NREL National Renewable Energy Laboratory
Innovation for Our Energy Future

Distributed Bio-Oil Reforming

S. Czernik, R. French,
M. M. Penev

National Renewable
Energy Laboratory

June 8-12, 2010

Project ID#
PD004

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 H_2)

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.

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:

$CH_{1.46}O_{0.67} \rightarrow 0.71CH_{1.98}O_{0.76} + 0.21CH_{0.1}O_{0.15} + 0.08CH_{0.44}O_{1.23}$

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

Catalytic Steam Reforming of Bio-oil:

Bio-oil - 90 wt% of feed + CH_3OH - 10 wt% of feed

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

H_2O (steam to carbon molar ratio = 2)

Overall Reaction:

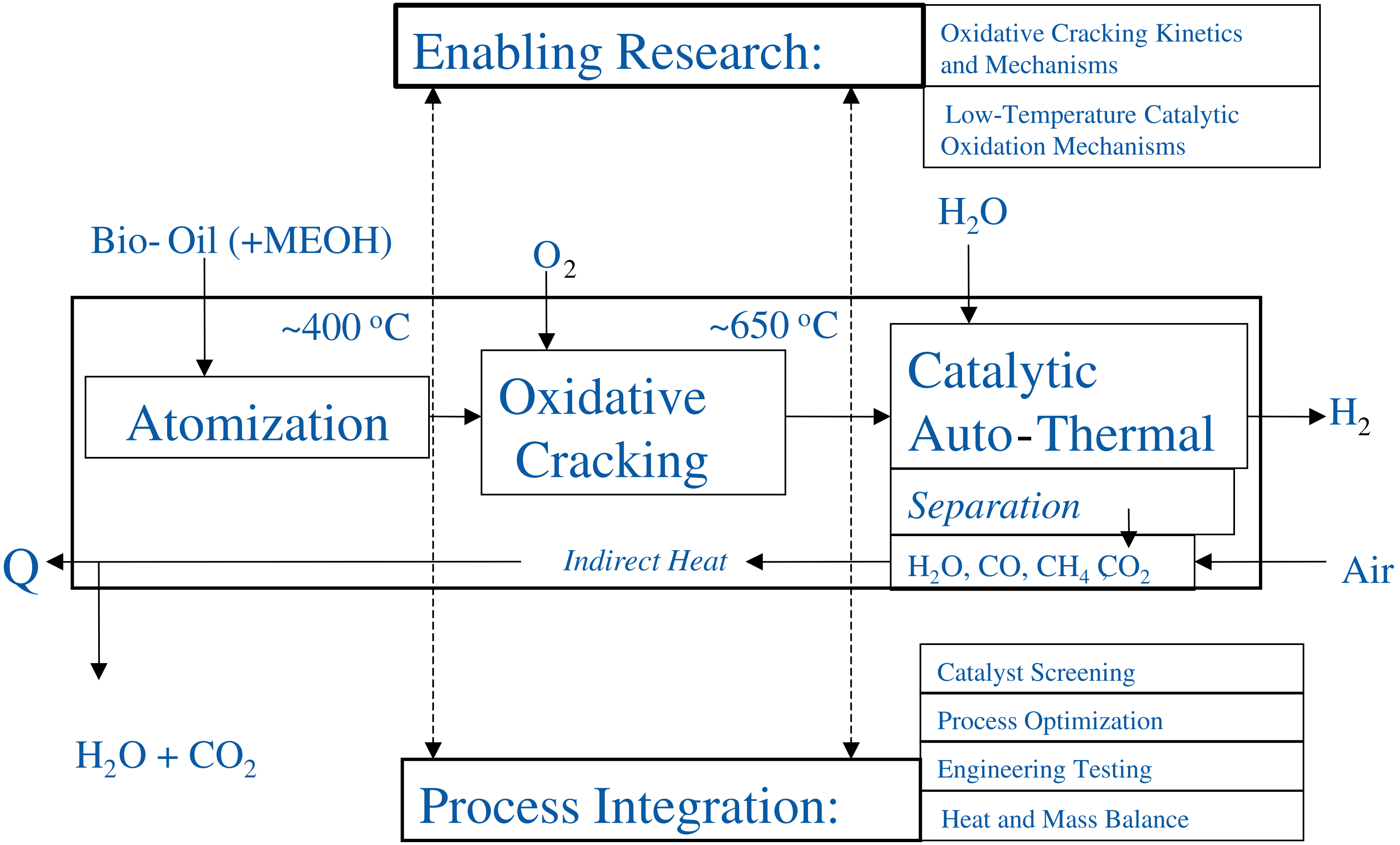
$CH_{2.18}O_{0.78} + 0.51O_2 + 0.19\ H_2O \rightarrow CO_2 + 1.28\ H_2$

***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

Bio- Oil (+MEOH)

O_2

H_2O

~400 °C

~650 °C

Atomization

Oxidative Cracking

Catalytic Auto-Thermal

Separation

H_2

Indirect Heat

H_2O, CO, CH_4 CO_2

Air

Q

$H_2O + CO_2$

Process Integration:

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

Objectives

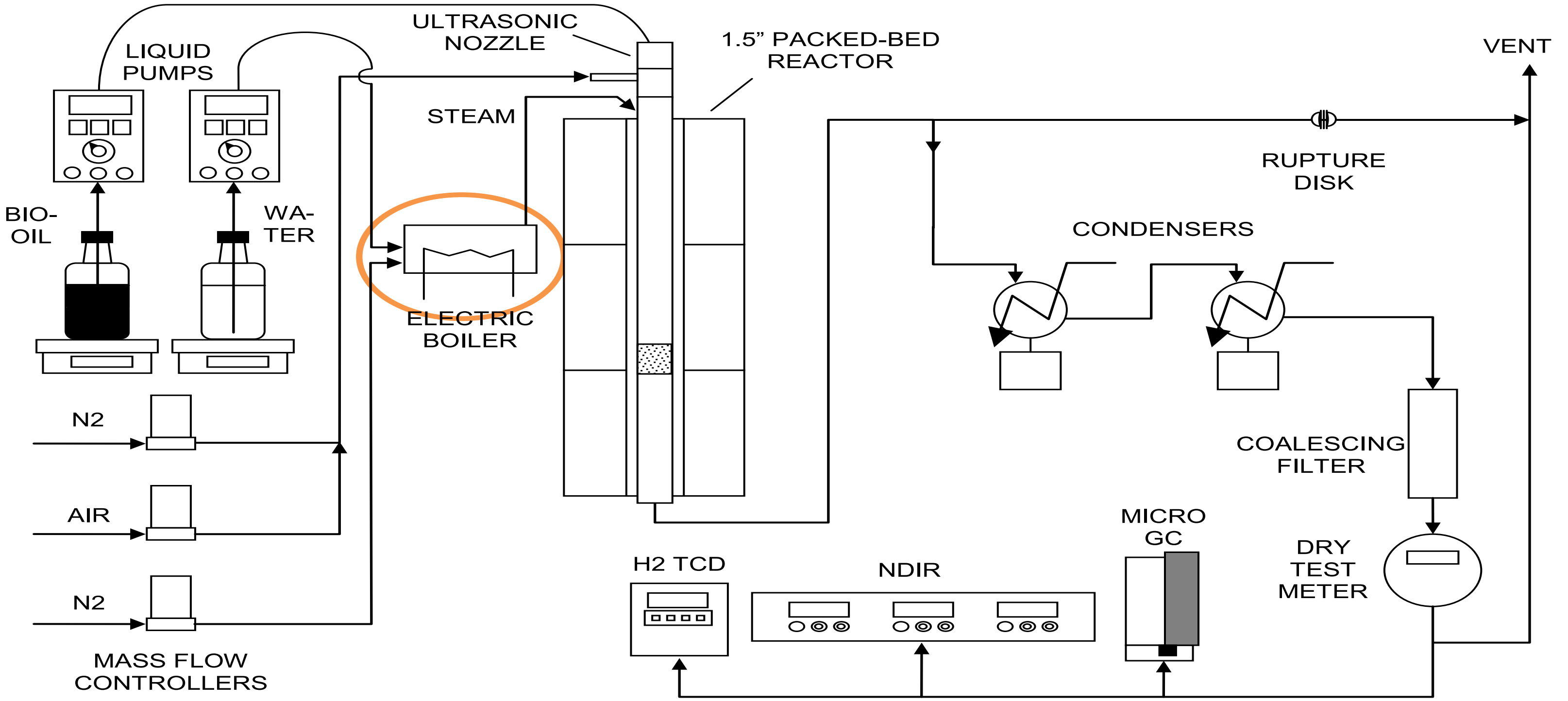
- Overall
  - Develop the necessary understanding of the process chemistry, compositional effects, catalyst chemistry, deactivation, and regeneration strategy as a basis for process definition for automated distributed reforming; demonstrate the technical feasibility of the process
- FY 2010
  - Demonstrate 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 CO_2
- **FY 2007**
  - Demonstrated equilibrium catalytic conversion to syngas at low temperature and low H_2O/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 H_2 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

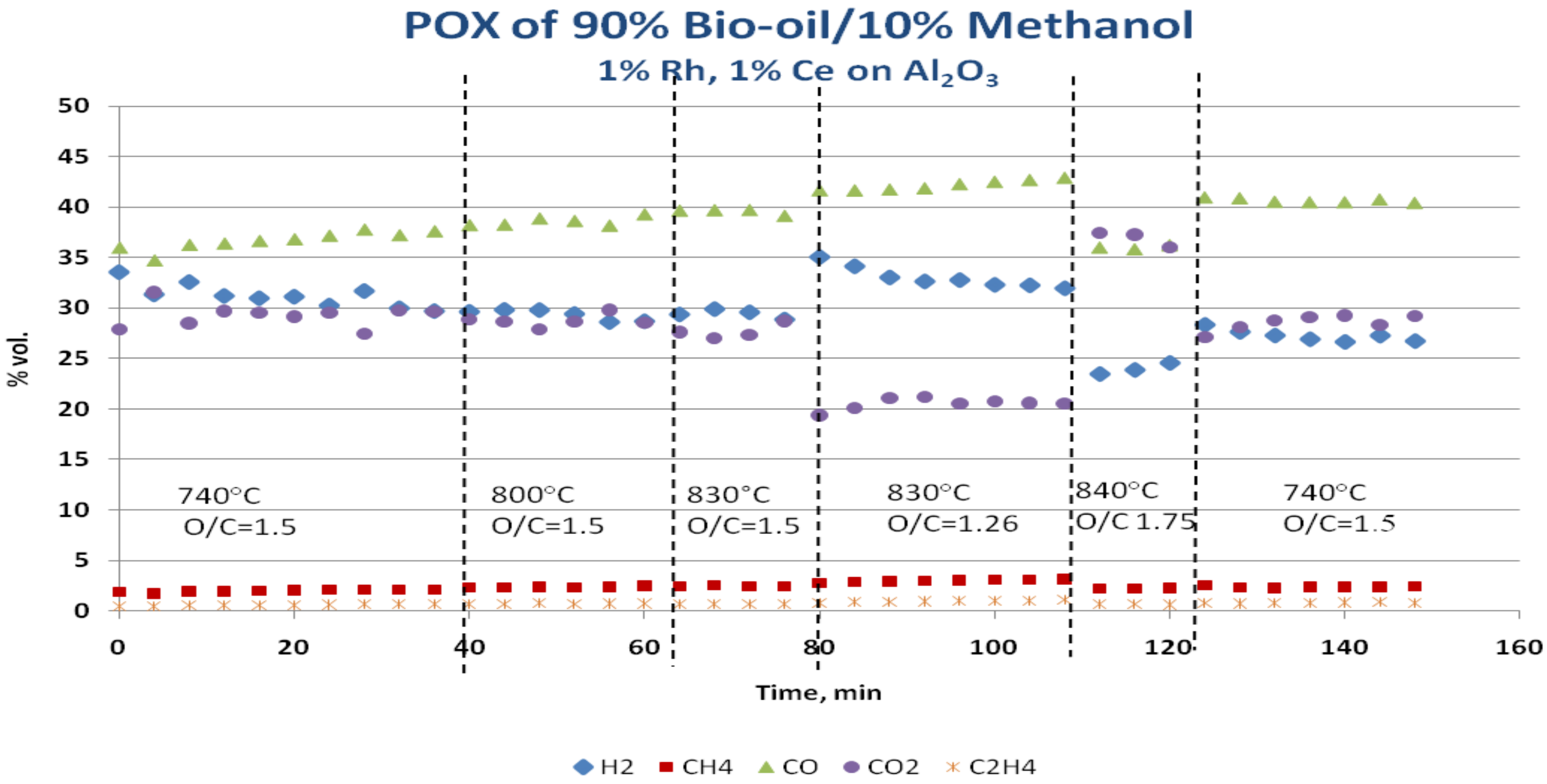


Continuous flow reactor for producing hydrogen from bio-oil

(micro steam generator added to the initial system)

Task 1. Process Performance Demonstration

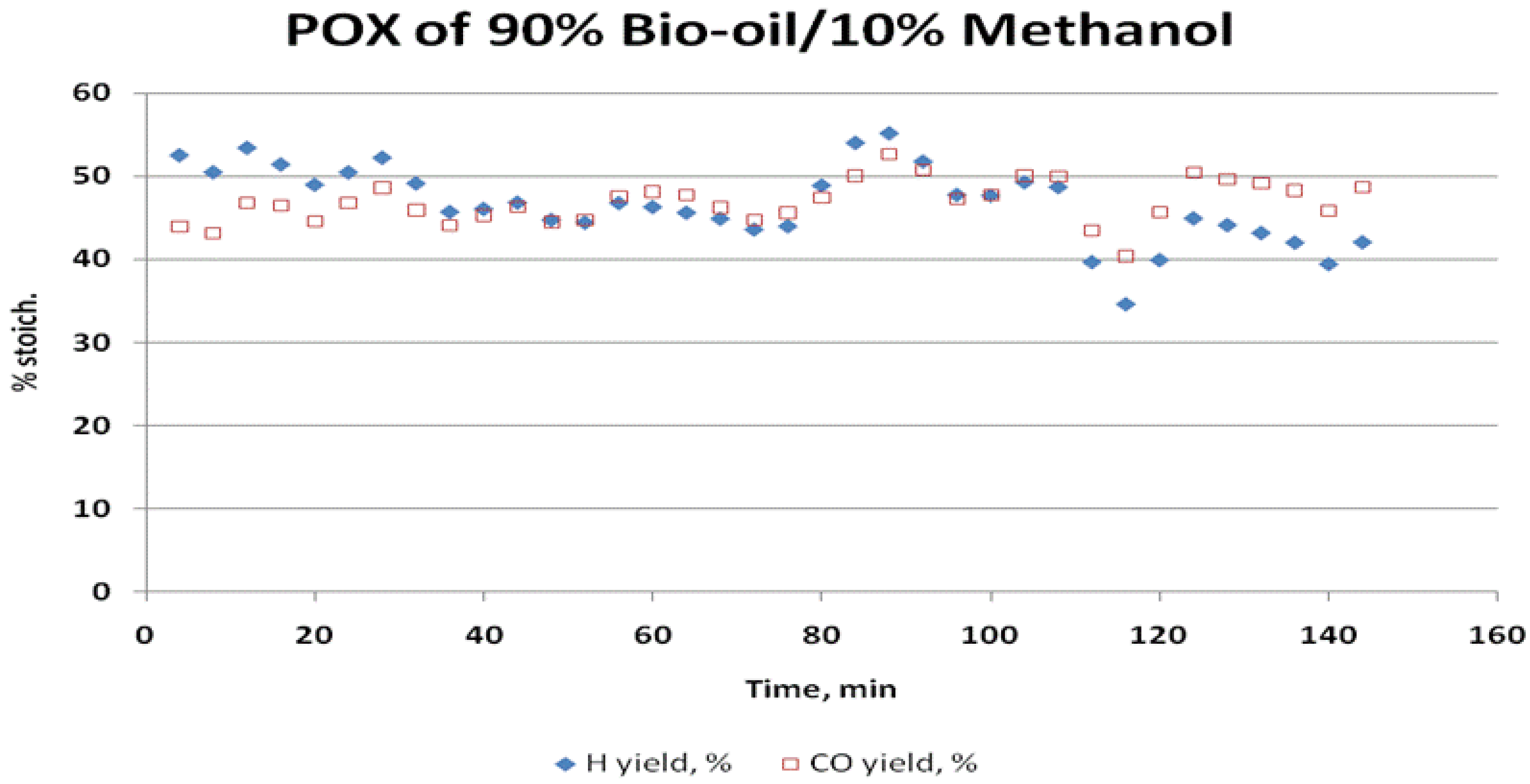
Syngas Composition at Different T and O/C levels



High temperature and low O/C favor higher yields of syngas (CO + H_2)

Task 1. Process Performance Demonstration

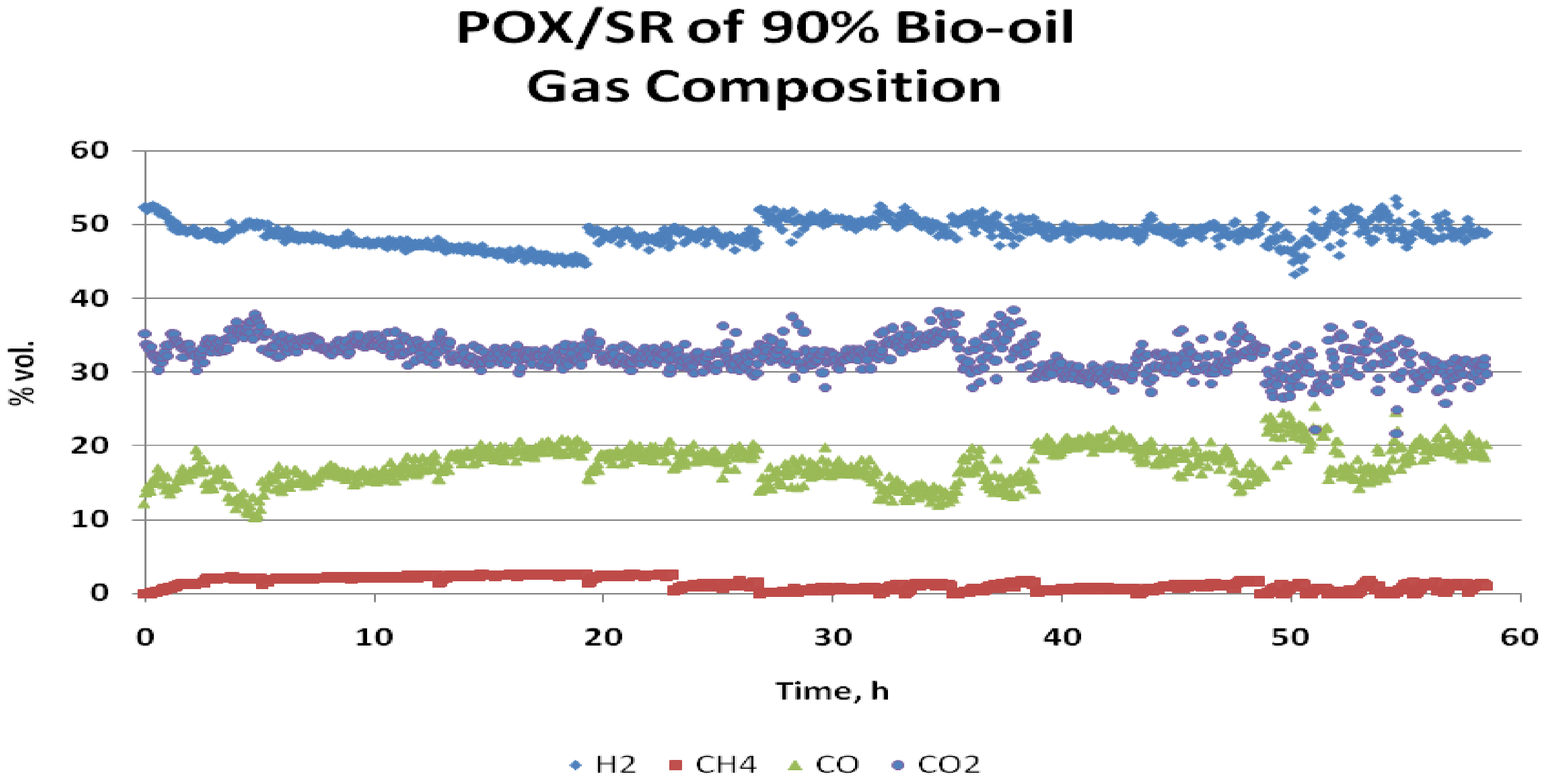
Yields of CO and H_2 by POX of Bio-oil



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

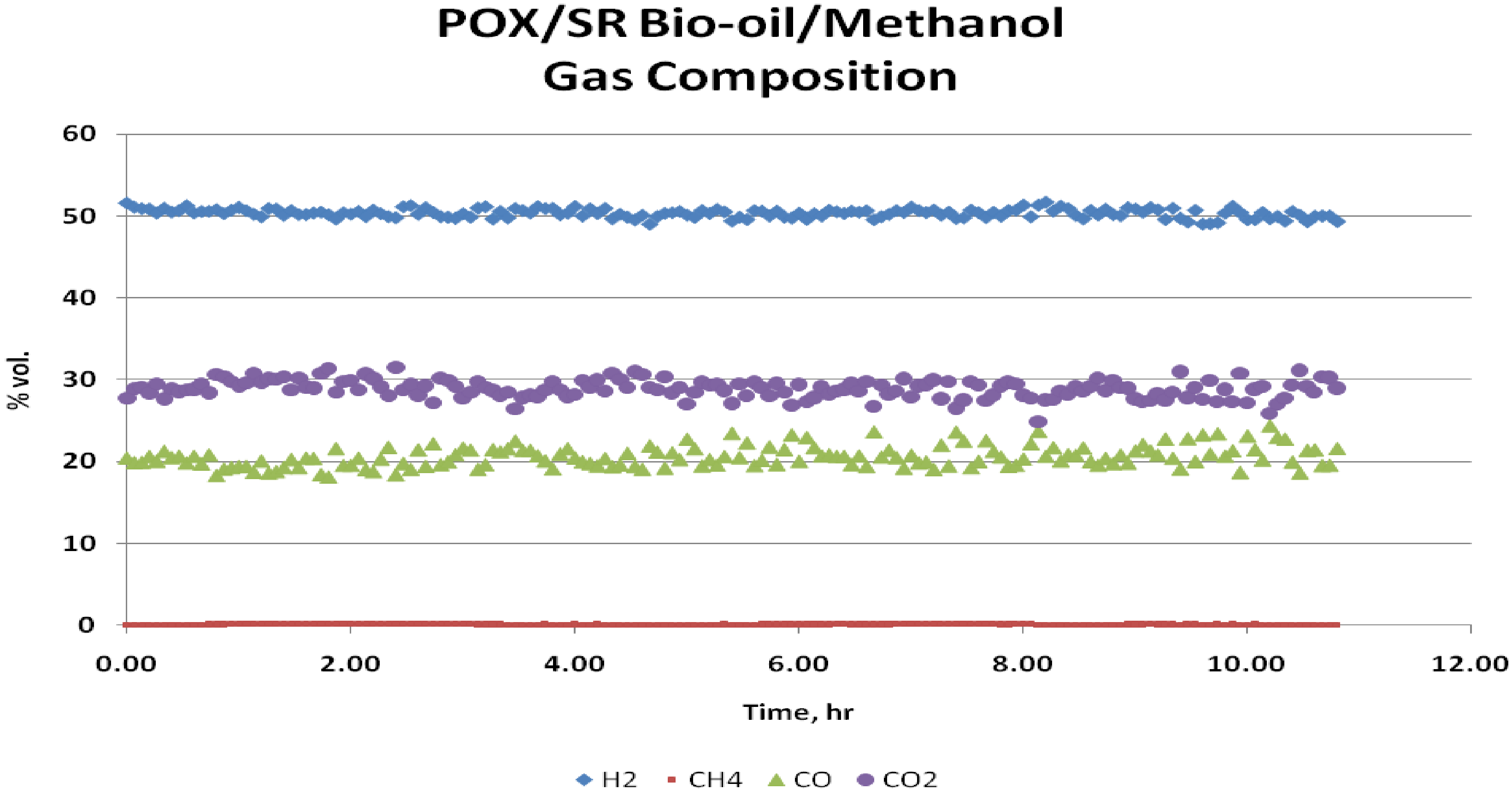
UMN 1% Rh, 1% Ce cat.; 850ºC; O/C=1.5; S/C= 1.6; GHSV=4200 h^{-1}



7.25 g H_2/100 g bio-oil (9.6 g H_2/100 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}



7.4 g H_2/100 g bio-oil (10.3 g H_2/100 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.

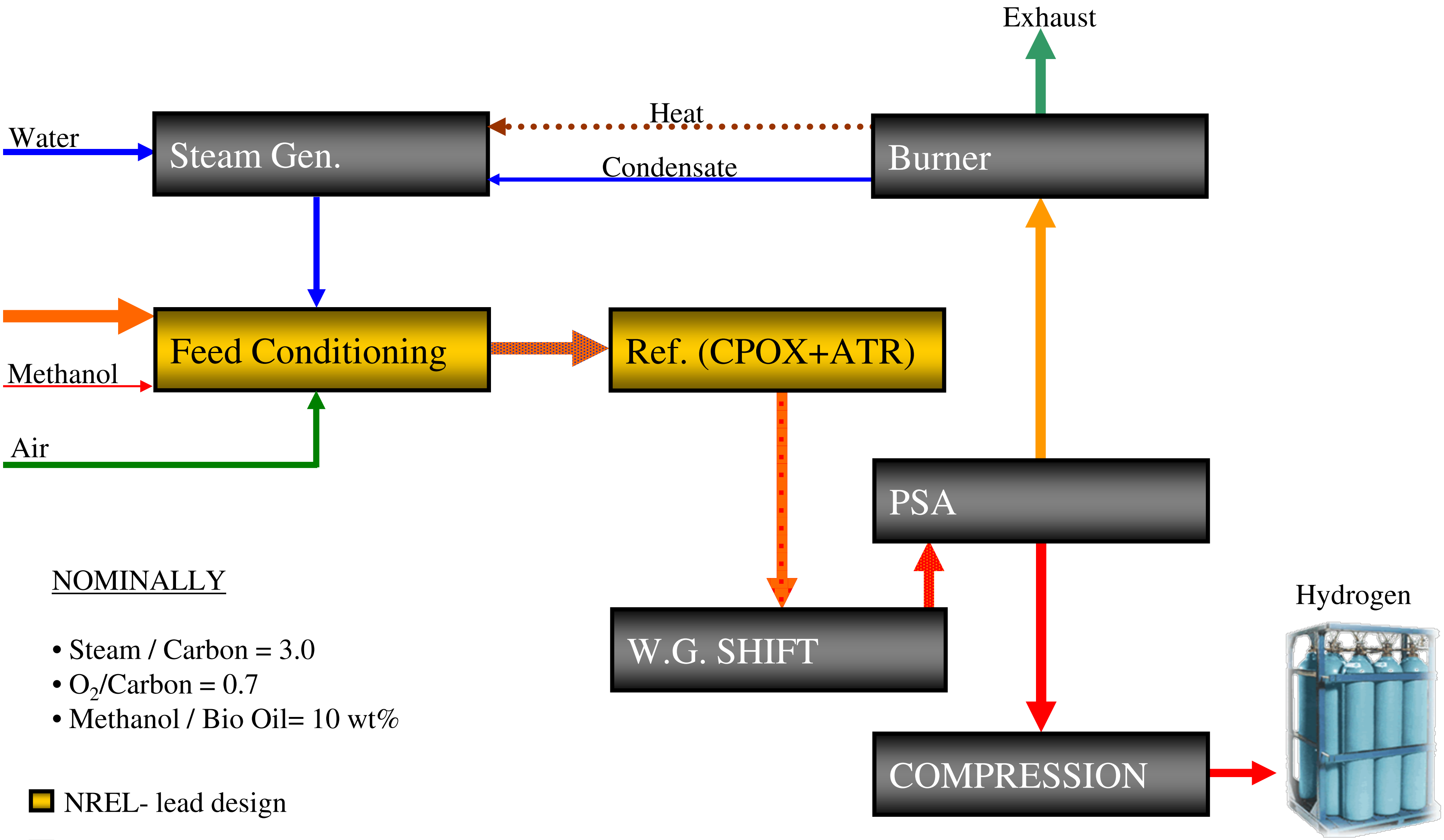
2. Best performing catalyst (1% Rh, 1% Ce on Al_2O_3) was provided for tests in the NREL POX/steam reforming system.

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



NOMINALLY

- Steam / Carbon = 3.0
- O_2/Carbon = 0.7
- Methanol / Bio Oil= 10 wt%

🟨 NREL- lead design

⬛ Industry - available subsystems

Task 3. Process Analysis

Hydrogen Cost *(2005$, nth 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

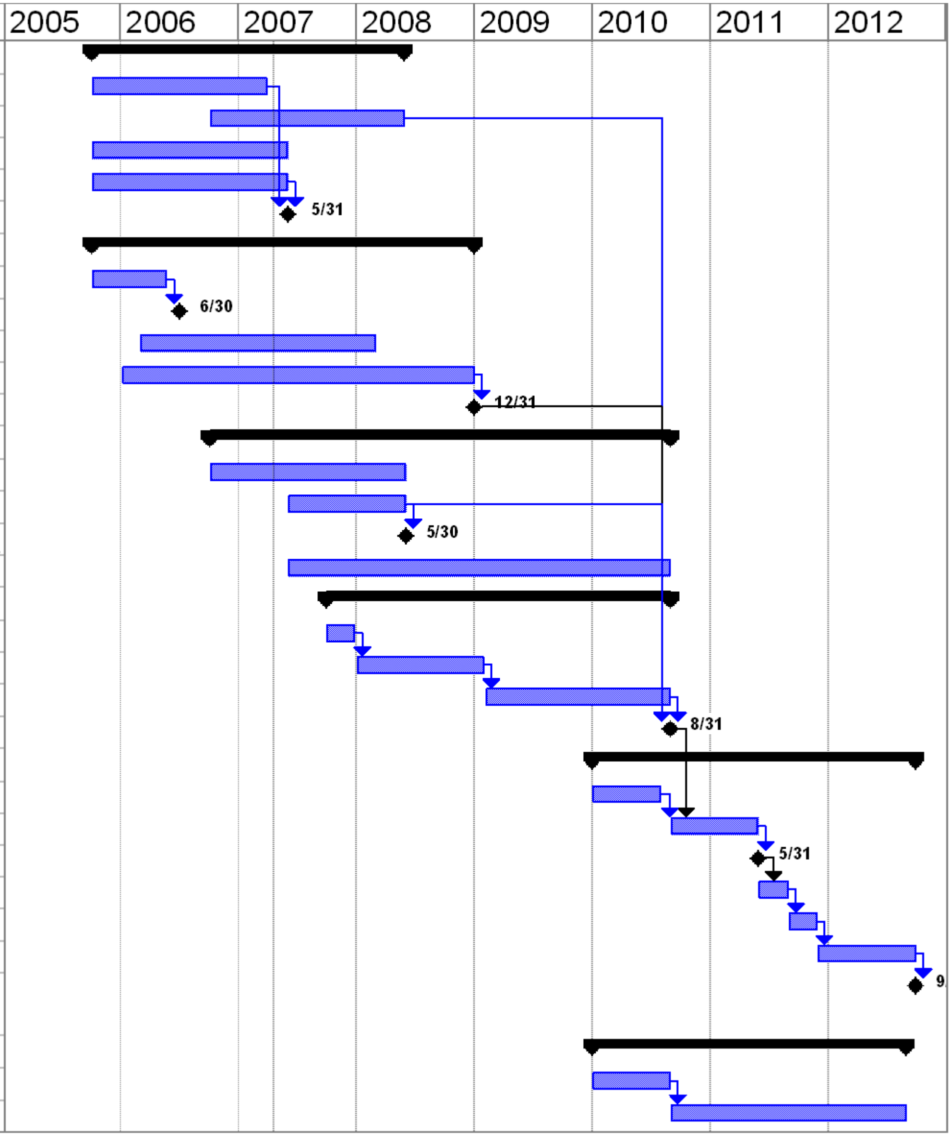
- University of Minnesota
    - ➢Catalyst development

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 Al_2O_3 prepared at University of Minnesota
    - 1% Ni, 1% Ce on Al_2O_3 prepared at University of Minnesota
    - 0.5% Rh on Al_2O_3 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

ID	Task Name
1	**Bio-Oil Volatilization**
2	Processing Options
3	Modification and Characterization
4	Injector Development
5	Coking Studies
6	***Go / No Go on Bio-Oil performance***
7	**Oxidative Cracking**
8	Proof of Concept
9	***Reduce Catalyst Loading by 50%***
10	Partial Oxidation Database
11	Modeling and Optimization
12	***Jon Marda Thesis***
13	**Catalytic Auto-Thermal Reforming**
14	Catalyst Screening
15	Catalyst Process optimization
16	***Demonstrate catalyst performance consistent with $3.80/gge h***
17	Catalyst Mechanistic Studies
18	**Integrated Separation**
19	Concept Evaluation
20	Materials Evaluation
21	Integrated Laboratory System Experiment
22	***Go / No Go on Conceptual Design***
23	**Systems Engineering**
24	Oxygen, Steam and Heat Integration
25	Engineering Design and Construction
26	***Prototype System Developed***
27	Heat and Mass Balances
28	Process Upsets
29	Long Duration Runs
30	***Demonstrate Distributed Hydrogen Production from Bio-Oil for $3.8/gge***
31	**Safety Analysis**
32	Review and Analysis of Pressure, O2, H2
33	Systems Integration



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**