Objectives

This work develops multi-disciplinary models of novel stationary fuel cell system (FCS) designs that co-produce hydrogen (H₂-FCS). The two main objectives of this work are to

- Develop novel H₂-FCS designs that release low greenhouse gas emissions, and
- Develop novel H₂-FCS designs with low H₂ production cost.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section (4.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Future Market Behavior
(B) Stove-piped/Siloed Analytical Capability
(D) Suite of Models and Tools

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achievement of the following DOE milestones for Systems Analysis within the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 5**: Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for various hydrogen scenarios. (4Q, 2009)
- **Milestone 8**: Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for technology readiness. (4Q, 2014)
- **Milestone 11**: Complete environmental analysis of the technology environmental impacts for the hydrogen scenarios and technology readiness. (2Q, 2015)
- **Milestone 26**: Annual model update and validation. (4Q, annually)

Accomplishments

A. Develop and apply integrated engineering, economic, and environmental optimization and analysis models

- Developed preliminary, alpha version integrated optimization models that show the economic and environmental advantages of H₂-FCS compared with competing separate generators for electricity, heat and H₂.
- Completed case studies showing the benefits of installing H₂-FCS for electricity, heat and H₂ consumers, FCS manufacturers, and the environment.
- Demonstrated that global carbon dioxide (CO₂) emissions are lowest with our approach of implementing H₂-FCS with electrical and thermal networking, variable heat-to-power ratio, variable H₂-to-heat ratio, first load-following heat, and then load-following H₂ (for the case studies explored). Less fuel energy content is wasted when these approaches are used. This approach achieves a reduction in CO₂ emissions of over 40%.
- Demonstrated for the case studies explored that global costs are lowest with our approach of implementing H₂-FCS with electrically and thermally networking, variable heat-to-power ratio, variable H₂-to-heat ratio, maximum electrical...
output, and then load-following both heat and H₂ in order of their relative expense. For a $4.00/kg market H₂ price, this approach achieves a cost savings of 10%.

- Showed that our novel H₂-FCS designs have the lowest CO₂ emissions and costs of any H₂ production method.

B. Develop and apply thermodynamic and chemical engineering models for analyses of complete FCSs

- Developed preliminary, alpha version analytical and chemical process plant engineering models to analyze the quantity of H₂ that can be co-produced with electricity from an auto-thermal FCS, requiring no additional fuel consumption for combustion heating of endothermic processes.

- Derived, from fundamental thermodynamics, that such an idealized one Megawatt electric (MWe) FCS can be designed to make between ~150 and 450 kg H₂/day, which is enough H₂ to fuel between 220 and 660 H₂ fuel cell cars per day with no added CO₂ emissions from fuel combustion for reformation processes.¹

- Calculated the theoretical maximum of H₂ co-production as a function of fuel consumption, electrical work output, internal reuse of heat, inlet fuel and oxidant conditions, fuel and oxidant quantity, fuel type (natural gas and biogas), fuel cell stack and reformer operating temperature, and fuel cell current density.

- Verified analytical thermodynamic models against chemical process plant engineering models in Aspen Plus.²

C. Develop and apply chemical engineering models for analyses of hydrogen separation and purification sub-systems

- Developed preliminary, alpha version chemical engineering process plant models of hydrogen separation unit (HSU) sub-systems coupled to FCSs.

- Conducted scenario analyses to evaluate different HSU sub-system designs and cycle configurations.

- Compared and contrasted two different HSU sub-system designs, referred to here as HSU 1 and HSU 2, that include anode offgas heat recovery for displacing heat recovery from combustion of anode off-gas H₂ water-gas shift reactors (WGSRs) for shifting carbon monoxide (CO) and water (H₂O) into CO₂ and H₂, and compression and heat exchange to required pressure swing adsorber (PSA) inlet pressures and temperatures.

- Demonstrated a superior design called HSU 1, which recovers 75% of the available thermal energy, with a compressor load of 11% of gross power, and increases the H₂ yield by 132% to 254 kg H₂/day (compared with a base case design with no heat recovery or WGSR that yields 110 kg H₂/day.)

- Developed a further refined design called HSU 2, which recovers 73% of the available thermal energy, with a compressor load of only 7% of gross power, and increases the H₂ yield by 172% to 298 kg H₂/day while also achieving neutral net water balance (compared with the base case design.)

Introduction

A. Develop and apply integrated engineering, economic, and environmental optimization and analysis models

In this first of three distinct modeling efforts, we developed integrated engineering, economic, and environmental models to optimize the design, installation, and control strategy of H₂-FCS for a particular location. To help achieve the DOE Hydrogen Program’s goals of H₂ production with low fuel consumption and CO₂ emissions and to help meet System Analysis Milestone 11, the model minimizes global CO₂ emissions or global costs for the provision of electricity and heat to building owners, and H₂ to vehicle owners, from any combination of generators (including H₂-FCS.)

B. Develop and apply thermodynamic and chemical engineering models for analyses of complete fuel cell systems

In this second of three distinct modeling efforts, we derive the theoretical upper bounds for cost savings, fuel savings, and the quantity of H₂ co-production with H₂-FCS. High-temperature FCSs such as solid oxide fuel cells (SOFC) and molten carbonate fuel cells (MCFC) generate heat and unconsumed H₂ fuel that can potentially be recycled for H₂ co-production. This work evaluates the amount of H₂ that can be co-produced under idealized system configurations.

C. Develop and apply chemical engineering models for analyses of hydrogen separation and purification sub-systems

In this third of three distinct modeling efforts, we model the thermodynamics of the overall H₂ separation sub-system using detailed chemical engineering simulations in Aspen Plus.³ A 1 MWe MCFC system, based on a similar product from FuelCell Energy (FCE), Inc., is thermally integrated with an HSU. PSA is evaluated as the H₂ separation technology due to its commercial readiness. We conduct a scenario analysis of different HSU designs, and report results for two

¹http://www.fueleconomy.gov/feg/fcv_sbs.shtml

²G          G          G          G          G

³G          G          G          G          G
different designs (HSU 1 and HSU 2), compared to a baseline configuration.

**Approach**

**A. Develop and apply integrated engineering, economic, and environmental optimization and analysis models**

In this first of three distinct modeling efforts, our integrated engineering, economic, and environmental model evaluates a combination of novel operating strategies for the design, installation, and control of H₂-FCS. For each novel strategy, the model minimizes total yearly electricity, heat, and H₂ costs or CO₂ emissions by changing the installed capacity of the H₂-FCS. Our model considers a particular location’s climatic region, building load curves, FCS type, and competitive environment. The model shows trade-offs between cost savings to building owners and H₂ consumers, CO₂ emission reductions, and fuel cell manufacturer sales. A FCS’s load-following controls will match the hourly demand if it is within the physical constraints of the system. All demand not supplied by the FCS is purchased from competing electricity, heat, and H₂ generators. Our model focuses on H₂-FCS designs that reuse heat from the FCS to provide heat for the endothermic steam methane reforming (SMR) process for H₂ production such that no additional fuel need be consumed. Consequently, heat generated by the fuel cell can be used either for building heating or for producing more H₂ fuel. The model leaves tunable the ratio of recovered heat for buildings to H₂ fuel. For the case studies evaluated here, the competing H₂ generators are stand-alone SMRs and the H₂-FCS are assumed to be connected to the grid, allowing them to sell back unused electricity at retail market prices (i.e., net metering). The model assumes that H₂ production is for just-in-time use with no H₂ storage, is limited at 5% of the total fuel energy entering the system, and the additional H₂ production and separation equipment results in a 25% increase in fixed costs over the standard FCS without H₂ co-production. The lowest cost strategies combine electrical and thermal networking, a variable heat-to-electric power ratio, a variable H₂-to-heat ratio, maximum electrical output, and then H₂ and heat load-following.

**B. Develop and apply thermodynamic and chemical engineering models for analyses of complete FCSs**

In this second of three distinct modeling efforts, we developed a high level analytical approach for benchmarking the quantity of H₂ co-production available from high-temperature FCSs. Sandia focused on FCS designs with no marginal increase in fuel consumption or greenhouse gas emissions from combustion of the primary feedstock fuel for providing heat for the endothermic fuel reforming processes. Sandia derives the theoretical limit of H₂ co-production from electrochemical heat production alone. The methodology involves hypothetically partitioning fuel cell stack heat into two quantities: (A) a quantity that meets the minimum energy requirement to provide heat to reform fuel solely to run the stack, and (B) a quantity that is potentially available to produce additional H₂. The steam reforming reactions can provide H₂ (A) for electrochemical conversion in the fuel cell anode compartment or (B) for H₂ co-production. For benchmarking an H₂ co-producing system against a standard system, we analytically separate the two processes – (A) and (B) – in two “virtually” separate steam reformers – Reformer “A” (REFA) and Reformer “B” (REFB). REFA produces enough H₂ for the fuel cell to produce electric power. REFB produces H₂ as a separate product (for vehicles, etc.) Following this methodology, we calculated the theoretical maximum of H₂ co-production as a function of a) fuel consumption, b) electrical work output, c) ideal and non-ideal system-wide heat transfer for internal reuse of heat, d) inlet fuel and oxidant conditions, e) fuel and oxidant quantity, f) fuel type (natural gas and biogas from waste water treatment plants), g) fuel cell stack and reformer operating temperature, h) fuel cell current density, i) ideal and non-ideal fuel cell operation, and j) different levels of fuel cell voltage losses (polarizations). The models use polarization expressions and constants from the peer-reviewed literature and from industry. Figure 1 shows example data for such expressions; SOFC polarization and power density curves are plotted as a function of fuel cell operating temperature. This conceptual model is analyzed theoretically through thermodynamic and chemical engineering models using Aspen Plus® software.

Sandia conducts scenario analyses to determine the effects of changes in fuel cell operating conditions on H₂ co-production. Table 1 summarizes the key scenarios evaluated. Scenario A evaluates different
VII. Systems Analysis

Whitney Colella – Sandia National Laboratories

levels of internal heat transfer within the system on $H_2$ co-production. Scenario A1 evaluates inlet reactant temperatures at the fuel cell/fuel reformer operating temperature (perfect heat transfer between hot exhaust gases and cold inlet gases.) Scenario A2 evaluates the inlet temperature of the reactant fuel at ambient temperature, and inlet oxidant and water temperature at system temperature. Scenario A3 evaluates conditions in which the inlet temperatures of all reactants are set to ambient temperature (no heat transfer between hot exhaust gases and cold inlet gases.) Scenario B evaluates excess $H_2$ with respect to a stoichiometric steam-to-carbon ratio (S/C) (equal to two) and to excess steam (S/C = 4). Scenario C evaluates pure oxygen as the oxidant, with a stoichiometric S/C of two, and serves as a base case. Scenario D evaluates air as the oxidant. Scenario E evaluates non-ideal cathode utilizations, with the percentage of oxygen reacting at the cathode as low as 25%. Scenario F evaluates excess $H_2$ from biogas fuel, derived from waste water treatment plant anaerobic digester gas. Biogas is modeled as being composed of 65% $CH_4$, 32% $CO_2$, and 3% $H_2O$ by mole fraction. These initial biogas analyses do not consider the upstream energy needed to run the low temperature anaerobic digester, which consumes the majority of available heat from the fuel cell.

C. Develop and apply chemical engineering models for analyses of hydrogen separation and purification sub-systems

In this third of three distinct modeling efforts, we developed detailed chemical engineering process plant models and analyses in Aspen Plus® and conduct scenario analyses using these models to better design one of the most important sub-systems within an $H_2$-FCS, the HSU. An HSU PSA unit requires inlet gas at relatively low temperature (323 K) and high pressure (20 bar). Since the anode-off gas of an MCFC is at high temperature (923 K) and low pressure (1.06 bar), a significant energy penalty could be associated with the required compression (146 kW) and heat extraction (600 kWt) for a 1 MWe FCS. In addition, currently, in most FCS designs, $H_2$ that is not consumed in the fuel cell anode compartment is exhausted from the stack in the anode off-gas (exhaust) and combusted in a catalytic afterburner to provide heat for upstream endothermic processes (such as fuel processing and preheating reactants). FCE, Inc. uses this approach in its standard system design. If instead, $H_2$ is separated prior to the afterburner for co-production, less $H_2$ and therefore less heat is available from the combustor for heating upstream processes. For a 1 MWe FCS, this lack of available $H_2$ for combustion can lead to an overall thermal energy deficit of 123 kWt for steam generation and for preheating air and fuel. This is the baseline case HSU design: heat is removed from the anode off-gas to drop the temperature from 923 K down to 323 K without recovering this heat for use in other parts of the system.

By contrast, we analyze alternative HSU designs, and propose new designs, called HSU 1 and HSU 2 (shown in the Figures 2 and 3), as improvements over the baseline case. Both HSU 1 and HSU 2 systems integrate the fuel cell balance of plant with the heat extraction steps required for the PSA. HSU 2 incorporates the same components as HSU 1: heat exchangers, compressors and WGSR. However, these

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Parameter Varied</th>
<th>Description</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Inlet stream temperature</td>
<td>Evaluate performance at the extreme inlet temperatures</td>
<td>1. Tinlet-all = Tsystem; 2. Tinlet-fuel = Tambient, 3. Tinlet-all = Tambient</td>
</tr>
<tr>
<td>B</td>
<td>Steam-to-carbon ratio (S/C)</td>
<td>Compare stoichiometric S/C relative to excess steam</td>
<td>S/C = 2, S/C = 4</td>
</tr>
<tr>
<td>C</td>
<td>Pure oxygen as oxidant</td>
<td>Baseline case</td>
<td>S/C = 2</td>
</tr>
<tr>
<td>D</td>
<td>Air as oxidant</td>
<td>Compare impact of pure air as feed</td>
<td>Air is 78% nitrogen and 22% oxygen by volume</td>
</tr>
<tr>
<td>E</td>
<td>Non-ideal cathode utilization</td>
<td>Compare the impact of inefficient oxidant utilization</td>
<td>Utilization of oxygen at the cathode is as low as 25%</td>
</tr>
<tr>
<td>F</td>
<td>Biogas fuel</td>
<td>Compare natural gas with a typical biogas feed stream</td>
<td>Biogas is modeled as 65% $CH_4$, 32% $CO_2$, and 3% $H_2O$ by mole fraction</td>
</tr>
</tbody>
</table>

FIGURE 2. HSU 1 Schematic Diagram
systems components are arranged in a different order for the two designs. With both configurations, enough heat is recovered to produce all of the high quality inlet steam needed for the FCS operation. Scenario analyses were performed to find appropriate design configurations that reduce the compression work requirements (parasitic loads that reduce gross power output) by reducing compressor inlet temperatures. In addition, scenario analyses were performed to achieve neutral system water balance, such that the overall FCS requires no net addition of liquid water input. Since anode-off gas temperature is dropped below its saturation point, steam condensation takes place in both evaporators. As a result, liquid water can be separated from the gas stream lowering compression work and providing a water supply for the upstream steam reforming process. In HSU 1, a WGSR has been integrated into the system after the compression stage. In HSU 2, the WGSR has been placed before the compressor steps. In both designs, H₂ yield increases by shifting CO and H₂O into H₂ and CO₂ compared to the baseline case. (The HSU baseline configuration is very similar to HSU 1 in terms of component order, but it does not recover the extracted heat to produce steam. Instead of raising steam, heat extracted is not recovered. It also does not include a WGSR.)

Results

A. Develop and apply integrated engineering, economic, and environmental optimization and analysis models

In this first of three distinct modeling efforts, our engineering, economic, and environmental model results show benefits of using H₂-FCS for electricity, heat and H₂ consumers; FCS manufacturers; and the environment.

Cost Optimization:

For the cases analyzed, our model shows that electricity, heat, and H₂ can be produced with the lowest costs for strategies that combine these novel features: (1) electrical and thermal networking, (2) variable heat-to-electric power ratio, (3) variable H₂-to-heat ratio, (4) maximum FCS electrical output, and then (5) H₂ and heat load-following. As long as H₂-FCS are grid-connected with a competitive electricity sell-back price, they can sell excess electricity not used to the local grid utility network for revenue. By contrast, both heat and H₂ demand are locally constrained, without storage in the current models. Less fuel is wasted when they are produced in load-following mode, yielding higher energy cost savings. The optimal order of H₂ and heat load-following depends upon the relative price of heat compared to H₂; as the competing generator price for H₂ rises relative to the heat price, global costs are lower when H₂-FCS first run in H₂ load-following mode followed by heat load-following mode. As the competing price of heat rises relative to H₂, it becomes more important for H₂-FCS to run in heat load-following mode first, and then H₂ load-following.

Figure 4 shows example results for cost optimization for thirteen different strategies evaluated at a competing H₂ generator price of $4/kg H₂. At this relatively low H₂ price, the most economical strategy is nine (ix) or NVYEXHP, which stands for electrical and thermal networking [N], variable heat-to-electric power ratio [V], variable H₂-to-heat ratio [Y], maximum FCS electrical output [EX], and then heat load-following [H], followed by H₂ load-following [P].

CO₂ Optimization:

For the cases analyzed, our model shows that electricity, heat, and H₂ can be produced with the lowest CO₂ emissions for strategies that combine these novel features: (1) electrical and thermal networking, (2) variable heat-to-power ratio, (3) variable H₂-to-heat ratio, (4) first load-following heat, then load-following H₂, and finally (5) operating with any of these three modes: electrical load-following, maximum electrical output, and minimum electrical output. With this approach, less fuel is wasted. These results indicate that a primary constraint to minimizing CO₂ emissions is to have the systems load follow heat first (over and above...
electricity). If systems are grid-connected, any electricity not consumed by the local energy area displaces grid electricity. By contrast, heat and H₂ demand are locally constrained without storage, which makes it important to load-follow with these outputs to maximize the amount of useful output per unit of fuel consumed. For the cases evaluated, heat load-following is more crucial than following H₂ demand due to the greater quantity of heat demand compared with H₂ demand in the scenarios investigated.

Figure 5 shows results for CO₂ minimization for thirteen different strategies. The strategies with lowest CO₂ emissions are five, six, and eight, or NVYHPEN, NVYHPE, and NVYHPEX, respectively. All three strategies prioritize electrical and thermal networking [N], a variable heat-to-electric power ratio [V], a variable H₂-to-heat ratio [Y], and then heat load-following [H], followed by H₂ load-following [P]. The strategies only vary by whether the H₂-FCS produces the minimum amount of electricity [EN], electrically load follow [E], or produce at their maximum electrical output [EX].

B. Develop and apply thermodynamic and chemical engineering models for analyses of complete FCSs

In this second of three distinct modeling efforts, we analyzed the H₂ co-production potential as a function of various input parameters. Summary results for one case are shown in Figure 6, which applies our simplified analytical model to daily operation. Figure 6 shows the daily H₂ output as a function of SOFC/reformer operating temperature between 600°C and 1,000°C and accounting for all of the cell polarizations (voltage losses) at several operating cell current densities. As shown in Figure 6, a 1 MWe SOFC operating between 800 and 1,000°C could make as much as ~150 to 450 kg of H₂/day without added fuel consumption or greenhouse gas emissions from fuel combustion for providing heat to the steam reforming reaction.

The quantity of H₂ co-production available is sensitive to several FCS operating conditions. At higher current densities, voltage losses (polarizations) increase and cell voltage declines. Cell voltage is proportional to the fuel cell stack electrical efficiency. As electrical efficiency declines, the potential for heat recovery increases. With a greater quantity of available heat, more H₂ can be generated. The H₂ co-production per unit of electrical work increases with higher irreversibilities (losses). This trend occurs to a greater extent as temperature decreases, because as the temperature decreases in the range of 600-1,000°C, the polarization increases, especially the ohmic polarization associated with ion conduction through the electrolyte. These results are for operation on oxygen (O₂) while operation on air would reduce the net electrical output of the fuel cell (due to slower parasitic loads,) it would not affect the quantity of H₂ co-produced significantly.

One of the most sensitive variables that affects H₂ co-production potential is the degree of internal heat transfer between hot outlet gases and cold inlet gases. A comparison of Figures 7 and 8 reveals the effects of this variable. Figure 7 shows the quantity of excess H₂ co-produced per unit of methane fuel input as a function of fuel cell/reformer operating temperature for Scenario A1 (100% heat transfer between hot outlet gases and cold inlet ones, with an S/C =2). Figure 8 shows both Scenario A3 (0% heat transfer between hot outlet gases and cold inlet ones, with a S/C =2) and Scenario B (comparison of S/C =2 and 4). The difference between H₂ co-production available in Scenario A1 and Scenario A3 is shown by comparing the solid lines of similar color in each figure. As shown in Figure 8, with no internal heat transfer, operating between 800°C and 1,000°C fuel cell/reformer operating temperature at current densities of 200 mA/cm² and below, no excess fuel cell heat is available and no excess H₂ can be produced. Over the full range of current densities within this temperature range, the H₂ yield is between about 0% and 50% of the H₂ yield with full internal heat transfer.

H₂ co-production potential is greater with more internal reuse of heat between hot outlet and cold inlet gases. Excess H₂ is greater with (A) ideal heat
transfer between hot FCS exhaust gases (CO\textsubscript{2}, H\textsubscript{2}O, H\textsubscript{2}) and cold inlet gases (O\textsubscript{2}, CH\textsubscript{4}, H\textsubscript{2}O) compared with (B) no heat transfer between hot exhaust and cold inlet streams. The quantity of H\textsubscript{2} co-production increases as the efficiency of heat exchange rises for preheating cold anode and cathode inlet gases with hot anode and cathode exhaust gases. The lower the temperature of inlet streams, the more pre-heating they require, and the less heat is available for H\textsubscript{2} co-production. Figure 8 also shows the impact of operating at a higher S/C. The solid lines represent a S/C of 2 and the dashed lines represent a S/C of 4. More inlet water at ambient temperature requires more pre-heating, and the excess heat available for H\textsubscript{2} declines.

**C. Develop and apply chemical engineering models for analyses of hydrogen separation and purification sub-systems**

In this third of three distinct modeling efforts, HSU 1 and HSU 2 designs integrate the fuel cell balance of plant with the heat extraction steps required for the PSA. Table 2 summarizes the performance of each design with respect to the base case design (no heat recovery). HSU 1 increases the H\textsubscript{2} yield by 132% to 254 kg H\textsubscript{2}/day and HSU 2 increases the yield by 172% to 298 kg H\textsubscript{2}/day, relative to a base case. For a 1 MWe FCS, both HSU 1 and HSU 2 recover 435 kWt of heat from the anode off-gas, or 73% of available heat, to produce high quality steam for the upstream steam reforming reactions. HSU 2 was specially configured so as to reduce compression work requirements by reducing the compressor’s inlet gas temperature and the quantity of water vapor in the anode off-gas stream entering the compressors. With the HSU 2 design, the anode-off gas temperature is dropped below its saturation point, such that steam condensation takes place in both evaporators. By condensing the water prior to the compressor, the gas flow and temperature were reduced, reducing the required compression work. Liquid water is separated from the gas stream lowering the compression work and PSA separation requirements. Consequently, HSU 1 compression work requires 114 kW, 11% of gross power, while HSU 2 compression work requires only 71 kW, or 7% of gross power.

**TABLE 2. Comparison of the Performance of Different HSU Designs**

<table>
<thead>
<tr>
<th>Molten Carbonate Fuel Cell System (MCFC) (1 MWe)</th>
<th>Base case</th>
<th>HSU 1</th>
<th>HSU 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2} Co-production</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Heat Recovery from the Hydrogen Separation Unit (HSU)</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Water-Gas Shift</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Generated Gross Power [kW]</td>
<td>1,000</td>
<td>1,000</td>
<td>1,000</td>
</tr>
<tr>
<td>Ancillary loads (compressors) [kW]</td>
<td>114</td>
<td>114</td>
<td>71</td>
</tr>
<tr>
<td>Thermal energy penalty to reach PSA levels [kW]</td>
<td>600</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>Heat recovered from HSU by steam production [kW]</td>
<td>0</td>
<td>435</td>
<td>435</td>
</tr>
<tr>
<td>Heat recovered from HSU by steam production [%]</td>
<td>n.a.</td>
<td>73 %</td>
<td>73 %</td>
</tr>
<tr>
<td>Hydrogen potential after WGSR (before PSA) [kmol/s]</td>
<td>0.00151</td>
<td>0.00173</td>
<td>0.00203</td>
</tr>
<tr>
<td>Hydrogen produced [kmol/s]</td>
<td>0.00063</td>
<td>0.00147</td>
<td>0.00173</td>
</tr>
<tr>
<td>Hydrogen produced [kg/day]</td>
<td>110</td>
<td>254</td>
<td>298</td>
</tr>
<tr>
<td>Marginal increase in H\textsubscript{2} compared with base case (kg H\textsubscript{2}/day)</td>
<td>n.a.</td>
<td>144</td>
<td>188</td>
</tr>
<tr>
<td>H\textsubscript{2} production increase (Benchmark: NO heat recovery; NO WGS)</td>
<td>n.a.</td>
<td>132%</td>
<td>172%</td>
</tr>
</tbody>
</table>

n.a. = not applicable

HSU 2 also achieves neutral water balance within the entire FCS, having condensed enough water for internal recycle to other parts of the system. In both
designs, the WGSR increases the \( \text{H}_2 \) yield by shifting CO and \( \text{H}_2\text{O} \) into \( \text{H}_2 \) and \( \text{CO}_2 \). In HSU 2, the WGSR inlet temperature is lowered to increase the \( \text{H}_2 \) yield. For the HSU 1 design, the individual contributions to the increase in \( \text{H}_2 \) yield are: 1) 102\% due to displaced \( \text{H}_2 \) combustion; 2) 15\% due to WGSR; and 3) 132\% due to both.

**Conclusions and Future Directions**

**A. Develop and apply integrated engineering, economic, and environmental optimization and analysis models**

- \( \text{H}_2 \)-FCS operating in novel configurations can be more economical and environmentally benign than state-of-the-art competing generators for electricity, heat and \( \text{H}_2 \).
- For the cases evaluated, global \( \text{CO}_2 \) emissions from \( \text{H}_2 \), electricity, and heat are lowest when \( \text{H}_2 \)-FCS are electrically and thermally networked, use a variable heat-to-power ratio, use a variable \( \text{H}_2 \)-to-heat ratio, and first load-follow either heat or \( \text{H}_2 \) demands, depending upon which energy quantity is greater. The electrical output control strategy is a lower priority for \( \text{CO}_2 \) emissions concerns. This is due primarily to the assumption that excess electricity can be exported to the grid and due to the comparable electrical efficiency of the FCS compared to that of state-of-the-art competing generators.
- Global energy costs for \( \text{H}_2 \), electricity, and heat are lowest when \( \text{H}_2 \)-FCS are networked, use variable heat-to-power ratio, use a variable \( \text{H}_2 \)-to-heat ratio, and first produce at their maximum electrical output continuously, and then load follow either heat and \( \text{H}_2 \) demands. High relative prices of heat compared to \( \text{H}_2 \) shift the optimal control towards heat load-following first and \( \text{H}_2 \) load-following second, and vice versa.

**B. Develop and apply thermodynamic and chemical engineering models for analyses of complete FCSs**

- An idealized 1 MW, fuel cell operating between 800 and 1,000°C could make between ~150 to 450 kg \( \text{H}_2 \)/day: enough to refuel between 220 and 660 \( \text{H}_2 \) fuel cell cars per day, without added fuel use or \( \text{CO}_2 \) emissions from combustion to provide heat for the endothermic steam reforming reaction.
- The quantity of excess \( \text{H}_2 \) available is very sensitive to the degree of internal heat transfer between cold inlet gases entering the system and hot anode and cathode off-gas streams.
- The quantity of \( \text{H}_2 \) co-production potential is very sensitive to the inlet temperature of fuel, oxidant, and water streams. Inlet streams at lower temperature require more preheating, and result in less heat for \( \text{H}_2 \) co-production.
- For example, an SOFC/reformer operating between 800°C and 1,000°C, and cells operating at 200 mA/cm\(^2\) with no internal heat transfer between hot outlet and cold inlet streams will have no excess fuel cell stack heat available for \( \text{H}_2 \) co-production without added fuel consumption for combustion. At higher current densities, the \( \text{H}_2 \) yield is between 0\% and about 50\% of the \( \text{H}_2 \) yield with full internal heat transfer.
- With no internal heat transfer, with an SOFC operating between 800°C and 1,000°C at current densities of 200 mA/cm\(^2\) and below, no excess fuel cell stack heat is available and therefore no excess \( \text{H}_2 \) can be produced.
- To maximize excess \( \text{H}_2 \) co-production, internal heat transfer to cold streams from hot ones must be maximized and ambient inlet stream temperatures increased through internal heat transfer.
- At higher current densities, voltage losses (polarizations) increase, cell voltage declines, available heat increases, and more \( \text{H}_2 \) can be co-produced.
- The excess \( \text{H}_2 \) per unit of electrical work increases with higher irreversibilities. This trend occurs to a greater extent as temperature decreases, because as temperature decreases in the range of 600-1,000°C, the polarizations (mainly ohmic and activation polarization) increase.

**C. Develop and apply chemical engineering models for analyses of hydrogen separation and purification sub-systems**

- We identified an optimal HSU cycle design that increases \( \text{H}_2 \) yield by 172\%.
- Our proposed design meets PSA unit inlet temperature and pressure requirements, recovers 75\% of available anode-off gas heat, consumes only 7\% of gross electricity, and increases \( \text{H}_2 \) yield by 172\% to 298 kg \( \text{H}_2 \)/day (compared with the base case with no heat recovery or WGS). This design also achieves neutral water balance, and minimizes fuel consumption and \( \text{CO}_2 \) emissions by re-using available heat and minimizing losses.
- One of the most important design conditions for enhancing \( \text{H}_2 \) yield is internal reuse of available heat.
- For separating out dilute \( \text{H}_2 \) from hot, low pressure anode off-gas, PSA technology is limited by requirements for: (1) gas delivery at high pressure, (2) low temperature, and (3) with high \( \text{H}_2 \) concentration; and (4) high ancillary loads for compression that diminish net electric power output. However, PSA technology is commercially available.
Sandia plans to pursue further research in these areas:

- Careful engineering design of the HSU can significantly increase H₂ yield, overall system efficiency, net electric power output, and the system ability to achieve neutral or positive net water balance.

- Enhance and integrate chemical engineering FCS and sub-system models.
- Enhance economic and environmental network models.
- Expand further chemical engineering FCS and sub-system models.
- Expand further economic and environmental network models.
- Integrate chemical engineering and economic and environmental models.
- Analyze case studies for controlling and operating advanced poly-generative fuel cell systems (PFCS).
- Independently verify PFCS costs based on industry best practice methods.
- Integrate PFCS models with models of advanced renewables and energy storage.
- Collaborate with other national labs on model development and integration.

**Special Recognitions & Awards/Patents Issued**


**FY 2009 Publications/Presentations**

Oral Presentations

Poster Presentations


Reports