

Distributed Bio-Oil Reforming



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Project ID#

PD04

Overview

T I M E L I N E

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

B U D G E T

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

B A R R I E R S

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)

P A R T N E R S

- 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.**

Distributed Production of Hydrogen - Process Concept

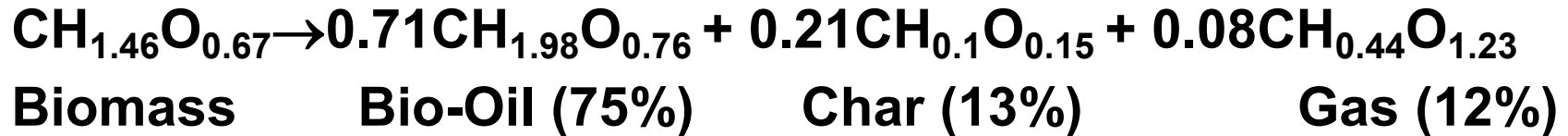
Biomass fast pyrolysis produces high yields of a liquid product, bio-oil, which can be stored and shipped to a site for renewable hydrogen production.

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



Process Chemistry Concept

Pyrolysis:



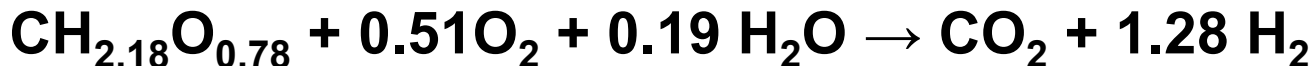
Catalytic Steam Reforming of Bio-oil:

Bio-oil - 90 wt% of feed + CH₃OH - 10 wt% of feed

Elemental formula of the combined feed: CH_{2.18}O_{0.78}

H₂O (steam to carbon molar ratio = 2)

Overall Reaction:

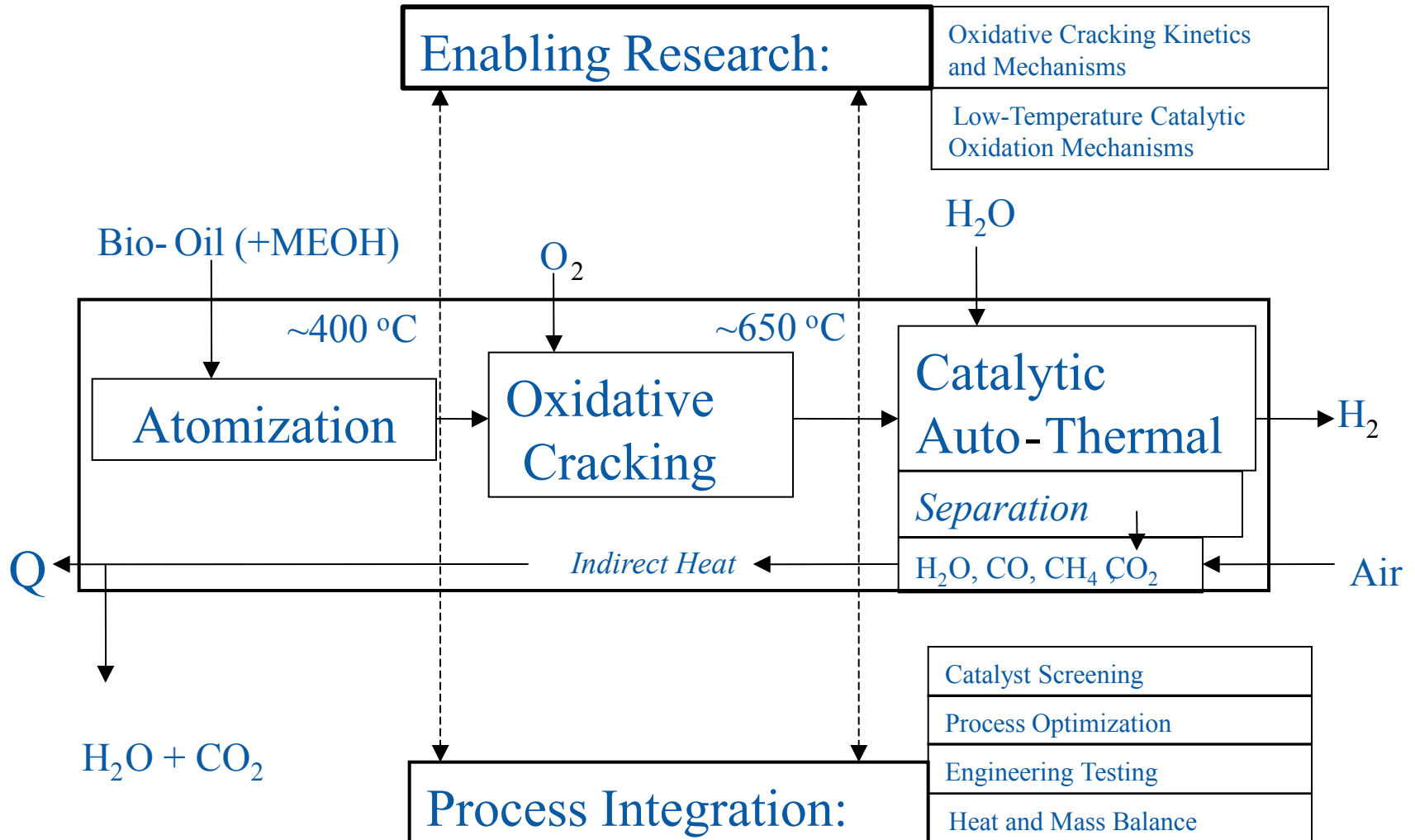


Estimated Practical Yield: 9.3 wt%

Estimated Energy Efficiency: 79% LHV H₂ out/(LHV in + input energy)

Distributed Bio-Oil Reforming Approach

Staged Process Concept and Related Research Areas



Objectives

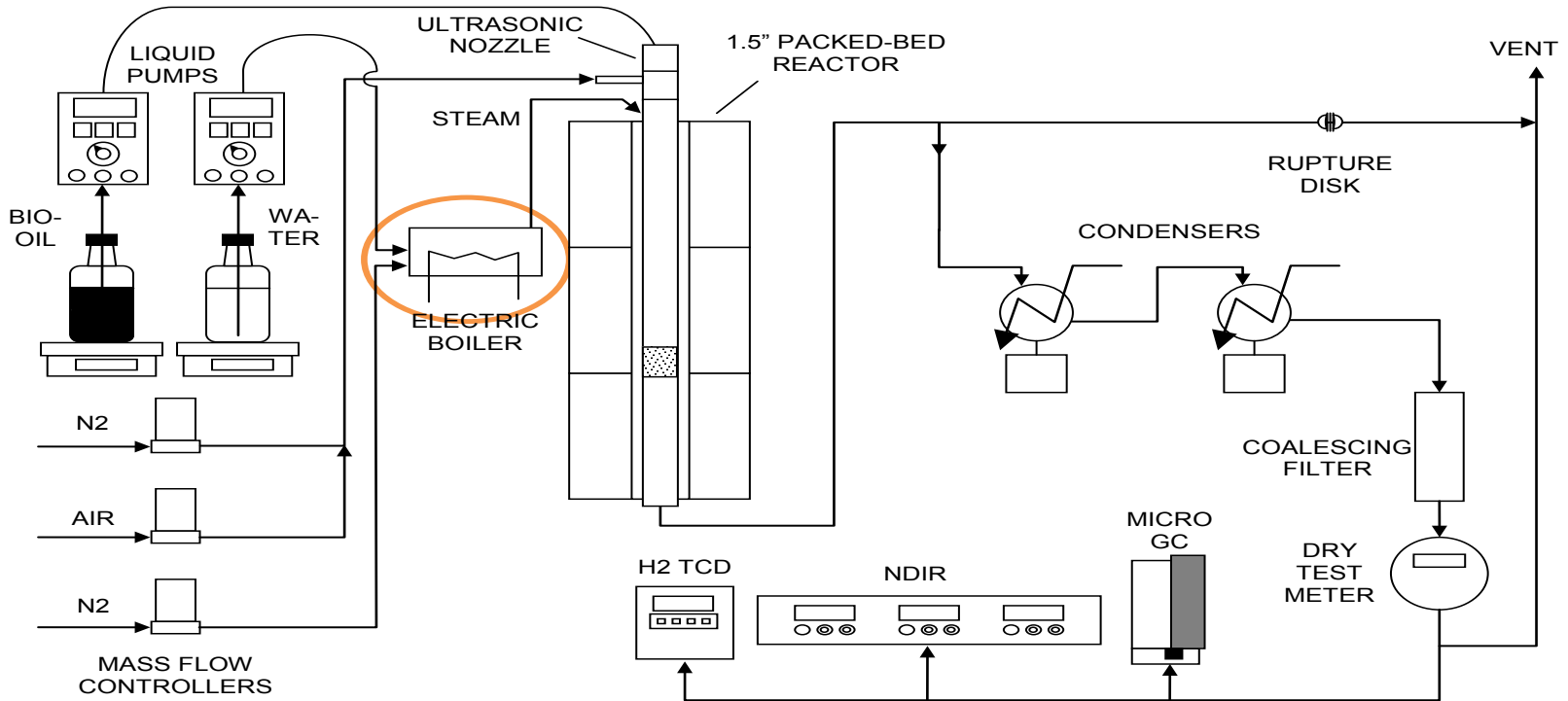
- Overall
 - Develop the necessary understanding of the process chemistry, compositional effects, catalyst chemistry, deactivation, and regeneration strategy as a basis for process definition for automated distributed reforming; demonstrate the technical feasibility of the process
- FY 2010
 - Demonstrate 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)

Task 1. Process Performance Demonstration

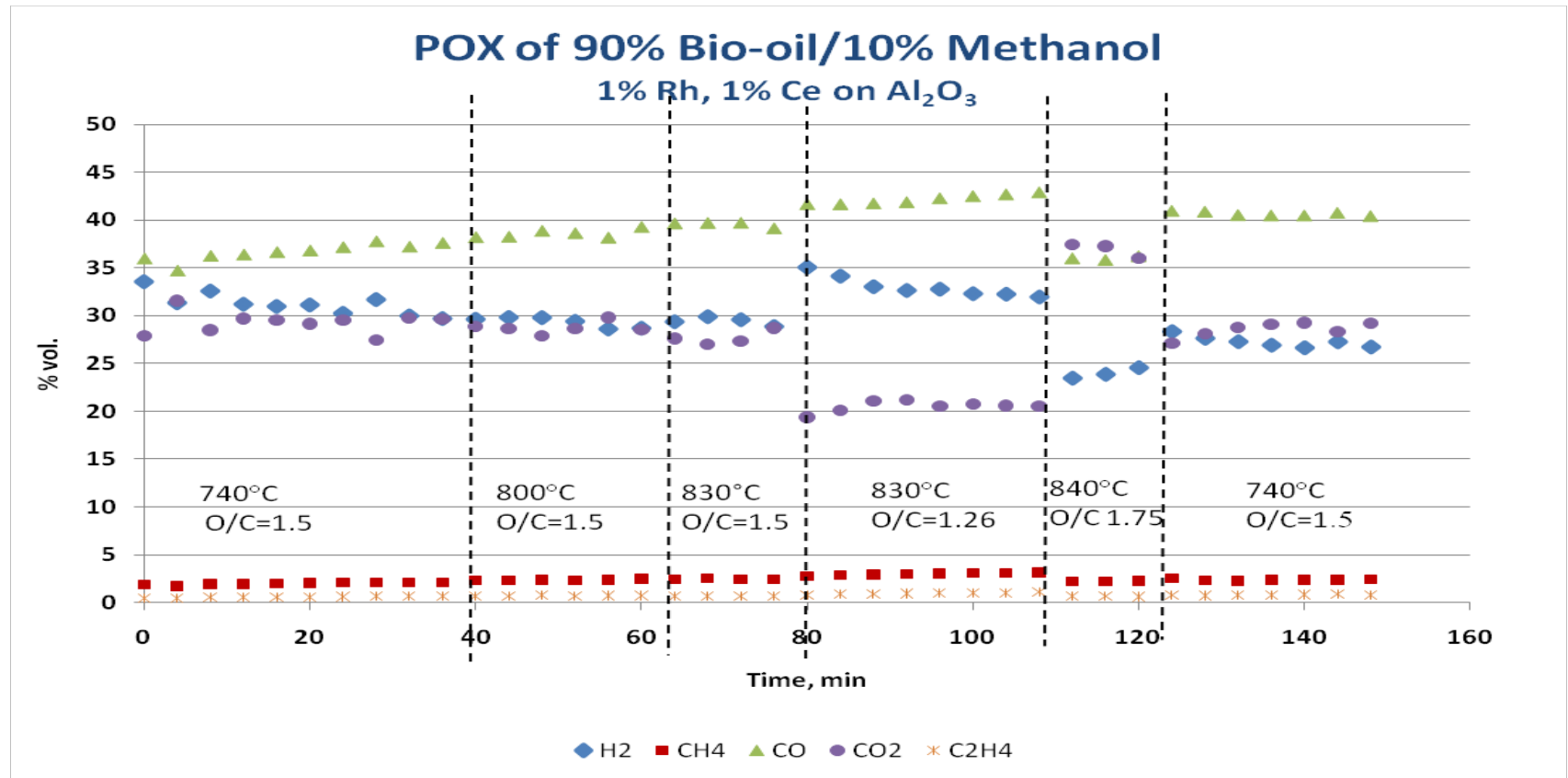
Bench-scale Reactor System



Continuous flow reactor for producing hydrogen from bio-oil
(micro steam generator added to the initial system)

Task 1. Process Performance Demonstration

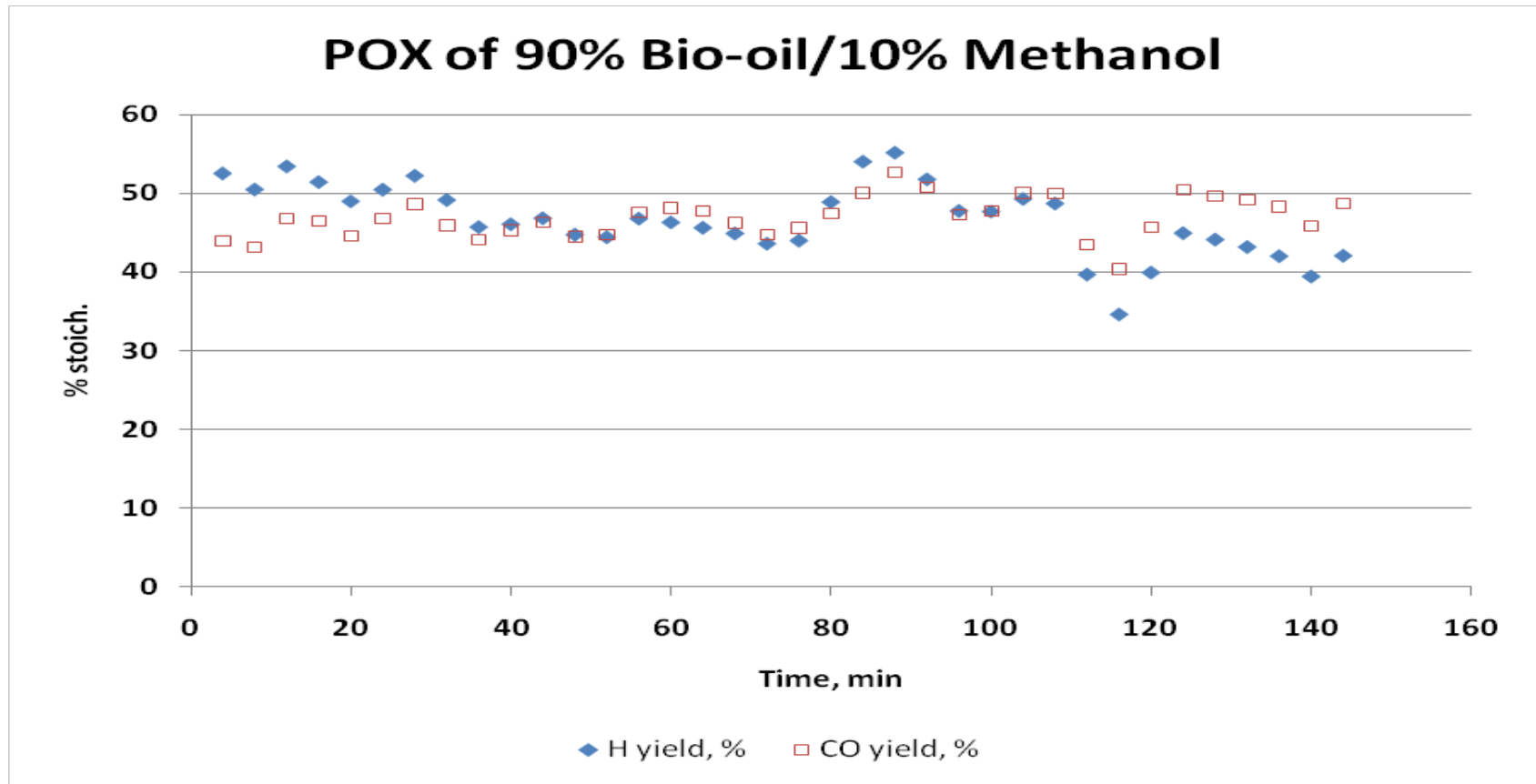
Syngas Composition at Different T and O/C levels



High temperature and low O/C favor higher yields of syngas (CO + H₂)

Task 1. Process Performance Demonstration

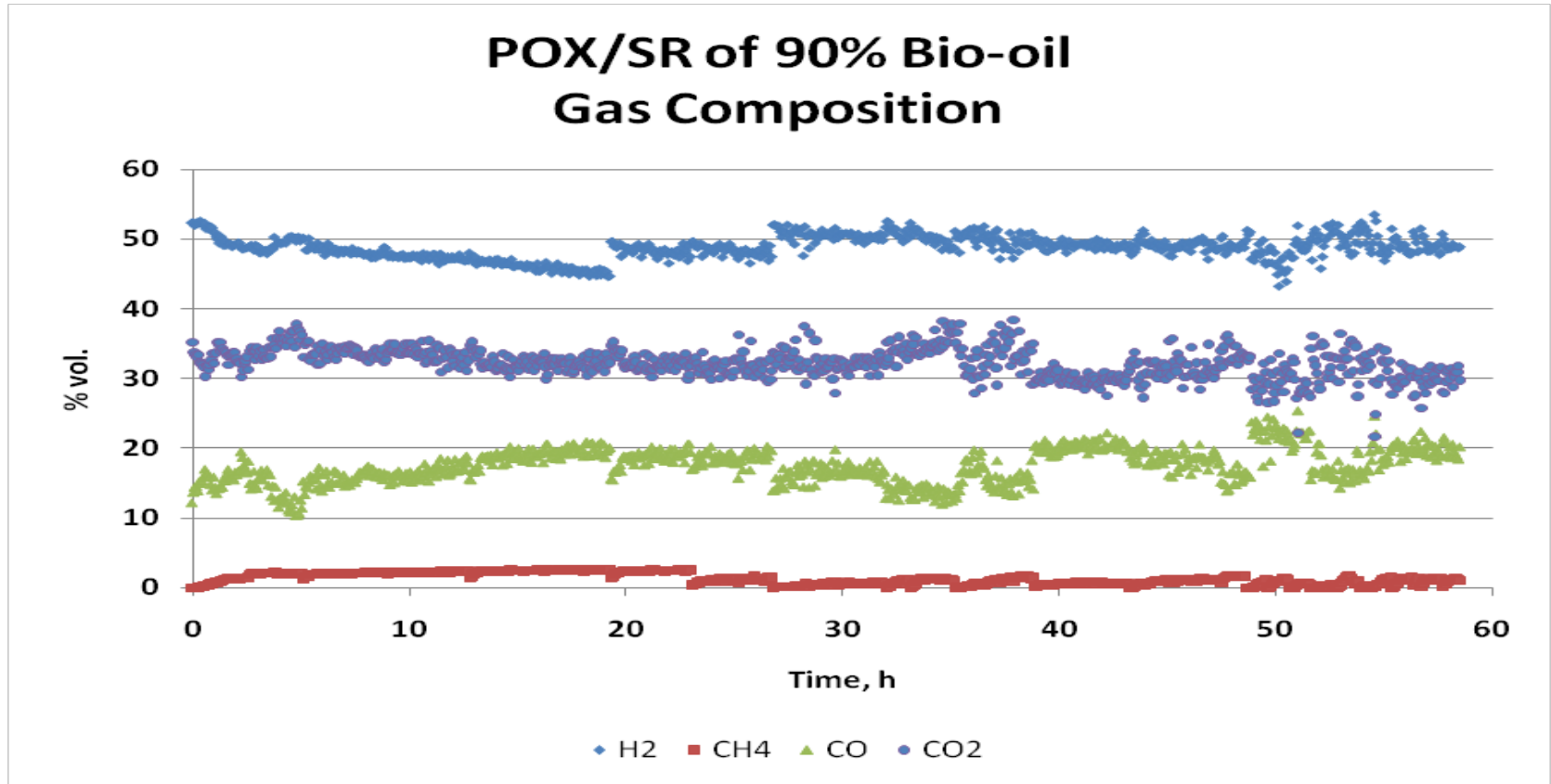
Yields of CO and H₂ by POX of Bio-oil



**3.5 g H₂/100 g bio-oil (7.5 g H₂/100 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

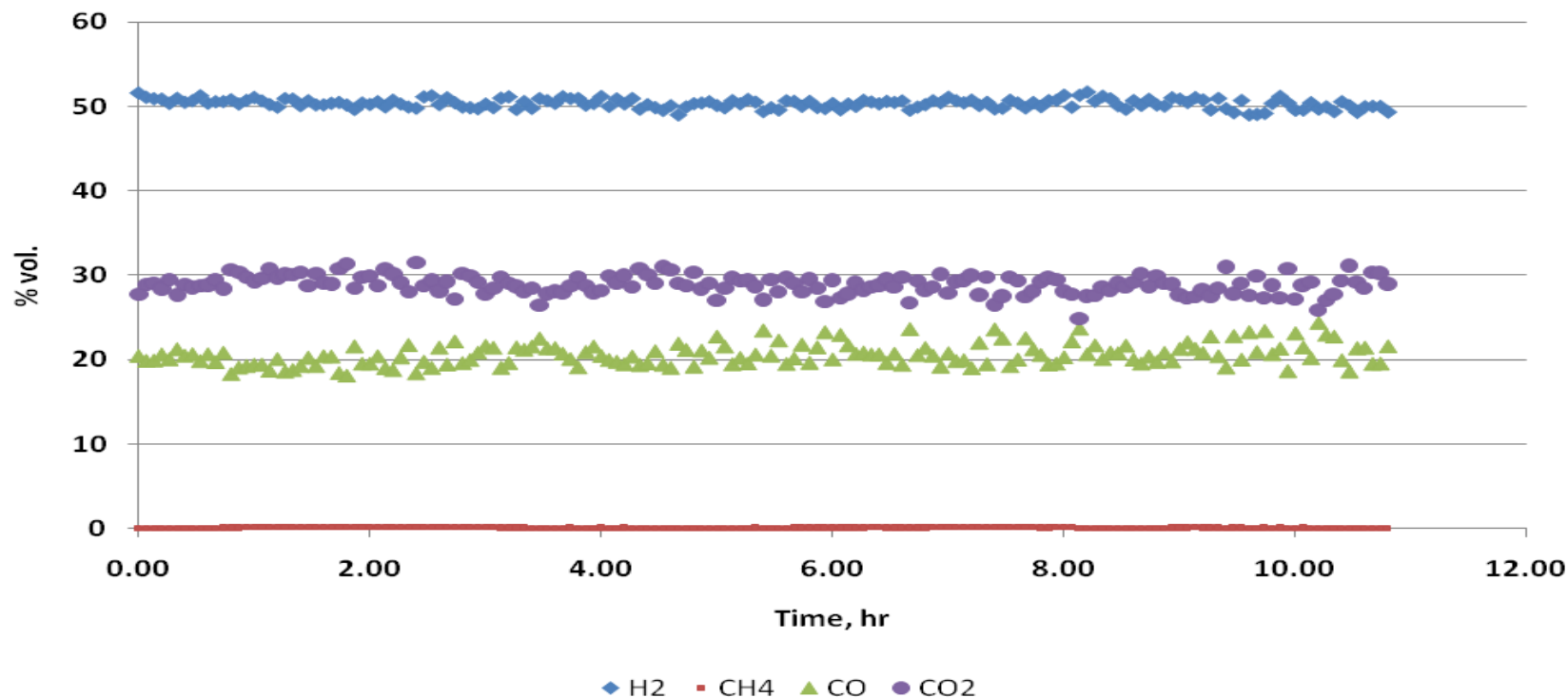


**7.25 g H₂/100 g bio-oil (9.6 g H₂/100 g after WGS complete)
Addition of steam significantly increased the hydrogen yield.**

Task 1. Process Performance Demonstration

BASF 0.5% Rh cat.; 850°C; 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)

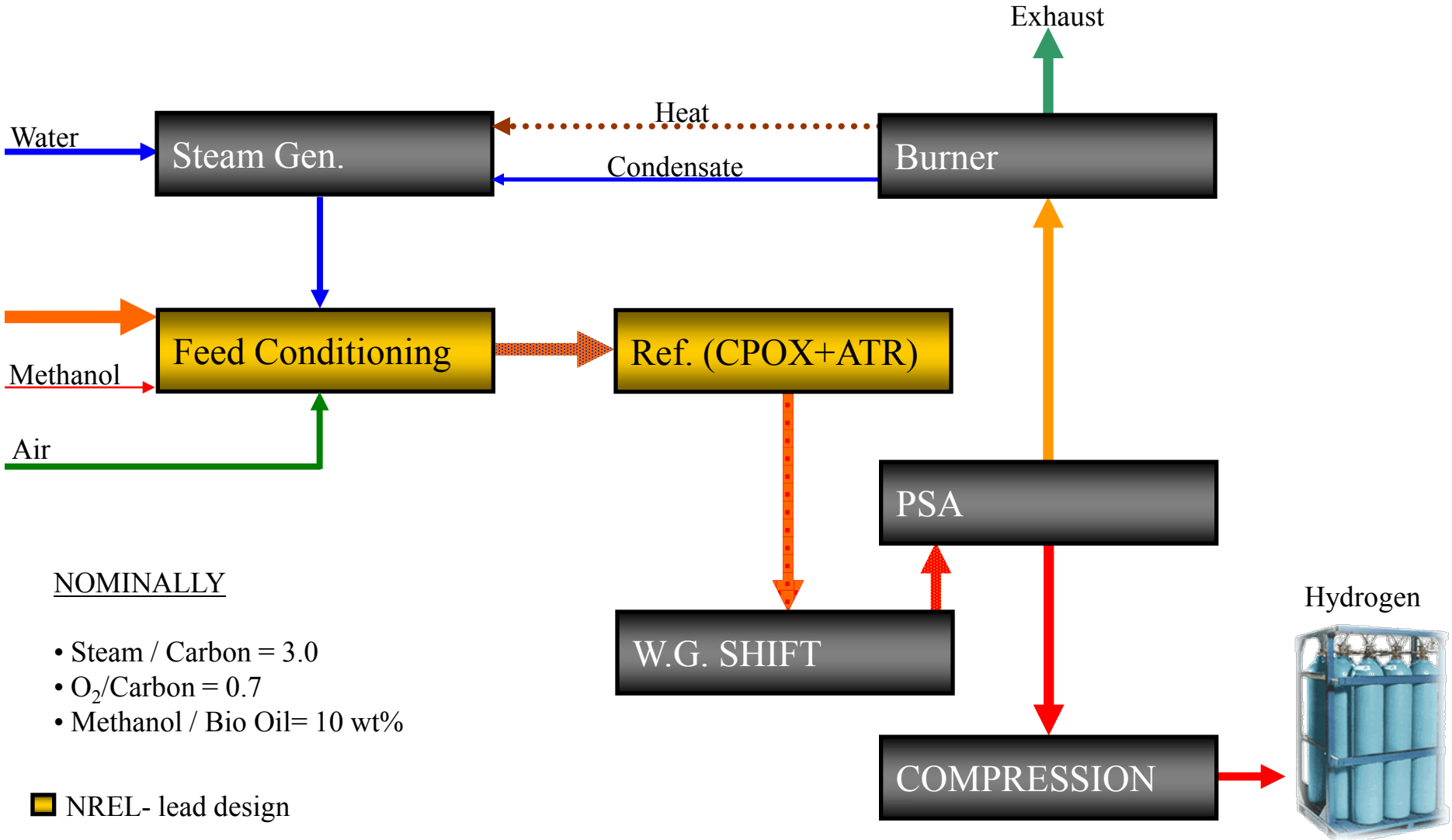
Very good performance of catalyst from a commercial manufacturer

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_2O_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



Hydrogen



Task 3. Process Analysis

Hydrogen Cost (2005\$, n^{th} 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**

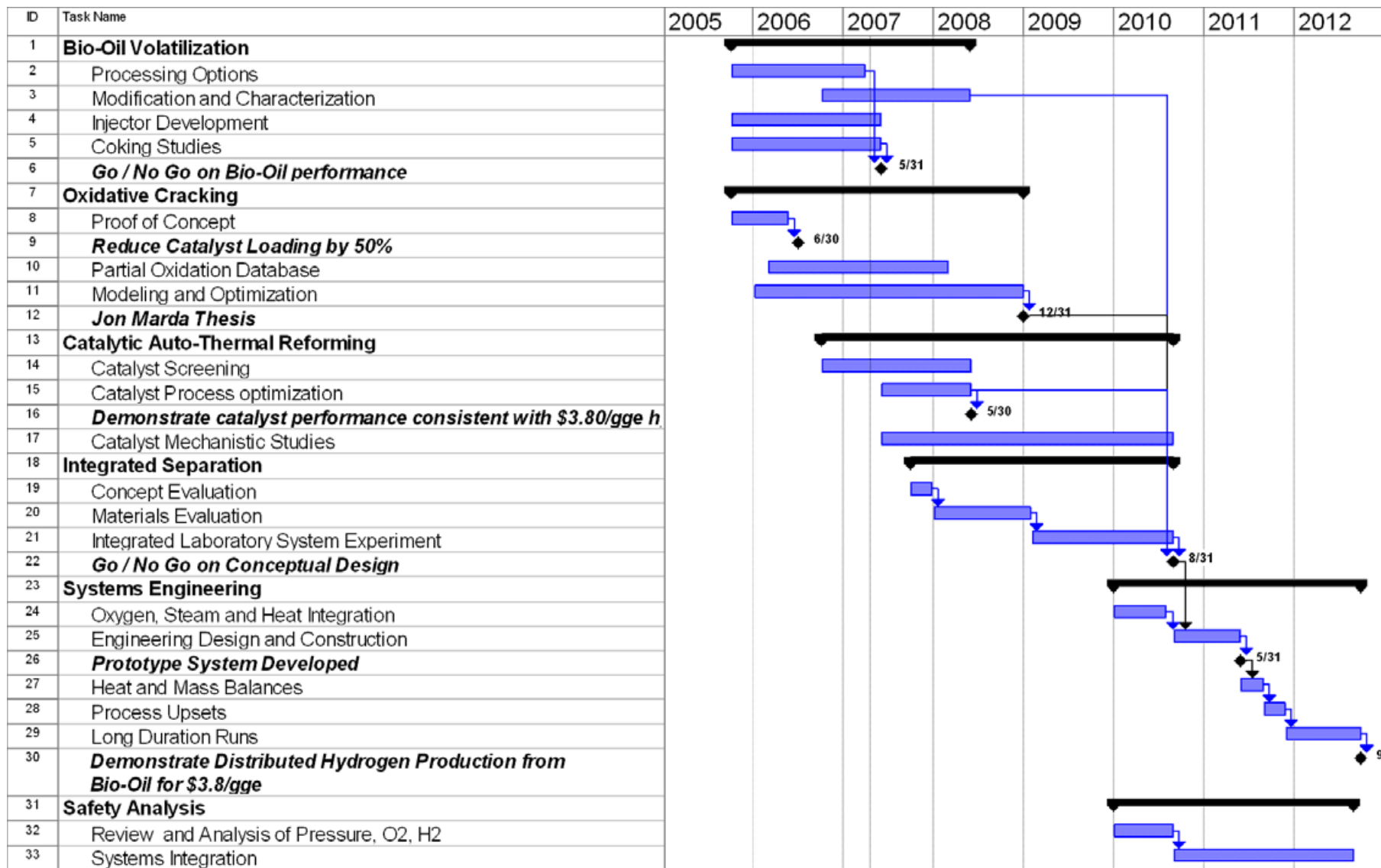
- **Chevron**
 - **Feedstock variability**

- **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.**

Project Timeline



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.

Publications and Presentations

1. Marda, J., DiBenedetto, J., McKibben, S., Evans, R., Czernik, S., French, R., and Dean, A., Non-Catalytic Partial Oxidation Of Bio-Oil To Synthesis Gas For Distributed Hydrogen Production, *International Journal for Hydrogen Energy*, 2009, 34, 8519-8534.
2. Rennard, D., French, R., Czernik, S., Josephson, T., Schmidt, L., Production of Synthesis Gas by Partial Oxidation and Steam Reforming of Biomass Pyrolysis Oils, *International Journal for Hydrogen Energy*, 2010, 35, 4048-4059.
3. Czernik, S. and French, R., Distributed Production of Hydrogen by Autothermal Reforming of Biomass Pyrolysis Oil, presented at ACS National Meeting, San Francisco, CA, March 21-25, 2010
4. Czernik, S. and French, R., Production of Hydrogen by Partial Oxidation/Steam Reforming of Biomass Pyrolysis Oil, 18th European Biomass Conference and Exhibition, Lyon, France, May 3-7, 2010.