

II.A.3 Analysis of Ethanol Reforming System Configurations

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Objectives

- Assess cost of hydrogen from bio-derived liquids:
 - Focus on 1,500 kg H₂/day distributed production forecourt systems
 - Consider both “conventional” and “advanced” systems
 - Conduct basic sensitivity analysis on the above reformation systems to assess the impact on hydrogen cost
- Reflect recent research:
 - Interact with DOE labs and contractors
 - Researchers to suggest catalysts composition, performance, potential configurations
 - Ground in reality with a focus on technical targets
- Output of work is:
 - System/configuration definition
 - Performance specification and optimization
 - Capital cost estimation
 - Projected hydrogen \$/kg

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Distributed Hydrogen Production from Natural Gas or Renewable Liquid Feedstocks:

- (A) Reformer Capitals Costs
- (B) Reformer Manufacturing

Hydrogen Separations:

- (R) Cost

Technical Targets

This project entails conducting configuration and cost analysis of current and future technology distributed bio-derived liquids reforming systems for the on-site production of hydrogen. Insights gained from these studies may be applied toward future system development that can meet the DOE 2017 targets for hydrogen production from bio-derived liquids.

TABLE 1. DOE Technical Targets

| Characteristic | 2006 | 2012 | 2017 |
|--|------------------|------------------|----------------------|
| System Efficiency | 70% | 72% | 65-75% |
| Production Unit Capital Cost (uninstalled) | \$1.4M | \$1.0M | \$600k |
| Total H₂ Cost | \$4.40/kg | \$3.80/kg | <\$3.00/kg |

Accomplishments

- Defined 18 different system configurations with a wide variety of approaches.
- Designed and analyzed an annular heat exchange reactor (HER) as an alternative to the conventional tubular reformer. A detailed and highly adjustable physical configuration model was constructed and used to determine appropriate reactor sizing and cost.
- Developed kinetics models of the reforming and water-gas shift (WGS) reactors to estimate reactor bed sizes.
- Developed a 1-dimensional, non-reacting chemistry model of a metal membrane separation unit to estimate membrane surface area requirements.
- Developed a detailed but modular sizing and costing model to handle each of the 18 system configurations.
- Postulated, developed, and analyzed multiple membrane/reformer/WGS systems.
- Developed HYSYS[®] performance models for each system configuration.

- Completed capital cost analysis of most of the different system configurations.
- Conducted literature reviews and interacted with industry to vet analysis.



Introduction

Small-scale distributed reforming of ethanol is one of the most promising renewable hydrogen production pathway options for the near- and mid-term. It offers the potential for both relatively low cost hydrogen and scalability to small production rates appropriate to the early years of the hydrogen economy. However within the class of distributed reforming systems there is considerable diversity and uncertainty regarding optimal choice of feedstock, conversion process, efficiency, and capital cost. A systematic approach needs to be developed as a tool to manage this area of the DOE Hydrogen Production program element.

The objective of this project is to examine forecourt ethanol reforming systems in sufficient detail to authoritatively estimate the performance and capital costs of the systems and thereby estimate the cost per kg of hydrogen created by the systems. Since there are multiple approaches to the conversion of the ethanol feedstock into hydrogen, both a baseline system and advanced alternative configuration systems will be assessed. The overall objective of the project will be to clearly define and document the performance and expected costs of leading near-term and advanced longer-term ethanol reformation systems as they pertain to small scale (~1,500 kg/day) forecourt hydrogen production systems.

Approach

This project seeks to quantitatively assess the projected cost of hydrogen produced by advanced configuration bio-derived liquids reformer systems. To achieve this objective, several bio-derived liquids (ethanol and glycerol) reformation system configurations are defined and evaluated for expected performance and capital cost. Figure 1 displays several general reformation pathways along with the commercial or national lab entity most closely associated with a given approach. Only steam reforming (ethanol) and liquid phase reforming (glycerol) are under consideration on this project. All selected systems are sized to produce 1,500 kg/day of purified hydrogen. While the focus of the work is determination of the capital cost and performance of the production system, the results will be combined with the standard DOE assumptions for hydrogen compression, storage and dispensing to arrive at the total delivered hydrogen cost for comparison with DOE targets.

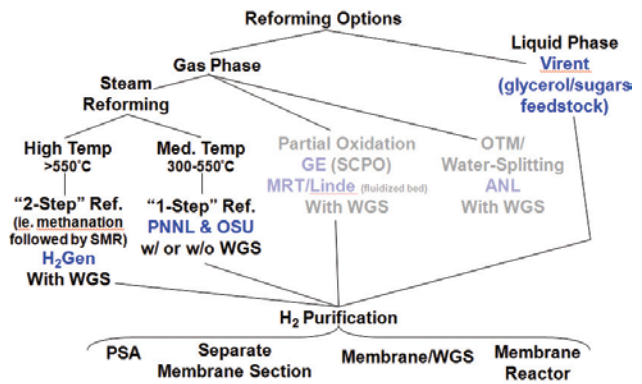


FIGURE 1. Ethanol Reforming Hierarchy

A baseline ethanol gas-phase reformation system using current technology catalysts and configuration has been examined to serve as a benchmark. The baseline utilizes steam reforming and employs discrete unit reactors (reformation, WGS, pressure swing adsorption, etc.). Catalyst beds are sized by experimental data and kinetics modeling to the extent possible. System performance is evaluated using HYSYS[®] simulations and system cost is estimated by a combination of scaling factors, previous estimates, and additional Design for Manufacture and Assembly (DFMA[®]) style calculation. The expected total delivered cost of hydrogen is then evaluated using DOE's H2A cost model, which provides a discounted cash flow methodology and standard assumptions regarding hydrogen compression, storage, and dispensing at the forecourt dispensing station.

Advanced technology on-site ethanol reforming systems are also examined. Emphasis is placed on unitized operations to achieve tighter heat integration, smaller reactor volume, enhanced efficiency, and lower capital cost. Integrated reformer/shift beds and integrated reformer/shift/membrane purification beds are examined. Advanced catalysts for lower temperature operation are considered. Like the baseline configuration, performance is evaluated in HYSYS[®], capital costs by a variety of methods, and total hydrogen cost by the H2A model. Sensitivity analysis will then be conducted on all configurations to assess the impact on hydrogen cost.

A low temperature aqueous phase reformer system utilizing glycerol as the bio-derived liquid feedstock will be configured in the next phase of the project. Reactor sizing will be based on a combination of published developer data and first principles reaction rates. Capital costs will be estimated based on a variety of methods as described above. Production systems performance and capital costs will be entered into the H2A model to obtain estimated delivered hydrogen cost for the total dispensing station.

Results

To date, we have defined and modeled 18 different systems with a variety of different components, and numerous permutations and combinations of those components. Complete DFMA[®] analyses have been conducted on most of them, replete with appropriate sizing parameters and material specifications.

The baseline configuration (see Figure 2) utilizes a two-step reforming approach where the ethanol is converted to methane in a pre-reformer and subsequently is converted to a hydrogen-rich gas using conventional high temperature ($\sim 900^{\circ}\text{C}$) steam methane reformer catalysts. A WGS bed followed by pressure swing adsorption (PSA) is used for CO shift and hydrogen purification, respectively. The baseline unit employs discrete unit reactors (reformation, WGS, PSA, etc.). Conventional tube-and-shell geometry was initially specified for each component, but careful analysis showed that an annular HER geometry was preferable in all cases.

Advanced configurations considered included one or more of the following elements:

- Medium temperature catalyst: catalyst based on data from Ohio State University (non-precious metals) and Pacific Northwest National Laboratory (precious metals) that have high conversion at $\sim 500^{\circ}\text{C}$.
- Pd-based hydrogen separators instead of PSA units.
- Integrated membrane reformers (where a separation membrane is used to preferentially remove hydrogen to drive the reforming and/or WGS reactions to a new equilibrium).
- HER configuration instead of conventional tubular layout.
- Advanced catalyst systems able to avoid coking at low steam to ethanol ratios.

Results of the configuration analysis are shown in Table 2.

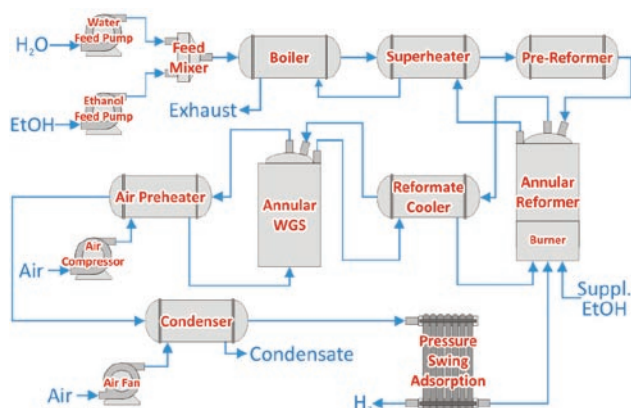


FIGURE 2. Baseline Configuration Diagram

TABLE 2. Configuration Results

| Case # | Description | Ethanol Efficiency (H_2 LHV/EtOH LHV) | Uninstalled Cap. Cost \$ | Production Cost \$/kg | Total Cost (Production/ Storage/Disp.) \$/kg |
|---|--|--|--------------------------------|-----------------------------|---|
| Baseline EtOH (High Temperature, Pre-Reformer) | | | | | |
| 6 | with PSA (75% H_2 Recovery) | 68.1% | \$830k | \$3.02/kg | \$5.04 |
| 11 | with Mem. Separator (90% H_2 Recovery) | 74.9% | \$909k | \$2.96/kg | \$4.98/kg |
| Medium Temperature EtOH (Steam/EtOH = 8 (PM) /10 (NPM) unless otherwise specified) PM= Precious Metal Catalyst NPM= Non-Precious Metal Catalyst | | | | | |
| 9 | with PSA (75% H_2 Recovery) | 67.3% (NPM) 67.5% (PM) | \$673k \$839k | \$2.95/kg \$3.04/kg | \$4.97/kg \$5.06/kg |
| 10 | with Mem. Separator (90% H_2 Recovery) | 64.5% (NPM) 66.8% (PM) | \$800k \$905k | \$3.28/kg \$3.25/kg | \$5.30/kg \$5.27/kg |
| 13a | with Integrated Ref./WGS/Mem. Sep. | 69.8% (NPM) (Steam/EtOH= 8) | \$711k (\$10/kg cat.) | \$3.02/kg | \$5.04/kg |
| 13d | | 67.6% (PM) (\$400/kg cat.) | \$929k | \$3.23/kg | \$5.25/kg |
| 13b | Future Integrated Ref./WGS/Mem. Sep. | 79.4% (NPM) (Steam/EtOH= 6) | \$608k (\$10/kg cat.) | \$2.67/kg | \$4.69/kg |

Conclusions and Future Directions

Key conclusions from the past year include:

- Medium and high temperature ethanol reformers have comparable efficiency.
- Alternative configurations to tubular designs may lower capital cost (but must have adequate heat transfer to support the endothermic steam reforming reaction).
- Low steam-to-ethanol ratios promote high system efficiency (but must not allow coking of the reactor).
- Methane in reformer product gas should be minimized:
 - Each CH_4 molecule in reformer exhaust robs four H_2 molecules from the product
 - “Methane make” is a key catalyst evaluation metric
- Catalyst cost is a key cost component. It is worthwhile to explore reduced/non-precious metal catalysts but they must have multi-year lifetimes.
- Achieving 90% hydrogen recovery in a membrane separator is feasible (at 20 atm reformate/1 atm permeate).
- Membrane systems (with $\sim 90\%$ recovery) can make significant efficiency improvements (up to 5%) over conventional PSA-based systems (at 75% recovery).
- Ethanol percent efficiencies in the mid 70s (lower heating value) are possible with multiple configurations.
- Hydrogen production-only cost of $< \$3/\text{kg}$ is feasible with advanced designs.
- Forecourt compression/storage/dispensing is currently very costly and adds $\sim \$2/\text{kgH}_2$ to the total hydrogen cost (DOE targets for compression/storage/dispensing need to be met to achieve the overall H_2 cost target of $< \$3/\text{kg}$).

- Integrated reformers have the advantages of:
 - Reduced operating temperature
 - Lower capital cost
 - Lower hydrogen cost
- While the cost and efficiency advantage of integrated reformers may not be decisive, integrated systems are compact and simpler: attributes very important for forecourt installations.
- The system that produces the lowest cost hydrogen is an integrated membrane reformer than can successfully utilize a non-precious metal catalyst at low steam-to-ethanol ratios. Development of such a system should be a DOE research goal.
- Aqueous phase reformers using low-cost feedstocks offer a potential pathway to low hydrogen cost.
 - Advantages include:
 - Low operating temperature
 - Low capital cost
 - Variety of low cost feedstocks
 - Cost and performance analysis of such systems is planned but not yet commenced.

To date, the project is roughly 75% complete. The remaining tasks include:

- Complete system performance and cost evaluations
- Examine aqueous reforming system
- Prepare the final report

FY 2008 Publications/Presentations

1. November 6th, 2007 – Laurel, MD: Ethanol Reformer Analysis Overview Delivered to the Bio-Derived Liquid Hydrogen Distributed Reforming Working Group (BILIWG).
2. November 7th, 2007 – Laurel, MD: Purification System Analysis Overview Delivered to the DOE Hydrogen Quality Working Group (PURIWG).
3. May 7th, 2008 – Arlington, VA: Cost Analysis of Advanced Ethanol Reforming Systems (Delivered to DOE Hydrogen office personnel).
4. June 10th, 2008 - Crystal City, VA: DOE H₂ Program Review Presentation.