

Environmental Impact of Fuel Cell Technology for Electric Power Generation: An Overview and Case Studies

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Abstract

The environmental impacts of fuel cell use depend upon the source of the hydrogen rich fuel used. By using pure hydrogen, fuel cells have virtually no emissions except water. Hydrogen is rarely used due to problems with storage and transportation, but in the future many people have predicted the growth of a 'solar hydrogen economy'. Photovoltaic cells convert sunlight into electricity. This electricity would be used to split water (electrolysis) into hydrogen and oxygen, to store the sun's energy as hydrogen fuel. In this scenario, fuel cell powered vehicles or generating stations have no real emissions of greenhouse or acid gases, or any other pollutants. It is predominantly during the fuel processing stage that atmospheric emissions are released by a fuel cell power plant. When methanol from biomass is used as a fuel, fuel cells have no net emissions of carbon dioxide (CO₂ a greenhouse gas) because any carbon released was recently taken from the atmosphere by photosynthetic plants. Any high temperature combustion, such as that which would take place in a spark ignition engine fuelled by methanol, produces nitrous oxides (NO_x), gasses which contribute to acid rain. Fuel cells virtually eliminate NO_x emissions because of the lower temperatures of their chemical reactions. Fuel cells, using processed fossil fuels, have emissions of CO₂ and sulfur dioxide (SO₂) but these emissions are lower than those from traditional thermal power plants or spark ignition engines due to the higher efficiency of fuel cell power plants. Higher efficiencies result

in less fuel being consumed to produce a given amount of electricity or to travel a given distance. This corresponds to lower CO₂ and SO₂ emissions. Fuel cell power plants also have longer life expectancies and lower maintenance costs than their alternatives.

This paper discusses an overview of the green house gas emissions, briefly looking in to the life cycle assessment of fuel cells. The paper also looks into some of the newer emission-free reformers for fuel cells. Atmospheric impacts of hydrogen are summarized along with some of the methods adopted to remove contaminants from fuel cells.

Introduction

Fuel cells are a future energy system with a high potential for environmentally-friendly energy conversion that can be used in stationary and mobile applications. Depending on the type of fuel cells, stationary applications include small residential, medium-sized cogeneration, or large power plant applications. In the mobile sector, fuel cells, particularly low-temperature fuel cells, can be used for heavy-duty and passenger vehicles, trains, boats, or auxiliary power units for air planes. Mobile applications also include portable low power systems for various uses.

The high efficiency can lead to a significant reduction of fossil fuel use and lower greenhouse gas (GHG) emissions. In addition, the electrochemical nature of the reaction, the low temperature in the reforming steps and the necessity to remove impurities in the fuel, such as sulfur, result in extremely low local emissions – an important feature especially in highly populated areas. In vehicle applications, particularly at low speed, reductions in noise emissions are expected. Other advantages include the elimination of gear shifts, the higher potential reliability, the compatibility with other electric or electronic devices, and new options with respect to the safety design of vehicles.

Thus, clear environmental advantages are expected in the applications of fuel cells. For an environmental evaluation of the different service supply options, an investigation of the complete life-cycle of these options is necessary to ensure that no environmental aspect is neglected. The appropriate instrument for this task uses life-cycle assessment (LCA).

With increasing environmental operation standards of modern energy conversion systems, the upstream and downstream processes, e.g., fuel supply or system production, are becoming increasingly relevant. In conventional road vehicles, the production of the vehicle contributes ~10% to the life-cycle GHG emissions, this share can increase to 30% in modern fuel saving vehicles. The absolute impact of production is more important than the relative contribution of the production. Often technologies exhibiting good characteristics in the use phase lead to higher absolute environmental impacts in the production phase due to the use of more sophisticated materials and components. For fuel cells, this implies that the LCA of producing the systems will be of higher importance.

GHG Emissions

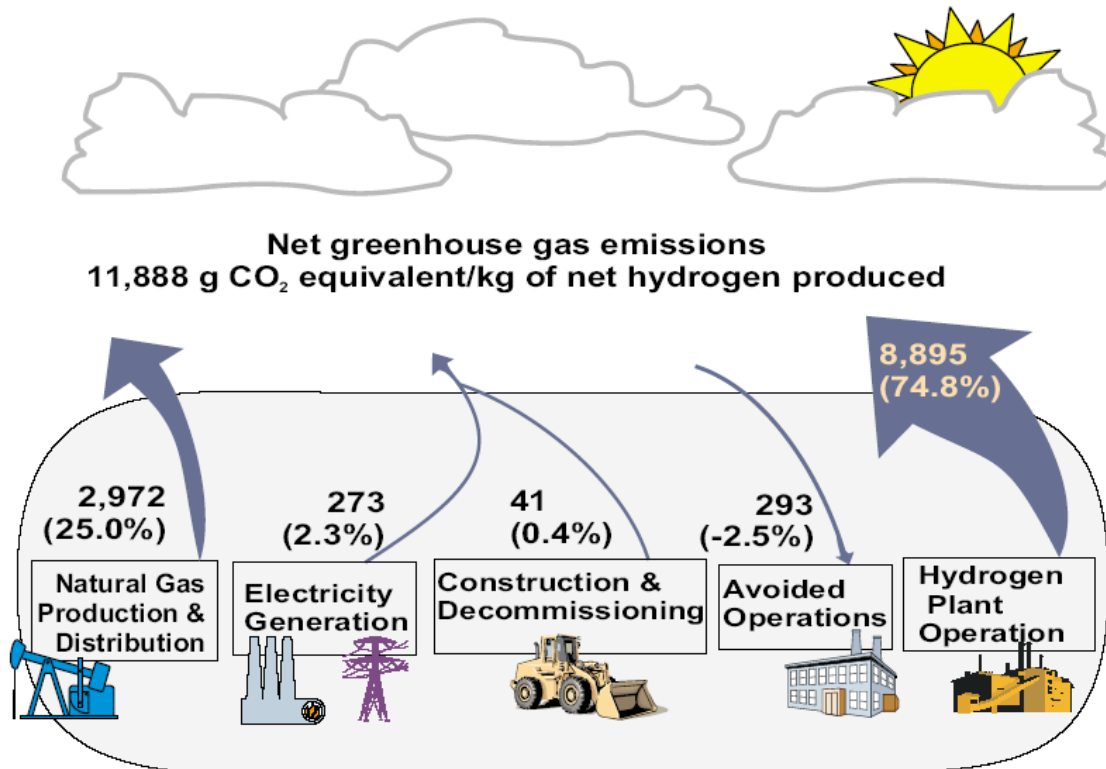
In terms of total air emissions, CO₂ is emitted in the greatest quantity, accounting for 99% (by weight) of the total air emissions. The CO₂ accounts for 89.3% of the system global warming potential (GWP), defined as a combination of CO₂, CH₄, and N₂O emissions expressed as CO₂-equivalence for a 100 year time frame. Methane accounts for 10.6% of the GWP. Sources of system global warming potential are summarized in Table 1 and Figure 1.

Table 1. Sources of System Global Warming Potential [Spath and Mann, 2001].

	Total (g/kg of H ₂)	% from construction and decommissioning ¹	% from natural gas production and transport	% from electricity generation	% from H ₂ plant operation	% from avoided operations ²
GHG Emissions (CO ₂ -eq)	11,888	0.4%	25%	2.3%	74.8%	-2.5%

¹Construction and decommissioning include plant construction and decommissioning as well as construction of the natural gas pipeline.

²Avoided operations are those that do not occur because excess steam is exported to another facility.



Avoided Operations = steam production from a natural gas boiler and natural gas production & distribution required to obtain the natural gas

Figure 1. Sources of net green house gas emissions [Spath and Mann, 2001].

Other than CO₂, methane is emitted in the next greatest quantity followed by non-methane hydrocarbons (NMHCs), NO_x, SO_x, CO, particulates, and benzene (see Figure 2). Most of these air emissions are a result of natural gas production and distribution. In terms of resource consumption, natural gas is used at the highest rate, followed by coal, iron (ore plus scrap), limestone, and oil. There is a large amount of water consumed primarily at the hydrogen plant, due to the steam requirements for reforming and the shift conversion. The majority of the system waste (72.3%) is generated during natural gas production and distribution. The remaining waste comes from electricity production (31.0%), and construction and decommissioning (3.8%). There is also a small amount of waste that is credited to the system due to avoided operations (-7.1%). Water emissions are small compared to the other emissions.

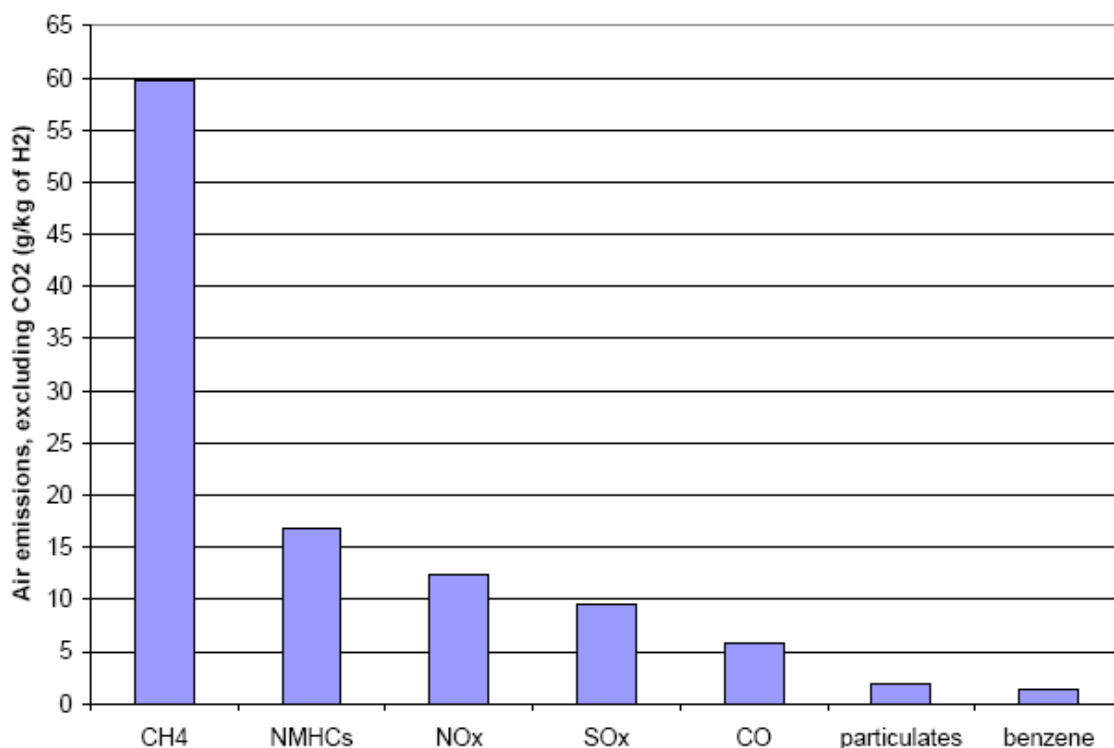


Figure 2. Air emissions from hydrogen production (excluding CO₂) [Spath and Mann, 2001].

Brief Introduction to Life Cycle Assessment (LCA)

The two key elements of an LCA are

- The assessment of the entire life-cycle of the investigated system, and
- The assessment of a variety of environmental impacts.

The first step is the goal and scope definition, in which the investigated product system, the intended application of the study, the data sources and system boundaries are described and the functional unit, i.e., the reference of all related inputs and outputs, is

defined. The criteria for selecting input and output flows or processes have to be specified. In this step, the data quality requirements, time-related and geographical coverage, the consistency, representatively and uncertainty of the data, and the critical review procedure have to be described. The life cycle inventory (LCI) analysis involves data collection and calculation procedures to quantify relevant inputs and outputs. These input and output flows involve consumed or produced goods as well as emissions, waste streams, etc. It is essential to consider all life-cycle stages, i.e., system production, operation, and disposal/recycling. Principally, there will be iterative steps leading to additional data requirements. The data collection usually follows the process chain, i.e., extraction, conversion, transport, production, use and disposal or recycling, respectively. The phases may be divided into smaller phases (unit processes). Every unit process of the chain has several incoming and outgoing material and energy flows that are carefully recorded. The main product or the byproducts, energy carriers, wastes and emissions into air, water, or soil, are outputs leaving the system boundaries (see Figure 3). The potential impacts of the inputs and outputs of the LCI are then determined by the impact assessment, which categorizes and aggregates the input and output flows to the biosphere to so-called impact categories, such as the global warming potential (GWP), by multiplication with characterization factors.

The life cycle of fuel cells in shown in the diagram below.

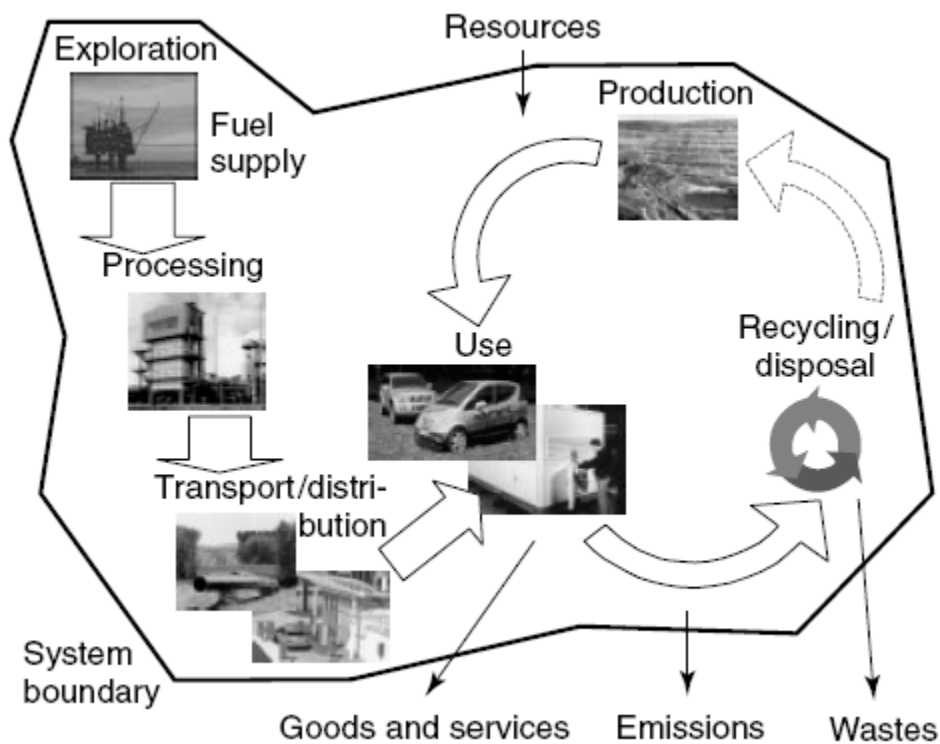


Figure 3. Inputs and outputs of fuel cell production in terms of its life cycle [Pehnt, 2003].

Impact categories include:

- Depletion of abiotic resources, such as fossil energy carriers and uranium, metals, or other materials;
- Depletion of biotic resources as a measure of overexploitation;
- GWP, because the emissions of GHGs influence the stability of solar irradiation and adsorption/reflection at the surface. These gases, e.g., carbon dioxide, methane, ozone and nitrous oxide, absorb the infrared radiation emitted by the earth and, thereby, increase the average temperature. A GWP can be attributed to these anthropogenic climate gases, which evaluate the efficacy in increasing the temperature relative to carbon dioxide for a given reference time;
- Depletion of stratospheric ozone particularly by chlorinated and brominated compounds, nitrous oxides, and indirectly by the greenhouse effect. Ozone depletion is usually quantified using the ozone depletion potential with CFC-11 as a reference substance;
- Acidification. Several substances, particularly sulfur dioxide, nitrogen oxides, and, indirectly ammonia, act as proton sources and acidify soil and water. The impact category can be operationalized using the acidification potential, which is the ratio of the number of potential proton equivalents per mass unit of a substance to the number of potential proton equivalents per mass unit of sulfur dioxide as a reference;
- Eutrophication involves the addition of mineral nutrients to soil and water, which results in shifts in increased algal growth, a reduction in ecological diversity and in some instances, a lack of oxygen. Mainly nitrogen and phosphorus components contribute to nitrification;
- Emission of ecotoxic and human toxic substances, such as pesticides, heavy metals and carcinogenic substances;
- Emission of radioactive substances; and
- Other impact categories, such as land use, noise, waste and odor.

Production of Fuel

The question of what is the right fuel is of high importance for the overall assessment of mobile fuel cells. Not only do the questions of storage systems and costs for fuel production or infrastructure considerations have to be answered, but also the environmental impacts for the different fuels are of importance. Fuel chains have been assessed in a number of different studies focusing on different environmental impacts, countries and applications [Pehnt, 2003].

Generally, the following factors are of relevance for the LCA of fuels:

- The primary energy carrier has an especially high impact on the impact categories of global warming and use of abiotic resources. The change from crude oil to natural gas, for instance, is associated with a decrease in CO₂ intensity due to the higher hydrogen to carbon ratio of natural gas. Switching to renewable primary energy carriers clearly reduces these impacts to low inputs of fossil energy along the production chain.
- The efficiencies and impacts of processing are also of importance. Today's crude oil-based fuels exhibit an extremely high energetic efficiency of more than 90%. In contrast, steam or combined reforming of natural gas for hydrogen and methanol production, respectively, have comparatively lower efficiencies. Thus, it is important to distinguish between the production of gasoline in average refineries (the so-called technology mix) and marginal

plants (new, single plants built to meet an increasing demand of a specific product and which, thus, exhibit significantly improved performance).

- The upstream and downstream processes involving different requirements for transportation or distribution, are the third important factor for the assessment of the fuel supply. The possible use of joint products (such as carbon black as a joint product of hydrogen production in the Kværner process or steam from H₂/steam reforming) can reduce environmental impacts if there is a market for the byproduct. Process steps involved in the production of gaseous and liquid hydrogen are shown schematically in Figure 4.

Hydrogen

Roughly 48% of the world wide hydrogen production is accomplished by steam reforming of natural gas, 30% by processing crude oil products, 18% by processing coal and 3% as a byproduct of the chlor-alkali process. The various hydrogen supply paths differ in terms of the distribution paths (pipeline transport of natural gas with onsite reforming, pipeline transport of gaseous hydrogen (GH₂), transport of liquid hydrogen (LH₂) by barge carriers and road trailers, and high voltage direct current (HVDC) transportation of electricity with hydrogen conversion close to the end user).

Natural gas steam reforming is one of the most common processes. The efficiency of that conversion depends on the use of the steam produced as a by-product. Gasification of biomass and water electrolysis using renewable electricity are attractive options for producing hydrogen with renewable primary energy carriers. However, the potentials of renewable energies must be taken into account because they can be used alternatively in stationary heat and power generation. Therefore, each option of using renewable energy should be assessed in terms of cost, efficiency, and storage requirements.

Stationary Systems

Fuel cells can be applied in various stationary applications, ranging from 1-kW_{el} systems for domestic heating and for combined heat and power production (CHP) for district heating or large buildings, up to megawatt applications for industrial cogeneration and electricity production without cogeneration. In each of these applications, different conventional systems are well-established, involving gas engine CHP, gas turbines, or combined cycle power plants. The environmental assessment needs to distinguish between the applications and compare fuel cells to different competitors.

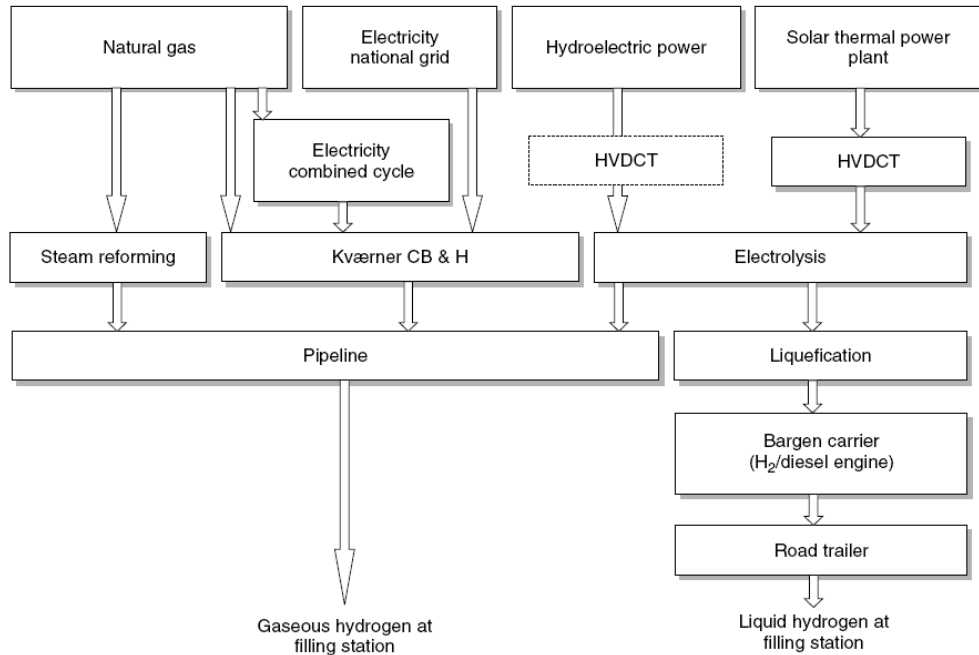


Figure 4. Process steps involved in the production of gaseous and liquid hydrogen [Pehnt, 2003].

Natural Gas

In the near- and mid-term future, natural gas will be the fuel of choice for stationary applications. The life-cycle of natural gas comprises the exploration, extraction, processing, and transport to the consumer. LCAs of the natural gas supply must be carried out specifically for each country. Parameters influencing the LCA of natural gas include:

- The transport mode and distance (pipeline distance, transportation as liquid natural gas, etc.);
- The specific energy requirements for compression and processing;
- The methane leaks in long-distance and the local distribution pipelines; this issue has been raised in connection with Russian natural gas where, due to the extreme climate and the poor pipeline conditions, leakage rates between 1 and 10% have been reported [Pehnt, 2003]. The high GWP of methane leads to a significant influence of that leakage rate; and
- SO₂ emission factors for the processing of sour natural gas.

Renewable Fuels

For long-term applications, biogen and other renewable fuels are considered suitable for use in fuel cells. Options include gasification of wood and other biomass, anaerobic digestion of biowaste, sewage, manure, etc. In the latter case, fuel cells are also attractive because of the low heat to power ratio. In many biogas plants, for instance, part of the heat produced in the cogeneration plant is wasted due to a lack of heat demand. Electricity, in contrast, can easily be fed into the grid. Generally, most applications (household, offices,

industries) will have reduced heat consumption in the future due to energy savings, whereas electricity consumption will grow or at least stay constant.

Operation of Fuel Cell Power Plants

The operation of fuel cell power plants leads to minimal direct emissions due to relatively low (compared to combustion engines or turbines) operating temperatures (leading to almost zero thermal NO_x emissions) and gas clean-up requirements (e.g., for required SO_2 removal). The emissions are typically dependent on the load only. As a first order approximation, these emissions can be applied to all natural gas reforming stationary plants as long as the fuel, the reformer type, temperature, and fuel utilization are comparable. Generally, these emissions are very low in comparison with emissions from other life cycle stages so that the uncertainty is not very relevant for the total results. It is important to consider emission developments in the conventional systems as well. Improved three-way catalysts for gas engines, low- NO_x combustion chambers and other primary and secondary measures for gas turbines, as well as NO_x and SO_2 abatement technologies for large power plants, have drastically reduced exhaust emissions.

Electrical Efficiencies

Essential for systems LCA are the assumed electrical and thermal efficiencies, which differ according to the system and the fuel cell type. The potentially high electrical efficiency of fuel cell power plants is a major advantage of this system. For each power range, fuel cells offer higher efficiencies than the conventional competitors, as shown in Figure 5.

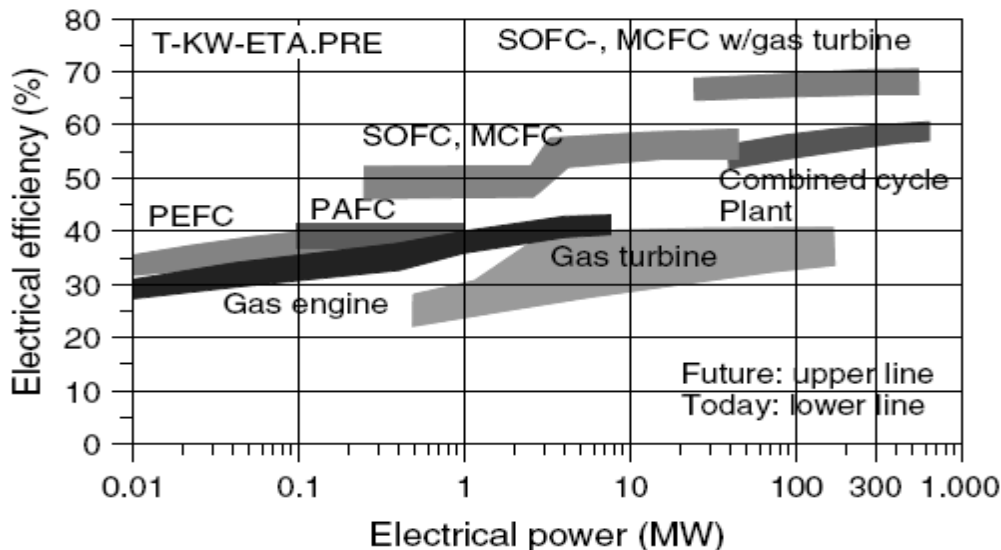


Figure 5. Typical electrical efficiency of various technologies as a function of the electrical power range with natural gas as fuel [Pehnt, 2003].

With natural gas as a fuel in the low power range, PEFCs have electrical efficiencies on the order of 32–35% for house heating systems and 40% in the 100 kW_{el} range. In a large

number of demonstration projects, these numbers have already been demonstrated for PAFCs. In some systems, especially of the early generations, however, degradation effects lowered the lifetime efficiency. High-temperature fuel cells offer efficiencies near 50% when used in lower power regimes.

Thermal/Total efficiency

For CHP, the thermal efficiency is also of importance. The thermal efficiencies of conventional systems have been a key parameter for past optimization of the systems. Gas engines, for instance, can reach total efficiencies approaching 100% (LHV) due to use of the condensing heat. In practice, more than 90% total efficiency is achievable. Combined cycle CHP plants can also reach thermal efficiencies of 50% resulting in total efficiencies of nearly 90%. Thermal efficiency is a function of the temperature of the heat medium. If only steam is needed, which is the case in many industrial applications, it will be lower than for a low temperature district or house heating system. Also, thermal efficiency is a function of the load. Generally, current target values for most fuel cell systems are approximately 80% total efficiency. To successfully compete with conventional systems, future work should also focus on increasing thermal efficiencies by using the reformer exhaust heat and other heat sources.

The Total Picture

In Figure 6, various environmental impacts of fuel cell energy production including all life-cycle stages are compared for competing technologies. The heat produced in cogeneration systems is credited with a modern natural gas burner; if the system produces x kWh of electricity and y kWh of heat simultaneously, the impacts of producing y kWh of heat with a modern natural gas are subtracted from the total impacts because this heat production is substituted by the cogeneration system. It is obvious that high-temperature fuel cells in this application offer significant advantages compared to the competing technologies. Considering the GWP, a solid oxide fuel cell (SOFC) in cogeneration is 12% more efficient than a gas turbine and even 47% more efficient than a German electricity mix. At the same time, a gas turbine in the 3MW_{el} power range produces less GHGs than a SOFC without cogeneration. Combined heat and power production generally should be promoted. In addition, both the electrical and total efficiency need to be optimized. This is even more important for PEFCs (polymer electrolyte fuel cells) in the $100\text{ kW}_{\text{el}}$ range where engine CHPs show total efficiencies exceeding 90% (LHV) because the heat of condensation is used. However, the development of high-efficiency centralized electricity production based on fuel cells decreases the gap between cogeneration and noncogeneration plants.

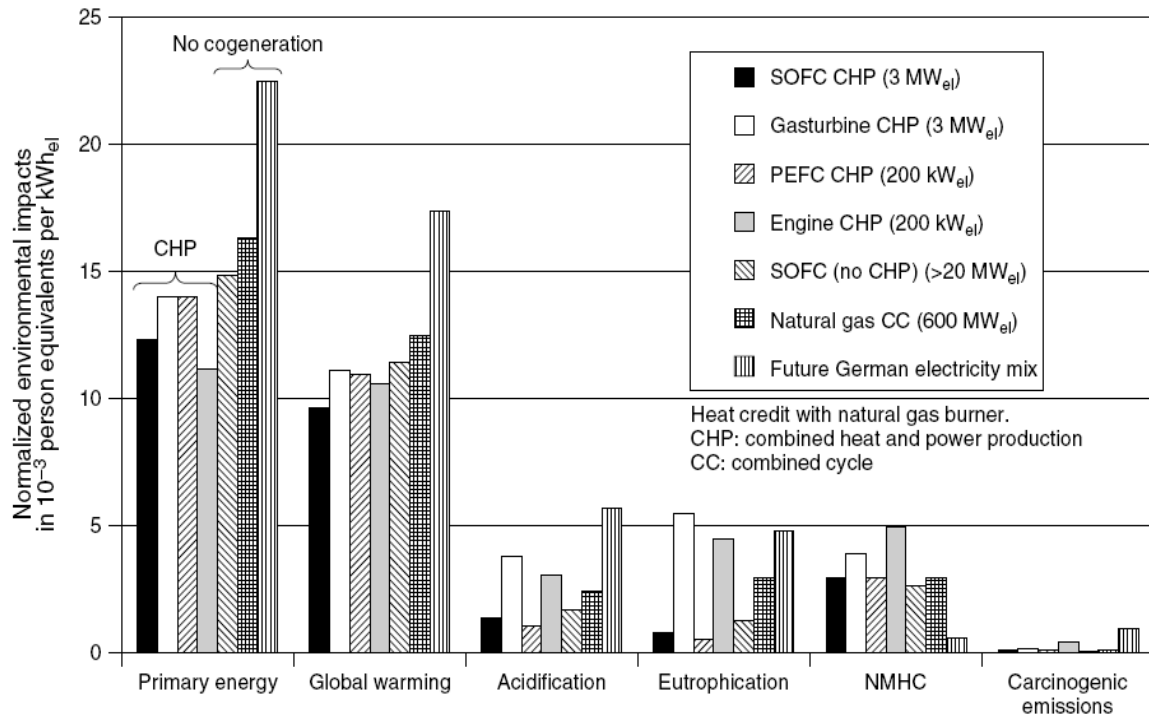


Figure 7. Environmental impacts associated with primary energy, global warming potential, acidification, eutrophication, nonmethane hydrocarbons, and carcinogenic emissions for various techniques employed to generate hydrogen [Pehnt, 2003].

Hydrogen Economy

Hydrogen, like electricity, is not an energy resource, but an energy carrier [Shinnar, 2003]. No hydrogen in a combustible form is available in nature. There is a vast amount of hydrogen in water, but it takes more energy to extract it than the hydrogen provides. This is a fundamental law of nature that no research can change. Hydrogen can be made from fossil fuels or by electrolysis of water. Hydrogen from fossil fuels would require more fossil fuel than presently used for the same purpose and would significantly increase our energy imports and the global warming potential. If the hydrogen is obtained by electrolysis using solar or nuclear derived electricity, the cost would be significantly higher. Moreover, direct use of electricity would cost half as much as via the hydrogen route. Electricity could be slowly introduced into the existing grid whereas it is nearly infeasible to switch to a radically new source of hydrogen that requires a new distribution system.

It is easier and more efficient to transport hydrogen than natural gas over large distances. The energy loss for transportation of hydrogen in pipelines depends on the design and cost. It has been proposed to use present pipe lines designed for natural gas, although there remain several severe questions whether it is safe to do so because of the potential leaking of hydrogen through the valves. For hydrogen, we need to triple the volume to supply the same energy as natural gas [Shinnar, 2003]. Therefore, if we were to use existing

pipelines, the velocity in the pipe would be tripled (pressure drop increases by a factor of nine), which makes hydrogen transport much less efficient than either electricity or natural gas in the natural distribution system. The transport losses of methane and electricity over large distances are nearly equal at 5–7% (with electricity having a slight advantage over large distances). Using the same pipe lines for hydrogen could increase the losses to ~20% [Shinnar, 2003]. In reality, it is very doubtful that we could use natural gas pipelines or local distribution system for hydrogen. Hydrogen requires totally different fittings and pipe specifications. Additionally, it would require installation of much larger compressors.

Safety Issues Concerning Hydrogen

The safety issues primarily focus on the flammability and explosive qualities of gaseous hydrogen, as any accident involving the exposure of liquid hydrogen to the environment means evaporation into a gaseous state. The possibility also exists of a leak in piping or industrial equipment, presenting problems of detection and fire suppression. As hydrogen ignites in air at very low concentrations, and ignition can be instigated by something as simple and commonplace as a static electric spark, these potential problems must be monitored very carefully. Another factor to be examined when considering pipeline delivery of hydrogen gas in a municipal energy setting is the efficiency with which energy can be transported from its point of origin to the consumer. Delivery of electric power from large power plants over high voltage power lines has a certain energy loss factored in, increasing its cost. With efficient pipeline delivery of hydrogen gas, a well-maintained system at our present level of technical ability can give the consumer equal or greater value for their energy dollar, as more of the energy put in to the system actually reaches the customer. Since gaseous hydrogen is 14 times lighter than air, if the gas escapes containment, it immediately disperses into the atmosphere with no toxic consequences. With improved storage mediums being developed, the likelihood of accidental release, already small, becomes an even lesser possibility. Metal hydrides, a chemical bonding of hydrogen with various metallic alloys, preclude the uncontrolled release of hydrogen, as heat energy must be applied to the hydrogen-bearing alloy to release its hydrogen load. Some types of hydride storage at ambient room temperatures can store larger amounts of hydrogen than an equal volume of liquid hydrogen. A new storage method using an experimental material known as activated carbon shows promise of storing ever greater volumes of hydrogen in smaller spaces [www.altenergy.org]. This is even more efficient than metal hydrides as a given volume of activated carbon can safely store 2.4 times the amount of hydrogen as the same volume of compressed gas stored at 3,000 psi [www.altenergy.org].

Energy Storage

Both hydrogen and electricity are storable. The question is what is the efficiency and cost involved? Electricity has several options of storage. For a thermal solar plant, there is an option to store the heat transfer fluid. While this is relatively cheaper and involves no efficiency losses, costs limit storage to one day. The cheapest storage is hydraulic, but it still has an efficiency of 80%. The same is true for batteries. Hydrogen storage by liquefaction is even more expensive and has larger efficiency losses. If we include the efficiency of making hydrogen from electricity, it is clearly more costly and less efficient. Hydrogen storage has one

advantage – it requires much less weight, which is important for cars. The best hope for the future is to reduce this by a factor of two (hydrogen generation from electricity including compression has very optimistically an efficiency of 70%, but currently is ~55%) [Shinnar, 2003].

Hydrogen as a Fuel

Hydrogen is the most attractive fuel for fuel cells having excellent electrochemical reactivity, providing adequate levels of power density in a hydrogen/air system for automobile propulsion, as well as having zero emissions characteristics. Historically, the trend in energy use indicates a slow transition from fuels with high carbon content, beginning with wood, to fuels with more hydrogen. Fossil fuels release varying quantities of carbon dioxide into the atmosphere: coal (having the highest carbon content), then petroleum, and finally natural gas the lowest carbon dioxide emitter per thermal unit. Hydrogen obviously releases no carbon dioxide emissions when burned. Hydrogen (H_2) is the most abundant element in the universe, although practically all of it is found in combination with other elements, for example, water (H_2O), or fossil fuels such as natural gas (CH_4). Therefore, hydrogen must be manufactured from either fossil fuels or water before it can be used as a fuel. Approximately 95% of all hydrogen is produced by steam reforming of natural gas, the most energy-efficient, large-scale method of production [www.hawaii.gov]. Carbon dioxide (CO_2) is a by-product of this reaction.

Hydrogen can also be produced by gasification of carbon containing materials such as coal, although this method also produces large amounts of carbon dioxide as a by-product. Electrolysis of water generates hydrogen and oxygen. The electricity required to electrolyze the water could be generated from either fossil fuel combustion or from renewable sources such as hydropower, solar energy or wind energy. In the longer term, hydrogen generation could be based on photo biological or photochemical methods. While there is an existing manufacturing, distribution, and storage infrastructure of hydrogen, it is limited. An expanded system would be required if hydrogen fuel were to be used for automotive and utility applications. While a single hydrogen production/distribution/storage system may not be appropriate for the diverse applications of fuel cells, it is certainly possible that a combination of technologies could be employed to meet future needs. All of the system components are currently available but cost-effective delivery and dispensing of hydrogen fuel is essential. If hydrogen were to become available and affordable, this would reduce the complexity and cost of fuel cell vehicle' enhancing the success of the technology. The hydrogen economy is an energy system based upon hydrogen for energy storage, distribution, and utilization [www.hawaii.gov]. Hydrogen fuel has been reported to be unsafe [www.hawaii.gov]. However, all fuels are inherently dangerous (e.g., how much thought do you give to the potential dangers of gasoline when you drive your car?). Proper engineering, education, and common sense reduce the risk in any potentially explosive situation. A hydrogen vehicle and supporting infrastructure can be engineered to be as safe as existing gasoline systems. Dealing with the perception and reality of safety will be critical to the successful widespread introduction of hydrogen into our energy economy.

The Potential for Hydrogen Energy

The element hydrogen offers the potential for a nearly inexhaustible supply of energy at reasonable cost without harmful impacts on the environment. The use of hydrogen as a fuel has been proposed to U.S. reliance on fossil fuels. In fact, many esteemed scientific and technical panels have predicted a future hydrogen energy economy that will use hydrogen to produce electricity via power plant's, fuel electric transportation, and serve domestic (heating and cooking) uses [www.hawaii.gov]. In the past 30 years, significant research and development activities have focused on improving the cost of manufacturing, delivering, and using hydrogen.

Hydrogen is viewed as a long-term energy solution due to the following reasons:

- It is potentially an inexhaustible supply of energy;
- It can be produced from many available primary energy resources;
- It easily converts to electricity with higher efficiencies than combustion processes;
- It improves the utilization of electricity from intermittent and distributed renewable resources;
- It is nonpolluting and nontoxic;
- When generated using renewable energy, it becomes a versatile, high-energy fuel with minimal environmental impact;
- It can drive fuel cells, which provide a highly efficient and reliable source of energy
- Modular means are available for providing distributed energy for the utility sector.

The drawback to the use of hydrogen energy has been cost, as it remains expensive to produce and use hydrogen when compared to fossil energy alternatives. However, significant progress and technological advances in the last five years for both producing and using hydrogen makes considering hydrogen energy today a prudent alternative.

There is an advantage for distributed electricity generation to save the cost and problems of long range distribution on the grid. This is partially true, but neither hydrogen nor fuel cells have any potential role. Today many natural gas fueled combined cycle power plants of 500 MW are built all over the country based on local needs. These are real distribution electricity generation reducing the load on the national grid. Small distribution units are only useful for remote locations and in under developed countries and even for such uses, fuel cells have to compete against small turbines and diesel generators. Compared to combined cycle power plants , distributed electricity generators have a smaller impact on the required carrying capacity of the grid, and no impact on the cost of the power company to maintain the local distribution system, almost half the cost of the power. The electric company has to maintain its generating capacity and maintain the distribution grid. All the fuel cells saves is the cost of electricity itself. The argument that it is cheaper then extending the natural grid is partially correct, but it is much cheaper to reduce the requirements of the national grid by the local combined cycle plant, which has only half the greenhouse emissions, compared to local fuel cells. Furthermore, it gives the power company the electricity whenever it needs it. When we ultimately go to solar energy, then transferring it to hydrogen and back to electricity makes no sense as we will get less than half the electricity back and a hydrogen distribution network would cost more than increasing the grid capacity.

Alternative Choices to Reduce Energy Imports and Global Warming

The main goals are reduction in oil imports, reducing carbon dioxide emissions, and in the long run, use of alternative energy. There are, however, much cheaper ways to achieve the same goals that can be gradually introduced starting now. The U.S. consumes 15 million barrels a crude oil daily, of which nine million barrels are imported. The main products are gasoline (8.8 million barrels a day), distillates (3.8 million barrels a day), and petrochemicals (approximately 1.0 million barrels a day). There are less expensive ways to cut about 4-5 million barrels of oil from imports, simultaneously reducing global emissions. It has been reported in a recent National Research Council study [Shinnar, 2003] that corporate average fuel economy standards could be cost effectively increased by as much as 12 to 27% for automobiles and 25 to 42% for vehicles built on light duty truck frames such as SUVs and vans. Only conventional technology was used and the cost of the additional technology was more than repaid by future fuel savings. This could reduce gasoline consumption by at least 20 to 30% a day and reduce green house gas emission proportionately. Even greater fuel savings are possible if additional technology is utilized such as hybrid vehicles, which are much more efficient than hydrogen cars. Although costs can be entirely recaptured in the future fuel savings, the costs could be significantly less than using hydrogen cars. One is the large scale introduction of hybrid cars, more efficient than either hydrogen cars or present cars, and introducing efficiency requirements for SUVs. This could reduce gasoline consumption by at least 20-30% reducing green house emissions by the same amount. Another reduction of both import and carbon dioxide emissions could be achieved by modifying the refinery process. Gasolines and distillates contain a mixture of paraffins (14.3% hydrogen), naphthenes and aromatics (7 to 11% hydrogen). Paraffins are environmentally superior to aromatics and naphthenes, as they have significantly lower emissions, and generate less carbon dioxide per BTU. Present gasoline and distillates contain about 30% aromatics. Ultimately, the only way to reduce global warming, to reduce pollution and achieve energy independence, is by developing alternative sources for electricity, especially solar energy. This would also require introducing electric cars. All these options require starting their implementation long before they are needed. Large scale implementation itself will reduce costs significantly , but how do we get there? In the 1970s, there was a large drive to reduce emissions from coal power plants. The technology to do so was available in the form of scrubbers. It would have cost 20 to 30 million dollars. Power companies strongly objected, as they had no assurance that they would be allowed to recover the costs. The U.S. spent the same 20 million dollars in research, but no performance results were obtained [Shinnar, 2003]. If instead, it would have found ways to implement scrubbers, competition would have reduced the cost and improved the technology. We will never sequester carbon dioxide unless it becomes profitable for those doing so. The US already captures 100 million tons of CO₂ a year and releases the CO₂ again [Shinnar, 2003].

Better Thermal Efficiency

For almost all applications, use of electricity is far more efficient than hydrogen. Generation of hydrogen involves a large energy loss. The most important alternative energy sources, solar and nuclear, generate electricity as the primary product. To generate hydrogen from electricity, it will be necessary to generate twice the amount of electricity and cost at least twice as much as using the electricity directly [Shinnar, 2003]. This alone clearly shows that a

hydrogen economy makes no sense. The thermal efficiency is lower for almost all the uses of hydrogen, as a result, it will cause more global warming.

Emission-Free Fuel Reformers for Fuel Cells

Conventional fuel reformers are complex, multi-component devices which produce large amounts of CO₂ emissions. Fossil fuel-based power sources are major producers of greenhouse gas (mostly, CO₂) emissions. Fuel cells (FCs) seem to be an answer to this environmental problem, however, the main question remains: what fuel and fuel processing technology should be used to produce hydrogen in fuel cells? Conventional fuel reformers are based on complex, multi-stage processes, such as steam–methane reforming (SMR), partial oxidation (POx) or autothermal reforming (ATR). Initially, hydrogen-containing compounds (e.g., hydrocarbons, alcohols, etc.) react with oxidants (water and/or oxygen) resulting in the production of the mixture of hydrogen and carbon monoxide (synthesis gas). This is followed by gas conditioning (e.g., low- and high-temperature water–gas shift (WGS) reactions, preferential oxidation, etc.) and gas separation and purification stages. As a result, the conventional fuel reformers produce large amounts of CO₂ emissions which significantly diminishes an environmental appeal of fuel cell-based power systems. One alternative to conventional fuel reforming technologies is pyrolysis (or cracking, decomposition) of hydrocarbons into hydrogen and carbon in an air/water-free environment.

No carbon oxides are formed during the process, due to the absence of oxidants in the reactor; instead, the process produces a valuable byproduct – clean carbon. Another advantage is the production of hydrogen in a single step, without the water-gas shift reaction (WGS) and CO₂ removal stages which significantly simplifies the system. The process is applicable to a variety of gaseous and liquid hydrocarbon fuels, and it potentially produces a stream of hydrogen with the purity up to 95 vol.% (the balance being methane). Thus, the major advantages of fuel reformers based on hydrocarbon pyrolysis (namely, pyrolytic fuel reformers, PFR) include: (i) fuel flexibility, (ii) relative simplicity and compactness, (iii) production of clean carbon byproduct, and (iv) significant reduction (potentially, elimination) in CO₂ emissions.

Thermal decomposition of hydrocarbons occurs at high temperatures (in case of methane, 1400°C and higher). The use of transition metal catalysts (e.g., Ni, Fe, Co) significantly reduces the maximum temperature of the process, however, there is a catalyst deactivation problem (fouling) associated with the carbon build-up on the catalyst surface. Fuel reformers operating in a cyclic pyrolysis-regeneration mode have been developed where carbon produced during hydrocarbon decomposition stage was combusted, providing heat for the endothermic reaction. Burning the carbon produces more heat than is required to drive the endothermic hydrocarbon decomposition reaction; this results in the reduction in the overall energy efficiency and production of significant amounts of CO₂ byproduct. The use of carbon-based catalysts can potentially solve catalyst regeneration and CO₂ emission problems. The main objective is the development of efficient CO₂-free fuel reformers based on catalytic pyrolysis of hydrocarbon fuels for mobile and portable fuel cell applications. CO₂-free production of hydrogen-rich gas and carbon byproduct can be accomplished via pyrolysis of selected hydrocarbons (e.g., propane, methane, gasoline vapor, etc.) in the presence of

carbon catalysts. A great deal of effort has been directed toward the development of efficient and stable carbon catalysts for the process [Muradov, 2003].

High-surface area carbons can be employed as catalysts in hydrocarbon pyrolysis experiments. The hydrocarbon feedstock enters the lower section of a catalytic reactor, thermally decomposed within the catalyst layer, and the products of its decomposition (hydrogen mixed with small amounts of methane) exit via a ceramic filter located at the top section of the reactor. The reactor temperature and the hydrocarbon residence time within the catalytic zone are maintained in the range of 850–950°C, and 20–50 s, respectively (depending on the hydrocarbon). Before the pyrolysis experiments, the reactor is purged with an inert gas (Ar) at 700°C for 1 h to remove all the adsorbed water and air from the catalyst surface. Methane and propane are directly introduced into the reactor, whereas, gasoline is evaporated and pre-heated to 250°C before entering the reactor. Initially, the catalyst fills approximately one-third of the reactor volume, leaving the rest of the space for the carbon to be produced during hydrocarbon pyrolysis. As the hydrocarbon pyrolysis reaction proceeds, the produced carbon gradually fills almost the entire volume of the reactor. At this moment, the introduction of hydrocarbon into the reactor is cut off, the reactor is allowed to cool down, and the carbon is dislodged from the reactor.

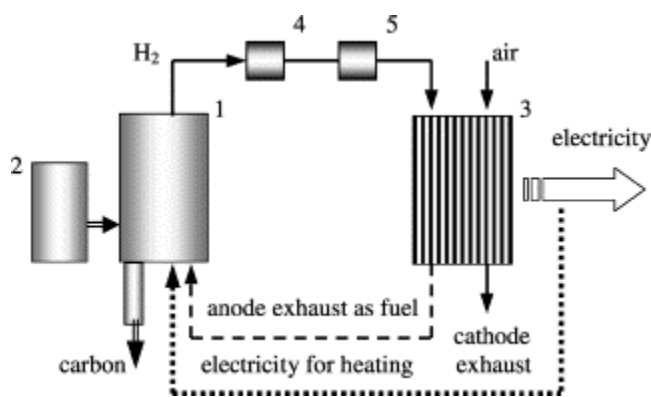


Figure 7. Emission-free fuel reformers for mobile and portable fuel cell applications [Muradov, 2003].

Figure 7 depicts the conceptual block-diagram of a power generation system comprising a pyrolytic fuel reformer combined with a fuel cell intended for mobile or portable applications. A hydrocarbon fuel (preferably, propane, compressed natural gas, or gasoline vapor) is directed from a fuel tank (2) to the PFR (1) where it is decomposed over the carbon catalyst at 850–950°C producing a stream of the hydrogen-rich gas with the average [H₂]=80 vol.%, the balance being methane (for the comparison, POx- and ATR-reformers produce the gas with [H₂]=35–40 vol.%). The hydrogen-rich gas enters the anode compartment of the fuel cell (e.g. polymer electrolyte membrane, PEM, FC) where it electrochemically reacts with oxygen (air) producing dc electricity.

If commercial hydrocarbon fuels are to be used in the power generator, then a sulfur trap and a methanator should be added to the scheme to prevent rapid

deactivation of PEM FC by the reactive impurities (e.g., CO and H₂S) originating from moisture and sulfurous compounds potentially present in these fuels. Alternatively, the reactor can be equipped with a hydrogen-selective membrane (e.g., Pd–Ag, or ceramic membrane). The advantages of using a membrane are two-fold: the production of high purity hydrogen (>99 vol.%) and possible decrease in the maximum temperature of the process (due to the shift in the equilibrium concentration of hydrogen in the presence of a membrane).

There are several options for providing the heat input to the reactor to drive endothermic hydrocarbon decomposition reactions. These options include (in the order of minimization of CO₂ emissions): (i) catalytic combustion of a fraction of the hydrocarbon fuel (in the case of propane, approximately 5% of the total amount), (ii) catalytic combustion of the anode exhaust gas (hydrogen–methane mixture), and (iii) the resistive heating of the reactor (equipped with a membrane) using a fraction of the electrical output of the FC (in case of propane, approximately 20% of the output) [Steinberg, 1999]. The latter case presents a near zero-emission option. PFR utilizes 50–60% (depending on the hydrocarbon) of the total chemical energy of the fuel leaving the remainder in the form of stored energy, i.e., carbon (rather than CO₂ byproduct).

The carbon product in the form of fine particulates remains within the reactor for the duration of a power generating cycle and is dislodged from the reactor during a refueling operation (e.g., by blowing with nitrogen into a special container). A quarter or third of the total amount of carbon particulates produced remains in the reactor as seed particles for a new cycle of pyrolytic reforming process. The production of 1 kg of hydrogen is accompanied with the co-production of approximately 3 kg of carbon (if natural gas is used as a fuel) or 4.5 kg of carbon (if propane is the fuel). The carbon product collected from mobile and portable power systems is to be directed to a central carbon storage and processing facility. There are several important potential application areas for the carbon product, e.g., metallurgical industry (carbon electrodes for the aluminum and ferro-alloys production), tires, plastics, construction materials, etc.

It is technically feasible to develop a hydrocarbon fuel reformer for mobile/portable fuel cell applications without (or drastically reduced) CO₂ emissions. The lack of bulky gas conditioning and separation stages potentially makes the reformer more compact and simple compared to conventional reformers. Furthermore, depending on the mode of operation, the pyrolytic reformer can produce either high purity hydrogen (membrane option), or CO/CO₂-free hydrogen-rich gas with the average [H₂]=80 vol.%, the balance being methane (which compares favorably with the quality of reformat gas, i.e., [H₂]=35–40 vol.%, produced by POx- and ATR-based reformers). Widely available and inexpensive propane is the preferred fuel for the pyrolytic reformer, however, gasoline or compressed natural gas could also be efficiently used for the production of hydrogen.

PFRFC-based power systems could be advantageously used in many emission-restricted application areas, e.g., mines, aerospace, recreational and emergency vehicles, etc. Potentially, their contribution to the general transportation

area will increase once CO₂ becomes a regulated pollutant. Due to the lack of emissions and moving parts, PFRFC power systems may find an important application in the military (soldier power). Besides the use in mobile and portable devices, PFRFC systems could be advantageous for the distributed power generation in many emission-sensitive areas (such as hospitals, recreational facilities, tunnels, etc.).

Atmospheric Impact of Hydrogen

Molecular hydrogen (H₂) is a trace component of the lower atmosphere. Molecular hydrogen can contribute to the following environmental issues:

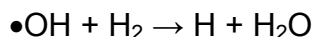
- ground-level ozone production;
- tropospheric ozone production;
- climate change; and
- stratospheric ozone chemistry.

These are discussed briefly below.

Ground Level Ozone production

During summertime, the United Kingdom [AEAS Technology, 2001] frequently experiences photochemical pollution episodes, which are characterized by concentrations of ozone which exceed environmental quality standards for the protection of human health and vegetation (e.g., crops). Ozone is not emitted directly into the troposphere, but is a secondary photochemical pollutant usually formed from the sunlight-initiated oxidation of volatile organic compounds (VOC, for example hydrocarbons) in the presence of nitrogen oxides (NO_x). Under conditions characteristic of photochemical pollution episodes, its formation and transport can occur over hundreds of kilometers, with the ozone concentration at a given location influenced by the history of the air mass over a period of up to several days.

One of the key factors in assessing episodic ozone production is the rate of reaction of ozone-precursor compounds with hydroxyl radicals (•OH).



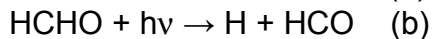
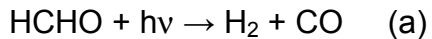
The reaction of H₂ with •OH is slow with a rate coefficient which is comparable to that for the reaction of •OH with methane. The atmospheric lifetime of methane (and hence hydrogen) with respect to this reaction is about 10 years.

Tropospheric Ozone Production

The complete oxidation of hydrogen to water in the troposphere leads to the production of ozone (O₃), as shown by the equation:



The tropospheric chemistry of hydrogen is strongly coupled to that of methane as the oxidation of methane produces formaldehyde (HCHO) as an intermediate. One of the photodissociation reactions with formaldehyde produces molecular hydrogen.



The molecular route (a) is a major source of atmospheric hydrogen [Simmonds *et al.*, 2000]. The free radical route (b) is a significant pathway in the formation of ozone and photochemical smog conditions. As HCHO is also produced in the oxidation of other organic compounds, these compounds are also sources of molecular hydrogen.

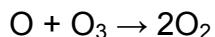
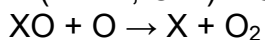
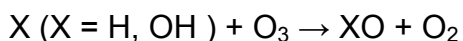
Climatic Change and Radiative Forcing

Hydrogen is not radiatively-active and therefore does not have a direct impact on climate change (i.e., it is not a greenhouse gas). This is due to two reasons: (1) the fundamental vibration of hydrogen is not infrared active and (2) the wavelength of the vibration (2.3 μm) is outside the key atmospheric window region between 7–13 μm .

Hydrogen does have an indirect impact on climate change as (a) it is involved in the production of tropospheric ozone (a strong greenhouse gas) and (b) it can modify the concentration of methane (another greenhouse gas) through its effect on the concentration of the hydroxyl radical ($\bullet\text{OH}$).

Stratospheric Ozone Chemistry

Together with water vapor itself and methane, molecular hydrogen is an important source gas that controls the stratospheric water vapor budget. These three species act as sources of odd hydrogen ($\bullet\text{H}$, $\bullet\text{OH}$), which can catalyze ozone destruction in the upper stratosphere.



Low Temperature Membranes and the Need for High Temperature Membranes

Polymer electrolyte membrane fuel cells operate at relatively low temperatures, typically around 80°C (176°F). Low temperature operation allows them to start quickly (less warm-up time) and results in less wear on system components, resulting in better durability. However, it requires that a noble-metal catalyst (typically platinum) be used to separate the hydrogen's electrons and protons, adding to system cost. Traditional low temperature fuel cells generally have problems when operating on reformat gas produced from hydrocarbons such as methanol, gasoline, or natural gas. In the fuel processing of the hydrocarbon to hydrogen, carbon monoxide (CO) is produced as a by-

product. This CO poisons the catalyst of the fuel cell; as a result, the CO has to be removed from the gas stream. Today's fuel cells cannot tolerate more than about 20 ppm CO in the reformat stream, making the required fuel processing complex and expensive. The platinum catalyst is extremely sensitive to CO poisoning, making it necessary to employ an additional reactor to reduce CO in the fuel gas if the hydrogen is derived from an alcohol or hydrocarbon fuel, further adding to the cost. Developers are currently exploring platinum/ruthenium catalysts that are more resistant to CO [Upadhyaya, 2004]. The low temperature can tolerate only a few ppm of sulfur compounds. By raising the operating temperature of the fuel cell above 150°C, this poisoning effect has little relevance. This greatly lowers the complexity of the fuel processor by removing the necessity for a multi-stage CO clean-up system. The CO cleanup system is generally the most space consuming reactor of the series required to produce the fuel cell feed gas. It is also the most expensive reactor and the most difficult to control. High temperature PEM fuel cell technology also makes it possible to simplify the overall power system with respect to water and thermal management, due to the fact that above 100°C the water management involves only a single phase (no liquid condensation), and the temperature gradient is larger for efficient cooling. Another advantage of high operating temperature is that high value heat can be recovered. Humidification is energy intensive and increases the complexity of the system. The use of water to humidify the gases limits the operating temperature of the fuel cell to less than the water's boiling point and therefore decreases the potential for co-generation applications. The low temperature is insufficient to perform useful co-generation.

High-temperature solid-polymer electrolyte membranes capable of operating at 150–200 °C are at an early stage of development [Doss *et al.*, 2002]. These are being advanced as alternatives to Nafion-based solid-polymer electrolyte membranes that operate at less than 90°C. An advantage of operating at higher temperatures is the reduced sensitivity of the electrocatalyst to carbon monoxide in the anode stream. Reduced CO sensitivity and higher temperature operation may make it possible to lower the loading of anode and cathode catalysts. This is important because studies indicate that the precious-metal (Pt and Ru) content of the electrocatalysts is the single largest contributor to the total estimated cost of Nafion-based polymer electrolyte fuel cell (PEFC) systems [Arthur D. Little, Inc., 2000]. Also, the reduction in overpotentials at higher temperatures can potentially lead to improvement in current density and a lighter and more compact stack. Specific weight and volume of PEFC stacks are of concern when dealing with Nafion-based membranes. For the high temperature membrane operated at 150°C, the water gas shift reaction is usually sufficient for producing hydrogen-rich fuel gas because the anode catalysts can tolerate CO limits greater than 10 ppm. The PROX (the preferential oxidation reactor) is eliminated. As a result, the cost, complexity and weight of the fuel processing system is reduced.

On the whole, high temperature membranes offer the following advantages:

- a higher resistance to carbon monoxide from reformed hydrogen gas;
- cost-effective water management within the cell;

- a higher operating temperature leads to more efficient use of heat for household and commercial use; and
- the large temperature difference enables a more efficient cooling system.

In conjunction with Argonne National Laboratory, we have simulated a 250KW natural gas reformed PEM fuel cell high temperature system operating at 150°C which is shown in Figure 8. The primary focus of the system was the generation of steam at 120°C to be used for industrial applications, although it did investigate some of the contaminants reduction such as sulfur, CO, and methane. The PROX reactor was eliminated in the fuel processor system. The system performance parameters used in the simulations are listed in Table 2.

Table 2. Important parameters of high temperature membrane system.

Operating Parameters	Values
Stack temperature	150°C
Fuel utilization	85%
Oxygen utilization	50%
Steam to carbon ratio	3.4
Oxygen to carbon ratio	1.2

The ease with which sulfur adsorbs on many metals means that sulfur is frequently a catalyst poison. This is particularly true for nickel based catalysts in which sulfur is normally adsorbed at high surface coverage even when present in the gas phase at low concentration. For some process routes, sulfur tolerant catalysts may exist, however, sulfur is an extreme poison for the shift stage catalysts and will generally be poisonous to the fuel cell stack itself. Consequently, we have designed to handle fuels containing sulfur using desulfurization techniques prior to the reformer. A large number of sulfur compounds are present in almost all fuels. For example, this may include hydrogen sulfide present in natural gas which needs to be removed before the stream enters the fuel cell stack. Desulfurization is a selected option as it is a mature technology practiced widely in industry and commercial processes. It involves a two bed system in which organic sulfides are first converted to hydrogen sulfide by hydrogenolysis and then removed, often using a bed of zinc oxide.

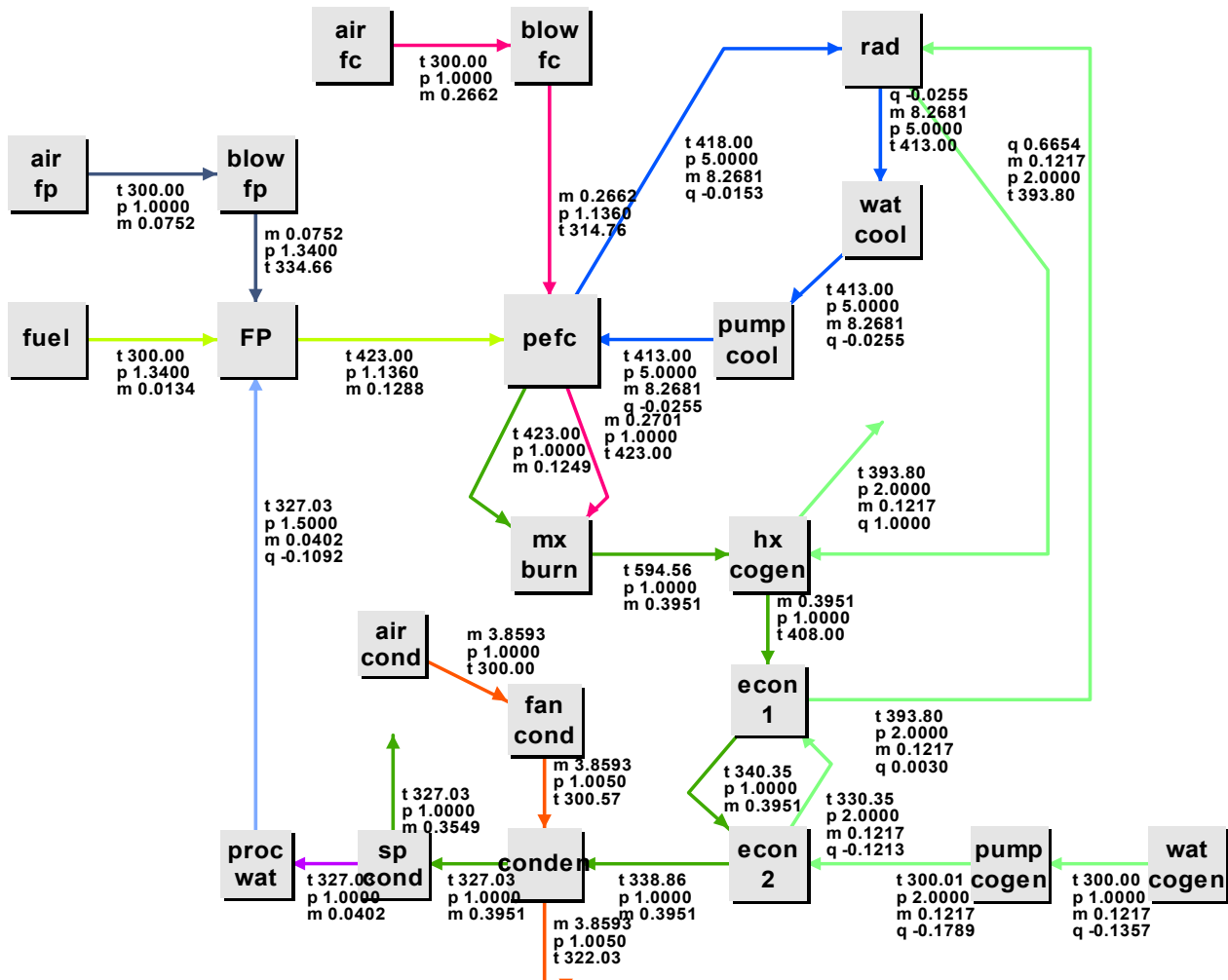


Figure 8. 250 kW natural gas reformed PEM fuel cell for combined heat and power.

In the above system, sulfur is desulfurized before it enters the system. The step by step processing of the fuel is as follows:

Reformer: The hydrocarbon and steam streams first pass through a high temperature reactor vessel, called a reformer, where most of the fuel is converted into a mixture of hydrogen and carbon monoxide. Some of the carbon monoxide produced in the reformer may also react with water to form carbon dioxide [Ferguson and Ugursal, 2002]. The reformer operating temperature is dependent on the fuel used, and may range from 250°C (methanol) to over 700°C (methane).

High Temperature Water Shift Reactor: The high temperature water shift reactor (HTWS) is used to convert carbon monoxide to carbon dioxide. The HTWS reactor typically operates at temperatures between 260–320°C.

Low Temperature Water Shift Reactor: The low temperature water shift (LTWS) reactor is used to convert the remaining carbon monoxide to carbon dioxide. The LTWS reactor typically operates at temperatures between 200–260°C. For the high

temperature membrane operated at 150°C, the water gas shift reaction is usually sufficient to produce hydrogen-rich fuel gas because the anode catalysts can tolerate CO limits greater than 10 ppm. The PROX (the preferential oxidation reactor) is eliminated. Thus the cost, complexity and weight of the fuel processing system is greatly reduced.

In this way, hydrogen rich reformat is fed in the anode end of the fuel cell and oxygen is fed in the cathode end of the fuel cell. They undergo an electrochemical reaction generating DC power, waste heat, and water. Only 85% of the fuel and 50% of oxygen is utilized in the fuel cell stack. The unconverted hydrogen and depleted oxygen are mixed in the catalytic burner (mx burn). The reformat is fed in to the heat exchanger (hx cogen) where the heat is recovered from the burner (see Figure 8). The water for cogeneration at 27°C is pumped into the low heat economizer and then to the high heat economizer where the temperature of the water is raised to 120°C with the help of the high temperature burner exhaust. There is a coolant, closed loop introduced which removes the heat generated by the cell reaction. Starting from the PEFC stack the water generated goes to the radiator where the excess heat is dissipated and the water is cooled and pumped back into the fuel cell stack. The reformat from the (hx cogen) is fed into the economizer 1 and 2 and then to the condenser where water is recovered from the exhaust. This water is then fed in the processed water tank for input into the fuel processor. Air for the cathode is introduced from the (air FC). Part of the exhaust is thrown away as waste from the (sp cond). The various heat exchangers and economizers are used for preheating the process steams and heat recovery between the different process steps. This thermal integration is essential for achieving a high efficiency in the fuel processor and in the entire fuel cell power system.

Auxiliary Systems

The above fuel cell systems also incorporate several ancillary devices necessary for their operation. These devices include:

- Electric motors that power the pumps and compressors.
- Mechanical cooling equipment that provides supplementary heat extraction required by the fuel cell stack and cooling processes.
- Power conditioning unit: This involves taking whatever electricity is produced by generator and converting it to meet the industry standards so that it can be used without damaging whatever is plugged in (such as a TV, etc.). Power conditioning for a fuel cell power plant includes an inverter which converts DC power into AC power, current, voltage, and frequency control.
- Hydrogen burner: The hydrogen burner is used to oxidize any hydrogen not reacted in the fuel cell stack. This prevents the release of combustible gasses to the atmosphere, and also produces thermal energy that may be used for process heating in the fuel processor.
- Auxiliary burner: The auxiliary burner is used to provide supplementary heat to the fuel processor for process heating if sufficient thermal energy cannot be recovered from hot process streams.

- Heat extraction equipment: During operation, the fuel cell produces heat that must be extracted to ensure that the stack remains at the optimal temperature. This may be done with a water loop that extracts heat for space heating and domestic hot water (DHW) purposes, and a mechanical cooling arrangement that provides cooling during periods of insufficient space heating and DHW demand.
- Heat Recovery: The arrangement of reactors in the fuel processor requires that the reactant streams be heated and then subsequently cooled. This is accomplished by a network of heat exchangers that transfers heat from streams requiring cooling to streams requiring heating.
- Air preheater: It is an indirect heat exchanger designed to transfer the heat from combustion gas to the air stream added to the combustion zone.
- Compressor: It is a device used for increasing the pressure and density of the gas. They are devices in which work is done on a gas passing through them in order to raise the pressure.
- Heat exchanger: It is a vessel in which heat is transferred from one medium to another. Devices that transfer energy between fluids at different temperatures by heat transfer modes are called heat exchangers or recuperators.
- Nozzle: It is a flow passage of varying cross sectional area in which the velocity of a gas or liquid increases in the direction of flow.
- Pumps: In pumps, the work input is used to change the state of a liquid passing through them.
- Expander: They are turbines in which gas expands, does work, and undergoes a drop in temperature.
- Turbines: A turbine is a device in which work is developed as a result of a gas or liquid passing through a set of blades attached to a shaft free to rotate.
- Turbocompressor: It supplies the cathode air as well as air needed for the fuel autothermal reformer.
- Condenser: It is used to recover water from the exhaust.

GCtool

For doing all the above simulation, GCtool (developed by Argonne National Laboratory) has been used. GCtool (General Computational Toolkit) is a software package that helps design, analyze, and optimize fuel cell and other power-plant configurations, including automotive and stationary distributed power generation systems [Geyer *et al.*, 1998]. Dynamic, total-system fuel cell modeling is one of its major strengths. Modules for polymer electrolyte and solid oxide fuel cells are available. GCtool provides a convenient, flexible framework for configuring various fuel cell and balance-of-plant components into simple or complex system configurations. An extensive library of component models and properties is available, and users can add their own models, if needed.

GCtool can be used to define arbitrary system configurations. It is able to handle models of any level of detail. It allows both steady-state and dynamic analyses, unlimited parameter sweeps, and constrained optimizations. It includes nested looping statements and other logical functions to automatically examine the effects of changes

in system parameters. GCTool's C-language interpreter and model design support rapid system prototyping. System configurations are set up with the help of on-screen graphics. Model parameters can be easily changed, and pop-up windows are used to display configurations and for line and surface plots. Other features include: A model library that offers four different types of fuel cells: polymer electrolyte (PEFC, often referred to as proton exchange membrane, or PEM), molten carbonate, phosphoric acid, and solid oxide fuel cells. Other ready-to-use component models include various types of heat exchangers (heat pipe, condenser, thermal radiator, etc.); fluid devices (splitter, nozzle, diffuser, gas turbine, pump, etc.); reactors and reformers; and vehicle systems (including electric motor/generator). Property codes that include a fast, gas-phase chemical equilibrium code capable of handling an arbitrary number of species; a multiphase chemical equilibrium code; a code for condensable pure substances; and a steam/water code. Mathematical utilities include a nonlinear equation solver, a constrained nonlinear optimizer (for both linear and nonlinear constraints), an integrator, and a solver for ordinary differential equations.

Application

This software tool has been used successfully in analyzing a variety of polymer electrolyte fuel cell (PEFC) systems using different fuels, fuel storage methods, and fuel processing techniques. Fuel cell systems have been analyzed for hydrogen, methanol, natural gas, and gasoline fuels. The analyses included off-design operation, dynamic and transient performance, and the effects of operation at extreme temperatures. Important issues involving heat, water, and air management have been identified, and alternative approaches to addressing those issues have been evaluated. Users have also analyzed system start-up from cold and warm conditions and determined system performance and efficiency during ramp-up and ramp-down transients.

Results

The results from this simulation are summarized in Table 3.

Table 3. System performance of HTM system.

Operating Parameters	Values
Fuel processor efficiency	80.8%
Electrical efficiency	37.3%
Thermal efficiency	47.2%
Water	28%
Nitrogen	61%
Oxygen	5%
Sulfur	Tolerant < 5ppm
CO	Tolerant 50ppm
CO ₂	6%

NO _x and VOC	Negligible
Methane slip	< 1%

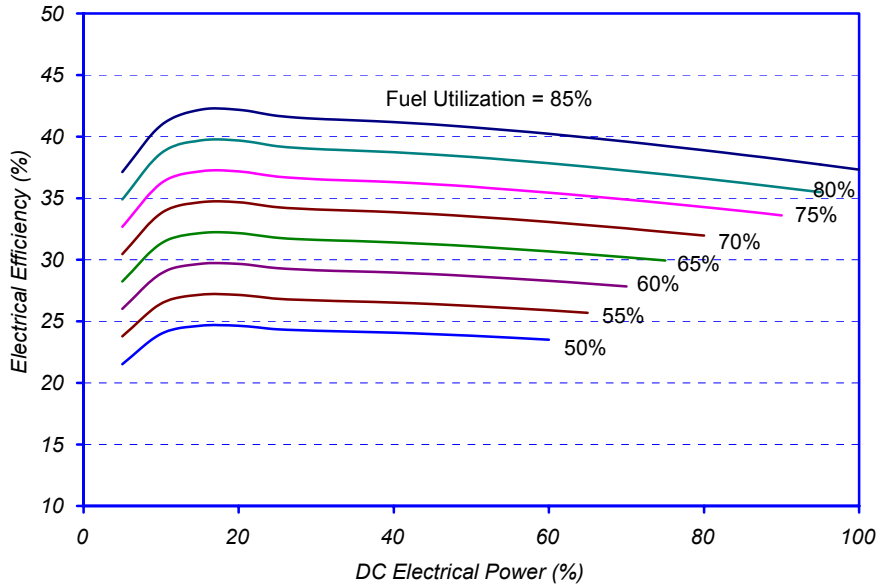


Figure 9. Electrical efficiency of high temperature membrane-fuel cell system as a function of different fuel utilization values.

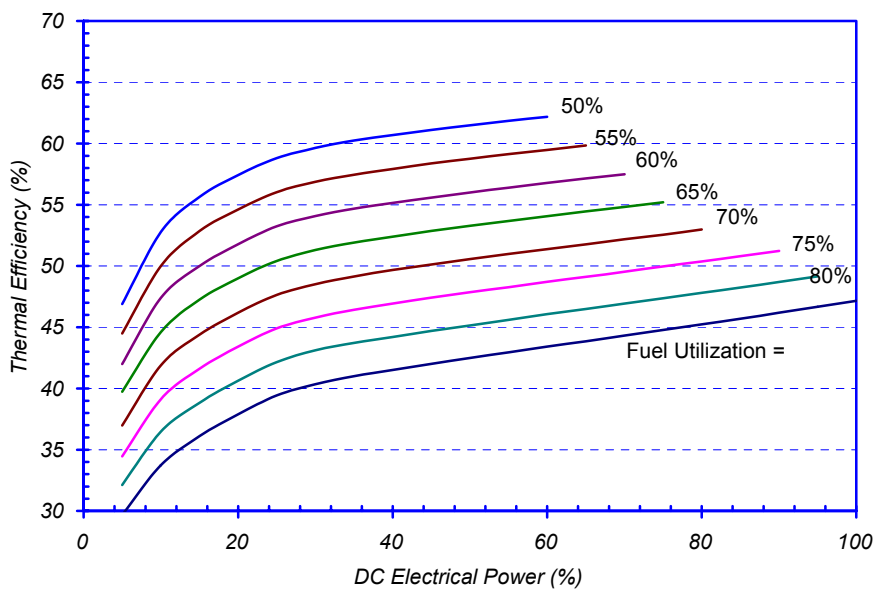


Figure 10. Thermal efficiency of high temperature membrane-fuel cell system as a function of different fuel utilization values.

Figures 9 and 10 show that the peak electrical efficiency occurs at ~85% fuel utilization which is 37.3%. The peak thermal efficiency at this utilization is 47.2%. These results are also shown in Figure 11.

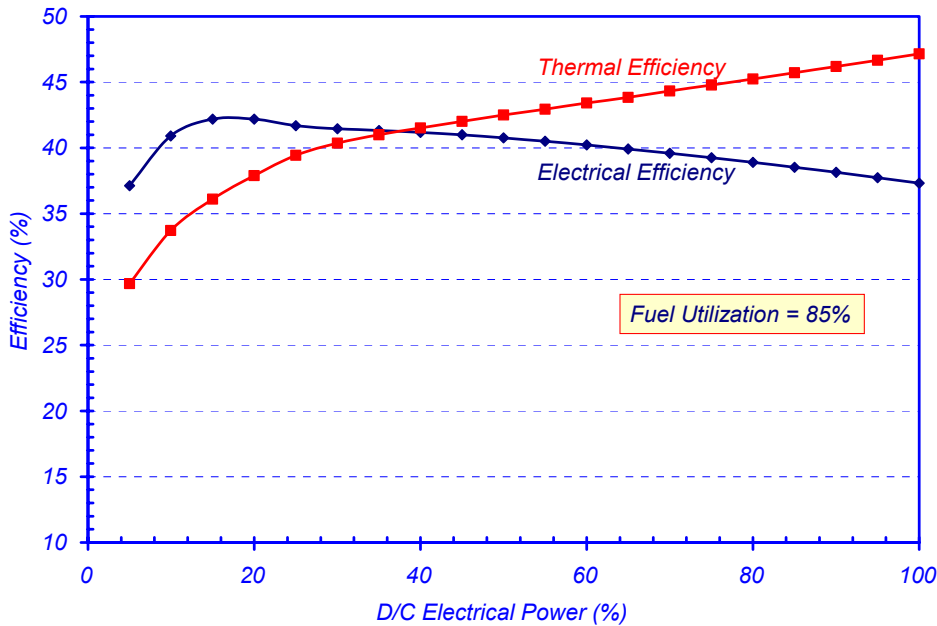


Figure 11. Natural gas reformed polymer electrolyte fuel cell system optimum efficiency.

At 85% fuel utilization, there is a point where the electrical and thermal efficiencies are optimum. Electric power generation in stationary fuel cells is in competition to thermal processes where the maximum energy efficiency is given by the Carnot cycle. The theoretical electrical efficiency for the electrochemical and the thermal processes are as follows:

$$\eta = T_2 / (T_2 - T_1) \quad \text{for Carnot cycle and}$$

$$\eta = \Delta G / (\Delta G + T\Delta S) \quad \text{for a fuel cell}$$

The theoretical electrical efficiency values will be reduced by additional process losses. In fuel cells, they are mainly caused by internal resistive and polarization losses producing Joule heat. Therefore, thermal energy in fuel cells (Q_{FC}) is generated as reversible heat (Q_R) and as Joule heat (Q_J).

$$Q_{FC} = Q_R + Q_J$$

At lower electrical loads, less Joule heat is generated. Therefore with decreasing load, not only will the electrical efficiency increase, but due to reduced resistive losses, it will also

increase. In practice, however, at very low loads, it decreases again, due to electricity consumption of auxiliary aggregates (e.g., pumps, etc.). This is shown in Figure 11.

Cleaning and Removing of Contaminants in the Fuel Cell

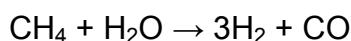
Fuel processors require the removal of impurities that degrade the fuel processor or fuel cell performance. Sulfur is the major contaminant encountered. Carbon monoxide reduction for low temperature fuel cells and avoidance of carbon deposition are addressed in this section. A typical processing chain for a low temperature fuel cell involves a hydrodesulfurizer, a halogen guard, a zinc oxide sulfur absorber, a catalytic reformer, a high temperature shift converter, a second halogen guard, and a low temperature shift converter. The function of all these components, except the reformer, is to remove impurities. For the PEFC cell, there needs to be an additional device to essentially remove all CO, such as a preferential oxidizer.

Sulfur Reduction

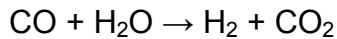
There are high temperature and low temperature methods to remove sulfur from a fuel reformat stream. Low temperature cleanup, such as hydrodesulfurization (limited to fuels with boiling end points below 205°C), is less difficult and lower in cost so it should be used wherever possible, certainly with low temperature cells. Sulfur species in the fuel are converted to H₂S, then the H₂S is trapped on zinc oxide. There is a vast difference between removing sulfur from a gaseous fuel and a liquid fuel. The sulfur in a liquid fuel is usually removed after it is converted to a gas. This occurs in the reformer reactor so that it has to handle the sulfur either by operating at significantly high temperature, by removing the sulfur in the reforming reactor vessel, or by incorporating sulfur resistant catalysts. Sulfur resistant catalysts are being developed but none are mature enough for use. Argonne National Laboratory, for example, has demonstrated that their catalyst can tolerate sulfur, but it has not been demonstrated on an engineering scale [Williams, 2000]. Some developers remove the sulfur immediately after vaporization and prior to the reforming. Hydrogen needs to be recirculated to the removal device to convert the sulfur species to H₂S so that it can be entrapped on zinc oxide. Zinc oxide beds are limited to operation at temperatures below 430°C probably because of pore plugging during sulfur removal and sintering. Thermodynamics also favors lower temperatures. At the higher temperatures, the H₂S cannot be reduced to levels low enough for shift catalyst or to reach fuel cell limits. Sulfur content in fuel and sulfur removal processor development are in a constant stage of change and the reader is referred to the literature to assess the latest status and techniques [Williams, 2000].

CO Poisoning

The fuel reforming system always involve a reaction producing carbon monoxide, just in the case of reaction between methane and steam.



For high temperature fuel cells, carbon monoxide is used as a fuel. However fuel cells using platinum as a catalyst most certainly cannot use carbon monoxide as a fuel. Even very small amounts of carbon monoxide have a significant effect on the anode. If a reformed hydrocarbon has to be used as a fuel, the carbon monoxide has to be shifted to carbon dioxide using more steam.



This reaction is called the “water gas shift reaction”. It does not easily go to completion, and there will always be some carbon monoxide in the reformed gas stream. A state of the art system will still have CO levels on the order of 0.25 to 0.50% (2500 to 5000 ppm).

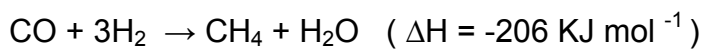
Carbon monoxide will occupy platinum catalysts sites – the compound has an affinity for platinum and it covers the catalysts, preventing the hydrogen fuel from reaching it. Experience has shown that a concentration of CO as low as 10 ppm has an unacceptable effect on the performance of the PEM fuel cell [Larminie and Dicks, 2003].

CO Removal

The requirement to remove carbon monoxide can be made somewhat less vigorous by the addition of small quantities of oxygen or air to the fuel stream. This reacts with the carbon monoxide at the catalysts sites, thus removing it. For example, by adding 2% oxygen to a hydrogen gas stream containing 100 ppm of CO, the poisoning effects of CO are eliminated. However, any oxygen not reacting with CO will certainly react with hydrogen, and thus waste fuel. The methods can only be used for CO concentrations in the 10s or 100s of ppm range, not 1000s of ppm concentration range from typical fuel reformers. In addition, the system to feed the precisely controlled amounts of air or oxygen will be fairly complex, as the flow rate has to carefully follow the rate of hydrogen use. For PEM fuel cells, further carbon monoxide removal is essential after the shift reactors. This is usually done in one of the three ways described below.

In the **selective oxidation reactor**, a small amount of air (typically around 2%) is added to the fuel stream, which then passes over a precious metal catalyst. This catalyst preferentially absorbs the carbon monoxide, rather than the hydrogen, where it reacts with the oxygen in the air. In addition to the previous problem of costs, these units need to be carefully controlled. Hydrogen, carbon monoxide and oxygen are present at an elevated temperature, with a noble metal catalyst. Measures must be taken to ensure that an explosive material is not produced. This is a special problem for cases where the flow rate of the gas is highly variable, such as with a PEM fuel cell in a vehicle.

The methanation of the carbon monoxide is an approach that reduces the danger of producing explosive gas mixtures. The reaction is the opposite of the steam reformation reaction.



This method has the obvious disadvantage that hydrogen is being consumed, and so the efficiency is reduced. However, the quantities involved are small. Carbon monoxide content is reduced from about 25%. The methane does not poison the fuel cell, but simply act as an diluent. Catalysts are available, which will promote this reaction so that at about 200C the carbon monoxide levels will be less than 10 ppm [Larminie and Dicks, 2003]. The catalysts will also ensure that any unconverted methanol is reacted with methane, hydrogen, or carbon dioxide.

Palladium/platinum membranes can be used to separate and purify the hydrogen. This is a mature technology that has been used for many years to produce hydrogen of exceptional purity. However, these devices are expensive.

A further method of hydrogen purification which can be applied, is that of **pressure swing absorption**. In this process, the reformer product gas is passed into a reactor containing absorbent material. Hydrogen gas is preferentially absorbed on this material. After a set time, the reactor is isolated and the feed gas is diverted into a parallel reactor. At this stage, the first reactor is depressurized, allowing pure hydrogen to desorb from the material. The process is repeated and the two reactors are alternatively pressurized and depressurized. The extra stages add considerably to the cost and complexity of the fuel.

Carbon Deposition Avoidance

The processing of hydrocarbons always has the potential to form coke. Coke formation is influenced by the composition of the fuel, the catalyst, and the process conditions (e.g., partial pressure of steam). Coke causes the greatest problems in gas flow paths and on the catalyst. Carbon deposition not only represents a loss of carbon for the reaction but more importantly also results in deactivation of the catalyst due to deposition at the active sites. Thermal cracking in overheated preheaters and manifolds can easily form carbon. If the fuel conversion reactor is not properly designed or operated, coking is likely to occur. Increasing steam, hydrogen, and carbon dioxide concentrations alleviates carbon deposition. Higher hydrocarbon fuels show a higher tendency for carbon formation than does methane. One method to alleviate carbon deposition problems in the fuel processor is to use special catalysts either containing alkali or catalysts that are based on an active magnesia support.

Coke formation resulting from the use of higher hydrocarbon fuels can also be eliminated with an adiabatic pre-reformer. The adiabatic reformer is a simple fixed bed reactor. By adiabatic pre-reforming, all higher hydrocarbons are converted at low temperature (below 500°C) with steam into methane, hydrogen, and carbon oxides at conditions where carbon formation does not occur. Coking can be also be avoided by operating at high temperatures and at high oxygen-to-carbon ratios. For a given O/C ratio, it is preferable that the oxygen feed be in the form of water. In other words, the coking tendency is reduced at high O/C and H/C ratios. Thus, less coke is formed in the order, POX > ATR > SR.

Methane Concentration in the Reformate

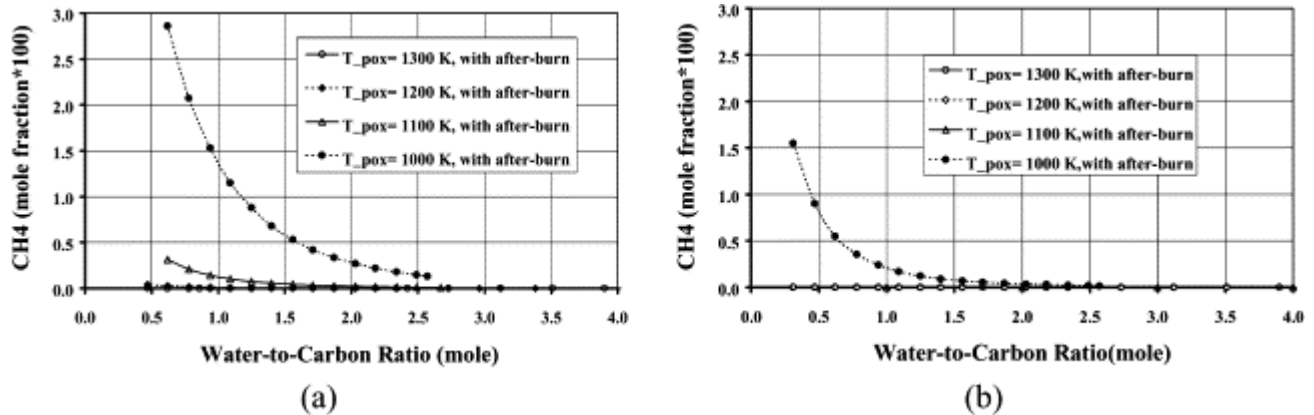


Figure 11. Methane formed as a function of the water-to-carbon ratio at various temperatures [Doss et al., 2001].

Any methane (CH₄) formed during the autothermal reforming step represents a corresponding decrease in the amount of hydrogen generated by the fuel processor, and a corresponding decrease in the amount of electrical energy generated in the fuel cell stack. This is because the CH₄ does not undergo any reaction in the rest of the fuel processor, and it is not electrochemically oxidized in the fuel cell stack. Its chemical energy is converted to heat at the fuel cell stack exhaust burner. Therefore, this CH₄ may or may not result in an efficiency penalty for the fuel processor or the total fuel cell system, depending on how effectively the burner heat can be used in the system. The concentration of CH₄ in the processed reformat is greatly affected by the value of T_{POX}, as shown in Figure 11. Figure 11a uses 3 atm system and figure 11b uses 1 atm system. At high T_{POX} (1100 K or higher) and/or high S/C (>1), the methane slip is less than 0.1%. Only at T_{POX}=1000 K is formation of CH₄ thermodynamically favored.

Environmental Impact of the Hydrogen Economy

According to conventional wisdom, hydrogen-fueled cars are environmentally friendly because they emit only water vapor -- a naturally abundant atmospheric gas. However, leakage of the hydrogen gas that can fuel such cars could cause problems for the upper atmosphere, new research has shown. In a recent article, researchers from the California Institute of Technology report that the leaked hydrogen gas that would inevitably result from a hydrogen economy, if it accumulates, could indirectly cause as much as a 10-percent decrease in atmospheric ozone [Tromp et al., 2003]. If hydrogen were to replace fossil fuel entirely, the researchers estimate that 60 to 120 trillion grams of hydrogen would be released each year into the atmosphere, assuming a 10–20% loss rate due to leakage. This is 4x to 8x as much hydrogen as is currently released into the atmosphere by human activity, and would result in doubling or tripling of inputs to the atmosphere from all sources, natural or human. Because molecular hydrogen freely moves up and mixes with stratospheric air, the result would be the creation of additional water at high altitudes and, consequently, an increased dampening of the stratosphere. This in turn could result in cooling of the lower stratosphere and disturbance of ozone chemistry, which depends on a chain of chemical reactions involving hydrochloric acid and chlorine nitrate on water ice. The estimates of potential damage to stratospheric ozone levels are based on an atmospheric modeling program that tests the

various scenarios that might result, depending on how much hydrogen ends up in the stratosphere from all sources, both natural and anthropogenic.

Ideally, a hydrogen fuel-cell vehicle has no environmental impact. Energy is produced by combining hydrogen with oxygen pulled from the atmosphere, and the tailpipe emission is water. The hydrogen fuel could come from a number of sources (Iceland recently started pulling it out of the ground). Nuclear power could be used to generate the electricity needed to split water, and in principle, the electricity needed could also be derived from renewable sources such as solar or wind power. By comparison, the internal combustion engine uses fossil fuels and produces many pollutants, including soot, noxious nitrogen and sulfur gases, and the "greenhouse gas" carbon dioxide. While a hydrogen fuel-cell economy would almost certainly improve urban air quality, it has the potential unexpected consequences due to the inevitable leakage of hydrogen from cars, hydrogen production facilities, and the transportation of the fuel. Uncertainty remains about the effects on the atmosphere because scientists still have a limited understanding of the hydrogen cycle. At present, it seems likely such emissions could accumulate in the air. Such a build-up would have several consequences, chief of which would be a moistening and cooling of the upper atmosphere and, indirectly, destruction of ozone. In this respect, hydrogen would be similar to the chlorofluorocarbons (once the standard substance used for air conditioning and refrigeration), which were intended to be contained within their devices, but which in practice leaked into the atmosphere and attacked the stratospheric ozone layer. The authors of the *Science* article say that the current situation is unique in that society has the opportunity to understand the potential environmental impact well ahead of the growth of a hydrogen economy. This contrasts with the cases of atmospheric carbon dioxide, methyl bromide, CFCs, and lead, all of which were released into the environment by humans long before their consequences were understood.

Summary of Environmental Impacts

The breakdown of organic pollutants and nitrogen oxides (which originate from the combustion of fossil fuels) in the lower levels of the atmosphere (troposphere) by sunlight can lead to excess formation of ozone ("photochemical smog"). This ozone can damage vegetation, building materials and human health. In the upper region of the troposphere, ozone can act as a significant greenhouse gas contributing to climate change. Replacing fossil fuels with hydrogen should therefore reduce these adverse impacts as a direct result of reducing polluting emissions. However, the situation is more complicated because hydrogen influences the reducing capacity of the atmosphere and therefore by its presence in the atmosphere affects the breakdown processes creating the ozone. While hydrogen is present in the atmosphere through natural processes, increased direct emissions of hydrogen to the atmosphere from human activity may alter the natural chemistry of the atmosphere and exacerbate problems relating to impacts of photochemical pollution (ozone) and climate change – particularly if high levels of organic pollutants continue to be emitted to the atmosphere even in the hydrogen economy. The impact of hydrogen in the highest parts of the atmosphere (the stratosphere) is also important given its potential to assist in the catalytic destruction of ozone and thereby the potential to confound measures taken under the Montreal Protocol. It is not possible to scope the scale of this problem without carrying out very detailed research. On balance, it is likely that substituting hydrogen for fossil fuels will have a positive

environmental impact in reducing both photochemical smog and climate change. There could be an adverse impact on the ozone layer but this is likely to be small, though potentially more significant if hydrogen was to be used as a aviation fuel. However, the highly complex nature of chemical reactions in the atmosphere means that we can not be certain about these assumptions without carrying out extensive modeling.

Outlook

Fuel cells are promising energy converters for mobile, portable and stationary applications. For an environmental evaluation of new technologies, however, an investigation of the complete life-cycle is necessary to ensure that no environmental aspect is neglected. In stationary applications, the potentially high electrical efficiency of fuel cell power plants, especially high temperature fuel cells, leads to clear resource and GHG emissions advantages compared to the competing technologies. Further advantages could be achieved if not only the electrical, but the total efficiency were simultaneously optimized. This is particularly important for low temperature fuel cells in CHP applications where some engine CHP plants show total efficiencies of more than 90%.

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