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Hydrogen Production from High-Temperature Fuel Cells

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Glossary

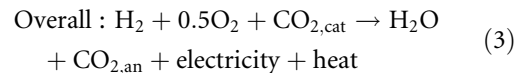
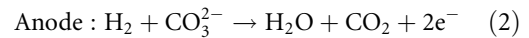
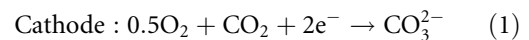
Distributed energy resources (DER) Small-scale power generation, energy conversion, storage, and/or control technologies (typically in the range of 3–10,000 kW) that are installed and operated close to the energy demand (e.g., a home or business). These resources can provide an alternative to or an enhancement of the existing electric power and thermal energy systems. Among the main advantages of the DER are the energy saving associated with the transport of energy from the centralized plants to the points of use and the potential to poly-generate power, heating, cooling, and/or fuels close to the point of use.

Distributed generation (DG) According to the California Energy Commission [7], distributed generation (DG) comprises small-scale power generation technologies (typically in the range of 3–10,000 kW) located close to where electricity is used (e.g., a home or business) to provide an alternative to or an enhancement of the existing electric power system. Among the main advantages of the distributed generation are the energy saving associated with the transport of energy from the centralized plants to the points of use and the potential for cogeneration of heat and power.

High-temperature fuel cells (HTFC) HTFC are electrochemical conversion devices that produce electricity directly from the chemical potential difference between a fuel and oxidant. There are two common types of high-temperature fuel cells: (1) molten carbonate fuel cells (MCFC) and (2) solid oxide fuel cells (SOFC).

The *molten carbonate fuel cell* uses a carbonate electrolyte, which is generally a mixture of lithium and potassium carbonates (salts). At the high

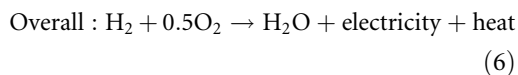
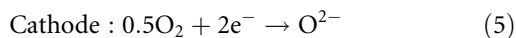
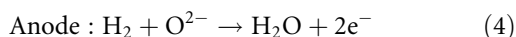
operating temperature (typically 550–650°C) the alkali carbonates become a highly conductive molten salt, with CO_3^{2-} ions providing ionic conduction. Anode materials are typically Ni–Cr/Ni–Al alloys and cathode materials are comprised of lithiated NiO [2]. The fuel cell operation is the result of a complex conjunction of physical, chemical, and electrochemical processes that together oxidize fuel and reduce oxidant in separate compartments to produce electricity, heat, and redox reaction products. The anode and cathode half reactions and overall electrochemical reaction are [3]



Note that carbon dioxide must be supplied to the cathode as well as oxygen. The CO_2 is converted to carbonate ions which provide the means of ion transfer between the cathode and the anode. Therefore, there is a net transfer of CO_2 from cathode to anode. There are different ways of CO_2 recycling. The most common method feeds the anode exhaust gas to an anodic gas oxidizer (AGO), which converts any unused hydrogen or carbon monoxide into water and CO_2 . A portion of the exhaust gas from the anodic gas oxidizer is then mixed with fresh air and fed into the cathode inlet. This process also serves to preheat the reactant air, burn the unused fuel, and bring the waste heat into one stream for use in a bottoming cycle [4].

The *solid oxide fuel cell* uses an oxide ion-conducting ceramic material as the electrolyte. Since only two phases (solid and gas) are required and CO_2 recirculation is not required, these systems are conceptually simpler than other fuel cells [5]. As in the molten carbonate case, no precious metal catalysts are needed due to the high operating temperatures (700°C–1,000°C). SOFC have typically used materials sets based upon a yttria-stabilized zirconia (YSZ) electrolyte comprised of 8–10% Y_2O_3 in ZrO_2 [2]. Above 700°C, YSZ becomes a conductor of oxygen ions (O^{2-}). The negatively charged ion (O^{2-}) is transferred

from the cathode to the anode [6]. The half-reactions produce water in the anode as follows:



The remaining SOFC fuel from the anode reactions is typically oxidized by the remaining oxygen from the cathode in a combustor to produce heat. This heat is used in the fuel cell plant to preheat the inlet streams and/or overcome the endothermicity of steam reforming reactions elsewhere in the system.

Hydrogen separation When hydrogen is produced by thermochemical processes such as steam methane reformation (SMR), the output gas is a hydrogen-rich gas (i.e., reformat) that contains water vapor, carbon monoxide, carbon dioxide, and other trace gases. Therefore, hydrogen must be separated from the reformat gas and purified to reach the specific requirements for hydrogen use.

Hydrogen separation in refineries has been traditionally done by established technologies such as pressure swing adsorption (PSA), selective permeation processes using polymer membranes, or cryogenic separation processes. Each process is based upon different separation principles. Economic aspects and other project considerations such as process flexibility, reliability, and scalability have to be taken into account to decide the hydrogen separation method [10].

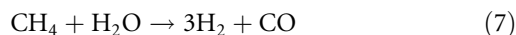
Besides the traditional methods, alternative techniques for hydrogen separation are being developed. These include the Electrochemical Hydrogen Separation method (EHS) and Hydrogen Separation Membrane Reactor (HSMR) [11].

Parasitic loads In power generation devices, parasitic loads are those loads associated with the normal operation of the system that are required to sustain the normal operation of the system in a safe and reliable manner. Typical parasitic loads are associated with the preparation of the reactants, handling of products, exchanging of heat and flows, and thermal management. The power required for these parasitic loads must be produced by the same

generator and subtracted from the generator power to produce the net system power output. Ideally, parasitic loads should be minimized in order to achieve higher system efficiencies.

Poly-generation Poly-generating systems include energy conversion systems that convert fuel chemical energy into multiple useful forms of energy or power. For instance, a specific poly-generation system instance that produces only two products is a combined heat and power (CHP) system that generates electrical and thermal power from fuel in a single, integrated system. Poly-generating systems are typically comprised of a number of individual components, including for example a heat engine, generator, heat recovery equipment, and electrical interconnection hardware that are configured into an integrated whole system. The primary energy conversion device (i.e., the prime mover) is typically used to identify the type of poly-generating system. Prime movers include reciprocating engines, gas or steam turbines, and fuel cells that can produce electrical and thermal power from a variety of fuels, including natural gas, coal, and biofuels. Thermal energy from the system can be used in direct process applications or indirectly to produce steam, hot water, hot air for drying, or chilled water for process cooling [8]. High-temperature fuel cells, in particular, can be designed and operated to poly-generate electricity, heat, and useful chemicals (such as hydrogen) in a variety of configurations [9].

Steam methane reformation (SMR) Steam methane reformation is a mature industrial technology that is typically used for hydrogen production. The basic reforming reaction for methane is

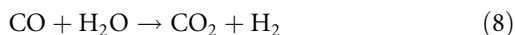


SMR is an endothermic reaction so that heat must be provided to drive the reaction forward to produce hydrogen. The overall process for hydrogen production typically also includes the water-gas-shift reaction defined below.

Synergy Synergy describes the complementary interaction of processes to create an outcome that is in some way of more value than the sum of the individual values that would otherwise have been

produced by the individual processes operating independently.

Water–gas shift (WGS) The reaction of carbon monoxide with water to produce hydrogen and carbon dioxide as follows:



The WGS reaction is reversible and exothermic.

Well-to-tank (WTT) efficiency Well-to-tank efficiency is defined as the total energy of a ready-to-be-used fuel (i.e., in the tank of the vehicle), divided by the total energy required for the extraction, preparation, transport, and dispensing of the same fuel. This efficiency calculation is widely used in the automotive sector to compare the energy intensity of different fuels. On the other hand, well-to-wheel (WTW) efficiency accounts for the inefficiencies of the vehicle propulsion system. WTT are higher than WTW efficiencies.

Definition of the Subject

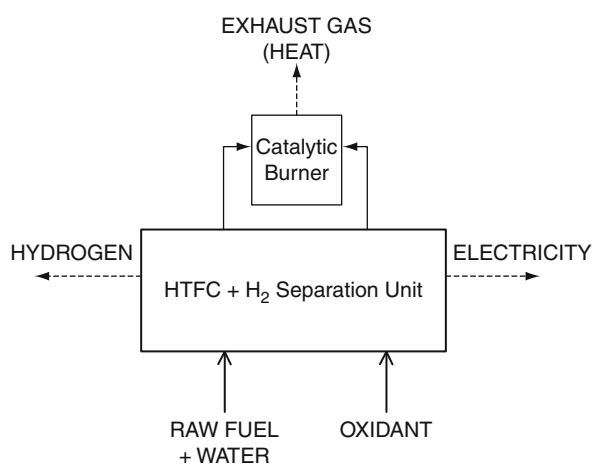
Hydrogen is a likely energy carrier of the future due to the absence of carbon, low emissions when converted in various end-use technologies, and ability to be cleanly and efficiently produced from various domestic primary energy sources. In 2003 the Federal government launched the Hydrogen Fuel Initiative with a total budget of \$1.2 billion over 5 years in order to accelerate research and development of fuel cell technologies [12]. Importantly, major automobile manufacturers are operating fuel cell vehicles that run on pure hydrogen gas, and several fuel cell buses are in operation in major cities around the world. Companies such as Shell, Air Products and Chemicals, Chevron, and Air Liquide are developing hydrogen production, distribution, and dispensing technologies for hydrogen vehicles along with strategies to deploy them. Moreover, the state of California intends to reduce the carbon content of transportation fuels through the Low Carbon Fuel Standard. Additional legislation in the areas of energy and climate, such as that contained in California laws entitled AB32, AB1493, SB76, and SB1368, highlight California's commitment to ensuring low greenhouse gas emissions for both electricity and transportation fuels [12]. Many other places around the world, including Germany and fellow European Union countries,

Japan, China, and Korea, are advancing hydrogen fueling and vehicle technology. Therefore, developing a highly efficient, low-emission, and economically viable hydrogen production and delivery methodology is of great importance from environmental, social, economic, and political perspectives.

The production of hydrogen from high-temperature fuel cells is accomplished by a synergistic integration of fuel processing, electrochemical conversion in a fuel cell, and hydrogen separation that leads to an ability to locally produce and deliver hydrogen with ultralow criteria pollutant and greenhouse gas emissions. The resulting system comprised of a high-temperature fuel cell that produces electricity, heat, and hydrogen fuel uses a hydrogen separation unit (HSU) that separates and purifies the hydrogen from the anode off-gas, and is typically referred to as a poly-generating or tri-generating fuel cell. Figure 1 shows a basic schematic of a poly-generating HTFC.

Introduction

Since it is not naturally occurring, hydrogen must be produced from water via electrolysis, photolysis, or thermal splitting, or from hydrocarbon fuels (e.g., natural gas, coal, biogas, biomass) via reformation or gasification. Currently, hydrogen is typically produced at large centralized steam methane reformation (SMR) plants from natural gas. SMR is a convenient and



Hydrogen Production from High-Temperature Fuel Cells. Figure 1

Basic schematic of a poly-generating HTFC

cost-effective method that has been implemented to produce a substantial commercial supply for petroleum refining, metals processing, and other industrial uses. Not only hydrogen production (e.g., SMR plants and a host of other cost-effective and environmentally sensitive production technologies) but also energy-efficient and environmentally sensitive technologies for transport, distribution, and dispensing of hydrogen will be needed in the future [13].

Distributed generation of hydrogen, while typically less efficient than centralized generation, is foreseen by many as a viable strategy to produce hydrogen due to the savings associated with transport and distribution of the hydrogen, which can be energy and emissions intensive. Significant efforts to develop small-scale hydrogen production plants have led to commercialization of relatively affordable systems. Ogden [14] reviewed the development and commercialization status of various types of small-scale reformers.

Conventional steam methane reformers consisting of long catalyst-filled tubes that operate at high pressures (15–25 atm) and high temperatures (850°C) have been successfully scaled down to units that produce as little as 10–100 kg/h. However, at such small sizes, relative capital costs are too high to compete with large-scale hydrogen production. In addition, the footprint of these systems may be too large to be placed at conventional fueling stations. For this reason, more compact and inexpensive designs have been, and are being, developed by many manufacturers. The average hydrogen production efficiency reported for good systems ranges between 60% and 77% (on a LHV basis) [14]. The main technical challenges of distributed reformers include relatively larger system heat losses at small scale and inability to produce hydrogen on demand that may require large hydrogen storage capabilities, especially during the early stages of hydrogen vehicle deployment.

Background

As indicated above, most hydrogen is produced today from fossil fuels in large SMR plants and is used at or near the production site [13]. As fuel cells and hydrogen vehicles become more widely used, an entire infrastructure for the distribution and dispensing of hydrogen will be needed with the additional goal of

producing and delivering hydrogen to consumers in an environmentally sensitive manner [15].

An integrated energy future that meets transportation fuel and stationary power and thermal energy demands could be made from the same primary energy sources. For example, the primary feedstock currently used for the production of hydrogen (i.e., natural gas) is also a significant primary energy source for electricity production. As both energy sectors (transportation and electricity generation) come to rely on the same primary energy sources, there are significant opportunities to integrate them, which can introduce profound changes in how our energy is converted and distributed. The integration of these two energy sectors at the level of a production plant via poly-generation of hydrogen, heat, and electricity could lead to lower prices for both transportation and stationary applications and ultimately enhance overall efficiency and flexible use of diverse resources [9].

Electricity and hydrogen poly-generation can be accomplished at large or at small scale. For the large-scale approach, hydrocarbon feedstocks such as coal, natural gas, or biomass can be converted via thermochemical processes to a syngas. Syngas is comprised of hydrogen, water, carbon monoxide, and carbon dioxide and can be used to generate electricity in a fuel cell, steam cycle, gas turbine, or combination of these technologies (i.e., combined cycle). Since the syngas produced has a high concentration of hydrogen, part of the gas stream can be diverted and the hydrogen can be separated from the rest of the gas to produce high-purity hydrogen for fuel cell vehicle use.

For the small-scale approach, poly-generating fuel cells represent a viable technology to produce hydrogen, electricity, and heat on demand in a distributed fashion. Excess heat released during the electrochemical fuel cell reactions can be used to produce hydrogen through steam reformation of hydrocarbon fuels. The highly synergistic nature of the poly-generating concept at high temperatures leads to higher production efficiencies compared to conventional hydrogen and electricity generation [16]. If successfully developed, poly-generating HTFC that produce electricity, heat, and hydrogen from a variety of hydrocarbon fuels will provide high efficiency and low emissions distributed hydrogen production and delivery. In addition, such a concept

could aid fuel cell market viability, stakeholder confidence, and energy security and sustainability together with emissions reduction [17].

Key Principles of Poly-Generation of H₂ with HTFC

The key principles that apply to high-temperature fuel cell systems that poly-generate electricity, heat, and hydrogen are as follows:

1. Fuel flexibility of high-temperature fuel cells
2. High-temperature fuel cell–fuel processing relationship
3. Low entropy associated with exchanging heat at similar temperature
4. Fuel utilization concept requires excess fuel processing
5. Lower fuel utilizations lead to higher electrochemical efficiencies
6. Endothermicity of hydrocarbon reformation provides needed cell cooling
7. Production of excess hydrogen produces higher fuel cell efficiency
8. Chemical synergy associated with reactant/product interactions
9. All synergies lead to lower fuel cell system parasitic losses
10. Electrochemical and catalytic processes are inherently low emissions
11. Processes are efficient even at small size enabling distributed production
12. Hydrogen transport involves emissions and energy penalties

A brief description of each of these key principles is presented in this section.

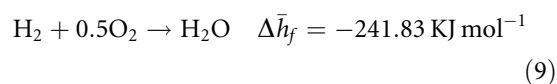
Fuel Flexibility of High-Temperature Fuel Cells

High-temperature fuel cells, such as the molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC), can be operated on a variety of hydrocarbon fuels including natural gas, digester gas, landfill gas, coal and biomass synthesis gases. MCFC and SOFC technologies comprise specific characteristics that make them especially amenable to operation on such hydrocarbon fuels. These characteristics include the use of an oxidizing ion in the electrochemical reactions (CO₃²⁻ for MCFC and O²⁻ for SOFC) and

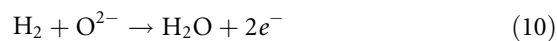
high-temperature operation (550–650°C for MCFC and 700–1,000°C for SOFC) which promotes sufficiently rapid chemical and electrochemical reactions.

High-Temperature Fuel Cell: Fuel Processing Relationship

Solid oxide fuel cells (SOFC) and molten carbonate fuel cells (MCFC) generate electricity and heat through exothermic electrochemical reactions. Oxidation of hydrogen takes place in the anode compartment, which overall thermodynamics are described by the global reaction:

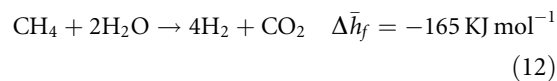


The electrochemical oxidation reactions that convert hydrogen to water in the SOFC and MCFC anode compartments are, respectively:



These reactions are complemented by corresponding oxidant reduction reactions in the cathode compartment, ion transport, and electron flow to perpetuate the electrochemical reactions. Since electricity is produced by these electrochemical reactions at less than 100% efficiency, the remaining portion of the enthalpy of reaction produces heat as reactants are converted to products.

HTFC system designs typically incorporate fuel processing with electrochemical conversion. The global fuel processing reaction includes steam methane reforming and water–gas–shift reactions and is described by:



The heat generated by the electrochemical reactions of Eq. 9 tends to be greater than the heat required by the endothermic fuel processing reactions of Eq. 12 for the amount of electricity produced [6]. Surplus heat is typically used to preheat the fuel and oxidant streams before they enter the fuel cell and to produce the steam required for system operations. Therefore, more hydrocarbon fuel than that required for the electric power

generation could be processed in a HTFC, creating a hydrogen-rich stream that could be subsequently purified and delivered to the point of use without the need of an additional reformer.

Low Entropy Associated with Exchanging Heat at Similar Temperature

To proceed at a sufficiently fast rate and to completion (i.e., consume all the hydrocarbon fuel to produce hydrogen-rich syngas), the fuel processing reactions (e.g., steam reformation reaction of Eq. 12) must occur at a reasonably high temperature. Irreversible heat transfer processes between the exothermic fuel cell reactions (i.e., heat source) and the endothermic reforming reactions (i.e., heat sink) increase the entropy generation of the system. This irreversible heat transfer must be provided to a typical reformer reactor in a fuel cell system, using either fuel combustion or fuel cell exhaust heat at temperatures above those at which the reformation reactions proceed. However, the operating temperatures of HTFC (550–650°C for MCFC and 700–1,000°C for SOFC) are similar to the temperatures at which hydrogen production rate and reaction completion are acceptable for steam methane reformation processes (i.e., ~700°C). Therefore, heat can be transferred from the exothermic to the endothermic process with minimal (or zero) temperature difference leading to low entropy generation for heat exchange, resulting in overall high efficiency.

Fuel Utilization Concept Requires Excess Fuel Processing

Fuel and oxidant utilization factors refer to the fractions of the total fuel and oxidant flowing through the anode and cathode compartments that are consumed to generate electricity. If fuel and/or oxidant species concentrations become too low, the chemical potential difference becomes unable to sustain a voltage difference. The Nernst potential (V_{Nernst}) describes the relationship between voltage and reactant and product concentrations that applies to a fuel cell

$$V_{\text{Nernst}} = E_0 + \frac{RT}{2F} \ln \frac{x_{\text{H}_2} x_{\text{O}_2}^{\frac{1}{2}}}{x_{\text{H}_2\text{O}}} \quad (13)$$

where E_0 is the ideal reversible potential, F is Faraday's constant [96,487 kC/kmol], R is the gas constant, T is

the operating temperature, and x_k is the concentration of the species k [6].

Since fuel cell electrodes are good electronic conductors (they act as equipotential surfaces), low reactant concentrations anywhere in the anode or cathode compartments leads to voltage that cannot be sustained. Therefore, fuel utilization (U_f) and oxygen utilization (U_{O_2}) must be always lower than 100%. In other words, the amount of fuel and oxidant fed into the fuel cell must always and continuously be greater than the amount consumed within the stack to produce electricity even when hydrogen is not produced.

Lower Fuel Utilizations Lead to Higher Electrochemical Efficiencies

In operational fuel cell systems, cell voltage increases as fuel utilization decreases, which results in higher electrochemical efficiencies. The electrochemical efficiency is defined as the actual cell voltage (V_{cell}) divided by the thermodynamically possible cell voltage (V_{max}), or

$$\eta_{\text{cell}} = \frac{V_{\text{cell}}}{V_{\text{max}}} \quad (14)$$

where V_{max} is defined as the maximum theoretical voltage that would be achieved if all the energy from the hydrogen fuel were transformed into electrical energy [16], or

$$V_{\text{max}} = \frac{-\Delta\bar{g}_f}{n_i F} \quad (15)$$

where $\Delta\bar{g}_f$ is the Gibbs free energy, n_i is the number of electrons transferred during the electrochemical oxidization of fuel species i ($n_i = 2$ for H_2 and CO , $n_i = 8$ for CH_4), and F is Faraday's constant.

From the Nernst voltage equation Eq. 13, it can be observed that higher species concentrations lead to higher cell voltages. At lower fuel utilizations, reactant species concentrations are higher along the electrode channels. Thus, it can be stated that lower fuel utilization results in higher cell voltages that raise the electrochemical efficiency of the fuel cell as described by Eq. 14.

An alternative concept that provided insight into the effects of the fuel utilization on the electrochemical

efficiency relates to the mixing of products with reactants to dilute the electrochemically active species concentrations. Water product mixes with the anode gas as it is formed by the electrochemical reactions in an MCFC or SOFC. The concentration of water product in the anode increases as the fuel utilization factor increases. Mixing processes are irreversible so they produce entropy. As a result, a completely reversible fuel cell operation would be only approached as $U_f \rightarrow 0$. In other words, irreversibilities increase as the utilization factor increases [18].

Consequently, one desires to operate a fuel cell at the lowest possible utilization factor to maximize the cell voltage and reduce mixing irreversibilities. However, unless one recycles or otherwise uses the anode off-gas then one alternatively desires high utilization to achieve high overall stack electrical efficiency. Typically, fuel utilization is selected in the 70–90% range to balance these considerations.

One of the key principles of poly-generating fuel cells is related to the capability of operating the fuel cell at lower fuel utilizations without compromising the overall system electrical efficiency. As already stated, hydrogen that is not electrochemically oxidized will be separated and considered as a valuable system output. Therefore, inasmuch as additional hydrogen is separated and used, there is the opportunity to take advantage of the higher electrochemical efficiency that is a natural by-product of the lower fuel utilizations required for hydrogen production.

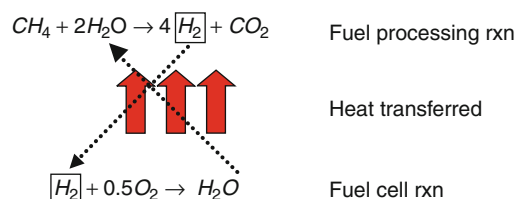
Endothermicity of Hydrocarbon Reformation Provides Needed Cell Cooling

The fact that fuel cells must be cooled to maintain steady state operating temperature allows for synergistic coupling of endothermic steam reforming with exothermic fuel cell electrochemical reactions to yield unprecedented efficiency. Adding more endothermic reforming reactions for the same amount of electrochemical reactions results in a reduced requirement for air cooling of the cell. The synergistic performance benefits related to these lower cooling requirements are caused by: (1) the additional endothermic reformation at lower fuel utilization that provides additional cooling to the fuel cell stack; and (2) less electrochemical heat generated per mol of input fuel due to the

higher voltages achieved at lower fuel utilizations. Both phenomena reduce the auxiliary power associated with forcing air through the cathode compartment, which is the primary means of otherwise removing heat from the fuel cell.

Chemical Synergy Associated with Reactant/Product Interactions

High-temperature fuel cells operate at high enough temperatures to convert methane into fuels that are more amenable to electrochemical oxidation such as hydrogen and carbon monoxide within the anode compartment. This concept is known as internal reformation (IR) and represents one of the key features of high-temperature fuel cells that can yield exceptionally high electrical efficiencies when compared with low-temperature fuel cells that process fuel in a separate reactor (i.e., external reformation). The main synergy associated with IR is related to the direct consumption of the hydrogen product of the reforming reaction by the electrochemical fuel cell reactions that produce water, a reformation reactant, which all occurs at the same time and physical location [17]. The immediate consumption of products and provision of reactants by the fuel cell reactions drives the reformation reaction forward and assures reaction completeness. Continual production of hydrogen and consumption of water by reformation also directly facilitates electrochemical reaction progress. This chemical synergy is introduced in addition to the heat exchange synergy between exothermic fuel cell reactions and endothermic fuel processing reactions with minimum losses since both reactions occur at the same time and place. Figure 2 shows the main



Hydrogen Production from High-Temperature Fuel Cells. Figure 2

Internal reformation chemical and thermal synergy mechanisms

reactions, chemical exchange synergy, and heat transfer processes occurring during internal reformation in high-temperature fuel cells.

All Synergies Together Work in the Same Direction to Increase Fuel Cell System Efficiency

At low fuel utilizations, the ratio between endothermic heat from the fuel processing reactions and exothermic heat from the electrochemical reactions increases, leading to a reduction of the auxiliary power required to circulate cooling air through the cathode. In addition, thermodynamic analyses demonstrate that cooling required per mol of fuel input drops at lower fuel utilizations due to the higher operational voltages at low fuel utilizations [16]. The design and operating changes that produce these synergies require changes in the same direction. Therefore, all of the described synergies of poly-generating high-temperature fuel cells can work together to result in higher fuel cell efficiencies compared to conventional fuel cell system designs that do not poly-generate. There remain design challenges, such as managing the fuel cell temperature gradient in poly-generating systems, but, the overall design and operating changes required for poly-generation work together to improve efficiency.

Integration with Hydrogen Separation Produces Higher System Efficiency

Fuel cells are by nature required to produce somewhat more hydrogen than is electrochemically converted in the anode compartment. However, operating at lower fuel utilization leads to higher electrochemical efficiency and the chemical synergies of internal reforming, and the endothermicity of fuel processing reactions leads to lower parasitic losses due to reduced air blower power. These features by themselves would not be beneficial to overall system efficiency until and unless they are integrated into a system design that produces a significant amount of product hydrogen leading to remarkably higher overall efficiency. This is accomplished by using the above principles in combination with hydrogen separation technology that is integrated with the system design requirements in a manner that exchanges more heat for useful electrochemical and hydrogen production purposes.

Electrochemical and Catalytic Processes Are Inherently Low Emissions

The inherent electrochemical and catalytic nature of high-temperature fuel cells and poly-generating fuel cells yields ultralow criteria pollution emissions.

- Thermal NO_x requires high-temperature combustion in air whereas in HTFC, all of the fuel is processed and converted either electrochemically or by catalytic processes at low temperature.
- SO_x cannot be produced since sulfur is removed from the fuel before entering the system.
- Particulate matter (PM) is not produced due to high water content, catalyst presence, and low-temperature conditions extant in the anode compartment, followed by catalytic and/or low-temperature oxidation of the anode off-gas.
- CO is amenable to the electrochemical oxidation to release electrons in the anode compartment and the remainder is consumed by catalytic and/or low-temperature oxidation of the anode off-gas.
- Hydrocarbons are usually converted into methane in a pre-converter reactor before entering the fuel cell stack and the remainder is consumed by catalytic and/or low-temperature oxidation of the anode off-gas.
- Air toxics, such as higher hydrocarbons, aldehydes, and alcohols, are not present or are removed from the incoming fuel and typically no air toxic compounds are produced by any of the processes involved in a fuel cell system. If any air toxics would be produced then they would likely be destroyed at the high-temperature catalytic conditions of the anode compartment or anode off-gas oxidizer.

Processes Are Efficient Even at Small Size Enabling Distributed Production

Heat engine energy conversion is driven by a temperature difference while fuel cell energy conversion is driven by a chemical potential difference. The efficiency of any heat engine is limited by the efficiency that could be achieved by the reversible cycle operating upon a temperature difference, known as the Carnot efficiency [19]. On the other hand, fuel cells are limited by the Nernst equation and chemical potential difference that can be established in the

cell, since they convert the chemical potential difference directly into electrical energy [6]. Heat engines for electricity production also have additional losses associated with the conversion of mechanical energy (e.g., piston movement, spinning turbine) to electricity through cranks, gears, and a generator.

Heat engines have reduced efficiency at reduced size because surface-to-volume ratios increase leading to higher percentage heat losses and inability to sustain the high cycle temperature for smaller engines. This leads to an inherent inability to establish a high temperature difference leading to a lower efficiency limit (i.e., lower Carnot efficiency). In addition, small-scale heat engines have proportionally larger friction, non-isentropic compressions and expansion, and other losses in comparison to larger heat engines. As a result, we currently tend to produce most of our power in very large central power plants based upon the heat engine – smaller plants are inherently less efficient.

On the other hand, fuel cell power production and efficiency depends upon the establishment of a chemical potential difference which can be established in equal difference regardless of the size of the cell.

Hydrogen Transport Involves Emissions and Energy Penalties

Today, most hydrogen is produced from natural gas in large steam methane reformation (SMR) plants in a centralized fashion. To produce hydrogen at large scale in centralized reformation plants is more efficient than producing hydrogen at small-scale reformation plants.

The main steps of a well-to-tank hydrogen supply chain may be defined as production, treatment, distribution, storage, and dispensing. Each step can be accomplished with a variety of different technologies which may be more or less energy intensive and environmentally friendly [20]. For long distances, transportation of liquefied hydrogen by diesel truck is the most common strategy. However, liquefaction of hydrogen is the most energy intensive process and it makes sense only for very long delivery distances. Shorter distance hydrogen transport may be resolved by the transportation of compressed hydrogen which takes less energy than liquefaction, but delivers less

hydrogen per unit truck volume. Hydrogen can also be transported via high-pressure pipeline, which is one of the least energy intensive methods. But, in comparison to other gaseous or liquid fuels, hydrogen pipeline delivery is more energy intensive [26]. In all of these cases, the relatively low volumetric energy density of hydrogen leads to relatively large energy and emissions penalties associated with hydrogen transport and delivery. These penalties can result in mediocre well-to-tank efficiencies compared to other fuels. These penalties can be averted by the production of hydrogen in a distributed fashion with a technology that scales down with high efficiency, such as poly-generating HTFC [16]. Nonetheless, energy and emissions penalties associated with hydrogen transport must be accounted for in all analyses.

Cycle Configurations for Poly-Generating HTFC

Brouwer and Leal [21] investigated the production of hydrogen with high-temperature fuel cells by analyzing and comparing eight different cycle configurations using solid oxide fuel cells (SOFC) and molten carbonate fuel cells (MCFC). Six of the eight configurations use fuel cell heat to drive hydrogen production in an external reformer placed in different positions in the cycle. The other two configurations use the internal reformation capabilities of high-temperature fuel cells to produce hydrogen.

Based upon the cycle configurations developed by Brouwer and Leal [21], Margalef et al. [9] investigated in detail how placing the external reformer in different positions affects the fuel cell performance and the hydrogen production efficiency. In addition, Margalef et al. investigated the performance of the poly-generating plant at different fuel utilizations together with the integration of commercially available hydrogen separation and purification technologies (i.e., pressure swing adsorption) with the fuel cell balance of plant (BOP).

High-Temperature Fuel Cell Subsystem

High-temperature fuel cells (HTFC) generate electricity and heat through exothermic electrochemical reactions. Generated heat by the fuel cell reactions is typically utilized internally or externally by the endothermic fuel processing reactions, which in turn

provide cooling to the system [22]. Surplus heat is used to preheat the fuel and oxidant streams before they enter the fuel cell and to produce the steam required for system operations. In addition, the remaining thermal energy contained in the exhaust gases can be used downstream of the fuel cell for poly-generation applications that require or value heat [22].

One possible configuration is to use the fuel cell heat to produce hydrogen via steam methane reforming in an external reformer (i.e., external reformation). Another possibility relies on the internal reforming capabilities of HTFCs and on the fact that the amount of high-quality heat produced by the exothermic reactions within the stack is typically greater than the heat required for fuel processing [6]. Therefore, more hydrocarbon fuel than that required for the electricity generation can be processed in an HTFC, creating a hydrogen-rich stream that could be subsequently purified and delivered at the point of production without the need of an external reformer [17] (i.e., internal reformation). This mode of operation implies lower stack fuel utilization factors and has been associated with synergies such as lower cell polarization losses and lower parasitic losses correlated with lower cooling air [16].

Separation/Purification Subsystem (Hydrogen Separation Unit (HSU))

Hydrogen separation and purification in refineries has been traditionally accomplished by using established technologies such as pressure swing adsorption (PSA), selective permeation processes using polymer membranes, or cryogenic separation process. Each process is based on a different separation principle, so each method differs significantly from each other. Economic aspects and other project considerations such as process flexibility, reliability, and scalability have to be taken into account to decide the hydrogen separation method [23].

Other hydrogen separation technologies include electrochemical hydrogen separation (EHS), which is foreseen as a promising technology to separate hydrogen fuel from a fuel cell anode exhaust stream. However, EHS technology is not currently mature and has not been used in poly-generating applications to date. In any case, the hydrogen-rich stream is treated

and prepared in the hydrogen separation unit (HSU) according to the selected separation/purification technology. For this work, PSA technology has been selected due to its commercial readiness and recent use in poly-generating systems [24].

The HSU configuration depends upon the specific requirements of the hydrogen separation technology and the anode off-gas conditions. PSA technology requires relatively low inlet temperatures and high inlet pressures. Additionally, hydrogen separation with PSA becomes more efficient at high hydrogen partial pressures [23]. Therefore, to extract the hydrogen from the anode off-gas of a HTFC using a PSA, the HSU is required to:

- Decrease the hydrogen-rich stream temperature
- Increase the hydrogen-rich stream pressure
- Increase the hydrogen partial pressure of the hydrogen-rich stream

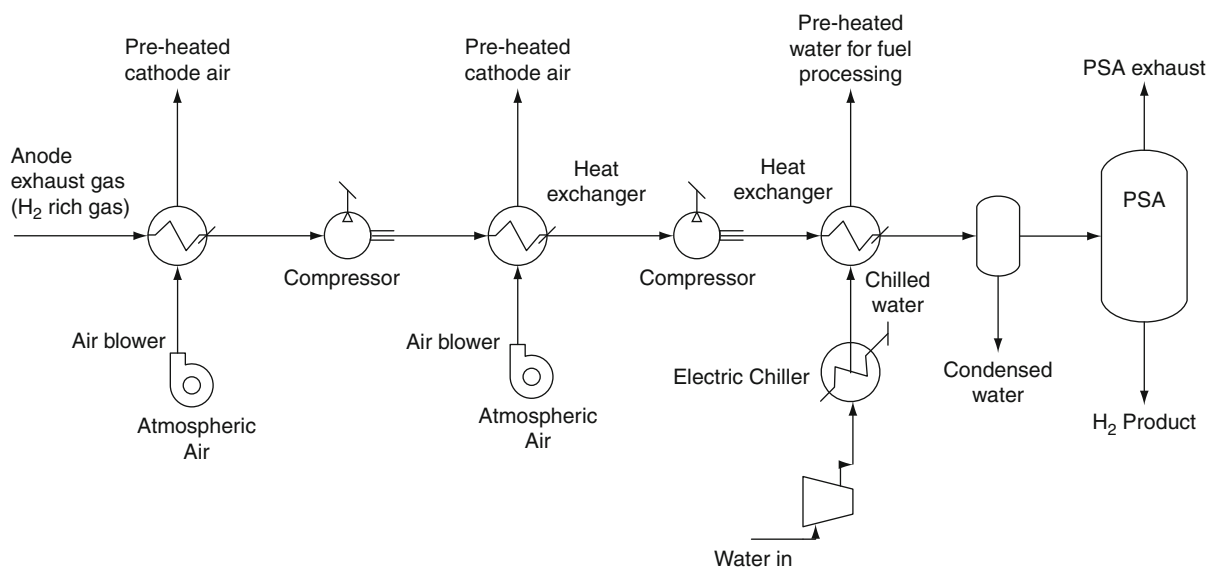
Table 1 shows representative PSA feed gas requirements and the current configuration design points.

A simplified HSU block consisting of a series of heat exchangers and compressors designed to meet the PSA temperature and pressure requirements is shown in Fig. 3.

As shown in Fig. 3, an electric chiller has been placed upstream of the PSA reactor to meet the temperature requirements when ambient air temperature (used as a cold media in the upstream heat exchangers) is too high. The electric chiller represents a small fraction of the total parasitic loads. Interestingly, required PSA inlet temperature is low enough to condense out sufficient water vapor from the gas stream. As shown in Fig. 3, condensed water may be removed upstream of the PSA reactor resulting

Hydrogen Production from High-Temperature Fuel Cells. Table 1 State-of-the-art PSA feed gas requirements

Parameter	State-of-the-art value range	Notes
Absolute pressure (kPa)	303–2,026	Based on the state of the art [25]
Temperature (°C)	4–50	Based on the state of the art [25]



Hydrogen Production from High-Temperature Fuel Cells. Figure 3
Hydrogen separation unit configuration

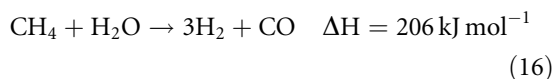
in higher hydrogen partial pressures and facilitating the PSA separation process.

In the internal reformation cases, the air and water that is heated in the HSU represents an opportunity to thermally integrate the HSU with fuel cell balance of plant. This thermal integration strategy is crucial in order to ensure overall thermal balance within the plant, which may be jeopardized at certain operating conditions if hydrogen is separated from the anode off-gas [16].

Integrated Poly-Generating HTFC Cycles According to Fuel Processing

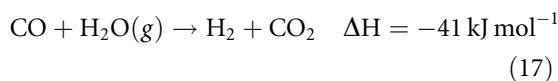
Steam methane reformation (SMR) and water–gas shift (WGS) are the main fuel processing reactions that convert raw fuel (i.e., natural gas) into fuels more amenable to electrochemical oxidation (i.e., hydrogen and carbon monoxide) occurring on the nickel-based anode of HTFC.

Steam methane reforming is an endothermic reaction that consists of the reaction of methane and steam over a supported nickel catalyst to produce a mixture of hydrogen, carbon monoxide, carbon dioxide, and methane. The basic reforming reaction for methane is



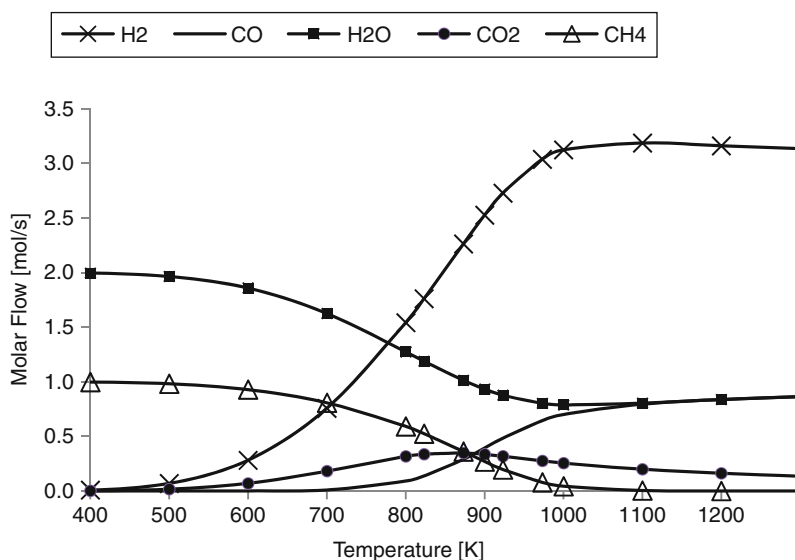
Heat has to be provided to drive the reaction forward to the hydrogen production direction. As shown in Fig. 4, hydrogen concentration under equilibrium conditions is highest between 900 and 1,100 K [17].

The water–gas-shift (WGS) reaction (starting from steam) is slightly exothermic and occurs at the same time as steam reforming [6]. During the shift reaction, additional hydrogen is produced. The basic water–gas-shift reaction for carbon monoxide is



In poly-generating HTFC, if external reformer is used to produce hydrogen, special attention has to be given to the temperature at which heat from the fuel cell stack is transferred to the external reformer. Therefore, it is important to analyze different cycle configurations consisting on different positions of the external reformer within the system.

In the internal reformation cases where additional hydrogen production occurs at the same physical location than fuel cell reactions (i.e., direct internal reformation) or in a location that is thermally connected with the anode (i.e., indirect internal reformation), the temperature at which heat is



Hydrogen Production from High-Temperature Fuel Cells. Figure 4
Equilibrium composition as a function of temperature (steam-to-carbon ratio $S/C = 2$) [17]

transferred to the fuel processing reactions corresponds to the operating stack temperature which is equal to the temperature at which hydrogen production is maximized. This feature constitutes one of the key principles that lead to unprecedented high efficiencies achieved by poly-generating HTFC [8].

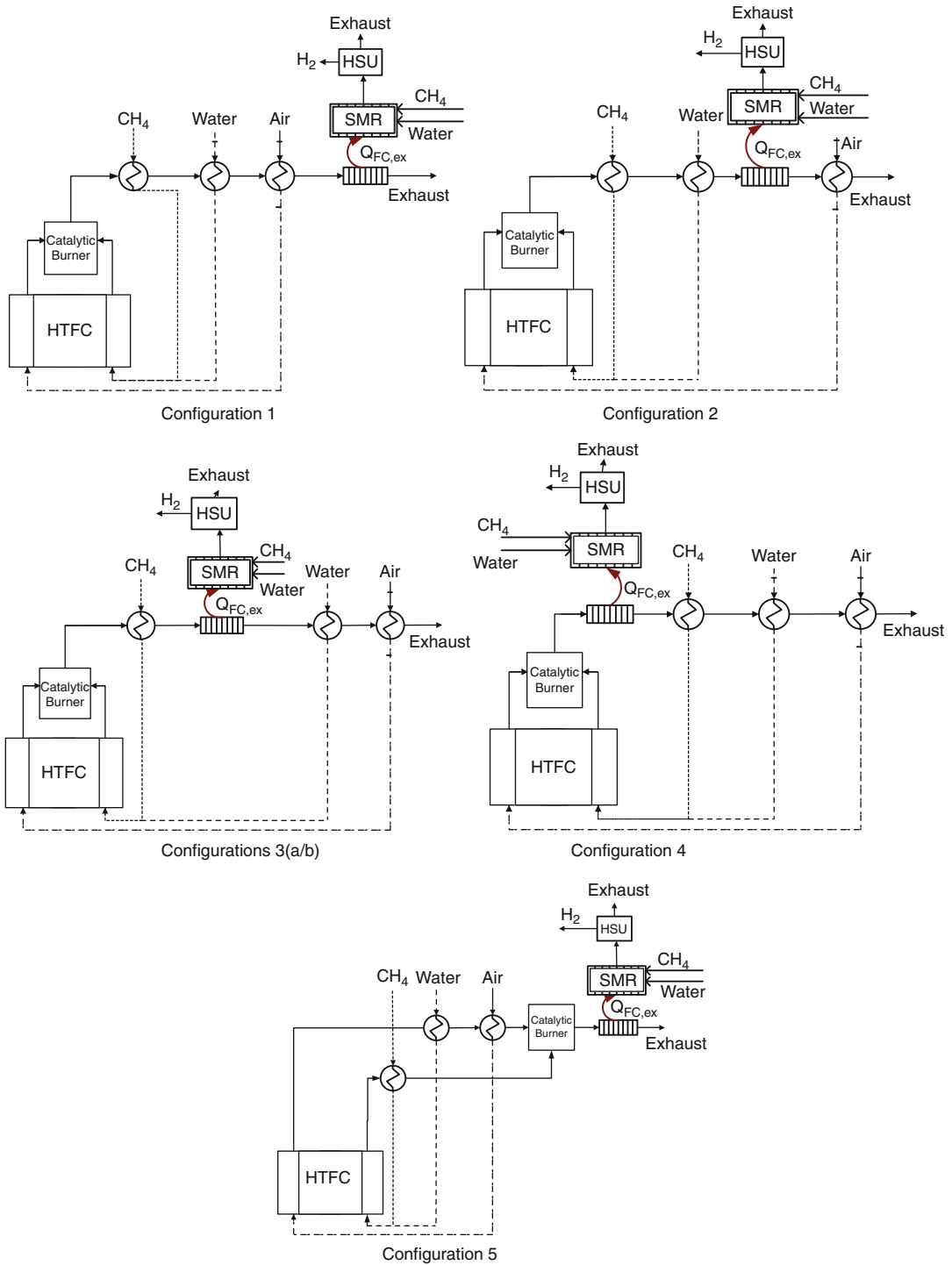
External Reformation Configurations High-temperature fuel cells (HTFC) can be integrated with an external reformer in multiple ways. Based on preliminary designs by Brouwer and Leal [17], Margalef et al. [9] analyzed in detail the external reforming configurations of poly-generating HTFC shown in Fig. 5.

In all cases, steam reformation is driven by the fuel cell exhaust heat in an external reformer, which takes as much heat as possible without compromising the fuel cell operating temperatures. Inlet temperatures of the fuel, steam, and air streams are kept constant at 1,173 K in order to sustain the electrochemical reactions within the stack. Therefore, depending upon the external reformer location, more or less heat is available to produce hydrogen with the external reformer. Note that in all the configurations, a hydrogen separation unit (HSU) block, based on PSA technology, is placed downstream of the reformer to separate and purify the hydrogen stream from the reformat gas.

Internal Reformation Configurations Internal reforming promotes hydrogen production within the fuel cell stack and provides cooling to the fuel cell stack due to its endothermic nature. Generally, fuel cell systems do not electrochemically consume all the fuel that is supplied (a fundamental limitation for all fuel cells) and they produce enough heat to reform much more fuel than the amount they consume. Remaining fuel exiting the anode presents a unique opportunity for low-cost hydrogen [17].

Margalef et al. [16] analyzed in detailed one internal reformation SOFC configuration at 80% and 60% fuel utilization (U_F). Figure 6 shows the schematic of this configuration. As shown, the HSU block is placed at the anode gas exit upstream the catalytic oxidizer.

Representative Performance Characteristics Modeling capabilities developed at the National Fuel Cell Research Center (NFCRC) of the University of California, Irvine have been used to evaluate the fuel cell performance and the hydrogen production capabilities of the presented poly-generating HTFC configurations. The complete model consists of an SOFC stack; heat exchangers to preheat the fuel, water, and air; an external SMR reactor placed in different locations for each of the different configurations; an adiabatic catalytic combustor that captures

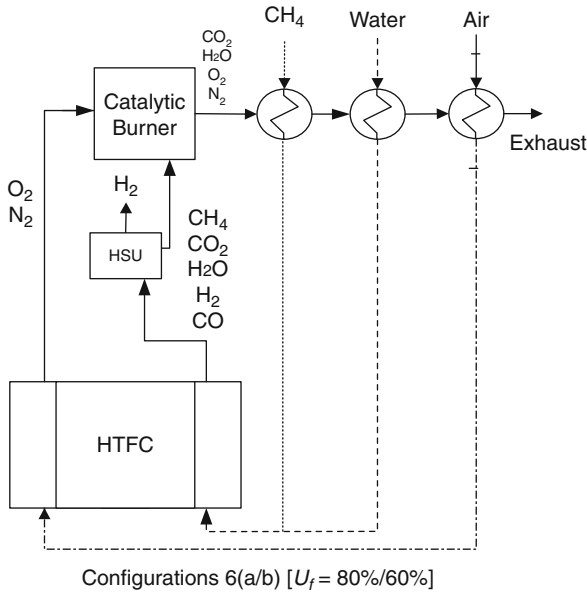


Hydrogen Production from High-Temperature Fuel Cells. Figure 5
 Poly-generating HTFC configurations based upon external reformation

the thermal energy of the unused fuel downstream of the stack; and an HSU block based on PSA technology.

Each configuration has been analyzed following the same approach. For the external reformation cases (Conf. 1–5), stack input temperatures of the fuel, air, and steam have been fixed at 1,173 K whereas the amount of reformed methane varies depending upon

how much heat is available after preheating all the input streams. Pinch analyses for each heat exchanger have been performed in order to avoid temperature crossovers within the heat exchangers. Similarly, for the internal reformation cases (Conf. 6a/6b), the amount of hydrogen extracted in the HSU block depends upon how much thermal energy has to be extracted from the anode off-gas in order to preheat the input streams to the specified temperatures [9].



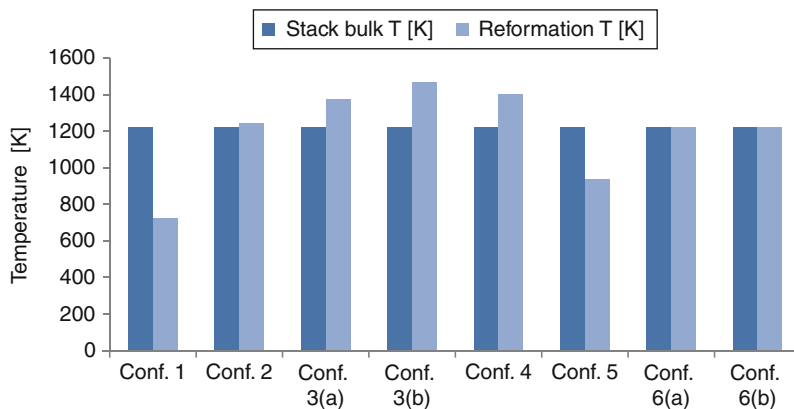
Hydrogen Production from High-Temperature Fuel Cells. Figure 6
Poly-generating HTFC based upon internal reformation

Bulk Stack and External Reformer Temperatures

For the external reformation cases, the heat available to produce hydrogen without compromising the thermal balance of the fuel cell determines how much methane will be taken by the external reformer. However, the hydrogen yield will be a function of the temperature at which the reformation takes places. As shown in Fig. 4, hydrogen yield peaks between 900 and 1,000 K and it flattens out after this point. Therefore, the external reformer should operate in this temperature range in order to maximize the hydrogen production.

Figure 7 shows both fuel cell stack and external reforming temperatures for all the configurations.

As expected, stack temperatures are the same for all cases since inlet stream temperatures have been fixed to a certain value. Importantly, in configurations 6a and 6b, stack and reformation temperatures are equal due to the fact that hydrogen is produced by internal reforming.



Hydrogen Production from High-Temperature Fuel Cells. Figure 7
Stack and reformer temperatures

Configuration 1 presents the lowest reformation temperature. This makes sense since the external reformer is placed downstream of all the heat exchangers where exhaust gas temperatures are lowest. Configuration 3b achieves the highest reformation temperature among the configurations. This configuration is the only external reforming configuration where the fuel utilization factor has been lowered to 60%. Therefore, more hydrogen will be oxidized in the catalytic combustor raising the exhaust gas temperature considerably. The rest of the configurations present similar reformation temperature values, all of them in range where hydrogen yield is high.

Hydrogen Production Rate Figure 8 shows the amount of hydrogen produced with each configuration. As observed, there is a significant difference between the hydrogen produced with the external reforming configurations and the amount of hydrogen produced with the internal reformation configurations.

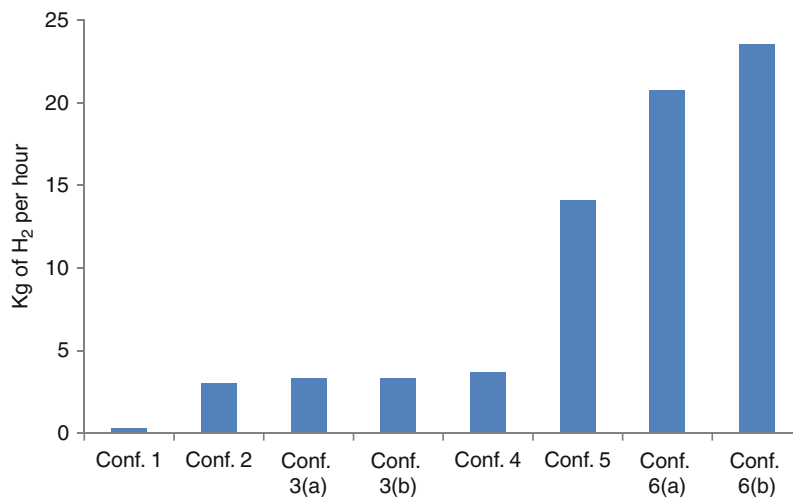
The amount of hydrogen produced with configuration 1 is low. As shown in Fig. 7, the temperature at which reformation occurs in configuration 1 is 724 K, at which temperature hydrogen yield under equilibrium conditions is very small.

Figure 7 shows that in configurations 2, 3a, 3b, and 4, external reforming occurs at temperatures at which

hydrogen yield is high. However, the amount of hydrogen produced is not comparable to the internal reformation cases or configuration 5. As mentioned previously, hydrogen production is a function of the temperature at which the reformation occurs but is also a function of the amount of transferred heat from the exhaust gas stream to the external reformer. Although in configurations 2, 3, and 4, steam reforming occurs at relatively elevated temperatures, the heat that can be transferred from the fuel cell exhaust to the reformer without compromising the fuel cell thermal balance is not enough to reform large amounts of methane. As a result, the amount of hydrogen that can be produced with these configurations is not large.

Configuration 5 presents higher hydrogen production than the other external reforming configurations. In this case, since the external reformer is placed after the catalytic combustor, the temperature at which the reformation occurs is high enough to achieve significant hydrogen yields. Importantly, since there is no preheater downstream of the reformer, more heat can be extracted from the fuel cell exhaust stream without affecting any fuel cell stream input temperatures.

Finally, configurations 6a and 6b achieve the highest hydrogen production. This is due to the fact that the reformation takes place within the SOFC stack, which operates within the range of temperatures



Hydrogen Production from High-Temperature Fuel Cells. Figure 8
Hydrogen production after PSA

at which hydrogen yield is high. Additionally, the reformation reactions and the fuel cell reactions occur in the same physical space. Therefore, heat from the source (i.e., exothermic fuel cell reactions) to the sink (i.e., endothermic reformation reactions) is directly transferred without the need of a heat exchanger. Thus, more heat can be captured resulting in higher hydrogen yields. The total hydrogen production for each configuration is shown in Fig. 8.

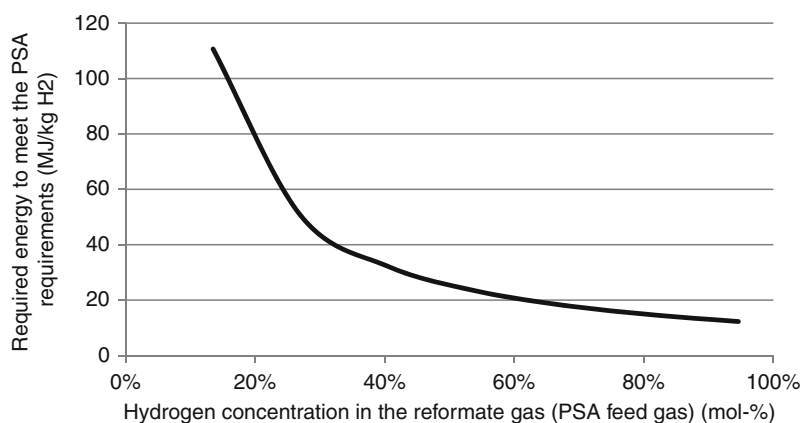
Parasitic Loads Associated with the Hydrogen Separation Unit Energy required to separate the hydrogen from the reformat stream varies in each configuration. The HSU is required to increase the pressure and drop the temperature of the reformat gas in order to meet the PSA requirements. This process requires energy and as a result, decreases the overall efficiency of the poly-generating plant. Margalef et al. [9] estimated the amount of energy required to separate 1 kg of hydrogen with the HSU design presented in Fig. 3. The HSU model consists of a series of heat exchangers and compressors that decrease the temperature and increase the pressure of the reformat gas to the design point levels, accordingly, for each configuration. Figure 9 shows the energy per kilogram of hydrogen required for the preparation of the reformat gas to meet the PSA requirements, as a function of the molar concentration of hydrogen.

As seen, the energy required to separate 1 kg of hydrogen from the reformat stream does not

decrease linearly with the hydrogen molar concentration and depends upon the hydrogen concentration in the anode off-gas. This is due to the fact that for lower hydrogen concentrations, relatively more gas has to be cooled and compressed to produce the same amount of hydrogen. Therefore, the amount of energy required to separate 1 kg of hydrogen with PSA technology is lower when the hydrogen concentration of the feed gas is high [9]. Figure 10 shows the molar hydrogen concentrations of the PSA feed gas for each configuration.

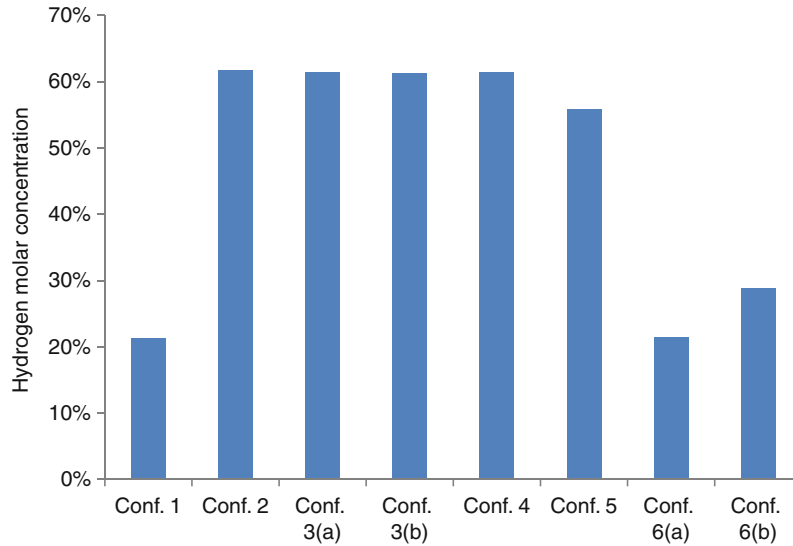
For all of the external reformation configurations except for configuration 1, hydrogen concentrations remain around 60%. Although the heat available to produce hydrogen in configuration 1 is comparable to the rest of the configurations, the temperature at which the reformation occurs is not high enough to achieve significant methane conversion. Similarly, configurations 6a and 6b present low hydrogen concentrations compared to the rest of the configurations. This makes sense since the produced hydrogen is mixed with the anode off-gas products which include all the carbon dioxide and steam products from the stack reactions, including internal reforming and electrochemical reactions. As a result, the hydrogen concentration of the reformat gas for the internal reformation cases is relative low when compared with the external reformation configurations.

Figure 11 shows the energy required to separate 1 kg of hydrogen with each configuration. As shown, higher



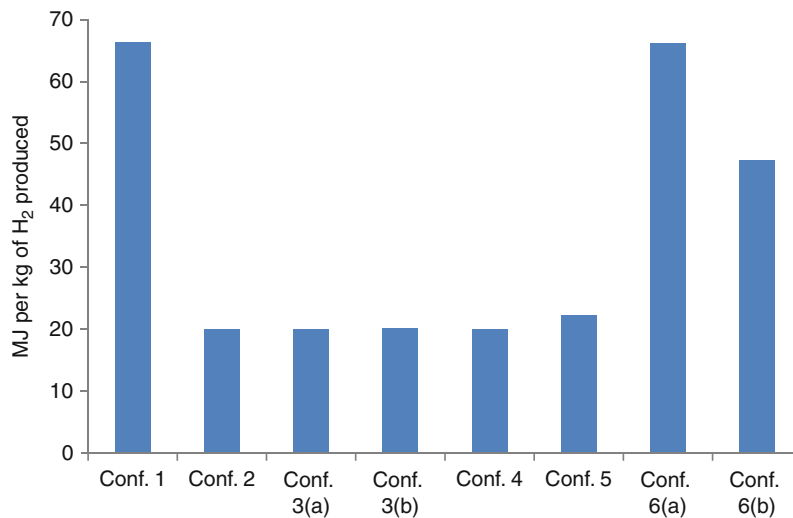
Hydrogen Production from High-Temperature Fuel Cells. Figure 9

Specific energy required for the PSA process



Hydrogen Production from High-Temperature Fuel Cells. Figure 10

Hydrogen concentration in the PSA feed gas



Hydrogen Production from High-Temperature Fuel Cells. Figure 11

Parasitic load required to separate 1 kg of H₂ at the HSU

hydrogen concentration streams require less energy to separate the hydrogen from the reformat gas.

Comparative Efficiency Analyses

Because a poly-generating HTFC simultaneously produces electricity, hydrogen, and useful thermal energy, efficiencies can be measured and expressed in a number

of different ways. Margalef et al. developed three different methods to appropriately calculate the overall and coproduct production efficiencies [8]. Table 2 shows the developed equations for each method. The methods have been labeled as: (1) *State-of-the-art Method*; (2) *Ideal Poly-generation Method*, and (3) *Supplemental Input Method*.

Hydrogen Production from High-Temperature Fuel Cells. Table 2 Efficiency equations for (1) state-of-the-art method, (2) ideal poly-generation method, and (3) supplemental input method [8]

	Electrical efficiency	Thermal efficiency	Hydrogen efficiency	Total mixed efficiency
1	$\frac{P_{net}}{E_{tot} - \frac{Q_{net}}{\eta_{boiler}} - \frac{H_2}{\eta_{SMR}}}$	$\frac{Q_{net}}{E_{tot} - \frac{P_{net}}{\eta_{CC}} - \frac{H_2}{\eta_{SMR}}}$	$\frac{H_2}{E_{tot} - \frac{P_{net}}{\eta_{CC}} - \frac{Q_{net}}{\eta_{boiler}}}$	$\frac{P_{net} + Q_{net} + H_2}{E_{tot}}$
2	$\frac{P_{net}}{E_{tot} + Q_{net} + H_2}$	$\frac{Q_{net}}{E_{tot} + P_{net} - H_2}$	$\frac{P_{PSA}}{E_{tot} - P_{net} - Q_{net}}$	$\frac{P_{net} + Q_{net} + H_2}{E_{tot}}$
3	External reforming	$\frac{Q_{net}}{Q_{net}} = \eta_{boiler}$ η_{boiler}	$\frac{H_2}{F_{H_2} + \frac{P_{PSA}}{\eta_{CC}}}$	$\frac{P_{net} + Q_{net} + H_2}{E_{tot}}$
	Internal Reforming.		$\frac{H_2}{(U_f - U_{f,H_2ES})E_{tot} + \frac{P_{PSA}}{\eta_{CC}}}$	
	$\frac{P_{net}}{E_{tot} - \frac{Q_{e^-}}{\eta_{boiler}} - \left(F_{H_2} + \frac{P_{PSA}}{\eta_{CC}} \right)}$			
	$\frac{P_{net}}{E_{tot} - \frac{Q_{e^-}}{\eta_{boiler}} - \left((U_f - U_{f,H_2ES})E_{tot} + \frac{P_{PSA}}{\eta_{CC}} \right)}$			

Hydrogen Production from High-Temperature Fuel Cells. Table 3 Efficiency results obtained with the Supplemental Input Method (LHV)

Configuration	1	2	3a	3b	4	5	6a	6b
Electrical efficiency	53.4%	53.3%	53.3%	46.9%	53.3%	52.8%	50.0%	58.4%
Hydrogen efficiency	18.0%	73.5%	73.2%	68.2%	73.2%	62.1%	90.7%	83.5%
Overall efficiency	52.3%	54.7%	54.8%	48.5%	55.0%	55.7%	70.0%	69.5%

These methods are based upon different and reasonable assumptions for the allocation of input energy to each of the coproducts. It should be clear that there is not a unique or superior method for calculating poly-generation efficiencies so that each of the methodologies proposed can be used in comparative analyses if based upon accurate assumptions. For the current specific analyses, the *Supplemental Input Method* is used to estimate the overall electrical and hydrogen production efficiencies for each configuration. Thermal efficiency has not been calculated since it depends upon the thermal requirements of each specific application and there may be cases when thermal energy is not required. Results are presented in Table 3.

The efficiency results shown in Table 3 correspond to the Supplemental Input Method [8] and do not include the heat products shown in the equations presented in Table 2. With this method, electrical

efficiency is the net power output P_{net} divided by the energy flow allocated exclusively for the electricity production, which corresponds to the total energy flow in E_{tot} minus the energy flow that has been specifically used to produce hydrogen product. The energy flow used to produce hydrogen product includes feedstock energy (i.e., additional fuel) as well as the necessary fuel to generate the electricity required for the hydrogen separation as if it was produced with a state-of-the-art combined cycle plant. The lowest electrical efficiency value corresponds to configuration 3b. In this case, hydrogen is produced externally and the fuel cell is operating at 60% utilization factor. As expected, the electrical efficiency is low since more fuel is used without obtaining any additional energy flow output (i.e., hydrogen fuel). On the other hand, the highest electrical efficiency value corresponds to configuration 6b, in which hydrogen is produced internally and the fuel cell is operated at 60% utilization factor.

Due to the synergies associated with higher voltages at lower fuel utilizations, electrical efficiency is significantly higher than the rest of the configurations. Nevertheless, one must recall the discussion associated with the key principles above that this analysis confirms that these synergies are only captured if hydrogen is separated from the anode off-gas. Otherwise, more fuel is being used to obtain the same mix of energy outputs. The rest of configurations present similar electrical efficiencies.

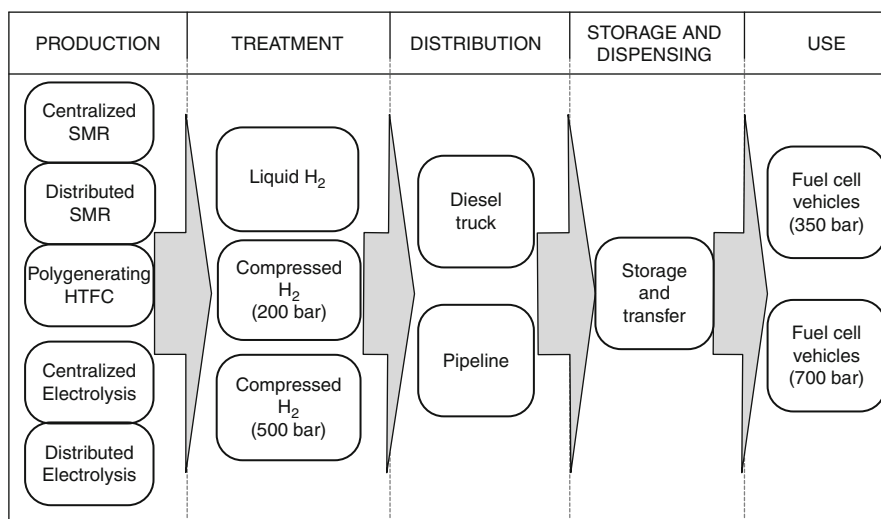
With the Supplemental Input Method, hydrogen efficiency is calculated in a similar way as specified in Table 2. The chemical power output of the hydrogen produced, H_2 , is divided by the energy flow input specifically allocated to produce hydrogen. Once again, it corresponds to the feedstock energy (i.e., additional fuel) as well as the necessary fuel to generate the electricity required for the hydrogen separation as if it was produced with a state-of-the-art combined cycle plant. As seen in Table 3, the highest values correspond to the internal reformation cases. Interestingly, although the parasitic load per kilogram of hydrogen produced is higher in configuration 6a than in configuration 6b (see Fig. 11), hydrogen production efficiency is greater in the former case due to the fact that when hydrogen is produced at 80% utilization factor,

the additional fuel feedstock allocated to produce hydrogen is equal to zero.

Finally, overall efficiency values are similar in all the external reformation cases, even for configuration 1 where the hydrogen output is almost negligible. This indicates that the hydrogen production does not affect the overall performance when the amount of hydrogen is relatively small (i.e., external reformation cases). As expected, both internal reformation cases achieve the highest overall fuel-to-product efficiency values.

Hydrogen Transport Impacts on Comparative Analyses

Today, most hydrogen is produced from natural gas in large steam-methane reformation (SMR) plants in a centralized fashion. To produce hydrogen at large scale in a centralized plant is more efficient than producing hydrogen at small scale [26]. Stephens-Romero et al. [20] define production, treatment, distribution, storage, and dispensing as the main steps of a well-to-tank hydrogen supply chain. Each step can be accomplished with a variety of different technologies. Figure 12 shows the main steps of a generic hydrogen supply chain from well to tank with the most widely used technologies.



Hydrogen Production from High-Temperature Fuel Cells. Figure 12

Steps in well-to-tank efficiency analysis of H_2

One of the main benefits of producing hydrogen in a distributed manner versus centralized manner is the elimination of the fuel transport and delivery steps (fuel distribution) which can be energy intensive. Furthermore, if hydrogen is produced on demand as in poly-generating HTFC, hydrogen storage may be considerably reduced compared with the distributed reformer case.

Comparative Analysis of Ten Different Hydrogen Supply Chains

To evaluate the benefits of producing hydrogen in a distributed fashion versus centralized production, different hydrogen supply chains with different technologies for each step are analyzed from an energy perspective, resulting in ten different cases. Details of each supply chain are provided in Table 4. As shown, two different final uses corresponding to the two available fuel cell vehicle tank pressures (i.e., 350 bar and 700 bar) [27]

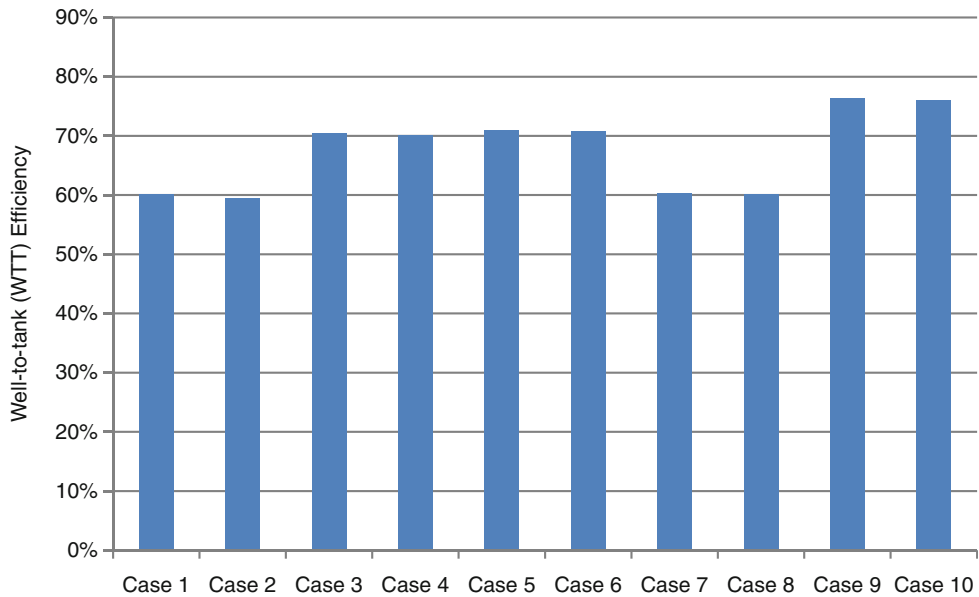
are evaluated. In addition, when hydrogen is produced in a centralized SMR plant, the three available treatment methodologies are investigated. As a result, ten different supply chains have been evaluated.

After evaluating the energy required for each step from *production* to *dispensing* of hydrogen, well-to-tank (WTT) efficiencies of the ten different hydrogen supply-chain scenarios were calculated. Figure 13 shows the main results obtained from the analyses.

As shown, the lowest WTT efficiency values are observed for the distributed steam- methane reformation (SMR) cases whereas the highest values correspond to poly-generating HTFC. As expected, due to the significant energy penalties associated with liquefaction processes, WTT efficiencies of centralized SMR with liquid hydrogen transportation are almost as low as the distributed SMR cases. Importantly, the production step includes the energy content of the fuel feedstock. The WTT efficiency values have

Hydrogen Production from High-Temperature Fuel Cells. Table 4 Definition of the ten unique hydrogen supply chain cases

Case	Production	Treatment	Distribution	Storage	Dispensing
1	Centralized SMR	Liquid H ₂	Diesel truck (100 km)	Liquid H ₂	Use = 350 bar (Transfer = 7 bar to 400 bar)
2	Centralized SMR	Liquid H ₂	Diesel truck (100 km)	Liquid H ₂	Use = 700 bar (Transfer = 7 bar to 800 bar)
3	Centralized SMR	Compressed H ₂ (200 bar)	Diesel truck (100 km)	Compressed H ₂ (200 bar)	Use = 350 bar (Transfer = 200 bar to 400 bar)
4	Centralized SMR	Compressed H ₂ (200 bar)	Diesel truck (100 km)	Compressed H ₂ (200 bar)	Use = 700 bar (Transfer = 200 bar to 800 bar)
5	Centralized SMR	Compressed H ₂ (500 bar)	Diesel truck (100 km)	Compressed H ₂ (500 bar)	Use = 350 bar (Transfer = 500 bar to 400 bar)
6	Centralized SMR	Compressed H ₂ (500 bar)	Diesel truck (100 km)	Compressed H ₂ (500 bar)	Use = 700 bar (Transfer = 500 bar to 800 bar)
7	Distributed SMR	Compressed H ₂ (500 bar)	n/a (0 km)	Compressed H ₂ (500 bar)	Use = 350 bar (Transfer = 500 bar to 500 bar)
8	Distributed SMR	Compressed H ₂ (500 bar)	n/a (0 km)	Compressed H ₂ (500 bar)	Use = 700 bar (Transfer = 500 bar to 800 bar)
9	Poly-generating HTFC	Compressed H ₂ (500 bar)	n/a (0 km)	Compressed H ₂ (500 bar)	Use = 350 bar (Transfer = 500 bar to 500 bar)
10	Poly-generating HTFC	Compressed H ₂ (500 bar)	(0 km)	Compressed H ₂ (500 bar)	Use = 700 bar (Transfer = 500 bar to 800 bar)



Hydrogen Production from High-Temperature Fuel Cells. Figure 13

Well-to-tank efficiencies of the evaluated supply-chains

been obtained by dividing the energy content of 1 kg of hydrogen (on a LHV basis) by the total energy required from WTT corresponding to each case.

From these energy-based comparative analyses, it is concluded that, of all the analyzed cases, poly-generating HTFC provide the most efficient way to produce and deliver hydrogen.

Discussion of Scientific Basis for Observed Performance

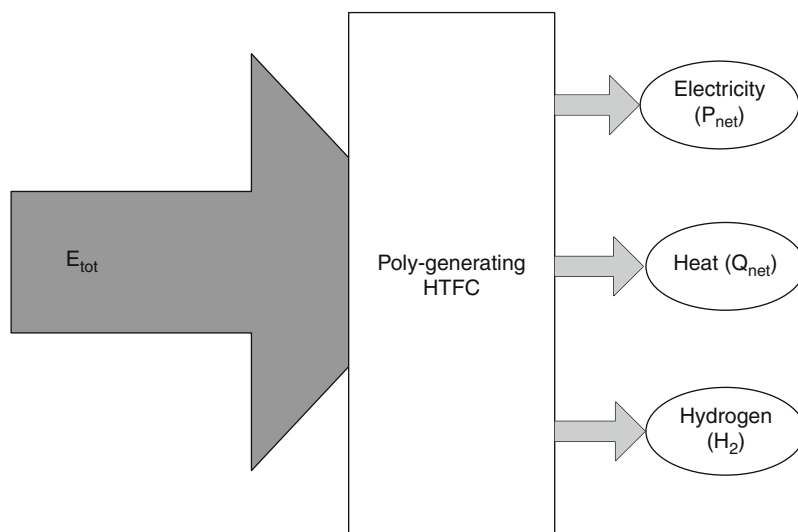
High-temperature fuel cells (HTFC) operate at high enough temperature and produce enough heat and water from the electrochemical reactions to provide heat to the internal fuel processing reactions (i.e., internal reformation). Importantly, the overall heat generated by the fuel cell reactions is typically greater than the heat consumed by the endothermic fuel processing reactions occurring within the fuel cell stack [6]. Surplus heat is partially used to preheat the fuel and oxidant streams before they enter the fuel cell and to produce the steam required for system operations. Therefore, more hydrocarbon fuel than that required for the electricity generation could be processed in an HTFC, creating a hydrogen-rich stream that could be subsequently

purified and delivered to the point of use without the need of an external reformer. This represents the main concept that defines and allows the production of hydrogen in addition to electricity and heat with an HTFC. Such systems have been identified as poly-generating HTFC or tri-generation systems (Fig. 14).

Poly-generation systems can produce and deliver hydrogen fuel with lower marginal costs, fuel use, and emissions than conventional hydrogen production and delivery methods [28]. Since hydrogen is produced in a distributed generation fashion there is no energy or emissions penalty associated with the transport and delivery of the hydrogen to its point of use. Recent studies performed at the National Fuel Cell Research Center (NFCRC) of the University of California Irvine demonstrate that less energy is needed to transport and deliver hydrogen to vehicles compared with distributed and centralized steam methane reforming (SMR) resulting in higher well-to-tank (WTT) efficiencies [16].

Definition and Quantification of the Synergies Associated with Poly-Generating HTFC

Among the main benefits associated with the production of hydrogen with HTFC, there are synergistic



Hydrogen Production from High-Temperature Fuel Cells. Figure 14

Inputs and outputs of a poly-generating HTFC

effects intimately related with operating the fuel cell at low fuel utilization factors:

1. Synergistic impact of lower fuel utilization leads to higher cell voltages which result in:
 - (a) Higher electrochemical efficiencies
 - (b) Less electrochemical heat generated per mol of input fuel
2. Synergistic impact of lower fuel utilization increases the heat sink associated with the endothermic SMR reaction (i.e., internal fuel processing), reducing excess air requirements for cooling.

Synergies 1(b) and 2 reduce the excess air requirements for the stack cooling. Consequently, lower cooling requirements will lower the parasitic loads from the cathodic air blowers, increasing the net power of the system and the overall system efficiency. In this section, more details about each of the identified synergies are provided.

Synergistic Impact of Lower Fuel Utilization Leads to Higher Electrochemical Efficiencies Ideal reversible voltage (E_0) drops as soon as current is being produced due to the changes in product and reactant concentrations. Importantly, reactants and products concentrations along the electrode channels vary at different utilization factors. Therefore, operating the fuel cell at different fuel utilizations may affect the cell

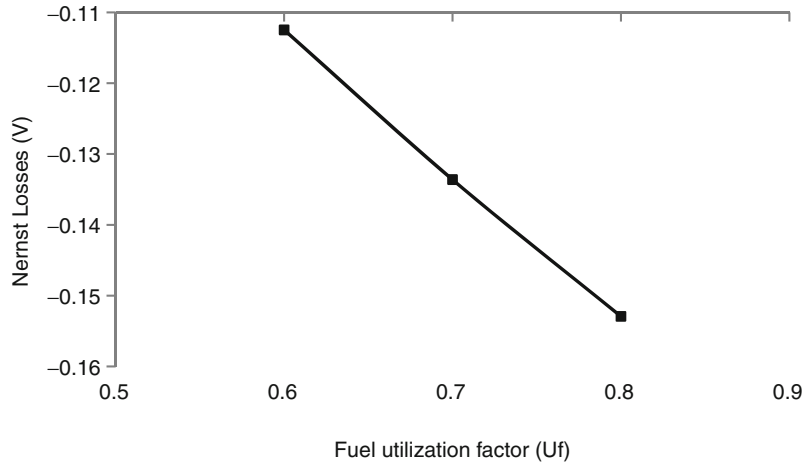
voltage. The voltage reduction caused by the change of species concentrations is known as *Nernstian losses* (η_{Nernst}), which added to the reversible voltage E_0 , results on the Nernst Voltage (V_{Nernst}).

$$V_{\text{Nernst}} = E_0 + \eta_{\text{Nernst}} = E_0 + \frac{RT}{2F} \ln(x_{\text{H}_2} x_{\text{O}_2}^{\frac{1}{2}}) / x_{\text{H}_2\text{O}} \quad (18)$$

Figure 15 shows the Nernstian losses (η_{Nernst}) as a function of the utilization factor obtained with the poly-generating SOFC modeling efforts by Li and Margalef [16, 30].

As shown in Fig. 15, voltage drop related with the Nernstian losses decreases at lower fuel utilizations. This effect represents in fact one of the synergies associated with poly-generating fuel cells, which typically operate at lower fuel utilizations than stand-alone fuel cells (i.e., electricity and heat production only).

To quantify this synergy, the system can be analyzed at two different fuel utilizations. The first value corresponds to the typical utilization factor of a stand-alone SOFC (e.g., $U_f = 0.9$) whereas the second value corresponds to the typical utilization factor of a poly-generating SOFC (e.g., $U_f = 0.6$). The difference in Nernst losses (V_{Nernst}) between both operating points represents the voltage gain of operating the fuel cell at lower fuel utilizations and quantifies this synergistic effect. Approximately, a gain of 0.06 V in the



Hydrogen Production from High-Temperature Fuel Cells. Figure 15

Nernst losses (η_{Nernst}) versus the fuel utilization factor

Nernst voltage has been observed by operating the fuel cell at typical utilization factor used in poly-generating fuel cells ($U_f = 0.6$ compared to $U_f = 0.9$).

Additionally, the utilization factor affects the fuel cell performance through reaction kinetics since they also depend upon the reactant and product concentrations at the reaction sites [22]. The voltage drop associated with the reaction kinetics at different fuel utilizations is known as *reaction loss* ($\eta_{\text{rxn rate}}$). However, previous analyses performed by Margalef et al. [16] show that reaction losses represent a small fraction of the total voltage drop related with the concentration changes associated with different fuel utilizations. Therefore, the overall effects of operating the fuel cell at lower fuel utilizations on the cell voltage can be defined as

$$\Delta V_{\text{cell,conc}} = \Delta V_{\text{cell,Nernstian}} + \Delta V_{\text{cell,rxn rate}} \sim \Delta V_{\text{cell,Nernstian}} \quad (19)$$

If all the energy from the hydrogen fuel were transformed into electrical energy, the cell voltage would correspond to the maximum voltage v_{max} . The maximum voltage would be given by

$$V_{\text{max}} = \frac{-\Delta \bar{g}_f}{n_i F} = 0.97 \text{ V if using the LHV} \quad (20)$$

where $\Delta \bar{g}_f$ is the Gibbs free energy at 900°C, n_i is the number of electrons transferred during the

electrochemical oxidation of fuel species i ($n_i = 2$ for H_2 and CO , $n_i = 8$ for CH_4), and F is the Faraday's constant. This voltage would be obtained from a 100% efficient system [6]. Therefore, the actual efficiency of the cell (or electrochemical efficiency) is the actual voltage divided by the maximum voltage, or

$$\eta_{\text{cell}} = \frac{V_{\text{cell}}}{V_{\text{max}}} = \frac{V_{\text{cell}}}{0.97} \text{ if using the LHV} \quad (21)$$

Therefore, the electrochemical efficiency gain associated with lower utilization factors can be written as

$$\Delta \eta_{\text{cell}} = \frac{\Delta V_{\text{cell,conc}}}{V_{\text{max}}} = \frac{0.06}{0.97} \times 100 = 6.2\% \text{ if using the LHV} \quad (22)$$

This result demonstrates and quantifies the first synergy associated with generating hydrogen with HTFC. As seen, by lowering the utilization factor at typical values of poly-generating SOFC, the electrochemical efficiency increases by 6.2%.

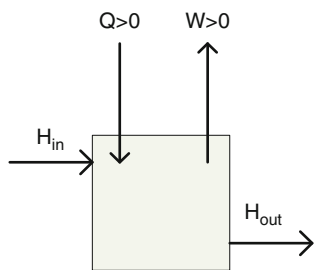
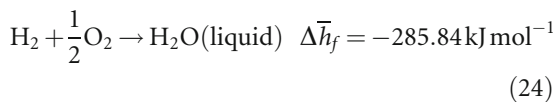
A more philosophical approach to explain the cell voltage drop as the fuel utilization factor increases is related to the mixing of products with reactants to dilute electrochemically active species concentrations. Water product mixes with the anode gas as it is formed throughout the electrochemical reactions. Note that mixing of products with reactants can occur in either the anode (e.g., MCFC, SOFC) or cathode (e.g., PEMFC, PAFC) compartments. The concentration of water product in the anode increases

as the fuel utilization factor increases. Mixing processes are irreversible so they produce entropy. As a result, a completely reversible SOFC operation would be only approached as $U_f \rightarrow 0$. In other words, irreversibilities increase as the utilization factor increases. Consequently, one wants to operate a fuel cell at the lowest possible utilization factor in order to reduce the mixing irreversibilities. However, there is a compromise between the cell efficiency and the fuel utilization efficiency that counterbalances this consideration with a desire for high utilization to achieve high overall system electrical efficiency.

Synergistic Impact of Lower Fuel Utilization Increases the Heat Sink Associated with the Endothermic SMR Reaction, Reducing Excess Air Requirements for Cooling A high-temperature fuel cell (HTFC) is an electrochemical device that converts chemical energy of a fuel and oxidant directly to electricity. Fuel cell electrochemical reactions are exothermic, thus electrochemical heat is produced. In addition, during the operation of an HTFC, ohmic resistance across the electrodes and bipolar plates generates heat. The specific electrochemical heat released q_{FC} can be calculated applying the first law of thermodynamics, according to Eq. 23. Sign convention for this analysis is specified in Fig. 16:

$$\Delta \bar{h}_f = q_{FC} - w_{FC} \quad (23)$$

where $\Delta \bar{h}_f$ is the enthalpy of combustion of hydrogen corresponding to the reaction



Hydrogen Production from High-Temperature Fuel Cells. Figure 16
Sign convention

and w_{FC} is the electric work produced by the fuel cell, given by the Eq. 23

$$w_{FC} = n_e F V_{\text{cell}} \quad (25)$$

where V_{cell} is the operational cell voltage, n_e is the number of electrons transferred during the electrochemical reactions (i.e., $n_e = 2$ for hydrogen), and F is the Faraday's constant. Combining Eq. 23 and Eq. 25, the specific heat generated during a real fuel cell operation can be calculated as follows:

$$q_{FC} = \Delta \bar{h}_f + w_{FC} = \Delta \bar{h}_f + n_e F V_{\text{cell}} \left[\frac{\text{kJ}}{\text{mol H}_2} \right] \quad (26)$$

In a real fuel cell, although part of the heat is exchanged and used in several ways, including fuel processing and air preheating, excess air is usually required to prevent overheating [29]. Assuming that the fuel processing consists of steam reformation (SMR) and water-gas shift (WGS), the total specific heat absorbed by the fuel processing reactions q_{FP} including the steam production is

$$\begin{aligned} q_{FP} &= \Delta \bar{h}_{SMR} + \Delta \bar{h}_{WGS} + 2 \times \Delta \bar{h}_{vap} \\ &= 206.1 - 41.2 + 2 \times 44.1 = 253.1 \left[\frac{\text{kJ}}{\text{mol CH}_4} \right] \end{aligned} \quad (27)$$

where $\Delta \bar{h}_{SMR}$ is the enthalpy of steam reforming reaction, $\Delta \bar{h}_{WGS}$ is the enthalpy of water-gas-shift reaction, and $\Delta \bar{h}_{vap}$ is the enthalpy of vaporization of water. Therefore, remaining heat that has to be transferred to the excess air for cooling purposes q_{cool} is the difference between the heat liberated during the fuel cell reactions q_{FC} and the heat absorbed by the fuel processing reactions q_{FP} :

$$q_{cool} = m \cdot q_{FC} + q_{FP} \left[\frac{\text{kJ}}{\text{mol CH}_4} \right] \quad (28)$$

where m is the number of moles of hydrogen produced during the fuel processing reactions. For this specific case, the overall fuel processing reaction includes SMR and WGS, and is given by Eq. 29.



Therefore, m is equal to 4. Combining Eqs. 27–29, the specific cooling required can be written as

$$q_{\text{cool}} = 4(\Delta\bar{h}_f + n_e F V_{\text{cell}}) + q_{FP} \left[\frac{\text{kJ}}{\text{mol of CH}_4} \right] \quad (30)$$

As expected, more electrochemical heat is liberated per mole of hydrogen q_{FC} at higher fuel utilizations. Consequently, by operating the fuel cell at lower utilization factors reduces the fuel cell cooling requirements per mole of input fuel, due to the higher cell voltages that result in less electrochemical heat generated. Lower cooling requirements mean lower parasitic loads from the air blowers, increasing the net power of the system and the overall system efficiency.

World's First Poly-Generating HTFC System

The world's first installation to poly-generate electricity and hydrogen with high-temperature fuel cells (i.e., a molten carbonate fuel cell) has been installed at the Orange County Sanitation District (OCSD) in Fountain Valley, California [24]. The system that has been installed at OCSD is the world's first hydrogen coproduction system installed at a customer site. In addition, it has begun to produce electricity, heat, and hydrogen from renewable digester gas fuel. The prime contractor in the effort is Air Products and Chemicals, Inc., who is working with FuelCell Energy and the National Fuel Cell Research Center and OCSD on the project. The main funding agencies are the US Department of Energy, California Air Resources Board, and the South Coast Air Quality Management District.

This important installation of a prototype poly-generating HTFC operating on digester gas at OCSD will provide important data and experience that will benefit the advancement of the poly-generation concept. The installation itself and measured performance characteristics may also identify important areas for research, development, improvement, and application of the concept.

Future Directions

Recommendations for future research work on poly-generating HTFC development include the development of a detailed dimensional and dynamic SOFC model that is required to solve the complicated internal temperature and species concentration profiles that are not resolved by nondimensional models.

Thermodynamic and nondimensional SOFC insights are nonetheless useful for system design and comparative analyses. In addition, the overall system performance obtained by these models generally sets the ideal system performance target. However, since the outlet flow temperatures do not necessarily represent the maximum temperatures in the SOFC, and peak temperatures often occur internal to the stack, a dimensional SOFC model and/or internal temperature measurements could be used to determine if the SOFC working voltage is achievable and practical.

All the analyses performed in previous literature have been performed at a fixed current density value. Therefore, the same analyses described in this chapter should be performed at lower current densities. At such operating conditions, it is likely that the operational cell voltage will rise, increasing the electrochemical efficiency. However, less electrochemical heat will be generated, which is likely to reduce the hydrogen production potential. Therefore, it is possible to adjust the system performance for each specific market depending upon which product is more valuable by varying the operational current density in addition to the fuel utilization.

It has been found that pressure swing adsorption (PSA) might not be the best technology for extraction and purification of the hydrogen from the anode off-gas due to the PSA feed gas requirements. A complex HSU configuration is required in order to meet pressure, temperature, and hydrogen concentration requirements. Therefore, different purification strategies such as electrochemical hydrogen separation and selective permeation membranes might be more suitable for the poly-generation application.

An economic analysis of poly-generating high-temperature fuel cells should be performed in detail. From an efficiency perspective and considering only the configurations presented herein, poly-generating HTFC are the best solution. However, the economics of such novel systems should be analyzed and compared with conventional production methods. Additionally, due to the poly-generating nature of these systems, different strategies to fit each of the specific market requirements should be designed. These strategies might be resolved by dynamic modeling efforts to investigate the ability of system configurations to dynamically dispatch each of the respective products depending upon demand profiles for each product.

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Hydrogen Production Science and Technology

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Article Outline

Introduction
 Review of Hydrogen Production Methods
 Reformation of Fossil Hydrocarbons and Bioderived Liquids
 Hydrogen Production Costs
 Conclusion
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