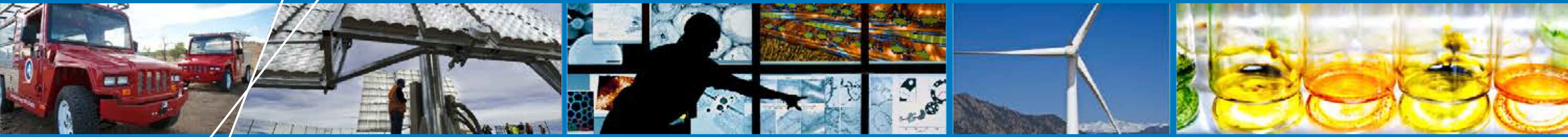
Distributed Bio-Oil Reforming



2013 Hydrogen & Fuel Cells Programs Annual Merit Review

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National Renewable Energy Laboratory

May 13-17, 2013

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: 6/2013*
- Percent complete: 95%

BARRIERS

Production Barriers

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

2015 Targets

- $5.90/gallon gasoline equivalent
- 70% energy efficiency (bio-oil to H_2)

BUDGET

- Total project funding: $2,950K
- Funding received in FY 2012: $450K
- Funding for FY 2013: $150K

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

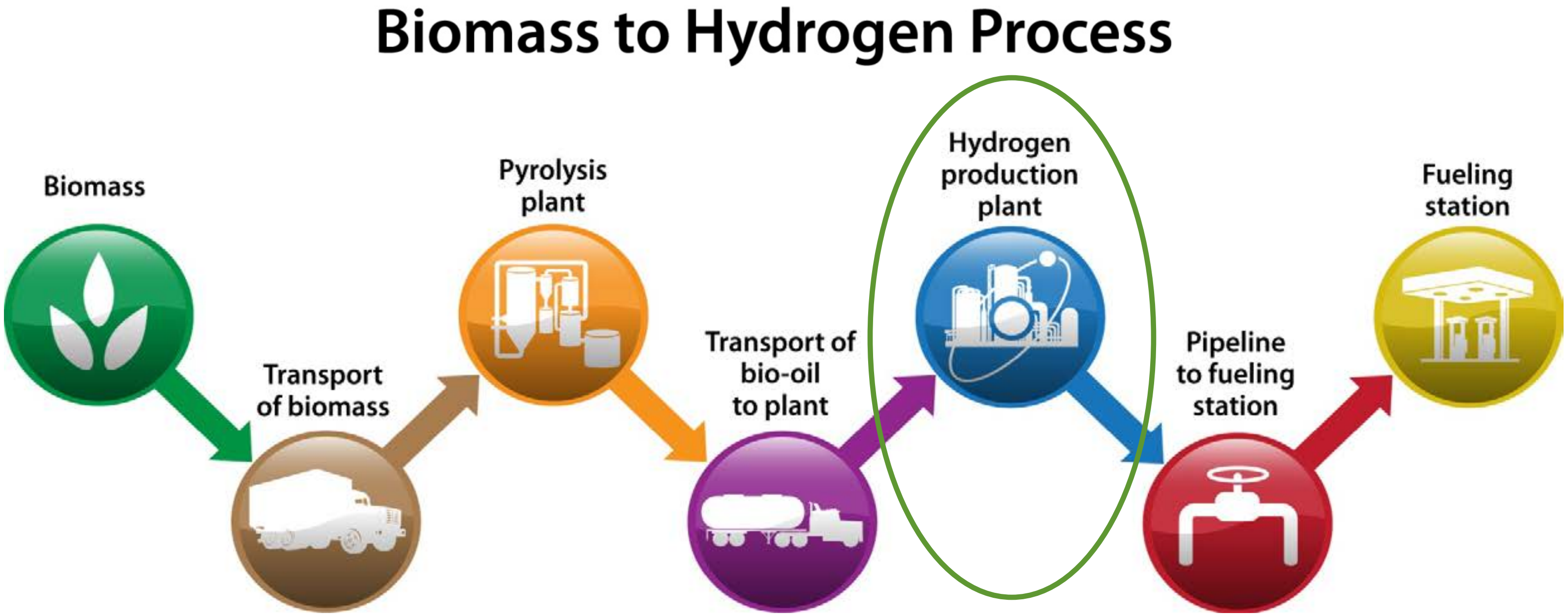
Biomass can be an important resource for hydrogen production.

- 1.3 Gt/year biomass is expected to be available in the U.S. for energy and fuels production. Potentially it could supply 130 Mt/year of hydrogen
- 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:

Reforming feed: 90 wt% bio-oil mixed with10 wt% methanol

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

Overall reaction:

$$CH_{2.18}O_{0.78} + 0.23O_2 + 0.76\,H_2O \rightarrow CO_2 + 1.8\,H_2$$

Theoretical yield: 13.5 wt%

Estimated energy efficiency: 72%; $E_{eff} = \dfrac{LHV\ H_2}{LHV\ biooil + process\ energy}$

Approach: Technical Progress

FY 2010

- Achieved hydrogen yield of 7.3 g per 100 g bio-oil in a bench-scale reactor.
- Demonstrated 60 hours of reforming catalyst performance using 90 wt% bio-oil/10 wt% methanol mixture as feedstock.

FY 2011

- Produced 50 L/h hydrogen at the yield of 10.1 g H_2 per 100 g bio-oil during short-term quartz reactor tests.
- 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.
- Produced 114 L/h of hydrogen with the yield of 11.0 g per 100 g of poplar bio-oil (the hydrogen yield produced from oak bio-oil was 9.1 g/100 g).

FY 2013

- Produced hydrogen from bio-oils derived from three different biomass feedstocks.
- For those bio-oils hydrogen yields varied from 9.1 g to 11.0 g per 100 g of bio-oil.

Objectives

Overall

- Develop the necessary understanding of the process chemistry, compositional effects, catalyst chemistry, deactivation, and regeneration strategy as a basis to define the process for automated distributed reforming; demonstrate the technical feasibility of the process.

FY 2013

- Provide mass balances for auto-thermal reforming of three pyrolysis liquids.
- Show relation between hydrogen yield and bio-oil composition and identify bio-oil that can deliver 10 g of hydrogen per 100 g bio-oil.
- Update the H2A analysis based on the validated performances to assess the process energy efficiency and the cost of hydrogen.

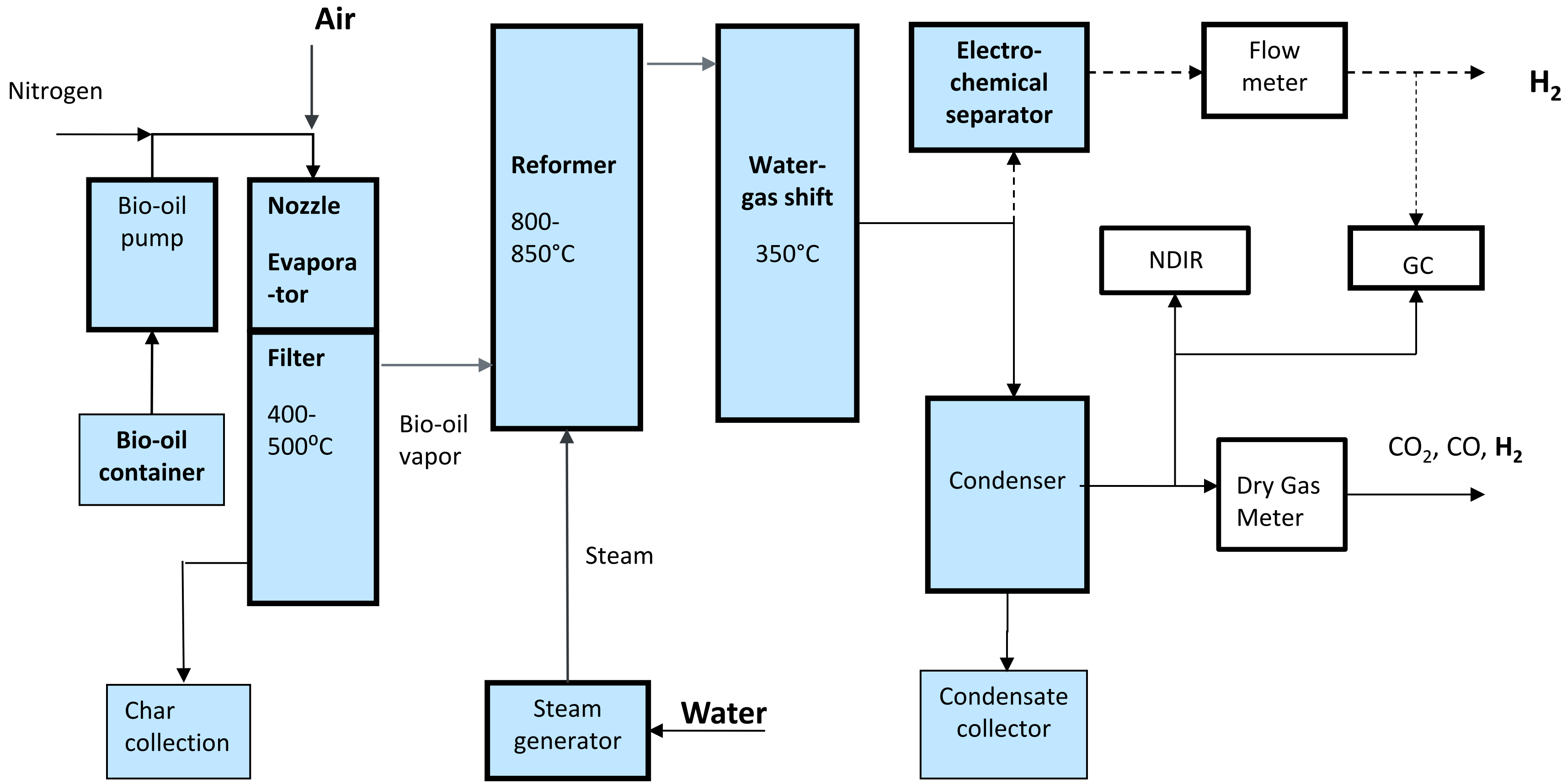
Technical Accomplishments: Bio-oil Characteristics

Feedstock	Poplar	Oak	Pine	Lignin-free oak
Elemental analysis				
C, wt.%	47.4	44.9	48.2	12.5
H, wt.%	7.5	7.2	7.4	10.0
O, wt.%	45.1	47.8	44.3	77.5
Water, wt.%	19.6	25.3	22.4	74.6
Lignin, wt.%	38.0	32.9	31.2	0
Mw, Da	670	860	710	290
Viscosity (25°C), cP	350	150	200	3.1
Surface tension, mNm	20	43	30	37
Maximum Hydrogen Yield, g/100 g bio-oil	**13.8**	**12.6**	**13.5**	**3.8** **(15.2)***

*potential hydrogen yield on water-free basis

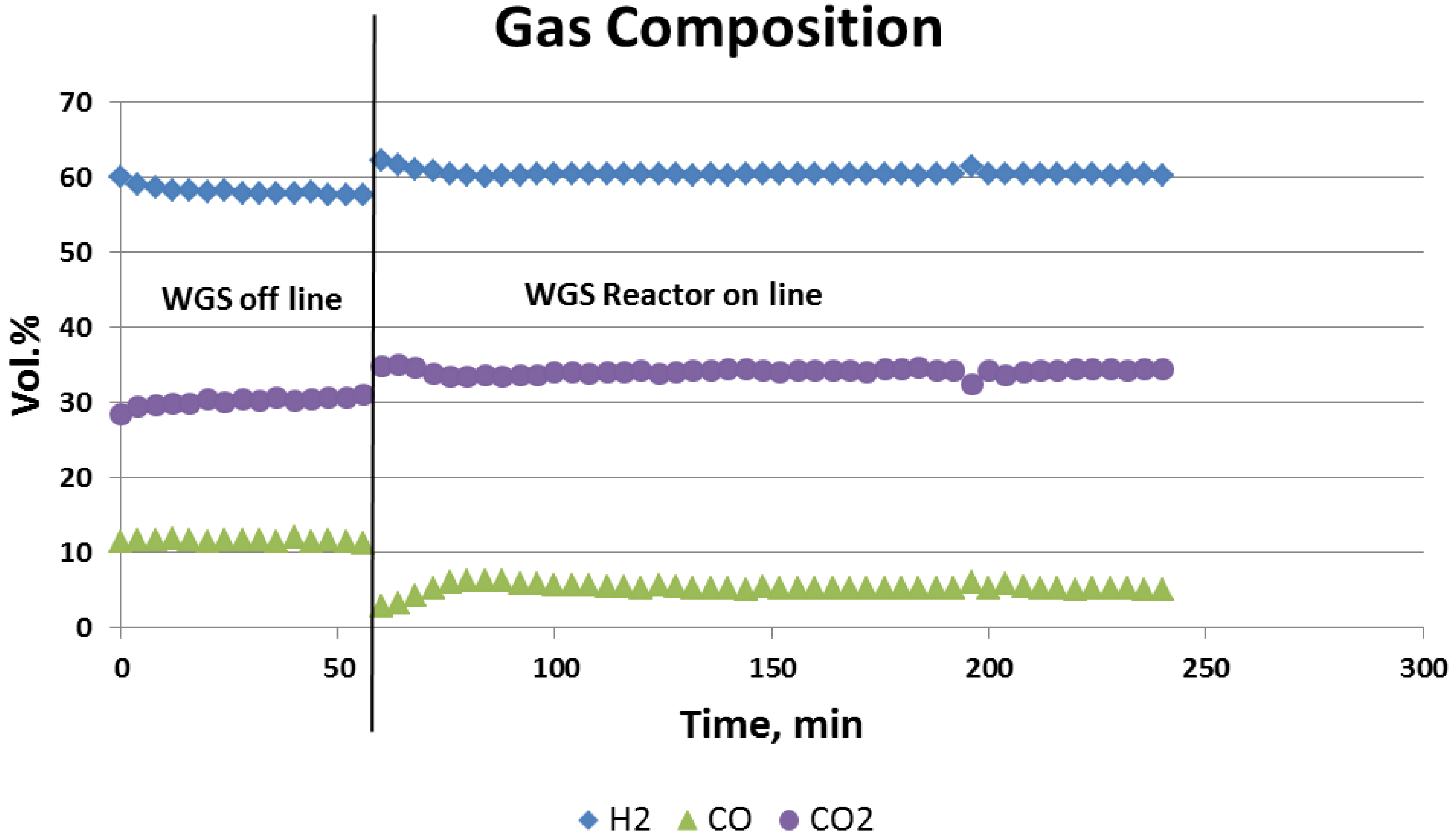
Technical Accomplishments: Integrated Bench-Scale System

Hydrogen was produced in the integrated bench-scale system by autothermal reforming of whole pyrolysis bio-oils obtained from three feed stocks: poplar, oak, and pine wood, and of the lignin-free fraction of the oak bio-oil.



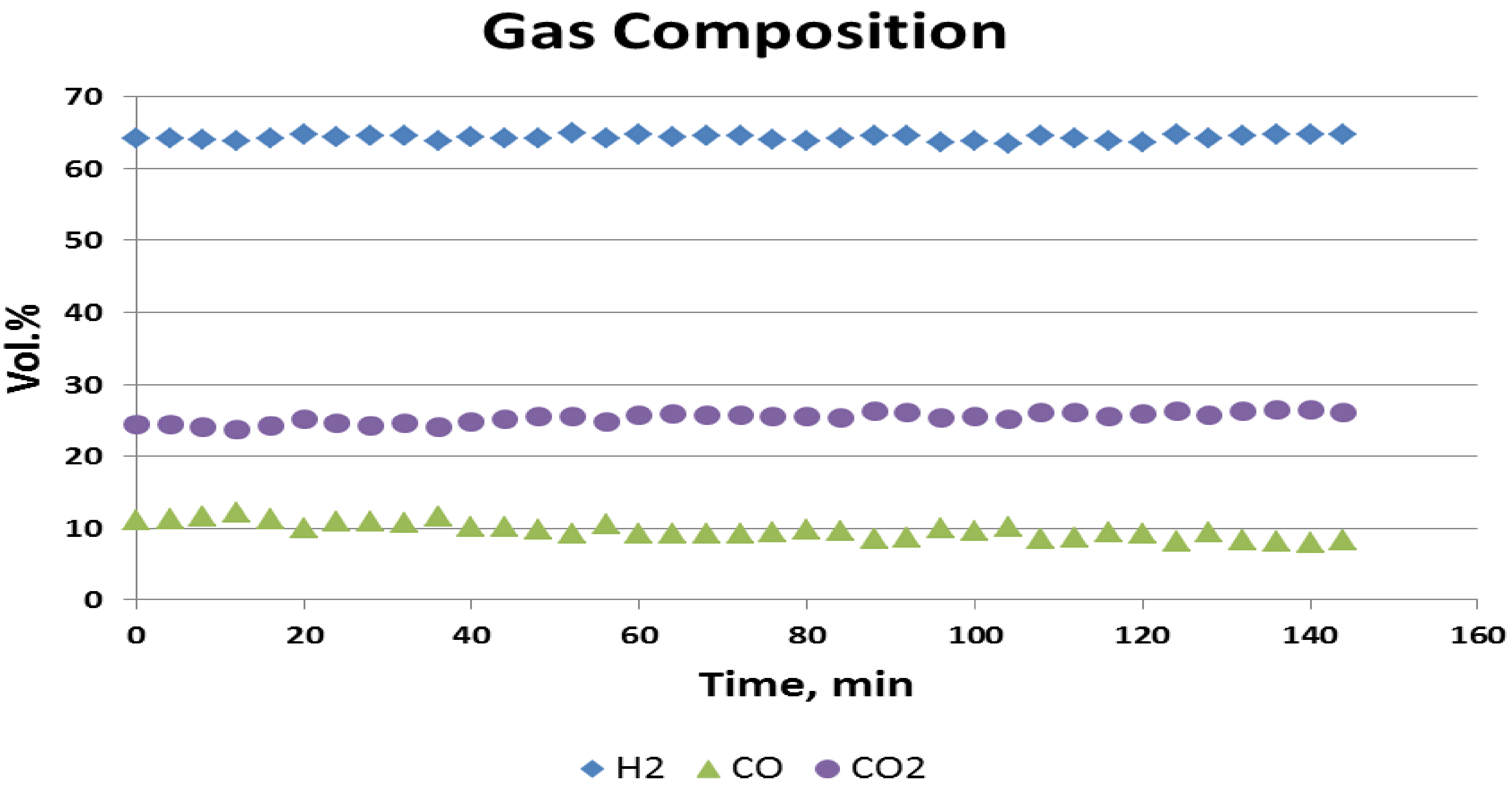
Technical Accomplishments: Process Performance Demonstration

Reforming of Lignin-free Oak Bio-oil



Technical Accomplishments: Process Performance Demonstration

Reforming Pine Bio-oil



Technical Accomplishments: Hydrogen Yields from Bio-oils

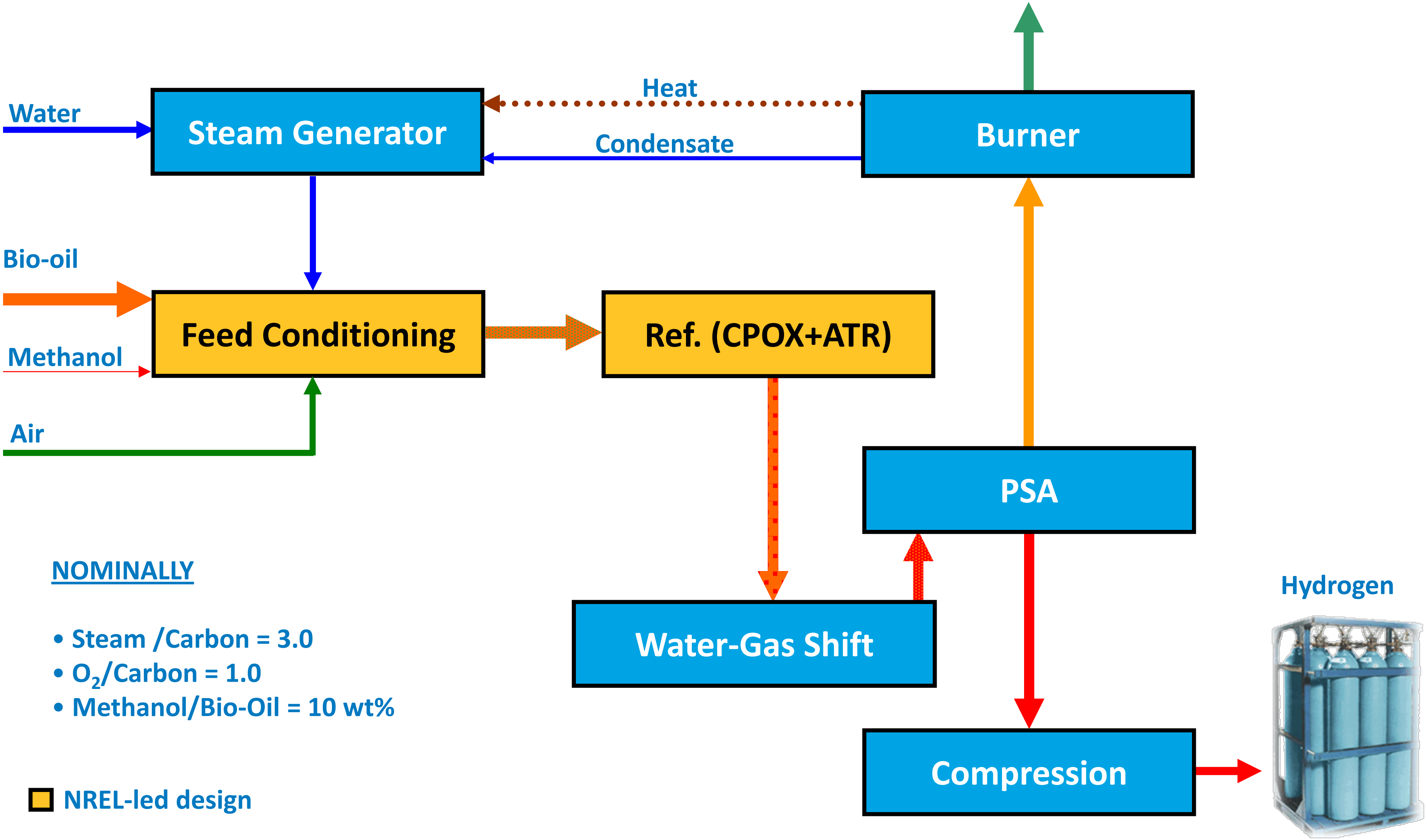
Feedstock	**VHSV h^{-1}**	**S/C**	**O/C**	**C conv. %**	**H_2 g/100g bio-oil**
Poplar	2000	3	0.9	89	**11.0**
Oak	2100	3.5	1.0	84	**8.5**
Pine	2100	2.8	0.85	86	**10.5**
Oak, lignin-free	1100	4	1.5	88	**3.0** **(12)***

VHSV – methane-equivalent volumetric hourly space velocity
S/C – molar steam-to-carbon ratio
O/C – atomic oxygen-to-carbon ratio
C conv. – carbon conversion from bio-oil to gas
*hydrogen yield on water-free basis (lignin-free oak bio-oil fraction contained 74.6% water)

Reforming of *poplar* and *pine* bio-oils delivered >10 g H_2 per 100 g bio-oil

Process Analysis

Conceptual Process Diagram



NOMINALLY

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

🟨 NREL-led design

🟦 Industry-available systems

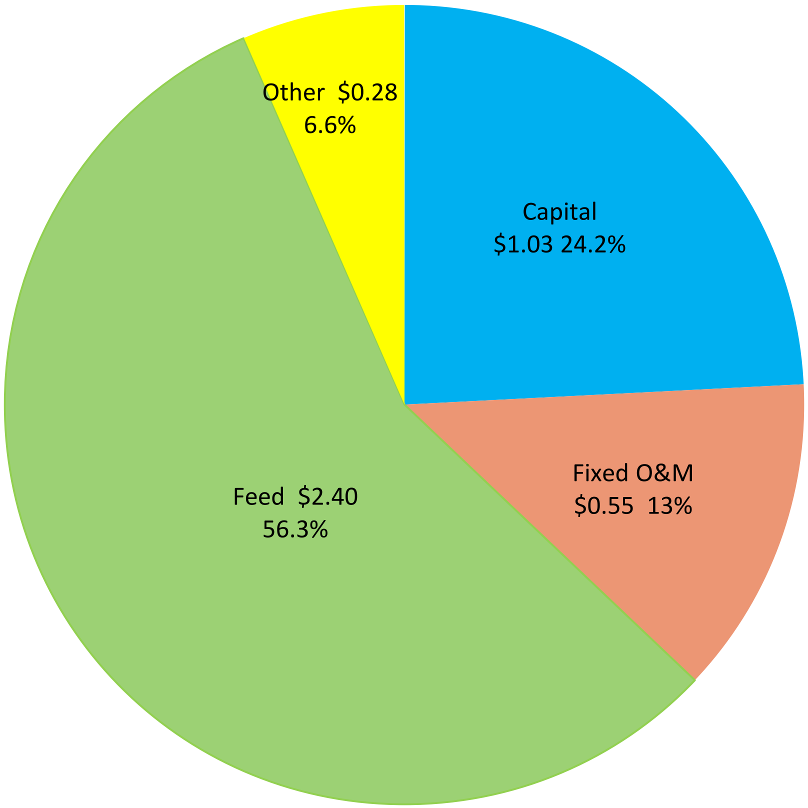
Process Analysis

Hydrogen production cost (H2Av3, 2007$, nth plant)

- 1,500 kg/day hydrogen plant
- Capital : $1,880,000
- Bio-oil price: $236/ton*
- **Cost of production: $4.26/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.

*estimated high-end value using biomass cost of $72/ton

Production Cost Break-down



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
- One CSM undergraduate student currently participates 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 2014

Submit proposal for R&D to explore novel hybrid approaches, including high-pressure reforming, to produce low-cost hydrogen from bio-oil.

Summary and Conclusions

Relevance: Production of hydrogen from biomass has potential to provide annually up to 130 Mt of hydrogen.

Approach: We propose a two-step biomass-to-hydrogen pathway: 1) fast pyrolysis that converts solid biomass into liquid product, bio-oil, 2) auto-thermal reforming of bio-oil to produce hydrogen. In this project we explore the second step: reforming of bio-oil.

Technical accomplishments: In a bench-scale integrated system we demonstrated hydrogen production >100 L/h, at a yield >10 g/100 g bio-oil, with the energy efficiency of 70%. The estimated cost of hydrogen production from poplar bio-oil was $4.26/gge, which exceeds the 2015 DOE target of $5.90/gge.

Collaboration: At different stages of the project we collaborated with two universities (Colorado School of Mines, University of Minnesota), and an oil company (Chevron). The reforming catalyst was provided by BASF.

Summary and Conclusions

- We identified optimum process parameters for the bio-oil auto-thermal reforming process: temperature 800-850°C, steam-to-carbon ratio of 2.5-3.5, oxygen-to-carbon ratio 0.9-1.1, catalyst – 0.5% Pt/Al_2O_3, methane-equivalent space velocity ~2000 h^{-1}.
- The hydrogen yields depended on both chemical composition and physical properties of bio-oils that were produced from different biomass feedstocks. The lower hydrogen yield obtained from oak bio-oil, compared to those from poplar and pine bio-oils, resulted from its lower carbon and higher oxygen content , as well as to the lower carbon-to-gas conversion.
- The incomplete carbon-to-gas conversion that ranged from 84% to 89% for different bio-oils was due to the incomplete evaporation of non-volatile compounds in bio-oils (oligomeric lignin and carbohydrates) that formed solid residue in the evaporator. The less-effective evaporation of oak bio-oil was most likely caused by its higher surface tension that resulted in larger size of bio-oil droplets generated by the ultrasonic nozzle.
- The hydrogen production from the lignin-free bio-oil fraction may be the most favorable economically but that strongly depends on the credit that can be obtained for the lignin fraction of bio-oil which could be used for the production of adhesives or liquid fuels (by hydroprocessing).