heat

Air

Q
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 process.

• FY 2009

Improve bio-oil atomization with less MeOH addition,
Demonstrate non-catalytic partial oxidation of bio-oil at bench scale
Demonstrate catalytic conversion of bio-oil to syngas at bench scale
Provide mass balance data for H2A
Technical Accomplishments

- **FY 2006**
  - Bio-oil volatilization method developed
  - Oxidative cracking to CO with minimal CO$_2$
- **FY 2007**
  - Demonstrated equilibrium catalytic conversion to syngas at low temperature and low H$_2$O/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
Progress in Process Development
1. Bio-Oil Volatilization

- The new ultrasonic nozzle can produce a fine mist even from high-viscosity liquids.
- Successful tests with 90 wt% bio-oil/10 wt% methanol mixture.
- Promising attempts of feeding neat bio-oil though 10 wt% methanol addition will likely be used to homogenize and stabilize bio-oil.
- Ultrasonic nozzle will likely be replaced by a high-pressure injector in larger-scale units.
Hydrogen yields are 25-30% of the stoichiometric potential; Those yields will significantly increase after completion of water-gas shift.
Overall CO Yield

>70% carbon can be converted to CO by non-catalytic POX;
O:C ratio has much stronger effect than temperature on CO yields
At O:C>1.4 temperature has little effect on benzene (aromatics) formation
University of Minnesota catalyst (Lanny Schmidt’s group): 1 wt % Rh and 1 wt % ceria on alumina

1 – 1.5 is the optimal range of O/C for catalytic POX of bio-oil
University of Minnesota catalyst (Lanny Schmidt’s group): 1 wt % Rh and 1 wt % ceria on alumina

Catalytic Steam Reforming of Hardwood Bio-oil
Hydrogen Yield

80-90% of stoichiometric yield of hydrogen was produced by catalytic steam reforming of bio-oil for the whole S/C range
Progress in Process Development
3. Catalytic Conversion

Product Gas Composition from Different Feedstocks

**Syn-gas Composition**

650 °C; O/C=1.3; S/C=2.5

- **H2**
- **CO**
- **CO2**
- **H2O**
Progress in Process Development
4. Bench-scale Reactor

- Built out of quartz: 
  \[ d = 30 \text{ mm}; \; h = 450 \text{ mm} \]
- Connected to the feeding and condensation systems
- Feed rate 1-2 g/min 90 wt% bio-oil/10 wt% methanol solution
- On-line product gas composition monitoring
- 1-4 hour runs
- Detailed product analysis
- Improved mass balance
Progress in Process Development
4. Bench Scale Reactor System
Progress in Process Development
4. Bench Scale Reactor System

Gas Composition from POX of Bio-oil/Methanol

POX of Bio-oil/Methanol Mixture
\( t = 730 \text{C}, \text{O:C} = 1.5 \)

![Graph showing gas composition](graph_image)
Gas Composition from Catalytic POX of Bio-oil/Methanol at different process conditions

**POX of 90% Bio-oil/10% Methanol**

1% Rh, 1% Ce on Al₂O₃

- 740°C, S/C=1.5
- 800°C, S/C=1.5, O/C=1.5
- 830°C, O/C=1.28
- 840°C, O/C=1.77
- 740°C, O/C=1.5

**Graph Elements:**
- H₂
- O₂
- CH₄
- CO
- CO₂
- C₂H₄

**Time (min):**
- 0 to 160

**Graph Values:**
- 0 to 50.0 (Vol%)

**Process Conditions:**
- Various temperatures and oxygen-to-carbon ratios.
Hydrogen Cost

1500 kg/day station used for H2A analysis.
Capital Costs $1,660,000 ($2.03/gge).
Total cost of delivered hydrogen $4.48/gge
$2.59/gge for the production
$1.88/gge for compression, distribution, and dispensing.
Process Subsystems Outline

**NOMINALLY**
- Steam / Carbon = 3.0
- O₂/Carbon = 0.7
- Methanol / Bio Oil = 10 wt%

- NREL - lead design
- Industry - available subsystems
Summary

• Bench-scale reactor system tests of non-catalytic and catalytic partial oxidation of bio-oil were performed using 90 wt% bio-oil/10 wt% methanol mixtures
• Carbon-to-gas conversion at bench-scale was slightly less than that achieved in micro scale system
• Rhodium catalyst enhanced bio-oil to syngas conversion by POX with and without added steam
• Bio-oils from herbaceous feedstock were more difficult to process and left more deposits than wood bio-oils
• Experimental results from bench-scale system will be used as to validate ASPEN simulations based on micro-scale data.
## Project Timeline

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<td><strong>Demonstrate catalyst performance consistent with $3.80/gge</strong></td>
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<td><strong>Demonstrate Distributed Hydrogen Production from Bio-Oil for $3.80/gge</strong></td>
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Future Work

- **FY 2009:** Produce process performance data as a function of process conditions (temperature, catalyst, O/C, S/C) using the bench-scale system
  - Integrated laboratory experiment
  - Optimization work
  - Long-term catalyst performance test
  - Assess the impact of the bench-scale results on the process design and on hydrogen production cost
- **FY 2010:** “Go/no-go” on conceptual design
- **FY 2011:** Prototype system
- **FY 2012:** Long duration runs to validate the process