Global Assessment of Hydrogen Technologies
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TASK 5 REPORT
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Use of Fuel Cell Technology in Electric Power Generation

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TABLE OF CONTENTS

TABLE OF FIGURES

TABLE OF TABLES

EXTENDED ABSTRACT

The purpose of this work was to assess the performance of high temperature membranes and observe the impact of different parameters, such as water-to-carbon ratio, carbon formation, hydrogen formation, efficiencies, methane formation, fuel and oxidant utilization, sulfur reduction, and the thermal efficiency/electrical efficiency relationship, on fuel cell performance. A 250 KW PEM fuel cell model was simulated [in conjunction with Argonne National Laboratory (ANL) with the help of the fuel cell computer software model (GCtool)] which would be used to produce power of 250 kW and also produce steam at 120^{o}C that can be used for industrial applications. The performance of the system was examined by estimating the various electrical and thermal efficiencies achievable, and by assessing the effect of supply water temperature, process water temperature, and pressure on thermal performance. It was concluded that increasing the fuel utilization increases the electrical efficiency but decreases the thermal efficiency. The electrical and thermal efficiencies are optimum at ~85% fuel utilization. The low temperature membrane (70^{o}C) is unsuitable for generating high-grade heat suitable for useful cogeneration. The high temperature fuel cells are capable of producing steam through 280^{o}C that can be utilized for industrial applications. Increasing the supply water temperature reduces the efficiency of the radiator. Increasing the supply water temperature beyond the dew point temperature decreases the thermal efficiency with the corresponding decrease in high-grade heat utilization. Increasing the steam pressure decreases the thermal efficiency.

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, the growth of a “solar hydrogen economy” has been projected. Photovoltaic cells convert sunlight into electricity. This electricity can 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 (CO_2, 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 fueled by methanol, produces nitrous oxides (NO_x), gases 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 CO_2 and sulfur dioxide (SO_2) but these emissions are much 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 CO_2 and SO_2 emissions. Fuel cell power plants also have longer life expectancies and lower maintenance costs than their alternatives.

This final task report presents an overview of the green house gas emissions, briefly looking in to the life cycle assessment of fuel cells. The report 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.

ACRONYMS

AC	Alternating current
Ag	Silver
ANL	Argonne National Laboratory
Ar	Argon
ATF	Autothermal reforming
CFC-11	Trichlorofluoromethane (freon-11)
CH_4	Methane
CHP	Combined heat and power
Co	Cobalt
CO	Carbon monoxide
CO_2	Carbon dioxide
DC	Direct current
e^-	Charge on an electron
E	Electric work of a fuel cell
E^o	Open circuit voltage
F	Faraday’s constant = 96,485 coulombs/mole
FCs	Fuel cells
ΔG	Gibb’s free energy released
GCtool	General Computational Toolkit (a fuel cell system model developed by Argonne National Laboratory)
GHC	Greenhouse gas
GH_2	Gaseous hydrogen

GWP	Global warming potential
Δh_f	Enthalpy of formation
ΔH	Enthalpy
•H	Hydrogen radicals
H/C	Hydrogen–to–carbon ratio
HCHO	Formaldehyde
H_2S	Hydrogen sulfide
HHV	Higher heating value
H_2O	Water
$h\nu$	Light
HVDC	High voltage direct current
I	Current
ICE	Internal combustion engine
KW	Kilowatt
LCA	Life cycle analysis
LCI	Life cycle inventory
LH_2	Liquid hydrogen
LHV	Lower heating value
MCFC	Molten carbonate fuel cell
N	Avogadro's number $= 6.023 \times 10^{23}$
Ni	Nickel
NMHC	Non-methane hydrocarbons
N_2	Nitrogen
N_2O	Nitrous oxide

NO_2	Nitrogen dioxide
NO_x	Nitrogen oxides
O/C	Oxygen–to–carbon ratio
O&M	Operations and maintenance
O_2	Oxygen
•OH	Hydroxyl radicals
PAFC	Phosphoric acid fuel cell
Pd	Palladium
PEFC	Polymer electrolyte fuel cell
PEMFC	Proton exchange membrane fuel cell
POx	Partial oxidation
PRF FC	Pyrolytic fuel reformer fuel cell
PROX	Preferential oxidation reactor
psi	Pounds per square inch
Pt	Platinum
Q_{in}	Heat released from the fuel cell
R	Resistance
Ru	Ruthenium
S/C	Sulfur–to–carbon ratio
SMR	Steam–methane reforming
SOFC	Solid oxide fuel cell
SO_2	Sulfur dioxide
SO_x	Sulfur oxides

SR	Steam reforming
SUVs	Sport utility vehicles
t	Time
T_H	High temperature in the thermodynamic cycle
T_i	Temperature of a heat engine
T_L	Low temperature in the thermodynamic cycle
UAB	University of Alabama at Birmingham
V	Voltage
WGS	Water−gas shift reaction
W_{net}	Mechanical work
Y_2O_3	Yttrium oxide
ZrO_2	Zirconium oxide

Greek Symbols:

η	Fuel cell efficiency
η_{th}	Thermal efficiency
$\eta_{th, Carnot}$	Maximum thermal efficiency
μ	Fuel equivalence ratio for blended fuels
μ_f	Mass of fuel reacted in the fuel cell/mass of fuel input in the fuel cell

1. 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 particularly 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 safe design of vehicles.

As a result, 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.

1.1 GHG Emissions

In terms of total air emissions, carbon dioxide (CO_2) is emitted in the greatest quantity, accounting for 99% (by weight) of the total air emissions. The CO_2 accounts for 89.3% of the system global warming potential (GWP), defined as a combination of CO_2, methane (CH_4), and N_2O emissions expressed as CO_2-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 decom-missionning[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%

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

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

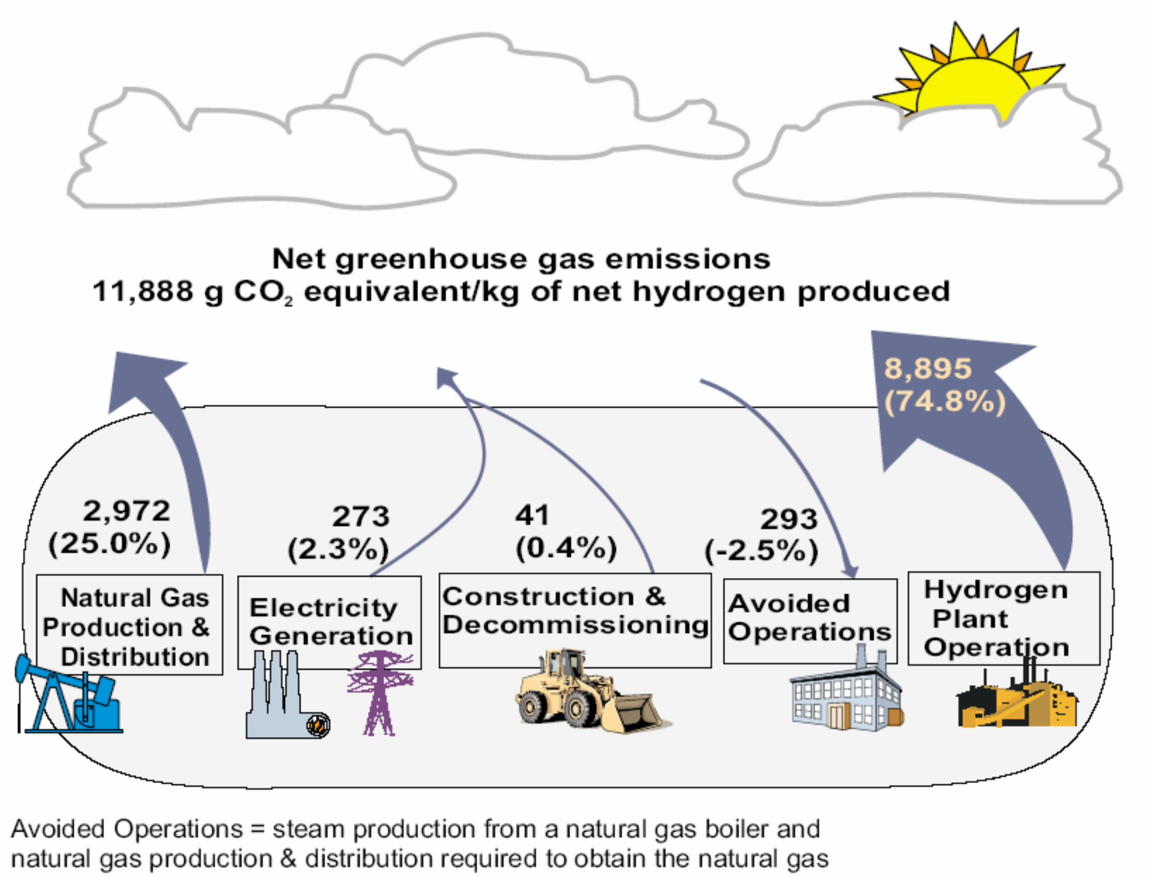


Figure 1. Sources of net green house gas emissions [Spath and Mann, 2001].

Other than CO_2, methane is emitted in the next greatest quantity followed by non-methane hydrocarbons (NMHCs), nitrogen dioxide (NO_x), sulfur oxides (SO_x), carbon monoxide (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.

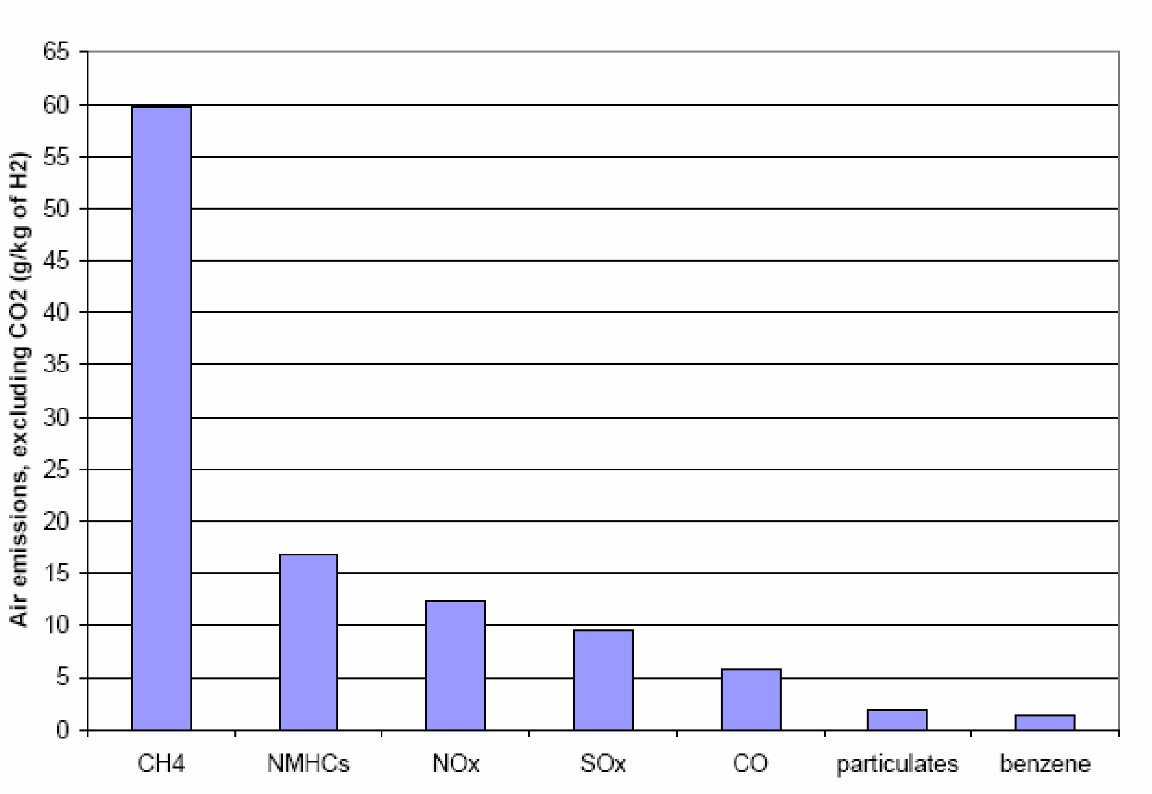


Figure 2. Air emissions from hydrogen production (excluding CO_2) [Spath and Mann, 2001].

1.2 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.

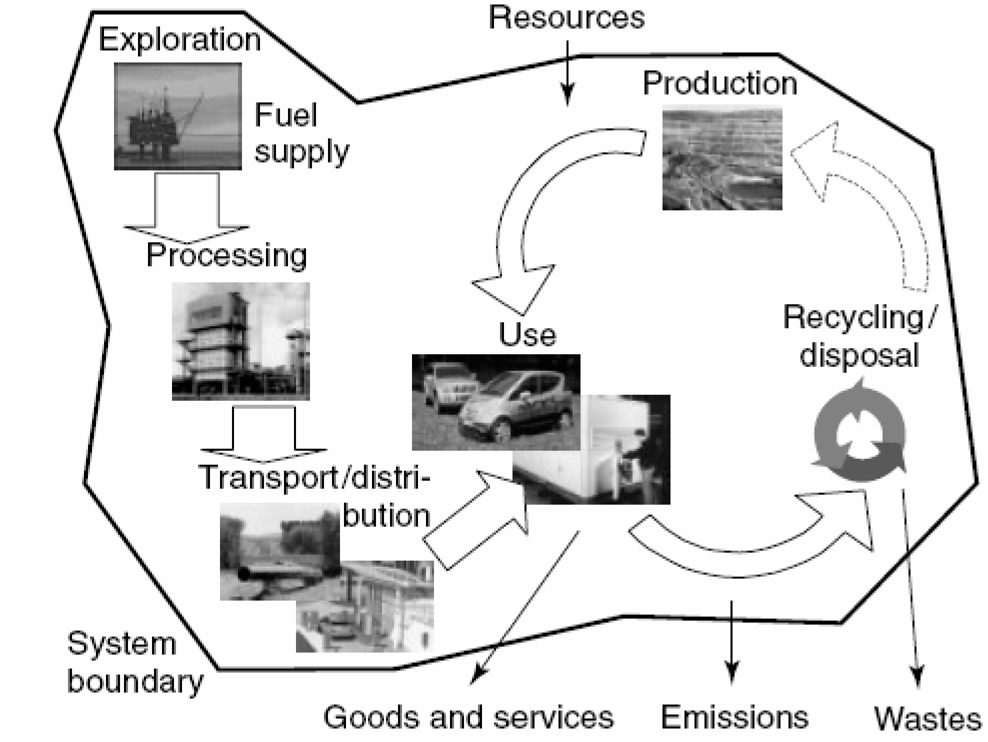


Figure 3. Inputs and outputs of fuel cell production in terms of its life cycle [Pehnt, 2003].

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. Nitrogen and phosphorus components primarily 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.

1.3 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 CO_2 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 H_2/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.

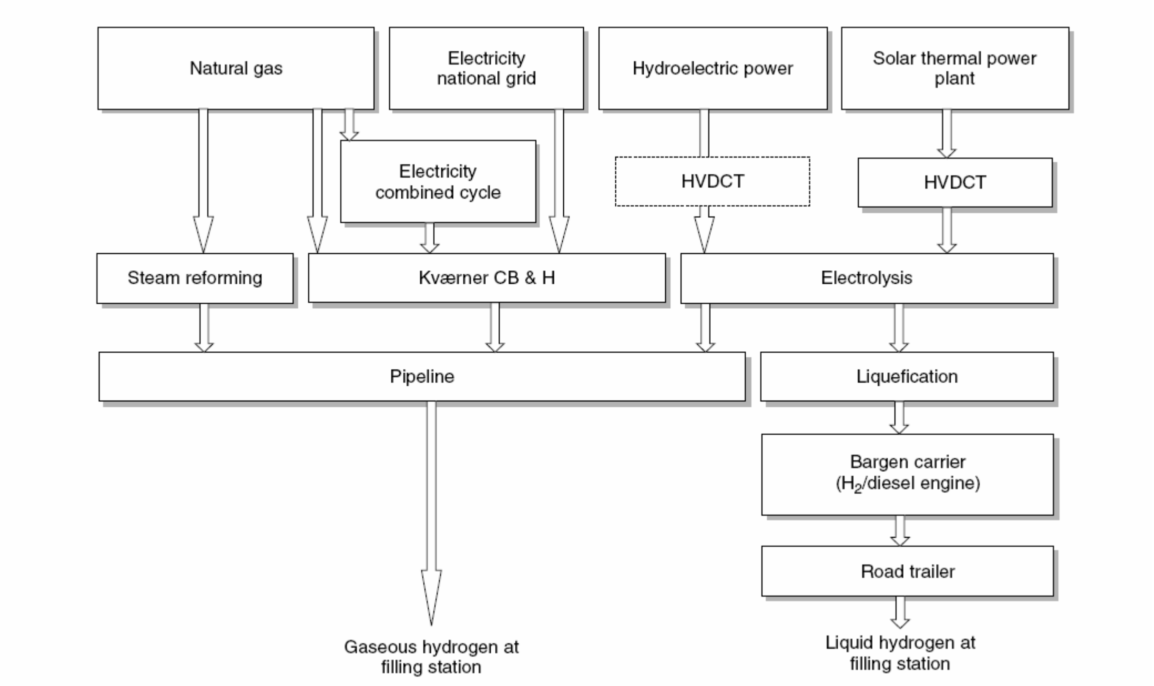


Figure 4. Process steps involved in the production of gaseous and liquid hydrogen [Pehnt, 2003].

1.3.1 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 (GH_2), transport of liquid hydrogen (LH_2) by barges 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, ecoefficiency, and storage requirements.

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

(1) It is potentially a nearly inexhaustible supply of energy;
(2) It can be produced from many available primary energy resources;
(3) It easily converts to electricity with higher efficiencies than combustion processes;
(4) It is “non” polluting and “non” toxic; and

(5) It can drive fuel cells, which provide a highly efficient and reliable source of energy

The drawback to the use of hydrogen energy has been cost, as it is expensive to produce and use hydrogen when compared to other fossil energy alternatives.

1.3.2 Hydrogen production

While hydrogen is abundant in our air and water, producing pure or free hydrogen for an energy supply can be costly. Molecular free hydrogen can be separated from naturally occurring compounds such as fossil fuels, water, or biomass using several processes, including steam reformation of natural gas (or other fossil fuels), electrolysis of water, or gasification of biomass. Since hydrogen does not occur in significant quantities naturally, it must be produced. There are a number of processes that can be employed to produce hydrogen from various feedstocks. Hydrogen can be produced from a wide variety of sources including reformation, electrolysis, biomass gasification and pyrolysis.

1.3.2.1 Reformation

Steam reforming of methanol is described by the following chemical reaction equation.

$$CH_3H\ (g) + H_2O\ (g) \rightarrow CO\ (g) + 3\ H_2 \qquad \Delta H = 49\ kJ\ mol^{-1}$$

Methanol and water are evaporated and react in a catalytic reactor to carbon dioxide and hydrogen, the desired product. The raw reformer output consists of hydrogen, carbon dioxide, and carbon monoxide. Carbon monoxide is converted to carbon dioxide and more hydrogen in a high temperature shift (HTS) stage followed by a low temperature shift (LTS) stage. In both stages, the water gas shift reaction takes place.

$$CO + H_2O\ (g) \rightarrow CO\ (g) + H_2 \qquad \Delta H = -41\ kJ\ mol^{-1}$$

The water gas shift is an exothermal reaction. Therefore, if too much heat is generated, it will eventually drive the reaction towards the reactant side. To prevent this, multiple stages with interstage cooling are used in practice. The best catalysts for the HTS reaction are a mixture of iron and chromium oxides with good activity between 400 and 500°C. LTS uses copper catalysts similar to and under similar operating conditions to those used in methanol steam reforming. Steam reforming of methane from natural gas is the standard way of producing hydrogen on an industrial scale. It is therefore of general importance to a hydrogen economy. In addition, smaller scale methane steam reformers have been developed to provide hydrogen for stationary power generation based on low temperature fuel cells. The methane steam reforming reaction is described by:

$$CH_4 + H_2O\ (g) \rightarrow CO + 3\ H_2 \qquad \Delta H = 206\ kJ\ mol^{-1}$$

1.3.2.2 Electrolysis

Electrolysis is the more desirable method used to produce hydrogen, but it is also one of the most costly. In this process, an electric current is used to split water into hydrogen and oxygen gases. Using an electric current to produce hydrogen from water permits the use of renewable energy sources, such as solar, wind, and hydropower. This can unfortunately make the process of producing hydrogen expensive, thereby creating a more favorable situation for the use of fossil fuels to produce the original electric current. Steam electrolysis may provide for a more efficient way of producing hydrogen when combined with the electric current method. Sunlight (solar radiation) can also be used to split water molecules. Photo electrolysis is accomplished using photovoltaic solar panels to harness the sun's energy and store it in a semiconductor. The solar energy is then used to split the water molecule and produce hydrogen. Another process involving sunlight, photolysis, adds a chemical catalyst to the collected sunlight to produce hydrogen in a process similar to photosynthesis. Certain photosynthetic organisms can also be used in a process called photobiological electrolysis.

1.3.2.3 Biomass gasification and pyrolysis

Production of hydrogen can also occur through the use of biomass resources. Biomass is a collective term used to describe such sources as wood chips, agricultural residues, and other organic wastes. All of these sources contain some amount of hydrogen, which can be isolated by high-temperature gasification or pyrolysis. Large stocks of biomass are required to produce a significant amount of hydrogen, making it more costly than using fossil fuels. Biomass also requires large land areas and does not contain a comparative amount of energy to fossil fuels.

1.3.2.4 Hydrogen storage and transport

Hydrogen storage is important if hydrogen energy systems are to become competitive alternatives to traditional energy systems. This is particularly evident for transportation applications where the need for high energy density and lightweight storage is clear. For utility and other stationary applications, the volume density and weight are not of prime consideration, but storage efficiency and system costs are major considerations.

1.3.2.5 Compressed gas storage tanks

Like other gases, hydrogen can be stored in pressurized tanks. However, since hydrogen is lighter than other gases, a higher pressure must be used to store a usable amount of the gas in a tank. To solve this problem, new materials have permitted the production of new high-pressure storage tanks. Storing hydrogen in this way would allow for easy transport.

1.3.2.6 Liquid hydrogen

Hydrogen can also be liquefied for storage. By condensing hydrogen gas into a liquid, a larger amount of hydrogen could be stored than in similar containers holding gaseous hydrogen. However, the process of condensing gaseous hydrogen can use significant amounts of energy and be very expensive.

1.3.2.7 Chemical hydrides and gas on solid adsorption

Hydrogen can also be combined with some pure or alloyed metals producing a metal hydride. The hydrogen can be stored by chemical combination with the metal and released from the hydride by the addition of heat. This process provides storage at a higher density than the simple compression of gaseous hydrogen. Hydrogen can also be adsorbed by activated carbon. This method can store an amount of hydrogen close to that of liquefaction. While all of these are successful methods for hydrogen storage, they still add large costs to hydrogen production. In comparison, consumers of both natural gas and electricity do not have to pay an added cost for storage. This added cost keeps hydrogen from being a competitor to more traditional fossil fuels. However, developments with new technology and innovations should help provide an answer to this problem in the near future.

1.3.3 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 significant factor 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 produced from the system actually reaches the customer [Muradov, 2003]. 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 even less of a 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.

1.4 Stationary Power Generation

The incentive for stationary power generation is quite different from that for the automotive fuel cell and other application. The single most important consideration for a commercial power generator is how to maximize the amount of electricity made out of a certain plant and a certain quantity of fuel. This problem takes in to account three important factors for a stationary power station: the hours of operation per year, the electrical efficiency of the electric generation process, and the capital investment.

Remote power generation is an issue in locations in the U.S. where grid connections are simply too expensive and fuel systems will enter direct competition with diesel or gasoline power generators.

Stationary power generation is viewed as the leading market for fuel cell technology. The reduction of CO_2 emissions is an important argument for the use of fuel cells in small stationary power systems, particularly in combined heat and power systems. In fact, fuel cells are currently the only practical engines for micro-combined heat and power systems in the domestic environment (5 to 10 kW). One of the characteristics of fuel cell systems is that their efficiency is nearly unaffected by size. This means that small, relatively high efficiency power plants can be developed, thus avoiding the higher cost exposure associated with large plant development. Smaller plants (several hundred KW to 1 to 2 MW) can be sited at the user's facility and are suited for cogeneration operation, i.e. the plants produce electricity and thermal energy. Larger, dispersed plants (1 to 100 MW) are likely to be used for distributed power generation. The plants are primarily fueled with natural gas. Once these plants are commercialized and price reduction takes place, fuel cells can be considered for large power plants [Watkins *et al*., 1986].

1.5 Conclusion

Large-scale central power generation using fuel cell technology will only be practicable when sufficiently high electric efficiencies can be achieved. Currently only the solid oxide fuel cell technology in the combined cycle process with gas turbines offers this potential, but cost reduction should also be considered [Watkins *et al*., 1986]. Domestic heat and power generation and grid-independent operation are currently the most promising applications for stationary fuel cell applications [Watkins *et al*., 1986]. In these areas, cost is less critical either because the systems replace other more expensive heating systems, or because they offer other benefits.

1.6 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.

1.7 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
- SO_2 emission factors for the processing of sour natural gas.

2. UNDERSTANDING FUEL CELLS

2.1 Introduction

Fuel cells are electrochemical devices that convert the chemical energy of a reaction directly into electric energy. As shown in Figure 5, the basic physical structure of a fuel cell consists of an electrolyte layer in contact with a porous anode and cathode on either side. In a typical fuel cell, gaseous fuel is fed continuously to the anode compartment and an oxidant, commonly oxygen from the air, is fed continuously to the cathode compartment.

The fuel or oxidant gases flow past the surface of the anode or cathode opposite the electrolyte and generate electric energy by the electrochemical oxidation of the fuel, usually hydrogen, and the electrochemical reduction of the oxidant, usually oxygen. A three-phase interface is developed among the reactants, electrolyte, and catalyst in the region of the porous electrode. The nature of this interface plays an important role in the electrochemical performance of a fuel cell, particularly in fuel cells with liquid electrolytes. In such fuel cells, the reactant gases diffuse through a thin electrolyte film that wets the portion of the porous electrodes and react electrochemically on their respective electrode surface. The electrolyte here provides a physical barrier preventing the fuel and oxidant gases from directly mixing. The electrolyte transports the dissolved reactants to the electrode and conducts an ionic charge between the electrodes, thereby completing the cell electric circuit.

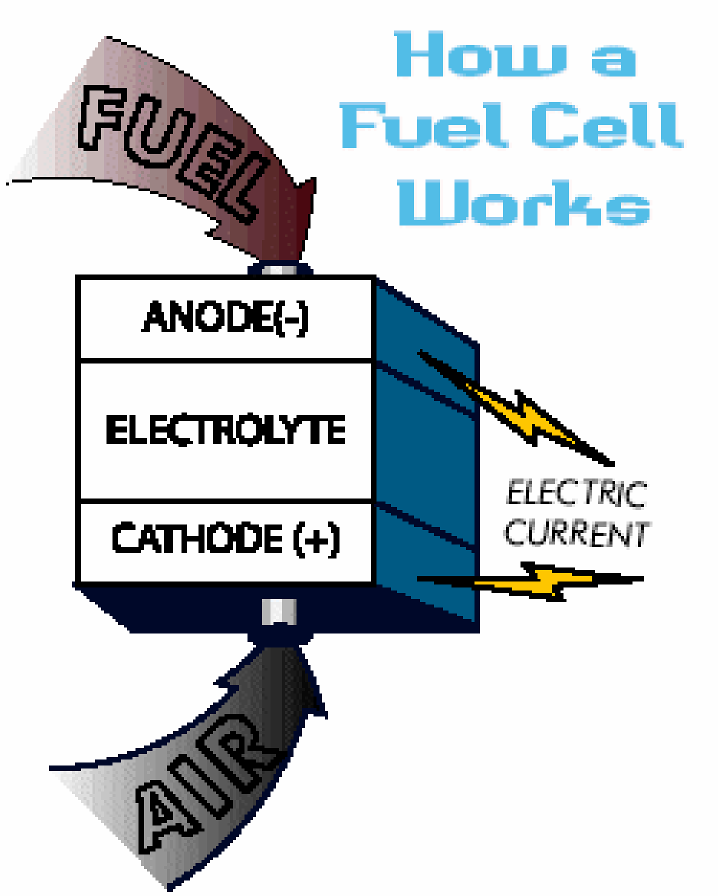


Figure 5. Working of fuel cells.

The porous electrodes provide a physical barrier separating the bulk gas phase and the electrolyte. It conducts the ions away from or into the three-phase interface once they are formed. They also provide a surface site where gas/liquid ionization/deionization takes place. In order to increase the rate of reactions, the electrode material should be catalytic as well as conductive, and porous rather than solid. The porous electrodes must be permeable to both the electrolyte and gases. Porous electrodes achieve much higher current densities because the electrode has a high surface area, relative to the geometric plate area, that significantly increases the number of reaction sites.

The operating temperature and useful life of a fuel cell dictate the physiochemical and thermomechanical properties of the materials used in the cell components. Aqueous electrolytes are limited to temperatures of about 200°C or lower because of their high water vapor pressure and/or rapid degradation at higher temperatures. The operating temperature also plays an important role in dictating the type of fuel that can be used in a fuel cell. In most practical applications the low temperature fuel cells with aqueous electrolytes are restricted to hydrogen as a fuel. In high temperature fuel cells, carbon monoxide or even methanol can be used due to the inherently rapid electrode kinetics and the smaller need for high catalytic activity at high temperatures. At the heart of the fuel cell membrane electrode assembly are two catalyst layers. These layers play a critical role in defining the performance of the membrane electrode assembly. Without them, the membrane electrolyte assembly would not function, and the fuel cell would not generate energy. The characteristics of the electrocatalysts are as follows:

(1) They should have good electrical conductivity to minimize resistive losses in the catalyst layer;
(2) They should be inexpensive to fabricate; and
(3) They should be manufacturable at high volume with good reproducibility.

Other requirements include the following [Watkins *et al.*, 1986]:

(1) Good interaction with ionomer;
(2) Reaction gas access; and
(3) Stability in contact with reactants, products, and electrolytes.

2.2 Electrochemistry of Fuel Cells

Oxidation half reaction: $2\,H_2 \rightarrow 4\,H^+ + 4\,e^-$ {1}

Reduction half reaction: $O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$ {2}

In the oxidation half reaction, gaseous hydrogen produces hydrogen ions that travel through the ionically conducting membrane to the cathode and electrons travel through an external circuit to the cathode. In the reduction half reaction, oxygen (supplied from air flowing past the cathode) combines with these hydrogen ions and electrons to form water and excess heat. These two half reactions occur very slowly at the low operating temperature, typically 70°C. Catalysts are used on both the anode and cathode to increase the rates of each half reaction.

2.3 Thermodynamics behind the Working of Fuel Cells

To understand the thermodynamics of the hydrogen fuel cells it is important to consider the following points. Some of them are explained in the following sections.

2.3.1 Energy and the EMF of the hydrogen fuel cell

The electrical power and the energy output can be easily calculated from these well known formulas [Williams, 2000].

$$\text{Power} = V\,I \qquad \{3\}$$

$$\text{Energy} = V\,I\,t \qquad \{4\}$$

where: V is the voltage, I is the current and t is the time.

In the case of fuel cells, it is the Gibb's free energy that is important. This can be defined as the energy available to do external work, neglecting any work done by changes in pressure and/or volume. In a fuel cell, the external work involves moving electrons around an external circuit. Any work done by a change in volume between the input and the output is not harnessed by the fuel cell. Enthalpy is the Gibbs free energy plus the energy connected with entropy. In a fuel cell, it is the change in Gibbs free energy of formation (G_f) that gives us the energy released. This change is the difference between the Gibbs free energy of the products and the Gibbs free energy of the reactants, which is as follows:

$$G_f = G_{f \text{ of products}} - G_{f \text{ of the reactants}} \qquad \{5\}$$

If there are no losses in the fuel cell, and if the process is reversible, then all of this Gibbs free energy is converted to electrical energy. For the hydrogen fuel cell, two electrons pass around the external circuit for each water molecule produced and each molecule of hydrogen used. So for one mole of hydrogen used, 2N electrons pass around the external circuit where N is the Avogadro's number (6.023×10^{23}). If e^- is the charge on one electron, then the charge that flows is given by:

$$-2\,Ne = -\,2F \text{ coulombs}$$

where F is the Faraday constant.

If E is the electric work of the fuel cell, then the electrical work performed in moving this charge around the circuit is:

$$\text{Electrical work done} = \text{charge x voltage} = -2\,FE \text{ joules}$$

If the system is reversible, then this electrical work will be equal to the Gibbs free energy released $\Delta G_f = -2\,FE$.

$$E = -\,\Delta G_f \,/\, 2F \qquad \{6\}$$

This fundamental equation gives the electromotive force or reversible open circuit voltage of the hydrogen fuel cell.

2.3.2 Efficiency and efficiency limits

If the maximum temperature of the heat engine is T_1 and the heated fluid is released at temperature T_2, then according to Carnot the maximum efficiency [Williams, 2000] possible is:

$$\text{Carnot limit} = (T_1 - T_2)/\ T_1 \qquad \{7\}$$

The temperatures are in ^{o}Kelvin (absolute temperature), where room temperature is about 290^{o}K, and so T_2 is never likely to be small. As an example, for a steam turbine operating at 400^{o}C (675^{o}K) with the water exhausted through a condenser at 50^{o}C (325^{o}K), the Carnot efficiency is 675–325/ 675 = 0.52 (i.e., 52%)

The reason for this limit on efficiency for heat engines is not particularly mysterious. There must be some heat energy, proportional to the lower temperature. T_2 which is always wasted. With the fuel cells the situation is slightly different. It is quite well known that fuel cells are not subject to the Carnot efficiency limit. Indeed, it is commonly supposed that if there were no irreversibilities, then the efficiency would be 100%. Therefore it is the Gibbs free energy that is converted into electrical energy. If there were no losses, then all of this energy would be converted into electrical energy, and the efficiency would be 100%. The efficiency is defined as electrical energy produced/Gibbs free energy change.

Since a fuel cell uses material that is usually burned to release their energy, it would be practical to compare the electrical energy produced with the heat that would be produced by burning the fuel. This is sometimes called the enthalpy of formation (Δh_f) There are two different values that can be used for Δh_f. For the burning of hydrogen:

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O \text{ (Steam)} \quad \Delta h_f = -241.83 \text{ kJ mol}^{-1}$$

whereas if the product water is condensed back to liquid, the reaction is:

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O \text{ (liquid)} \qquad \Delta h_f = -285.84 \text{ kJ mol}^{-1}$$

The difference between these two values (44.01 kJ mol^{-1}) is the molar enthalpy of vaporization of water. The higher value is called the higher heating value (HHV) and the smaller value is called the lower heating value (LHV).

If all the energy from the hydrogen fuel cell were transformed into electrical energy, then the electromotive force [Williams, 2000] would be given by:

$$E = -\Delta h_f / 2F \quad = 1.48 \text{ V}$$

if using the high heating value and 1.25 if using the low heating value.

In practice, not all of the fuel that is fed to a fuel cell anode is used. A fuel use coefficient can be defined as $\mu_f =$ mass of the fuel reacted in the fuel cell/mass of the fuel input in the fuel cell. This is equivalent to the ratio of fuel cell current and the current that would be obtained if all the fuel were reacted. The fuel cell efficiency is given by:

$\eta = \mu_f V / 1.48 \times 100\%$ (in case of the HHV) [Williams, 2000]

2.3.3 Fuel cell irreversibilities

The fuel cell irreversibilities include the various losses associated with the fuel cell system. Some of the common losses are explained in the following sections.

2.3.3.1 Activation losses

These irreversibilities are caused by the slowness of the reactions taking place on the surface of the electrodes. A proportion of the voltage generated is lost in driving the chemical reaction that transfers the electrons to or from the cathode.

2.3.3.2 Fuel crossover and internal currents

This energy loss results from the waste of fuel passing through the electrolyte and, to a lesser extent, from electron conduction through the electrolyte. The electrolyte should only transport ions through the cell. However, a certain amount of fuel diffusion and electron flow is sometimes possible [Williams, 2000].

2.3.3.3 Ohmic losses

This voltage drop is the resistance to the flow of electrons through the material of the electrodes and the various interconnections, as well as the resistance to the flow of ions through the electrolyte. This voltage drop is ideally proportional to current density [Williams, 2000].

2.3.3.4 Mass transport or concentration losses

These losses result from the change in concentration of the reactants at the surface of the electrodes as the fuel is consumed. That concentration affects the voltage, and so this type of irreversibility is sometimes called concentration loss. Because the reduction in concentration is the result of a failure to transport sufficient reactant to the electrode surface, this type of loss is sometimes called mass transport loss.

2.3.4 Maximum thermal efficiencies

The thermal efficiency of a heat engine is determined by the amount of work the engine can perform with the thermal energy supplied to the system. The heat (Q_{in}) is released from the fuel cell when it is oxidized and is transferred to the working fluid [in the case of an internal combustion engine (ICE)]. The expansion of the working fluid (the combustion gases themselves in an ICE) is harnessed by machinery and converted into mechanical work, W_{net} by the following equation:

$$\eta_{th} = W_{net}/Q_{in} \qquad \{8\}$$

where η_{th} is the thermal efficiency.

The maximum thermal energy that can be achieved by a heat engine is given by the theoretical Carnot cycle, which is thermodynamically reversible.

$$\eta_{th,\ Carnot} = 1 - (T_L/T_H)$$

This equation shows that the thermal efficiency of reversible heat engines, depends on the ratio of the low (T_L) and high (T_H) temperatures in the thermodynamic cycle. Because the low temperature is usually fixed at the ambient condition, the efficiency is determined by the highest temperature in the cycle. The higher the temperature, the higher the efficiency. To reach the highest possible temperature, however, the fuel loses a portion of its chemical energy to irreversible processes that occur during combustion. Electrochemical cells such as fuel cells, on the other hand, operate at constant temperatures with products of the reaction leaving at the same temperature as the reactants. Because of this isothermal reaction, more of the chemical energy of the reactants is converted to chemical energy instead of being consumed to raise the temperature of the products; therefore, the electrochemical conversion process is less irreversible then the combustion reaction. In the electrochemical cell, none of the conditions that define heat engines is satisfied, so the Carnot efficiency, which limits the maximum work to the highest temperature of the cycle, is irrelevant to electrochemical fuel cells.

To make a direct comparison between heat engines and electrochemical cells, the first law-based efficiency is used. For the higher heating value (HHV) of the fuel, water in the combustion products is in the condensed form.

$$\eta_{th,\ cell} = W_{cell}/HHV = \eta eFE/(HHV)$$

The maximum thermal efficiency of an electrochemical cell is given at the open circuit voltage, E^0, the equilibrium condition in which no current is being drawn from the cell.

$$\eta_{th,\ cell,max} = \eta_e FE^0/(HHV) \qquad \{9\}$$

2.3.5 Cell efficiency

The thermal efficiency of an energy conversion device is defined as the amount of useful energy produced relative to the change in stored chemical energy that is released when a fuel has reacted with an oxidant.

$$\eta = \text{Useful energy} / \Delta H \qquad \{10\}$$

In the ideal case of an electrochemical converter, such as a fuel cell, the change in Gibb's free energy, ΔG, of the reaction is available as useful electric energy at the temperature of the conversion. The ideal efficiency of a fuel cell, operating irreversibly, is then:

$$\eta = \Delta G / \Delta H \tag{11}$$

The most widely used efficiency of a fuel cell is based on the change in the standard free energy for the cell reaction.

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O \quad \text{is given by}$$

$$\Delta G_r = G_{H2O} - G_{H2} - \tfrac{1}{2} G_{O2}$$

where the product (water) is in liquid form.

The efficiency of an actual fuel cell can be expressed in terms of the ratio of the operating cell voltage to the ideal cell voltage. The actual cell voltage is less than the ideal cell voltage because of the losses associated with cell polarization and the *iR* loss. The thermal efficiency of the fuel cell can then be written in terms of the actual cell voltage,

$$\eta = \frac{useful\ power}{\frac{\Delta G}{0.83}} = \frac{Volts\,actual\ x\ current}{Volts\,ideal\,x\,current / 0.83} = \frac{Volts\,actual\,x\,0.83}{Volts\,ideal}$$

A fuel cell can be operated at different current densities, expressed as mA/cm^2 or A/ft^2. The corresponding cell voltage then determines the fuel cell efficiency. Decreasing the current density increases the cell voltage, thereby increasing the fuel cell efficiency.

2.3.6 Fuel cells in comparison to internal combustion engines (ICE) and batteries

What internal combustion engines, batteries, and fuel cells have in common is their purpose: all are devices that convert energy from one form to another. The ICE operates on noisy, high temperature explosions resulting from the release of chemical energy by burning fuel with oxygen from the air. The ICE changes the chemical energy of the fuel to thermal energy to generate mechanical energy. The ICE is less efficient because it includes the conversion of thermal to mechanical energy, which is limited by the Carnot cycle. In an automotive fuel cell, hydrogen and oxygen undergo a relatively cool, electrochemical reaction that directly produces electrical energy. This electricity would be used by the motors to power the wheels of the vehicles. The direct hydrogen fuel cell will have no emissions even during idling. Batteries and fuel cells are similar in that they both convert chemical energy into electricity very efficiently both require minimal maintenance because neither has any moving parts. However, unlike a fuel cell, the reactants in a battery are stored internally and, when used up, the battery must be recharged or replaced.

2.3.7 Types of fuel cells

The different types of fuel cells are polymer electrolyte fuel cells, phosphoric acid fuel cells, molten carbonate acid fuel cells, and solid oxide fuel cells.

An ordinary electrolyte is a substance that dissociates into positively charged and negatively charged ions in the presence of water, thereby making the water solution electrically conducting. The electrolyte in a polymer electrolyte membrane fuel cell is a polymer and is usually referred to as a membrane. The appearance of the electrolyte varies depending upon the manufacturer, but the most prevalent membrane, Nafion^{TM} produced by DuPont, resembles the plastic wrap used for sealing foods. Typically, the membrane material is more substantial than common plastic wrap, varying in thickness from 75 to 200 microns.

In an operating fuel cell, the membrane is well humidified so that the electrolyte looks like a moist piece of thick plastic wrap. Polymer electrolyte membranes are somewhat unusual electrolytes in that, in the presence of water, the negative ions are held rigidly within their structure. Only the positive ions contained within the membrane are mobile and are free to carry positive charges through the membrane [Larmanie and Dicks, 2003]. In polymer electrolyte membrane fuel cells, these positive ions are hydrogen ions (or protons), hence the term proton exchange membrane fuel cell. The movement of the hydrogen ions through the membrane in one direction only, from anode to cathode, is essential to fuel cell operation. Without this movement of ionic charges within the fuel cell, the circuit defined by the fuel cell, wires, and load remains open, and no current can flow. Because their structure is based on a Teflon^{TM} backbone, polymer electrolyte membranes are relatively strong, stable substances. Although thin, a polymer electrolyte membrane is an effective gas separator. It can keep the hydrogen fuel separated from the oxidant air, a feature essential to the efficient operation of a fuel cell. Although they are ionic conductors, polymer electrolyte membranes do not conduct electrons. The organic nature of the polymer electrolyte membrane structure makes them electronic insulators, another feature essential to fuel cell operation. As electrons cannot move through the membrane, the electrons produced at one side of the fuel cell must travel, through an external wire, to the other side of the fuel cell to complete the circuit. It is in their route through the circuitry external to the fuel cell that the electrons generate electrical power. Because of the intrinsic nature of the materials used, low-temperature operation of approximately 70^{o}C is possible.

The cell is also able to sustain operation at very high current densities. These attributes lead to a fast start capability and the ability to make a compact and lightweight cell. Other beneficial attributes of the cell include no corrosive fluid hazard and a lower sensitivity to orientation. As a result, the polymer electrolyte fuel cell is particularly suited for vehicular power application. Transportation applications mean that the fuel of choice will likely be methanol, although hydrogen storage on-board in the form of pressurized gas and the partial oxidation of gasoline should be considered [Doss and Kumar, 2003]. The cell is also being considered for stationary power applications, which will use natural gas or other hydrogen-rich reformate [Hoogers, 2003]. The lower operating temperature of a PEFC results in both advantages and disadvantages. Low temperature operation is advantageous because the fuel cell can start from ambient conditions quickly, especially when pure hydrogen fuel is available. A disadvantage is that expensive platinum catalysts are required to promote the electrochemical reaction. CO binds strongly to platinum sites at temperatures below 150°C, which reduces the number of sites available for hydrogen chemisorption and electro-oxidation. Due to CO affecting the anode, only a few ppm of CO can be tolerated with the platinum catalyst at 70°C. Because reformed and shifted hydrocarbons contain about 1% of CO, a mechanism to reduce the level of CO in the fuel gas is required. The low temperature of operation also means that little heat is available from the fuel cell for any endothermic reforming process.

Water management has a significant impact on cell performance because, at high current densities, mass transport issues associated with water formation and distribution limit cell output. Without adequate water management, an imbalance will occur between the water produced and the water consumed within the fuel cell. Adverse effects include dilution of reactant gases by water vapor, flooding of the electrodes, and dehydration of the solid polymer electrolyte fuel cell membrane (PEFC) [Hoogers, 2003]. The adherence of the membrane to the electrode will also be adversely affected if dehydration occurs. Intimate contact between the electrodes and the electrolyte membrane is important because there is no free liquid electrolyte to form a conducting bridge. If more water is exhausted than produced, then it is important to humidify the incoming anode gas. If there is too much humidification, however, the electrode floods, which causes problems with diffusing the gas to the electrode [Hoogers, 2003].

The primary contaminants of a PEFC are CO, CO_2, and the hydrocarbon fuel. Reformed hydrocarbon fuels typically contain at least 1% CO. However, even small amounts of CO in the gas stream will preferentially adsorb on the platinum catalyst surface and block access of the hydrogen to the catalyst sites. Tests indicate that approximately 20 ppm of CO in the gas stream begins to impact cell performance. Fuel processing can reduce CO content by several ppm, but there are other system costs associated with an increased fuel purification process [Hoogers, 2003]. Platinum/ruthenium catalysts that have intrinsic tolerance to CO are being developed. These electrodes have been shown in controlled laboratory experiments to be CO tolerant up to 250 ppm [Williams, 2000]. Although much less significant than CO poisoning, CO_2 affects anode performance through the reaction of CO_2 with adsorbed hydrides on platinum.

This reaction is the electrochemical equivalent of the “water gas shift reaction”. A number of system approaches can be used to clean up the fuel feed. These include pressure swing adsorption, membrane separation, methanation, and selective oxidation [Hoogers, 2003]. Although selective oxidation does not remove CO_2, it is usually the preferred method for CO removal because of the parasitic system loads and energy required by the other methods. In selective oxidation, the reformed fuel is mixed with air or oxygen either before the fuel is fed into the cell or within the stack itself. Current selective oxidation technology can reduce CO levels to less than 10 ppm, but this is difficult to maintain under actual operating conditions.

Another approach involves the use of a selective oxidation catalyst that is placed between the fuel stream inlet and the anode catalyst. Introducing an air bleed to the fuel stream appears to be the most effective way to reduce CO to an acceptable level. Work is continuing in this field to identify methods and materials that are more tolerant to impurities in the fuel cell feed [Hoogers, 2003].

The electrolyte in the phosphoric acid fuel cell is 100% concentrated phosphoric acid, which operates at 150 to 200°C. The use of 100% concentrated acid minimizes the water vapor pressure, so water management in the cell is not difficult. The matrix used to retain the acid is silicon carbide, and the electrocatalyst in both the anode and cathode is platinum.

The PC-25 fuel cell is the first to enter the commercial market. The plant was developed by the International Fuel Cells Corporation. The onsite plant is proving to be an economic and beneficial addition to the operating systems of commercial buildings and industrial facilities because it is superior to conventional technologies in terms of reliability, efficiency, environmental impact, and ease of siting [Hoogers, 2003]. Because of its attributes, the PC-25 is being installed in hospitals, hotels, large office buildings, manufacturing sites, waste water treatment plants, and institutions [Hoogers, 2003] to meet the following requirements:

(1) Onsite energy;
(2) Continuous power- back up;
(3) Uninterrupted power supply;
(4) Premium power quality;
(5) Independent power source;

Results from the operating units as of August 2000 are as follows [Hoogers, 2003]:

(1) Total fleet operation was about 3.5 million hr;
(2) The plants achieve 40% LHV electric efficiency and the overall use of fuel energy approaches 80% for cogeneration applications;
(3) Operations confirm that rejected heat from the initial PAFC plants can be used for cogeneration;
(4) One plant has completed over 50,000 h of operation, and a number of plants have operated over 40,000 hr;
(5) It is estimated that cell stacks can achieve a life of approximately 5 to 7 years;
(6) Emissions are so low that the PC-25 plant is exempt from the environmental quality standards, which have the most stringent limits in the United States; and
(7) The sound pressure level is 62 dba at 9 meters from the fuel cell.

This fuel cell operates at 600 to 700°C. At high operating temperatures, Ni (anode) and nickel oxide (cathode) are adequate to promote reaction. Noble metals are not required. The electrolyte in this fuel cell is usually a combination of alkali carbonate, which is retained in the ceramic matrix of $LiAiO_2$.

The electrolyte in the solid oxide fuel cell is a solid, nonporous metal oxide, usually Y_2O_3 stabilized ZrO_2. The anode is Co-ZrO_2 and the cathode is Sr doped $LaMnO_3$.

2.3.8 Characteristics of fuel cells

The two very important merits that have been instrumental in driving the interest for terrestrial applications are the combination of relatively high efficiency and very low environmental intrusion. Measured emissions from the phosphoric acid fuel cell unit are less than

1 ppm of NO_x, 4 ppm of CO, and less then 1 ppm of reactive organic gases. In addition the fuel cells operate at a constant temperature, and the heat from the electrochemical reaction is available for cogeneration applications. Other characteristics that the fuel cell plants offer include the following:

(1) Direct energy conversion (no combustion);
(2) No moving parts in the energy converter;
(3) Quiet;
(4) Fuel flexibility;
(5) Size flexibility;
(6) Modular installations to match load and increase reliability;
(7) Clean; and
(8) Environmentally safe (lack of emissions).

The two major impediments to the wide spread use of fuel cells are the high initial cost and high-temperature cell endurance operation. Other drawbacks [Hoogers, 2003] include the unfamiliar technology to the power industry, undeveloped infrastructure, and high cost of platinum catalyst.

2.3.9 Advantages/disadvantages of different types of fuel cells

The advantages and disadvantages of different fuel cells depend upon their usage, performance, costs, and size. The advantages of polymer electrolyte fuel cells [International Fuel Cells, 2001] include the following:

(1) They are tolerant of carbon dioxide. As a result, PEM fuel cells can use unscrubbed air as oxidant, and reformate as fuel;
(2) They operate at low temperatures;
(3) They use a solid, dry electrolyte;
(4) They use a “non-corrosive” electrolyte;
(5) They have high voltage, current and power density;
(6) They operate at low pressure, which increases safety;
(7) They have good tolerance to differential reactant gas pressures; and
(8) They use stable materials of construction.

The disadvantages [Ledjeff, 1992] include the following:

(1) They cannot tolerate more then 50 ppm carbon monoxide;
(2) They can tolerate only a few ppm of total sulfur compounds;
(3) They need reactant gas humidification;
(4) They use an expensive platinum catalyst; and
(5) They use an expensive membrane that is difficult to work with.

The advantages of phosphoric acid fuel cells [Ledjeff, 1992] include the following:

(1) They are tolerant to carbon dioxide up to a certain extent. As a result, these fuel cells can use unscrubbed air as oxidant, and reformate as fuel;
(2) They operate at low temperature, but at higher temperatures than other low-temperature fuel cells. Thus, they produce higher grade waste heat that can potentially be used in cogeneration (combined heat and power) applications; and
(3) They have stable electrolyte characteristics with low volatility even at operating temperatures as high as 200ºC.

The disadvantages [Ledjeff, 1992] are as follows:

(1) They can tolerate very less carbon monoxide;
(2) They can tolerate only about 50 ppm of total sulfur compounds;
(3) They use a corrosive liquid electrolyte at moderate temperatures, resulting in material corrosion problems;
(4) They have a liquid electrolyte, introducing liquid handling problems;
(5) They are large and heavy; and
(6) They cannot auto reform hydrocarbon fuels.

The advantages of molten carbonate fuel cells [Ledjeff, 1992] are as follows:

(1) They generate high-grade waste heat;
(2) They have fast reaction kinetics;
(3) They have high efficiency; and
(4) They do not need noble metal catalysts.

The disadvantages include [Ledjeff, 1992]:

(1) They require the development of suitable materials that are resistant to corrosion, have high endurance and ease to fabrication;
(2) They have a high intolerance to sulfur;
(3) They have a liquid electrolyte, which introduces liquid handling problems; and
(4) They require a considerable warm up period.

The advantages of solid oxide fuel cells [Ledjeff, 1992] include the following:

(1) They support spontaneous internal reforming of hydrocarbon fuels;
(2) They generate high-grade waste heat;
(3) They have fast reaction kinetics;
(4) They have very high efficiency;
(5) They have a solid electrolyte, avoiding problems associated with handling liquids; and
(6) They do not need noble metal catalysts.

The disadvantages [Ledjeff, 1992] include the following:

(1) They have a moderate intolerance to sulfur;
(2) They do not yet have practical fabrication processes; and

(3) The technology is not yet mature.

2.3.10 Environmental impacts of fuel cells

The environmental impacts of fuel cell use depend upon the source of the hydrogen-rich reformate used. If pure hydrogen is used, fuel cells have virtually no emissions except water. However, hydrogen is seldom used due to problems with storage and transportation, but in the future many people have visualized the growth of a hydrogen economy [Kaarsberg *et al.*, 1999]. 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 $CO_{2,}$ because any carbon released can be taken from the atmosphere by photosynthetic plants. Any high temperature combustion, such as that which would take place in a spark ignition engine fueled by methanol, produces NO_x, gasses which contribute to acid rain. Fuel cells virtually eliminate NO_x emissions because of the lower temperatures of their chemical reactions. If fossil fuels are processed, fuel cells have emissions of carbon dioxide and sulfur dioxide, but these emissions are lower than those from traditional combustion processes because of the higher efficiency of fuel cell power plants. Higher efficiencies result in less fuel being consumed to produce a given amount of electricity. This reduces the carbon dioxide and sulfur dioxide emissions [Kaarsberg *et al.*, 1999].

2.3.11 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.

2.3.12 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 6.

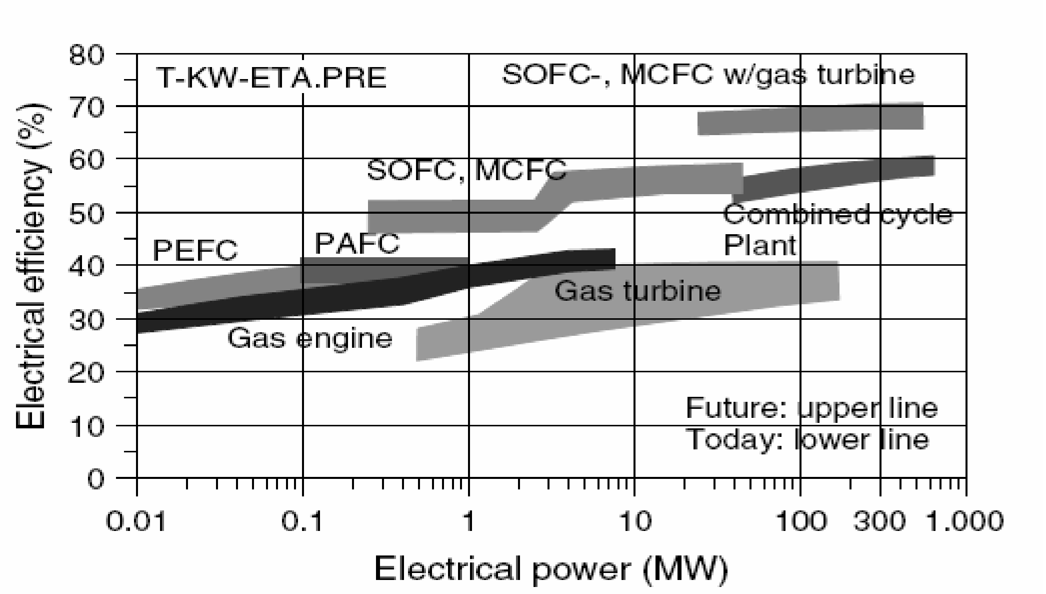


Figure 6. Typical electrical efficiency of various technologies as a function of the electrical power range with natural gas as fuel [Pehnt, 2003].

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 phosphoric acid fuel cells (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.

2.3.13 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.

2.3.14 The total picture

In Figure 7, 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 kW_{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.

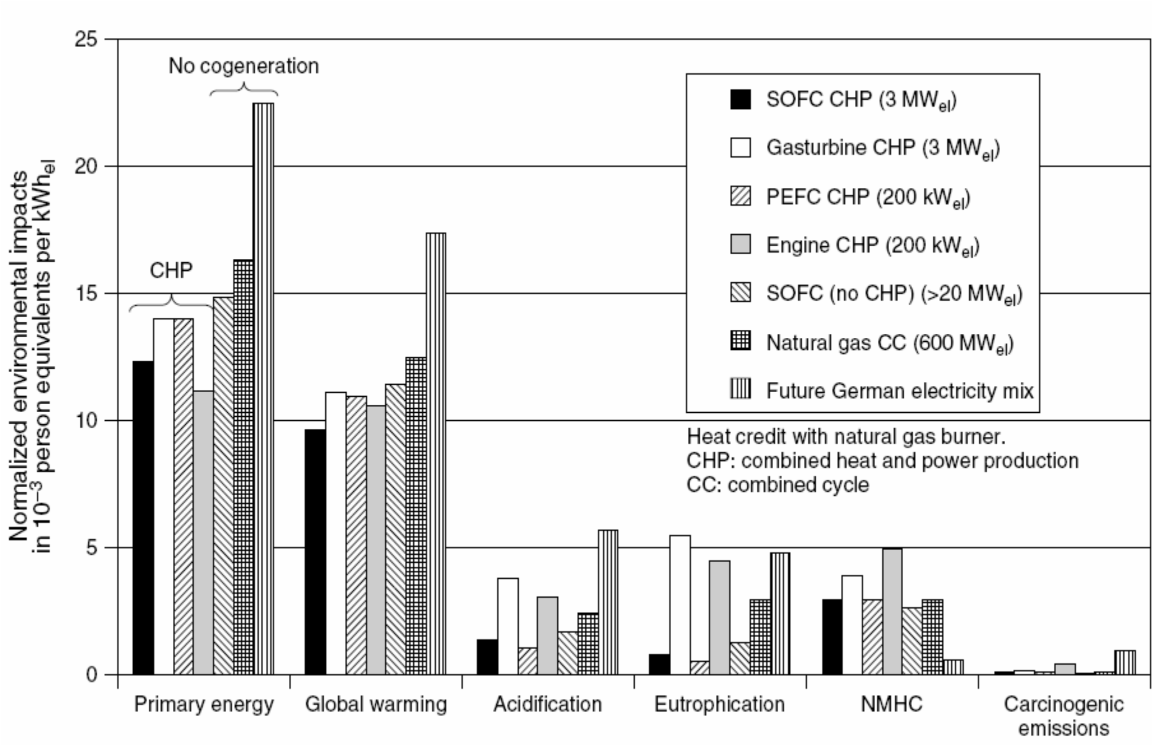


Figure 7. Environmental impacts associated with primary energy, global warming potential, acidification, eutrophication, nonmethane hydrocarbons, and carcinogenic emissions for various techniques employed to generate hydrogen [Pehnt, 2003].

2.3.15 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% to 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.

2.3.16 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].

2.3.17 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 limits 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].

2.3.17.1 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 sport utility vehicles (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 cares 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 U.S. already captures 100 million tons of CO_2 a year and releases the CO_2 again [Shinnar, 2003].

2.3.17.2 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.

2.3.18 Emission-free fuel reformers for fuel cells

Conventional fuel reformers are complex, multi-component devices which produce large amounts of CO_2 emissions. Fossil fuel-based power sources are major producers of greenhouse gas (mostly, CO_2) 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 CO_2 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 CO_2 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 CO_2 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 CO_2 byproduct. The use of carbon-based catalysts can potentially solve catalyst regeneration and CO_2 emission problems. The main objective is the development of efficient CO_2-free fuel reformers based on catalytic pyrolysis of hydrocarbon fuels for mobile and portable fuel cell applications. CO_2-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 sec, respectively (depending on the hydrocarbon). Before the pyrolysis experiments, the reactor is purged with an inert gas, argon (Ar), at 700°C for 1.0 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 8 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 $[H_2]$=80 vol.%, the balance being methane (for the comparison, POx- and ATR-reformers produce the gas with $[H_2]$=35–40 vol.%). The hydrogen-rich gas enters the anode compartment of the fuel cell (e.g., proton exchange membrane, PEM, FC) where it electrochemically reacts with oxygen (air) producing dc electricity.

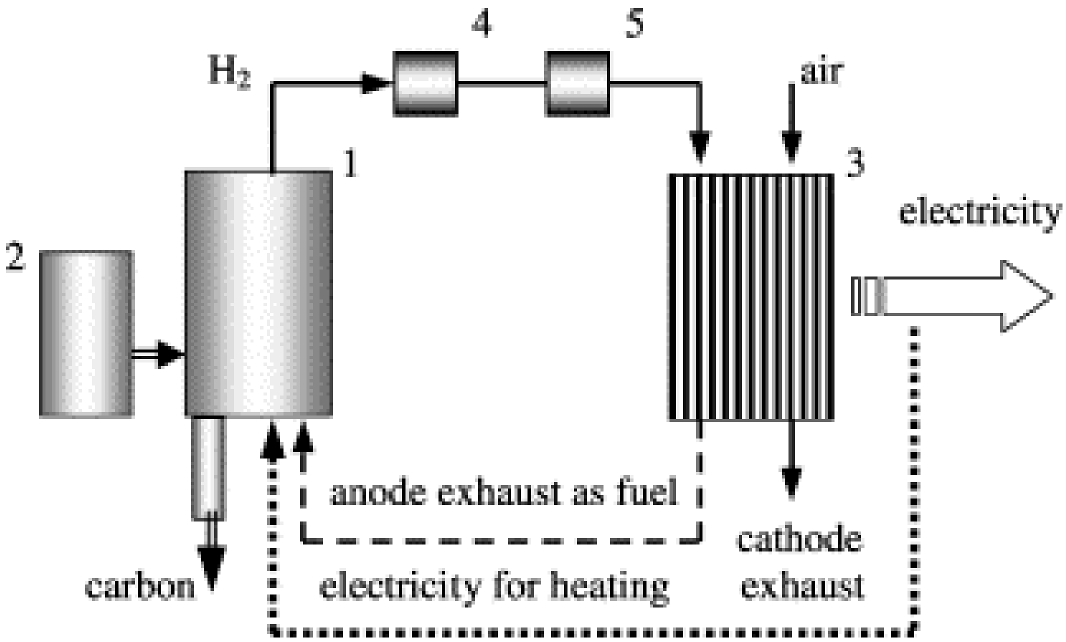


Figure 8. Emission-free fuel reformers for mobile and portable fuel cell applications [Muradov, 2003].

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 H_2S) 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 CO_2 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 CO_2 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) CO_2 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/CO_2-free hydrogen-rich gas with the average $[H_2]$=80 vol.%, the balance being methane (which compares favorably with the quality of reformate gas, i.e., $[H_2]$=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 CO_2 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.).

2.3.19 Atmospheric impact of hydrogen

Molecular hydrogen (H_2) 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.

2.3.19.1 Ground level ozone production

During summertime, the United Kingdom [AEA 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).

$$\bullet OH + H_2 \rightarrow H + H_2O$$

The reaction of H_2 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.

2.3.19.2 Tropospheric ozone production

The complete oxidation of hydrogen to water in the troposphere leads to the production of ozone (O_3), as shown by the equation:

$$H_2 + 2\ O_2 + h\nu \rightarrow H_2O + O_3$$

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.

$$HCHO + h\nu \rightarrow H_2 + CO \qquad \{12\}$$
$$HCHO + h\nu \rightarrow H + HCO \qquad \{13\}$$

The molecular route {12} is a major source of atmospheric hydrogen [Simmonds *et al.*, 2000]. The free radical route {13} 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.

2.3.19.3 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 it is involved in the production of tropospheric ozone (a strong greenhouse gas) and it can modify the concentration of methane (another greenhouse gas) through its effect on the concentration of the hydroxyl radical (•OH).

2.3.19.4 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 reactive hydrogen (•H, •OH), which can catalyze ozone destruction in the upper stratosphere.

X (X = H, OH) + $O_3 \rightarrow XO + O_2$
$XO + O \rightarrow X + O_2$
$O + O_3 \rightarrow 2\ O_2$

3. FUEL CELL TECHNOLOGIES

3.1 Distributed Generation

Distributed generation involves small, modular power systems that are sited at or near their points of use. The typical system is less than 30 MW, used for generation or storage, and is extremely clean. The market for distributed generation is aimed at customers dependent on reliable energy, such as hospitals, manufacturing plants, grocery stores, restaurants, and banking facilities. There are many applications for distributed generation systems:

(1) Peak shaving;
(2) Cogeneration;
(3) Grid support;
(4) Standby power; and
(5) Remote/stand alone.

Distribution generation systems have small footprints, and are modular and mobile, making them very flexible in use. The systems provide benefits at the customer level, the supplier level, and the national level. Benefits to the customer include high power quality, improved reliability, and flexibility to react to electricity price spikes. Supplier benefits include avoiding investments in transmission and distribution capacity upgrades by locating power where it is most needed and opening new markets in new areas. At the national level, the market for distributed generation establishes a new industry, boosting the economy. The improved efficiencies also reduce greenhouse gas emissions.

The barriers include technical, economic, institutional and regulatory issues. Many of the proposed technologies have not yet entered the market and will need to meet the performance and pricing targets before entry. Lack of standardized procedures creates delays and discourages customer-owned projects. Siting, permitting, and environmental regulations can also delay and increase the costs of distributed generation projects. Fuel cells in distributed generation have been hindered by high initial costs. However, costs are expected to decline as manufacturing capacity and capability increase and designs and integration improve. The fuel cell systems offer many potential benefits as distributed generation systems. They are small and modular, and capital costs are relatively insensitive to scale. This makes them ideal candidates for a diverse amount of applications where they can be matched to meet specific load requirements. The systems are unobtrusive with very low noise levels and have negligible air emissions. These qualities enable them to be placed close to the source of power demand. Fuel cells also offer higher efficiencies than conventional plants. The efficiencies can be enhanced by utilizing the quality waste heat derived from the fuel cell reactions for cogeneration and combined cycle applications.

3.2 Cogeneration

Cogeneration, also known as Combined Heat and Power (CHP), is the production of electricity and heat in a single process for dual output streams. In conventional electricity generation, 35% of the energy potential contained in the fuel is converted on average into electricity, while the rest is lost as waste heat as shown in Figure 9. Cogeneration uses electricity and heat and therefore results in an efficiency of almost 90%, giving energy savings around 30% when compared with the separate production of electricity from conventional power stations and of heat from boilers as shown in Figure 10. It is the most efficient way to use fuel.

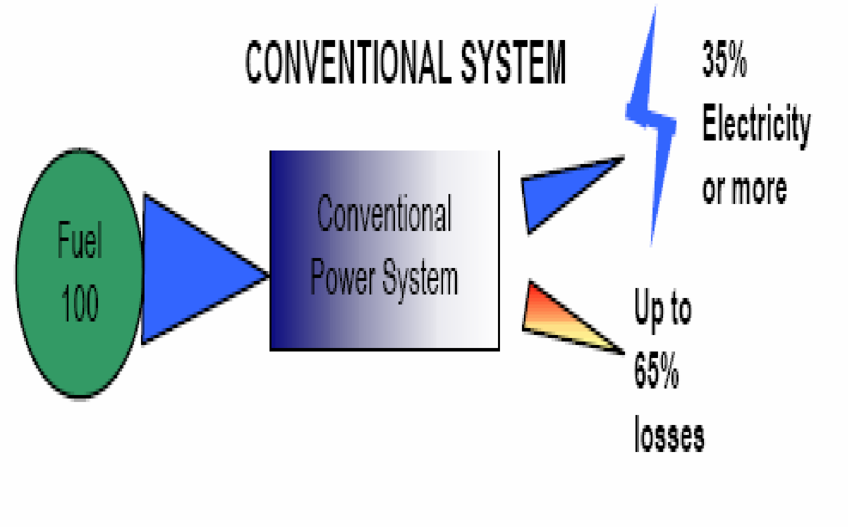


Figure 9. Conventional power system.

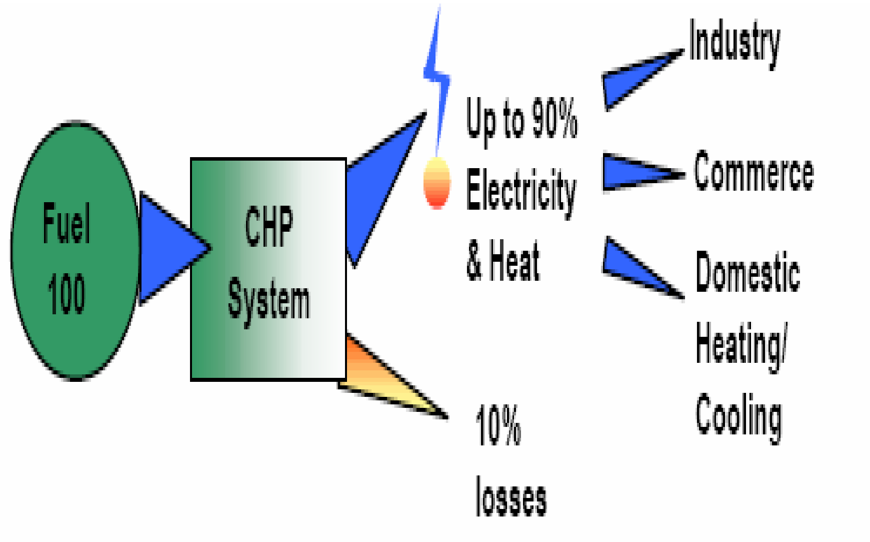


Figure 10. Combined heat and power system.

Cogeneration helps in reducing energy costs, thus improving the energy security of supply. The heat produced by cogeneration can be delivered through various mediums, including warm water, steam, or hot air. It is also possible to do trigeneration, the production of electricity, heat, and cooling in a single process. Trigeneration is also an attractive option, such as in production processes with cooling requirements. Cogeneration schemes are usually sited close to the heat and cooling demand and, ideally, are built to meet this demand as efficiently as possible. Under these conditions more electricity is usually generated than is needed. In recent years cogeneration has become an attractive and practical proposition for a wide range of applications in the United States. These include the process industries including pharmaceuticals, and paper and board, commercial and public sector buildings and district heating schemes. A range of technologies can be applied to cogenerate electricity and heat. All cogeneration schemes include an electricity generator and a system to recover the heat. The following technologies are currently in widespread use: Steam and gas turbines, combined cycle, diesel and Otto engines.

These technologies are readily available, mature, and reliable. Three other technologies to be commercialized in the market within the next few years are micro-turbines, fuel cells; and stirling engines.

Cogeneration schemes can have different sizes, ranging from an electrical capacity of less than 10 kW_e to 500 MW_e. Cogeneration can be based on a wide variety of fuels, and individual installations may be designed to accept more than one fuel. While solid, liquid, or gaseous fossil fuels dominate currently, cogeneration from biomass fuels is attracting attention. Sometimes, fuels are used that otherwise would produce waste. These substances increase the cost efficiency of cogeneration.

3.2.1 Cogeneration power plants

Distributed generation is a term used for small power generators located near the point of electricity use as opposed to central power plants using transmission grids. As shown in Figures 1 and 2, the production of both electricity and thermal energy from a cogeneration system leads to more efficient energy use. A typical cogeneration system can convert 30 to 35% of the energy in the fuel to electricity, with another 50 to 55% produced as steam and/or hot water.

By locating energy production near the user, loads on existing transmission systems can be reduced, negating the need for expensive upgrades or new transmission lines. Reducing the load on existing transmission systems also improves the operating stability of the system. Cogeneration plants sized to supply the thermal load to a facility may produce excess electricity that can be sold back to the grid.

Cogeneration systems are often installed and operated by the electricity user and can be maintained to provide more dependable power. Existing transmission systems may also act as a backup to the cogeneration system.

Improving the overall efficiency of fuel energy use also leads to reduced emissions of pollutants and greenhouses gases into the atmosphere. The cogeneration system supplies both electricity and thermal energy, in place of purchasing electricity from the grid and firing natural gas in a separate boiler to generate thermal energy for plant use.

Cogeneration power plants are usually small plants sized to either the user's electricity demand or thermal demand. The availability of a number of cogeneration plants operated by independent companies leads to increased competition in the production and sale of electricity that may lead to improved quality and reduced cost to the user.

3.2.2 Summary of benefits of CHP

Some of the key benefits of combined heat and power are as follows:

(1) It produces over 10% of the electric power generated in the U.S.;
(2) It saves users over $5 billion each year in energy costs;
(3) It reduces NO_x emissions by 0.5 million tons per year;
(4) It reduces sulfur dioxide emissions by 1 million tons per year; and
(5) It prevents the release of over 35 million metric tons of carbon equivalent in to the atmosphere.

3.2.3 Barriers to increased use of cogeneration

There are some barriers to the greater use of cogeneration.

Large central power plants and the associated transmission grid can be installed at government cost. This usually leads to an artificially low price that is difficult for new cogeneration facilities to compete with.

Although fuel use efficiency is higher, the economies of scale usually result in a high capital equipment cost per kilowatt of electricity produced for small cogeneration plants.

In addition, safety aspects and power quality requirements increase the cost of the equipment required to connect cogeneration systems to an existing transmission grid.

3.2.4 CHP technologies

Among the most widely used and most efficient prime movers are reciprocating engines. Electric efficiencies of 35% make them an economic cogeneration option in many applications [Watkins *et al*., 1986]. In addition to CHP applications, diesel engines are widely used to provide standby or emergency power to commercial and industrial facilities for critical power requirements. Reciprocating engines have electric efficiencies of 35% (LHV) and are among the most efficient of any commercially available prime mover [Watkins *et al*., 1986].

Energy in the fuel is released during combustion and converted to shaft work and heat. Approximately 65% of the total energy input is converted to heat, while smaller amounts are also available from the oil cooler and the turbocharger's intercooler and aftercooler [Watkins *et al*.,, 1986]. Steam or hot water can be generated from recovered heat that is typically used for space heating, reheat, domestic hot water and absorption cooling [Watkins *et al*., 1986].

Reciprocating engines are typically used in CHP applications where there is a substantial hot water or low pressure steam demand. When cooling is required, the thermal output of a reciprocating engine can be used in a single-effect absorption chiller.

Steam turbines are one of the most versatile and oldest prime mover technologies used to drive a generator or mechanical machinery. The capacity of steam turbines can range from a horsepower to more than 1,500 MW for large utility power plants [Watkins *et al.*, 1986].

Modern, large condensing steam turbine plants have efficiencies approaching 40–45%; however, efficiencies of smaller industrial or turbines can range from 15–35% [Watkins *et al.*, 1986].

Heat recovery methods from a steam turbine use exhaust or extraction steam. Heat recovery from a steam turbine is somewhat misleading, since waste heat is generally associated with the heat source, in this case a boiler with an economizer or air preheater. A steam turbine can also be used as a mechanical drive for a centrifugal chiller.

In industrial applications, steam turbines may drive an electric generator or equipment, such as boiler feedwater pumps, process pumps, air compressors, and refrigeration chillers.

Gas turbines represent only 20% of the power generation market since 20 years ago [Watkins *et al.*, 1986]. Gas turbines have been long used by utilities for peaking capacity; however, with changes in the power industry and increased efficiency, the gas turbine is now being used for base load power.

Efficiency generally increases for higher power outputs and aeroderivative designs. Simple cycle efficiencies can vary between 25–40% LHV. Next-generation combined cycles are being advertised with electric efficiencies approaching 60% [Watkins *et al.*, 1986].

The simple cycle gas turbine is the least efficient arrangement since there is no recovery of heat in the exhaust gas. Hot exhaust gas can be used directly in a process or, by adding a heat recovery steam generator, exhaust heat can generate steam or hot water.

Gas turbines are a cost-effective CHP alternative for commercial and industrial end users, with a base load electric demand greater than about 5 MW. Gas turbines are frequently used in district steam heating systems since their high quality thermal output can be used for most medium pressure steam systems.

Most manufacturers are developing competing engines in the 25–250 kW range; however, multiple units can be integrated to produce higher electrical output while providing additional reliability [International Fuel Cells, 2001]. Microturbines are a relatively new entry in the CHP industry and therefore many of the performance characteristics are estimates based on demonstration projects and laboratory testing. Most designs offer a recuperator to maintain high efficiency while operating at combustion temperatures below NO_x formation levels. With recuperation, efficiency is currently in the 20%–30% LHV range [Watkins *et al.*, 1986].

Hot exhaust gas from the turbine section is available for CHP applications. Most designs incorporate a recuperator that limits the amount of heat available for CHP. Recovered heat can be used for hot water heating or low pressure steam applications.

Markets for the microturbine include commercial and light industrial facilities. Manufacturers will target several electric generation applications, including standby power, peak shaving, and base-loaded operation with and without heat recovery [Watkins *et al*., 1986].

Fuel cells offer the advantages of clean, quiet, and very efficient power generation, benefits that have driven their development in the past two decades. Fuel cells offer the ability to operate at electrical efficiencies of 40–60% (LHV) and up to 85% in CHP [Watkins *et al*., 1986]. Development of fuel cells for commercial use began in earnest in the 1970's for stationary power and transportation applications. Although several fuel cell designs are under development, only the PAFC is commercially available. The price of the most competitive PAFC is still around $3000/kW, which is too high for most industrial and commercial applications.

The electric efficiency of fuel cells is dramatically higher than that of combustion-based power plants. The current efficiency of PAFC is 40% with an estimated target of 40–60% (LHV). With the recovery of the thermal energy, overall fuel utilization could approach 85% [Watkins *et al*., 1986]. Fuel cells retain their efficiency at part load.

Significant heat is released in a fuel cell during electrical generation. The PAFC and polymer electrolyte fuel cells operate at lower temperatures and produce lower grades of waste heat generally suitable for commercial and industrial CHP applications. The molten carbonate fuel cells and solid oxide fuel cells operate at much higher temperatures and produce heat that is sufficient to generate additional electricity with a steam turbine or a microturbine hybrid gas turbine combined cycle.

The type of fuel cell determines the temperature of the heat liberated during the process and its suitability for CHP applications. Low temperature fuel cells generate a thermal product suitable for low-pressure steam and hot water CHP applications. High temperature fuel cells produce high-pressure steam that can be used in combined cycles and other CHP process applications. Although some fuel cells can operate at part load, other designs only operate under continuous base load conditions.

For stationary power, fuel cells are being developed for small commercial and residential markets and as peak shaving units for commercial and industrial customers. In a unique innovation, high temperature fuel cells and gas turbines are being integrated to increase electric efficiencies [Watkins *et al*., 1986]. Combined cycle systems are being evaluated for sizes up to 25 MW with electric efficiencies in the range 60–70% (LHV) [Watkins *et al*., 1986]. The hot exhaust from the fuel cell is combusted and used to drive the gas turbine. Energy recovered from the turbine's exhaust is used in a recuperator that preheats air from the turbine's compressor section. The heated air is then directed to the fuel cell and the gas turbine [Watkins *et al*., 1986]. The comparison of different CHP technologies is summarized in Table 2 and comparisons of different fuel cells for CHP applications are summarized in Table 3.

Table 2**.** Comparison of CHP technologies.

	Diesel Engine	**Natural Gas Engine**	**Steam Turbine**	**Gas Turbine**	**Micro-Turbine**	**Fuel Cells**
Electric efficiency (LHV)	30–50%	25–45%	30–42%	25–40%	20–30%	40–70%
CHP Installed cost($/kW)	800–1500	800–1500	800–1000	700–900	500–1300	>3000
O&M cost ($/kW)	0.005-0.008	0.007-0.015	0.004	0.002-0.008	0.002-0.01	0.003-0.015
Availability	90-95%	92-97%	Near 100%	90-98%	90-98%	>95%
Start up time	10 s	10s	1 h–1day	10 min-1h	60 s	3 days
Fuel pressure (psi)	<5	1–4.5	n/a	120–500	40–100	0.5–4.5
Fuels	Diesel and residual oil	Natural gas, biogas, propane	all	Natural gas, biogas, propane, distillate oil	Natural gas, biogas, propane, and distillate oil	Hydrogen, natural gas, propane
Noise	Moderate to high	Moderate to high	Moderate to high	Moderate	Moderate	Low
NO_x emission (lb/mWhr)	Mar-33	2.2–28	1.8	0.3–4	0.4–2.2	<0.02
Uses for heat recovery	Hot water, LP steam, district heating	Hot water, LP steam, district heating	LP -Hp, steam, district heating	Direct heat, hot water, LP steam, district heating	Direct heat, hot water, LP steam	Hot water, LP-Hp steam
Useable temperature for CHP (^oF)	180–900	300–500	n/a	400–650	400–650	140–700

Table 3. Comparison of fuel cell types.

	AFC	**PEM**	**PAFC**	**MCFC**	**SOFC**
Typical unit sizes, (kW)	<<100	0.1–500	5–200 and up to 5000	800–2000 and up to 100,000	2.5–100,000
Electric efficiency	Up to 70%	Up to 50%	40-45%	50-57%	45-50%
Installed cost, (\$/kW)		4000	300-3500	800-2000	1300-2000
Commercial availability	Not for CHP	R and D	yes	Rand D	R and D
Electric/thermal energy		1	1	Up to 1.5	Up to 1.5
Oxidation media	Oxy+gen	Oxygen from air	Oxygen from air	Oxygen from air	Oxygen from air
Cooling medium		water	Boiling water	Excess air	Excess air
Fuel	H_2	H_2 and reformed H_2	H_2 reformed from natural gas	H_2 and CO reformed from natural gas or coal gas	H_2 and CO reformed from natural gas or coal gas
Operating temperature, (^{o}F)	160–210	120–210	320–410	1250	1500–1800
Operating pressure, (psig)		14.7–74	14.7–118	14.7–44	14.7–>150
Applications	Space and military	Stationary power, bus, and rail road automotive	Stationary power, rail road propulsion	Stationary power	stationary

3.3 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 reformate 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 reformate 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, 2004a]. 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 waters 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.

4. OBJECTIVES

The objective of this task is to promote and establish a hydrogen infrastructure and application base in the southeast with attention focused on the application of fuel cells for stationary electric power generation.

The specific objectives of this task are as follows:

- Assess the ability of hydrogen production and utilization to be competitive with other forms of energy generation.
- Review various case histories involving the use of hydrogen-based fuel cells for electric power generation.

5. RESEARCH TASK

This task addresses the use of hydrogen-based fuel cell technology in stationary electric power generation. Attention also focuses on demonstrations in major commercial and residential applications. Feasibility studies are conducted comparing fuel cell electrical generation with other power generation systems. Alternate power generation systems are compared from an economic, environmental, and public health (emissions) perspectives. Case studies of fuel cell power generation are reported for the purpose of evaluating actual performance and public perception of hydrogen-based fuel cell technology. In support of the simulation and analysis, an extensive fuel cell system model (GCtool) was used to model the system, evaluate potential changes in components or trade-offs in operating parameters, in an effort to optimize fuel cell system performance. GCtool is discussed in more detail in the publication by Geyer and Ahluwalia [1988].

6. TYPICAL RESIDENTIAL FUEL CELL SYSTEM

Figure 11 summarizes the different components in a typical fuel cell system. It consists of a fuel processor that converts the fuel to a hydrogen-rich reformate suitable for the fuel cell anode. The processed fuel is fed in the fuel cell stack which converts hydrogen and air in to DC power. A power conditioner (inverter) is used to convert DC power to AC power. Some of the heat from the fuel cell stack is rejected as waste heat and the rest is recovered for useful cogeneration.

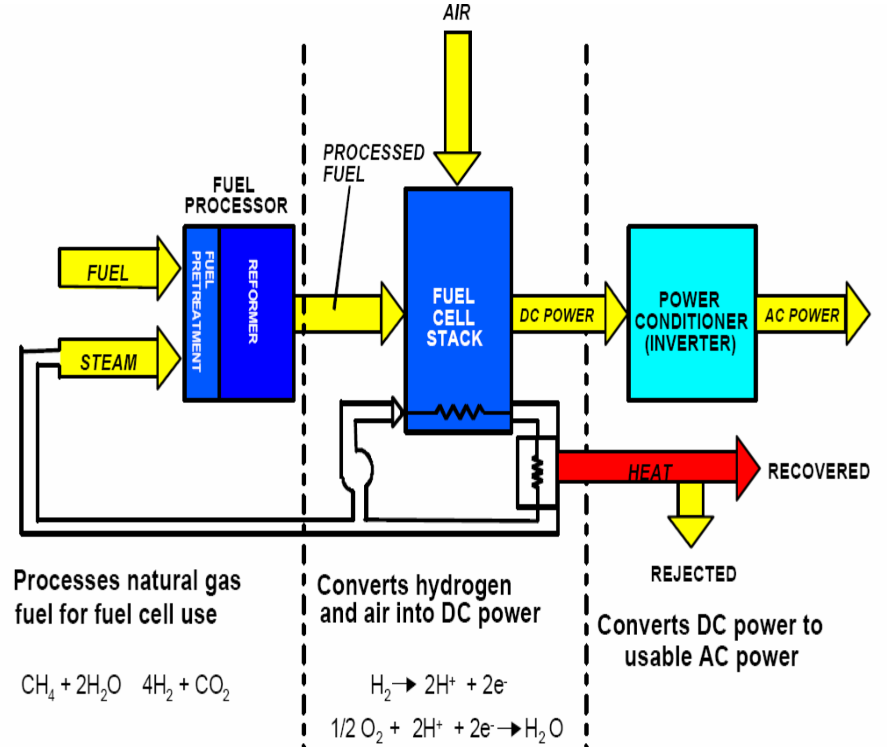


Figure 11. Simplified fuel cell system.

6.1 Fuel processor

Fuel processing is defined as the conversion of a commercially available gas, liquid, or solid fuel to a fuel gas reformate (rich in hydrogen) suitable for the fuel cell anode reaction. As shown in Figure 12, it also consists of cleaning and removing the harmful species in the raw fuel. Fuel cleaning involves the removal of sulfur, hydrides, ammonia, and other impurities to prevent fuel processor and fuel cell catalysts poisoning [Hoogers, 2003]. Reformate gas alteration involves converting carbon monoxide and water in the fuel gas reformate to hydrogen and carbon dioxide via the high and low temperature water gas shift reaction; selective oxidation to reduce CO to a few ppm; or removal of water by condensing to increase the concentration of hydrogen [Hoogers, 2003]. The fuel conversion and reformate gas alteration process can take place either external to the fuel cell or within the fuel cell anode compartment. The former is referred to as external reforming and the latter is referred to as internal reforming.

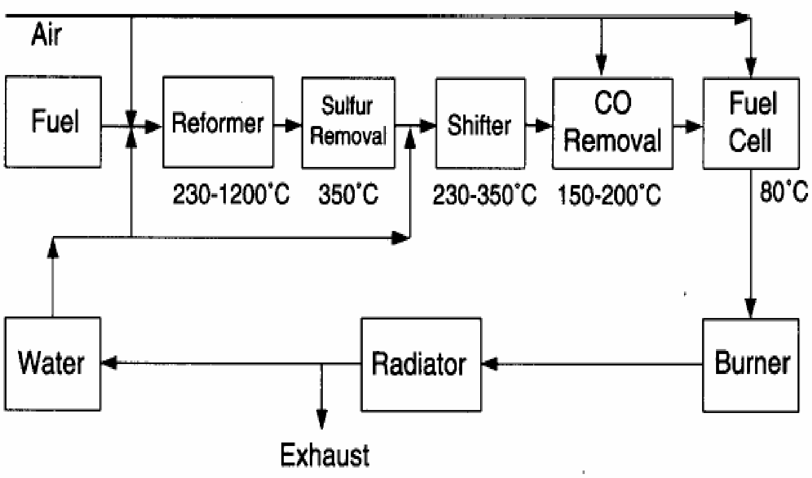


Figure 12. Fuel processing for fuel cell power systems.

The step-by-step process is as follows: 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 [International Fuel Cells, 2001]. The reformer operating temperature is dependent on the fuel used, and may range from 250°C (methanol) to over 700°C (methane) [International Fuel Cells, 2001].

The high temperature water shift reactor is used to convert carbon monoxide to carbon dioxide. The above reactor typically operates at temperatures between 250–320°C [International Fuel Cells, 2001]. The low temperature water shift reactor is used to convert the remaining carbon monoxide to carbon dioxide. The low temperature reactor typically operates at temperatures between 200–250°C [International Fuel Cells, 2001]. The low temperature PEM fuel cells use a preferential oxidation (PROX) reactor to shift any remaining carbon monoxide to carbon dioxide by introducing a suitable amount of oxygen to the reformate stream. This is done because trace amounts of carbon monoxide will be absorbed on the platinum catalyst and block access of hydrogen to the catalyst sites, reducing the performance of the cell [International Fuel Cells, 2001].

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. The cost, complexity, and weight of the fuel processing system is greatly reduced.

Four separate reactions occur in the fuel processor:

$$C_xH_yO_z + (x - z)\,H_2O \leftrightarrow x\,CO + (x + y/2 - z)\,H_2$$

This reaction involves direct conversion of a hydrocarbon fuel ($C_xH_yO_z$) into a mixture of hydrogen and carbon monoxide, and occurs exclusively in the reformer.

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

This describes a shift reaction in which carbon monoxide produced in the reformer is reacted with water vapor to produce additional hydrogen and carbon dioxide. This shift reaction is exothermic and occurs in the reformer, high temperature water shift, and low temperature water shift reaction vessels.

$$CO + \frac{1}{2} O_2 \leftrightarrow CO_2$$

$$H_2 + \frac{1}{2} O_2 \leftrightarrow H_2O$$

These reactions occur exclusively in the PROX reactor vessel, where remaining carbon monoxide is converted to carbon dioxide by means of a reaction with oxygen. Oxygen that enters the PROX reactor and does not oxidize with carbon monoxide will reacts with hydrogen to form water vapor.

6.2 Fuel Cell Stack

The fuel cell stack is the electrode electrolyte structure where energy conversion occurs. The electrode in contact with the fuel stream is called the anode, while the electrode in contact with the oxidant is termed the cathode. In PEM fuel cell systems, the stack typically operates at 70°C. The reactions occurring in the PEM fuel cell stack proceed as follows:

Anode: $H_2 \rightarrow 2\,H^+ + 2\,e^-$
Cathode: $2\,H^+ + \frac{1}{2} O_2 + 2\,e^- \rightarrow H_2O$
Overall: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

The theoretical maximum amount of electrical energy that can be obtained from the electrochemical reactions occurring in the fuel cell stack is equal to the change in the Gibbs free energy within the cell. The total amount of energy released in the electrochemical reactions is equal to the enthalpy change within the cell. The theoretical maximum efficiency of conversion from chemical to electrical energy, $\acute{\eta}_{max}$, is obtained as the ratio between the change in the Gibbs free energy (ΔG_{stack}) and the change in the enthalpy (ΔH_{stack}) that occur in the cell stack:-$\eta_{max} = \Delta G_{stack} / \Delta H_{stack}$.

6.3 Thermal Integration and Water Management System

This system maintains the fuel stack and fuel processor in thermal and mass equilibrium. It uses pumps, fans, heat exchangers, and controls, which create a constant power requirement on the fuel cell generator whenever it is running. The process is described as follows.

As shown in Figure 13, the gasoline fuel is mixed with preheated air and superheated steam and fed to a catalytic autothermal reformer (ATR) where fuel is partially oxidized and reformed to produce hydrogen. The bulk of the carbon monoxide that is also produced is converted to carbon dioxide and additional hydrogen by the water gas shift reaction. The remaining carbon monoxide is selectively oxidized to carbon dioxide through a preferential oxidizer. The reformate mixture is then cooled and fed to the fuel cell anode. A turbo-compressor supplies the cathode air, as well the air needed for the fuel autothermal reformer. A condenser is used to recover water from the exhaust.

Other factors to be considered for the water recovery process include the FC utilization and the supplied air relative humidity. Any oxygen utilization below than 100% means that more air is supplied to the fuel cell stack than is required for the hydrogen reaction [Au *et al*., 2003]. This leads to more process water being added for air humidification. Furthermore, the amount of moisture added increases if the relative humidity of the ambient air is low. A separate coolant loop is usually configured in the fuel cell (FC) system to remove the heat generated by the fuel cell reaction. This energy can be used to preheat the incoming air and fuel. Any excess heat is dissipated in a conventional air water radiator.

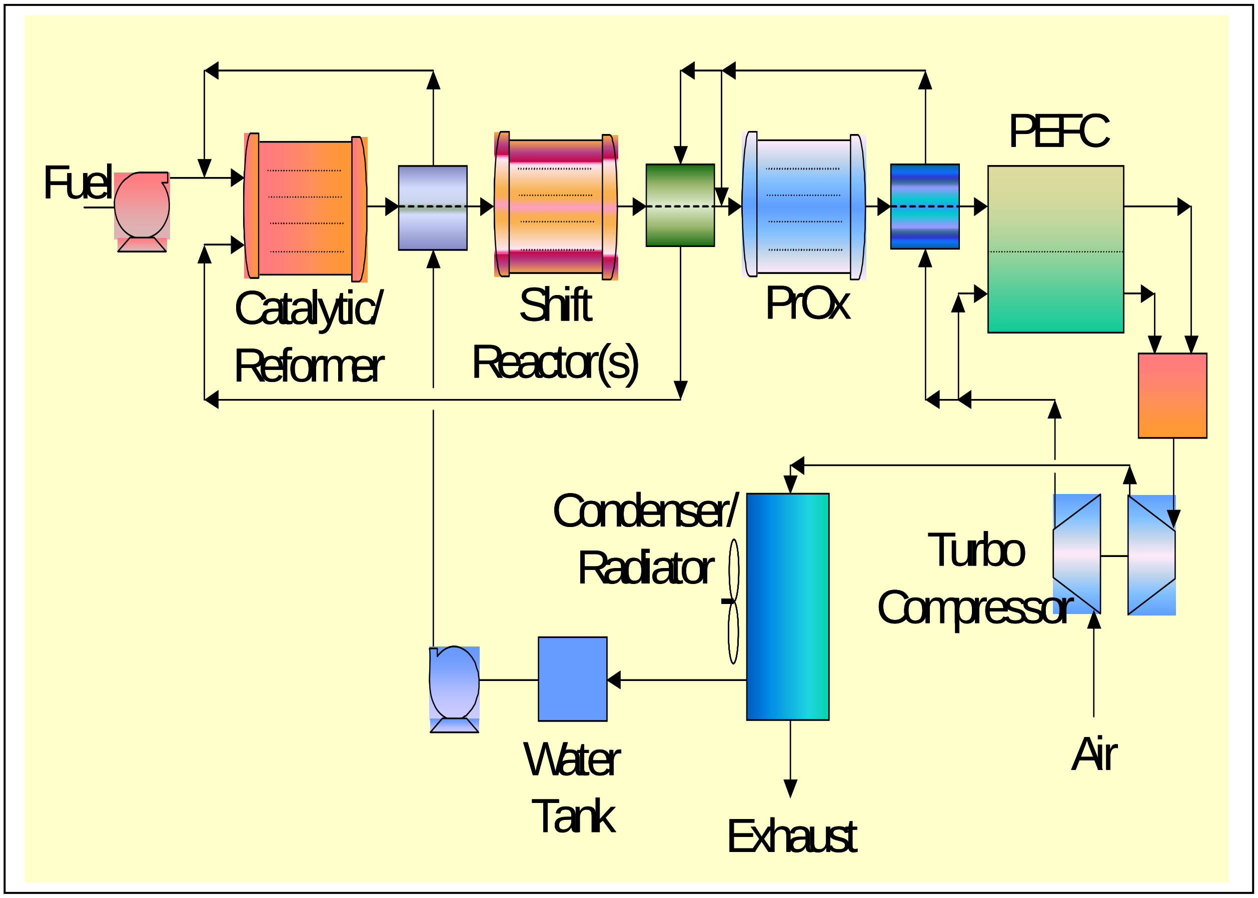


Figure 13. A conceptual diagram of a pressurized gasoline-fueled fuel cell system.

7. Fuel Processing for Fuel Cell Power Systems

7.1 Fuel Choice

The fuel cell is a power generation technology that is in the early stages of its commercial use. The fuel choice for small stationary power plants is pipeline gas due to its availability for multiple commercial, light industrial, and residential applications. As environmental regulation becomes more stringent for megawatt-size power plants and fuel cells are scaled larger in size, there is a possibility to use coal. Large power station operators require an alternate fuel, usually heavy oil. Several views and suggestions from Exxon Mobil [Bernardi, 1990] are as follows.

Fuels that are directly suitable to the fuel cell are the most difficult, costly to produce, and distribute. Gasoline and methanol are the leading contributors to power fuel cell engines. Due to methanol's corrosivity and its affinity for water, it cannot be readily distributed in today's fuel infrastructure. Methanol is more acutely toxic than gasoline. Gasoline fuel processing has the ability to use the existing infrastructure. It is more flexible than the low temperature methanol processor, allowing different fuel use in the same system. The gasoline processor is also more tolerant of contaminants contained in the fuel. Due to the higher energy density of gasoline, the gasoline system offers the potential for up to twice the vehicle range of the methanol system. Despite the increased vehicle efficiency of the methanol fuel cell system, the resultant wheel-to-wheel efficiency would be only 20%, lower than either gasoline hybrids or gasoline fuel cell vehicles. A customized gasoline for fuel cells could offer better performance and be produced at lower cost because many of today's conventional gasoline's more expensive ingredients would not be required. Naphtha is a common refinery stream that is an inexpensive alternative to conventional gasoline. Although its octane is too low for today's ICE, naphtha is ideal for fuel cells and could supplied to retail stations within the existing gasoline infrastructure. For automotive fuel cell systems, the commercially available fuels are conventional gasoline and diesel, with limited availability of alternative fuels, such as methanol, ethanol, natural gas, and various other fuel blends.

For stationary fuel cell systems, natural gas is an attractive fuel because of its ready availability in most urban areas. Methanol is the easiest of the potential transportation fuels to convert to hydrogen. Methanol dissociates to CO and hydrogen at temperatures below 400^{o}C and can be catalytically steam reformed at 250^{o}C or less. This low conversion temperature is advantageous for rapid start up of the reformer, a capability that is essential for vehicular applications. Further, methanol can be converted to hydrogen with efficiencies of greater than 90%. Methanol is produced largely from natural gas. The conversion process itself requires energy, and thus methanol is less attractive than gasoline on the basis of a wheel to wheel efficiency.

Other comparisons with gasolines are based on factors related to the production capacity relative to the needs of the automotive sector, including the cost per mile, the environmental impact, and the refueling infrastructure. Gasoline has more than twice the energy content of methanol, may be less expensive in the U.S., and has a well-established infrastructure that would allow the fuel cell vehicle a smoother entry into the market.

However its conversion to hydrogen requires temperatures greater than 500°C and tends to produce considerable amounts on carbon monoxide, methane, and possibly coke. Furthermore, petroleum-derived fuels such as gasoline contain sulfur and trace amounts of metal which, if not effectively removed, can damage the fuel cell. Although these contaminants may be removed more effectively at the refinery than in an on-board fuel processor, that decision will eventually emerge from market drivers and possibly government regulations. Natural gas is not a strong contender for fueling vehicles because of its relatively low energy density. It requires reforming temperatures of 700°C or higher. Natural gas typically contains over 90% methane along with higher hydrocarbons, carbon dioxide and nitrogen. Converting methane to hydrogen can be highly efficient because of its hydrogen to carbon ratio.

Methane is also less prone to coking, compared to other hydrocarbon fuels. The existing natural gas infrastructure in most urban areas makes it very attractive for use in stationary fuel cells. Natural gas-fueled PAFC power plants that can generate 200 kW have been commercially available for some time. In higher temperature fuel cells, such as SOFC and MCFC, stationary power generation ranges from 200 kW to 2 MW. In almost all of these stationary fuel cell applications, the natural gas fuel is converted to hydrogen by catalytic steam reforming, often within the fuel cell stack or bundle, but not necessarily in the anode compartment of the fuel cell.

7.2 Reformer Technologies

There are different commercially available reformer technologies. Some of them are as follows.

Steam reforming of methanol is described by the following chemical reaction equation:

$$CH_3O(g) + H_2O(g) \rightarrow CO_2(g) + 3\ H_2 \qquad \Delta H = 49\ \text{kJ mol}^{-1}$$

Methanol and water are evaporated and react in a catalytic reactor to carbon dioxide and hydrogen, the desired product. The raw reformer output consists of hydrogen, carbon dioxide, and carbon monoxide. Carbon monoxide is converted to carbon dioxide and more hydrogen in a HTS stage followed by a LTS stage. In both stages, the water gas shift reaction is described by the following chemical equation.

$$CO + H_2O(g) \rightarrow CO_2(g) + H_2 \qquad \Delta H = -41\ \text{kJ mol}^{-1}$$

The water gas shift is an exothermal reaction. Therefore, if too much heat is generated, it will eventually drive the reaction towards the reactant side. To prevent this, multiple stages with interstage cooling are used. The best catalysts for the high temperature shift reaction are a mixture of iron and chromium oxides with good activity between 400 and 550°C. The low temperature shift reaction uses copper catalysts and operating conditions similar to those used in methanol steam reforming. Steam reforming of methane from natural gas is the standard way of producing hydrogen on an industrial scale. It is therefore of general importance to a hydrogen economy. In addition, smaller scale methane steam reformers have been developed to provide hydrogen for stationary power generation based on low temperature fuel cells. The methane steam reforming reaction is described by:

$$CH_4 + H_2O\,(g) \rightarrow CO + 3\,H_2 \qquad \Delta H = 206\ \text{kJ mol}^{-1}$$

Partial oxidation is the partial, or incomplete, combustion of a fuel.

$$CH_4 + \tfrac{1}{2}\,O_2 \rightarrow CO + 2\,H_2 \qquad \Delta H_{298} = -35.7\ \text{kJ mol}^{-1}$$

$$C_8H_{18} + 4\,O_2 \rightarrow 8\,CO + 9\,H_2 \qquad \Delta\,H_{298} = -158.1\ \text{kJ mol}^{-1}$$

A substoichiometric amount of air, or oxygen, is used. This partial oxidation process is highly exothermic and raises the reactants to a high temperature. The resulting high temperature reaction products, still in a reduced state, are then quenched through the introduction of superheated steam. The addition of the steam promotes the combined water-gas shift and steam reforming reactions, which further cools the gas. In most cases, and if sufficient preheating of the reactants is used, the overall reaction is exothermic and self-sustaining.

For some applications, particularly small-scale configurations, a catalyst can be used to increase reaction rates at lowered reaction temperatures. POX reactor exit temperatures vary widely. Noncatalytic processes for gasoline reforming require temperatures in excess of 1,200°C [Hoogers, 2003]. These temperatures require the use of special materials and significant preheating and integration of process streams. The use of a catalyst can substantially reduce the operating temperature, allowing the use of more common materials, such as steel. Lower temperature conversion leads to less carbon monoxide, so that the shift reactor can be smaller.

Lower temperature conversion will also increase system efficiency. For some heavy hydrocarbon fuels, typical values range from as low as 850°C for catalytic POX upwards to 1400°C for non-catalytic POX [Hoogers, 2003]. For sulfur-bearing diesel fuel, a catalytic POX reactor will usually operate at approximately 900°C. This relatively elevated temperature is needed to overcome catalyst degradation due to the presence of sulfur. Noncatalytic POX reactors operate at around 1200°C on diesel fuel [Hoogers, 2003]. Advantages of POX that make this type of fuel conversion suitable for transportation power include the following: POX does not need indirect heat transfer so the processor is more compact and lightweight, POX and ATR are capable of higher reforming efficiencies than are steam reformers.

Partial oxidation should be reacted so that the overall reaction is exothermic, but at a low oxygen-to-fuel ratio where the higher hydrogen yields and concentrations are favored. POX is thought to lead to lower efficiency than steam reforming due to the POX reaction being exothermic [Hoogers, 2003]. However, a thorough examination of the thermodynamics shows that POX and ATR have higher reforming efficiencies than steam reforming technology [Hoogers, 2003]. This gives rise to the question as to why there is a need to use steam reforming or an ATR if the POX's efficiency is higher. The minimum oxygen-to-carbon (O/C) ratio allowable is 1.0 for the POX process [Hoogers, 2003]. This generates high-grade heat that leads to undesirable high temperatures (low H_2, CO_2 selectivity, etc). The steam reformer and

ATR allow lower O/C ratios, keep the temperature down, and result in higher CO_2 and H_2 selectivity (more H_2 yield per mole of fuel) [Hoogers, 2003].

7.3 Autothermal Reforming

ATR involves the reaction of oxygen, steam, and fuel to produce H_2 and CO_2:

$$CH_4 + \frac{1}{2} O_2 + H_2O \rightarrow CO_2 + 3 H_2 \qquad \Delta H_{298} = -18.4 \text{ kJ mol}^{-1}$$
$$C_8H_{18} + 4 O_2 + 8 H_2 O \rightarrow 8 CO_2 + 17 H_2 \qquad \Delta H_{298} = -236.7 \text{ kJ mol}^{-1}$$

The coupling of SR with POX is termed ATR. ATR is carried out in the presence of a catalyst that controls the reaction pathways and thereby determines the relative extents of the POX and SR reactions. The SR reaction absorbs part of the heat generated by the POX process reaction, limiting the maximum temperature in the reactor. The net result is a slightly exothermic process. Autothermal reforming provides a fuel processor compromise that operates at a lower O/C and lower temperature than the POX; is smaller, quicker starting, and quicker responding than the SR; and results in good H_2 concentration and high efficiency [Hoogers, 2003]. A catalytic POX must be used to reduce the reaction temperature to a value compatible with the SR temperature. Once started, surplus heat from other parts of the unit can be sent to the ATR to increase its efficiency.

7.4 Comparison of Reforming Technologies

Table 4 lists typical compositions of reformate using different reforming technologies. SR gives the highest hydrogen concentration. At the same time, a system relying entirely on SR operates best under steady-state conditions because it does not lend itself to rapid dynamic response. This also applies to start up. In contrast, partial oxidation offers compactness, fast start up, and rapid dynamic response as compared to SR while producing lower concentrations of hydrogen [Watkins *et al*., 1986]. In addition to differences in product stoichiometries between SR and POX reformers, the output of a POX reformer is necessarily further diluted by nitrogen. Nitrogen is introduced to the system from air, which is usually the only economical source of oxygen, and carried through as an inert gas. ATR offers a compromise. Steam reforming is highly endothermic. Heat is usually supplied to the reactor, for example, by burning extra fuel. In a fuel cell system, (catalytic) oxidation of excess hydrogen exiting from the anode provides a convenient way of generating the required thermal energy. Steam reforming may be suitable here, whereas ATR could be considered in a PEFC system, which has only low-grade heat available. Fuel efficiency also deserves attention. Though always important, the cost of fuel is the most important factor in stationary power generation. Hence, the method offering the highest overall hydrogen output from the chosen fuel, usually natural gas, is selected. Steam reforming delivers the highest hydrogen concentrations. Therefore, the fuel cell stack efficiency at the higher hydrogen content may compensate for the higher fuel demand for steam generation. This is probably the reason why steam reforming is currently the reforming natural gas of choice in stationary power plants based on polymer electrolyte fuel cells [Watkins *et al*., 1986]. A partial oxidation reformer offers the required dynamic behavior then SR and is likely to be the best choice with higher hydrocarbons [Watkins *et al*., 1986].

Table 4. Typical compositions of reformate from different reforming technologies.

Output Composition	**SR**	**POX**	**ATR**
H_2	68	47	56
CO_2	23	20	22
N_2	---	23	22
CO	---	---	2

8. OVERALL FUEL CELL SYSTEM AND FUEL PROCESSORS SUBSYSTEM

8.1 Introduction of Polymer Electrolyte Fuel Cell System

The polymer electrolyte fuel cell systems is being developed for powering clean and efficient automobiles in the future require a fuel gas that is either pure hydrogen, or a gas mixture that contains a significant concentration of hydrogen. Thus, the vehicles with methanol as the on-board fuel use a fuel processor, also referred to as a reformer, to convert the methanol to a fuel gas, reformate, that contains hydrogen, carbon dioxide, water vapor, and nitrogen, with trace levels of other species, such as carbon monoxide and unconverted methanol.

In an autothermal fuel processor, the fuel, air, and water (steam) are fed in controlled proportions to generate a reformate gas mixture. This reformate must be processed further to convert all of the carbon monoxide to carbon dioxide, remove hydrogen sulfide (produced from the organic sulfur typically present in gasoline at 30–300 ppm, by weight), cool and humidify the reformate to the desired fuel cell inlet conditions. The amount and concentration of hydrogen generated from a given amount of gasoline, and the quality of the raw reformate (i.e., CO, CO_2, CH_4 and other hydrocarbons, H_2O, and N_2), are influenced by the reforming conditions. The amount of H_2 produced determines the efficiency of the fuel processor; the greater this amount, the higher the fuel processor efficiency. The fuel processor efficiency is defined as the ratio of the lower heating value of the total amount of hydrogen in the processed reformate (at the entrance to the fuel cell) to the lower heating value of the gasoline used in the fuel processor. The concentration of H_2 in the reformate influences the performance of the fuel cell stack, with higher hydrogen concentrations yielding better fuel cell performance. The quality of the raw reformate determines the extent of subsequent processing required, primarily for CO and H_2S removal. This subsequent reformate processing has a significant effect on the design, efficiency, volume, weight, and cost of the fuel processing subsystem and, in turn, on the total fuel cell power system. The primary operating variables in autothermal reforming are the fuel-to-air and fuel-to-water ratios. These two ratios, along with the degree of preheat of the fuel, air, and water (or steam) determine the reaction temperature in the reformer.

The main electric power generator in the system is the fuel cell stack (pefc) shown in the upper-right part of the diagram. Fuel gas containing H_2 is fed to the fuel side inlet, and the oxidation air is fed to the air side inlet to the stack. Further discussion is provided by Upadhyaya [2004b]

Ambient air is compressed (in cp_air) and split into two main streams (at sp_pox). The smaller airflow to the left is preheated (in air_htr) and fed to the ATR partial-oxidation reactor (pox). From the larger airflow to the right, a small amount is split off (at sp_prox) for injection at the preferential oxidation unit (prox) for CO removal. The bulk of the airflow is humidified and cooled by injecting liquid water, and then supplied to the cathode inlet of the fuel cell stack (pefc). The fuel flow circuit begins at the fuel tank (fuel). From the tank, it is pumped (by pump fuel) to the fuel vaporizer (fuel_vap), where it is heated and vaporized by the hot system exhaust gas. It is then fed to the ATR (pox) where it is reacted with the preheated air and superheated steam to yield the raw reformate.

The hot reformate is used to preheat the ATR air feed (at air_htr), superheat the ATR steam feed (at super_heat), and boil the primary process water for the ATR. It may then be mixed with additional process water (at mx_hts) and fed to the high-temperature water-gas shift reactor (hts). After removal of H_2S by ZnO or other suitable sorbent, the reformate is further cooled by boiling the process water (boiler). The reformate may be then mixed with more water (at mx_lts) before entering the low-temperature water-gas shift reactor (lts). The fuel gas leaving this reactor is cooled by heating/boiling water in an economizer and then fed to the preferential oxidation unit (prox) for CO removal. The gas exiting prox is cooled to the fuel cell stack temperature in another economizer. Any water condensed out is separated, and the fuel gas is then fed to the fuel cell stack (pefc).

The water for fuel processing is taken from a surge tank (water_proc) by a water pump (pump_proc). Fractions of the process water stream may be split off for the high-temperature shift (at mx_hts), the low-temperature shift , the shift reactor exit gas cooler (at sp_proxw), the prox exit gas cooler (at sp_econ0), and the humidifier for the fuel cell air feed. The main process water stream then picks up combined water from the water separator on fuel cell anode feed and the water condensed out of the fuel cell cathode exhaust. The process water stream then picks up any liquid water from the water boilers, and the water from the steam drum (at mx_proc3). It then flows to the process water radiator (proc_rad) where it is cooled and then returned to the process water tank (water_proc). Any excess process water is removed from the return line from the steam drum at.

The fuel cell cathode exhaust is cooled (in condsr) to recover water for the fuel processor and then combined with the anode exhaust in a catalytic burner (burner). The hot gas leaving the burner can be used to heat the process water through a heat exchanger (war_econ2). The hot gas is then used to vaporize the fuel (in fuel_vap) before being expanded in a turbine (gt_1) for power recovery. The turbine exhaust is the only exhaust from this fuel cell system.

The last subsystem is the stack coolant circuit which is used to remove the waste heat from the fuel cell stack. Coolant from the tank (water_fc) is pumped to the cooling plates in the fuel cell stack. The heated coolant then flows to the main radiator (radiat) and then back to the coolant tank (water_fc).

8.2 The Fuel Processor Subsystem

The process of converting gasoline to a fuel gas suitable for feeding to the anode of the fuel cell stack consists of several steps. First, the gasoline is reacted with air and water in the ATR to form a gas mixture of H_2, CO, CO_2, N_2, H_2O, CH_4, and possibly other species, such as H_2S and ammonia. To achieve fuel cell quality gas, all of the CO must be converted to CO_2, and any H_2S, ammonia, or other contaminants must be removed (or reduced to acceptably low levels of a few ppm or less). The processes for the subsequent processing of the gas mixture produced at the ATR reactor are carried out at successively decreasing temperatures, as discussed in the following paragraphs.

The first step, the autothermal reforming reaction, is carried out at the highest temperature in the fuel processing train. Depending on the catalyst used, this reaction may require temperatures more then 1000−1200°K. At these temperatures, most of the carbon in the fuel is converted to CO or CO_2, with the possible formation of relatively small amounts of CH_4 and other hydrocarbons. The reaction conditions must be maintained such that no graphitic or amorphous carbon is formed in this step.

The bulk of the CO in the raw reformate is converted to CO_2 using the water-gas shift reaction, $CO + H_2O \rightarrow CO_2 + H_2$, which generates additional H_2 as well. While kinetics would dictate the use of higher temperatures for this reaction, the reaction equilibrium favors the conversion of CO to CO_2 at lower temperatures. In the fuel processors, this water-gas shift reaction is carried out in two stages. The high-temperature shift reactor (hts) is used to convert part of the CO, followed by the low-temperature shift reactor (lts) to provide further reduction in the concentration of CO in the reformate.

At the shift reactor temperatures of around 450 through 700°K, the CO concentration at the exit from low temperature water gas shift reactor is typically less than 1% by volume. This level of carbon monoxide is still too high for the fuel cell stack, which can tolerate only a few parts per million of CO by volume in the fuel gas [Doss *et al.*, 2002]. The final reduction of CO to these levels is carried out in the preferential oxidizer (prox) where the reformate is reacted with a controlled amount of air over a suitable catalyst. In case of high temperature fuel cells the PROX is eliminated. In the low temperature ones the effectiveness factor for the catalyst is assumed to be 50%, so, the amount of air added at the prox is such that the amount of O_2 in it is twice the amount of CO at the inlet to the PROX. The gas leaving the PROX is then assumed to have no CO in it [Doss *et al.*, 2002].

The other major components of the fuel processing subsystem are the various heat exchangers, boilers, and economizers used for preheating the process streams 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. .

8.3 Fuel Processing Parameters

The influence of varying several different fuel processor and fuel cell system design configurations and operating parameters are as follows: the temperature of the autothermal reactor, the water-to-carbon ratio in the ATR reactor, the water used in the ATR reactor is usually called the primary water, the system pressure (1 and 3 atmosphere nominal), and the electrochemical fuel utilization in the fuel cell stack In general, varying the first two parameters affects the other operating parameters [Doss *et al.*, 2002].

8.4 Operating Factors Influencing the Fuel Cell Performance

The total water-to-carbon mole ratio used in the fuel processor increases with increasing T_{POX} and with increasing S/C in the reactant feed to the ATR reactor. This increase results from the increased thermal mass of the raw reformate, which permits a greater amount of water to be used.

For a given T_{POX}, increasing the amount of water fed to the ATR reactor requires an increase in the amount of air that must also be fed to that reactor. The reforming conditions at the ATR reactor are defined by the water-to-fuel and the oxygen-to-fuel ratios, along with the inlet temperatures of the fuel (420°K), air, and water/steam. While the water-to-fuel ratio is often given in terms of S/C, the oxygen-to-fuel feed rate is conveniently stated as a fuel equivalence ratio, μ, for blended fuels. For a given amount of air, μ is the ratio of the actual amount of fuel reacted to the stoichiometric amount of fuel that would be completely oxidized by the given amount of air. Thus, at a μ less than 1, the gasoline would be completely oxidized to CO_2 and H_2O, with some O_2 also present in the product gas. At μ greater than 1, there is not enough oxygen to convert all of the carbon in the fuel to carbon dioxide and all of the hydrogen in the fuel to water. Under these conditions, the product gas would contain H_2 and/or CO, along with H_2O and CO_2. As μ increases above 1, the amounts of H_2 and CO also increase (assuming the same percentage conversion of the fuel). It is desirable to operate with as high a value of μ as possible for maximum generation of H_2 and CO [Doss *et al.*, 2002]. The high-temperature reforming reaction at the partial-oxidation reformer (pox) generates substantial amounts of carbon monoxide, which is converted to carbon dioxide and additional hydrogen in the water-gas shift reactors, hts and lts. However, even after the shift processing, high levels of CO can be present in the fuel gas, depending on the amount of S/C fed into partial oxidation reactor and on the operating temperature of the ATR.

This remaining CO must be almost completely removed in the catalytic preferential oxidizer (prox), where it is reacted with 100% excess oxygen. Since this process also consumes an equivalent amount of H_2, it is desirable to reduce the CO concentration by the shift process as much as possible, before it reaches the prox. Increasing steam-to-carbon ratio increases the total amount of water used in the fuel processor, with a resultant decrease in the concentration of CO.

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.

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O \quad (\Delta H = -206\ \text{kJmol}^{-1})$$

This method has the obvious disadvantage that hydrogen is being consumed, and so the efficiency is reduced. However, the quantities involved are small. We are reducing carbon monoxide content from about 25%. The methane does not poison the fuel cell, but acts as an diluent. Catalysts are available, that will promote this reaction so that at about 200°C, the carbon monoxide levels will be less than 10 ppm. The catalyst will also ensure that any unconverted methanol is reacted to 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. Another method of hydrogen purification is 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 period of 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. These extra stages add considerably to the cost and complexity of the fuel. The permissible amount [Hoogers, 2003] for CO is 50 ppm for the polymer electrolyte fuel cell and 1.0% for the phosphoric acid fuel cell.

Any methane 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 CH_4 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 CH_4 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 CH_4 in the processed reformate, after lts, is greatly affected by the value of partial oxidation temperature.

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. Coke causes the greatest problems in gas flow paths and on catalyst. Carbon deposition not only represents a loss of carbon for the reaction but more importantly 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 based on alkali or 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 $500^{o}C$) 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.

There are high temperature and low temperature methods to remove sulfur from a fuel reformate stream. Low temperature cleanup, such as hydrodesulfurization (limited to fuels with boiling end points below $200^{o}C$), is less difficult and lower in cost and should be used where possible, certainly with low temperature cells. Sulfur species in the fuel are converted to H_2S, if necessary, then the H_2S 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 the catalyst developed by them can tolerate sulfur, but it has not been demonstrated on an engineering scale. Hydrogen needs to be recirculated to the removal device to convert the sulfur species to H_2S so that it can be entrapped on zinc oxide, a complication. Zinc oxide beds are limited to operation at temperatures below 400^{o}C, probably because of pore plugging during sulfur removal and sintering. At the higher temperatures, the H_2S cannot be reduced to levels low enough for shift catalyst or to reach fuel cell limits. The permissible amount for sulfur is 1 ppm for the polymer electrolyte fuel cell, and 20 ppm for the phosphoric acid fuel cell.

The concentration of hydrogen in the fuel gas supplied to the fuel cell stack affects the performance of the fuel cell, while the amount of total hydrogen obtained from a given amount of gasoline affects the energy conversion efficiency of the fuel cell system. To obtain high performance in the fuel cell, it is desirable to achieve the highest possible hydrogen concentration in the processed reformate.

In the preferential oxidizer, as additional oxygen (air) is injected to react with CO to form CO_2, it also reacts with H_2 and forms H_2O. This process leads to a reduction in the total amount of H_2 going to the fuel cell stack. Also, as the S/C ratio decreases and T_{POX} decreases, the amount of methane formed in pox increases. This increase in the amount of methane formed leads to a corresponding decrease in the amount of H_2 formed in the fuel processor. The use of the burner heat in the fuel processor increases the maximum concentration of H_2 by enabling the use of higher values of S/C at lower values of partial oxidation temperature.

8.5 Heat Recovery and Electrical Efficiencies

Heat is generally recovered in the form of hot water or low-pressure steam (< 30 psig), but the quality of heat is dependent on the type of fuel cell and its operating temperature. The one exception to this is the PEM fuel cell, which operates at temperatures below 200°F, and therefore has only low-quality heat. Generally, the heat recovered from fuel cell CHP systems is appropriate for low temperature process needs, space heating, and potable water heating. In the case of SOFC and MCFC technologies, medium-pressure steam (up to about 150 psig) can be generated from the fuel cell's high temperature exhaust gas, but the primary use of this hot exhaust gas is in recuperative heat exchange with the inlet process gases. The simplest thermal load to supply is hot water. Primary applications for CHP in the commercial/institutional sectors are those building types with relatively high and coincident electric and hot water/space heating demand, such as colleges and universities, hospitals and nursing homes, and lodging. Technology developments in heat-activated cooling/refrigeration and thermally regenerated desiccants will enhance fuel cell CHP applications by increasing the thermal energy loads in certain building types. Use of these advanced technologies in applications such as restaurants, supermarkets, and refrigerated warehouses provides a base thermal load that opens these applications to CHP.

The overall electrical efficiency of the cell is the ratio of the power generated and the heating value of the hydrogen consumed. The maximum thermodynamic efficiency of a hydrogen fuel cell is the ratio of the Gibbs free energy and the heating value of the hydrogen.

The Gibbs free energy decreases with increasing temperatures, because the product water produced at the elevated temperature of the fuel cell includes the sensible heat of that temperature, and this energy cannot be converted into electricity without the addition of a thermal energy conversion cycle (such as a steam turbine). Therefore, the maximum efficiency of a pure fuel cell system decreases with increasing temperature. Irreversibilities are changes in the potential energy of the chemical that are not reversible through the electrochemical process. Typically, some of the potential energy is converted into heat even at open circuit conditions when current is not flowing. A simple example is the resistance to ionic flow through the electrolyte while the fuel cell is operating. This potential energy loss is really a conversion to heat energy, which cannot be reconverted into chemical energy directly within the fuel cell.

The electrical efficiency increases as the operating temperature and size of the fuel cell increases. As electrical efficiency increases, the absolute quantity of thermal energy available to produce useful thermal energy decreases per unit of power output, and the ratio of power to heat for the CHP system generally increases. A changing ratio of power to heat impacts project economics and may affect the decisions that customers make in terms of CHP acceptance, sizing, and the desirability of selling power.

The economics of fuel cells in on-site power generation applications depend less on the effective use of the thermal energy recovered than is the case with lower efficiency prime movers, but thermal load displacements improve operating economics, as in any CHP application. Generally, the stack and reformer subsystems contain 25% of the inlet fuel energy in the form of higher quality thermal energy. The exhaust gases (includes the latent heat of the product water generated in the fuel cell) contain another 25% of the recoverable energy. The most common use of this heat is to generate hot water or low-pressure steam for process use or for space heating, process needs, or domestic hot water. Heat can generally be recovered in the form of hot water or low-pressure steam (<30 psig), but the quality of heat is dependent on the type of fuel cell and its operating temperature. The one exception to this is the PEM fuel cell, which operates at temperatures below 100°C, and therefore has only low-quality heat. As an example, there are four primary potential sources of usable waste heat from a fuel cell system: exhaust gas including water condensation, stack cooling, anode-off gas combustion, and reformer heat. The PAFC system approximately achieves a 36% electric efficiency and a 72% overall CHP efficiency, which means that it has a 36% thermal efficiency or a power-to-heat ratio of one. Of the available heat, 25–45% is recovered from the stack-cooling loop that operates at approximately 400°F and can deliver low- to medium-pressure steam. The exhaust gas-cooling loop provides the balance of the heat and serves two functions. The first is condensation of product water, thus rendering the system water self-sufficient, and the second is the recovery of by-product heat. Since its primary function is water recovery, the balance of the heat available from the PAFC fuel cell is recoverable with 120°F return and 300°F supply temperatures. This tends to limit the application of this heat to domestic hot water applications. Maximum system efficiency occurs when all of the available anode-off gas heat and internal reformer heat is used internally.

Air is fed to the cathode side of the fuel cell stack to provide the oxygen needed for the power generation process. Typically, 50–100% more air passes through the cathode than the fuel cell reactions require. The fuel cell operated at near-ambient pressure, or at elevated pressures to enhance stack performance. Increasing the pressure, and therefore the partial pressure of the reactants, increases stack performance by reducing the electrode over potentials associated with moving the reactants into the electrodes where the catalytic reaction occurs. It also improves the performance of the catalyst.

8.6 Impact of Operating Pressure and Temperature

Operating temperature has a significant influence on PEFC performance. An increase in temperature lowers the internal resistance of the cell, mainly by decreasing the ohmic resistance of the electrolyte. In addition, mass transport limitations are reduced at higher temperatures. The overall result is an improvement in cell performance. Experimental data suggest a voltage gain in the range of 1.1 mV to 2.5 mV for each degree (^{o}C) of temperature increase [Ledjeff, 1992]. Operating at higher temperatures also reduces the chemisorption of CO because this reaction is exothermic. Improving the cell performance through an increase in temperature is limited by the high vapor pressure of water in the ion exchange membrane. This is due to the membrane's susceptibility to dehydration and the subsequent loss of ionic conductivity. Although the open circuit voltage decreases with increasing temperature, the performance at operating current densities increases with increasing temperature due to reduced mass transfer polarizations and ohmic losses. The increased temperature also yields higher quality rejected heat stream. An additional benefit to an increased temperature in the PAFC is an increased tolerance to CO levels, a catalyst poison. The temperatures at which the various fuel cells can operate are, however, limited by material constraints. The PAFC and MCFC are both limited by life-shortening corrosion at higher temperatures.

Operating pressure also impacts cell performance. Research has demonstrated that an increase in the pressure of oxygen results in a significant reduction in polarization at the cathode. Performance improvements due to increased pressure must be balanced against the energy required to pressurize the reactant gases. The overall system must be optimized according to output, efficiency, cost, and size. Operating at pressure above ambient conditions would most likely be reserved for stationary power applications.

8.7 Utilization

Utilization refers to the amount of gases that are reacted within the fuel cell compared to that supplied. Both fuel and oxidant utilizations involve trade-offs with respect to the optimum utilization for a given system. High utilizations are considered desirable (particularly in smaller systems) because they minimize the required fuel and oxidant flow, for a minimum fuel cost and compressor/blower load and size. However, utilizations that are pushed too high result in significant voltage drops. One study states that low utilizations can be advantageous in large fuel cell power cycles with efficient bottoming cycles because the low utilization improves the performance of the fuel cell and makes more heat available to the bottoming cycle. Like almost all design parameters, the selection of optimum utilizations requires an engineering trade-off that considers the specifics of each case.

8.7.1 Fuel utilization

High fuel utilization is desirable in small power systems, because in such systems the fuel cell is usually the sole power source. However, because the complete utilization of the fuel is not practical, except for pure H_2 fuel, and other requirements for fuel exist, the selection of utilization represents a balance between other fuel/heat requirements and the impact of utilization on overall performance. The designer has the ability to increase the overall utilization of fuel (or the oxidant) by recycling a portion of the spent stream back to the inlet. This increases the overall utilization while maintaining a lower per-pass utilization of reactants within the fuel cell to ensure good cell performance. The disadvantage of recycling is the increased auxiliary power and capital cost of the high temperature recycle fan or blower. By varying the fuel cell utilization, the electric power generation split between the fuel cell, steam turbine, and gas turbine are changed. The low fuel utilization decreases the percentage of power from the fuel cell while increasing the fuel cell performance. The increased power output from the gas turbine and steam turbine also results in their improved performance and economy of scale. The specific analysis results depend upon the assumed stack costs.

8.7.2 Oxidant utilization

A major fraction of the hydrogen fed to the fuel cell anode is electrochemically oxidized within the fuel cell. This fraction is referred to as the fuel utilization. Similarly, only a fraction of the oxygen fed to the cathode is consumed in the electrochemical reaction with hydrogen. The fraction of oxygen thus consumed is referred to as the oxidant utilization. The inverse of the oxygen utilization is also referred to as the air stoichiometry. For example, 40% oxygen utilization corresponds to an air stoichiometry of 2.5.

8.8 Water Management in PEM Fuel Cells

The fuel processor converts the available fuel into a hydrogen-containing fuel gas suitable for the fuel cell. This fuel conversion process, often referred to as reforming, typically requires water for either steam reforming or autothermal reforming. Even for systems fueled with direct hydrogen, water management and self-sufficiency may be an issue if humidification of the anode and/or cathode gases is needed to achieve high performance in the fuel cell. The need for an external water supply is determined by the amount of water consumed by the fuel processor, produced by the fuel cell, and recovered within the system. The ability to operate without an external water supply allows the fuel cell system to be independent of the local infrastructure. This feature is essential for portability and use in rural or remote locations.

As seen in Figure 14, the hydrogen-containing reformate gas from the fuel processing subsystem enters the anode side of the fuel cell stack, and air is fed to the cathode side. The hydrogen and oxygen react electrochemically to produce electricity, heat, and water. The electric fraction of the total electric and thermal energy generated in the fuel cell stack is often referred to as the cell or stack efficiency. The efficiency of the total system is, of course, less than the cell efficiency because of less-than-total fuel utilization, heat losses, and parasitic power consumption. As mentioned above, not all of the hydrogen fed to the fuel cell stack is electrochemically oxidized, i.e., fuel utilization is less than 100%. The hydrogen present in the anode effluent is burned in the spent-gas burner, with the cathode effluent as the oxidant. The burner product gas is cooled to condense and recover some of the water, which is then recycled back to the water tank. This cooling of the burner exhaust occurs in the condenser, with ambient air as the coolant. Since the exhaust gas is saturated with water vapor as it leaves the system, the amount of water that can be condensed out and recovered depends on the temperature to which the exhaust is cooled. This exhaust gas temperature is determined by the temperature of the ambient air and the approach temperature for which the condenser is designed. The amount of water that can be recovered at the condenser depends on the concentration of water in the burner product gas and the saturation water vapor content of the exhaust gas. The latter depends on the exhaust gas pressure and temperature. The ability to operate with a smaller approach temperature would lower the exhaust gas temperature and favor the recovery of water.

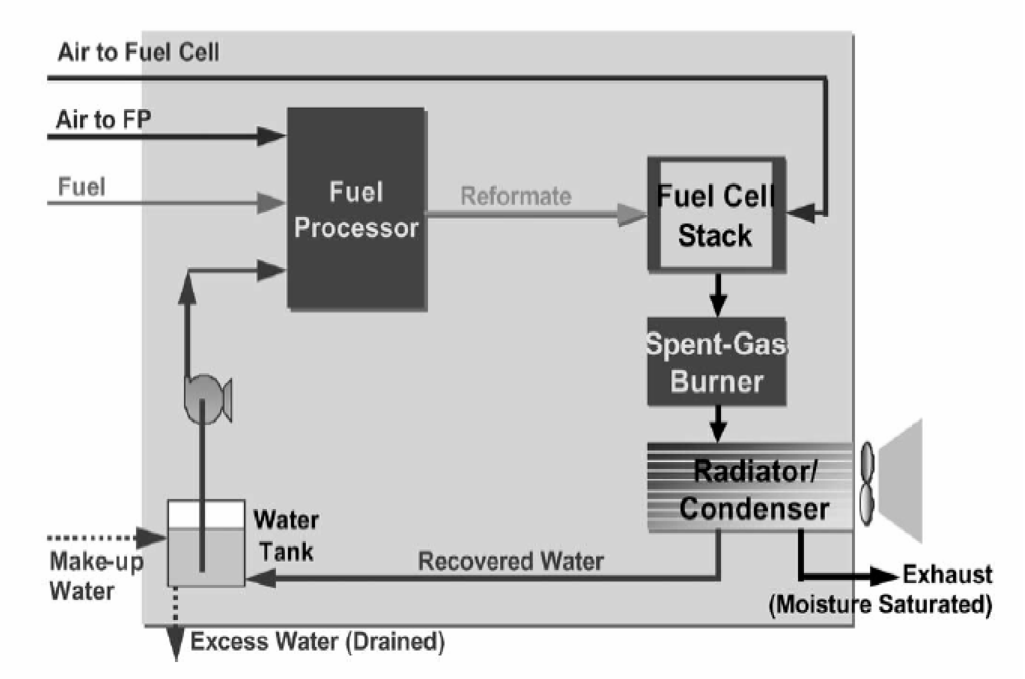


Figure 14, Water balance in polymer electrolyte fuel cell system.

Not all of the hydrogen produced by the fuel processor can be converted in the fuel cell stack. The fraction of hydrogen that is electrochemically converted, the fuel utilization, has a direct impact on the electric power generated by the fuel cell. Higher fuel utilization leaves less hydrogen available for combustion in the burner, and thus, less heat is generated at the burner. This is an important consideration for thermal integration of the system, since the heat generated at the burner is typically recovered and used to preheat feeds. With less heat generated at the burner, it may be necessary to operate at higher oxygen-to-fuel ratios to maintain the temperatures needed in the fuel processor. This becomes an optimization problem, since changing x affects many different parameters in the total system.

The effects of changing the fuel and oxidant utilizations on the system's water balance are in opposite directions, i.e. net water production decreases with increasing fuel utilization, but increases with increasing oxygen utilization. Ultimately, the effects of changing these utilizations are really due to the change in the cathode air requirement, which affects the moisture concentration in the burner product and, therefore, the amount of water that can be recovered. In addition to affecting the water balance in the system, the fuel and oxygen utilizations have significant impacts on the performance of the fuel cell itself. Lower utilizations permit operation at higher cell voltages, thereby yielding higher stack efficiencies. However, the electric power generated by the fuel cell system is lower. There are also operational constraints on how high or low these utilizations can be. Selection of the appropriate fuel and oxidant utilizations must be considered as part of the tradeoff analyses necessary for the system to meet the water balance, efficiency, and other constraints of the application.

Many fuel cell applications may be constrained by the availability of a consumable water supply for fuel processing and gas humidification. Several factors govern whether the fuel cell system will operate as a net water producer or consumer. These include such parameters as the steam-to-carbon ratio, the oxygen-to-fuel ratio, the fuel and oxygen utilizations in the fuel cell stack, and the water recoverable at the condenser which in turn is determined by the system (or ambient) pressure and temperature. More water is recoverable when systems operate at higher pressures, or at lower fuel and higher oxygen utilizations. More water is also recoverable if the fuel processor is operated with a higher oxygen-to-fuel ratio, though fuel processor and fuel cell system efficiency are lower as a consequence. The choice of fuel can have a significant impact on the water balance in the fuel cell system. Fuels with higher H/C tend to produce more net water. Such fuels can, in principle, be used in fuel cell systems that operate more efficiently and as net-water-producers even in climates with lower ambient pressures and higher ambient temperatures.

9. DESIGN OF HIGH TEMPERATURE MEMBRANES

9.1 Low Temperature Membranes and the Need for High Temperature Membranes

Polymer electrolyte membrane fuel cells operate at relatively low temperatures, typically around 70 °C. 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 the system cost. Traditional low temperature fuel cells generally have problems when operating on reformate gas produced from hydrocarbons, such as methanol, gasoline, or natural gas. In the fuel processing of the hydrocarbon to hydrogen, 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 50 ppm CO in the reformate stream [Hoogers, 2003], 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 [Wilkinson and Thompsett, 1997]. 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 significance. 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 temperatures 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 boiling point of water and therefore decreases the potential for cogeneration applications. The low temperature is insufficient to perform useful cogeneration. In low temperature fuel cells operating around 90^oC extra humidification is an issue. At 60^oC say product water is formed at the cathode, which can tend to flooding; this water needs to be removed. The cathode air must be dry enough to evaporate the product water but not so dry that it dries too much. A balance needs to be maintained. For doing all of this expensive equipments are needed. This all leads to extra costs. The higher the operating temperature, the better the performance, as there is no liquid water formed. Additionally the cathode over voltage reduces. Operating at low temperature the humidification problems increase, and the extra weight and cost of the humidification equipment can exceed the savings coming from smaller, lighter fuel cells.

High-temperature solid-polymer electrolyte membranes capable of operating at 150-200°C are at an early stage of development [Doss and Kumar, 2003]. These are being advanced as alternatives to Nafion-based solid-polymer electrolyte membranes that operate at around 70°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 PEFC systems. The reduction in overpotentials at higher temperatures can also potentially lead to improvement in current density and a lighter and more compact stack. The 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. 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 advantages as compared to low temperature membranes as follows. 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 elimination of the PROX reactor reduces the cost and the weight of the fuel processor and the entire fuel cell system.

9.2 250 KW Combined Heat and Power High Temperature Membrane Polymer Electrolyte Fuel Cell System

In conjunction with Argonne National Laboratory, we have simulated a 250 KW natural gas reformed PEM fuel cell high-temperature system operating at 150°C shown in Figure 15. The primary focus of the system was the generation of steam at 120°C to be used for industrial applications, although it did focus on the reduction of contaminants 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 5.

Table 5. 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 stack temperature selected was 150°C. This was not based on any studies but was done only for thesis. A wide range of fuel utilization ranging from 85% to 50% was taken in to consideration. This simulation was performed assuming a 85% fuel utilization. The steam-to-carbon ratio used in the simulation was 3.4.

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 tolerate 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.

In this system, sulfur is desulfurized before it enters the system. The step by step processing of the fuel is as follows: 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 [International Fuel Cells, 2001]. The reformer operating temperature is dependent on the fuel used and may range from 250°C (methanol) to over 700°C (methane). The high temperature water shift reactor is used to convert carbon monoxide to carbon dioxide. The high temperature water shift reactor typically operates at temperatures between 250–300°C.

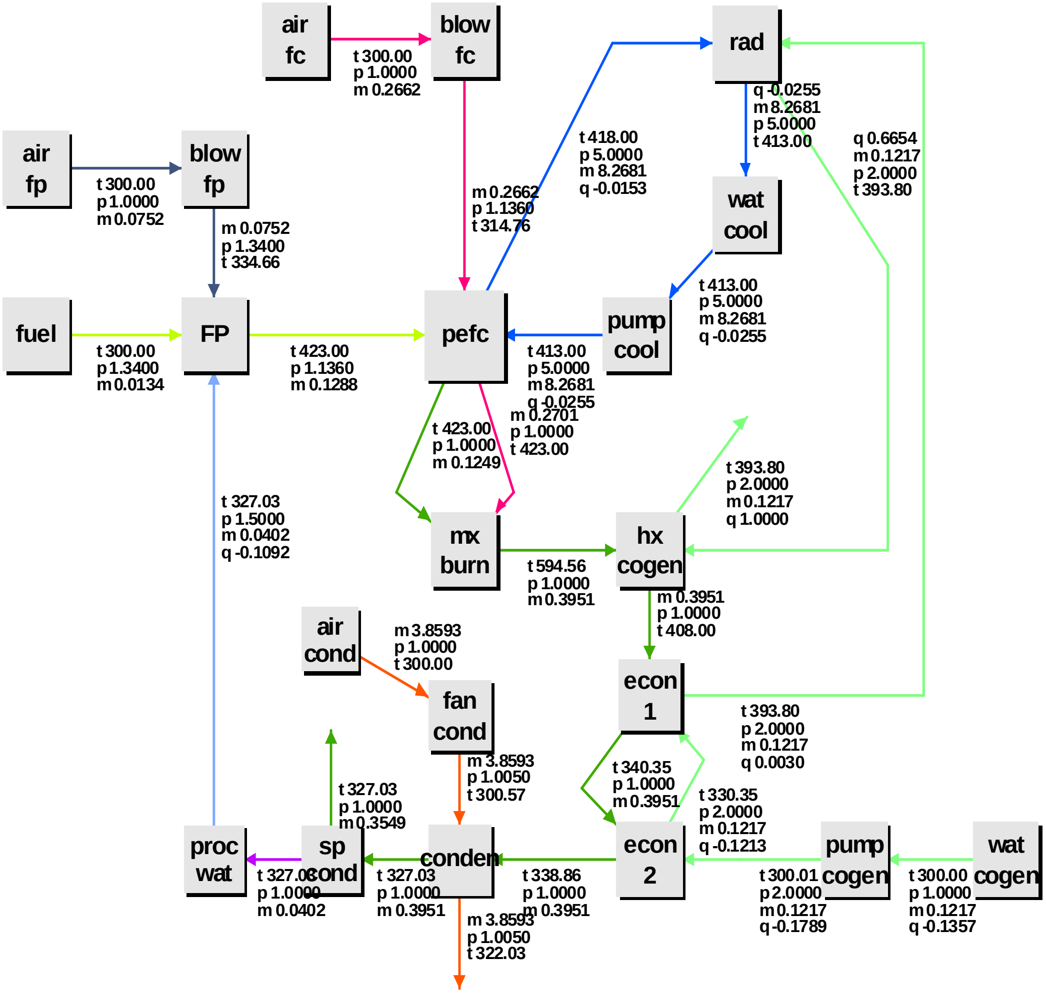


Figure 15. Combined 250 KW power-steam HTM-PEM system.

The low temperature water shift reactor is used to convert the remaining carbon monoxide to carbon dioxide. The LTWS reactor typically operates at temperatures between 200–250°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. The cost, complexity, and weight of the fuel processing system are greatly reduced.

In this way, hydrogen-rich reformate is fed into the anode end of the fuel cell and oxygen is fed into 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 the oxygen is used in the fuel cell stack. The unconverted hydrogen and depleted oxygen are mixed in the catalytic burner (mx burn). The reformate is fed into the heat exchanger (hx cogen) where the heat is recovered from the burner (refer to Figure 15). 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 loop (closed) 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. The water is cooled and pumped back into the fuel cell stack. The reformate from the heat exchanger 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 into the processed water tank for input into the fuel processor. Air for the cathode is introduced from the blower. Part of the exhaust is thrown away as waste from the condenser. The various heat exchangers and economizers are used for preheating the process steams and for 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.

9.3 Process Steps

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. As a result, the cost, complexity and weight of the fuel processing system is greatly reduced.

In this way, hydrogen-rich reformate is fed into the anode end of the fuel cell and oxygen is fed into 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 the oxygen is used in the fuel cell stack. The unconverted hydrogen and depleted oxygen are mixed in the catalytic burner (mx burn). The reformate is fed into the heat exchanger (hx cogen) where the heat is recovered from the burner (refer to Figure 15). 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 loop (closed) 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. The water is cooled and pumped back into the fuel cell stack. The reformate from the heat exchanger 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 into the processed water tank for input into the fuel processor. Air for the cathode is introduced from the blower. Part of the exhaust is thrown away as waste from the condenser. The various heat exchangers and economizers are used for preheating the process steams and for 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.

9.4 Auxiliary Systems

These fuel cell systems also incorporate several ancillary devices necessary for their operation:

(1) Electric motors that power the pumps and compressors.
(2) Mechanical cooling equipment that provides supplementary heat extraction required by the fuel cell stack and cooling processes.
(3) Power conditioning unit: This involves taking whatever electricity is produced by the generator and converting it to meet the industry standards so that it can used without damaging whatever is plugged in (e.g., a TV). Power conditioning for a fuel cell power plant includes an inverter that converts DC power into AC power, current, voltage, and frequency control.
(4) Hydrogen burner: The hydrogen burner is used to oxidize any hydrogen not reacted in the fuel cell stack. This prevents the release of combustible gases to the atmosphere and also produces thermal energy that may be used for process heating in the fuel processor.
(5) 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.
(6) 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 purposes, and a mechanical cooling arrangement that provides cooling during periods of insufficient space heating and demand.
(7) 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.
(8) 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.
(9) 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.
(10) 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.

(11) Nozzle: It is a flow passage of varying cross-sectional area in which the velocity of a gas of liquid increases in the direction of flow.
(12) Pumps: In pumps, the work input is used to change the state of a liquid passing through them.
(13) Expander: They are turbines in which gas expands, does work, and undergoes a drop in temperature.
(14) 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.
(15) Turbocompressor**:** It supplies the cathode air as well as air needed for the fuel autothermal reformer.
(16) Condenser: It is used to recover water from the exhaust.

9.5 GCtool

GCtool (developed by Argonne National Laboratory) has been used for all of the above simulations. 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 and Ahluwalia, 1988]. 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: PEFC, often referred to as proton exchange membrane), 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 motors/generators). Property codes 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.

This software tool has been used successfully in analyzing a variety of 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.

The GCtool program's great strength is its flexibility; it can be used to define arbitrary system configurations, handling models of any level of sophistication and permitting arbitrary flows and system constraints [Geyer and Ahluwalia, 1988]. Unlike other software it performs both steady-state and dynamic analysis, allows unlimited parameter sweeps, and performs constrained optimization (in contrast to other software where specifying constraints has often been a problem). Users need not run GCtool over and over again to examine each individual change in system parameters; loping statements and other logical functions automate the process. GCtool's C language interpreter and model design support rapid system prototyping. Models can be in any C linkable language, at any level of complexity. The GCtool environment is highly user friendly; users are capable of actively programming in less than a week. Other important features include the following: The model library offers four different types of fuel cells PEM, molten carbonate, phosphoric acid, and solid oxide cells. Other ready-to-use component models include various kinds of heat exchangers (heat pipes, condenser, thermal radiator, etc.), fluid devices (splitter, nozzles, diffuser, gas turbine, pump, etc.), reactors and reformers, and vehicle systems (including an electric motor and generator). The property codes include a fast gas-phase chemical equilibrium code capable of handling an arbitrary number of species, a multiphase chemical equilibrium code, one for condensable pure substances, and a steam/water code. Special-purpose procedures are also available for dealing with sodium and potassium. GCtool uses a system of "stacks" (the gas stack, shaft stack, power stack, etc.) to pass information between models; each model takes from a given stack the inputs it requires and adds to the stack the outputs it generates. The program's powerful mathematical utilities include a nonlinear equation solver, a constrained nonlinear optimizer (which handles both linear and nonlinear constraints), an integrator, and a solver for ordinary differential equations. With its tremendous adaptability, GCtool can be applied to a broad range of power-plant types: Fuel cell systems, including polymer electrolyte, molten carbonate, phosphoric acid, and solid oxide designs; Pressurized fluidized-bed combustion and integrated gasification/combined-cycle plants, Coal combustion systems, and space power systems.

This software tool has been used successfully in analyzing a variety of the polymer electrolyte fuel cell (PEFC) systems using different fuels, fuel storage methods, and fuel processing techniques. Examples include compressed hydrogen systems; metal hydride, glass microsphere, and sponge-iron hydrogen storage systems; and fuel cell systems with reformers for methanol, natural gas, and gasoline, using either partial-oxidation or steam reforming.

9.6 Results for 250 KW Combined Heat and Power High Temperature Membrane Polymer Electrolyte Fuel Cell System

The results from this simulation are summarized in Table 6.

Table 6. System performance of high temperature membrane system**.**

Operating Parameters	**Values**
Fuel processor efficiency	80.80%
Electrical efficiency	37.30%
Thermal efficiency	47.20%
Water	28%
Nitrogen	61%
Oxygen	5%
Sulfur	Tolerant < 5ppm
CO	Tolerant 50ppm
CO_2	6%
NO_x and VOC	Negligible
Methane slip	< 1%

9.6.1 Electrical and thermal efficiencies

As shown in Figure 16 at 85% fuel utilization, there are two points 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.

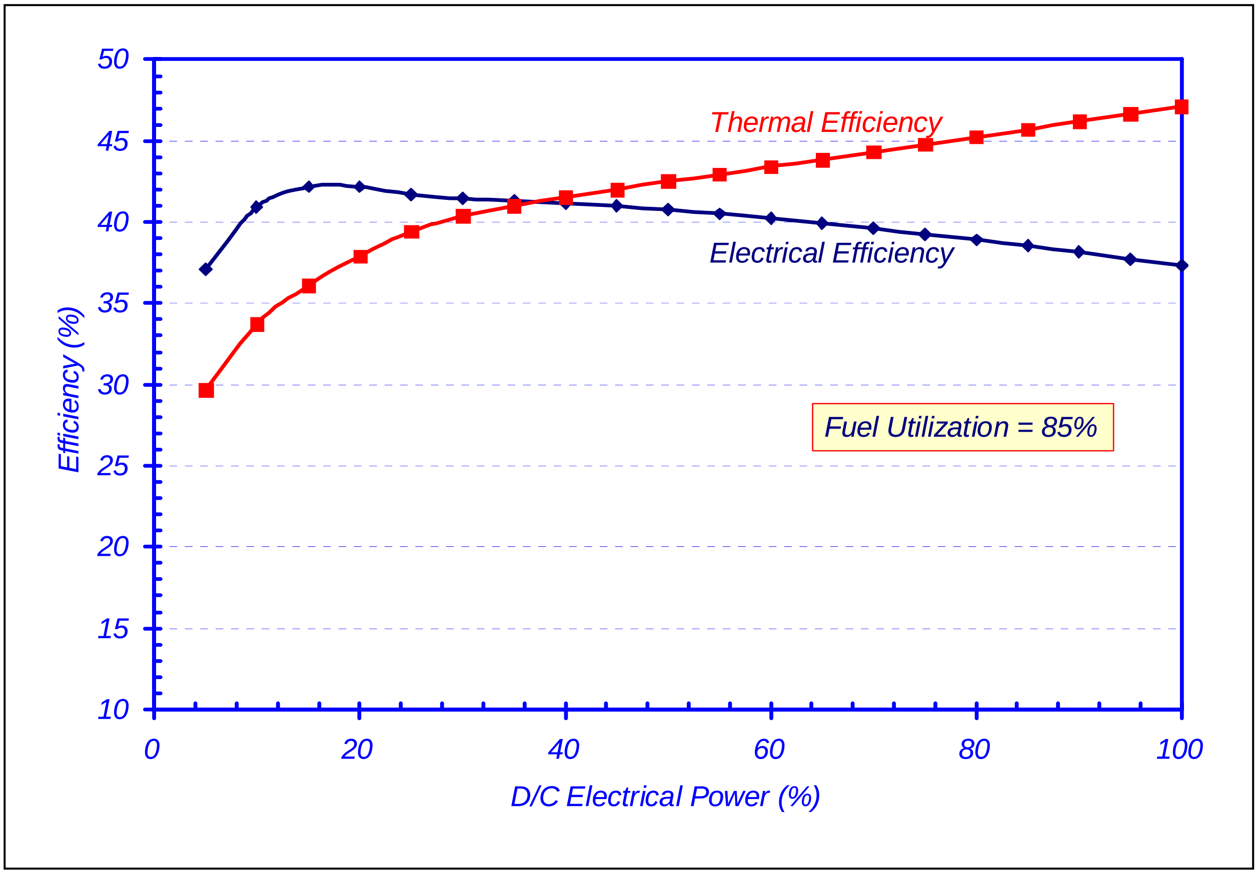


Figure 16. Electrical and thermal efficiency of a PEM fuel cell versus load.

The quotient of the electrical energy and usable thermal energy is an important operating parameter of the fuel cell system. This electrical energy-thermal energy-relation A is defined as follows:

A = electrical energy / thermal energy and is strongly dependent on the electrical load.

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:

$$\eta = T_2 / (T_2 - T_1) \qquad \text{for Carnot cycle and}$$
$$\eta = \Delta G / (\Delta G + T\Delta G) \qquad \text{for a fuel cell}$$

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).

Total thermal energy of fuel cell = reversible heat + Joule heat.

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

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 16.

9.6.1.1 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.

9.6.1.2 Sulfur reduction

There are high temperature and low temperature methods to remove sulfur from a fuel reformate stream. Low temperature cleanup, such as hydrodesulfurization (limited to fuels with boiling end points below 205^{o}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 H_2S, then the H_2S 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 H_2S so that it can be entrapped on zinc oxide. Zinc oxide beds are limited to operation at temperatures below 430^{o}C probably because of pore plugging during sulfur removal and sintering. Thermodynamics also favors lower temperatures. At the higher temperatures, the H_2S 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].

9.6.1.3 CO poisoning

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

$$CH_4 + H_2O \rightarrow 3\,H_2 + CO$$

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.

$$CO + H_2O \rightarrow H_2 + CO_2$$

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 [Larmanie and Dicks, 2003].

9.6.1.4 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 then 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.

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O \qquad (\Delta H = -206 \text{ KJ mol}^{-1})$$

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 200°C, the carbon monoxide levels will be less than 10 ppm [Larmanie and Dicks, 2003]. The catalysts will also ensure that any unconverted methanol is reacted with methane, hydrogen, or carbon dioxide.

*Palladium/platinum membrane***s** 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.

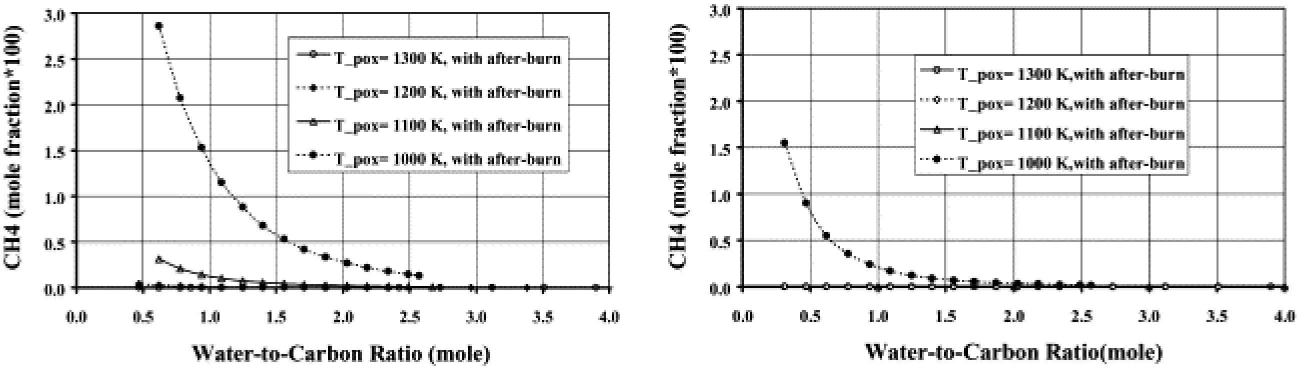
9.6.2 Carbon deposition avoidance

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.

9.6.3 Methane concentration in the reformate

Any methane (CH_4) 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 CH_4 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 CH_4 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 CH_4 in the processed reformate is greatly affected by the value of T_{POX}, as shown in Figure 17. Figure 17a uses 3 atm system and Figure 17b_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 CH_4 thermodynamically favored.



(a) (b)

Figure 17. Methane formed as a function of the water-to-carbon ratio at various temperatures [Doss *et al*., 2001].

9.6.4 Electrical efficiency

Figure 18 shows that, upon increasing the fuel utilization, the electrical efficiency keeps on increasing as more hydrogen is being consumed, leading to more efficient fuel utilization.

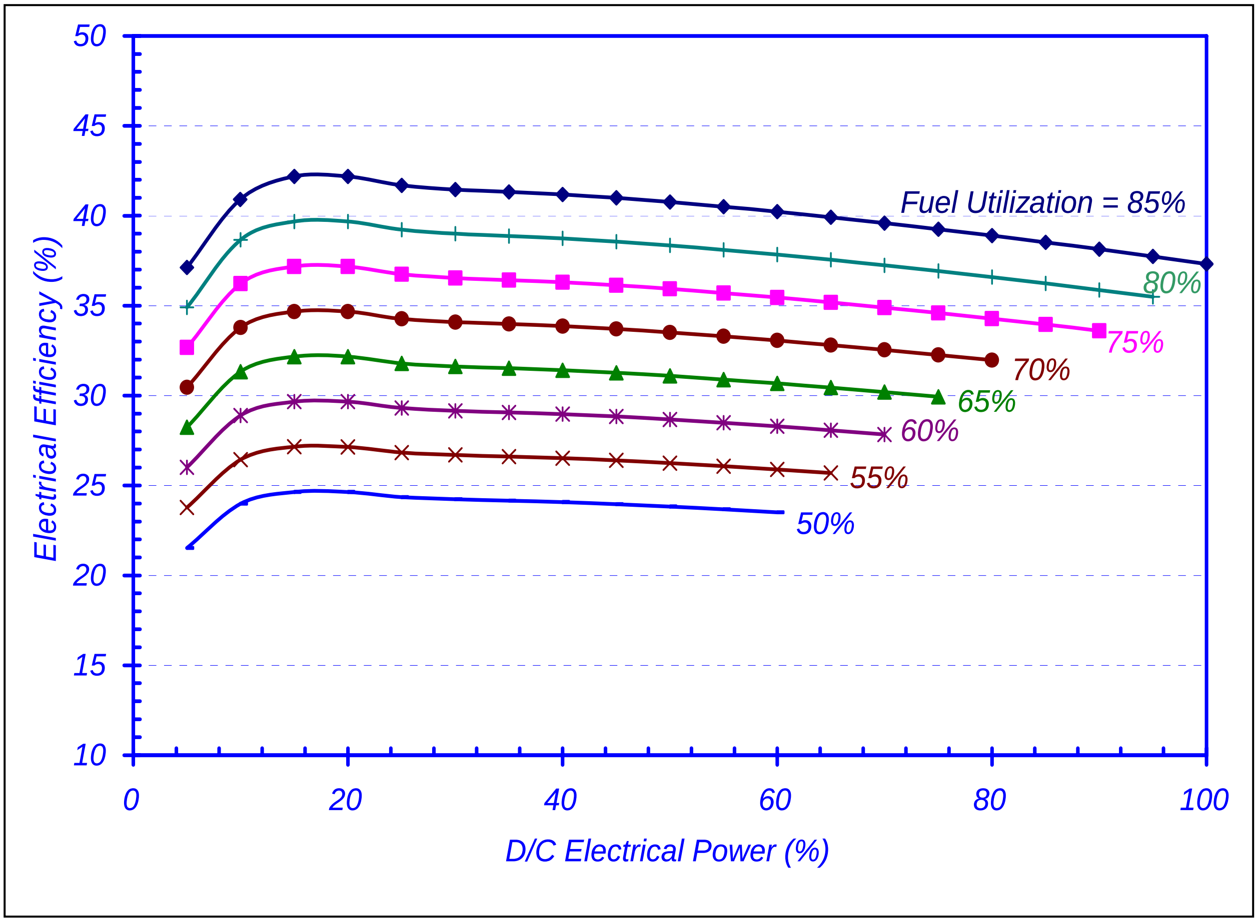


Figure 18. Plot of electrical efficiency.

9.6.5 Thermal efficiency

Figure 19 shows the variation of thermal efficiency with different fuel utilization. This is opposite of the previous figure (Figure 18) where the electrical efficiency increased with the fuel utilization. Here, if more fuel is utilized, then less hydrogen will be left in the catalytic burner and the result will be less generation of heat from the burner power generation. The peak electrical efficiency achieved is 42.5% for 85% fuel utilization.

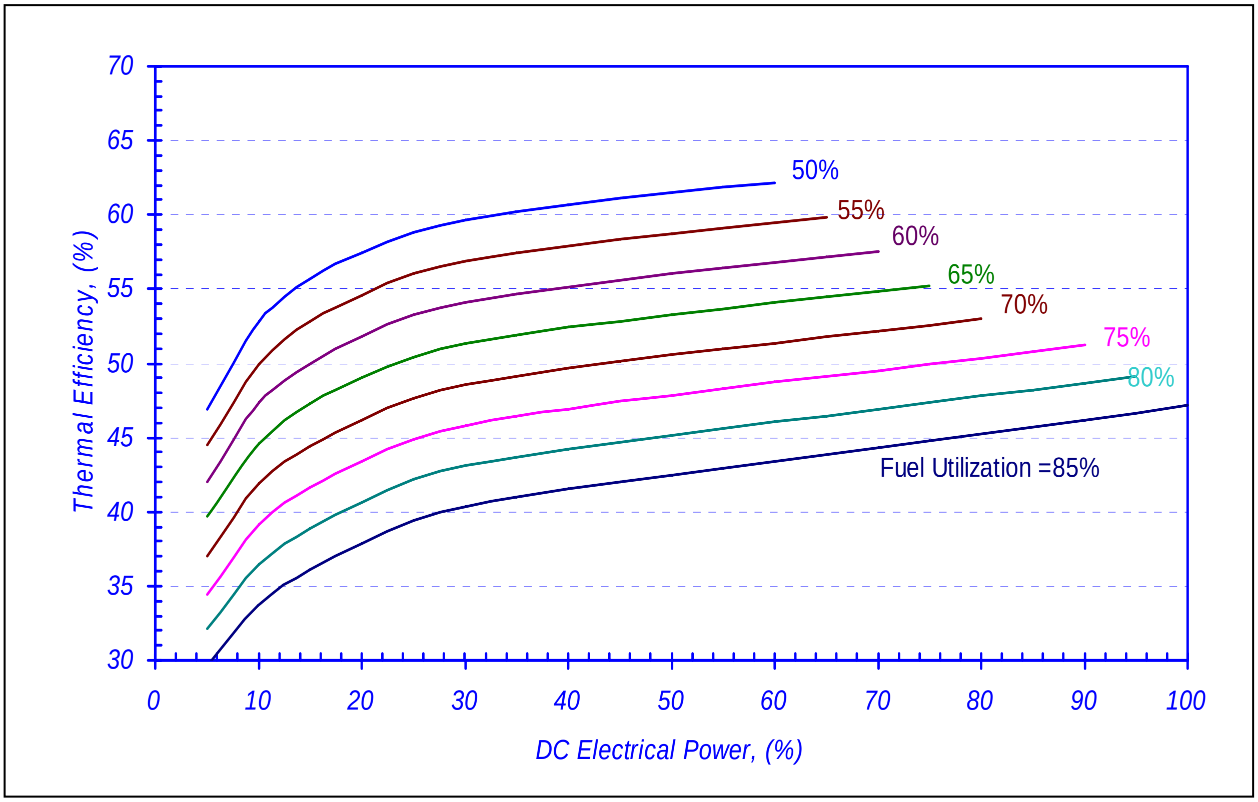


Figure 19. Plot of thermal efficiency

Figures 18 and 19 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%.

9.6.6 Electrical performance map

Figure 20 shows that at the intersection of thermal input and electrical efficiencies, the different power is produced and the heat available for cogeneration are obtained. For example, if it is required to generate a power of 160 kW and the desired electrical efficiency required is 40% then, the available heat for co-generation would be 170 kW and the thermal input would be 60%.

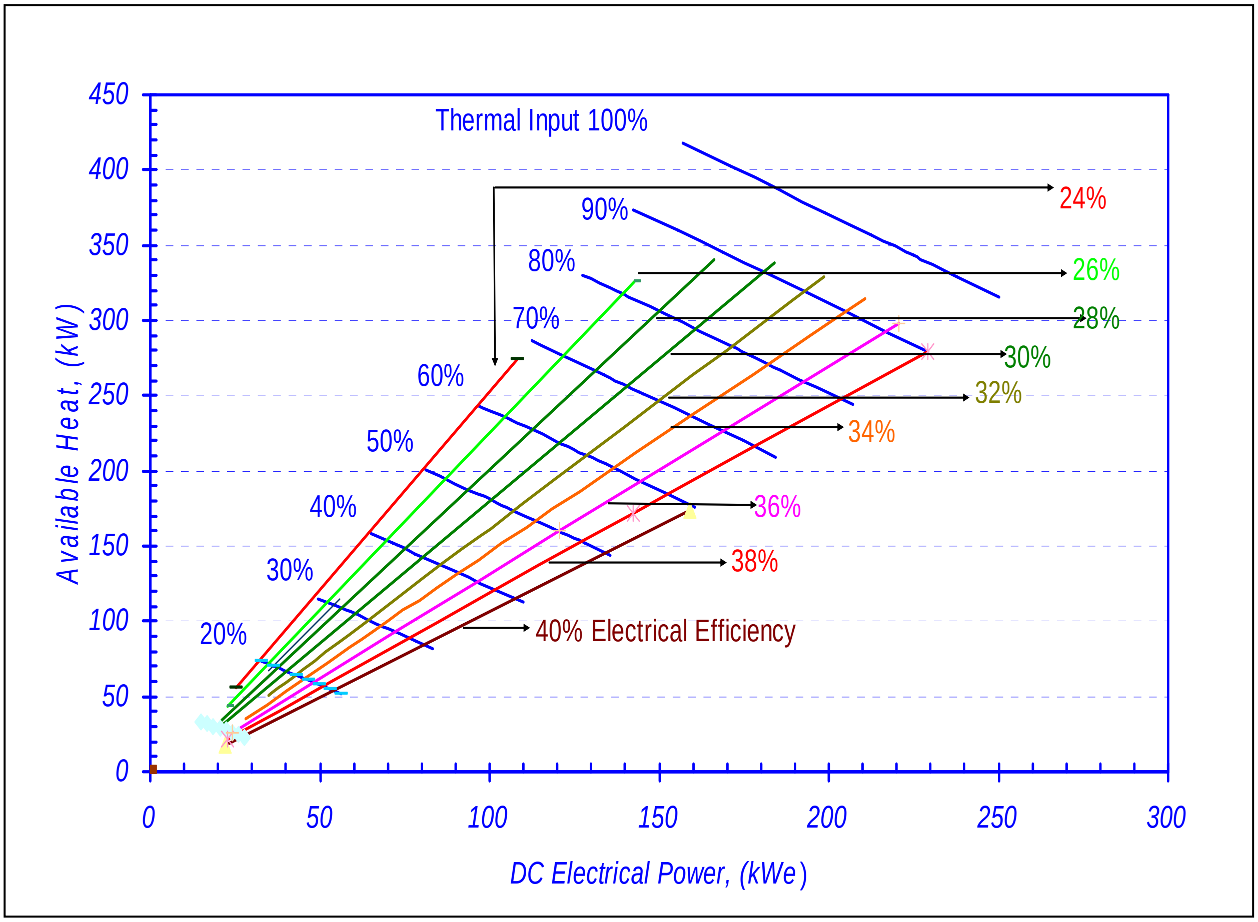


Figure 20. Electrical performance map.

9.6.7 Thermal performance map

Figure 21 shows that at the intersection of thermal input and thermal efficiencies, different power is produced and the heat available for cogeneration is obtained. For example, if it is required to generate a power of 160 kW and the desired thermal efficiency required is 45%, then the available heat for co-generation would be 180 kW and the thermal input would be 60%.

It is important to understand the concept of water drag in case of low temperature fuel cells. When the hydrogen ions travel across the membrane from the anode to the cathode, they tend to drag some water molecules with them. This phenomenon is known as “electro-osmotic” drag. The electro-osmotic drag is a result of the proton transport mechanism in the membrane. Water is produced at the cathode, and some water tends to accumulate at the cathode from the electro-osmotic drag.

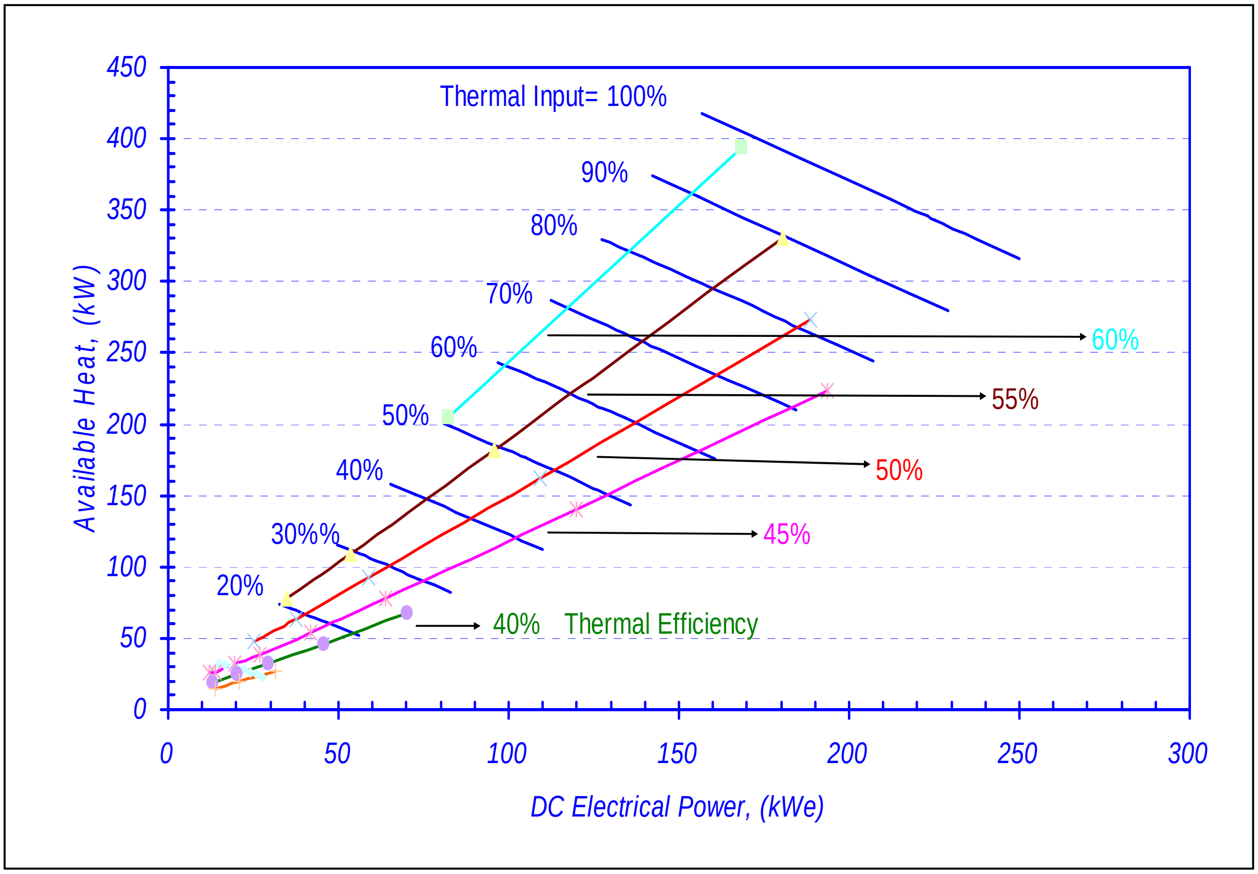


Figure 21. Thermal performance map.

Under most operating conditions, the concentration of water becomes higher on the cathode than on the anode side, leading to "back diffusion" of water towards the anode side. There are two components to water drag "electro-osmotic" drag and "back diffusion". The amount of water dragged can play an important role in the performance of the fuel cell. The water that is dragged across the membrane helps in keeping the membrane humidified.

A membrane that is not well humidified can have high resistance, leading to substantial voltage losses in the fuel cell. In general, the anode stream (and maybe also the cathode stream) has to be humidified with the intention of keeping the membrane well hydrated. The total amount of water dragged adds to the total amount of water produced at the cathode layer, so a large water drag brings up the concern of cathode "flooding", which can substantially bring down the performance of the fuel cell. This happens because liquid water blocks the pores and thereby hinders the transport of oxygen in the cathode. In our analysis, we neglected the flooding of the membrane.

It is important to understand the concept of high grade heat and low grade heat. We have defined high grade heat, which is related to the catalytic burner exhaust. The low grade heat is related to the fuel cell stack exhaust. The purpose of the radiator is to maintain the fuel cell stack temperature near the operating temperature. The purpose of the condenser is to aid in water recovery for the system.

In low temperature fuel cells, the water in the cathode exhaust is from four different sources: water produced by the reaction between hydrogen and oxygen, water used to cool and humidify the cathode, net water dragged from the anode to the cathode, and water in the cathode due to ambient relative humidity. Figure 22 shows a plot of the thermal efficiency for a low temperature fuel cell.

Under certain operating conditions, the amount of water in the cathode of the fuel cell stack can be much more than the air stream can hold in the vapor state, resulting in condensation inside the stack. This condensation imposes an additional load on the radiator as the radiator has to remove the heat due to condensation. As a result, the stack load can be much more then the radiator can support efficiently, causing the thermal efficiency of the radiator to decrease.

The low temperature fuel cell operating at about 70°C is insufficient to perform useful cogeneration due to its low operating temperature. The low grade heat generated is insufficient to produce water/steam greater then 70°C. As shown in Figure 23, only 42.6% of the high-grade heat is used and the rest is cooled in a condenser.

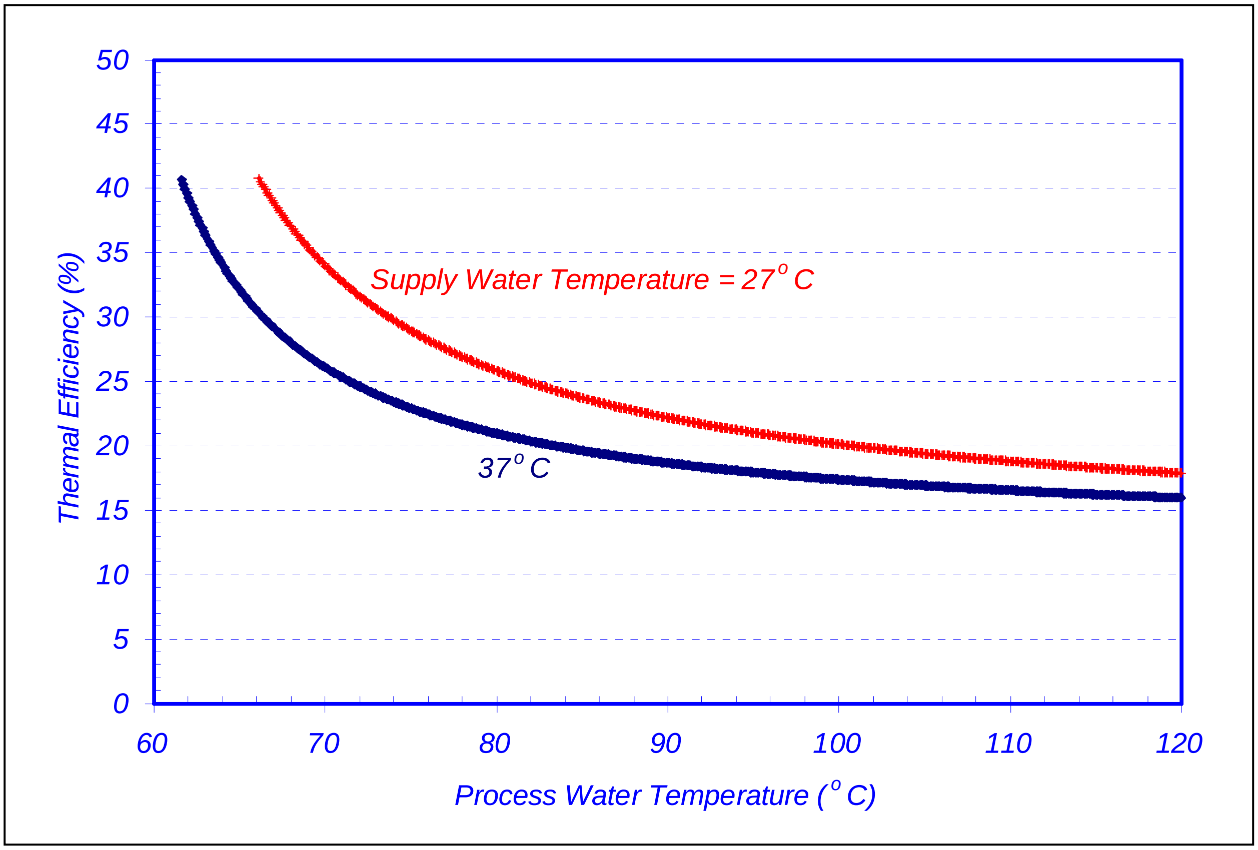


Figure 22. Plot of thermal efficiency (low temperature fuel cell).

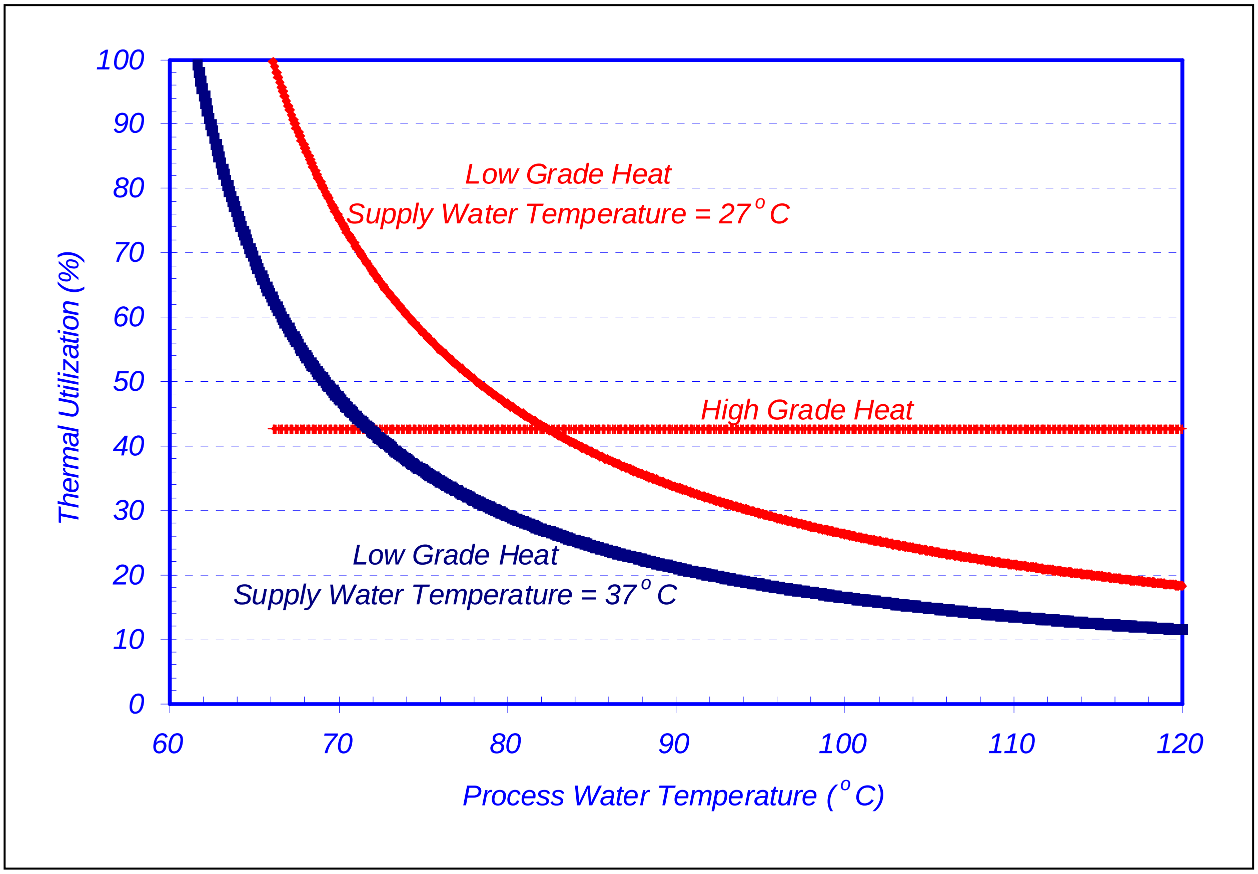


Figure 23. Plot of thermal utilization (low temperature fuel cell).

The efficiency of the low-grade heat decreases as we increase the supply water temperature. Here we designate the water for cogeneration purposes as supply water. It is the water for cogeneration that is used in generating steam with the help of the low grade heat from the stack (radiator) and part of the high-grade heat from the catalytic burner.

The fuel cell cathode exhaust is cooled in a condenser to recover water for the fuel processor. The hot gas leaving the burner can be used to heat the water through a heat exchanger. The stack coolant loop is used to remove the water heat the fuel cell stack. Coolant from the tank is pumped into the fuel cell stack. The heated coolant then flows in to the radiator (where the excess heat due to the inefficiency of the fuel cell is dissipated) and then back to the coolant tank. The supply water provides water to the coolant circuit. If the supply water temperature is increased the load on the radiator increases. The supply water temperature imposes an additional load on the radiator in the form of heat. As a result the efficiency of the radiator decreases. The radiator has to take care of the extra heat from the supply water temperature. The radiator then throws some of the extra heat in the condenser which increases its load.

The low temperature fuel cells are inefficient for generating steam. Use of low-grade heat decreases with the process water temperature. The high-grade heat used (as shown in Figure 23) is only 42.6%. The operating temperature limits the formation of the low-grade heat temperature through which it can be utilized. Figure 24 shows a plot of the thermal efficiency versus the process steam temperature, and Figure 25 shows a plot of thermal utilization versus process steam temperature.

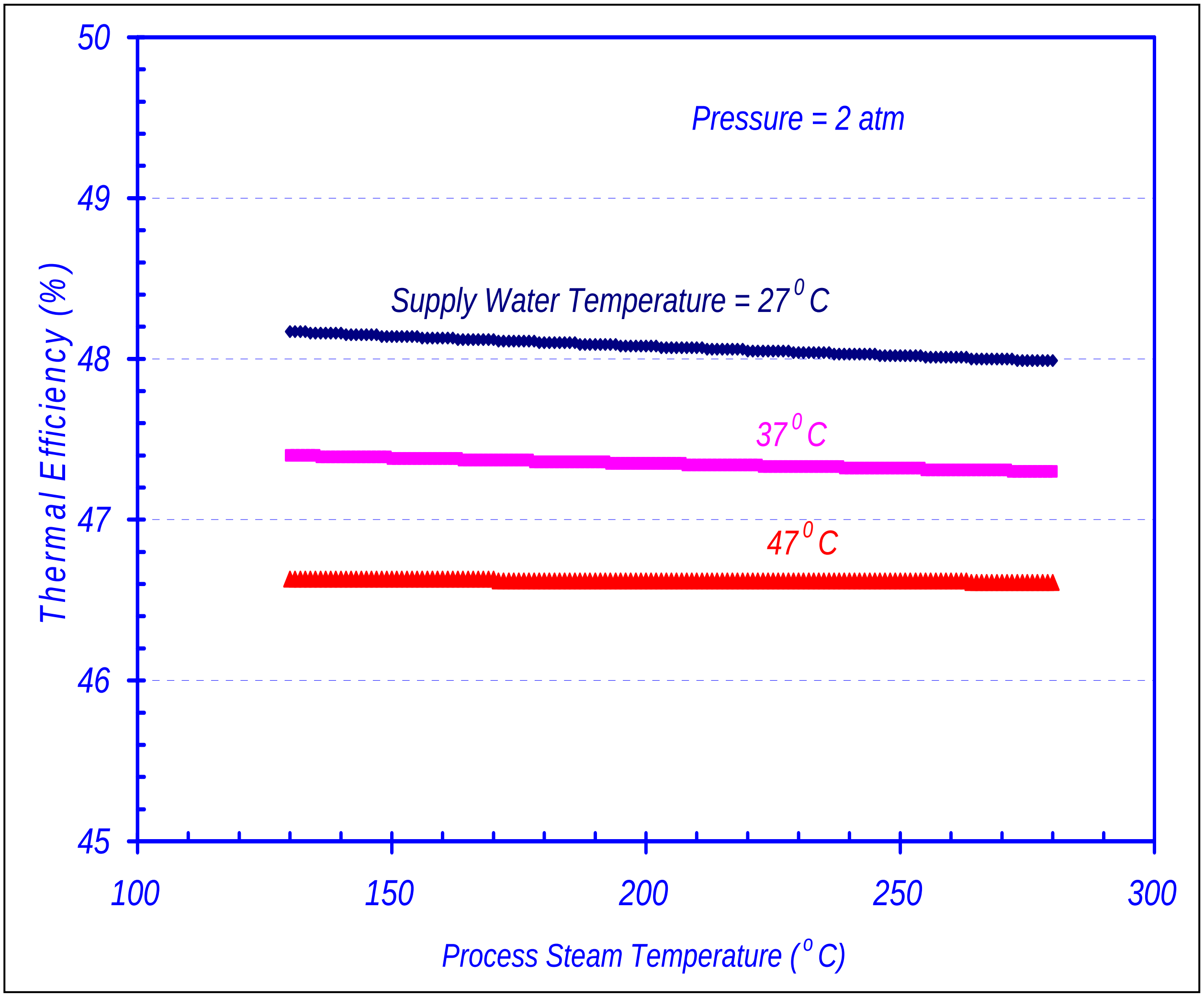


Figure 24. Thermal efficiency versus process steam temperature.

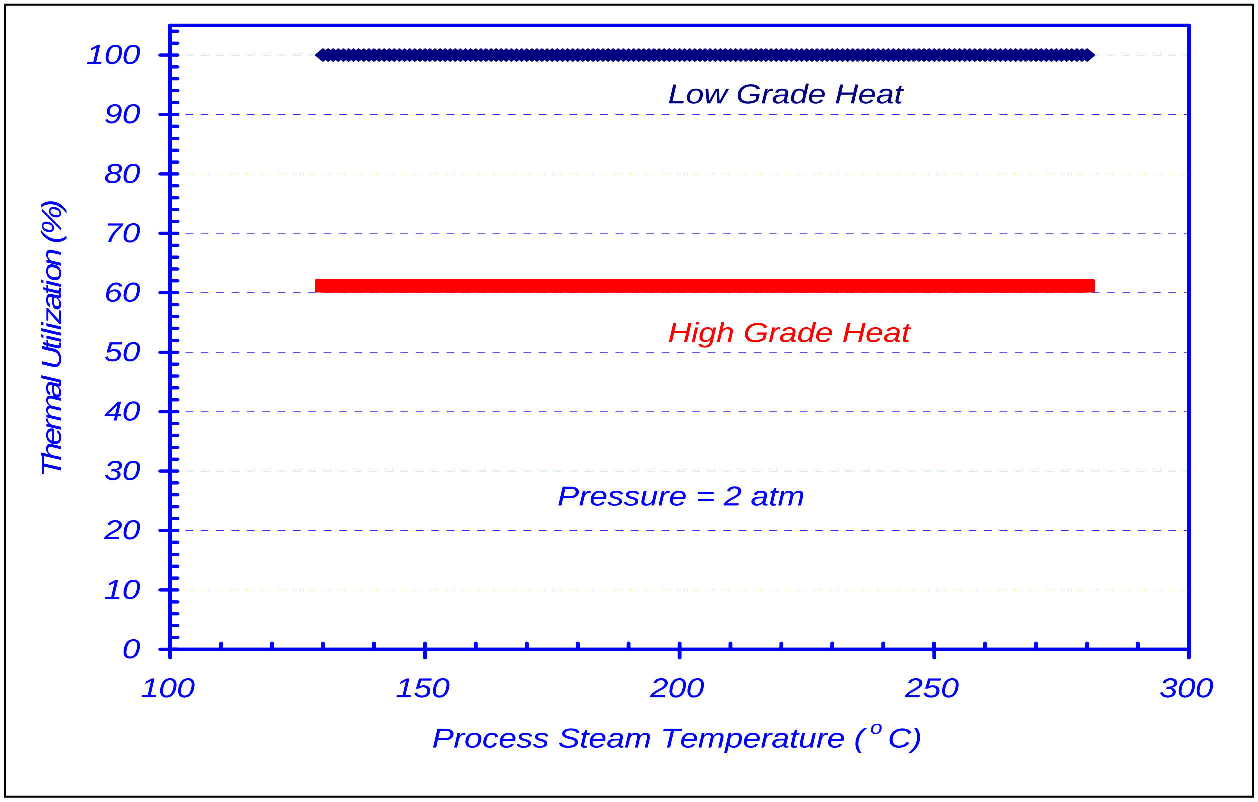


Figure 25. Thermal utilization versus process steam temperature.

In high temperature fuel cells, steam (and not water) is produced. Since there is no product water produced, there is no additional load on the stack. In low temperature fuel formed at the cathode which may tend to flooding. This water needs to be removed, increasing the stack heat load which has to be removed by the radiator. The higher the operating temperature, the better the performance as there is no liquid water formed. Additionally the cathode over voltage reduces. So the stack heat load of the high temperature fuel cell is less as compared to low temperature ones.

Further the supply water temperature is a function of the dew point temperature, which is a measure of the amount of water vapor in the current air mass. The higher the dew point, the more water vapor there is in the air. The dew point temperature in our simulations was about 50°C. As shown in Figure 26, as the supply water temperature increased beyond the dew point temperature, the thermal efficiency decreases. The reason for this is that the amount of water vapor in the air increased, leading to condensation of water in the cathode exhaust, which in turn increased the stack load. The heat due to the increased condensation had to be removed by the radiator putting an additional load on it and decreasing its efficiency.

The stack coolant loop is used to remove the water heat the fuel cell stack. Coolant from the tank is pumped into the fuel cell stack. The heated coolant then flows in to the radiator (where the excess heat due to the inefficiency of the fuel cell is dissipated) and then back to the coolant tank. The supply water provides water to the coolant circuit. If the supply water temperature is increased, the load on the radiator increases. The supply water temperature imposes an additional load on the radiator in the form of heat. As a result the efficiency of the radiator decreases. The radiator has to take care of the extra heat from the supply water temperature. The radiator then throws some of the extra heat in the condenser which increases its load. This is shown in Figure 27.

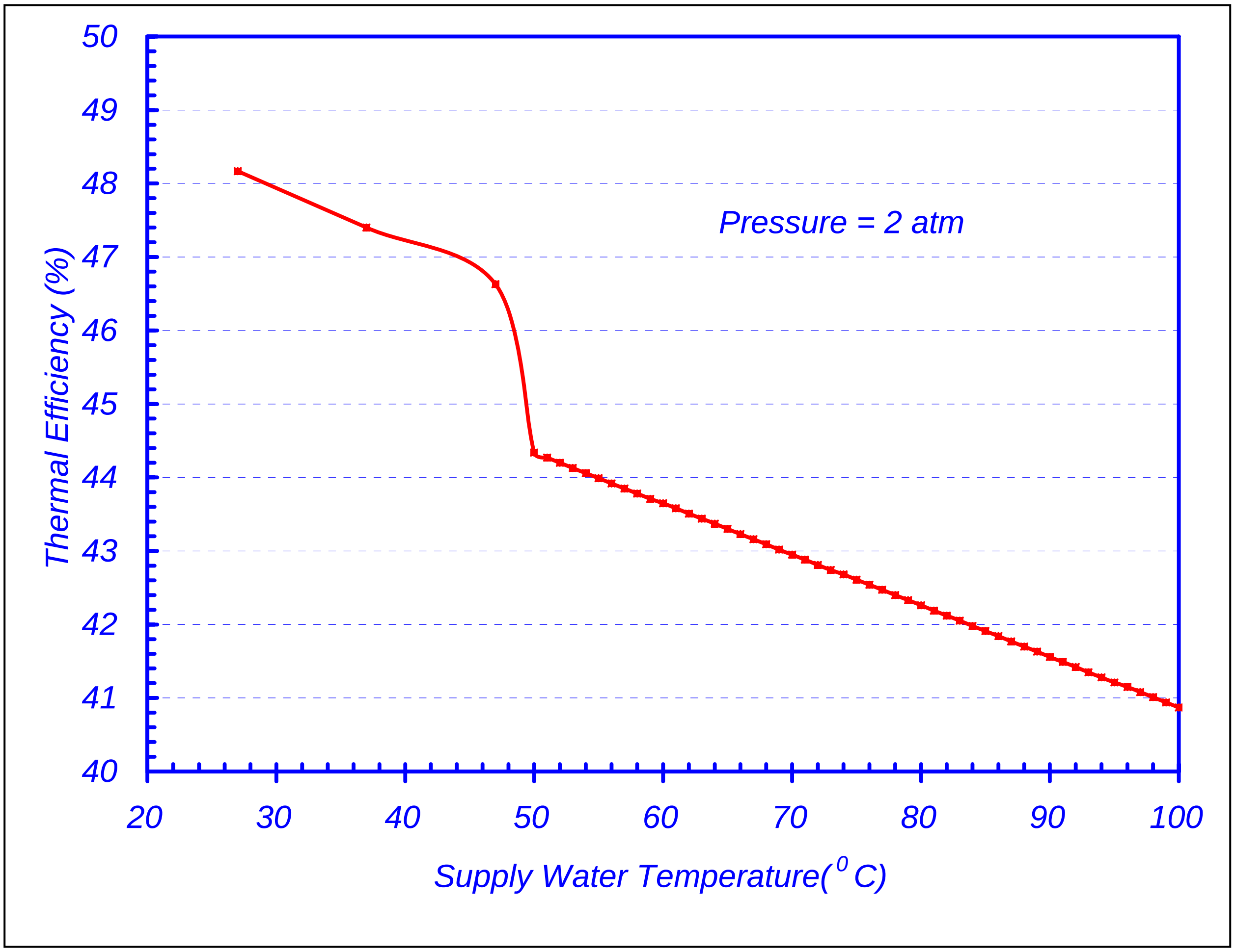


Figure 26. Thermal efficiency versus supply water temperature.

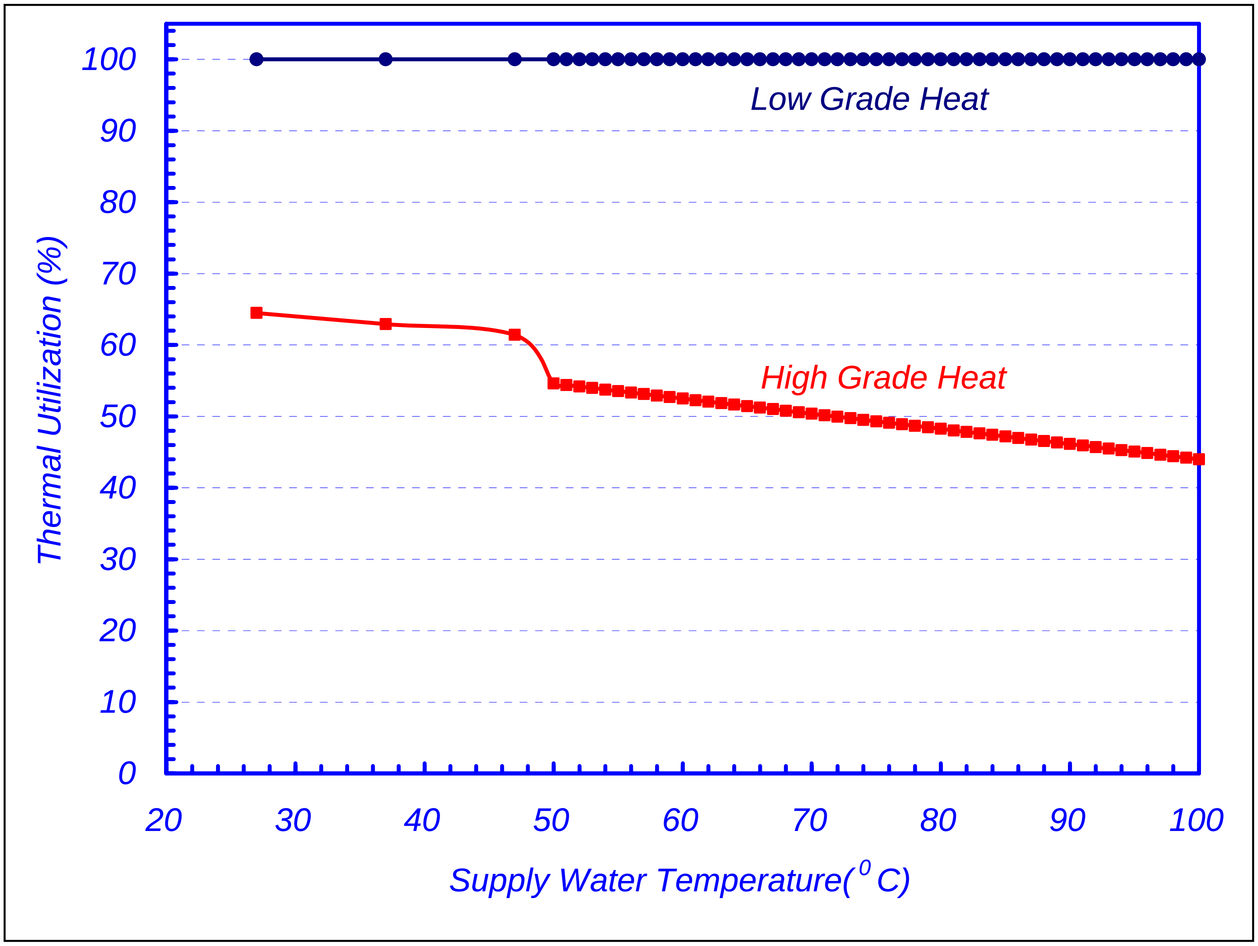


Figure 27**.** Thermal utilization versus supply water temperature.

Figures 28 and 29 show that, if the steam pressure is increased while keeping the mass flow rate of air and water constant, the partial pressure of water vapor in the cathode exhaust increases and water begins to condense out of the stream, leading to an increased condensation of water. As a result, the amount of water that condenses out of the stream depends on the steam pressure. Consequently, with an increase in pressure, the required water condenses out at higher temperatures in the condenser. Table 7 presents a comparison of low temperature and high temperature fuel cells for Cogeneration

The increasing saturation temperature decreases the condenser fan power with increasing steam pressure (the lower the temperature drop in the condenser the lower the condenser loads). This effect continues as long as there is still water remaining to be removed in the condenser. For the radiator, the load decreases gradually, due to the fact that as the pressure of the air supplied to the stack is increased, the partial pressure of the oxygen is increased at the catalyst sites, thereby reducing the cathode overpotential and increasing the stack efficiency accordingly. Up to a certain point, all of the water required for the system is condensed within the condenser and the radiator load accommodates only the heat rejection due to the efficiency losses in the stack. When the steam pressure is increased further, under the given conditions, liquid water begins to condense within the stack; this condensation within the stack increases the radiator duty and parasitic load.

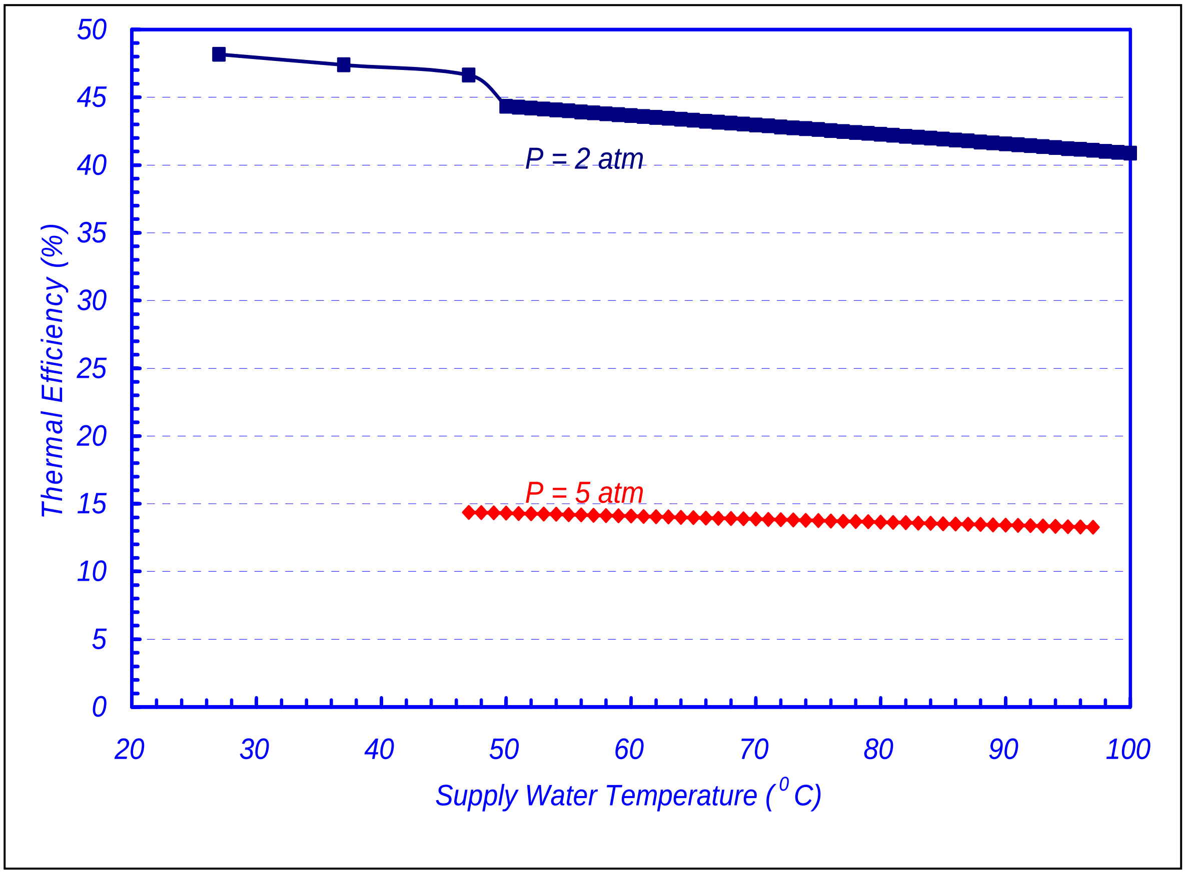


Figure 28. Effect of pressure on thermal efficiency.

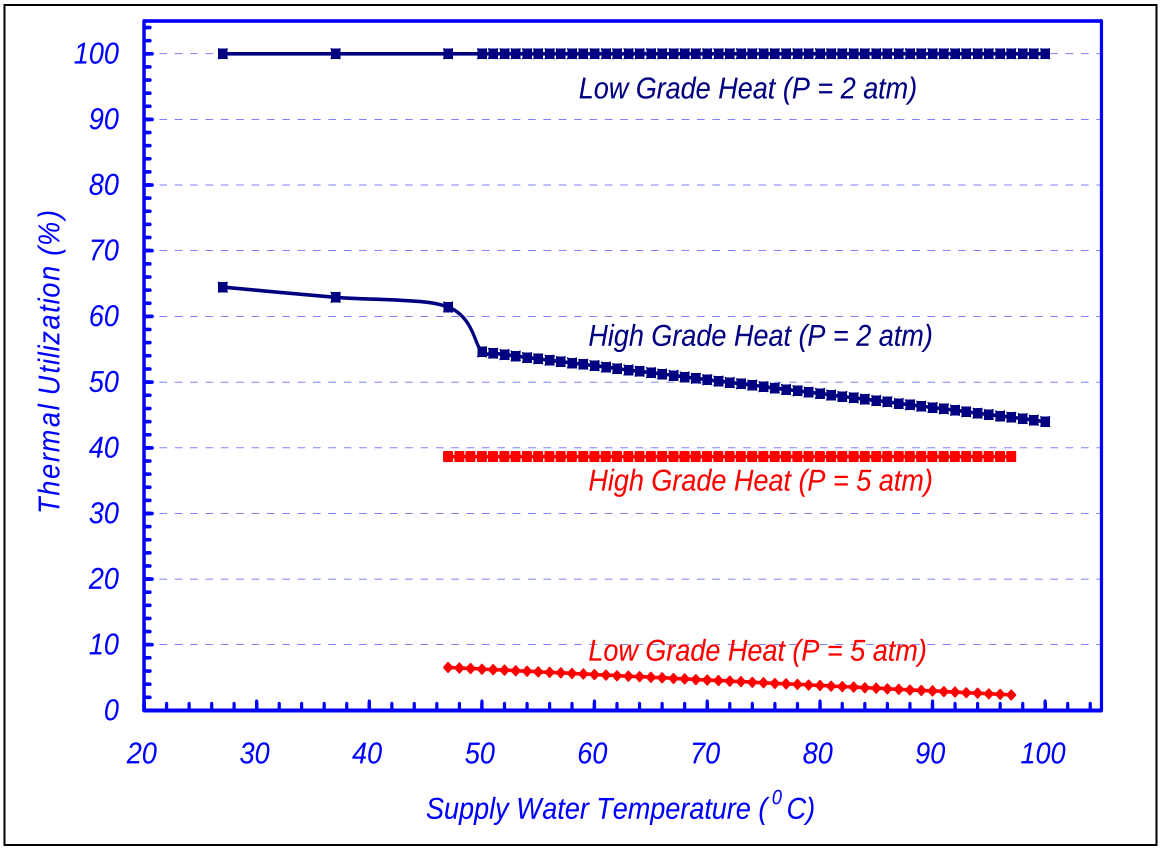


Figure 29. Effect of pressure on thermal utilization.

Table 7. Summary table comparison of low temperature and high temperature fuel cells for Cogeneration

Low Temperature Fuel Cell	**High Temperature Fuel Cell**
Stack heat load = 235 kW	Stack heat load = 178 kW
Radiator load = 184 kW	Radiator load = 178 kW
Condenser heat load = 112 kW	Condenser heat load = 85 kW
High grade heat utilized = 42.5%	High grade heat utilized = 61.3%
Inefficient for cogeneration	Steam generation possible through 280^{o}C
Tail gas burner temperature = 245^{o}C	Tail gas burnet temperature = 322^{o}C
Low grade heat utilization decreases	Low grade heat utilization is 100%

9.7 Observations and Results

The performance of high-temperature membrane, polymer electrolyte fuel cell systems was studied with particular attention paid to the effects of the water-to-carbon ratio, carbon formation, hydrogen formation, methane formation, fuel and oxidant utilization, sulfur reduction, and thermal efficiency/electrical efficiency relationship, on fuel cell performance. The high temperature and the low temperature fuel cells were compared on the basis of carbon monoxide production, co-generation, and humidification issues.

The major conclusions are as follows: Increasing the fuel utilization increases the electrical efficiency, but decreases the thermal efficiency. Higher fuel utilization leaves less hydrogen available for combustion in the catalytic burner leading to less heat generated in the burner. The electrical and thermal efficiencies are optimum at 85% fuel utilization. Any methane formed in the autothermal reactor 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. At S/C greater than 1, methane slip is less than 1%. The simulations have used a S/C ratio of 3.4. In our simulations, we have assumed that sulfur is desulfurized before it entered the fuel processor.

The disadvantages of low temperature fuel cells (70^{o}C) include: The low temperature membrane (70^{o}C) is unsuitable for generating high grade heat suitable for useful cogeneration. The high-grade heat generated is only 245^{o}C. The high-grade heat used is 42.5%. The low temperature membrane is suitable for producing process water with temperature less than 70^{o}C. In low temperature fuel cells, carbon monoxide is produced as a byproduct is extremely sensitive to the platinum catalyst, requiring additional PROX to remove it, adding to the cost, weight, space, and complexity of the fuel cell system. The PROX is very difficult to control. The PROX reduces the amount of hydrogen going to the fuel cell stack. The PROX allows oxygen and hydrogen to react with carbon monoxide to form water and carbon dioxide, thereby consuming hydrogen in the reaction. Extra humidification is an issue in low temperature fuel cells, as the product water formed in the fuel cell stack needs to be removed, requiring extra humidification equipment which adds to the weight and cost of the fuel cell system. The radiator load increases as the heat due to condensation of water has to be removed by the radiator.

High temperature fuel cells (150^{o}C) offer the following advantages: They are suitable for generating high-grade heat suitable for useful cogeneration. The high-grade heat generated is near 322^{o}C. The high grade heat utilized is 61.3%. The high temperature fuel cells are capable of producing steam at 280^{o}C that can be utilized for industrial applications. High temperature fuel cells offer higher resistance to carbon monoxide, eliminating the PROX, thereby reducing the cost and weight of the fuel processor and the entire fuel cell system. Thus more hydrogen will be consumed in the fuel cell stack generating more power. Extra humidification is not an issue as product water is not formed in the fuel cell stack.

Other observations include: Increasing the supply water temperature reduces the efficiency of the radiator. In low temperature fuel cells, the fuel cell stack heat load (produced due to the increased condensation of water) of 235 kW is greater than the radiator heat load of 184 kW (radiator size), decreasing the low grade heat utilization. The rest of the heat is discarded as waste heat. For high temperature fuel cells, the stack heat load and the radiator heat load is 178 kW making 100% low-grade heat utilization. Increasing the supply water temperature beyond the dew point temperature decreases the thermal efficiency, with a corresponding decrease in high grade heat utilization. Increasing the steam pressure decreases the thermal efficiency. The partial pressure of water vapor increases, leading to the condensation of water in the fuel cell stack. This induces an additional load on the radiator, decreasing its efficiency. As a result, the low grade heat utilization decreases. With an increase in the steam pressure, the water condenses at high temperature in the condenser, increasing its load and decreasing its efficiency. The condenser heat load is 112 kW in a typical low temperature fuel cell and 85 kW of a typical high temperature fuel cell.

9.8 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.

9.9 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 fossils 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 fossils 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.

9.10 Recommendations and Future Work

We simulated a 250 kW polymer electrolyte fuel cell system capable of producing combined heat and power. In this simulation we did not look into the economics of developing such a system, although we tried to reduce the cost of the fuel cell system by eliminating the PROX reactor and extra humidification. Additionally, we have reduced some of the emissions generated, such as sulfur, carbon monoxide, and methane. There is a need to control the CO_2 generated. In our simulations, the carbon dioxide generated was about 6%. That could be reduced further in the future. Practical applications require attention, as this was only a hypothetical analysis.

10. SUMMARY AND CONCLUSIONS

Polymer electrolyte membrane fuel cells operate at relatively low temperatures, around 70°C. 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 the system cost. The platinum catalyst is also 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. This also adds cost. The PEM system allows compact designs and achieves a high energy-to-weight ratio. Another advantage is a quick start-up when hydrogen is applied. The stack runs at a relatively low temperature of about 70°C. The efficiency is approximately 50%. (In comparison, the internal compaction motor has an efficiency of about 15%). The limitations of the PEM system are high manufacturing costs and complex water management issues. The stack contains hydrogen, oxygen, and water. If dry, the input resistance is high, and water must be added to get the system going. Too much water causes flooding. The PEM fuel cell has a limited temperature range. Freezing water can damage the stack. Heating elements are needed to keep the stack within an acceptable temperature range. The warm up is slow and the performance is poor when cold. Heat is also a concern if the temperature rises too high.

The PEM fuel cell requires heavy accessories. Operating compressors, pumps, and other apparatus consume around 30% of the energy generated. The PEM stack has an estimated service life of around 4000 hours if operated in a vehicle. The relatively short life span is caused by intermittent operation. Start and stop conditions induce drying and wetting, which contributes to membrane stress. If run continuously, the stationary stack is good for about 40,000 hr. The replacement of the stack is a major expense. The PEM fuel cell requires hydrogen-rich reformate. There is little tolerance for contaminates, such as sulfur compounds or carbon monoxide. Carbon monoxide can poison the system. A decomposition of the membrane takes place if different grade fuels are used. Testing and repairing a stack are difficult. The accumulation of product water within the oxidant stream effectively limits operating temperatures to below 212ºF (100ºC). At this temperature, the water boils and the resulting steam severely reduces the partial pressure of the oxygen. This, in turn, drastically reduces cell performance due to oxygen starvation. This can damage the fuel cells and reduce their life. To some extent, higher temperatures can be achieved by operating at higher pressures since these increases the water boiling point accordingly. However, this effect is slight at the practical PEM fuel cell operating pressures. The net effect is that fuel cell voltage increases with temperature until the temperature approaches the boiling point of water at which point the voltage begins to decline.

Insufficient humidification water dehydrates the membrane and can lead to cracks or holes in the membrane. This results in a chemical short circuit, local gas mixing, hot spots, and the possibility of fire. Conversely, excess humidification water leads to condensation and flooding within the flow field plates. This, in turn, can result in a phenomenon known as cell reversal where the affected cells produce a zero or negative voltage. If a large enough negative voltage occurs, the affected fuel cells start to act like an electrolyzer. This produces a lot of heat and can potentially destroy the cell. Cell monitoring systems are typically installed to detect cell reversal before cell damage occurs. Humidity is typically measured as relative humidity; relative since it depends on the pressure and temperature of the gas. When a gas has absorbed as much water as it is physically able to at a given pressure and temperature, it is said to be saturated and has a relatively humidity of 100%. If that saturated gas then becomes hotter (without the addition of more water), the relative humidity drops. If the gas cools, some of the water condenses and the gas remains saturated at the new temperature. Fuel cells are typically operated at or near saturated conditions at the fuel cell operating temperature (as set by the stack coolant temperature). This provides the maximum amount of water possible while preventing flooding. A further consideration is that the humidifier water must remain nonconductive. Failure to do so causes short circuits and corrosion currents within the fuel cell stack. Water becomes conductive as it absorbs ions from its surroundings. To eliminate these ions, the water must continuously flow through a deionizing filter.

High-temperature solid-polymer electrolyte membranes capable of operating at 150-200°C are at an early stage of development [Au *et al.*, 2003]. These are being encouraged 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). In addition, the reduction in overpotentials at higher temperatures can potentially lead to improvement in current density and a lighter, 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. 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 elimination of the PROX reactor reduces the cost and the weight of the fuel processor and the entire fuel cell system.

Some of the other conclusions include: Fuel processor efficiencies are slightly affected by reducing the electrochemical fuel utilization below 85% in the fuel cell stack. However the total system efficiency is reduced significantly by lowering the fuel utilization. The total water to carbon that can be used in the fuel processing subsystem is strongly affected by the autothermal reforming temperature. Increasing the reforming temperature increases the amount of water that can be used in the fuel processor. Use of thermal energy from the fuel cell stack exhaust burner in the fuel processing subsystem permits the use of larger amounts of water in fuel processing. This is due to the increase of the total thermal energy available to heat the process water. The analyses indicate the potential for increased fuel processor and fuel cell system efficiencies if more active catalysts can be developed for lower temperature operation. With such catalysts it might be possible to suppress or reduce methane formation. This could lead to a higher content of hydrogen and a better fuel processor performance. The results for the overall system performance are also subject to several assumptions such as the average cell operating voltage in the fuel cell stack, fuel and oxidant utilizations, and the efficiencies of the compressors and expander and of the various pumps, blowers and fans, radiator and condenser that are used in the balance of plant in the fuel cell system. Changes in those assumptions would affect the actual system efficiencies attained.

11. FUEL CELL DEMONSTRATION PROJECT

A 200 kW phosphoric acid fuel cell (PC25) power plant operating at 200°C was installed in the main street facility in Los Angeles in February 2002 by ONSI Corporation. The fuel cell helps to supply an additional load of 200 kW of power in to Los Angeles department of water and power. A more significant reason for the installation of this fuel cell was to continue the demonstration of fuel cell applications and to verify reliability under real world operating conditions. The fuel cell demonstration project can help advance fuel cell technology by using independence performance teat data over an extended period of time. The cost analysis showed that the installation of the PC25 is not economically viable because of the initial high cost of the fuel cell. Forecasters predict that with the continuous growth in fuel cell application in the commercial area, the cost would come down from approximately \$4000/kW to less then \$1000/kW [Wilkenson and Thompsett, 1997]. For mass production of fuel cells to become a reality, fuel cells cost, reliability, and efficiency (infrastructure) must be improved. However, this fuel cell has minimal NO_x and SO_x emissions, which make the fuel cell an environmentally friendly form of electric power generation. The achievement of this project contributed to the evaluation of the fuel cell technology, providing technical and commercial data that will be valuable for further fuel cell technology development. The phosphoric acid fuel cell was selected because it is believed to be the most commercialized fuel cell technology in terms of technology and maturity activities. It has an advantage in that it can operate at a high temperature of around 200°C which makes it most suitable for CHP applications. The installation of PC25 reduced the amount of such harmful air pollutants as NO_x and SO_x. In Table 8, it can be seen that the amount of NO_x produced is negligible, along with the other harmful emissions, thus confirming the use of fuel cell technology as a virtually pollution-free source of energy.

Table.8. Emissions resulting from the PC25 fuel cell [Wilkenson and Thompsett, 1997].

Emissions	Amount
NO_x	1ppm
SO_x	Negligible
NO_2	Negligible
SO_2	2ppmv
CO	5ppmv
Particulates	Negligible
Smoke	None
Hydrocarbons	6ppm

Operating data shows that the power plant is reliable and its electrical performance complies with premium power supply requirements. In terms of efficiency, the power plant performs better than other conventional combustion technologies. During 2002, the PC25C supplied a total of 1,354 MWh into the Los Angeles Department of Water and Power. It also provided valuable technical and operational data, helping the Los Angeles Department of

Water and Power with future fuel cell installations. Fuel cells are highly efficient and environmentally friendly but, due to the high initial costs, it is difficult to afford them. Fuel cell power plants are becoming attractive in combined systems where its heat output can be utilized. By using fuel cell power plants to generate power, the Los Angeles Department of Water and Power is able to reduce the amount of such harmful air pollutants such as NO_x and SO_x. Los Angeles Department of Water and Power is also able to promote fuel cells and eventually reduce the equipment costs of fuel cells. This will allow more companies to install fuel cells and further promote the maturing concept of distributed generation.

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13. THESES, PUBLICATIONS, CONFERENCE PROCEEDINGS AND TECHNICAL PRESENTATIONS

Theses:

Upadhyaya, Jaimini, 2004 – "Hydrogen-Based Fuel Cell Technology for Combined Heat and Power Generation", M.S. Thesis completed Fall semester, University of Alabama at Birmingham, Birmingham, Alabama, 2004, (*graduated*).

Publications:

None at this time.

Conference Proceedings:

Upadhyaya, J., R.W. Peters, F.H. Fouad, T. Das, J.F. Miller, and W.F. Podolski, 2004. "Environmental Impact of Fuel Cell Technology for Electric Power Generation: An Overview and Case Studies", Paper included in ***Proceedings of the 2004 Annual American Institute of Chemical Engineers (AIChE) Meeting***, Topic: T3 on Fuel Cells, 35 pages, Austin, Texas, (November 7–12).

Technical Presentations:

Upadhyaya, J., R.W. Peters, F.H. Fouad, T. Das, J.F. Miller, and W.F. Podolski, 2004. "Environmental Impact of Fuel Cell Technology for Electric Power Generation: An Overview and Case Studies", Paper presented in the session on "Environmental Impact of Fuel Cell Technology" at the 2004 Annual American Institute of Chemical Engineers (AIChE) Meeting, Austin, Texas, November 7–12, 2004.

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Poster Paper Presentations:

University of Alabama at Birmingham (F.H. Fouad, R.W. Peters, A. Sullivan, V.P. Sisiopiku, and S. Jones) and Argonne National Laboratory (D. Hillebrand, M. Mintz, H. Ng, R. Ahluwalia, and A. Rousseau), 2005. "Global Assessment of Hydrogen-Based Technologies (TVP-13)", Poster paper presented at the DOE Hydrogen Program Review Meeting, Arlington, Virginia, (May 23-26).

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University of Alabama at Birmingham (F.H. Fouad, R.W. Peters, A. Sullivan, S. Jones, and V. Sisiopiku, 2004. "Global Assessment of Hydrogen-Based Technologies", Poster paper presented at the Hydrogen, Fuel Cells, and Infrastructure Technologies Program of the U.S. Department of Energy, Philadelphia, PA, (May 24-27).

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