# II.A.1 Hydrogen Pathways Analysis for $H_2$ Production via a Monolithic Piston Reforming Reactor and Reformer-Electrolyzer-Purifier Technology

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Contract Number: DE-EE0006231

Project Start Date: March 15, 2013
Project End Date: September 30, 2016

## Overall Objectives

The objectives of this project are to:

- Analyze hydrogen production and delivery (P&D) pathways to determine the most economical, environmentally-benign, and societally-feasible paths for the P&D of hydrogen fuel for fuel cell vehicles.
- Identify key technical and economic barriers to the success of these pathways, primary cost drivers, and remaining research and development challenges.
- Assess technical progress, benefits and limitations, levelized hydrogen costs, and potential to meet U.S. Department of Energy (DOE) P&D cost goals of <$4 per gasoline gallon equivalent (gge) (dispensed, untaxed) by 2020.
- Provide analyses that assist DOE in setting research priorities.
- Apply the H2A Production Model as the primary analysis tool for projection of levelized hydrogen costs (U.S. dollars per kilogram of $H_2$ [$/kg $H_2$]) and cost sensitivities.

## Fiscal Year (FY) 2016 Objectives

In 2015–2016, these overall project objectives were applied to:

- Complete documentation for high temperature solid oxide electrolysis cell and dark fermentation of bio feedstocks.
- Develop hydrogen pathway case studies for hydrogen generation via:
  - Pacific Northwest National Laboratory's (PNNL's) Monolithic Piston-Type Reactor for hydrogen production.
  - Fuel Cell Energy Inc.'s (FCE) Reformer-Electrolyzer-Purifier (REP) electrolyzer technology.

## Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

Hydrogen Generation by Water Electrolysis

(F) Capital Cost

(G) System Efficiency and Electricity Cost

(K) Manufacturing

Reformer-Electrolyzer-Purifier

(F) Capital Cost

(G) System Efficiency and Electricity Cost

(K) Manufacturing

Fermentative Hydrogen Production

(AX) Hydrogen Molar Yield

(AY) Feedstock Costs

(AZ) Systems Engineering

Monolithic Piston Reforming of Bio-oil to Hydrogen

(AX) Hydrogen Molar Yield

(AY) Feedstock Costs

(AZ) Systems Engineering

## Technical Targets

This project conducts cost modeling to attain realistic cost estimates for the production and delivery of hydrogen fuel for fuel cell vehicles. These values can help inform future technical targets.

- DOE P&D cost goals < $4/gge of $H_2$ (dispensed, untaxed) by 2020

## FY 2016 Accomplishments

- A no-cost extension was granted to SA by DOE.
- Finalized documentation for hydrogen production via dark fermentation of corn stover.
  - H2A cases and DOE record are to be published upon final approval of DOE.
- Finalized documentation for hydrogen production via high temperature solid oxide electrolysis cell.
  - H2A cases and DOE record were published online after receiving approval from DOE.
- Initiated case studies for hydrogen production via the Monolithic Piston-Type Reactor.
  - Initial design completed using generic bio-oil feedstock.
  - Defined reactors and estimated cost using Design for Manufacturing and Assembly methodology commonly used by Strategic Analysis Inc.
  - Completed ASPEN Hysys® simulations to verify all stream properties and production capacity.
    - Several system components are sized according to the production capacity, including heat exchangers and pumps.
  - Pyrolysis oil is selected as the preferred feedstock based on PNNL recommendation.
    - Pyrolysis oil is modeled on a synthesis of H2A default values and data from recent National Renewable Energy Laboratory (NREL) reports.
    - Models are to be updated as information is provided by NREL.
  - Created a future case H2A model for the process.
    - The project is assessed at a low technology readiness level (TRL), and a current case analysis is not appropriate at this time.
    - Conducted a sensitivity analysis.
    - Preliminary cost estimate is $3.69/kg for $H_2$ production from pyrolysis oil.
- Initiated case studies for $H_2$ production via FCE's REP technology.
  - Received process data from FCE.
    - Utilized FCE inputs as a comparison point. All FCE inputs (capital cost, fuel usage, electrical inputs, and water usage) were put into H2A with SA's "standard" indirect and replacement costs.
    - Examined both an Integrated Configuration (FCE plus REP) and Standalone Configuration (REP alone).
  - Completed ASPEN Hysys® simulations of REP to identify reactant and product stream thermodynamic properties which were used to appropriately size system components and provide input values for the H2A cases.
  - Preliminary results suggest $1.77/kg $H_2$ and $2.51/kg $H_2$ for the integrated and standalone REP systems, respectively. Results are similar to past FCE published costs.

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## INTRODUCTION

This report reflects work conducted in the third year of a three-year project to analyze innovative hydrogen production and delivery pathways and their potential to meet the DOE hydrogen P&D cost goal of <$4/gge by 2020. Work in the first year of the project concentrated on hydrogen production from proton exchange membrane electrolysis. Work in the second year focused on solid oxide electrolysis cell technology and dark fermentation. Work in the third year has focused on hydrogen production from the monolithic piston-type project being researched by PNNL and the Reformer-Electrolyzer-Purification work developed by Fuel Cell Energy, Inc. The analysis methodology utilizes DOE's H2A distributed and central hydrogen production models.[1] Those models provide a transparent modeling framework and apply standard mass, energy, and economic analysis methods agreed upon by DOE's hydrogen and fuel cell technology teams.

## APPROACH

The following steps summarize the analysis methodology applied to each of the hydrogen production pathways examined in the project.

- Conduct literature review.
- Develop, circulate, and analyze results from an industry survey covering the targeted technology.
- Define generalized cases for systems of different sizes and TRLs.
- Run H2A models with general case input data to calculate the levelized cost of hydrogen ($/kg $H_2$).
- Perform sensitivity analyses (including tornado and waterfall charts) to identify key cost drivers.
- Document case study results.
- Vet case study results with DOE, industry, and team partners.
- Repeat these steps until agreement attained among project partners.

[1] http://www.hydrogen.energy.gov/h2a_analysis.html

## Specific Approach to Monolithic Piston System

Initial system designs were developed from the published 2015 U.S. Department of Energy Hydrogen and Fuel Cells Program Annual Merit Review (AMR) documentation delivered by the PNNL principle investigator [2]. All system designs were based on a forecourt model with a target production of 1,500 kg $H_2$/d. The monolithic piston plant was considered at only a future technological development time horizon due to its assessed low TRL (as determined by SA and NREL). The future case represents a 2025 technology year with system manufacturing and design maturity.

System designs were simulated in both Excel and ASPEN Hysys®. The system is primarily a two-bed, cyclic reactor which toggles between steam-oil reforming and catalyst regeneration mode. Figure 1 shows a partial schematic of the system, with one reactor operating in reformer mode and the other in regeneration mode. The chemical reforming process consists of the oil feedstock and steam being supplied at approximately 300°C and 24 bar to a reactor which contains a $TiO_2$ monolith that is coated with a non-precious metal catalyst. The steam-oil reaction that occurs produces $H_2$, $CO_2$, and a coking compound. The reactor monolith also contains a composite sorbent primarily made of dolomite that captures the $CO_2$ upon production. It is assumed that approximately 90% of the $CO_2$ is captured in the process. The coke produced deposits on the reactor internals. The reactor exhaust is a relatively pure stream (~97%) of $H_2$ with some $CO_2$, unreacted oil, and steam. The exhaust gas stream passes through several heat exchangers and a condensation tank in which the unreacted oil and steam condense and can be recovered and recycled. The gas is passed onto a pressure swing adsorption column for further purification.

After 10 minutes of reforming, the flow of oil and steam is stopped. Air is then passed through the reactor, burning the deposited coke, regenerating the reactor. The heat produced during this regeneration process provides heat to the reactor and the reactor internals. At the end of the regeneration reaction, the reactor internals are expected to be at 700°C. After 10 minutes of regeneration, air flow is stopped and the reactor returns to reforming mode. When the next reforming reaction occurs in the recently regenerated reactor, the reactor has an internal temperature of 700°C, which provides sufficient heat to complete the 10 minute cycle of reforming. To minimize downtime and maintain flow of $H_2$ out of the system, two reactors are proposed operating out of sync is proposed, so that one reactor is reforming while the other is regenerating.

Data from the reforming and regeneration simulations were used to size the equipment. Quotes were solicited for equipment and the reactor prices were generated by Design for Manufacturing and Assemblymethods. The capital costs were incorporated into an H2A analysis. H2A results were further supplemented with a sensitivity analysis in order to identify the primary cost identifiers.

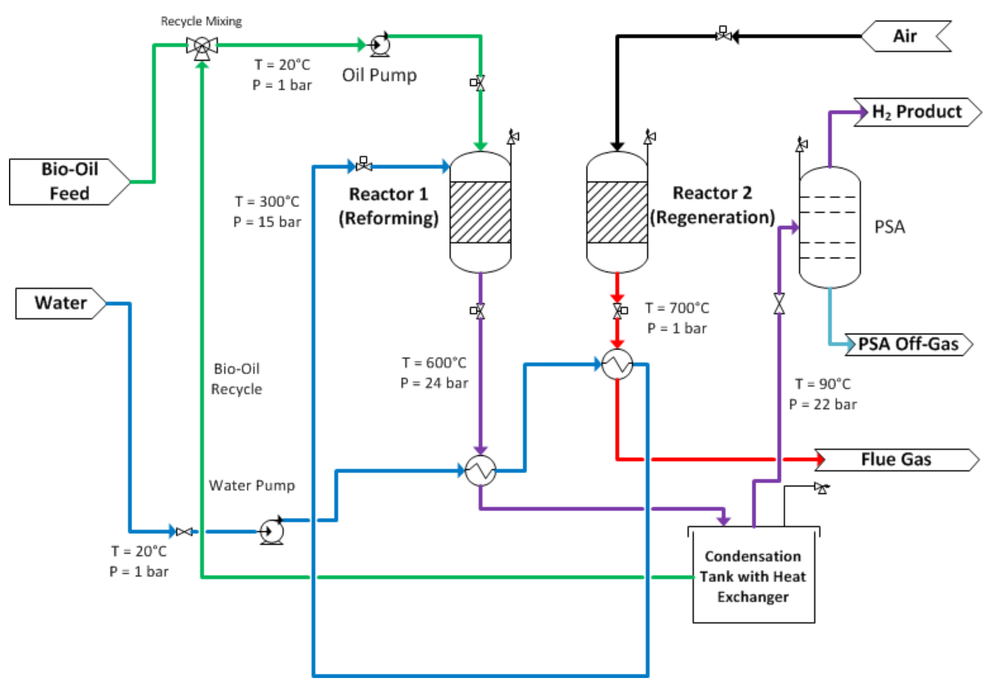



**FIGURE 1.** Partial system diagram for monolithic piston-type reforming project. Process flow diagram shows Reactor 1 in reforming mode and Reactor 2 in regeneration mode. For simplicity and clarity of operation, not all system connections are shown.

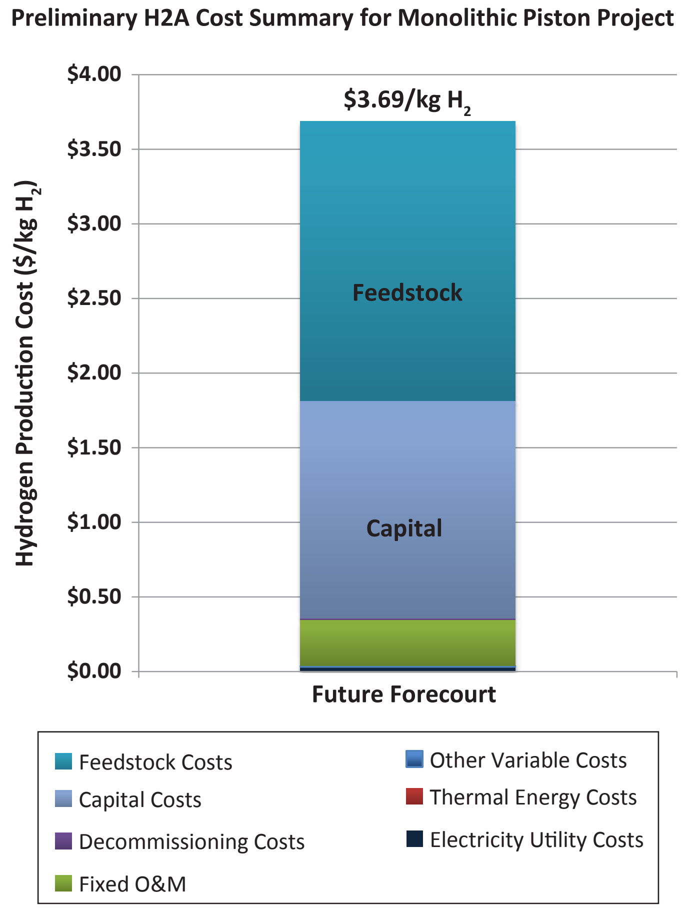
### Specific Approach to Reformer-Electrolyzer-Purifier

Initial system designs were developed from the published 2015 AMR documentation [1] and additional input from FCE. All system designs were based on a forecourt model with a target production of 1,500 kg $H_2$/d. SA assesses the TRL of this project as very high because the technology in question is essentially the same as Fuel Cell Energy's molten carbonate fuel cell which is already in production. Further, FCE has demonstrated pilot scale systems operating in REP mode. As such, a current case analysis has been conducted for forecourt operation. Two system designs were analyzed:

- Standalone Configuration: Natural gas is fed to a reformer in two streams. One stream is fed to a combustion system which provides heating for the system. The other stream is mixed with water and heated by the combustion chamber, converting some of the methane into $H_2$ and $CO_2$. The pre-reformed gas enters the REP unit, which further reforms the gas. The $CO_2$ in the gas then reacts with steam at the anode to form $CO_3$ that is transported across the molten carbonate electrolyte leaving a purified stream of $H_2$ on the anode. This process is the same operation as a standard molten carbonate fuel cell, but run in electrolyzer mode and therefore requires an electrical input as opposed to producing electricity. The $H_2$ is then sent to a pressure swing adsorption unit for further purification to reach fuel cell vehicle requirements.
- Integrated Configuration: This system utilizes existing Fuel Cell Energy's molten carbonate direct fuel cell (DFC). A surplus of natural gas is fed to a commercial DFC. The surplus fuel (approximately 15% of the feed) is reformed within the reforming section of the DFC but is pulled from the system before reaching the fuel cell anode. The removed fuel is heated, passed through an external reformer to further convert any remaining natural gas into $H_2$ and $CO_2$, and fed to an REP unit. The REP unit then finishes any reforming of the natural gas and purifies the gas by removing $CO_2$ from the stream. Electrical energy for the REP unit can be supplied from the DFC. The purified $H_2$ is sent to a pressure swing adsorption unit to create an ultra-pure $H_2$ stream suitable for alternative fuel vehicles.

## RESULTS

Monolithic Piston System Cost Results: Current H2A analysis is still ongoing, but preliminary results indicate hydrogen production costs from a pyrolysis oil feedstock are approximately \$3.69/kg $H_2$. Figure 2 details the cost breakdown. Cost drivers are, predictably, the feedstock and capital cost. Figure 3 identifies the sensitivity of the cost drivers, providing a potential range of prices from \$3.21–\$4.17/kg $H_2$.




O&M – Operating and maintenance

**FIGURE 2.** Preliminary H2A cost summary for piston-type reforming reactor with pyrolysis oil feedstock

While pyrolysis oil is the targeted and experimentally demonstrated fuel, a side analysis was conducted using soybean oil as the feedstock to assess the hydrogen cost from a currently available commodity bio-oil with high specific energy. Comparatively, the specific energy of soybean oil (~37 MJ/kg) [3] is approximately double the specific energy of pyrolysis oil (~17 MJ/kg) [4] but costs a factor of 2.5 more (\$0.66/kg oil[2] compared to \$0.245/kg oil [4] for pyrolysis oil). The estimated hydrogen cost from soybean oil is \$4.07/kg $H_2$ using the monolithic oil reforming process described above.

REP System Cost Results: A preliminary current forecourt H2A analysis of the REP systems was conducted based on inputs from FCE for fuel feedstock, energy usage, water usage, and maintenance costs. To the extent possible, SA independently validated these values and augmented then with standard H2A analysis assumptions to estimate hydrogen cost. Preliminary hydrogen production for the integrated REP system and standalone REP

[2] Price reflects soybean commodities price index between January and February of 2016.

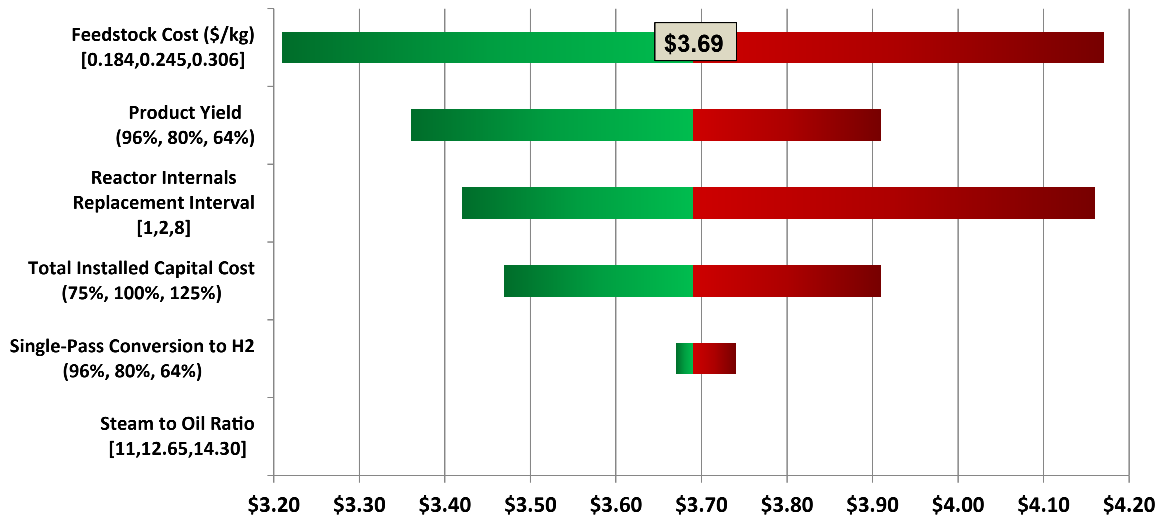



**FIGURE 3.** Tornado chart for hydrogen production via piston-type reforming reactor with pyrolysis oil feedstock. Replacement of reactor internals encompasses replacement of the monolith, catalyst, and sorbent in the reactor.

system are $1.77/kg ($3.92/kg delivered) and $2.51/kg ($4.58/kg delivered), respectively. These results are in general alignment with published cost results released by FCE. Additionally analysis is planned to further vet assumptions and finalize the cost projections.

## CONCLUSIONS AND FUTURE DIRECTIONS

In its third year, this project made key observations and important achievements.

- Representative pathway analysis cases were completed for $H_2$ generation via the Monolithic Piston System and FCE's REP technology.
- Costs were estimated for the Monolith Piston System with a feedstock of pyrolysis oil.

## FY 2016 PUBLICATIONS/PRESENTATIONS

### Presentations

**1.** Cassidy Houchins, Brian James, and Daniel DeSantis. "Techno-Economic Analysis: Assessing Progress of Emerging Technologies towards Meeting Cost and Performance Targets." 2016. Presentation. 3/7/2016, Solar Fuels Workshop, University of Delaware.

**2.** Brian James, Cassidy Houchins, and Daniel DeSantis. "Techno-Economic Analysis: Water Splitting Technologies and Metrics." 2016, Presentation. 4/14/2016, Water Splitting Workshop, Stanford University.

**3.** Brian James, Cassidy Houchins, Genevieve Saur, Jennie M. Huya-Kouadio, and Daniel DeSantis. "Analysis of Advanced H2 Production Pathways." 2016. Presentation. 6/8/2016, AMR, Washington, D.C.

## REFERENCES

**1.** Jahnke, F. "Reformer-Electrolyzer-Purifier (REP) for production of Hydrogen." in *AMR* (2015).

**2.** Liu, W., "Monolithic Piston-Type Reactor for Hydrogen Production through Rapid Swing of Reforming/Combustion Reactions." in *AMR* (2015).

**3.** Patzek, T.W., "A First Law Thermodynamic Analysis of Biodiesel Production From Soybean." *Bull. Sci. Technol. Soc.* **29,** 194–204 (2009).

**4.** Ringer, M., Putsche, V. & Scahill, J., "Large-Scale Pyrolysis Oil Production: A Technology Assessment and Economic Analysis." *NREL/Tp-510-37779* 1–93 (2006). doi:10.2172/894989