

PG&E GAS R&D AND INNOVATION

Hydrogen Technical Analysis

7/3/2018



Together, Building
a Better California



“The opinions, findings, and conclusions in the whitepaper are those of the authors and not necessarily those of PG&E. Publication and dissemination of the whitepaper by PG&E should not be considered an endorsement by PG&E, or the accuracy or validity of any opinions, findings, or conclusions expressed herein.

In publishing this whitepaper, PG&E makes no warranty or representation, expressed or implied, with respect to the accuracy, completeness, usefulness, or fitness for purpose of the information contained herein, or that the use of any information, method, process, or apparatus disclosed in this whitepaper may not infringe on privately owned rights. PG&E assumes no liability with respect to the use of, or for damages resulting from the use of, any information, method, process, or apparatus disclosed in this report. By accepting the whitepaper and utilizing it, you agree to waive any and all claims you may have, resulting from your voluntary use of the whitepaper, against PG&E.”



Table of Contents

| | |
|--|----|
| 1 What is Hydrogen | 5 |
| 2 How to Create Hydrogen | 5 |
| 2.1 Electrolysis | 5 |
| 2.2 Steam Methane Reforming..... | 7 |
| 2.3 Partial Oxidation | 8 |
| 2.4 Tri-Generation..... | 9 |
| 2.5 Technology Comparison | 10 |
| 3 New Technologies..... | 12 |
| 3.1 Thyssenkrupp: Chlorine-Alkaline Electrolysis | 12 |
| 3.2 HyTech: Internal Combustion Assistance (ICA) On-Board Hydrogen Generator | 13 |
| 3.3 HyperSolar – Nanotechnology for Making Hydrogen from Sunlight | 14 |
| 3.4 The Linde Group..... | 15 |
| 3.5 Air Products: Hydrogen Plants | 19 |
| 3.6 GTI: Compact Hydrogen Generator (CHG)..... | 21 |
| 3.7 Combined Heat, Hydrogen, and Power (CHHP) System | 24 |
| 4 Hydrogen and Natural Gas Pipeline Infrastructure | 26 |
| 4.1 Hydrogen Embrittlement | 27 |
| 5 R&D Opportunities | 28 |
| 6 References | 28 |

Table of Figures

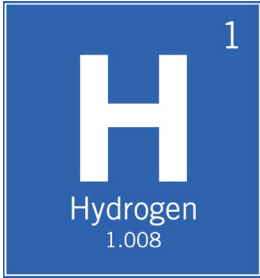
| | |
|--|----|
| Figure 1 Electrolysis Process (South Coast Air Quality Management District (SCAQMD), 2018) | 5 |
| Figure 2 Schematic representation of technology development potential (International Energy Agency (IEA), 2015)..... | 7 |
| Figure 3 Flow chart of steam methane reforming (South Coast Air Quality Management District (SCAQMD), 2018) | 7 |
| Figure 4 Illustration of a molten carbonate fuel cell (Fuel Cell Today (FCT), n.d.)..... | 9 |
| Figure 6 Hydrogen production cost results with revenue (Melaina & Eichman, 2015)..... | 12 |
| Figure 7 Illustration of an electrolysis cell (thyssenkrupp, 2018) | 12 |
| Figure 8 Illustration of the nanotechnology (HyperSolar, Inc., 2012)..... | 14 |
| Figure 9 Flowsheet for Linde's large capacity hydrogen plant (The Linde Group)..... | 16 |
| Figure 10 HYDROPRIME® (The Linde Group, 2015) | 18 |
| Figure 11 Steam methane reforming plant (Air Products and Chemicals, Inc., 2013)..... | 19 |
| Figure 12 System Concept (Gas Technology Institute (GTI), 2018) | 21 |
| Figure 13 Compact Hydrogen Generator (Gas Technology Institute (GTI), 2018)..... | 22 |
| Figure 14 Efficiency and Capital Costs (CHG vs. SMR) (Gas Technology Institute (GTI), 2018) | 22 |
| Figure 15 Tri-Generation Concept (U.S. Department of Energy, 2013) | 25 |
| Figure 16 Limitations on the blend share of hydrogen by application – the most important applications to the blend share are gas turbines, compressing stations and CNG tanks (International Energy Agency (IEA), 2015)..... | 27 |



Table of Tables

| | |
|---|----|
| Table 1 Current performance of key hydrogen generation technologies (International Energy Agency (IEA), 2015) | 10 |
| Table 2 Costs of Production for Renewable Hydrogen Pathways (doesn't include compression/storage/delivery) (South Coast Air Quality Management District (SCAQMD), 2018) | 10 |
| Table 3 Summary Table - Key Data and Figures for Hydrogen Production (2014) (IEA Energy Technology Network, 2014).... | 11 |
| Table 4 Comparison of the 5 MW versus 20 MW module (thyssenkrupp, 2018)..... | 13 |
| Table 5 Typical Performance Figures of a Steam Reforming based Hydrogen Plant (The Linde Group)..... | 17 |

1 What is Hydrogen



(South Coast Air Quality Management District (SCAQMD), 2018)

Hydrogen is the lightest, smallest and most abundant element in the universe (it is the first element in the periodic table). It naturally carries a very high amount of energy relative to its weight. Hydrogen does not exist freely in nature: it is only produced from other sources of energy, so it is often referred to as an energy carrier. Hydrogen can be found in combination with other elements in nature, such as H₂O or CH₄. Hydrogen needs to be isolated or “produced” by breaking the chemical bonds in the molecules that form these substances. (South Coast Air Quality Management District (SCAQMD), 2018)

Hydrogen is needed for large-scale industrial processes such as oil refining and ammonia production but its use as a transportation fuel, industrial heating feedstock and storage medium for renewable electricity is growing. It is a clean-burning fuel, and when combined with oxygen in a fuel cell, it produces heat and electricity with only water vapor as a by-product. (NREL, n.d.)

Some envision a future "hydrogen economy," where hydrogen is produced from a variety of energy sources, stored for later use, piped to where it is needed, and then converted cleanly into heat and electricity. (South Coast Air Quality Management District (SCAQMD), 2018)

2 How to Create Hydrogen

2.1 ELECTROLYSIS

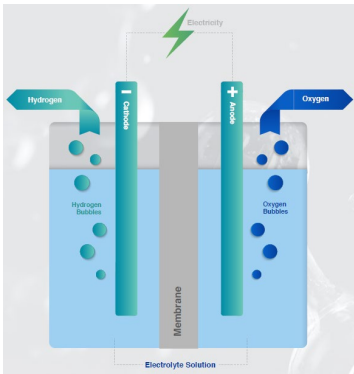


Figure 1 Electrolysis Process (South Coast Air Quality Management District (SCAQMD), 2018)

Electrolysis uses electricity to split water into hydrogen and oxygen. This reaction takes place in an electrolyzer. Similar to fuel cells, electrolyzers consist of an anode and cathode separated by a membrane, in an electrolyte solution. There are three main types of electrolyzers: (1) Polymer Electrolyte Membrane (PEM); (2) Alkaline; (3) Solid Oxide (SO). (Office of Energy Efficiency & Renewable Energy, n.d.)



PEM electrolyzers – polymer material electrolyte

At the anode, water reacts to form oxygen and positively charged hydrogen ions (protons). The electrons flow through an external circuit and the hydrogen ions selectively move across the PEM to the cathode. At the cathode, hydrogen ions combine with electrons from the external circuit to form hydrogen gas. (Office of Energy Efficiency & Renewable Energy, n.d.)

Anode Reaction $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$

Cathode Reaction $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$

Alkaline electrolyzers - liquid alkaline electrolyte solution of sodium or potassium hydroxide (South Coast Air Quality Management District (SCAQMD), 2018)

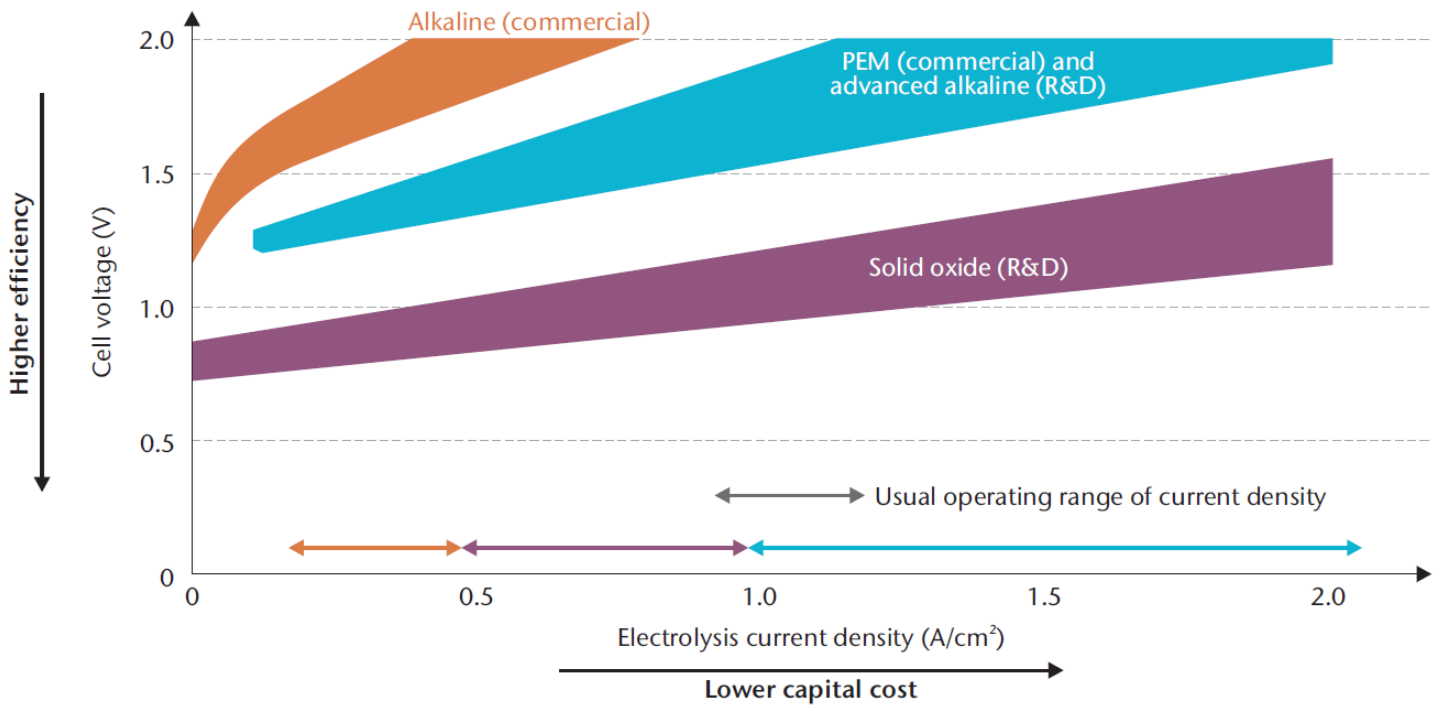
Note: Newer approaches using solid alkaline exchange membranes as the electrolyte are showing promise on the lab scale.

Alkaline electrolyzers operate via transport of hydroxide ions (OH^-) through the electrolyte from the cathode to the anode with hydrogen being generated on the cathode side. (Office of Energy Efficiency & Renewable Energy, n.d.)

SO electrolyzers - solid ceramic material electrolyte (South Coast Air Quality Management District (SCAQMD), 2018)

At the cathode, water combines with electrons from the external circuit to form hydrogen gas and negatively charged oxygen ions. The oxygen ions pass through the solid ceramic membrane and react at the anode to form oxygen gas and generate electrons for the external circuit.

Solid oxide electrolyzers need to operate at 700°–800°C, compared to PEM electrolyzers, which operate at 70°–90°C, and commercial alkaline electrolyzers, which operate at 100°–150°C. The electrolyzers can use heat available at these elevated temperatures (from various sources, including nuclear energy) to decrease the amount of electrical energy needed. (Office of Energy Efficiency & Renewable Energy, n.d.)



Note: A/cm² = ampere per square centimetre.

Figure 2 Schematic representation of technology development potential (International Energy Agency (IEA), 2015)

2.2 STEAM METHANE REFORMING



Figure 3 Flow chart of steam methane reforming (South Coast Air Quality Management District (SCAQMD), 2018)



Methane (e.g. from natural gas) reacts with high-temperature steam (700°C – 1,000°C) under 3–25 bar pressure in the presence of a catalyst to produce hydrogen, carbon monoxide, and a small amount of carbon dioxide (Office of Energy Efficiency & Renewable Energy, n.d.). Steam reforming is endothermic and requires heat to be supplied. In the "water-gas shift reaction," carbon monoxide and steam react over a catalyst to produce carbon dioxide and more hydrogen. Finally, in "pressure-swing adsorption," carbon dioxide and other impurities are removed from the gas stream, leaving essentially pure hydrogen.

Steam-methane reforming reaction $\text{CH}_4 + \text{H}_2\text{O} (+ \text{heat}) \rightarrow \text{CO} + 3\text{H}_2$

Water-gas shift reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 (+ \text{small amount of heat})$

2.3 PARTIAL OXIDATION

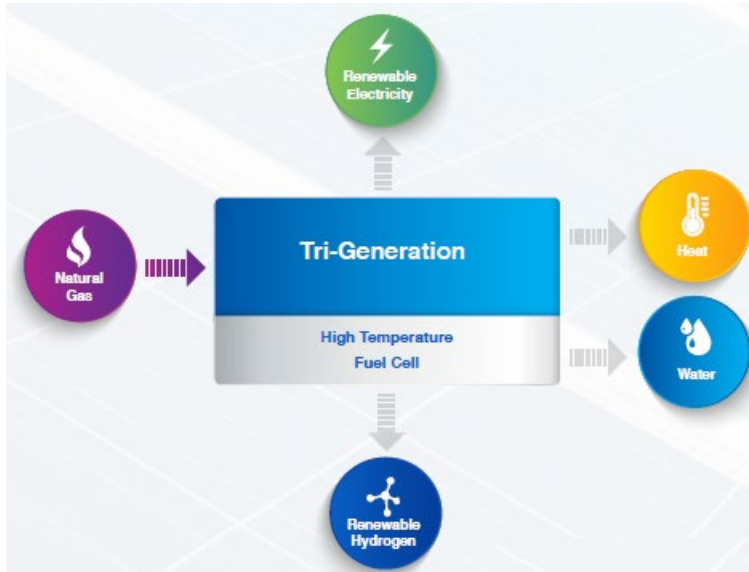
Methane and other hydrocarbons in natural gas react with less than the stoichiometric amount of oxygen (e.g. from air) that is not enough to completely oxidize the hydrocarbons to carbon dioxide and water. This results in products of primarily hydrogen and carbon monoxide (and nitrogen, if the reaction is carried out with air rather than pure oxygen), and a small amount of carbon dioxide and other compounds. In a "water-gas shift reaction," the carbon monoxide reacts with water to form carbon dioxide and more hydrogen.

Partial oxidation is an exothermic process, and gives off heat. The process is, typically, faster than steam reforming and requires a smaller reactor vessel. The process initially produces less hydrogen per unit of the input fuel than is obtained by steam reforming of the same fuel. (Office of Energy Efficiency & Renewable Energy, n.d.)

Partial oxidation of methane reaction $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 (+ \text{heat})$

Water-gas shift reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 (+ \text{small amount of heat})$

2.4 TRI-GENERATION



(South Coast Air Quality Management District (SCAQMD), 2018)

Tri-generation uses molten carbonate fuel cells to produce hydrogen, electricity, heat and water from natural gas or biogas. Trigeneration systems produce hydrogen through the reforming process, but don't require additional hydrocarbon fuel to create heat and steam. By-product heat and steam or waste energy from power production occurring within the same system is used. The amount of fuel input needed to power the reformation process is less than in SMR, which yields less GHG emissions.

Molten Carbonate Fuel Cells (MCFCs)

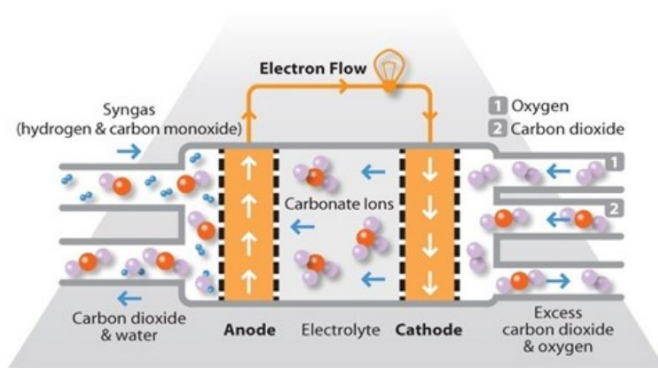


Figure 4 Illustration of a molten carbonate fuel cell (Fuel Cell Today (FCT), n.d.)

MCFCs operate at high temperatures (~650°C) and use a molten carbonate salt suspended in a porous ceramic matrix as the electrolyte. Salts commonly used include lithium carbonate, potassium carbonate and sodium carbonate.



2.5 TECHNOLOGY COMPARISON

Table 1 Current performance of key hydrogen generation technologies (International Energy Agency (IEA), 2015)

| Application | Power or capacity | Efficiency* | Initial investment cost | Life time | Maturity |
|-------------------------------------|---|--------------|-------------------------|---------------------|---------------|
| Steam methane reformer, large scale | 150-300 MW | 70-85% | 400-600 USD/kW | 30 years | Mature |
| Steam methane reformer, small scale | 0.15-15 MW | ~51% | 3 000-5 000 USD/kW | 15 years | Demonstration |
| Alkaline electrolyser | Up to 150 MW | 65-82% (HHV) | 850-1 500 USD/kW | 60 000-90 000 hours | Mature |
| PEM electrolyser | Up to 150 kW (stacks) Up to 1 MW (systems) | 65-78% (HHV) | 1 500-3 800 USD/kW | 20 000-60 000 hours | Early market |
| SO electrolyser | Lab scale | 85-90% (HHV) | - | ~1 000 h | R&D |

* = Unless otherwise stated efficiencies are based on LHV.

** = All investment costs refer to the energy output.

Notes: PEM = proton exchange membrane; SO = solid oxide.

Table 2 Costs of Production for Renewable Hydrogen Pathways (doesn't include compression/storage/delivery) (South Coast Air Quality Management District (SCAQMD), 2018)

| Pathway | Renewable Level | Technology | Input | Plant Capacity | Levelized Cost of Production (\$/kg) |
|--------------------------------------|-----------------|------------------|--------------------------------------|----------------|--------------------------------------|
| Solar PV + CA Grid to H2 - 1MW | 32% | PEM Electrolysis | Grid and Solar Electricity, Water | 398kg/day | \$8.02 |
| 100% Solar PV Generation to H2 - 1MW | 100% | PEM Electrolysis | Grid Electricity, Water | 126kg/day | \$15.43 |
| Biogas to H2 | 100% | SMR | Landfill, Wastewater or Dairy Biogas | 1500kg/day | \$2.94 |
| Tri-Generation Biogas to H2 | 100% | Tri-Generation | Biogas | 1500kg/day | \$5.99 |
| Natural Gas to Hydrogen | 0 | SMR | Natural Gas | 398kg/day | \$2.17 |

Table 3 Summary Table - Key Data and Figures for Hydrogen Production (2014) (IEA Energy Technology Network, 2014)

| Technical Performance by Technology Variants | Typical current international values and ranges | |
|--|--|--|
| | SMR | Electrolysis |
| Energy input | Natural Gas + Electricity | Electricity |
| Energy efficiency (%) | 70 - 85 | 62 - 82 |
| Typical size (Nm ³ /h) | 10.000 – 20.000 | 0.5 - 10 |
| Technical lifetime | 2 – 5 years | 40.000 hours |
| Market share (%),(2012) | 48% | 4% |
| Costs (€2011) | | |
| Production cost, (€/Nm ³ H ₂) | 0.05 – 0.1 | 0.16 – 0.30 |
| Typical cost breakdown, (%) (material, process, labour) | 30% material, 40% process, 30% labour | 50% material, 30% process, 20% labour |
| Data Projections 2015 - 2030 | | |
| Efficiency (%), | 70 - 85 (2015) 70 - 85 (2020) 75 - 85 (2030) | 50 - 80 (2015) 55 - 80 (2020) 60 - 85 (2030) |
| Product cost (€/Nm ³ H ₂), | 0.090 (2015) 0.085 (2020) 0.080 (2030) | 0.15 – 0.27 (2015) 0.13 – 0.20 (2020) 0.10 – 0.15 (2030) |
| Lifetime, | 2 – 5 years (2015) 2 – 5 years (2020) 2 – 5 years (2030) | 40,000 hrs (2015) 45,000 hrs (2020) 65,000 hrs (2030) |
| Market share (%), | 48% (2015) 45% (2020) 40% (2030) | 5% (2015) 15% (2020) 30% (2030) |

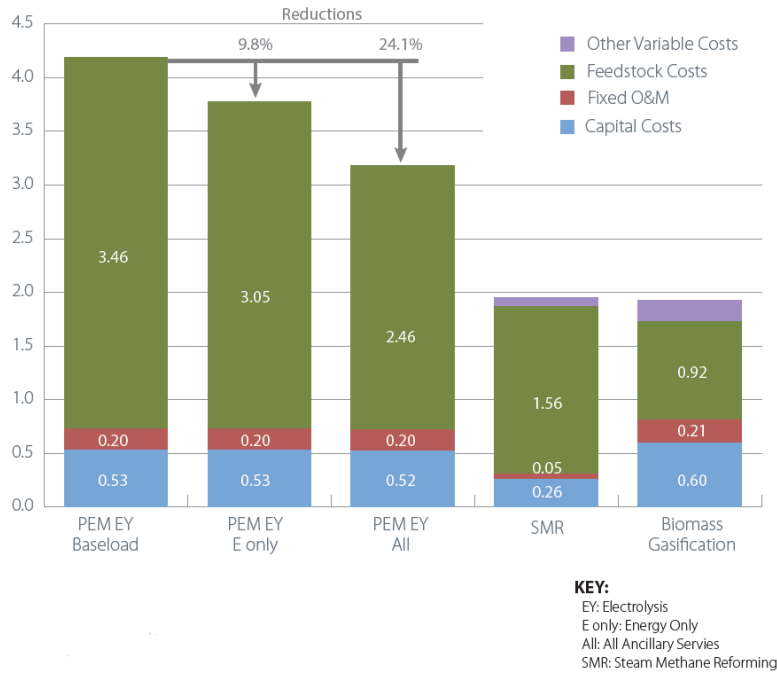


Figure 5 Hydrogen production cost results with revenue (Melaina & Eichman, 2015)

A breakdown of future costs associated with hydrogen that is produced via central electrolysis, with a baseload reference case slightly above \$4 per kg of hydrogen produced. When energy services revenue from HES is taken into account, total costs are reduced (offset) by 9.8%; including all ancillary services, this results in a 24.1% reduction, equal to approximately \$1 per kg. Production costs from central steam methane reforming (SMR) and biomass gasification are shown for reference.

3 New Technologies

3.1 THYSSENKRUPP: CHLORINE-ALKALINE ELECTROLYSIS

Chlorine-Alkaline electrolysis technology producing hydrogen from the splitting of water.

An initial lab-scale plant has already been built. The next planned step in the development process is a pilot plant.

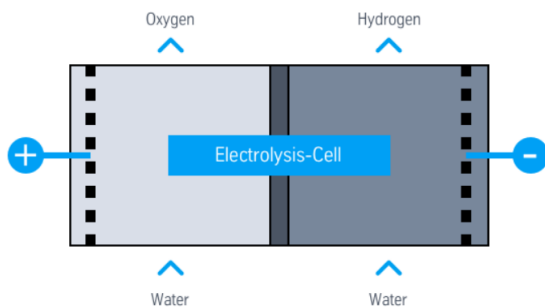


Figure 6 Illustration of an electrolysis cell (thyssenkrupp, 2018)

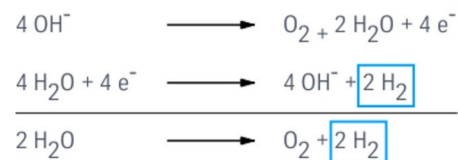


Table 4 Comparison of the 5 MW versus 20 MW module (thyssenkrupp, 2018)

| | 5 MW module | 20 MW module |
|---|---|---|
| Design capacity H ₂ | 1000 Nm ³ /h | 4000 Nm ³ /h |
| Efficiency electrolyzer (DC) | > 82% _{HHV} * | > 82% _{HHV} * |
| Power consumption (DC) | max. 4.3 kWh/Nm ³ H ₂ | max. 4.3 kWh/Nm ³ H ₂ |
| Water consumption | <1l/Nm ³ H ₂ | <1l/Nm ³ H ₂ |
| Standard operation window | 10% - 100% | 10% - 100% |
| H ₂ product quality at electrolyzer outlet | > 99.95% purity (dry basis) | > 99.95% purity (dry basis) |
| H ₂ product quality after treatment (optional) | as required by customer, up to 99.9998 % | as required by customer, up to 99.9998 % |
| H ₂ product pressure at module outlet | ~300 mbar | ~300 mbar |
| Operating temperature | up to 90 °C | up to 90 °C |

* HHV = calculated with reference to higher heating value of hydrogen.
 All values may vary depending on operating conditions.

Benefits

- Modular, skid-mounted water electrolyzers
- Up to 80 percent efficiency
- Investment costs 3.5 times lower

Limitations

(Marini, et al., 2012)

- May have low operating current density
- System complexity

3.2 HYTECH: INTERNAL COMBUSTION ASSISTANCE (ICA) ON-BOARD HYDROGEN GENERATOR

HyTech Power's Internal Combustion Assistance, or ICA, utilizes electrolysis to create hydrogen from water and injects the hydrogen gas into the engine cylinders. The hydrogen gas accelerates the clean burn of the diesel fuel and greatly increases its efficiency while eliminating or significantly reducing harmful emissions. The HyTech patented ICA solution is currently in the commercialization phase. It is the among the first HHO systems that

incorporates computer technology to optimize injection timing and injected quantity based upon engine demand. The HTP ICA system is listed on the U.S. Environmental Protection Agency (EPA) website as a compliant alternative fuel conversion system and has received the CARB Exemption Executive Order (California Air Resources Board). (Roberts, 2018)

Author’s Note: Information on the technology is not available

3.3 HYPERSOLAR – NANOTECHNOLOGY FOR MAKING HYDROGEN FROM SUNLIGHT

Technology uses sunlight energy to power a traditional water electrolysis process. On June 5, 2018, HyperSolar surpassed 294 hours without any degradation. The next milestone is 1000 hours of continuous operation. The design of the device serves as the foundation of the Company’s first generation commercial renewable hydrogen generator. (HyperSolar, Inc., 2018)

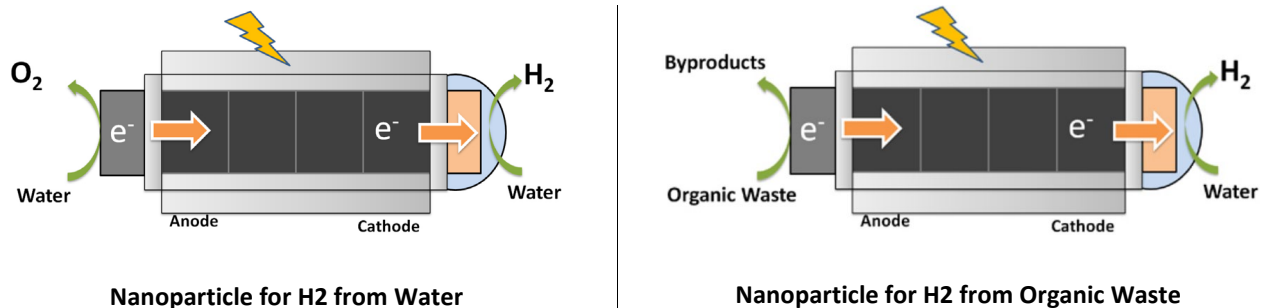


Figure 7 Illustration of the nanotechnology (HyperSolar, Inc., 2012)

Cathode (reduction): $2 \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$

Anode (oxidation): $4 \text{OH}^- \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^-$

To address the fundamental electron transfer efficiency problem, HyperSolar is developing a nanoparticle to ensure that all electrons are utilized in splitting a water molecule. The nanoparticle has two important features (HyperSolar, Inc., 2012):

- **Self-contained Photoelectrochemical Nanosystem** — Nano-size particle technology is designed to mimic photosynthesis and contains a solar absorber that generates electrons from sunlight, as well as integrated cathode and anode areas to readily split water and transfer those electrons to the molecular bonds of

hydrogen. The nanoparticles are optimized to ensure maximum electron generation and utilization efficiency, thereby using fewer photovoltaic elements, an expensive material, than conventional solar panels to achieve the same system level efficiency.

- **Protective Coating** — A protective coating is used to encapsulate key elements of the nanoparticle to allow it to function for long periods of time in a wide range of water conditions (e.g. sea water, runoff water, river water, waste water) without corrosion or short circuiting.

Benefits

- Uses renewable electricity to produce hydrogen
- Nanoparticles being designed to utilize most if not all electrons to split the water molecules

Limitations

- Solar energy is only available for certain periods of time in a day and varies per season
- Risks of corrosion of the nanoparticle due to submersion in a water environment

3.4 THE LINDE GROUP

Linde is a leading supplier of steam reformer plants with more than 200 constructed units producing capacities of synthesis gas from 1,000 to over 120,000 Nm³/h of (Linde, 2018).

The basic process steps for a large capacity hydrogen plant (The Linde Group)

1. Hydrodesulfurization of feed stock
2. Steam reforming
3. Heat recovery from reformed and from combustion flue gas to produce process and export steam
4. Single stage adiabatic high temperature CO-shift conversion
5. Final hydrogen purification by pressure swing adsorption

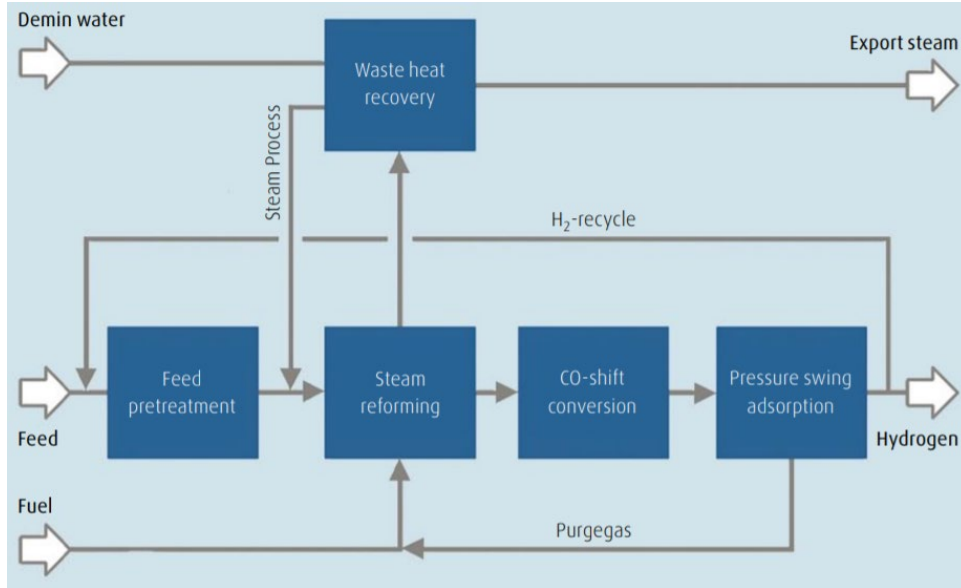
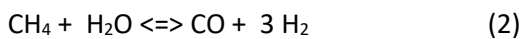
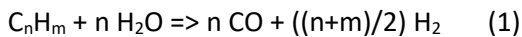


Figure 8 Flowsheet for Linde's large capacity hydrogen plant (The Linde Group)

The desulfurized hydrocarbon feed is mixed with superheated process steam in accordance with the steam/carbon relationship necessary for the reforming process. After that, this gas mixture is heated up and then distributed on the catalyst-filled reformer tubes. The gas mixture flows from top to bottom through tubes arranged in vertical rows. While flowing through the tubes heated from the outside, the hydrocarbon/steam mixture reacts, forming hydrogen and carbon monoxide in accordance with the following reactions (Linde, 2018):



To minimize the methane content in the synthesis gas while simultaneously maximizing the H₂ yield and preventing the formation of elemental carbon and keeping it from getting deposited on the catalyst, the reformer is operated with a higher steam/carbon relationship than theoretically necessary. As the heat balance for the main reactions (1) - (3) is endothermic, the required heat must be produced by external firing. The burners for the firing are arranged on the ceiling of the firing area between the tube rows and fire vertically downward. The residual gas from the pressure swing adsorption unit as well as heating gas from battery limits is used as fuel gas. The flue gas is then cooled down in a convection zone, generating steam.



Table 5 Typical Performance Figures of a Steam Reforming based Hydrogen Plant (The Linde Group)

| | | | Natural gas | LPG | Naphtha | Refinery gas |
|---|-------------------------|---|-------------|-----------|-----------|--------------|
| Product hydrogen | flow rate | Nm ³ /h | 50,000 | 50,000 | 50,000 | 50,000 |
| | | MMSCFD | 44.8 | 44.8 | 44.8 | 44.8 |
| | pressure | bara | 25.0 | 25.0 | 25.0 | 25.0 |
| | purity | mol-% | 99.9 | 99.9 | 99.9 | 99.9 |
| Export steam | flow rate | T/hr | 31 | 28.9 | 28.6 | 29.2 |
| | temperature | °C | 390 | 390 | 390 | 390 |
| | pressure | bara | 40 | 40 | 40 | 40 |
| Feed and fuel consumption | | Gcal/hr | 177.8 | 181.8 | 182.9 | 175.8 |
| | | GJ/hr | 744.4 | 761.2 | 765.8 | 736.0 |
| Energy consumption (incl. steam credit) | | Gcal/1,000 Nm ³ H ₂ | 3.070 | 3.210 | 3.222 | 3.072 |
| | | GJ/1,000 Nm ³ H ₂ | 12.853 | 13.440 | 13.490 | 12.862 |
| Utilities | demin. water | T/hr | 55.6 | 57.5 | 60.6 | 53.2 |
| | cooling water | T/hr | 160 | 165 | 168 | 157 |
| | electrical energy | kW | 850 | 920 | 945 | 780 |
| Design flexibility | export steam production | T/1,000 Nm ³ H ₂ | 0.5 - 1.2 | 0.4 - 1.2 | 0.4 - 1.2 | 0.4 - 1.1 |
| | fuel consumption | GJ/1,000 Nm ³ H ₂ | 0.9 - 3.5 | 1.8 - 4.3 | 1.9 - 4.4 | 0.7 - 2.9 |

Linde also has modular hydrogen generators using SMR. Their technology, called HYDROPRIME[®], provides hydrogen capacities from 0.3 – 0.9 MM SCFD, with high purity of 99.999%+, at 200 psig (The Linde Group, 2015). The modular, open skid design allows for easy site installation (indoor / outdoor) and easy accessibility for maintenance.

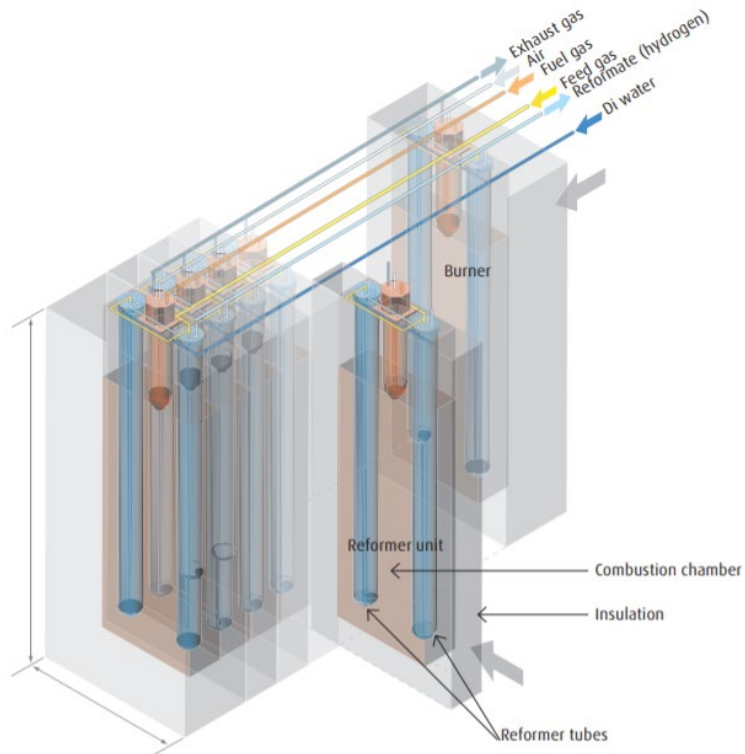


Figure 9 HYDROPRIME® (The Linde Group, 2015)

Benefits

- High thermal efficiency and low utility consumption for low operating cost
- Fully automatic with fail-safe controls
 - Remote start-up, operation, and monitoring
 - Automatic load-following controls to reduce production, resulting in lower natural gas and power consumption during periods of reduced demand

Limitations

- The use of fossil fuels as the feedstock for the SMR doesn't eliminate GHG

3.5 AIR PRODUCTS: HYDROGEN PLANTS

Air Products operates 60+ SMR/POx facilities worldwide in addition to many off-gas plants, all of which deliver hydrogen directly or via pipeline networks to more than 80 customers (Air Products and Chemicals, Inc., 2013).

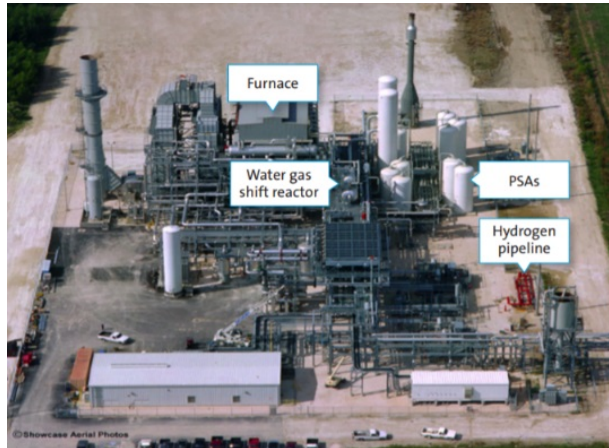
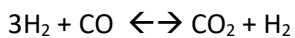
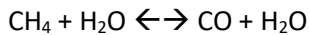


Figure 10 Steam methane reforming plant (Air Products and Chemicals, Inc., 2013)

Steam methane reforming is the most common and economical way to make hydrogen. There are two primary reactions: the reforming reaction and the water gas shift reaction. In the reforming reaction, natural gas is mixed with steam, heated to over 1,500 degrees Fahrenheit, and reacted with nickel catalyst to produce hydrogen (H₂) and carbon monoxide (CO).



Furnace

The furnace is where the process of liberating hydrogen from natural gas and steam begins. The gas-and-steam mixture travels down into reformer tubes that hang in vertical rows surrounded by gas burners that heat the mixture. The reformer tubes are full of nickel catalyst, which triggers a reaction, causing the methane in natural gas to react with water vapor to form hydrogen, carbon monoxide, and carbon dioxide.

Water gas shift reactor

Additional hydrogen is created in the water gas shift reactor. The water gas shift reactor is filled with an ironchrome based catalyst that causes steam (H₂O) to break into oxygen and hydrogen. The hydrogen moves through the plant, while the oxygen joins carbon monoxide from the furnace (reforming reaction) and becomes carbon dioxide (CO₂).



Pressure swing absorbers (PSAs)

The PSAs are used to filter out remaining traces of carbon monoxide, carbon dioxide, steam, and methane from the hydrogen. These leftover gases are used as fuel for the furnace, while the hydrogen is ready for customers. The hydrogen can be put into a hydrogen pipeline or liquefied and moved by truck.

Output

SMRs primarily produce hydrogen. They can also create CO, syngas mixtures (various combinations of hydrogen and carbon monoxide), steam, and electric power for customer use.

Benefits

- High operating efficiency, good heat integration which lowers feedstock consumption

Limitations

- The use of fossil fuels as the feedstock for the SMR doesn't eliminate GHG

3.6 GTI: COMPACT HYDROGEN GENERATOR (CHG)

GTI's technology is an alternative solution to generating hydrogen from natural gas. The technology came from a concept to pilot scale by Aerojet Rocketdyne and is now owned by GTI. The Compact Hydrogen Generator (CHG) process utilizes calcium oxide (CaO) as a sorbent for the in-situ removal of by-product carbon dioxide which directly produces a 92+ vol% pure H₂ product, resulting in lower equipment costs, higher H₂ yields and a concentrated CO₂ product stream suitable for Carbon Capture and Sequestration (CCS) or other applications.

The ability to utilize CaO is made possible by the use of a bubbling fluidized bed of catalyst particles with the CaO being injected as a reactant with the steam/methane mixture. The CaO used has a fine particle size and is elutriated through the catalyst bed during which it picks up the CO₂ and gets converted to calcium carbonate (CaCO₃). Once the CaO reactant passes through the catalyst bed, it is entrained with the product H₂ and separated using internal cyclones. The CaCO₃ is then transferred to a second unit operation wherein it is rapidly heated in a gas phase transport calciner to reject the CO₂ and produce CaO for reuse in the H₂ generator reactor.

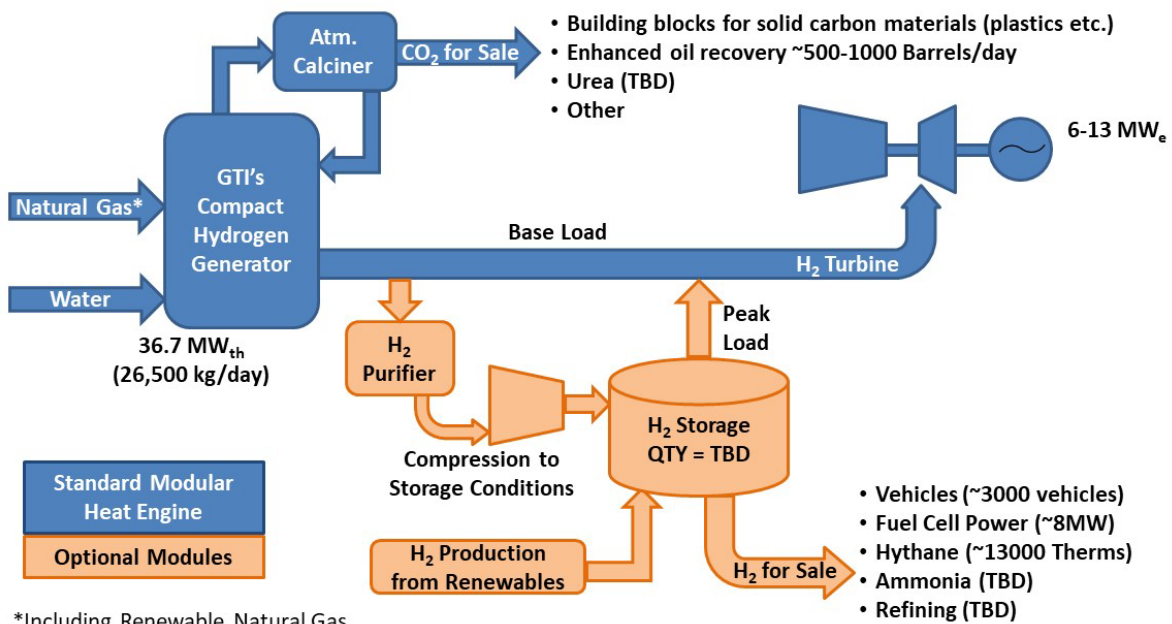
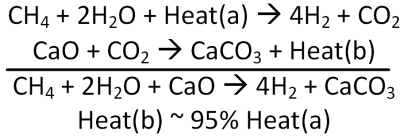


Figure 11 System Concept (Gas Technology Institute (GTI), 2018)

**Sorption Enhanced
Steam Methane Reforming**



700°C, 20-35 psig

Catalyst:

Commercially Available
Ni on Alumina
2mm diameter

Sorbent:

Natural Solid Sorbent:
Limestone or Dolomite
<0.2mm diameter

- Catalyst
- Sorbent
- Sorbent with CO₂

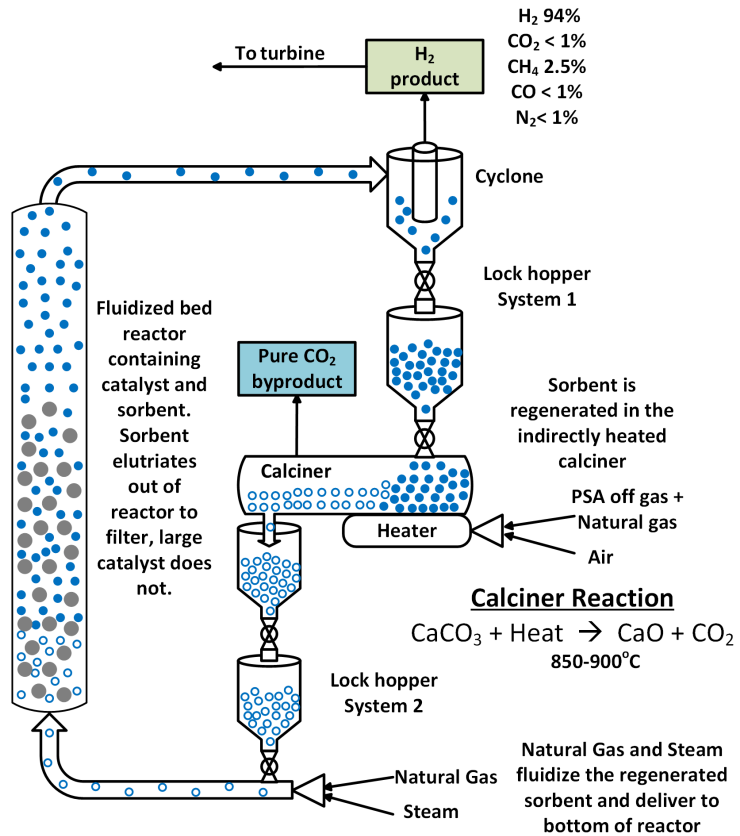


Figure 12 Compact Hydrogen Generator (Gas Technology Institute (GTI), 2018)

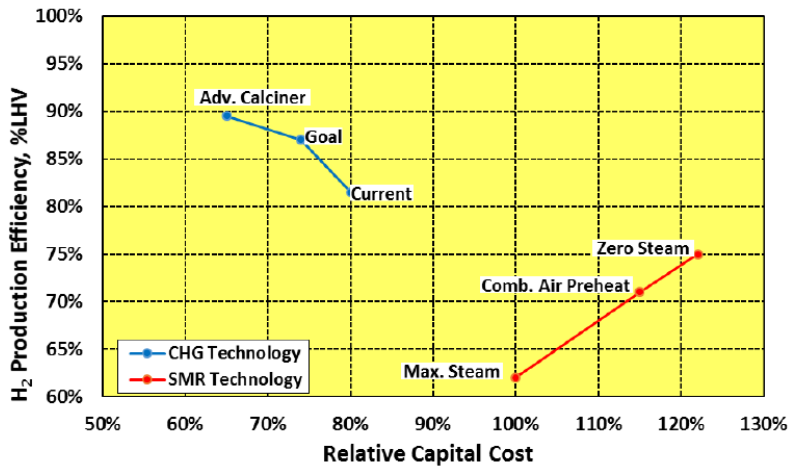


Figure 13 Efficiency and Capital Costs (CHG vs. SMR) (Gas Technology Institute (GTI), 2018)



Benefits

- No syngas production step
- No indirect firing/heat transfer approach
- Recapturing sensible heat from direct fired calciner
- Steam neutral process

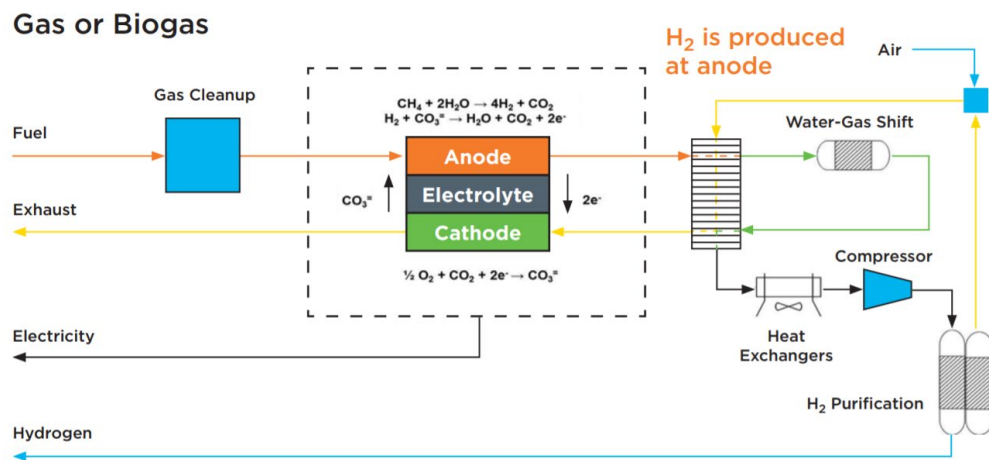
Limitations

- Thermodynamic feasibility not proven yet
- Catalyst activity may diminish with each run

3.7 COMBINED HEAT, HYDROGEN, AND POWER (CHHP) SYSTEM

Project Information: The Fountain Valley energy station, is the world’s first tri-generation hydrogen energy and electrical power station to provide transportation fuel to the public and electric power to an industrial facility. Located at the Orange County Sanitation District’s wastewater treatment plant in Fountain Valley, California, the unit is a combined heat, hydrogen, and power (CHHP) system that co-produces hydrogen in addition to electricity and heat, making it a tri-generation system. The hydrogen produced by the system supplies a hydrogen fueling station that is open to the public and can support between 25 and 50 fuel cell electric vehicle fills per day. The fuel cell also produces approximately 250 kW of power for use by the wastewater treatment plant with nearly zero criteria pollutant emissions. Since the power is made from a renewable waste stream, greenhouse gas emissions are substantially reduced. (U.S. Department of Energy, 2013)

Anaerobically digested biogas from the municipal wastewater treatment plant is used as the fuel for a fuel cell. The CHHP system uses a molten carbonate fuel cell, chosen for its high efficiency and the capability to co-produce hydrogen. The system is integrated with a hydrogen purification system to produce approximately 100 kg of hydrogen per day. The hydrogen is stored on-site in high pressure tubes at < 7000 psi near the tri-generation system and next to the fueling station. (U.S. Department of Energy, 2013)



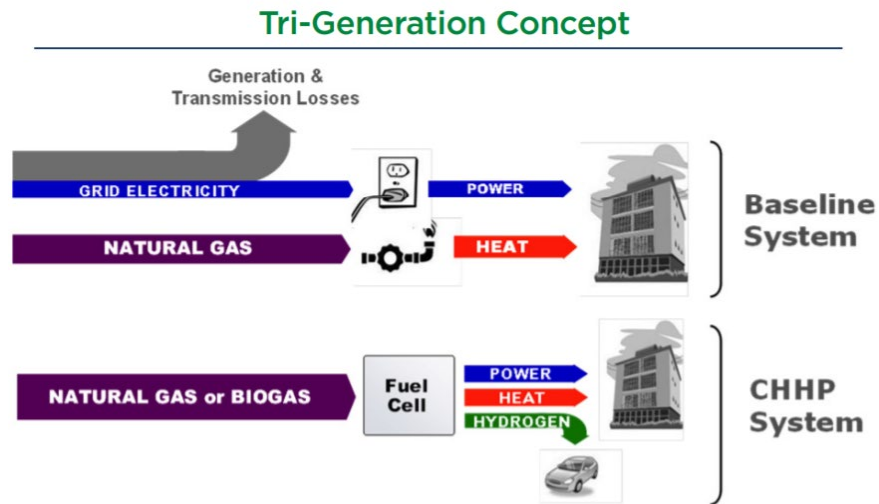


Figure 14 Tri-Generation Concept (U.S. Department of Energy, 2013)

Benefits

(Fuel Cell Today (FCT), n.d.)

- High operating temperature
 - Improves reaction kinetics, eliminating the need to boost this with a noble metal catalyst
 - Makes the cell less prone to CO poisoning
 - Allows different fuels as feedstock, e.g. coal-derived gas, methane or natural gas, eliminating need for external reformers

Limitations

(Fuel Cell Today (FCT), n.d.)

- Uses liquid electrolyte instead of a solid and requires injection of CO₂ at the cathode as carbonate ions are consumed in anode reactions
- Molten carbonate fuel cells have durability issues due to high operating temperatures (> 600°C) and corrosive electrolyte

4 Hydrogen and Natural Gas Pipeline Infrastructure¹

Hydrogen is viewed as an important energy carrier for the future which offers carbon free emissions at the point of use. The use of hydrogen gas as a renewable and practical energy source partly depends on whether it can be distributed safely and efficiently to consumers. The existing natural gas piping infrastructure could provide such a means if it is compatible.

A network designed for natural gas cannot be used for pure hydrogen without modifications to network components or the way it is operated and maintained. However, the existing natural gas transmission, distribution and end use systems could be used for mixtures of natural gas and hydrogen given appropriate modifications. The mixture can be used as such and, if required, hydrogen appliances could be fueled with “pure” hydrogen by developing devices to extract hydrogen selectively from the mixture.

For the accommodation of gases which contain a certain percentage of hydrogen, it is important that the physical and chemical characteristics related to the composition of the gas fit with the characteristics of natural gas, and do not create unacceptable risks (e.g. integrity of gas system). The physical and chemical properties of hydrogen differ from natural gas and adding a certain percentage of hydrogen may impact combustion properties, diffusion into materials and behavior of the gas mixture in air. The following aspects may be impacted:

- Safety related to the transmission, distribution and use of gas
- Integrity of pipelines
- Gas quality management
- Performance of end user appliances

Up to 30% by volume hydrogen could be added to the natural gas within the current gas infrastructure without adversely affecting the risk to the public significantly and without any additional mitigation measures. The addition of 40 to 50% by volume hydrogen would probably also be achievable without unacceptably increasing the risk to the public from the pipeline system or from explosions in properties. However, it is recognized that in some circumstances the increase in the severity of the explosions may be undesirable and pose an additional hazard. Therefore, it would be prudent to consider the adoption of mitigation measures in situations where the explosion severity could be increased.

¹(Lowesmith & Hankinson, 2009) (Dirven, Mueller-Syring, & Noort, 2018) (Ersoy, 2015)

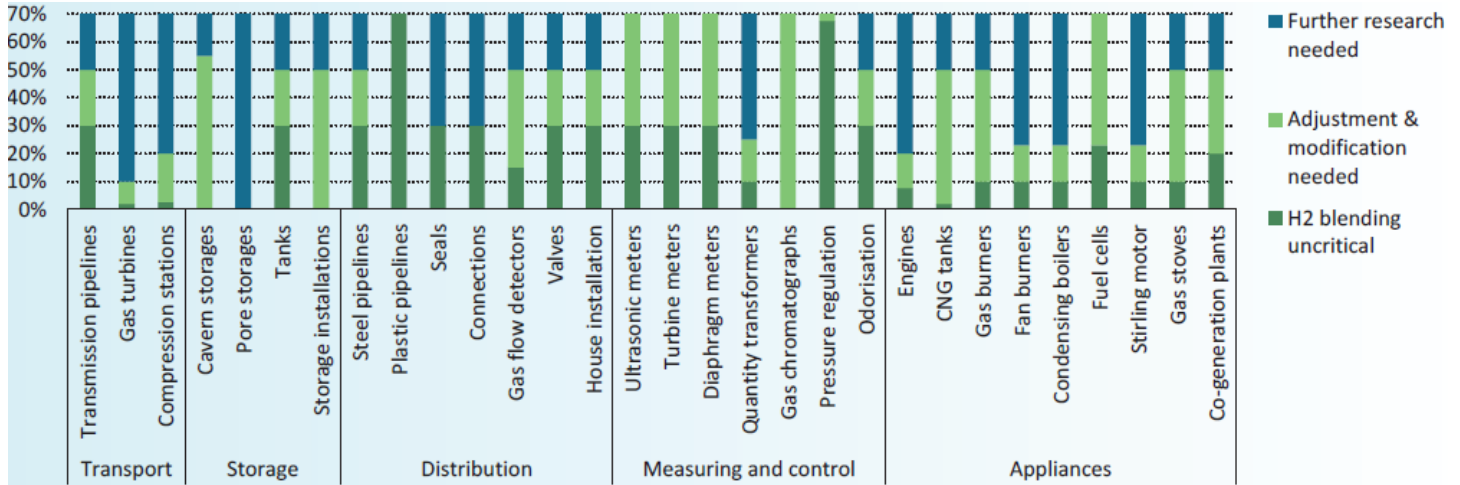


Figure 15 Limitations on the blend share of hydrogen by application – the most important applications to the blend share are gas turbines, compressing stations and CNG tanks (International Energy Agency (IEA), 2015)

4.1 HYDROGEN EMBRITTLEMENT

One major and known concern related to hydrogen exposure of ferritic steels is hydrogen embrittlement. There are many factors involved that relate and contribute to the likelihood of hydrogen embrittlement of pipeline steels, specifically *Hydrogen-Environment Embrittlement (H-E)*. This is the degradation of mechanical properties when metal is exposed to a hydrogen environment. It occurs when the metal is under stress and cracks are present. There is no time delay, it occurs once the local stress level exceeds yield strength. H-E is believed to be the most important mechanism for hydrogen pipelines or hydrogen injection into natural gas pipelines.

Hydrogen gas reduces the fracture toughness, crack propagation resistance, and ductility (as measured by reduction in area), and increases the fatigue crack growth rates for pipeline steels and their welds. This is also true for hydrogen-natural gas blends, and even when hydrogen partial pressures are low, especially for crack growth rates. A short summary of findings are presented below. The welds and their heat affected zones followed the same trends as the pipe body materials. (Melaina, Antonia, & Penev, 2013)

1. Reduction of Area (RA). It is reflective of the steels toughness. There is a significant reduction in the RA%'s with notched steel specimens when typical pipeline steels are exposed to a hydrogen pressure of 6.9MPa (1,000 psi) and these results were typically independent of pressure. The reduction was as high as 80%.
2. Fracture Toughness. There is a significant reduction in both the fracture toughness of pipeline steels exposed to gaseous hydrogen. Even at lower hydrogen pressures of 2.0 MPa (290 psi) there was a reduction in fracture toughness of over 22%. As toughness and reduction area decrease, the pipeline steel and its welds become more susceptible to



brittle failure mechanisms and pipeline leaks and/or ruptures at defects like poor quality welds, steel inclusions, and other features that act as stress risers.

3. Crack Propagation Resistance. There is a reduction in the crack propagation resistance when hydrogen is present. The effect is more pronounced on crack propagation than fracture toughness.
4. Fatigue Crack Growth Rates. The fatigue crack growth rates in hydrogen become increasingly greater relative to those in air or nitrogen as ΔK (stress intensity factor range) increases; the difference can be an order of magnitude (10X) or greater. Gases containing even low partial pressure of hydrogen may accelerate fatigue crack growth in carbon steels. As for blends with natural gas, the crack growth rate in air and natural gas are the same, whereas a blend of hydrogen with natural gas shows a similar crack growth rate as pure hydrogen, even at low absolute pressures.

5 R&D Opportunities

- Collaboration with GTI to prove CHG technology (existing project with funding from DOE)
- Collaboration with NYSEARCH to update the RANGETM model to incorporate impacts of hydrogen on end-use appliances (proposed project)
- Joint Industry collaboration to put together engineering guidelines on the impact of hydrogen on transmission and distribution system operations (existing project - HYREADY)

References

- Air Products and Chemicals, Inc. (2013). *Air Products and Technip*. Retrieved from H2Alliance: http://www.h2alliance.com/pdf/Final%20_H2Alliance_DS_1-22-13.pdf
- Air Products and Chemicals, Inc. (2013). *Steam methane reformer*. Retrieved from Air Products: <http://www.airproducts.com/~media/Files/PDF/industries/energy/energy-hydrogen-steam-methane-reformer-datasheet.pdf>
- Dirven, J., Mueller-Syring, G., & Noort, A. v. (2018). *HYREADY Engineering guidelines*. DNV GL.
- Ersoy, D. (2015). *Steel Pipe and Welds - Hydrogen Environmental Embrittlement*. Des Plaines: GTI.
- Fuel Cell Today (FCT). (n.d.). *MCFC*. Retrieved from Fuel Cell Today: <http://www.fuelcelltoday.com/technologies/mcfc>
- Gas Technology Institute (GTI). (2018). *A Modular Heat Engine for the Direct Conversion of Natural Gas to Hydrogen and Power Using Hydrogen Turbines*. GTI.
- HyperSolar, Inc. (2012). *Breakthrough Nanotechnology for Making Renewable Hydrogen from Sunlight*. Retrieved from HyperSolar: <http://www.hypersolar.com/technology.php>
- HyperSolar, Inc. (2018, June 5). *HyperSolar Announces a Record 294 Hours of Successful Hydrogen Production*. Retrieved from HyperSolar: http://www.hypersolar.com/news_detail.php?id=96
- IEA Energy Technology Network. (2014). *Hydrogen Production & Distribution*. IEA Energy Technology Network. Retrieved from https://iea-etsap.org/E-TechDS/PDF/P12_H2_Feb2014_FINAL%203_CRES-2a-GS%20Mz%20GSOK.pdf
- International Energy Agency (IEA). (2015). *Technology Roadmap Hydrogen and Fuel Cells*. Paris: International Energy Agency (IEA). Retrieved from <https://www.iea.org/publications/freepublications/publication/TechnologyRoadmapHydrogenandFuelCells.pdf>
- Linde. (2018). *Steam reforming*. Retrieved from Linde Engineering: https://www.linde-engineering.com/en/process_plants/hydrogen_and_synthesis_gas_plants/gas_generation/steam_reforming/index.html
- Lowesmith, B., & Hankinson, G. (2009). *NATURALHY: Adding Hydrogen to the Natural Gas Infrastructure: Overall Conclusions on the Risk to the Public*. Loughborough: Loughborough University.
- Marini, S., Salvi, P., Nelli, P., Kirov, Y., Pesenti, R., Villa, M., . . . Zangari, G. (2012, November). Advanced alkaline water electrolysis. *Electrochimica Acta*, 82:384. Retrieved from https://www.researchgate.net/publication/255791873_Advanced_alkaline_water_electrolysis
- Melaina, M. W., Antonia, O., & Penev, M. (2013). *Blending Hydrogen into Natural Gas Pipeline Networks: A Review of Key Issues*. Golden: NREL.



- Melaina, M., & Eichman, J. (2015). *Hydrogen Energy Storage: Grid and Transportation Services*. Golden: National Renewable Energy Laboratory.
- NREL. (n.d.). *Hydrogen Basics*. Retrieved from U.S. Department of Energy: <https://www.nrel.gov/workingwithus/eds-hydrogen.html>
- Office of Energy Efficiency & Renewable Energy. (n.d.). *Hydrogen Production: Electrolysis*. Retrieved from Office of Energy Efficiency & Renewable Energy: <https://www.energy.gov/eere/fuelcells/hydrogen-production-electrolysis>
- Office of Energy Efficiency & Renewable Energy. (n.d.). *Hydrogen Production: Natural Gas Reforming*. Retrieved from Office of Energy Efficiency & Renewable Energy: <https://www.energy.gov/eere/fuelcells/hydrogen-production-natural-gas-reforming>
- Roberts, D. (2018, February 16). *This company may have solved one of the hardest problems in clean energy*. Retrieved from Vox: <https://www.vox.com/energy-and-environment/2018/2/16/16926950/hydrogen-fuel-technology-economy-hytech-storage>
- South Coast Air Quality Management District (SCAQMD). (2018). *Renewable Hydrogen Roadmap*. Energy Independence Now (EIN). Retrieved from https://static1.squarespace.com/static/58e8f58d20099ea6eb9ab918/t/5afd25a9f950b7543abe21ba/1526539702668/EIN_RH2_Paper_Lowres.pdf
- The Linde Group. (2015, January). *HYDROPRIME®. Modular hydrogen generators using*. Retrieved from Linde: https://www.linde-engineering.com/en/images/HydroPrime%20Cut%20Sheet%20January%202015_tcm19-160823.pdf
- The Linde Group. (n.d.). *Hydrogen*. Retrieved from Linde: https://www.linde-engineering.com/en/images/H2_1_1_e_12_150dpi_NB_tcm19-4258.pdf
- thyssenkrupp. (2018). *Hydrogen from large-scale electrolysis*. Germany. Retrieved from 14. <https://www.thyssenkrupp-uhde-chlorine-engineers.com/en/download?p=AB1E80C53A1DDA095AA013B71CCF9DF2B9E33916AF40B53CBF8E83B5CA5B994030094D79C08F1A15E7EDF523170C54D605F79C6872F9FD91B3C9A47A0BCAC09D91CD1AE37307A0297EC5192AE0686513B85FB5AECC87EFCBFE103F52>
- thyssenkrupp. (2018). *Water electrolysis: Power to gas*. Retrieved from thyssenkrupp: <https://www.thyssenkrupp.com/en/company/innovation/technologies-for-the-energy-transition/water-electrolysis.html>
- U.S. Department of Energy. (2013, March). *Tri-Generation Success Story*. Retrieved from U.S. Department of Energy: https://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/tri-generation_fountainvalley.pdf