

Water balance in a polymer electrolyte fuel cell system[☆]

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Abstract

Polymer electrolyte fuel cell (PEFC) systems operating on carbonaceous fuels require water for fuel processing. Such systems can find wider applications if they do not require a supply of water in addition to the supply of fuel, that is, if they can be self-sustaining based on the water produced at the fuel cell stack. This paper considers a generic PEFC system and identifies the parameters that affect, and the extent of their contribution to, the net water balance in the system. These parameters include the steam-to-carbon and the oxygen-to-carbon ratios in the fuel processor, the electrochemical fuel and oxygen utilizations in the fuel cell stack, the ambient pressure and temperature, and the composition of the fuel used. The analysis shows that the amount of water lost from the system as water vapor in the exhaust is very sensitive to the system pressure and ambient temperature, while the amount of water produced in the system is a function of the composition of the fuel. Fuels with a high H/C (hydrogen to carbon atomic ratio) allow the system to be operated as a net water producer under a wider range of operating conditions.

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1. Introduction

Fuel cells generate electricity through the electrochemical oxidation of hydrogen to produce water. Although hydrogen is the preferred fuel for fuel cells, it is often desirable to operate a fuel cell system with a conventional or alternative fuel, such as natural gas or propane for stationary applications, or gasoline or an alcohol for automotive applications. Of course, other fuels may also be available in specific situations, such as naphtha or other products in the hydrocarbon or chemical processing industry. If such a fuel is used, the fuel cell power plant must include a fuel processor. 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 [1]. Direct hydrogen-fueled fuel cell systems are not considered in this paper, however.

The need for an external water supply is determined by three quantities: 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. Indeed, the suitability or commercial viability of fuel cell power may become questionable for certain applications (e.g. transportation, portable power) if the systems require a supply of consumable water.

This paper examines a generic polymer electrolyte fuel cell (PEFC) system and discusses the design and operating parameters that affect the water balance in such a system. Options that can make the system self-sufficient in water (or make it operate as a net water producer) are identified and discussed. The analysis examines the following parameters:

- Steam-to-carbon ratio in the fuel processor.
- Oxygen-to-fuel ratio in the fuel processor.
- Fuel and oxidant utilizations in the fuel cell stack.

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- Exhaust gas temperature and pressure.
- Fuel composition.

2. The fuel cell system

Fig. 1 shows a highly simplified schematic of a generic PEFC system. The shaded box represents the system boundary and shows some of the key components in the device. Streams flowing into and out of the system boundary include a generic carbonaceous fuel ($C_nH_mO_p$) feed, air feeds to the fuel processor (FP) and the fuel cell cathode, and a gaseous exhaust. The two dotted lines at the lower left of the box are for the drainage of excess water in the case of a net-water-producer system, or for the supply of make-up water in the case of a net-water-consumer system.

In the fuel reforming process, the fuel, air, and water are converted into a mixture of hydrogen, carbon dioxide, and nitrogen according to the idealized reaction

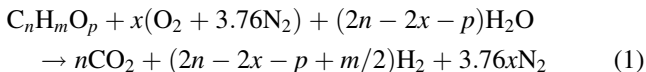


Fig. 1 shows that all the gases from the fuel processor enter as a single stream into the fuel cell. This implies an auto-thermal reforming process. In fuel processors based on steam reforming, the reformat and combustion streams would be kept separate. The combustion products (generating the heat for the steam reforming reaction) would then be fed either into the burner or into the radiator/condenser, located after the fuel cell stack. This alternative arrangement would change some of the mass flow rates in the fuel cell and burner but would not affect the net water excess or deficit,

since that parameter is calculated from the outlet of the radiator/condenser.

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, a 40% oxygen utilization corresponds to an air stoichiometry of 2.5 (i.e. 1.0/0.4). Depending on the type of fuel cell, the cell reaction produces water either at the cathode (polymer electrolyte and phosphoric acid fuel cells) or at the anode (solid oxide and molten carbonate fuel cells).

The hydrogen present in the anode effluent is burned in the spent gas burner, typically with the cathode effluent supplying the needed oxygen. The heat generated at the burner is reused within the system, for example, to preheat the incoming feeds or to generate steam used in the fuel processor. The burner product gas is cooled (by heat exchange with ambient air) in the radiator/condenser, where part of its water content is condensed out and recovered for reuse in the process.

Water may also be collected at other points in the system where the moisture content of the process gas exceeds the saturation vapor pressure of water and a heat sink is available to absorb its latent heat of condensation. This can occur, for example, when the reformat gas is cooled, typically to 60–80 °C, before being fed to the anode in a PEFC. On the other hand, water may be used to humidify the air fed to the cathode for optimum operation of the PEFC.

If the total amount of water recovered at the condenser and at other locations is greater than the total amount of

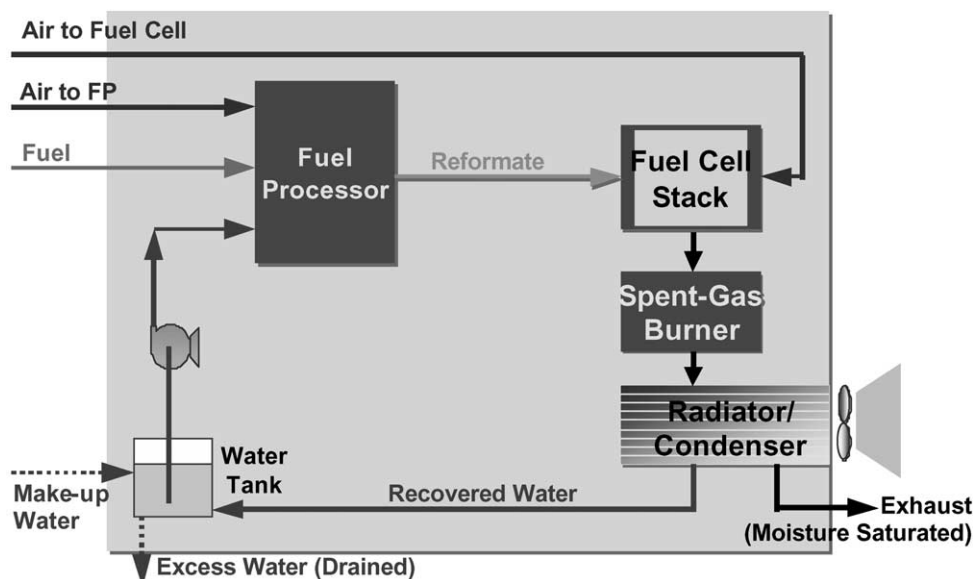


Fig. 1. Simplified schematic of a fuel cell power system showing the various streams entering and leaving the system.

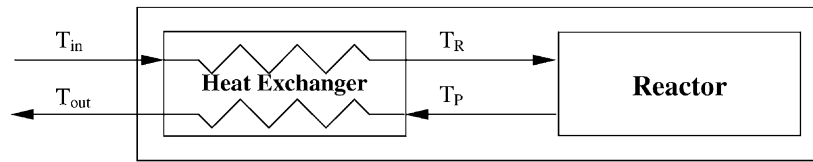


Fig. 2. Fuel processing subsystem showing idealized heat exchange between reactants and products to achieve $T_{\text{out}} = T_{\text{in}}$.

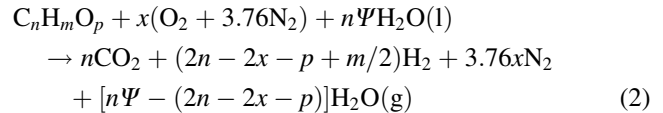
water needed for fuel processing and humidification, the system is a net water producer. In such a case, the excess water can be drained from the water tank, as represented by the dotted stream leaving the fuel cell system at the lower left of Fig. 1. Alternatively, the excess water can be discharged from the system by allowing the exhaust gas to leave the condenser at a higher temperature, thereby carrying out more water as vapor. Conversely, if the amount of water recovered is less than that used in the system, the system is a net water consumer. For sustained operation in this mode, make-up water would be needed. This mode would require a continuously available water source or periodic refilling of the water tank. For many applications, the option of providing make-up water may not be available or acceptable.

3. The fuel cell system model

The fuel cell system shown schematically in Fig. 1 may be configured in a variety of ways. For the present analysis, however, we consider a system operating on a generic carbonaceous fuel, $C_nH_mO_p$, which is converted to hydrogen and carbon dioxide (in a mixture with nitrogen and traces of other species) by an overall reforming process represented by Eq. (1). A major fraction of the hydrogen in the reformat is then consumed in the fuel cell to produce electricity. Further, the fuel cell stack operates with no prior humidification of the air fed to the cathode. Thus, the overall fuel cell system takes in fuel and air (and possibly water), producing electric power and an exhaust gas containing carbon dioxide, water vapor, and nitrogen.

The amount of water needed to convert the input fuel to hydrogen and CO_2 by the overall reaction given by Eq. (1) is determined by the fuel composition (i.e. the values of n and p) and by the oxygen-to-fuel molar ratio ($x = O_2:C_nH_mO_p$). Thus, $(2n - 2x - p)$ is the minimum water-to-fuel molar ratio ($H_2O:C_nH_mO_p$) that must be provided in the feed to the fuel processor to convert all of the carbon in the input fuel to CO_2 . In terms of the steam-to-carbon ratio (Ψ), the minimum ratio required, Ψ_{min} , is $(2n - 2x - p)/n$. In practice, an excess of water is used in the fuel processor (i.e. Ψ is usually greater than the minimum required). For the base case analysis discussed below, a Ψ of 1.5 was used. When the fuel is methane, this corresponds to 44%¹ more water than the minimum required.

In the case where an excess of water is used, i.e. where $\Psi > (2n - 2x - p)/n$, the overall fuel processing reaction becomes



The oxygen-to-fuel ratio (x) for this reaction is calculated such that the reaction is thermoneutral, i.e. the heat of reaction ($\Delta H_{r,298}$) for Eq. (2) is equal to zero [2]. In such a case, there is no change in temperature between the incoming reactants and the outgoing products of the fuel processor, assuming that there is no heat loss from the reactor. Although the above assumption restricts the products and reactants to be at the same temperature (i.e. $T_{\text{out}} = T_{\text{in}}$), note that the actual temperature in the reformer is not being specified. An integrated fuel processor subsystem can contain a heat exchanger, as shown in Fig. 2, that transfers heat from the product to the reactant stream. In this design, it is theoretically possible for the reactor to operate at any temperature needed for the desired conversion and kinetics, while maintaining $T_{\text{out}} = T_{\text{in}}$. Of course, for a practical device in which the reactor operates at an elevated temperature, T_{out} must exceed T_{in} by the amount of the approach temperature (the minimum temperature difference, ΔT , between the product gas and the ambient air) at the heat exchanger.

The hydrogen-containing reformat 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

¹ This number is obtained after setting the air-to-fuel ratio such that the heat of the idealized reforming reaction, Eq. (1), is zero.

Table 1
Water balance in a fuel cell system operating on methane

Input/assumptions		Calculated parameters	
Fuel: methane (CH ₄); basis: 1 gmol/min of fuel			
Molecular weight	16	O ₂ /fuel molar ratio into FP, x	0.478
$\Delta H_{f,298}$ (kcal/gmol)	-17.9	Air feed into FP (gmol/min)	2.270
$\Delta H_{c,298}$ (kcal/gmol)	192	O _{air} /C ratio	0.956
System pressure (atm)	1.0	Water feed into FP (gmol/min)	1.500
H ₂ O/C ratio into FP, Ψ	1.5	Idealized FP products	
Heat of reaction, $\Delta H_{r,298}$ (kcal/gmol)	0	H ₂ (gmol/min)	3.05
Fuel (H ₂) utilization (%)	80	H ₂ conc. in reformat (%-dry)	48.4
O ₂ utilization (%)	40	LHV of H ₂ (kW(t))	12.3
Ambient temperature, T_{air}	35 °C, 95 °F	Fuel processor efficiency (%)	91.8
Condenser approach temperature, $T_{approach}$	11 °C, 20 °F	H ₂ O in reformat (gmol/min)	0.46
		H ₂ O conc. in Reformat (%-wet)	7.2
		Air stoichiometry in fuel cell	2.50
		Air into cathode (gmol/min)	14.5
		Burner product (gmol/min)	19.3
		H ₂ O in burner product (gmol/min)	3.5
		H ₂ O conc. in burner product (%-wet)	18.2
		Exhaust gas temperature, $T_{exhaust} = T_{air} + T_{approach}$	46 °C, 115 °F
		Saturated moisture content in exhaust gas (%-wet)	10.0
		Recoverable water (gmol/min)	1.75
		Net water produced (gmol/min)	+0.25
		Net water produced (ml/min)	+4.6

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.

Table 1 shows the parameters and a summary of results for a base case water balance calculation for a simple hydrocarbon fuel, methane. The left side of the table contains the input parameters and assumptions, while the right side displays the calculated results. Additional computational details and results for a variety of fuels are given in Appendix A. The calculations are based on a methane feed rate of 1 gmol/min. For these calculations, the simplified fuel cell system is assumed to operate at a pressure of 1 atm absolute (neglecting pressure drops within the system) and a steam-to-carbon molar ratio of 1.5 in a thermoneutral fuel processor. For the specified Ψ of 1.5, thermoneutrality is achieved at an oxygen-to-fuel ratio, x , of 0.478, which corresponds to an air feed rate of 2.27 gmol/min. The product gas from the fuel processor, as defined by Eq. (2), contains 3.05 gmol/min of hydrogen (48.4% on a dry basis), with a lower heating value (LHV) of 12.3 kW(t). Thus, the fuel processor efficiency is 91.8%, where efficiency is defined as the LHV of hydrogen produced relative to the LHV of the fuel fed to the fuel processor. The fuel processor product gas also contains 0.46 gmol/min of water vapor, or 7.2% of this reformat stream. Assuming that the fuel cell operates at 60 °C, for a water vapor pressure of 0.193 atm, no water is condensed out of the reformat as it is cooled to the fuel cell operating temperature.

With the assumed fuel and oxidant utilizations of 80 and 40%, respectively, the air feed rate to the fuel cell cathode is

14.5 gmol/min. By the time the reformat gas passes through the fuel cell and the spent-gas burner, all of the hydrogen in it, 3.05 gmol/min, is converted to water. Thus, the total water content in the burner product gas is 3.5 gmol/min (which equals the 2 gmol/min formed from the oxidation of the methane feed and the 1.5 gmol/min of water fed to the fuel processor), corresponding to a water concentration of 18.2% of the burner product.

With an ambient temperature of 35 °C (95 °F) and a condenser designed for an approach temperature of 11 °C (20 °F), the exhaust gas can leave the system at 46 °C (115 °F). The saturation water vapor concentration at this temperature and 1 atm pressure is 10%. Therefore, cooling the burner exhaust to 46 °C (115 °F) would condense out 1.75 gmol/min of water. Comparing this amount of recovered water with the amount of water fed to the fuel processor, it is seen that the system recovers 0.25 gmol/min of water more than it consumes. Thus, this system operates as a net water producer.

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. However, the approach temperature used in this analysis, 11 °C (20 °F), is already quite small. With smaller approach temperatures, the temperature-difference driving force also gets smaller, necessitating a larger, heavier, and more expensive condenser.

Table 2
Effect of varying the steam-to-carbon ratio Ψ on fuel processor operation and system water balance

Basis: 1 gmol/min of methane	Base case			
H ₂ O/C ratio into FP, Ψ	1.2 (–20%)	1.5	1.8 (+20%)	3.0 (+100%)
Water feed into FP (gmol/min)	1.2	1.5	1.8	3.0
O ₂ /fuel molar ratio into FP, x	0.450	0.478	0.523	0.614
Air feed into FP (gmol/min)	2.14	2.27	2.40	2.92
Idealized FP products				
H ₂ (gmol/min)	3.10	3.05	2.99	2.77
H ₂ conc. in reformat (–dry)	52.6	48.4	44.6	33.4
LHV of H ₂ (kW(t))	12.5	12.3	12.1	11.2
Fuel processor efficiency (%)	93.4	91.8	90.1	83.5
H ₂ O in reformat (gmol/min)	0.10	0.46	0.81	2.23
H ₂ O conc. in reformat (–wet)	1.71	7.2	12.1	26.8
Air into cathode (gmol/min)	14.8	14.5	14.2	13.2
H ₂ O in burner product (gmol/min)	3.2	3.5	3.8	5.0
H ₂ O conc. in burner product (–wet)	16.8	18.2	19.6	24.9
Exhaust gas temperature, $T_{\text{exhaust}} = T_{\text{air}} + T_{\text{approach}}$	46 °C, 115 °F	46 °C, 115 °F	46 °C, 115 °F	46 °C, 115 °F
Saturated moisture content in exhaust gas (–wet)	10.0	10.0	10.0	10.0
Recoverable water (gmol/min)	1.43	1.75	2.06	3.32
Net water produced (gmol/min)	+0.23	+0.25	+0.26	+0.32
Net water produced (ml/min)	+4.2	+4.6	+4.8	+5.8

4. Effect of steam-to-carbon ratio

Hydrocarbons heavier than methane have a tendency to form coke during processing at temperatures where thermolysis reactions can occur. This is a highly undesirable by-product, since it can foul and shut down the reactors. To suppress coke formation, reformers are typically operated at relatively high steam-to-carbon ratios. Table 2 shows the calculated effect of varying the steam-to-carbon ratio, while keeping all other assumptions and input parameters the same as in Table 1.

Table 2 shows the effect of changing Ψ by $\pm 20\%$ from the base case value of 1.5 (i.e. to 1.2 and to 1.8); the last column shows the effect of using a much higher Ψ of 3.0, as is done in some fuel processors. Maintaining thermoneutrality at these different values of Ψ requires adjusting the oxygen-to-fuel ratio, x , as shown in Table 2. The increasing amount of oxygen fed to the fuel processor is needed to generate the heat to vaporize the increasing amount of water in the feed. This successively increasing x leads to lower hydrogen and higher water contents in the product gas from the fuel processor, as shown in Table 2. As the table also shows, the lower hydrogen yields lead to lower heating values of the reformat gas and lower fuel processor efficiencies.

Another effect of the decreasing hydrogen yields with increasing Ψ and x is that the air feed rate to the cathode is decreased, since the electrochemical fuel and oxygen utilizations are kept constant. This decrease is greater than the increase in the air feed to the fuel processor, so that the total air fed into the system (the sum of the air feeds to the fuel processor and the cathode) is actually reduced as Ψ increases. At the same time, the water contained in the burner product is also higher, because more water is fed to the fuel processor. This increased amount of water in the

decreased total gas flow leads to a higher concentration of water in the burner product gas.

Fig. 3 shows the effect of varying Ψ on the net water produced and the total system efficiency. The sensitivities of both parameters, especially the system efficiency, are significantly damped, i.e. only 9% change in efficiency resulting from a 100% change in Ψ . Their responses are also in opposite directions, indicating that net water production is inversely correlated with efficiency.

With the exhaust gas temperature held constant at 46 °C, the water vapor concentration in it remains constant at 10%. Thus, with increasing values of Ψ , increasing amounts of water can be recovered at the condenser. Fig. 4 shows that the amount of this recovered water is greater than the increased amount of water fed to the fuel processor, and the difference (i.e. surplus) increases as Ψ is increased. The difference between the extra² water recovered and the diagonal line can be traced to additional water that would be produced from the extra fuel consumed to compensate for efficiency losses.

5. Effect of the oxygen-to-fuel ratio in the fuel processor

The base case required an oxygen-to-fuel molar ratio $x = 0.478$, such that the fuel processing reaction is thermoneutral, i.e. the heat of reaction given by Eq. (2) is zero. For a given value Ψ , the thermoneutral value of x yields the maximum efficiency of the fuel processor [2]. In practice, however, the reforming reaction is conducted so as to be slightly exothermic to compensate for the heat loss from the

² Additional water fed or recovered with respect to the water fed or recovered at the base condition.

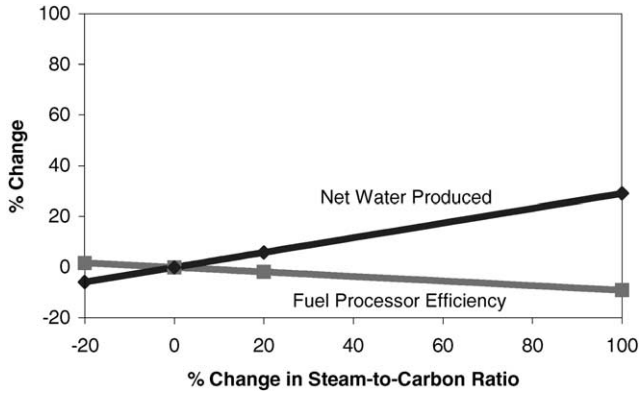


Fig. 3. Parametric effect of steam-to-carbon ratio on the net water production and the fuel processor efficiency.

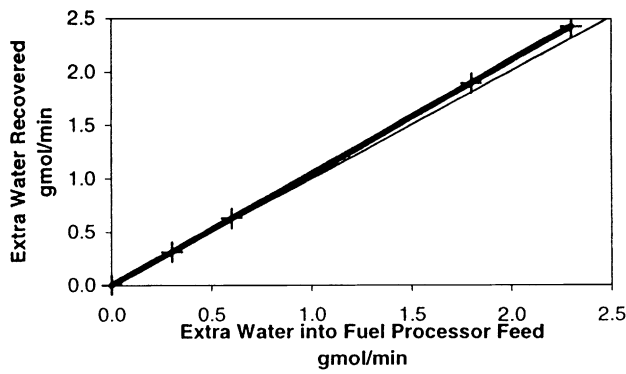


Fig. 4. Sensitivity of water recovery as a function of the extra water added at the fuel processor. “Extra” refers to the additional water with respect to the base case.

fuel processor to the environment and for the reformat exit temperature being higher than the reactant inlet temperatures. The extra thermal energy needed is obtained by increasing x , which also affects various other system parameters. The third and fourth columns in Table 3 show the

effect of increasing the oxygen-to-fuel ratio by 10 and 20% over the base case. The major effects of the higher oxygen-to-fuel ratio are lower hydrogen yields, lower fuel processor efficiencies, and higher water content in the reformat fed to the fuel cell stack.

With less hydrogen going to the fuel cell stack, the cathode air feed requirement is reduced (since oxygen utilization is held constant). The total water content in the burner exhaust remains the same, however, since the total quantity of hydrogen introduced into the fuel processor (as methane and water) stays the same. The concentration of water in the burner product increases, because the total gas flow rate is lower as a result of the lower total air fed into the system (air fed to the fuel processor plus the air fed to the fuel cell cathode). Since the exit temperature of the exhaust gas is held constant at 46 °C, its moisture content is maintained at 10%. Thus, more water is recovered at the condenser as x is increased. It should be noted, however, that as x increases, the system efficiency (the product of the fuel processor efficiency, fuel utilization, and stack efficiency) decreases.

6. Effect of fuel and oxygen utilizations in the fuel cell stack

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. The effect of varying the fuel utilization on the water balance can be seen in Table 4, where the outcomes from using three different values of fuel utilization (70, 80, and 90%) may be compared.

The air feed rate to the cathode (operating at a constant 40% oxygen utilization) increases with increasing fuel utilization. The total water contained in the burner product

Table 3
Effect of the oxygen-to-fuel ratio x on fuel processing and water balance

Basis: 1 gmol/min of methane	Base case		
O ₂ /fuel molar ratio into FP, x	0.478	0.526 (+10%)	0.574 (+20%)
Air feed into FP (gmol/min)	2.27	2.50	2.73
Heat of reaction, $\Delta H_{r,298}$ (kcal/gmol)	0	-5.6	-11.1
Idealized FP products			
H ₂ (gmol/min)	3.05	2.95	2.85
H ₂ conc. in reformat (%-dry)	48.4	45.5	42.9
LHV of H ₂ (kW(t))	12.3	11.9	11.5
Fuel processor efficiency (%)	91.8	88.9	86.0
H ₂ O in reformat (gmol/min)	0.46	0.55	0.65
H ₂ O conc. in reformat (%-wet)	7.2	8.5	9.7
Air into cathode (gmol/min)	14.5	14.0	13.6
H ₂ O in burner product (gmol/min)	3.5	3.5	3.5
H ₂ O conc. in burner product (%-wet)	18.2	18.4	18.6
Recoverable water (gmol/min)	1.75	1.77	1.80
Net water produced (gmol/min)	+0.25	+0.27	+0.30
Net water produced (ml/min)	+4.6	+4.95	+5.4

Table 4
Effect of fuel utilization in the fuel cell stack on water balance

Basis: 1 gmol/min of methane	Base case		
H ₂ into fuel cell stack (gmol/min)	3.05	3.05	3.05
Fuel (H ₂) used in FC (%)	70	80	90
Air into cathode (gmol/min)	12.7	14.5	16.3
Burner product (gmol/min)	17.5	19.3	21.1
H ₂ O in burner product (gmol/min)	3.5	3.5	3.5
H ₂ O conc. in burner product (%-wet)	20.1	18.2	16.6
Recoverable water (gmol/min)	1.95	1.75	1.55
Net water produced (gmol/min)	+0.45	+0.25	+0.05
Net water produced (ml/min)	+8.1	+4.6	+0.9

remains unchanged³ at 3.5 gmol/min. However, the larger air feed rate to the cathode lowers the concentration of water vapor in the exhaust gas, and consequently the amount of water recoverable at the condenser also decreases. Thus, the overall effect of increasing the fuel utilization from 70 to 90% is to decrease the net amount of water recovered from 0.45 to 0.05 gmol/min (8.1–0.9 ml/min).

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, as discussed earlier.

The effect of varying the oxygen utilization in the fuel cell stack is shown in Table 5. With the oxygen utilization reduced from 40 to 30%, the cathode air feed rate increases from 14.5 to 19.3 gmol/min, and the burner product gas flow rate increases from 19.3 to 24.1 gmol/min. With the same amount of water contained in the higher burner product gas flow, the corresponding moisture concentration is lowered from 18.2 to 14.5%. At the specified exit gas temperature (46 °C), the reduction in water recovery is sufficient to make the fuel cell system a net water consumer, as shown by the negative numbers in the last two rows of Table 5. The opposite effect is seen if the oxygen utilization is increased from 40 to 50%, i.e. the system becomes even more of a net water producer.

Thus, 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.

³ All the H atoms entering the system are contained in the burner product in the form of H₂O. Since the rates of feeds containing H (CH₄ and H₂O) are unchanged, the amount of H₂O in the burner product also remains unchanged.

Table 5
Effect of oxygen utilization in the fuel cell stack on water balance

Basis: 1 gmol/min of methane	Base case		
H ₂ into fuel cell stack (gmol/min)	3.05	3.05	3.05
Oxygen used in cathode (%)	30	40	50
Air into cathode (gmol/min)	19.3	14.5	11.6
Burner product (gmol/min)	24.1	19.3	16.4
H ₂ O in burner product (gmol/min)	3.5	3.5	3.5
H ₂ O conc. in burner product (%-wet)	14.5	18.2	21.4
Recoverable water (gmol/min)	1.21	1.75	2.07
Net water produced (gmol/min)	−0.29	+0.25	+0.57
Net water produced (ml/min)	−5.2	+4.6	+10.3

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.

7. Effect of exhaust gas temperature and pressure

Water leaves the system with the exhaust gas.⁴ The exhaust gas is saturated with water vapor, and its water content is determined by the temperature and pressure of the exiting gas. The temperature is determined directly by the ambient temperature and the approach temperature for the condenser, since $T_{\text{exhaust}} = T_{\text{ambient}} + T_{\text{approach}}$. Fig. 5 shows the effect of the gas exit temperature on the water balance in the fuel cell system. The net water produced falls off rapidly with increasing exhaust gas temperature, reflecting the dependence of the saturation partial pressure of water on temperature. The fuel cell system defined in Table 1 becomes a net water consumer when the exhaust temperature exceeds 49 °C (120 °F). This means that with an approach temperature of 11 °C (20 °F), the system will remain self-sufficient in water only as long as the ambient temperature remains below 38 °C (100 °F).

Although the saturation partial pressure of water is a function of temperature only, the mole fraction of water at which the exhaust gas is saturated is determined by

$$y_{\text{H}_2\text{O}} = \frac{p_{\text{sat}}(T)}{p} \quad (3)$$

where $y_{\text{H}_2\text{O}}$ is the mole fraction of saturation water vapor in the exhaust gas, $p_{\text{sat}}(T)$ the saturation partial pressure of water

⁴ This discussion refers to the water exiting the system continuously, as opposed to water that may be drained from the water tank to prevent overflowing of water tank.

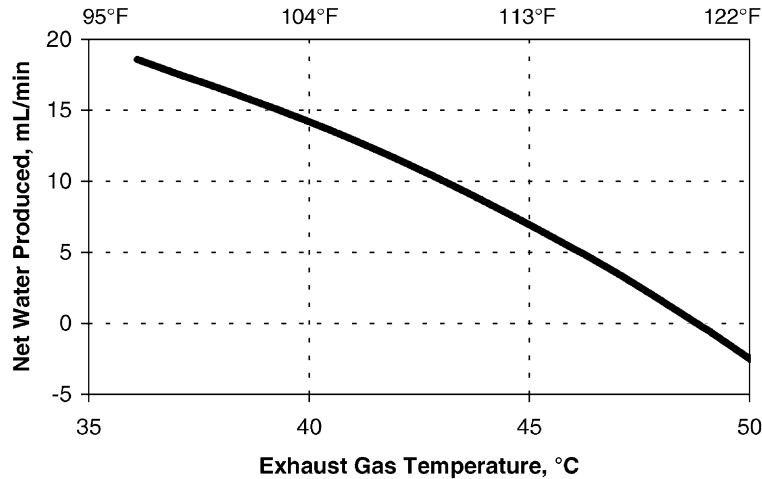


Fig. 5. Effect of exhaust gas exit temperature on the water balance in the fuel cell system (all other parameters as given in Table 1).

(a function of temperature), and P the total pressure. As is evident from Eq. (3), for a given exhaust gas exit temperature and its corresponding saturation partial pressure, the mole fraction of water in the exhaust and, therefore, the amount of water leaving with the exhaust, will be lower if the gas pressure (P) in the condenser is higher. Consequently, more water can be condensed out and recovered at higher pressures.

For nonpressurized systems, the condenser gas pressure is determined by the ambient pressure. This factor can have a serious impact on the water balance at high-altitude locations, such as Los Alamos, New Mexico, where the ambient pressure averages 580 mmHg (0.76 atm). The lower ambient pressure contributes to greater water loss with the exhaust gas and, therefore, less recoverable water. Indeed, as shown in Table 6 and Fig. 6, the base case fuel cell system discussed above would operate as a net water consumer in Los Alamos, but as a net water producer at sea level. Pressurized systems can operate as net water producers, as shown in Table 6, if

Table 6

Effect of condenser pressure on water balance

Basis: 1 gmol/min of methane	Los Alamos	Base case		
Ambient/system pressure (atm)	0.76	1.0	1.5	3.0
H ₂ O in burner product (gmol/min)	3.5	3.5	3.5	3.5
H ₂ O conc. in burner product (%-wet)	18.2	18.2	18.2	18.2
Recoverable water (gmol/min)	1.12	1.75	2.38	2.96
Net water produced (gmol/min)	-0.38	+0.25	+0.88	+1.46
Net water produced (ml/min)	-6.9	+4.6	+15.9	+26.4

the condenser is placed before the pressure let-down to the ambient pressure.

8. Effect of fuel composition

The discussion thus far has been limited to the use of methane as the fuel. In the following section, we examine the

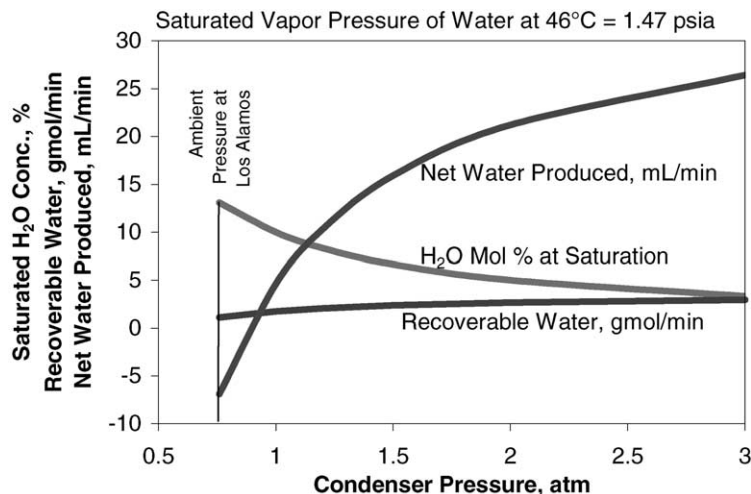


Fig. 6. Effect of system/ambient pressure on the fuel cell system water balance.

Table 7
Water balance in a fuel cell system operating on methane or oxygenated hydrocarbons

Basis: 1 gmol/min of fuel	Methane (base case)	Methanol	Ethanol	Ethylene glycol	Acetic acid
Fuel	CH ₄	CH ₃ OH	C ₂ H ₆ O ₁	C ₂ H ₆ O ₂	C ₂ H ₄ O ₂
Molecular weight	16	32	46	62	60
$\Delta H_{f,298}$ (kcal/gmol)	-17.9	-57.1	-66.2	-108.6	-116.4
$\Delta H_{c,298}$ (kcal/gmol)	192	152	295	253	187
O ₂ /fuel molar ratio into FP, x	0.478	0.317	0.718	0.585	0.653
Air feed into FP (gmol/min)	2.28	1.51	3.42	2.79	3.1
Water feed into FP (gmol/min)	1.5	1.5	3.0	3.0	3.0
Idealized FP products					
H ₂ (gmol/min)	3.05	2.37	4.56	3.83	2.7
H ₂ conc. in reformat (%-wet)	48.4	41.6	42.6	37.5	28.5
LHV of H ₂ (kW(t))	12.3	9.5	18.3	15.4	10.9
Fuel processor efficiency (%)	91.8	89.7	89.3	87.5	83.2
H ₂ O in reformat (gmol/min)	0.46	1.13	1.44	2.17	2.31
H ₂ O conc. in reformat (%-wet)	7.2	19.9	13.4	21.3	24.4
Air into cathode (gmol/min)	14.5	11.3	21.7	18.2	12.8
Burner product (gmol/min)	19.3	15.8	30.1	26.5	20.9
H ₂ O in burner product (gmol/min)	3.5	3.5	6.0	6.0	5.0
H ₂ O conc. in burner product (%-wet)	18.2	22.2	19.9	22.6	23.9
Recoverable water (gmol/min)	1.75	2.14	3.32	3.72	3.23
Net water produced (gmol/min)	+0.25	+0.64	+0.32	+0.73	+0.23
Net water produced (ml/min)	+4.6	+11.6	+5.8	+13.1	+4.2
Net water produced (ml/(Mcal fuel))	+23.8	+75.9	+19.5	+52.0	+22.6

Non-fuel-related parameters (same as base case, Table 1): system pressure = 1 atm; H₂O/C ratio into FP, $\Psi = 1.5$; heat of reforming reaction, $\Delta H_{r,298} = 0$; fuel utilization = 80%; oxygen utilization = 40%; ambient temperature = 35 °C; approach temperature = 11 °C; exhaust temperature = 46 °C; saturated H₂O in exhaust = 10.0%-wet.

Table 8
Water balance of a fuel cell system operating on heavier hydrocarbons

Basis: 1 gmol/min of fuel	<i>n</i> -Hexane	<i>iso</i> -Octane	Toluene	Cyclohexane	Trimethylbenzene	Gasoline
Fuel	C ₆ H ₁₄	C ₈ H ₁₈	C ₇ H ₈	C ₆ H ₁₂	C ₉ H ₁₂	C _{7.3} H _{14.8} O _{0.1}
Molecular weight	86	114	92	84	120	104
$\Delta H_{f,298}$ (kcal/gmol)	-40.0	-62.0	+2.9	-38.0	-13.0	-53.0
$\Delta H_{c,298}$ (kcal/gmol)	929	1,210	892	873	1,180	1,061
O ₂ /fuel molar ratio into FP, x	2.28	3.12	2.24	2.26	3.02	2.77
Air feed into FP (gmol/min)	10.9	14.9	10.6	10.8	14.4	13.2
Water feed into FP (gmol/min)	9.0	12.0	10.5	9	13.5	10.95
Idealized FP products						
H ₂ (gmol/min)	14.4	18.8	13.5	13.5	18.0	16.4
H ₂ conc. in reformat (%-dry)	47.2	46.1	45.2	45.6	45.1	45.4
LHV of H ₂ (kW(t))	58.2	75.6	54.5	54.3	72.4	66.0
Fuel processor efficiency (%)	89.8	89.6	87.6	89.2	88.0	89.1
H ₂ O in reformat (gmol/min)	1.57	2.24	0.97	1.53	1.54	1.98
H ₂ O Conc. in reformat (%-wet)	5.1	5.5	3.24	5.2	3.86	5.49
Air into cathode (gmol/min)	68.7	89.3	64.4	64.1	85.5	77.9
Burner product (gmol/min)	92.1	120.7	87.5	86.9	116.4	105.8
H ₂ O in burner product (gmol/min)	16.0	21.0	14.5	15.0	19.5	18.4
H ₂ O Conc. in burner product (%-wet)	17.4	17.4	16.6	17.3	16.8	17.4
Recoverable water (gmol/min)	7.55	9.93	6.39	7.0	8.76	8.64
Net water produced (gmol/min)	-1.45	-2.07	-4.1	-1.99	-4.7	-2.3
Net water produced (ml/min)	-26.3	-37.5	-74.4	-36.0	-85.7	-41.9
Net water produced (ml/(Mcal fuel))	-28.3	-31.0	-83.4	-41.2	-72.6	-39.4

System pressure = 1 atm; H₂O/C ratio into FP, $\Psi = 1.5$; heat of reforming reaction, $\Delta H_{r,298} = 0$; fuel utilization = 80%; oxygen utilization = 40%; ambient temperature = 35 °C; approach temperature = 11 °C; exhaust temperature = 46 °C; saturated H₂O in exhaust = 10.0%-wet.

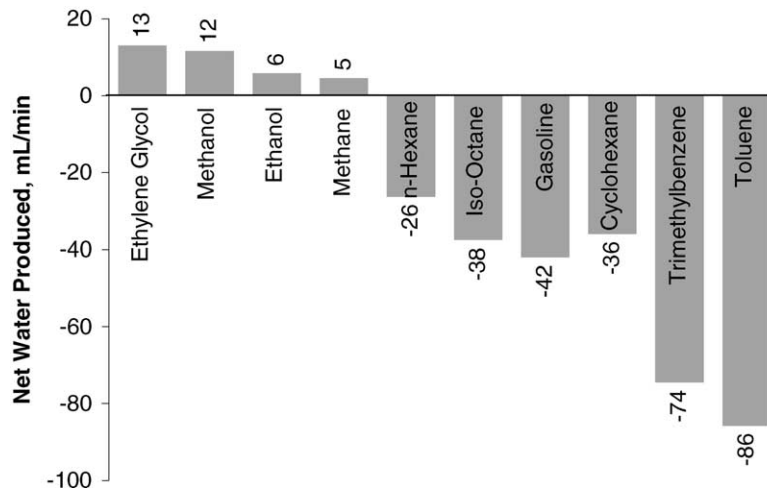


Fig. 7. Effect of fuel composition on the net water produced or consumed by the fuel cell system, based on 1 gmol/min of fuel feed.

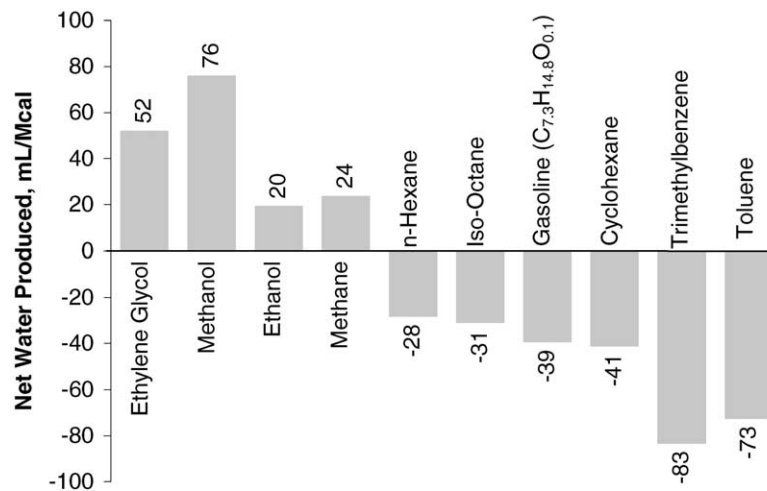


Fig. 8. Effect of fuel composition on the net water produced by the fuel cell system, normalized to 1 Mcal of the lower heating value of the fuel.

effect of using different fuels while the fuel cell system characteristics remain unchanged (i.e. all non-fuel-related parameters are the same as those given in Table 1). The results for a number of fuels and/or oxygenated species are summarized in Tables 7 and 8. The net water production or consumption is shown graphically in Fig. 7, which shows that fuel cell systems operated with methane or oxygenated hydrocarbons are net water producers, while systems using heavier hydrocarbons tend to be net water consumers.

Fig. 8 gives the energy-specific water production, i.e. the net water produced (ml/min) normalized to the input rate of the fuel in terms of its lower heating value (Mcal/min). This figure shows the same general characteristics for the different fuels as Fig. 7, in terms of whether the fuel cell system is a net water producer or consumer. However, it also shows that the energy content of the fuel does affect the amount of water produced or consumed. Thus, on this basis, methanol produces more water than ethylene glycol, while toluene consumes less water than trimethylbenzene.

The energy-specific water production (ml/Mcal) may also be examined as a function of the H/C ratio for the different fuels. Fuels with higher H/C ratios lead to more net water production and show a strong correlation in Fig. 9.⁵ A closer look at Table 7 shows that fuels with low H/C ratios require more water during fuel processing, which may not be recovered at the condenser. Oxygenated hydrocarbons also show a similar trend, but are more favorable fuels in terms of net water production. It may be observed that even though both ethane and ethylene glycol (C₂H₆O₂) have H/C = 3, ethylene glycol produces more water than ethane. This difference can be traced to the reaction stoichiometry (moles of H₂O needed versus moles of H₂ produced); the specified value of the steam-to-carbon ratio (1.5), which changes the actual moles of water entering the reformer; the oxygen (air)

⁵ The energy-specific values for the hydrocarbon species show a strong correlation with the H/C ratio and can be fit with a second-order polynomial with an *R* value of 0.9997.

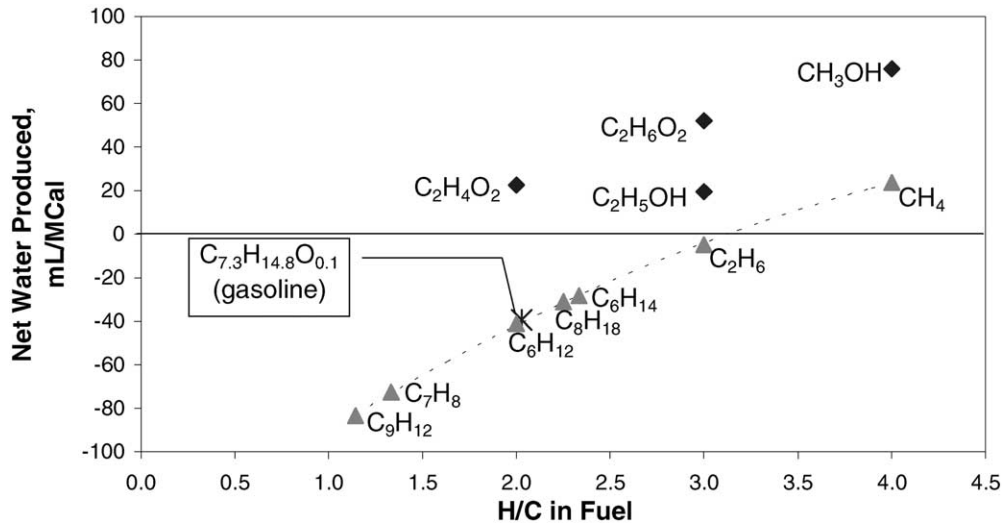


Fig. 9. Effect of the H/C of the fuel on the net water produced by the fuel cell system, normalized to the fuel's heating value.

needed to maintain thermoneutrality; the air needed in the cathode; and other factors.

The fuel composition is thus found to have a significant impact on the net water balance in the fuel cell system. Fuels that produce more net water allow a wider latitude in operating conditions. That is, fuels such as methanol and methane can be operated in the net-water-producing mode even when ambient temperatures are high (except at high altitudes). On the other hand, heavy hydrocarbons, although favored because of their high heating values, tend to make the fuel cell system operate as a net water consumer.

9. Conclusions

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.

Acknowledgements

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Appendix A

$C_nH_mO_p$	n	m	p	
	1	4	0	Methane
	Mol. Wt.	$-\Delta H_f$	ΔH_c	ΔH_c
	(g/mol):	(cal/gmol):	(cal/gmol):	(Btu/lb):
	16	17,889	191,758	21,573
<i>Fuel properties</i>				
Fuel feed	1 gmol			
Oxygen	0.478 gmol			
Nitrogen	1.797 gmol			
Required S/C	1.045			

Appendix A. (Continued)

Operating S/C	1.500		
Excess water (%)	43.6		
Water feed	1.500 gmol		
<i>Ideal products</i>			
H ₂	3.045 gmol	48.35%-wet	12.3 kW(t)
CO ₂	1.000 gmol	15.88%-wet	
N ₂	1.797 gmol	28.54%-wet	
H ₂ O(g)	0.455 gmol	7.23%-wet	
Total	6.297 gmol	100%-wet	
Heat of reaction	0.0 cal	–ve: exo; +ve: endo	
Reactor <i>T</i> estimate for <i>C_p</i> calculations	500 °C		
Efficiency (%)	91.8		
Anode gas temperature	60 °C	139.4 °F	
Saturated vapor pressure	2.833 psia	0.193 atm	19.27%-wet
Fuel utilization stack	80%		
H ₂ reacting in stack	2.44 gmol		
Air stoich in stack	2.5		
Oxygen into cathode	3.045 gmol		
Nitrogen into cathode	11.448 gmol		
<i>Combined product after burner</i>			
CO ₂	1.000 gmol	5.19%-wet	
N ₂	13.245 gmol	68.74%-wet	
O ₂	1.522 gmol	7.90%-wet	
H ₂ O	3.500 gmol	18.17%-wet	
Total	19.267 gmol	100.00%-wet	
System pressure	1.0 atm		
Ambient temperature	35.3 °C	95 °F	
Radiator/condenser approach <i>T</i>	11.1 °C	20 °F	
Exhaust gas temperature	46.4 °C	115 °F	
Saturated pressure	1.470 psia	0.100 atm	10.00%-wet
Water recovered at radiator	1.748 gmol		
<i>Radiator exhaust gas</i>			
CO ₂	1.000 gmol	5.71%-wet	
N ₂	13.245 gmol	75.60%-wet	
O ₂	1.522 gmol	8.69%-wet	
H ₂ O	1.752 gmol	10.00%-wet	
Total	17.519 gmol	100.00%-wet	
Excess water in FP = water recovered – water used	0.25 gmol	4.5 ml/(gmol of fuel); 23.4 ml/(Mcal)	

Basis: 1 min.

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