VII.17 Thermodynamic, Economic, and Environmental Modeling of Hydrogen (H_2) Co-Production Integrated with Stationary Fuel Cell Systems (FCS)

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Objectives

This work develops multi-disciplinary models of novel stationary fuel cell system (FCS) designs that co-produce hydrogen (H_2-FCS). The two main objectives of this work are to

- Develop novel H_2-FCS designs that release low greenhouse gas emissions, and
- Develop novel H_2-FCS designs with low H_2 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)
- **Milestone 41**: Annual Analysis Conference for the hydrogen community. (4Q, 2008; 4Q, 2009; 4Q, 2010; 4Q, 2011; 4Q, 2012; 4Q, 2013; 4Q, 2014; 4Q, 2015)

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 H_2-FCS compared with competing separate generators for electricity, heat and H_2.
- Completed case studies showing the benefits of installing H_2-FCS for electricity, heat and H_2 consumers, FCS manufacturers, and the environment.
- Demonstrated that global carbon dioxide (CO_2) emissions are lowest with our approach of implementing H_2-FCS with electrical and thermal networking, variable heat-to-power ratio, variable H_2-to-heat ratio, first load-following heat, and then load-following H_2 (for the case studies explored). Less fuel energy content is wasted when these approaches are used. This approach achieves a reduction in CO_2 emissions of over 40%.
- Demonstrated for the case studies explored that global costs are lowest with our approach of implementing H_2-FCS with electrically and thermally networking, variable heat-to-power ratio, variable H_2-to-heat ratio, maximum electrical

output, and then load-following both heat and H_2 in order of their relative expense. For a $4.00/kg market H_2 price, this approach achieves a cost savings of 10%.

- Showed that our novel H_2-FCS designs have the lowest CO_2 emissions and costs of any H_2 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 H_2 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 H_2/day, which is enough H_2 to fuel between 220 and 660 H_2 fuel cell cars per day with no added CO_2 emissions from fuel combustion for reformation processes.[1]
- Calculated the theoretical maximum of H_2 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®.

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 H_2, water-gas shift reactors (WGSRs) for shifting carbon monoxide (CO) and water (H_2O) into CO_2 and H_2, and compression and heat exchange to required pressure swing adsorber (PSA) inlet pressures and temperatures.
- Demonstrated a superior design called HSU 1, which recovers 73% of the available thermal energy, with a compressor load of 11% of gross power, and increases the H_2 yield by 132% to 254 kg H_2/day (compared with a base case design with no heat recovery or WGSR that yields 110 kg H_2/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 H_2 yield by 172% to 298 kg H_2/day while also achieving neutral net water balance (compared with the base case design.)

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

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 H_2-FCS for a particular location. To help achieve the DOE Hydrogen Program's goals of H_2 production with low fuel consumption and CO_2 emissions and to help meet System Analysis Milestone 11, the model minimizes global CO_2 emissions or global costs for the provision of electricity and heat to building owners, and H_2 to vehicle owners, from any combination of generators (including H_2-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 H_2 co-production with H_2-FCS. High-temperature FCSs such as solid oxide fuel cells (SOFC) and molten carbonate fuel cells (MCFC) generate heat and unconsumed H_2 fuel that can potentially be recycled for H_2 co-production. This work evaluates the amount of H_2 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 H_2 separation sub-system using detailed chemical engineering simulations in Aspen Plus®. 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 H_2 separation technology due to its commercial readiness. We conduct a scenario analysis of different HSU designs, and report results for two

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 H_2-FCS. For each novel strategy, the model minimizes total yearly electricity, heat, and H_2 costs or CO_2 emissions by changing the installed capacity of the H_2-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 H_2 consumers, CO_2 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 H_2 generators. Our model focuses on H_2-FCS designs that reuse heat from the FCS to provide heat for the endothermic steam methane reforming (SMR) process for H_2 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 H_2 fuel. The model leaves tunable the ratio of recovered heat for buildings to H_2 fuel. For the case studies evaluated here, the competing H_2 generators are stand-alone SMRs and the H_2-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 H_2 production is for just-in-time use with no H_2 storage, is limited at 5% of the total fuel energy entering the system, and the additional H_2 production and separation equipment results in a 25% increase in fixed costs over the standard FCS without H_2 co-production. The lowest cost strategies combine electrical and thermal networking, a variable heat-to-electric power ratio, a variable H_2-to-heat ratio, maximum electrical output, and then H_2 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 H_2 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 H_2 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 H_2. The steam reforming reactions can provide H_2 (A) for electrochemical conversion in the fuel cell anode compartment or (B) for H_2 co-production. For benchmarking an H_2 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 H_2 for the fuel cell to produce electric power. REFB produces H_2 as a separate product (for vehicles, etc.) Following this methodology, we calculated the theoretical maximum of H_2 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 H_2 co-production. Table 1 summarizes the key scenarios evaluated. Scenario A evaluates different

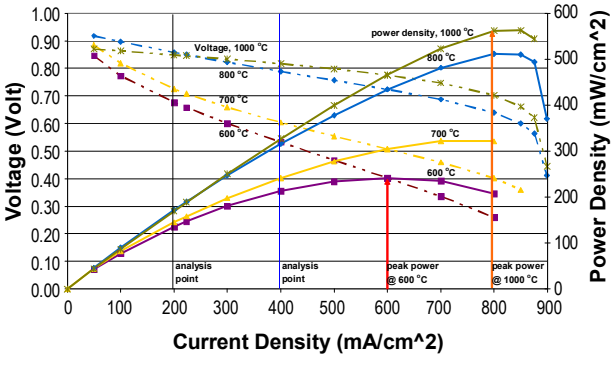

FIGURE 1. Hydrogen co-production available for vehicles is analyzed as a function of fuel cell stack polarization, cell power density, and cell operating temperature (600°C to 1,000°C).

TABLE 1. Analysis Scenarios for Excess Hydrogen Calculations

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

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 kWe) 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

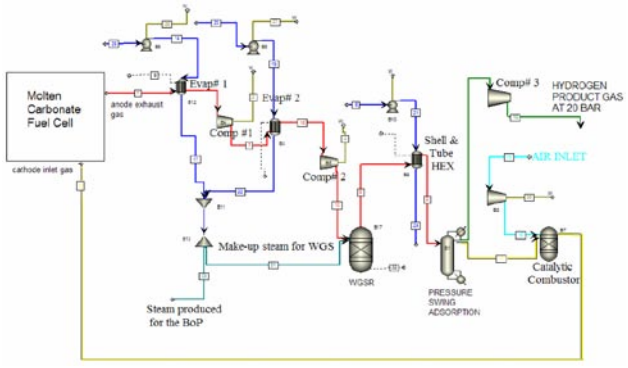

FIGURE 2. HSU 1 Schematic Diagram

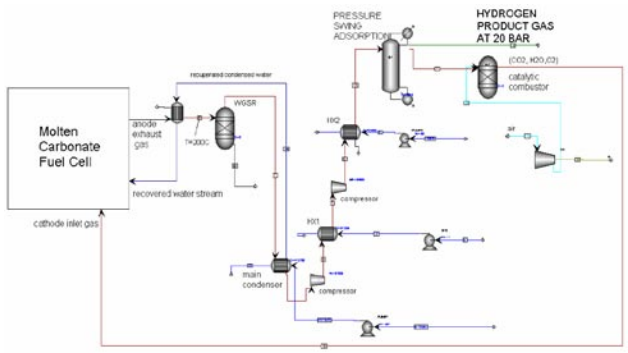

FIGURE 3. HSU 2 Schematic Diagram

system 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, H_2 yield increases by shifting CO and H_2O into H_2 and CO_2 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 H_2-FCS for electricity, heat and H_2 consumers; FCS manufacturers; and the environment.

Cost Optimization:

For the cases analyzed, our model shows that electricity, heat, and H_2 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 H_2-to-heat ratio, (4) maximum FCS electrical output, and then (5) H_2 and heat load-following. As long as H_2-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 H_2 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 H_2 and heat load-following depends upon the relative price of heat compared to H_2; as the competing generator price for H_2 rises relative to the heat price, global costs are lower when H_2-FCS first run in H_2 load-following mode followed by heat load-following mode. As the competing price of heat rises relative to H_2, it becomes more important for H_2-FCS to run in heat load-following mode first, and then H_2 load-following.

Figure 4 shows example results for cost optimization for thirteen different strategies evaluated at a competing H_2 generator price of \$4/kg H_2. At this relatively low H_2 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 H_2-to-heat ratio [Y], maximum FCS electrical output [EX], and then heat load-following [H], followed by H_2 load-following [P].

CO_2 Optimization:

For the cases analyzed, our model shows that electricity, heat, and H_2 can be produced with the lowest CO_2 emissions for strategies that combine these novel features: (1) electrical and thermal networking, (2) variable heat-to-power ratio, (3) variable H_2-to-heat ratio, (4) first load-following heat, then load-following H_2, 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 CO_2 emissions is to have the systems load follow heat first (over and above

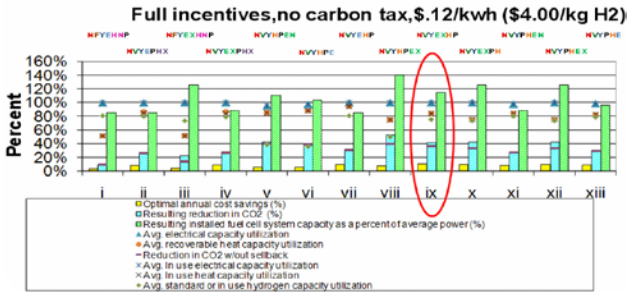

FIGURE 4. Optimizing For Lowest Energy Costs

electricity). If systems are grid-connected, any electricity not consumed by the local energy area displaces grid electricity. By contrast, heat and H_2 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 H_2 demand due to the greater quantity of heat demand compared with H_2 demand in the scenarios investigated.

Figure 5 shows results for CO_2 minimization for thirteen different strategies. The strategies with lowest CO_2 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 H_2-to-heat ratio [Y], and then heat load-following [H], followed by H_2 load-following [P]. The strategies only vary by whether the H_2-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 H_2 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 H_2 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 H_2/day without added fuel consumption or greenhouse gas emissions from fuel combustion for providing heat to the steam reforming reaction.

The quantity of H_2 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 H_2 can be generated. The H_2 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 (O_2.) While operation on air would reduce the net electrical output of the fuel cell (due to blower parasitic loads,) it would not affect the quantity of H_2 co-produced significantly.

One of the most sensitive variables that affects H_2 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 H_2 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 H_2 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/cm^2 and below, no excess fuel cell heat is available and no excess H_2 can be produced. Over the full range of current densities within this temperature range, the H_2 yield is between about 0% and 50% of the H_2 yield with full internal heat transfer.

H_2 co-production potential is greater with more internal reuse of heat between hot outlet and cold inlet gases. Excess H_2 is greater with (A) ideal heat

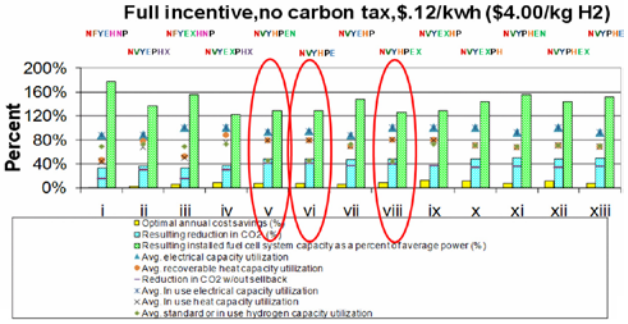

FIGURE 5. Optimizing for Minimum CO_2 Emissions

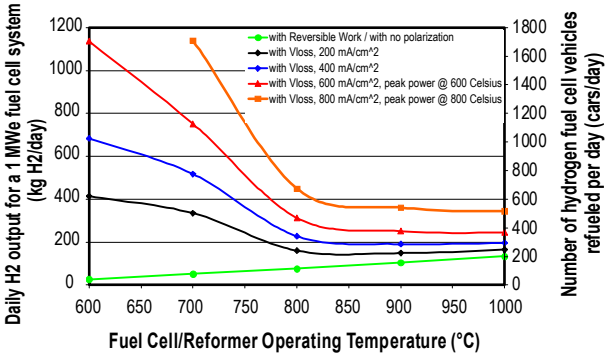

FIGURE 6. Excess hydrogen as a function of fuel cell operating temperature and polarization.

transfer between hot FCS exhaust gases (CO_2, H_2O, H_2) and cold inlet gases (O_2, CH_4, H_2O) compared with (B) no heat transfer between hot exhaust and cold inlet streams. The quantity of H_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_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_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_2 yield by 132% to 254 kg H_2/day and HSU 2 increases the yield by 172% to 298 kg H_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.

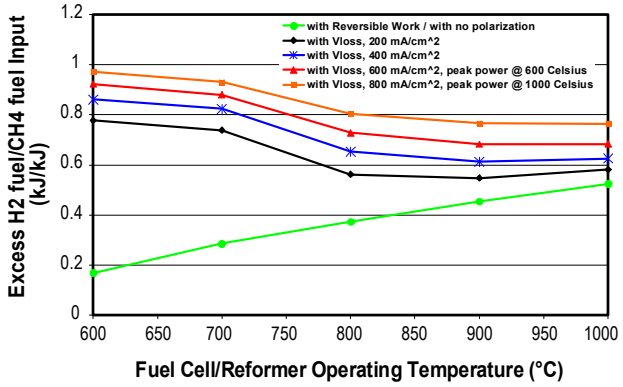

FIGURE 7. Excess hydrogen relative to fuel (methane) input for 100% heat transfer between hot and cold streams, S/C = 2.

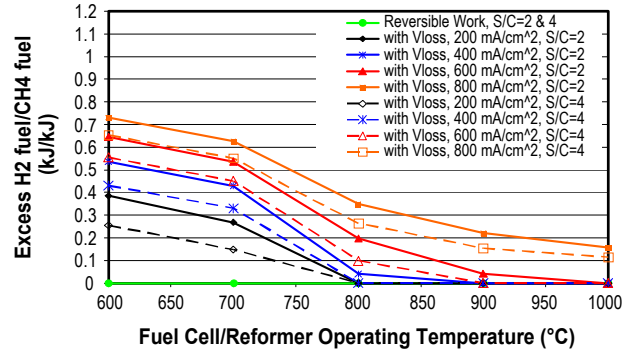

FIGURE 8. Excess hydrogen relative to fuel input for 0% heat transfer between hot and cold streams, S/C = 2 and 4.

TABLE 2. Comparison of the Performance of Different HSU Designs

Molten Carbonate Fuel Cell System (MCFC) (1 MWe)	Base case	HSU 1	HSU 2
H_2 Co-production	Yes	Yes	Yes
Heat Recovery from the Hydrogen Separation Unit (HSU)	No	Yes	Yes
Water-Gas Shift	No	Yes	Yes
Generated Gross Power [kW]	1,000	1,000	1,000
Ancillary loads (compressors) [KW]	114	114	71
Thermal energy penalty to reach PSA levels [kW]	600	600	600
Heat recovered from HSU by steam production [kW]	0	435	435
Heat recovered from HSU by steam production [%]	n.a.	73 %	73 %
Hydrogen potential after WGSR (before PSA) [kmol/s]	0.00151	0.00173	0.00203
Hydrogen produced [kmol/s]	0.00063	0.00147	0.00173
Hydrogen produced [kg/day]	110	254	298
Marginal increase in H_2 compared with base case (kg H_2/day)	n.a.	144	188
H_2 production increase (Benchmark: NO heat recovery; NO WGS)	n.a.	**132%**	**172%**

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 H_2 yield by shifting CO and H_2O into H_2 and CO_2. In HSU 2, the WGSR inlet temperature is lowered to increase the H_2 yield. For the HSU 1 design, the individual contributions to the increase in H_2 yield are: 1) 102% due to displaced 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

- 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 H_2.
- For the cases evaluated, global CO_2 emissions from H_2, electricity, and heat are lowest when H_2-FCS are electrically and thermally networked, use a variable heat-to-power ratio, use a variable H_2-to-heat ratio, and first load-follow either heat or H_2 demands, depending upon which energy quantity is greater. The electrical output control strategy is a lower priority for 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 H_2, electricity, and heat are lowest when H_2-FCS are networked, use variable heat-to-power ratio, use a variable H_2-to-heat ratio, and first produce at their maximum electrical output continuously, and then load follow either heat and H_2 demands. High relative prices of heat compared to H_2 shift the optimal control towards heat load-following first and 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_e fuel cell operating between 800 and 1,000°C could make between ~150 to 450 kg H_2/day: enough to refuel between 220 and 660 H_2 fuel cell cars per day, without added fuel use or CO_2 emissions from combustion to provide heat for the endothermic steam reforming reaction.
- The quantity of excess 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 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 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 H_2 co-production without added fuel consumption for combustion. At higher current densities, the H_2 yield is between 0% and about 50% of the 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 H_2 can be produced.
- To maximize excess 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 H_2 can be co-produced.
- The excess 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 H_2 yield by 172%.
- Our proposed design meets PSA unit inlet temperature and pressure requirements, recovers 73% of available anode-off gas heat, consumes only 7% of gross electricity, and increases H_2 yield by 172% to 298 kg 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 CO_2 emissions by re-using available heat and minimizing losses.
- One of the most important design conditions for enhancing H_2 yield is internal reuse of available heat.
- For separating out dilute 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 H_2 concentration; and (4) high ancillary loads for compression that diminish net electric power output. However, PSA technology is commercially available.

- Careful engineering design of the HSU can significantly increase H_2 yield, overall system efficiency, net electric power output, and the system ability to achieve neutral or positive net water balance.

Sandia plans to pursue further research in these areas:

- 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

1. *American Society of Mechanical Engineers (ASME) Keynote Speaker Award* for presenting this keynote paper: Whitney Colella, Aerel Rankin, Amy Sun, Pere Margalef, Jack Brouwer, "Engineering Design and Control of Polygenerative Fuel Cells," *ASME 7th International Fuel Cell Science, Engineering, and Technology Conference*, Newport Beach, CA, USA, June 8–10th, 2009.

FY 2009 Publications/Presentations

Oral Presentations

1. Colella, W.G., Rankin, A., Margalef, P., Brouwer, J., Sun, A., "Releasing Low, Zero, or Negative Net Carbon Dioxide Emissions by Polygenerating Electricity, Recoverable Heat, Cooling Power, and Hydrogen Fuel with Novel Fuel Cell Designs," *2nd Annual Earth, Wind, and Sun Conference*, Sandia National Laboratories, Albuquerque, NM, July 22nd, 2009.

2. Whitney Colella, Aerel Rankin, Pere Margalef, Jack Brouwer, Amy Sun, "Polygenerating Electricity, Recoverable Heat, Cooling Power, and Hydrogen Fuel with Fuel Cell Systems," *Energy Seminar at the Solar Thermal Power Tower*, Sandia National Laboratories, Albuquerque, NM, USA, July 13th, 2009.

3. Whitney Colella, "Implementing Stationary Fuel Cell Systems in Novel Ways to Poly-generate Electricity, Recoverable Heat, Cooling Power, and Hydrogen Fuel Based on Thermodynamic, Economic, and Environmental Models," *Energy Systems Analysis Department Colloquia*, Sandia National Laboratories, Albuquerque, NM, USA, July 13th, 2009.

4. Pere Margalef, "Hydrogen Generation with High-Temperature Fuel Cells". *Advanced Power and Energy Program Seminar Series*. University of California, Irvine. Irvine, California, June 26th, 2009.

5. Whitney Colella, Aerel Rankin, Melahn Parker, "Economic and Environmental Optimization Models for Refining Fuel Cell Use," *32nd International Association of Energy Economics (IAEE) International Conference -- Energy, Economy, Environment: The Global View*, San Francisco, CA, June 21st-24th, 2009.

6. Whitney Colella, Aerel Rankin, Amy Sun, Pere Margalef, Jack Brouwer, "Designing Next-Generation Fuel Cells for Poly-generating Electricity, Recoverable Heat, Cooling Power, and Transportation Fuels," *Electric Power Conference*, Rosemont, Illinois, May 12th, 2009.

7. Whitney Colella, "Innovative Fuel Cells for Poly-generating Electricity, Heat, and Transportation fuels," *ENG300 Energy Systems Course Seminar*, Sandia National Laboratories, Albuquerque, NM, USA, May 5th, 2009.

8. Whitney Colella, Aerel Rankin, Amy Sun, Melahn Parker, Jack Brouwer, Pere Margalef, "Optimal Design, Installation, and Control Strategies for Cogenerative Distributed Fuel Cells," *École Polytechnique Fédérale de Lausanne (EPFL) Seminar*, Laboratoire d'énergétique industrielle, Lausanne, Switzerland, April 2nd, 2009.

9. Whitney Colella, Aerel Rankin, Amy Sun, Melahn Parker, Jack Brouwer, Pere Margalef, "Advanced Low Carbon Distributed Generation," *E4Tech Seminar*, Lausanne, Switzerland, April 1st, 2009.

10. Whitney Colella, Amy Sun, Jack Brouwer, Pere Margalef, "Advanced Strategies for Stationary Fuel Cell Systems (FCS)," *International Energy Agency (IEA) Advanced Fuel Cells Annex: Stationary applications Annex XIX Meeting*, Vienna and Güssing, Austria, March 25th–26th, 2009.

11. Whitney Colella, Aerel Rankin, Amy Sun, Melahn Parker, Jack Brouwer, Pere Margalef, "Advanced Cogenerative and Polygenerative Fuel Cell System Design," *Fraunhofer Institute for Solar Energy (ISE) Systems Seminar,* Freiburg, Germany, March 31st, 2009.

12. Whitney Colella, Aerel Rankin, Amy Sun, Jack Brouwer, Pere Margalef, "Dynamic System Modeling of Integrated Fuel Cell Systems with Hydrogen Co-Production," *Fuels Pathways Integration Technology Team (FPITT) Meeting*, National Renewable Energy Laboratory (NREL) offices, Washington, D.C. (remotely delivered), March 17th 2009.

13. Pere Margalef, Jack Brouwer, Scott Samuelsen, "Tri-Generation of Electricity, Hydrogen, and Heat on Demand from High-Temperature Fuel Cells," *International Colloquium on Environmentally Preferred Advanced Power Generation (ICEPAG)*, Newport Beach, California, Feb. 10th–12th, 2009.

Poster Presentations

1. Whitney Colella, Aerel Rankin, Amy Sun, Pere Margalef, Jack Brouwer, "Thermodynamic, Economic, and Environmental Modeling of Hydrogen (H2) Co-Production Integrated with Stationary Fuel Cell Systems (FCS)," *2009 U.S. Department of Energy Hydrogen Program Annual Merit Review & Peer Evaluation Meeting*, Arlington, VA, May 18–22nd, 2009.

Reports

1. Whitney Colella, Aerel Rankin, Pere Margalef, Amy Sun, Jack Brouwer, "Thermodynamic, Economic, and Environmental Modeling of Hydrogen (H_2) Co-Production Integrated with Stationary Fuel Cell Systems (FCS), *2009 U.S. Department of Energy Hydrogen Program Annual Report*, Albuquerque, NM, July 1st, 2009.