NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Distributed Bio-Oil Reforming

2012 Annual Merit Review & Peer Evaluation Meeting

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Project ID# PD004

Overview

TIMELINE

- Start date: 2005
- End date: 10/2012*
- Percent complete: 90%

BARRIERS

Production Barriers

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

2012 Targets

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

BUDGET

- Total project funding: $2,800K
- Funding received in FY 2011: $450K
- Planned funding for FY 2012: $450K

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

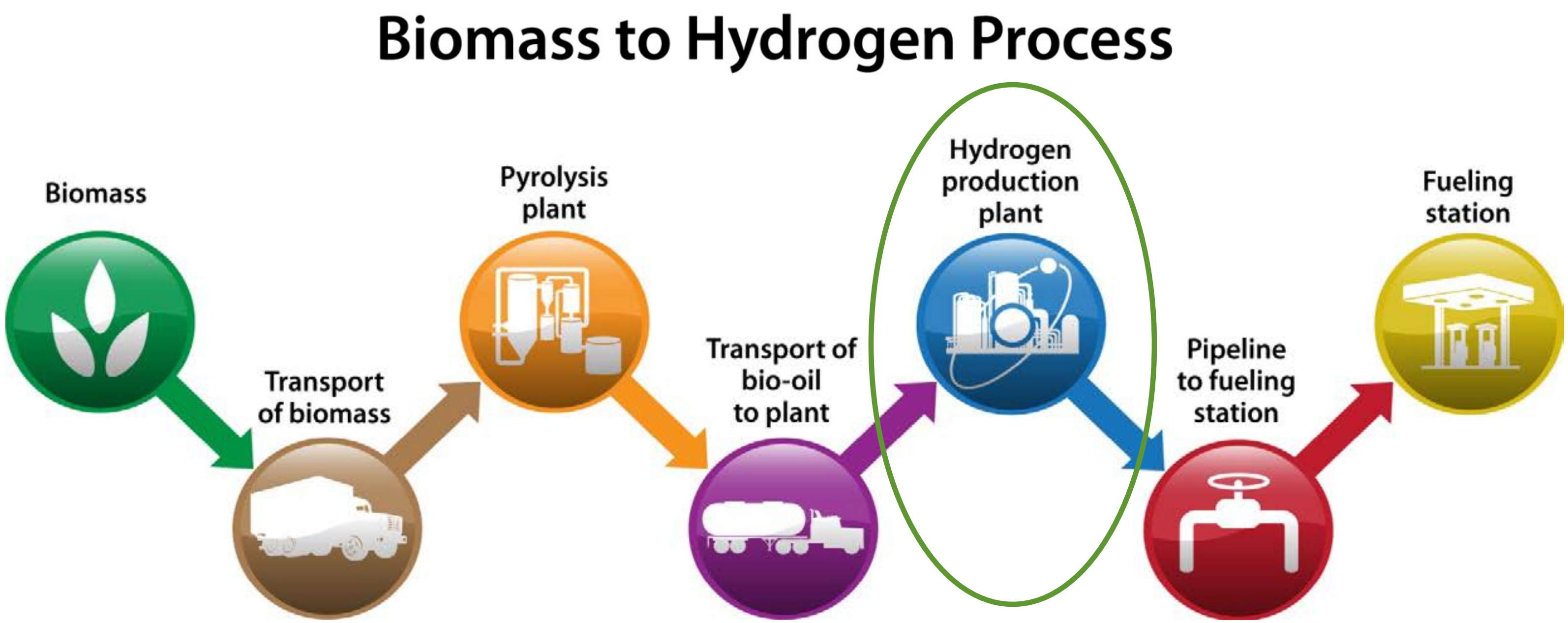
Biomass can be an important resource for hydrogen production.

- 1.3 Gt/year biomass is expected to be available in the U.S. for energy and fuels production.
- Producing hydrogen from domestic resources, such as biomass, can reduce dependence on petroleum and yield virtually zero greenhouse gas emissions.
- This project addresses the technical and economic challenges of hydrogen production from renewable liquids.

Approach: Process Concept

The proposed *biomass-to-hydrogen* process includes two production steps:

- *Fast pyrolysis* that converts biomass into a liquid product, bio-oil
- ***Autothermal reforming* of bio-oil to produce hydrogen.**



This project explores the bio-oil to hydrogen step

Approach: Process Chemistry

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 autothermal reforming of bio-oil:

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

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

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)

Approach: Technical Progress

FY 2009

- Built a bench-scale reactor system and demonstrated operation of the unit using 90 wt% bio-oil/10 wt% methanol mixture

FY 2010

- Demonstrated 60 hours of catalyst performance
- Achieved hydrogen yield of 7.3 g H_2 per 100 g bio-oil

FY 2011

- Achieved yield of 10.1 g H_2 per 100 g bio-oil during short-term quartz reactor tests producing hydrogen at 50 L/h
- Built an integrated bench-scale system for the production of 100 L/h hydrogen from biomass pyrolysis oil

FY 2012

- Demonstrated 100 hours of the commercial catalyst performance in the integrated bio-oil to hydrogen system.

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 2012

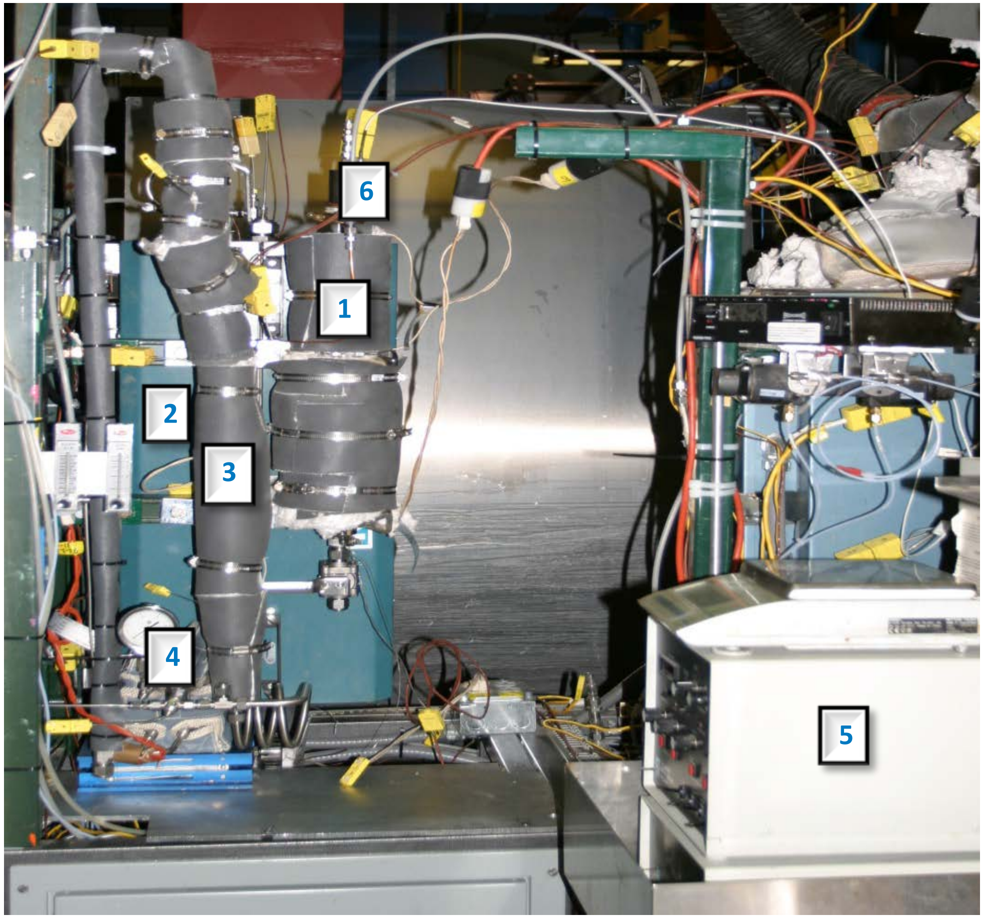
- Demonstrate 100 hours of the commercial catalyst performance in the integrated bench-scale system.
- Achieve the production of 100 L/h of hydrogen at a yield of 10 g H_2/100 g bio-oil.
- Assess the process energy efficiency and the cost of hydrogen.

Technical Accomplishments

1. The integrated bench-scale system for the production of 100 L/h hydrogen from pyrolysis bio-oil has been constructed. Except for the gas compression, this system includes all the basic unit operations as the design for the 1500 kg/day hydrogen plant.
2. The system was tested using the following process parameters:
   - commercial catalyst (BASF 0.5%Pt/Al_2O_3),
   - process temperature 800-850^oC,
   - oxygen to carbon ratio (O/C) 1.2-1.6,
   - steam to carbon ratio (S/C) 2-3, and
   - space velocity GHSV 1800-2500 h^{-1}.
3. For the new batch of bio-oil, the hydrogen yield achieved so far was 9.1 g/100 g bio-oil and the bio-oil carbon to gas conversion was >85%.

Technical Accomplishments

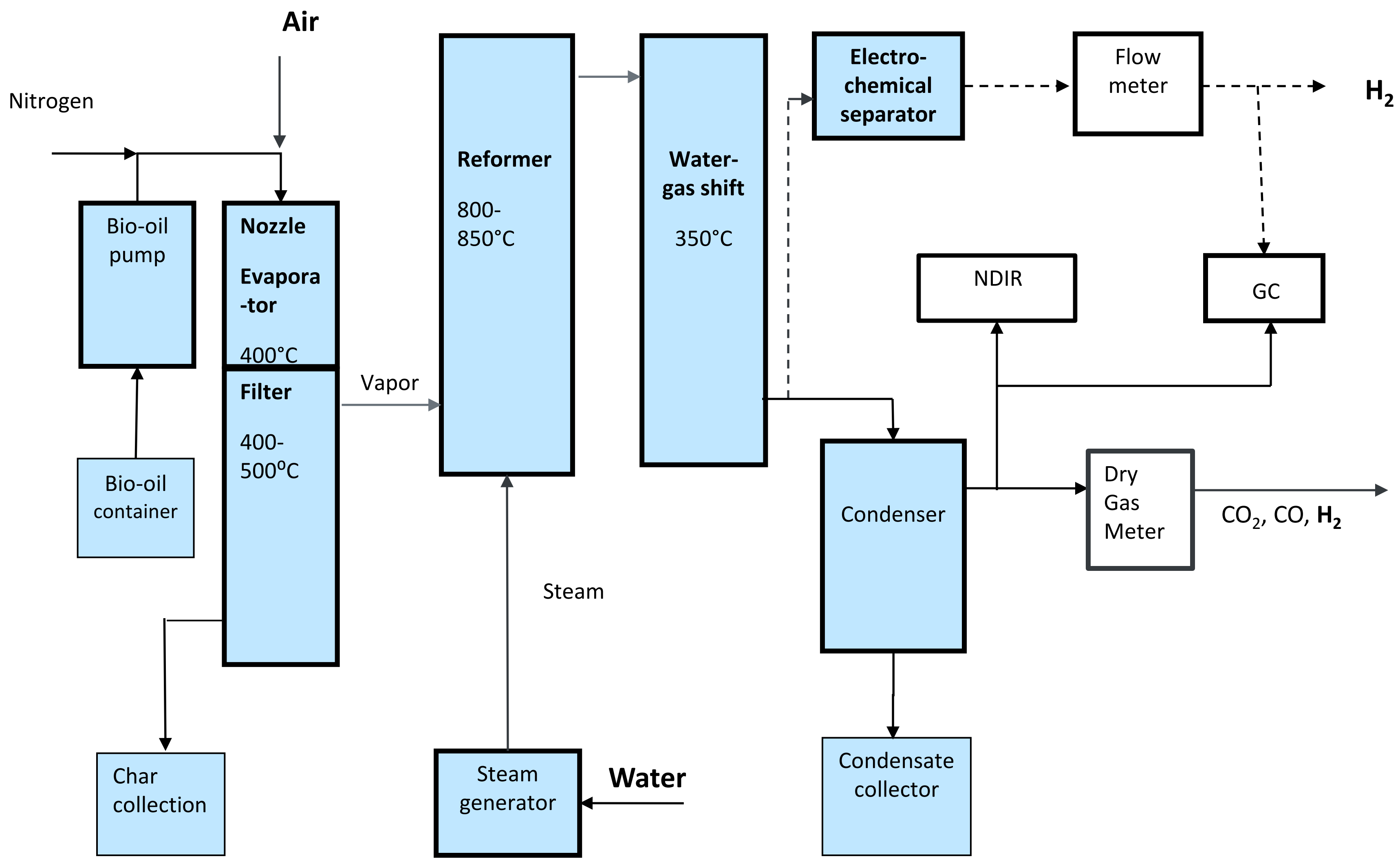
Integrated bio-oil to hydrogen system is comprised of the following units:



1. Bio-oil evaporator/filter
2. Reformer
3. Water/gas shift reactor
4. Electrochemical hydrogen separator
5. Bio-oil pump
6. Ultrasonic bio-oil atomization nozzle
7. Steam condenser *(not shown)*

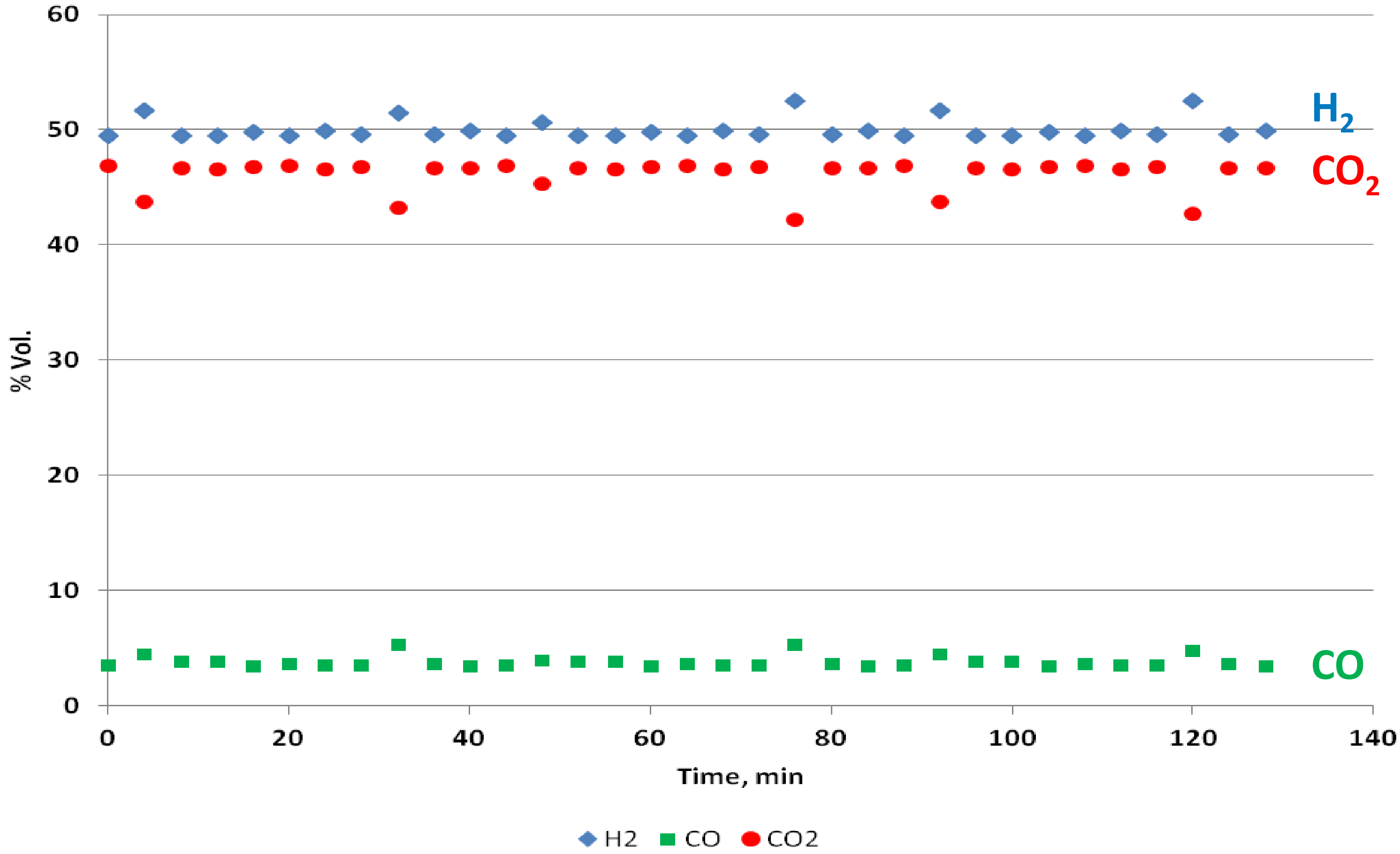
The 50 L/h bench-scale system used in 2010-2011 did not have the evaporator, the water-gas shift reactor or the hydrogen separator

Schematic of Integrated Bio-Oil to Hydrogen System



Integrated System Process Performance Demonstration

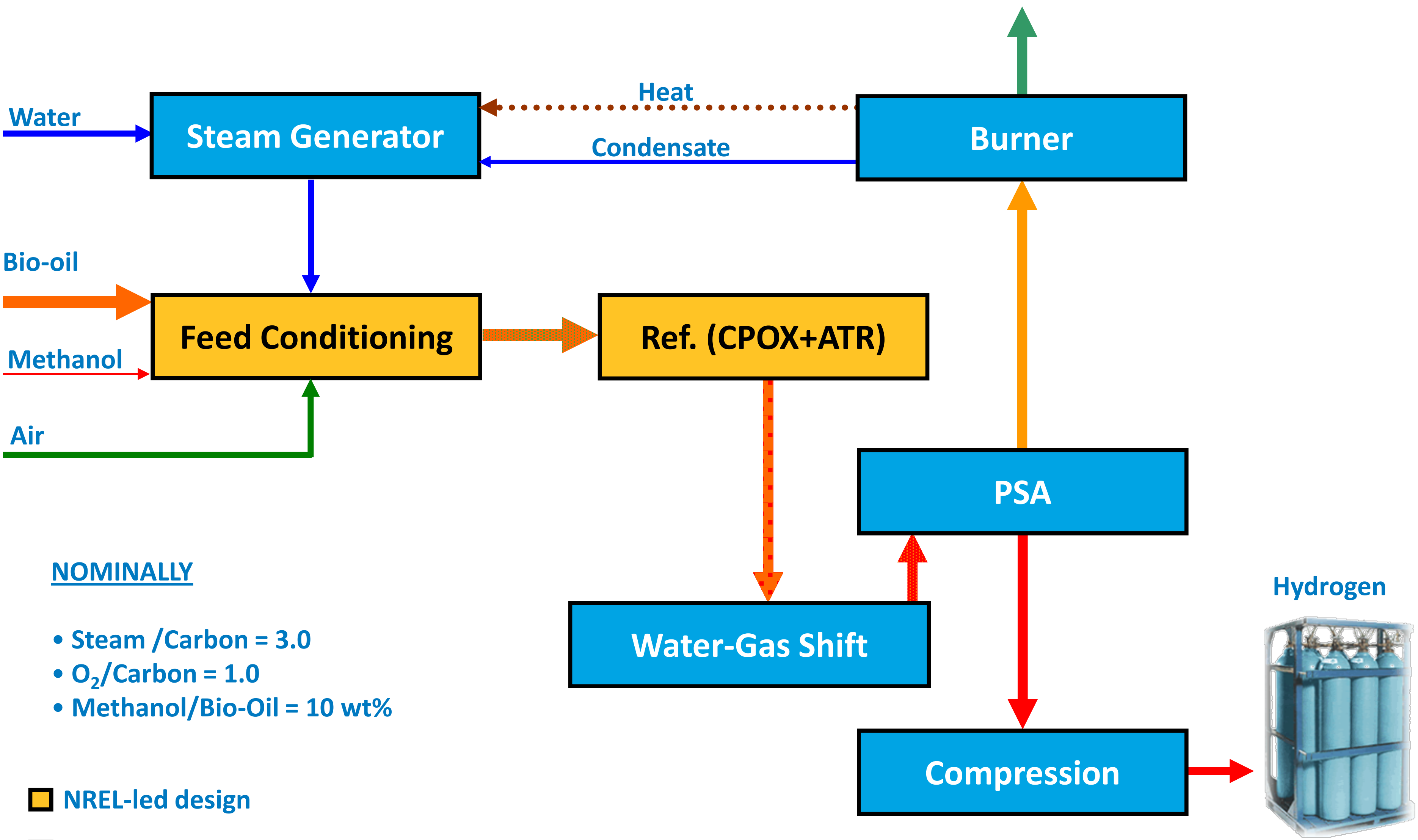
BASF 0.5% Pt/Al_2O_3 catalyst; 850 C; O/C=1.5; S/C= 3.0; GHSV=1950 h^{-1}



Yield = 9.1 g H_2/100 g bio-oil
Carbon to gas conversion = 85%

Process Analysis

Conceptual Process Diagram



<u>NOMINALLY</u>

- Steam /Carbon = 3.0
- O_2/Carbon = 1.0
- Methanol/Bio-Oil = 10 wt%

■ NREL-led design

■ Industry-available systems

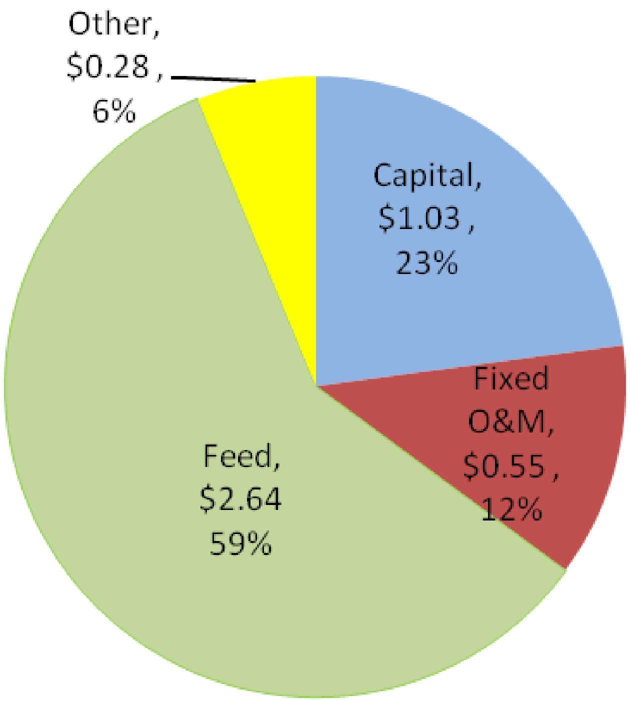
Process Analysis

Hydrogen production cost (H2Av3, 2007$, n^{th} plant)

- **1,500 kg/day hydrogen plant**
- **Capital : $1,880,000**
- **Bio-oil price: $236/ton**
- **Cost of production: $4.60/gge**

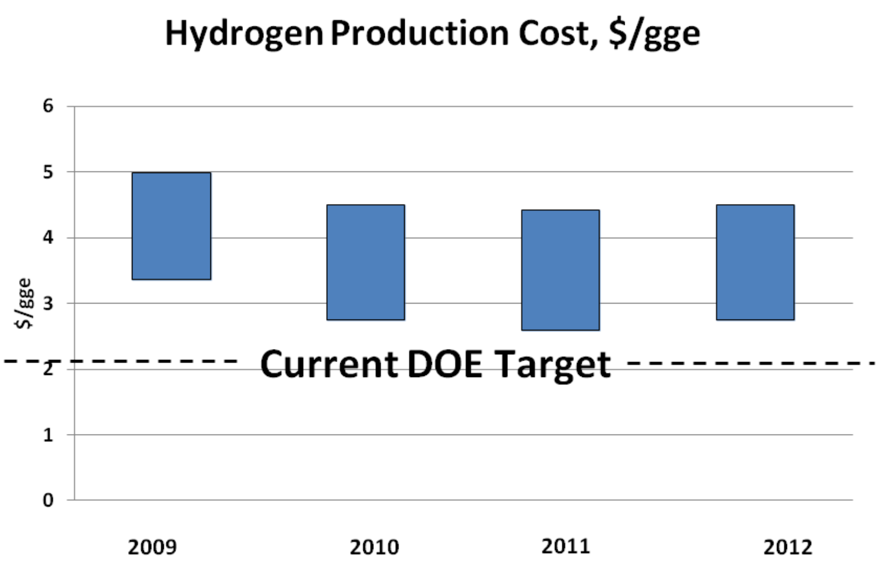
  (compression, storage, and distribution not included)
- **Additional $2.00/kg H_2 is assumed as the cost of compression, storage, and distribution consistent with the delivery portion of $2-4/gge hydrogen production threshold goal.**

Production Cost Break-down



Progress Toward DOE Targets

- In the integrated bench-scale system we achieved the hydrogen yield of 9.1 g H_2/100 g bio-oil; last year the yield reached 10.1 g H_2/100 g bio-oil for a different batch of bio-oil.
- For a 1,500 kg/day hydrogen plant, the total production cost was estimated at $4.60/gge.
- Compression, storage, and dispensing are assumed to add $2.00/gge to the total cost of hydrogen.
- The main reasons for not achieving the cost target is the increase in the price of bio-oil from $100/ton to $236/ton and higher than previously assumed capital costs.



The hydrogen cost values correspond to bio-oil prices in a range of $100–$236/ton ($0.46 - $1.08/gal).

The increase in the last year cost is due to a lower yield of hydrogen produced from a new batch of bio-oil (contains higher fraction of non-volatile compounds).

Collaborations

Colorado School of Mines

- Development of a model of partial oxidation of bio-oil and definition of conditions for the auto-thermal reforming process
- Ph.D. thesis, M.S. thesis, one peer-reviewed journal paper, and four conference presentations
- Two CSM undergraduate students currently participate in bench-scale experiments at NREL

University of Minnesota *(ended in 2011)*

- Synthesis of different types of reforming catalysts
- Ph.D. thesis, three peer-reviewed journal papers, several conference presentations

Chevron *(ended in 2009)*

- Impact of feedstock variability on bio-oil quality and on the efficiency of the reforming process (wood-derived bio-oil proved to be superior to that produced from herbaceous feedstocks)

Proposed Future Work

FY 2012

- Continue bio-oil reforming tests to validate and optimize the process
- Demonstrate 100 hours of performance of the commercial catalyst in the integrated bench-scale system
- Achieve the production of 100 L/h of hydrogen at a yield of 10 g H_2/100 g bio-oil
- Assess the process energy efficiency and the cost of hydrogen

FY 2013

- Construct and test a high-pressure (200 psig) bio-oil reforming system which is expected to improve the process performance and to reduce the cost of compression.

Summary

- An integrated bench-scale system for the production of 100 L/h of hydrogen by autothermal reforming of biomass pyrolysis oil was constructed.
- The system includes a bio-oil pump and atomizer, an evaporator/filter unit, reformer, water-gas shift reactor, electrochemical hydrogen separator, steam condenser, and analytical instrumentation.
- At present, the achieved bio-oil carbon-to-gas conversion is 85%–88%. This conversion was >90% for the previously used batch of bio-oil that contained less non-volatile fraction.
- At 850°C, O/C = 1.4, S/C = 3.0, and GHSV = 2000, 9.1 g hydrogen was produced from 100 g bio-oil/methanol feed. This yield depends on the composition of bio-oil and decreases with the concentration of non-volatile compounds.
- With that yield, the estimated cost of hydrogen production is $4.60/gge.
- Ongoing tests are aimed at optimizing the system operation, especially the volatilization of bio-oil.