NATIONAL RENEWABLE ENERGY LABORATORY

Distributed Bio-Oil Reforming

2011 Annual Merit Review and Peer Evaluation Meeting

Stefan Czernik

May 9-13, 2011

Project ID# PD004

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Overview

TIMELINE

- Start date: 2005
- End date: 10/2011*
- Percent complete: 85%

BUDGET

- Total Project Funding: 2,350K
- Funding received in FY 2010: $500K
- Funding for FY 2011: $400K

BARRIERS

Production Barriers

A. Fuel processor capital
C. Operations and maintenance
D. Feedstock issues
F. Control and safety

2012 Targets

- $3.80/gallon gasoline equivalent
- 72% energy efficiency (bio-oil to H_2)

PARTNERS

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

Project continuation and direction determined annually by DOE.

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 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 = 2-3)

Overall Reaction:

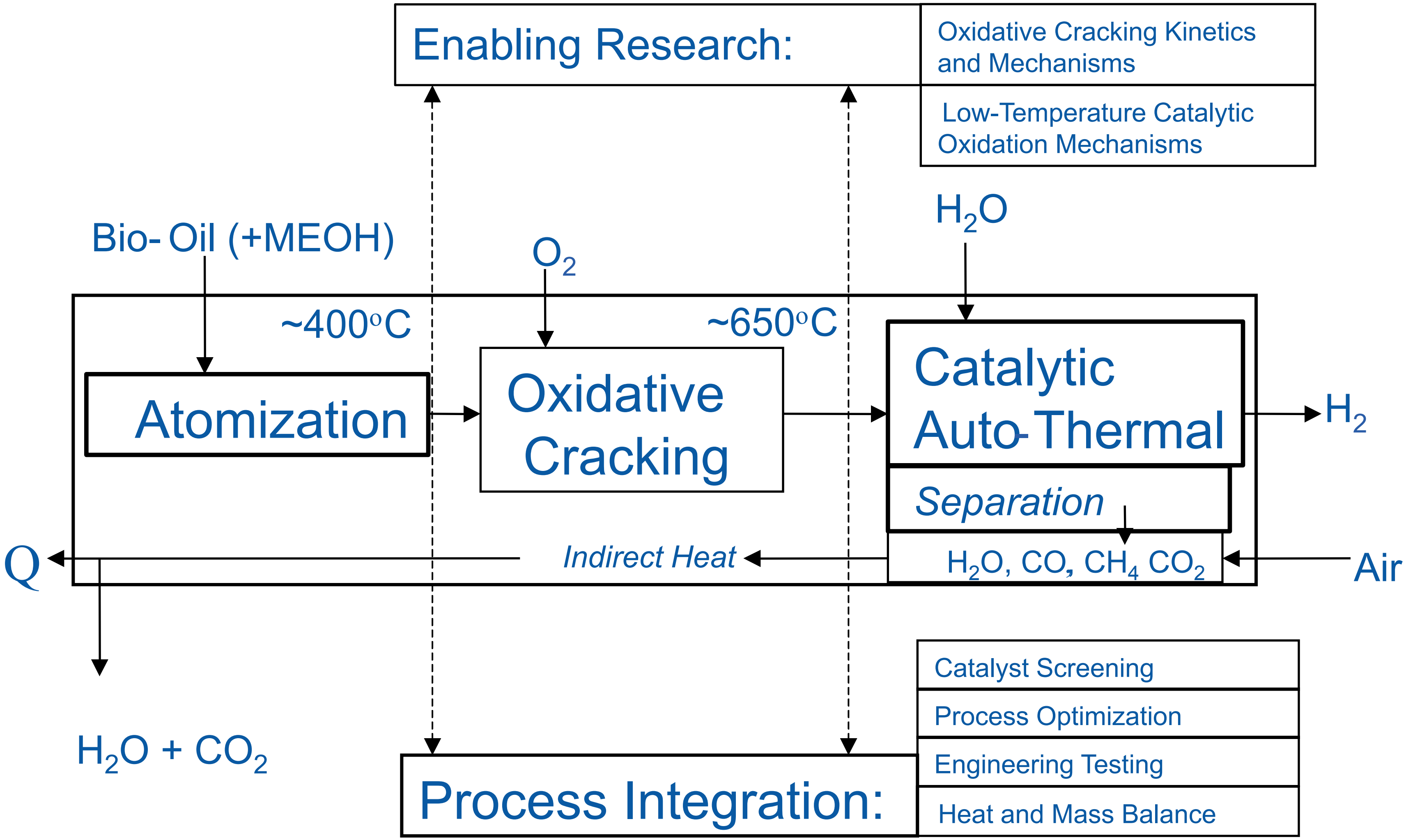
$CH_{2.18}O_{0.78} + 0.51O_2 + 0.19\ H_2O \rightarrow CO_2 + 1.28\ H_2$

***Estimated Practical Yield:* 10 wt%**

Estimated Energy Efficiency: 72% LHV H_2 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 2011

- Select a commercial catalyst for autothermal reforming of bio-oil.
- Construct an integrated system for producing hydrogen from bio-oil.
- Demonstrate operation of the integrated autothermal system for producing hydrogen from bio-oil at 100 L/h.

Technical Accomplishments

FY 2008

- 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)

FY 2011

- Achieved yield of 10.1 g H_2 per 100 g bio-oil

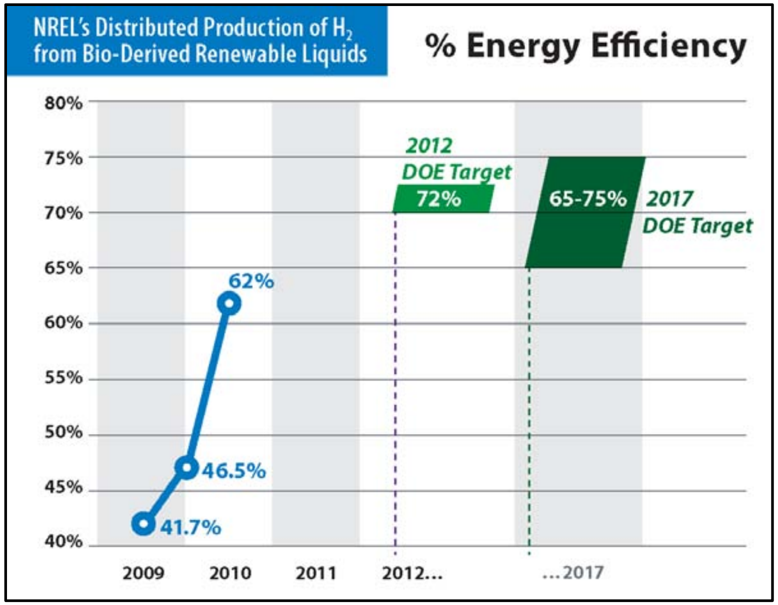
Progress Toward DOE Targets

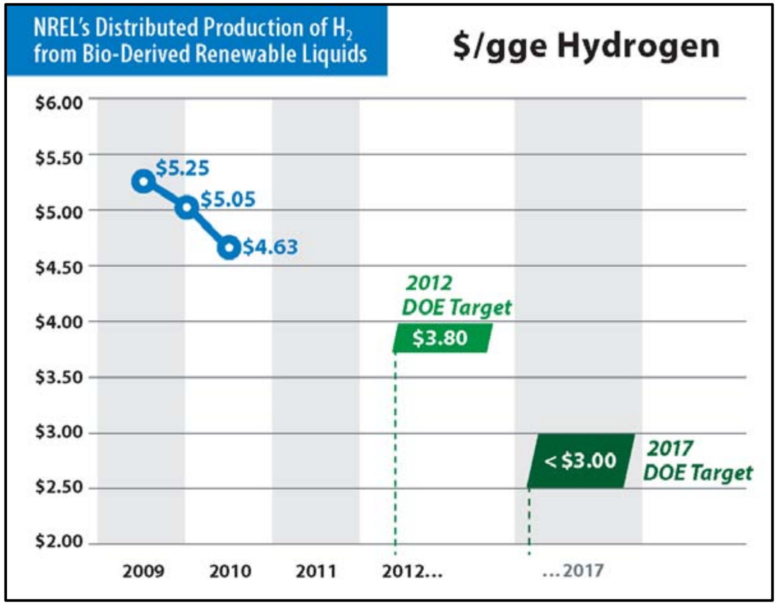
We demonstrated hydrogen production by auto-thermal reforming of bio-oil in a bench-scale reactor system in FY 2009/2010.

Using a commercial catalyst, the hydrogen yield was 10.1g/100g bio-oil in Sept., 2010 (compared to 6.6g/100g bio-oil at the end of 2009).

For a 1,500 kg/day hydrogen plant, the total production cost was estimated at $2.70/gge.

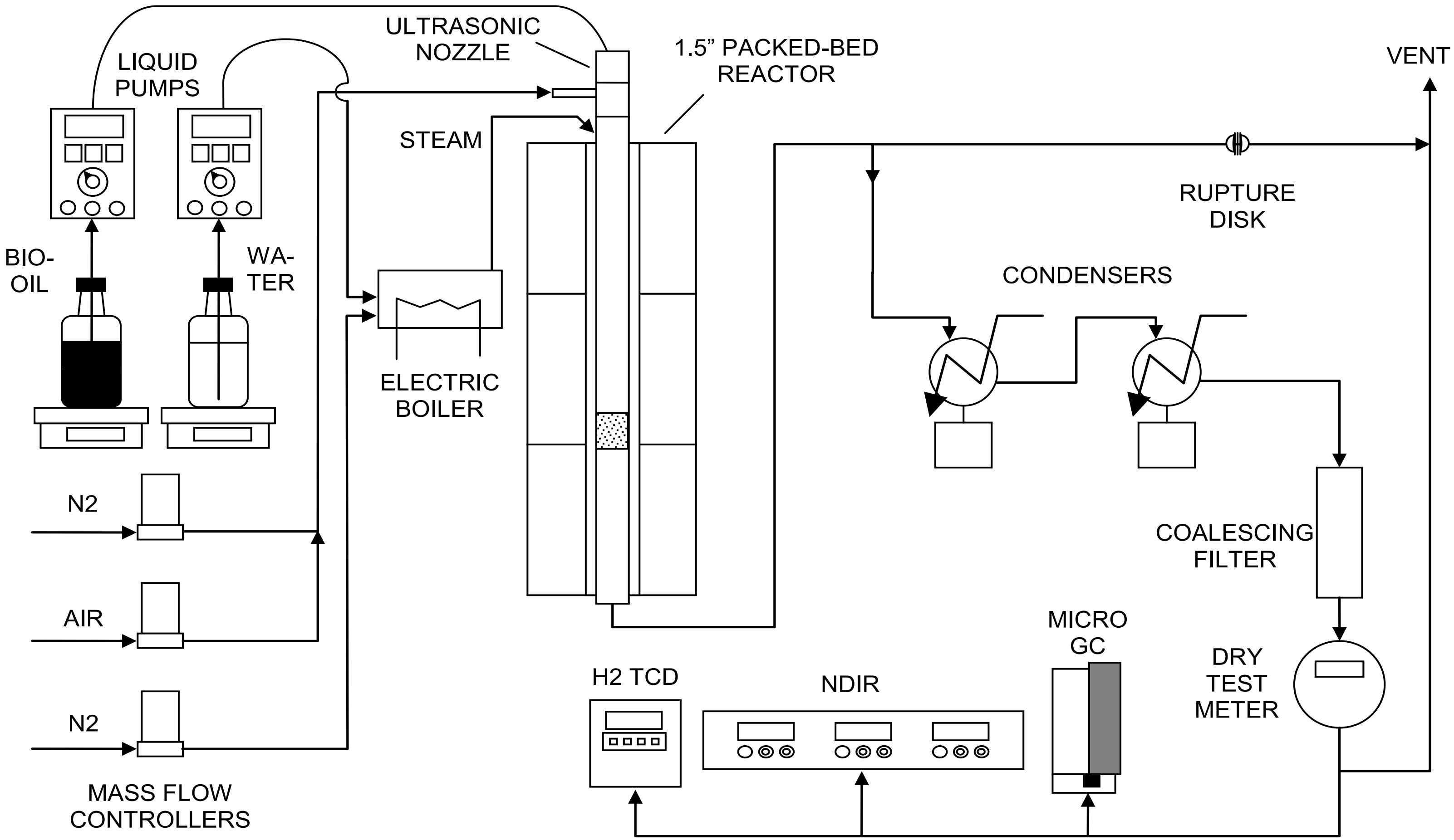
Compression and dispensing costs bring the total projected cost of hydrogen to $4.63/gge.





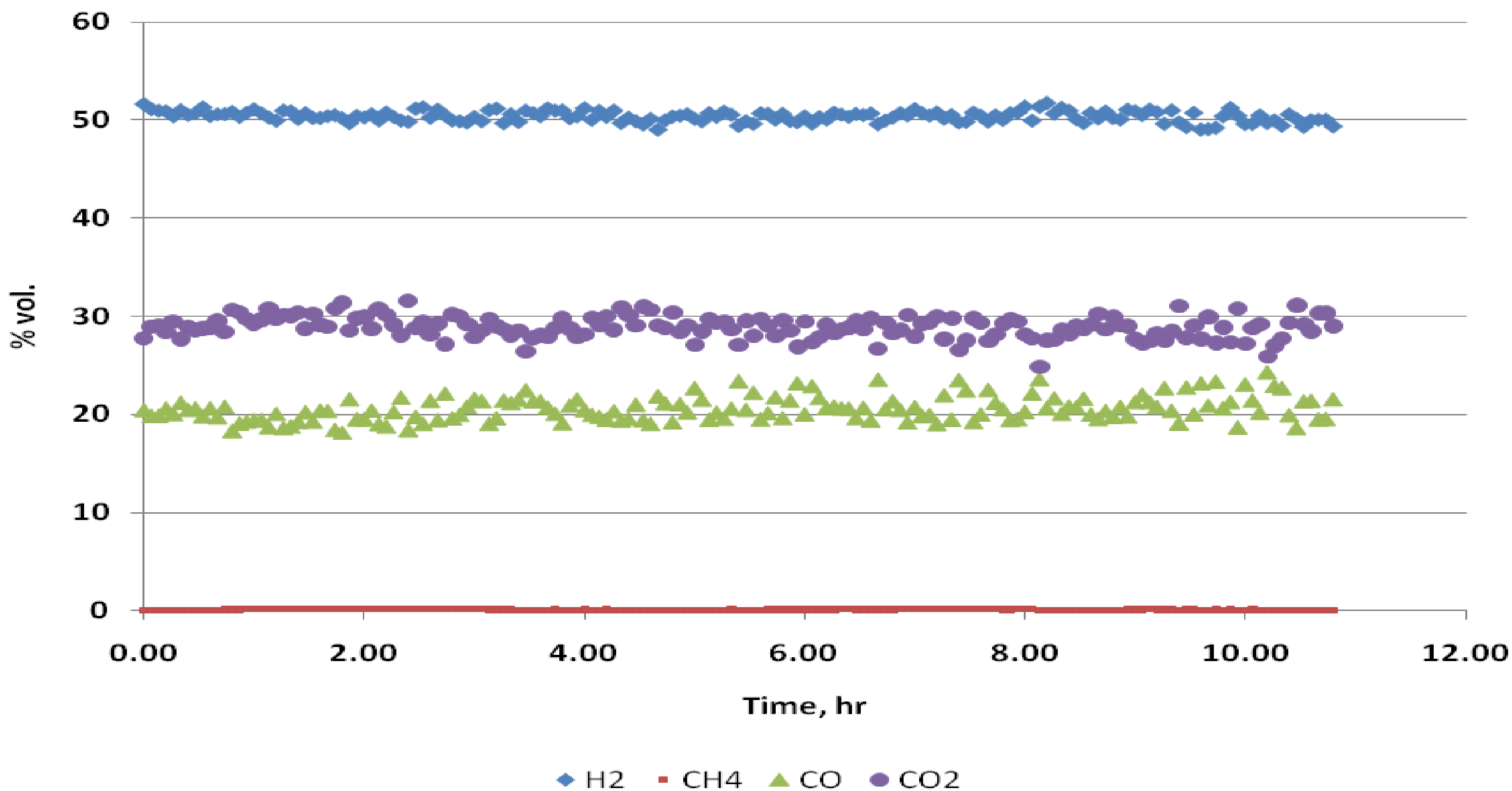
Process Performance Demonstration

Bench-Scale Fixed-Bed Continuous Flow Reactor System



Process Performance Demonstration

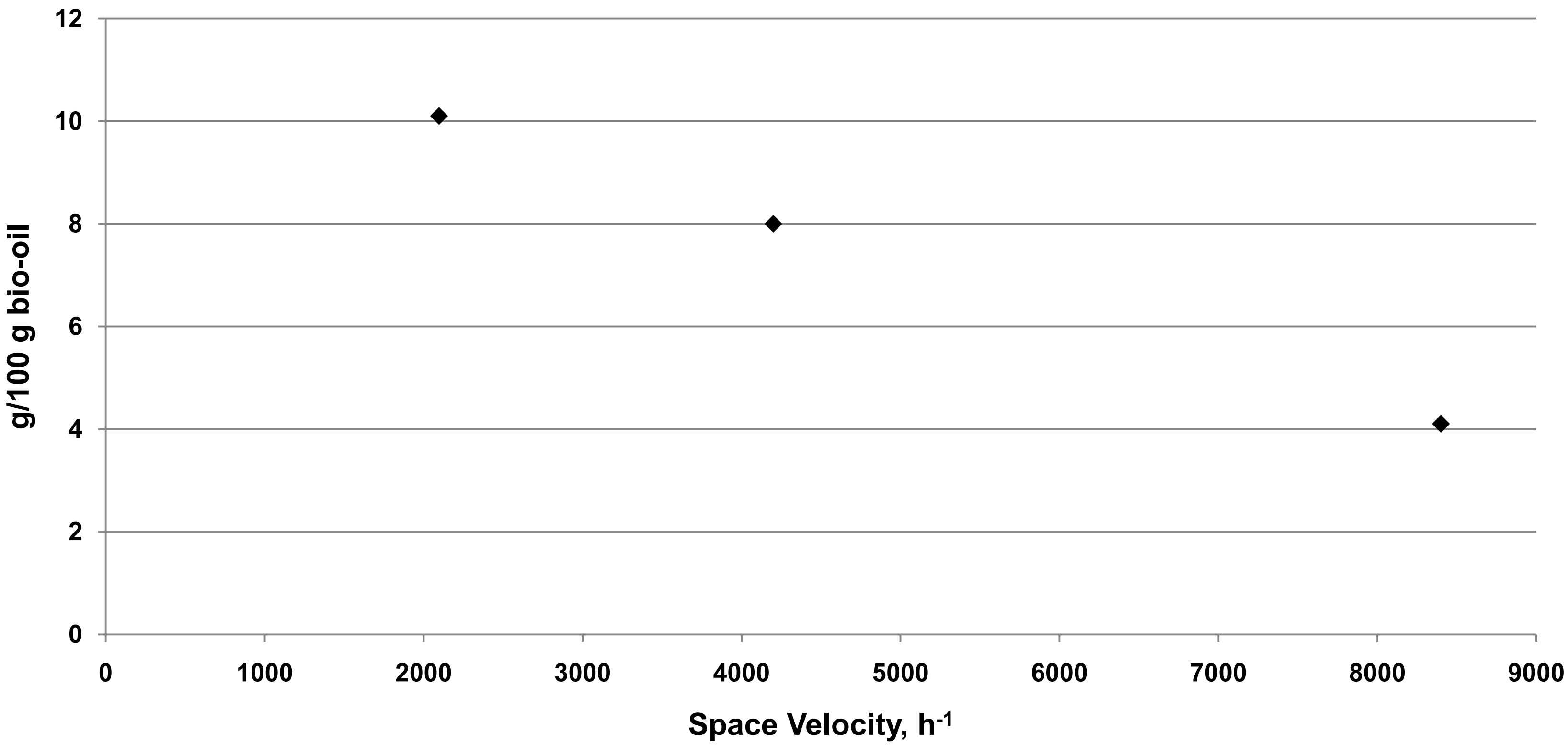
BASF 0.5% Pt/Al_2O_3 catalyst; 850ºC; O/C=0.9; S/C= 2.9; GHSV=2100 h^{-1}



10.1 g H_2/100 g bio-oil

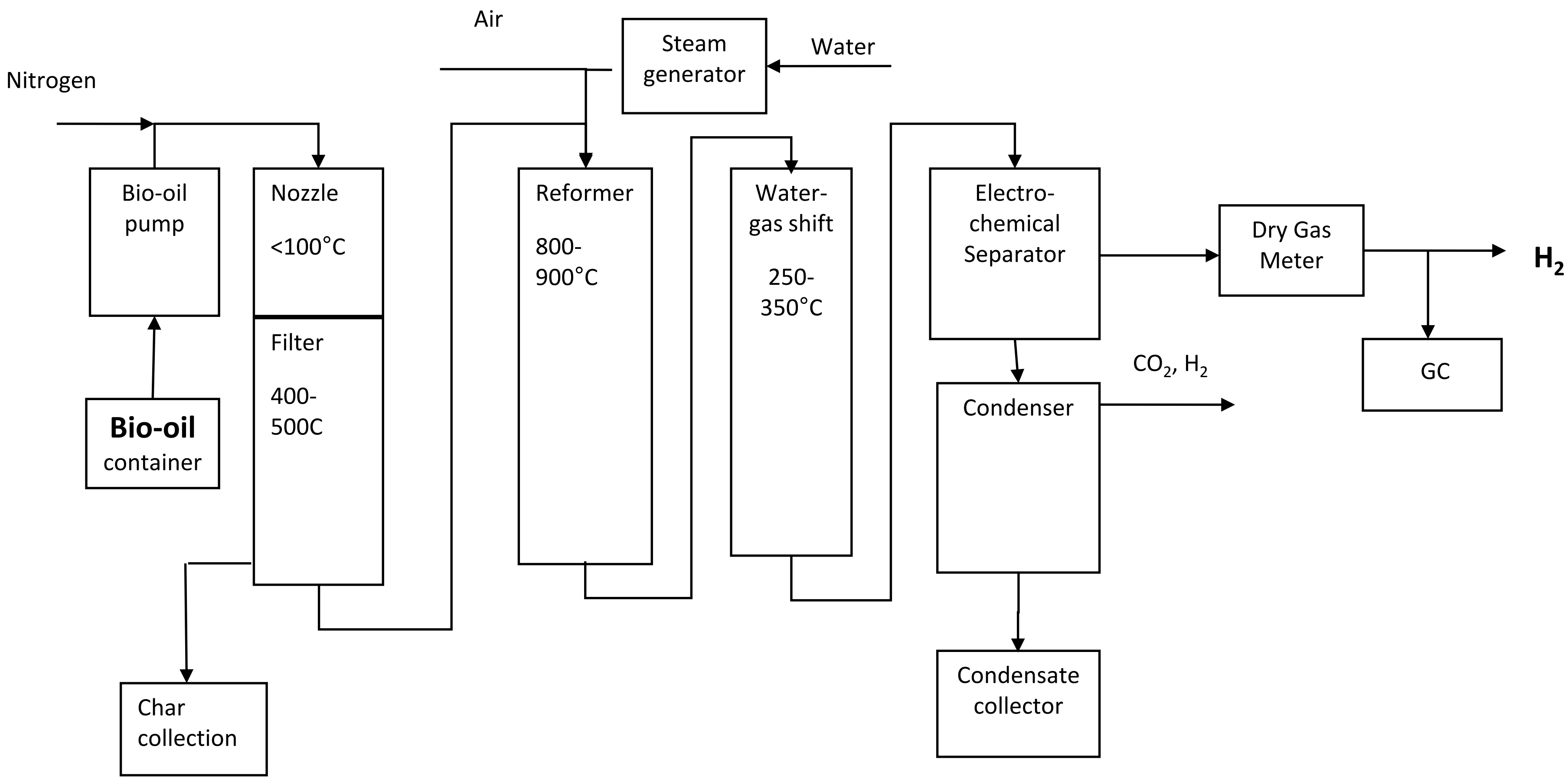
Yield of Hydrogen at Different Space Velocities

BASF 0.5% Pt/Al_2O_3 catalyst; 850ºC O/C=0.9; S/C=2.9



WHSV=0.6 is required to produce high yields of hydrogen

Construction and Shakedown of Integrated System

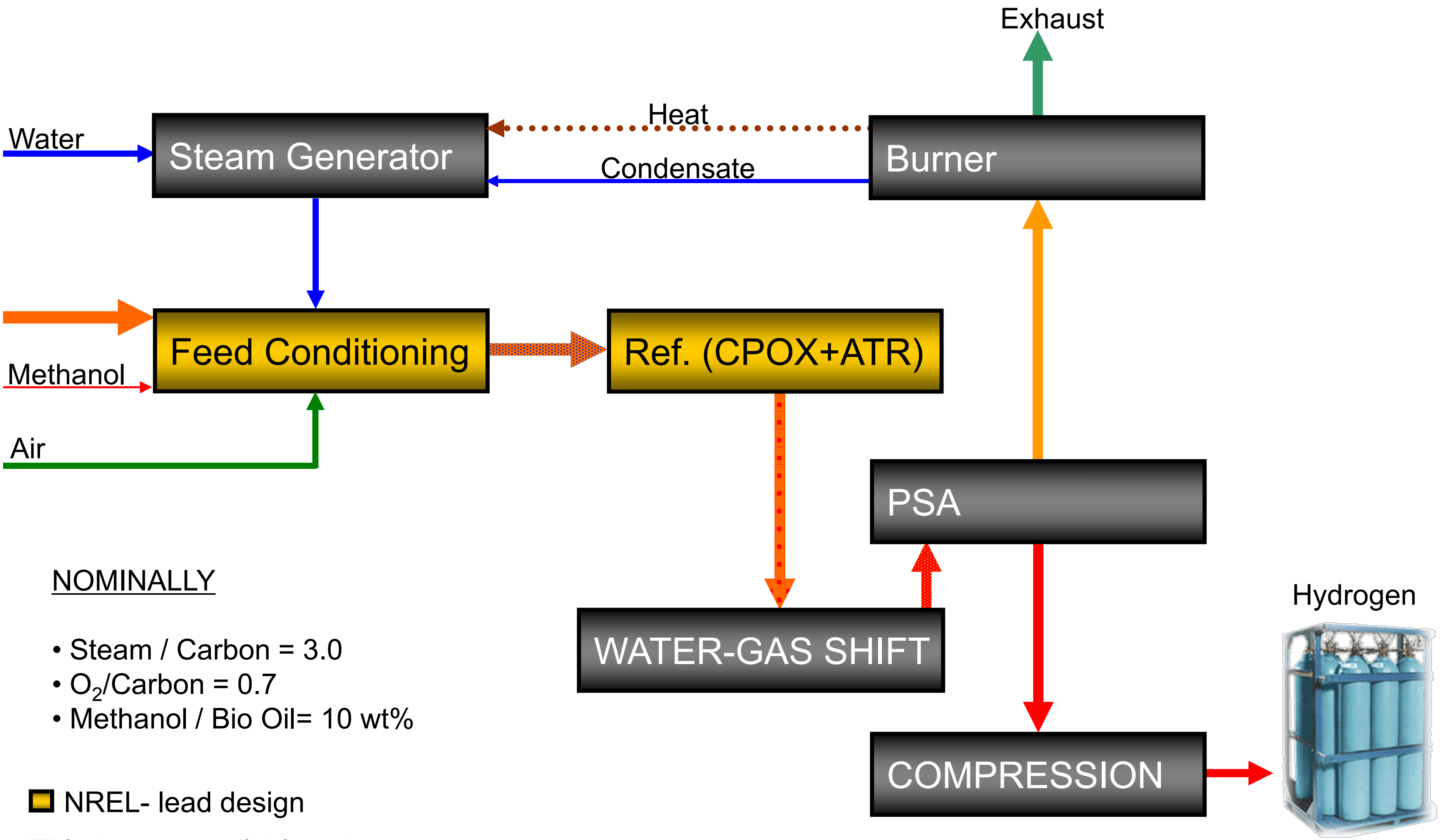


Construction of the reactors in progress

Hydrogen separator will be loaned from H2Pump

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

Process Analysis

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

1500 kg/day station used for H2A analysis

(Current projected high volume cost based on 2011 performance)

- **Capital costs *$1,780,000* *or* *$2.13/gge***

  ***$1.29/gge* for compression and distribution**

  ***$0.84/gge* for production**

- **Total cost of delivered hydrogen *$4.63/gge***

  ***$2.75/gge* for production**

  ***$1.88/gge* for compression and distribution**

Collaborations

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

  CSM undergraduate students participate in bench-scale experiments at NREL

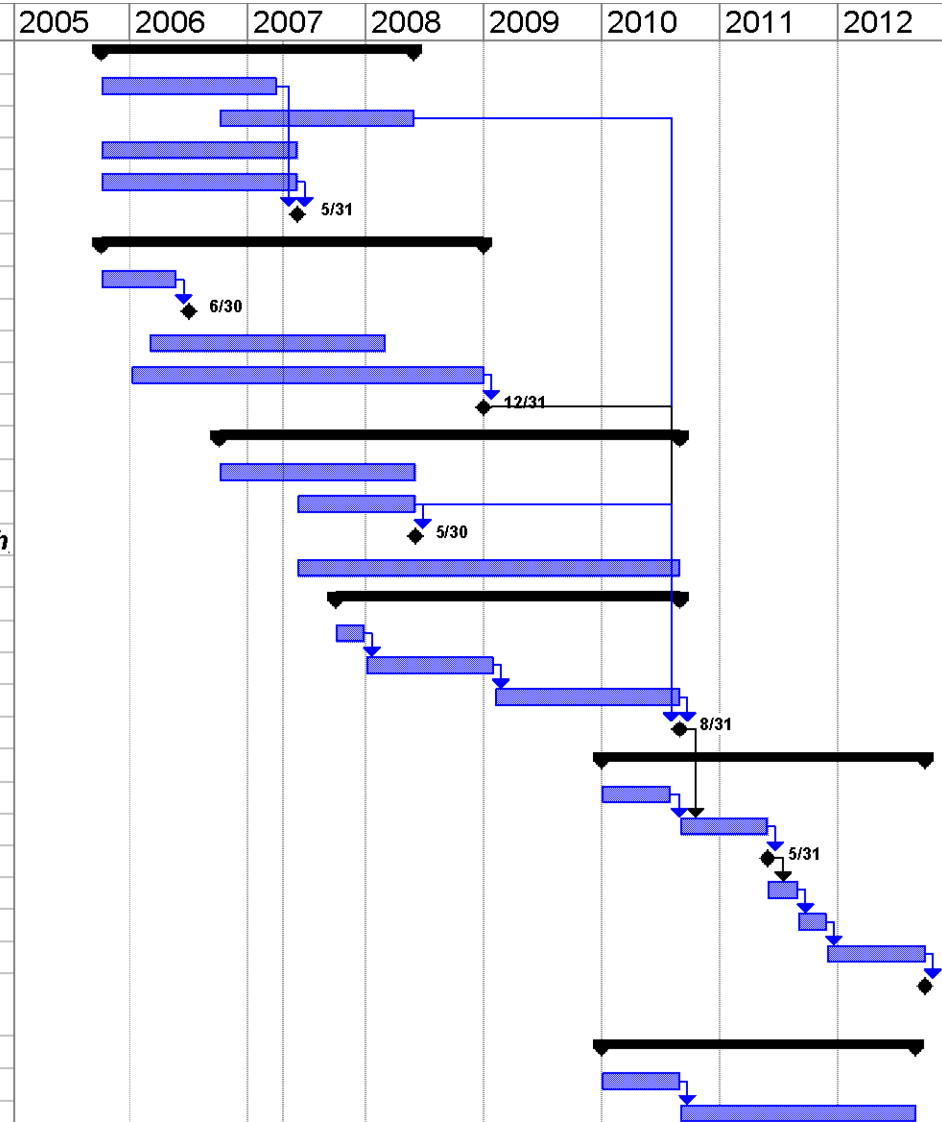
- Chevron
  - Feedstock variability
- University of Minnesota
  - Catalyst development

Summary

- Bench-scale reactor system tests of catalytic autothermal reforming of bio-oil continued using 90 wt% bio-oil/10 wt% methanol mixtures.
- The catalysts:
  - 0.5% Pt on Al_2O_3 pellets and monolith provided by BASF were tested using different space velocities.
- Carbon-to-gas conversion was 88%–91%.
- At 850°, O/C=1.5, S/C=2.9, and GHSV=2100, 10.1 g hydrogen was produced from 100 g bio-oil/methanol feed.
- The estimated cost of hydrogen production: $2.73/gge.
- The construction of an integrated system for producing 100 L/h of hydrogen by autothermal reforming of bio-oil is in progress.

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 2011: Complete integrated prototype system producing 100L/h hydrogen from bio-oil**
- **FY 2012: Long duration runs to demonstrate at least 100 hours of the catalyst performance and to validate the operation of the integrated system.**