

II.A.8 Analysis of Ethanol Reforming System Configurations

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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.

Objectives

- Assess cost of H₂ from bio-derived liquids:
 - Focus on 1,500 kgH₂/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 H₂ cost.
- Reflect recent research:
 - Interact with DOE labs and contractors.
 - Researchers to suggest catalysts composition, performance, potential configurations.
 - Grounded in reality but with a focus on technical targets.
- Output of work is:
 - System/configuration definition.
 - Performance specification and optimization.
 - Capital cost estimation.
 - Projected hydrogen cost (\$/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

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 H ₂ Cost	\$4.40/kg	\$3.80/kg	<\$3.00/kg

Accomplishments

- Defined 21 different system configurations with a wide variety of approaches.
- Designed and analyzed an annular heat exchange reactor 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 21 system configurations.
- Postulated, developed, and analyzed multiple membrane/reformer/WGS systems.

- Developed HYSYS^{®1} performance models for each system configuration.
- Completed capital cost analyses of the 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 H₂ and scalability to small production rates appropriate to the early years of the H₂ 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 was 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, a baseline system and advanced alternative configuration systems were all assessed. The overall objective of the project was 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 sought 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 glucose) 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. Although methane systems were examined for comparison to existing technologies, only steam reforming (ethanol) and liquid phase reforming (glucose) were under consideration in this project. All selected systems were sized to produce 1,500 kg/day of purified hydrogen. While the focus of the work was determination of the capital cost and performance of the

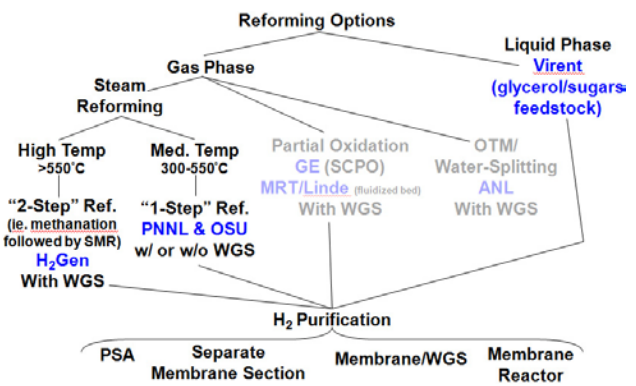


FIGURE 1. Ethanol Reforming Hierarchy

production system, the results were 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.

A baseline ethanol gas-phase reformation system using current technology catalysts and configuration was examined to serve as a benchmark. This baseline system utilizes steam reforming and employs discrete unit reactors (reformation, WGS, pressure swing adsorption [PSA], etc.). Catalyst beds were sized by experimental data and kinetics modeling to the extent possible. System performance was evaluated using HYSYS[®] simulations and system cost was 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 was 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 were also examined. Emphasis was 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 were examined, and advanced catalysts for lower temperature operation were considered. As with the baseline configuration, the performance was evaluated with HYSYS[®], the capital costs by a variety of methods, and the total hydrogen cost by the H2A model.

A low temperature (225°C) aqueous phase reformer system utilizing glucose as the bio-derived liquid feedstock was also examined. Reactor size was based on published data and projections from Virent Energy Systems, a manufacturer of aqueous phase reformer systems. Capital costs and system performance were estimated using the same methods as described above for gaseous phase ethanol reformers. The H2A model was used to obtain estimated delivered hydrogen cost for the

¹ A process modeling software package from Aspen Technology, Inc.

total dispensing station. Two aqueous reformer cases were analyzed: a current-performance case representing the state of the technology as presented in the published literature and a future-performance case representing specifically-quantified improvements in technology, efficiency and achievement of the DOE 2017 cost target for bio-liquid fuel (\$0.14/kg glucose).

Results

We defined and modeled 21 different systems with a variety of different components, and numerous permutations and combinations of those components. Complete DFMA[®] analyses were conducted on most of these systems, replete with appropriate sizing parameters and material specifications.

The baseline ethanol 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 (~900°C) steam methane reformer catalysts. A WGS bed followed by 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 heat exchange reactor geometry was preferable in all cases.

Advanced ethanol reformer 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 the Pacific Northwest National Laboratory (precious metals) that have high conversion at ~500°C.
- Pd-based hydrogen separators instead of PSA units.
- Integrated membrane reformers (where a separation membrane is used to preferentially remove hydrogen

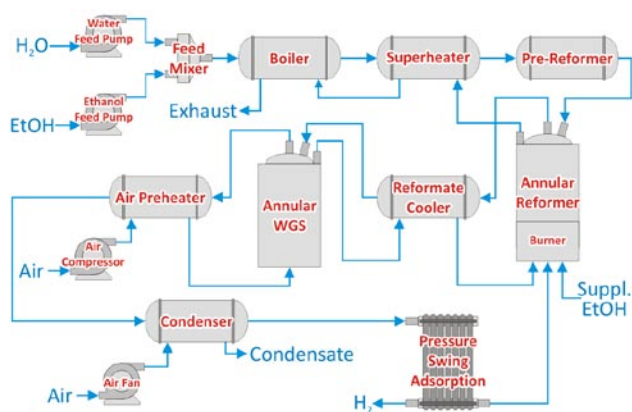


FIGURE 2. Baseline Configuration Diagram

to drive the reforming and/or WGS reactions to a new equilibrium).

- Heat exchange reactor configuration instead of conventional tubular layout.
- Advanced catalyst systems able to avoid coking at low steam to ethanol ratios.
- Advanced PSA systems than can achieve high H₂ recovery (85%) on ethanol reformers while still maintaining five-nines H₂ gas purity (at 300 psi operating pressure).

Table 2 summarizes the configuration and cost results for the main systems of interest. Overall, we note that there is a surprising convergence of performance and cost with three different technology approaches expected to achieve nearly identical performance (68% efficiency and ~\$3/kg H₂ cost): high-temperature reformer with PSA separation, medium-temperature reformer with PSA separation, and medium-temperature integrated (reformer, membrane) systems. We also note that for the “future performance” systems – advanced PSA systems and advanced integrated reactors – there is also a surprising convergence of performance and cost: 75-80% lower heating value (LHV) efficiency and \$2.67/kgH₂. This suggests there are multiple pathways to lower system cost and that no single configuration is clearly favored.

Table 2 also reports the cost results for the aqueous glucose reformer systems. A substantial efficiency and H₂ cost gap is observed to exist between current performance and future performance systems. Efficiency is low primarily due to the currently low hydrogen yield: due to an undesirable side reaction which produces alkanes, only 45% of theoretical amount of hydrogen is currently produced in the reactor. The low hydrogen production efficiency results in high feedstock cost. Additionally, high catalyst loading, and low reactor space velocity results in a high catalyst cost for the current performance aqueous reformer. Projected improvement in efficiency and reduction in hydrogen cost for the future performance system stem from four main assumptions:

- Improvement in catalyst activity (weight hourly space velocity increase from 1/hour to 10/hour).
- Reduction in catalyst loading (from 5% wt to 1% wt Pt loading).
- Improvement in hydrogen selectivity (from 45% to 75% H₂ yield).
- Reduction in feedstock cost (from \$0.23/kg to \$0.14/kg glucose).

Results indicate that the current performance aqueous reformer system results in a very expensive production cost for renewable hydrogen (\$8.28/kgH₂) but achievement of the expected parameter improvements will allow future hydrogen costs of \$2.10/kgH₂.

TABLE 2. Configuration Results

Case #	Description	Feedstock Efficiency (H ₂ LHV/ Feedstock LHV)	Uninstalled Cap. Cost \$	Production Cost \$/kg	Total Cost (Production/ Storage/Disp.) \$/kg
Baseline Ethanol Systems (High Temperature, Pre-Reformer)					
6	- with PSA (75% H ₂ Recovery)	68.1%	\$830k	\$3.01/kg	\$5.03
11	- with Membrane Separator (90% H ₂ Recovery)	74.9%	\$859k	\$2.92/kg	\$4.94/kg
Medium Temperature Ethanol Systems PM = Precious Metal Catalyst (Steam/EtOH = 8 (PM) /10 (NPM) unless otherwise specified) NPM = Non-Precious Metal Catalyst					
9	- with PSA (75% H ₂ Recovery)	67.3% (NPM)	\$682k	\$2.97/kg	\$4.99/kg
15		67.5% (PM)	\$891k	\$3.06/kg	\$5.08/kg
9b	- with Future PSA (85% H ₂ Recovery & Steam/EtOH = 4)	75% (NPM)	\$641k	\$2.68/kg	\$4.70/kg
10	- with Membr. Sep. (90% H ₂ Recovery)	64.5% (NPM)	\$567k	\$3.16/kg	\$5.18/kg
17		66.8% (PM)	\$905k	\$3.25/kg	\$5.27/kg
13a	- with Integrated Reformer/	69.8% (NPM)	\$711k	\$3.02/kg	\$5.04/kg
13d	WGS/Membrane System	(Steam/EtOH = 8) 67.6% (PM)	(\$10/kg catalyst) \$929k	\$3.23/kg	\$5.25/kg
			(\$400/kg catalyst)		
13b	- Future Integrated Reformer/	79.4% (NPM)	\$608k	\$2.67/kg	\$4.69/kg
	WGS/Membrane System	(Steam/EtOH = 6)	(\$10/kg catalyst)		
Aqueous Phase Glucose Systems (Precious metal catalyst)					
16a	- Current Performance Sys.	28.6%	\$1.9M	\$8.28/kg	\$10.30/kg
16b	- Future Performance Sys.	52.6%	\$500k	\$2.10/kg	\$4.12/kg

Conclusions and Future Directions

Key conclusions 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 CH₄ molecule in reformer exhaust robs four H₂ 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% H₂ recovery in a membrane separator is feasible (at 20 atm reformat/1 atm permeate).
- Membrane systems (with ~90% H₂ recovery) can make significant efficiency improvements (up to 5%) over conventional PSA-based systems (at 75% H₂ recovery).
- Ethanol efficiencies (LHV) in the mid 70% are possible with multiple configurations.
- H₂ Production-only cost of <\$3/kg is feasible with advanced designs.
- Forecourt compression/storage/dispensing is currently very costly and adds ~\$2/kgH₂ to the total hydrogen cost.
 - DOE targets for compression/storage/dispensing need to be met to achieve the overall H₂ cost target of <\$3/kg.
- Integrated reformers have the advantages of:
 - reduced operating temperature
 - lower capital cost
 - lower H₂ \$/kg
 - 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 are of interest due to their potential for:

- Operation at low temperature.
- Low capital cost (due to the low temperature and potential for small size).
- Use of a variety of low cost, renewable feedstocks.
- However, current performance aqueous phase reformers using renewable feedstocks such as glucose result in comparatively high hydrogen cost due to:
 - Currently low hydrogen yield and resulting low H₂ energy conversion efficiency.
 - High precious metal catalyst loading.
 - Low reactor space velocity.
 - Relatively high feedstock cost.
- Future performance aqueous phase reformer systems are expected to improve upon of these deficiencies and when combined with achievement of the DOE 2017 bioliquids cost targets, offer hydrogen costs <\$3/kg.
- Feedstock price was found to be the largest contributor to H₂ cost.

FY 2009 Publications/Presentations

1. “Cost Analysis of Distributed Bio-Derived Liquid Reforming Systems for Hydrogen Production”, Directed Technologies Inc., Project Final Report.