15
Exergy Analysis of a Micro Fuel Processing System for Hydrogen and Electricity Production – A Case Study

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15.1
Introduction

Today, fuel cells (FCs) are regarded as the best solution for future energy systems with increased energy efficiency and low environmental impact. It is expected that FCs will find successful applications in stationary power plants and in mobile power sources, particularly in vehicles [1]. Currently, due to the common use of portable electrical and electronic devices, efficient low-power generators are needed as alternatives to batteries [2].

Proton exchange membrane (PEM) FCs are a very promising technology for mobile power applications because of their very low emissions, low operating temperature, fast response and relatively high efficiency. For this type of FC, hydrogen is the fuel of choice. The main advantages of using hydrogen as a fuel in PEM FCs are a high electrochemical reactivity and environmental friendly reaction products.

15.1.1
Need for a Fuel Processor for Hydrogen Generation

Two fundamentally different methods can be used to supply hydrogen to the FC. In the first method, an appropriate storage tank is used that contains hydrogen, which has been produced previously by any suitable production method. It is commonly known that hydrogen is very difficult to store either as a gas or a liquid or when using storage media, such as metal hydrides or carbon nanotubes [3]. Therefore, this method is usually limited to stationary applications. In the case of mobile applications the second method of hydrogen supply to the FC, that is, on-board hydrogen production, is much more promising. This method is actually

based on chemical storage of hydrogen in liquid fuels. In this case, a fuel processor (FP) is needed to convert the liquid fuel into hydrogen gas, which can be subsequently fed to the FC [4].

15.1.2
Integrated Fuel Processor–Fuel Cell (FP–FC) System

Different primary liquid fuels can be considered as a source of hydrogen, including alcohols, hydrocarbons and ammonia. In order to convert alcohols or hydrocarbons into hydrogen, catalytic steam reforming or catalytic partial oxidation can be used, whereas in the case of ammonia a catalytic cracking step is needed. Several selection criteria can be considered for selecting a suitable primary liquid fuel for a mobile FP–FC system. The most important are a high energy content, possibility of liquefaction at moderate pressures and fuel cost. Other essential criteria involve easy refueling, few health, safety and environmental hazards and robust and easy to down-size conversion processes [5]. A very promising primary fuel for mobile FP–FC systems is methanol, which can be safely handled and easy stored by conventional methods and is fully miscible with water [6]. Moreover, methanol can easily be converted into hydrogen and generally it can be produced from renewable resources such as biomass or municipal wastes. In order to achieve portability of the FP–FC system, microreactor technology should be used [7, 8].

15.1.3
Goal

Various design criteria can be used for FP–FC systems involving efficient fuel utilization, energy density and life cycle cost in addition to environmental impact and safety. Power generation systems are traditionally analyzed by energetic analysis based on the first law of thermodynamics only. However, this type of analysis shows only the mass and energy flows and does not take into account how the quality of the energy and material streams degrades through the process. In this chapter, exergy analysis, which is based also on the second law of thermodynamics, is used to analyze FP–FC systems. Exergy analysis directly detects process losses due to thermodynamic imperfections of the system. Using exergy analysis, it is possible to reduce energy use and improve integration of the components in a micro-FP–FC system. In this way, miniaturization of the system can be realized, which is needed in the case of micropower devices.

In Section 15.2, thermodynamic analysis to evaluate the maximum amount of electricity generated from an FP–FC system is presented. Section 15.3 is devoted to design and exergy analysis of methanol FP–FC processors that can produce 100 W of electricity. Finally, Section 15.4 shows a comparison of FP–FC systems with alternative devices such as rechargeable batteries and combustion engines.

15.2
## Thermodynamic Evaluation of FP–FC Systems

15.2.1
### Methanol Processor Integrated with PEM Fuel Cell

A block diagram of the FP integrated with FC is presented in Figure 15.1. In this system the fuel is methanol, which is stored in a storage tank as an aqueous solution. Excess water in the feed is needed to reduce CO formation in the reformer and avoid dehydration of the FC. Methanol is evaporated in the vaporizer as all reactions in the FP–FC system take place in the gas phase. In the reformer methanol is converted into a hydrogen-rich gas at 250 °C over a Cu-based catalyst according to the endothermic steam reforming reaction.

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \qquad \Delta H = +48.8 \text{ kJ mol}^{-1} \qquad (15.1)$$

The gas produced in the reformer contains in addition to hydrogen also CO_2 and small amounts of CO, which is produced in the methanol decomposition reaction:

$$CH_3OH \rightarrow CO + 2H_2 \qquad \Delta H = +89.2 \text{ kJ mol}^{-1} \qquad (15.2)$$
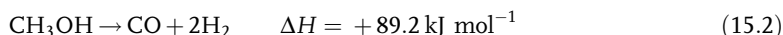
The concentration of CO should not be higher than 10–100 ppm as this gas is a poison for the PEM FC anode. In the reformer the exothermic water gas shift reaction also takes place, which affects the composition of the product gas:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41.0 \text{ kJ mol}^{-1} \qquad (15.3)$$
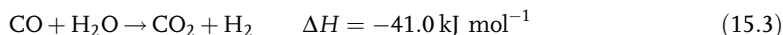
In order to reduce CO formation, the reformer should operate with excess of water and at lower temperature. Compared with all other common liquids, such as gasoline and ethanol, methanol is a promising liquid fuel candidate as it can be reformed into hydrogen at a relatively low temperature (about 250 °C). The usual reforming temperature for other liquids is higher (450–900 °C), which results in much higher CO concentration in the product gas.

CO is removed from the product gas in the gas-clean-up step, where selective CO oxidation takes place at 150 °C over a Pt-based catalyst:
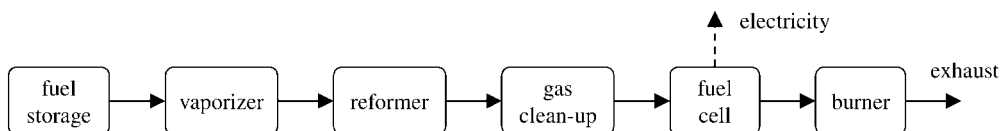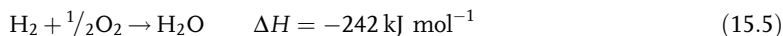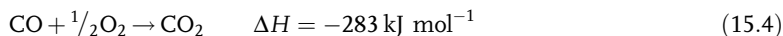
$$CO + {}^1\!/_2 O_2 \rightarrow CO_2 \qquad \Delta H = -283 \text{ kJ mol}^{-1} \qquad (15.4)$$

$$H_2 + {}^1\!/_2 O_2 \rightarrow H_2O \qquad \Delta H = -242 \text{ kJ mol}^{-1} \qquad (15.5)$$

Figure 15.1 Schematic of the integrated fuel cell–fuel processor system.

Finally, a clean hydrogen-rich gas enters the FC, where electricity is produced. In the catalytic burner, the unconverted hydrogen is combusted to deliver heat necessary for the vaporizer and reformer.

15.2.2
Maximum Electricity Generation from Various Fuels

The thermodynamic evaluation of the FP–FC system is performed in two steps. The first step is evaluation of the maximum amount of work available from the system. The maximum amount of work (electricity) gives the theoretical energy density of a fuel in an ideally operated FP–FC system. Subsequently, in the second step, the overall thermodynamic efficiency is evaluated using exergy analysis. Moreover, the exergy analysis indicates system units where the highest exergy losses occur.

The maximum electricity produced from the FP–FC system can be evaluated from the energy and entropy balances for this system:

$$\Delta H_T = H_P - H_F = Q + W_x \tag{15.6}$$

$$\Delta S_T = S_P - S_F = \Pi + \frac{Q}{T} \tag{15.7}$$

From these equations, one can derive the expression for work produced:

$$W_x = \Delta H_T - T\Delta S_T + T\Pi = \Delta G_T + T\Pi \tag{15.8}$$

The maximum amount of electricity is obtained from Equation (15.8) if the entropy production Π is equal to zero. In real systems, the amount of produced work is always lower than the maximum due to the positive value of the entropy production. Table 15.1 presents the changes in enthalpy, entropy and Gibbs free energy for various investigated primary fuels, including alcohols (methanol, ethanol), hydrocarbons (gasoline, natural gas), ammonia and methane and hydrogen for comparison. They are calculated using thermodynamic data from [9], which are true for any process to convert fuel to electricity. All primary fuels are assumed to be in the

Table 15.1 Change of enthalpy, entropy and Gibbs free energy for conversion of primary fuels to electricity, and the associated heat effect; values at 298 K and 1 bar.

Fuel	Enthalpy change [kJ (mol fuel)$^{-1}$]	Entropy change [J (mol fuel)$^{-1}$ K^{-1}]	Gibbs free energy change [kJ (mol fuel)$^{-1}$]	Heat effect [kJ (mol fuel)$^{-1}$]
Methanol (CH_3OH)	−676	44	−689	13
Ethanol (C_2H_5OH)	−1277	96	−1300	29
n-Octane (C_8H_{18})	−5116	380	−5229	113
Ammonia (NH_3)	−317	33	−326	10
Methane (CH_4)	−802	−5.1	−801	−1.5
Hydrogen (H_2)	−242	−44	−229	−13

gaseous state. The final products from the FP–FC system are CO_2 and H_2O for alcohols and hydrocarbons, H_2O for hydrogen and N_2 and H_2O for ammonia, according to the following chemical reactions.

$$CH_3OH + 1\frac{1}{2}O_2 \rightarrow CO_2 + 2H_2O \tag{15.9}$$

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \tag{15.10}$$

$$C_8H_{18} + 12\frac{1}{2}O_2 \rightarrow 8CO_2 + 9H_2O \tag{15.11}$$

$$NH_3 + \frac{3}{4}O_2 \rightarrow \frac{1}{2}N_2 + 1\frac{1}{2}H_2O \tag{15.12}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{15.13}$$

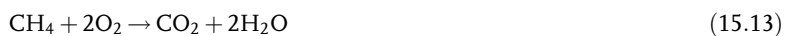$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{15.14}$$

Table 15.2 shows the maximum amount of electricity available expressed in different units. The maximum amount of work available from the FP–FC system shows different values for various fuels, when it is represented per kilomole and per kilogram of fuel. However, in the case of carbon-containing compounds, the maximum amount of work per kilomole of C present in a fuel is approximately similar. Moreover, when the maximum amount of work produced in the FP–FC system is expressed per kilomole of H_2 generated via steam reforming in the case of alcohols and hydrocarbons and via catalytic cracking in the case of ammonia, it is approximately the same for each fuel. The heat effect of an ideal conversion system is relatively low compared with the maximum amount of work for all investigated fuels.

Pure hydrogen shows the highest value of energy density (113 MJ kg^{-1} fuel), followed by methane and n-octane (50 and 46 MJ kg^{-1}, respectively) and the remaining fuels have an energy density in the range 19–28 MJ kg^{-1}. The corresponding energy density for state-of-the-art batteries such as Li ion or Zn–air is much lower,

Table 15.2 Maximum amount of work for the conversion of primary fuels to electricity expressed in various units; values at 298 K and 1 bar.

Fuel	Maximum amount of work				
	MJ (mol fuel)$^{-1}$	MJ (kg fuel)$^{-1}$	MJ (L fuel)$^{-1}$	MJ (mol C in fuel)$^{-1}$	MJ (mol H_2 via reforming)$^{-1}$
Methanol	−0.69	−22	−17[a]	−0.69	−0.23
Ethanol	−1.31	−28	−22[a]	−0.65	−0.22
n-Octane	−5.23	−46	−32[a]	−0.65	−0.21
Ammonia	−0.33	−19	−10[a]		−0.22
Methane	−0.80	−50	−3.9[b]	−0.80	−0.20
Hydrogen	−0.23	−113	−0.89[b]		−0.23

[a]Density of the liquid fuels calculated at 298 K and 1 bar, for ammonia at 10 bar.
[b]Density of the gaseous fuels calculated at 298 K and 100 bar.

about 1 MJ kg^{-1} [2]. Similarly, the volumetric energy density of typical fuels, such as *n*-octane and methanol (32.2 and 17.0 MJ L^{-1} fuel, respectively) exceeds those of batteries (lower than 2 MJ L^{-1}). It is also interesting to note that for the fuels with a positive entropy change (positive heat effect) the maximum amount of work is higher then the enthalpy change. This means that the direct processing of these fuels in an FP–FC system is, from the thermodynamic point of view, more energy efficient than the traditional combustion.

The maximum amount of work and corresponding heat effect for the fuels considered depend only slightly on the temperature of the FP–FC system. Generally, for fuels with a positive entropy change, such as methanol, the maximum amount of work increases with temperature, whereas for fuels with a negative entropy change, it decreases with temperature.

15.3
Exergetic Analysis of Integrated FP–FC Systems

15.3.1
Design of Methanol FP Integrated with FC

The flow-sheeting program Aspen Plus is used to design the FP–FC system, which produces 100 W of electricity. The process has been modeled and simulated for a standard set of conditions shown in Table 15.3 and subsequently the process

Table 15.3 Temperature, molar flow rate and exergy flow rate for the FP–FC system (at standard conditions; see also Figure 15.2).

| Stream	Temperature (K)	Molar flow rate (mmol s^{-1})							Exergy flow rate (J s^{-1})
		CH$_3$OH	H$_2$O	H$_2$	O$_2$	CO$_2$	CO	N$_2$	
1	298	0.37	0.75	–	–	–	–	–	267
2	423	0.37	0.75	–	–	–	–	–	276
3	523	–	0.39	1.11	–	0.36	0.01	–	274
4	517	–	0.39	1.11	0.01	0.36	0.01	0.05	274
5	423	–	0.39	1.11	0.01	0.36	0.01	0.05	272
6	423	–	0.40	1.10	–	0.37	–	0.05	266
7	338	–	0.40	1.10	–	0.37	–	0.05	265
8	335	–	1.23	0.27	0.33	0.37	–	3.47	70
9	365	–	1.23	0.27	0.33	0.37	–	3.47	71
10	400	–	1.23	0.27	0.33	0.37	–	3.47	72
11	433	–	1.23	0.27	0.33	0.37	–	3.47	74
12	642	–	1.49	–	0.20	0.37	–	3.47	33
13	344	–	1.49	–	0.20	0.37	–	3.47	12
Air1	298	–	–	–	0.01	–	–	0.05	0
Air2	298	–	–	–	0.75	–	–	3.42	0
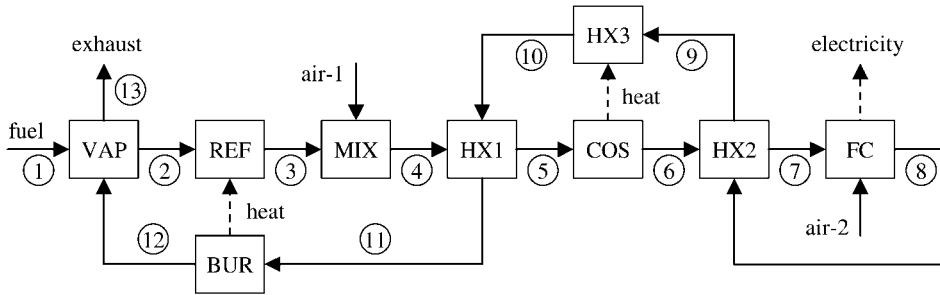
Figure 15.2 Flow sheet of the integrated fuel processor–fuel cell system (see text for abbreviations).

conditions have been modified to determine the influence of the operating conditions on the overall efficiency of the system.

Figure 15.2 shows the flow sheet of the FP–FC system. The fuel for the system is an aqueous solution of methanol at the molar ratio of methanol to water of 1 : 2 for the standard case. The fuel is evaporated in the vaporizer (VAP) at 150 °C. In the reformer, the vaporized methanol and water react at 250 °C to form a hydrogen-rich gas, which contains also some CO_2 and CO. The steam reformer is modeled as a Gibbs reactor assuming chemical equilibrium between the species at the outlet of the reactor. At the reforming temperature of 250 °C, the equilibrium conversion of methanol is almost 100%. The selectivity of methanol to CO_2 is about 97% and to CO about 3%. In the mixer (MIX), the hydrogen-rich gas from the reformer is mixed with a small quantity of air, which is needed for the oxidation of CO present in the product gas from the reformer. The selective CO oxidation takes place in the COS reactor at 150 °C. The COS reactor is modeled as a stoichiometric reactor where 50% of the supplied O_2 from the air is used for complete oxidation of CO and the remaining 50% of O_2 reacts with H_2.

Finally, the CO-free H_2-rich gas is oxidized in the PEM FC. The excess of O_2 from air used in the cell is assumed to be 80% with respect to reacting H_2. The operating temperature of the PEM FC is about 60 °C, as calculated from a balance between water entering the FC and formed in the cell and water leaving the FC as saturated vapor. The water flows into and out of the FC have to be balanced, to avoid dehydration or flooding of the cell. The amount of water vapor leaving the cell is directly related to the operating temperature of the cell, when equilibrium is assumed between the exhaust gas and liquid water present in the cell. The conversion of H_2 in the cell is calculated assuming a generation of 100 W of electricity and an LHV FC efficiency of 50% of the FP–FC system. In contrast to the FP part of the FP–FC system, the FC part is not modeled in detail, which is beyond the scope of this chapter. Therefore, only the overall FC efficiency is taken into account.

The heat integration system consists of a catalytic burner reactor (BUR) and three heat exchangers (HX1, HX2, HX3). In the catalytic burner reactor, the unconverted hydrogen is combusted at 370 °C to deliver the heat necessary for the vaporizer and the reformer. The whole FP–FC system operates autothermally.

Table 15.4 Work and heat transfer rate for the FP–FC system
(at standard conditions; see also Figure 15.2).

Transfer rate	VAP	REF	BUR	COS	FC	HX1	HX2	HX3
Heat $(J\,s^{-1})$	53.0	27.0	−27.0	−6.1	−96.8	6.0	5.0	6.1
Work $(J\,s^{-1})$					−100			

Table 15.3 summarizes temperature and molar flow rate for all process streams in the standard case. An overview of the electrical work and heat transfer rate is shown in Table 15.4. For the FP–FC system described in this section, a detailed exergy analysis is presented in the next section.

15.3.2
Exergy Concept

Exergy analysis is a relatively new method of thermodynamic analysis that has recently been applied in different fields of engineering and science [10]. The exergy method takes into account not only the quantity of materials and energy flows, but also their quality. The main reason of exergy analysis is to detect and evaluate quantitatively the losses that occur in thermal and chemical processes.

Exergy is defined as the maximum amount of work that can be obtained from a material stream, heat stream or work interaction by bringing this stream to environmental conditions. The environmental state is a crucial concept in exergy analysis. The term environment is regarded as a medium composed of common substances existing in abundance within the Earth's atmosphere, oceans and crust. The reference state is usually taken to be at standard temperature ($T_0 = 298.15$ K) and pressure ($p_0 = 1$ atm). Some reference species include CO_2, O_2 and N_2, having mole fractions of 0.0003, 0.2099 and 0.7903 in dry air, respectively.

Among the different forms of exergy, three forms are the major contributors to total exergy: thermal exergy, work exergy and exergy of material. The exergetic value of a heat flow, that is, its quality of energy, is the maximum amount of work that could be obtained from it by using the environment as a reservoir of zero-grade thermal energy:

$$E^Q = Q\tau = Q\left(1 - \frac{T_0}{T}\right) \tag{15.15}$$

Work interaction is a completely ordered form of energy and therefore the exergy value E^W equals to the amount of work done:

$$E^W = W_x = W_e \tag{15.16}$$

The quality of a material stream can be expressed using their physical and chemical exergy:

$$\varepsilon_t = \varepsilon_{ph} + \varepsilon_{ch} \tag{15.17}$$

The physical exergy $\varepsilon_{\mathrm{ph}}$ is equal to the maximum amount of work obtainable when a compound or mixture is brought from its temperature T and pressure P to environmental conditions, characterized by environmental temperature T_0 and pressure P_0. The standard chemical exergy of a pure chemical compound $\varepsilon_{\mathrm{ch}}$ is equal to the maximum amount of work obtainable when a compound is brought from the environmental state, characterized by the environmental temperature T_0 (298.15 K) and environmental pressure P_0 (1 atm), to the dead state, characterized by the same environmental conditions of temperature and pressure, but also by the concentration of reference substances in a standard environment.

The exergy balance of a process can be represented in the following form using exergy values of all streams entering and leaving the process:

$$\sum_{\mathrm{IN}} E_j + E^Q + E^W = \sum_{\mathrm{OUT}} E_k + I \tag{15.18}$$

where $\sum_{\mathrm{IN}} E_j$ and $\sum_{\mathrm{OUT}} E_k$ are exergy flow of all entering and leaving material streams, respectively, and E^Q and E^W are the sums of all thermal exergy and work interactions involved in a process. The difference between the concept of exergy and those of mass and energy is that exergy is not conserved but subjected to dissipation. This means that the exergy leaving any process step will always be less than the exergy in. The difference between all entering exergy streams and that of leaving streams is called irreversibility I. Irreversibility represents the internal exergy loss in the process as the loss of quality of materials and energy due to dissipation. Irreversibility relates also to entropy production in the system and can be expressed as follows:

$$I = T_0 \Pi \tag{15.19}$$

15.3.3
Exergy Efficiency and Exergy Losses

Exergy flow rates, calculated according to Szargut *et al.* [10], for all process streams of the FP–FC systems are shown in Table 15.3. The overall exergetic efficiency of the FP–FC system for the standard case is calculated as the ratio between the useful exergy output and the exergy input, using the following overall exergy balance:

$$E_1 + E_{\mathrm{air1}} + E_{\mathrm{air2}} = E_{13} + E_{\mathrm{FC}}^Q + W_{\mathrm{e}} + I \tag{15.20}$$

where $(E_1 + E_{\mathrm{air1}} + E_{\mathrm{air2}})$ represents exergy input to the FP–FC system, W_{e} exergy output, $(E_{13} + E_{\mathrm{FC}}^Q)$ external exergy losses and I irreversibility.

The exergy input is equal to the exergy of methanol, 267 J s^{-1}, as the exergy of both air streams is equal to zero. The exergy output is the electrical work from the FC and this is set to 100 J s^{-1}. This means that the overall exergetic efficiency of the FP–FC system is equal to 37.5% and the total exergy losses are equal to 167 J s^{-1}. The contributions of internal and external exergy losses are 144 and 23 J s^{-1}, respectively. The external exergy losses are the exergy of exhaust gas from the vaporizer (exergy value 12 J s^{-1}) and waste heat from the FC (exergy value 11 J s^{-1}).
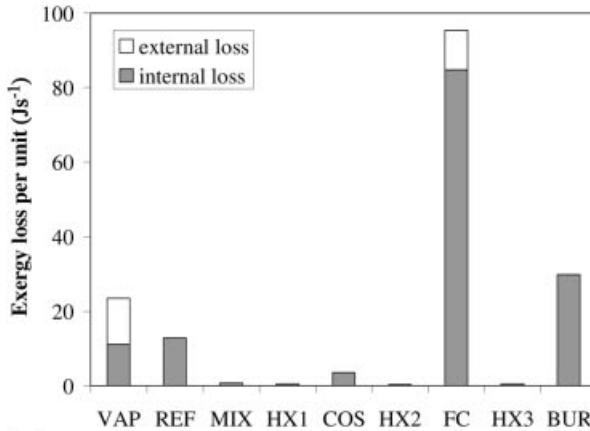
(a)
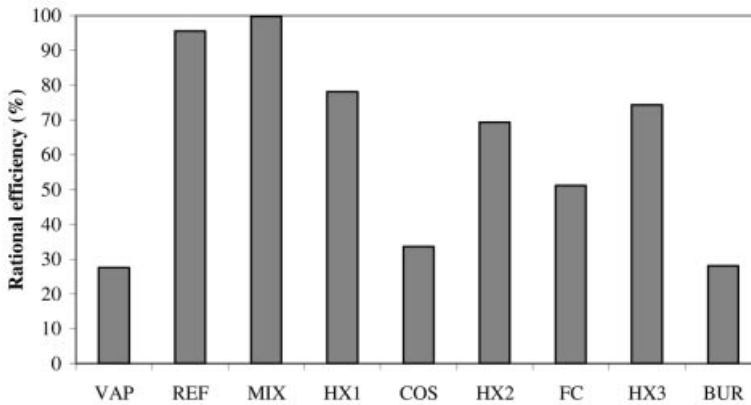
(b)

Figure 15.3 Exergy analysis results for the process units in the FP–FC system. (a) Internal and external exergy losses; (b) rational efficiencies.

The detailed results of the exergy analysis are presented in Figure 15.3. Figure 15.3a shows the internal and external exergy losses for all process units and Figure 15.3b shows the rational efficiency of these process units. External exergy losses take place only in the vaporizer (stream 13) and the FC (heat losses); heat losses in the other process units are neglected. The main exergy losses occur in the FC, burner, reformer and vaporizer. The exergy losses in the FC are caused by activation polarization, ohmic and concentration polarization. In the vaporizer, only physical exergy accounts for the losses there, mainly due to the high temperature difference between the hot and cold sides of the heat exchanger. In the reformer and burner both chemical and physical exergy losses occur. The sum of the exergy losses in the mixer, the COS reactor and the heat exchangers HX1, HX2 and HX3 is less than 5% of the total loss.

Figure 15.3b shows the performance of all process units in terms of rational efficiency. The rational efficiency is defined as the ratio between the desired output of a process unit and the necessary input to this unit [11]. The performance expressed in terms of rational efficiency only shows the relative efficiency of individual system units and is sensitive to the definition of the input and output streams. In Figure 15.3a, the performance of the system is shown as the absolute exergy losses of these units. Figure 15.3b shows that the reformer and mixer perform very well in terms of relative efficiency, followed by the heat exchangers HX1, HX2 and HX3, whereas the performance of the FC, burner, vaporizer and COS reactor is lower.

15.3.4
Optimization of the FP–FC System

Based on the absolute exergy losses shown in Figure 15.3a, only the reformer, burner, vaporizer and especially the FC should be considered when optimizing the efficiency of the overall FP–FC system. Therefore, we studied the influence of the following operating conditions on the overall exergy loss of the FP–FC system: the methanol concentration in the feed, the reformer temperature, the FC temperature and the LHV efficiency of the FC. Figure 15.4a demonstrates that the total exergy loss decreases with increasing methanol concentration in the feed. Almost all units contribute to this improvement (Figure 15.4b), with the exception of the COS reactor (the exergy losses in the FC were assumed to be independent of the methanol feed concentration). Figure 15.5 shows a small increase in total exergy loss with temperature increase of the FC, whereas the total exergy loss increases only slightly on increasing reformer temperature, as shown in Figure 15.6. Finally, increasing the LHV-based efficiency of the FC from 40 to 60% resulted in a substantial decrease in the total exergy loss from 234 to 123 J s^{-1}. Increasing the efficiency of the PEM FC can be realized at the expense of a lower power density. In that case, a larger FC is needed, which is not practical for a small-scale application.

15.4
Discussion

Efficient autonomous portable power generators are required due to the common use of portable electrical and electronic devices, such as laptop computers and cell telephones. Currently, rechargeable batteries are the predominant technology for these applications. Moreover, mobile power generators are needed for residential and recreational purposes to replace small combustion engines, for example diesel generators on board (sailing) yachts. In all these applications, small FP–FC systems are convenient alternatives.

Exergy analysis can be used to compare FP–FC systems with rechargeable batteries and combustion engines. Other important aspects, in addition to exergetic efficiency, are environmental impact, safety and life cycle cost. Efficient fuel utilization is particularly important for larger FP–FC systems. For small systems, the energy
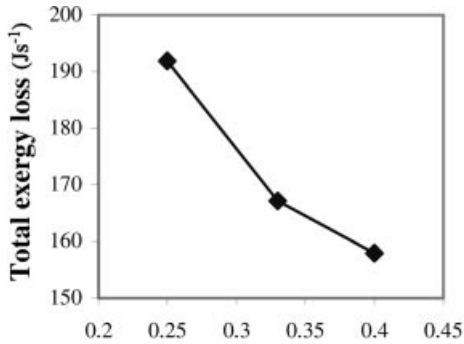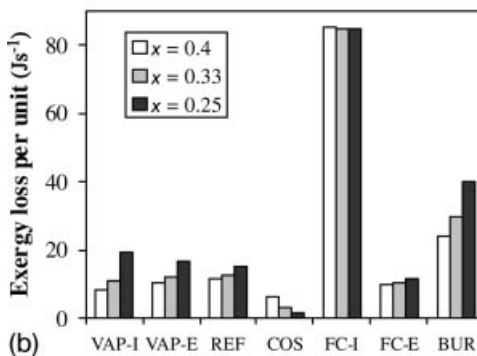
Figure 15.4 Influence of the methanol concentration in the feed on the exergy losses in the FP–FC system. (a) Total exergy losses; (b) exergy losses (I = internal, E = external) per unit.

density is also important, being higher for FCs than for batteries. Moreover, FP–FC systems have the advantages of less sound generation and less pollution in comparison with combustion engines. In this section, a comparison of the second-law efficiency is presented between the FP–FC system, rechargeable batteries and small combustion engines, for the conversion of a chemical fuel to electrical and mechanical work. As a standard value of the exergetic efficiency for the fuel-to-electricity conversion in an FP–FC system, a value of 37% is used, as calculated in the previous section.

15.4.1
Exergetic Comparison Between FP–FC Systems and Alternatives

In this section, an exergetic comparison is presented between FP–FC systems and rechargeable batteries and small combustion engines. For typical batteries, including Ni–MH, Ni–Cd, Li ion and lead acid batteries, the exergetic efficiency has been evaluated as the ratio of the amount of energy released from the battery while discharging to the amount of energy delivered to the battery during charging. For the investigated batteries the calculated efficiency is between 55% for an Ni–Cd battery and 88% for an Li ion battery. On the other hand, the exergetic efficiency of small-
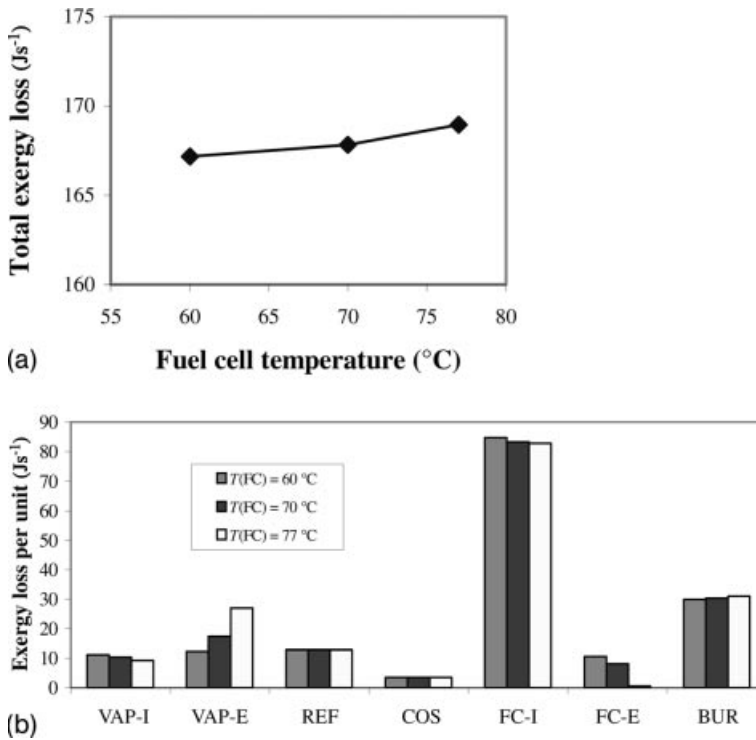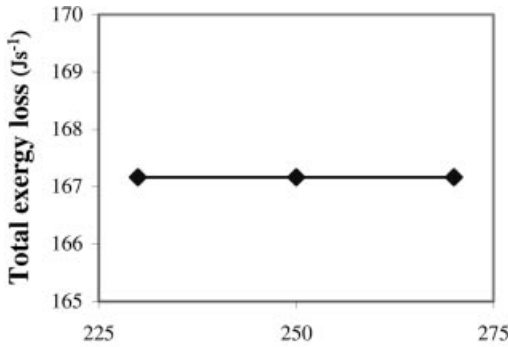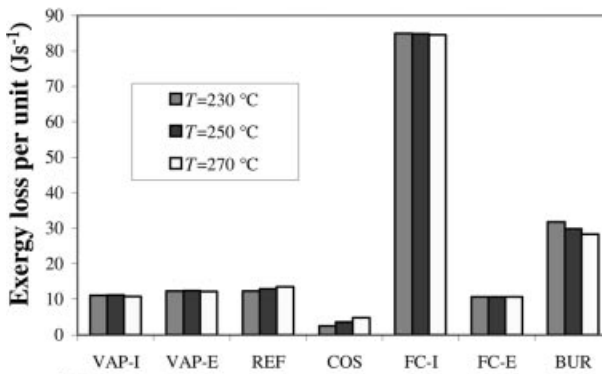
Figure 15.5 Influence of the fuel cell temperature on the exergy losses in the FP–FC system. (a) Total exergy losses; (b) exergy losses (I = internal, E = external) per unit.

scale combustion engines, such as used for electricity generation, has been evaluated as the ratio between the engine power (mechanical work production) and the chemical exergy of the fuel. Typical fuels used in the considered combustion engines are gasoline and diesel. The calculated efficiency ranged between 8% for small engines (<1 kW) to 30% for larger engines (about 100 kW) [12].

The comparison between FP–FC systems, rechargeable batteries and combustion engines based on exergetic efficiency is shown in Figure 15.7. It should be noted that the presented comparison relates to the energy conversion from fuel to electrical and subsequently to mechanical work. The additional assumption was made that the fuel-to-electricity conversion efficiency in a large power plant is 40% and that the conversion efficiency between mechanical and electrical work is 90%. The results show that FP–FC systems have higher fuel-to-electricity and fuel-to-mechanical energy efficiency than batteries and combustion engines. Combustion engines have the lowest efficiency, due to limitation by the Carnot efficiency. The comparison shown in Figure 15.7 assumes that the same fuel, such as a hydrocarbon (natural gas, gasoline, oil), is used in all considered conversion devices. If methanol is used as a fuel for an FP–FC system, it has to be produced from hydrocarbons (currently from natural gas), which will reduce the overall efficiency.

(a) **Reformer temperature (°C)**

(b)

Figure 15.6 Influence of the reformer temperature on the exergy losses in the FP–FC system. (a) Total exergy losses; (b) exergy losses (I = internal, E = external) per unit.
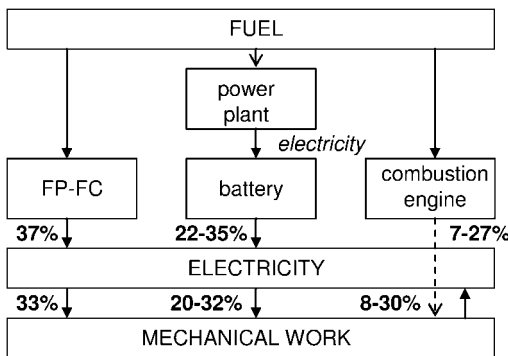

Figure 15.7 Comparison of exergetic efficiency between the FP–FC system, rechargeable batteries and combustion engines.

15.4.2
Other Criteria to Compare FP–FC Systems with Alternatives

Several additional criteria can be used to compare FP–FC systems with batteries and combustion engines. The most important are discussed below.

• *Energy density:* The methanol powered FC system has an energy density higher than that of batteries. Table 15.5 shows a comparison between the energy density of methanol FCs and that of lithium-ion batteries which have the highest energy density compared to other battery types.

• *Economy.* Because FCs are an emerging technology, they tend to be more expensive than other forms of power generation. However, with future research and development, new cell designs promise to make FC costs competitive.

• *Lifetime.* FCs and combustion engines are preferred choices for applications of longer duration. They are devices that can be continuously refueled. On the other hand, combustion engines require regular maintenance.

• *Safety.* FCs, batteries and combustion engines have relatively similar safety records. Fuel such as methanol used in FCs is flammable and the chance of explosion is high.

• *Environment.* Alcohol fuels and components of FCs are relatively environmentally friendly. On the other hand, batteries and combustion engines have environmental problems. Furthermore, FCs and batteries are quiet devices whereas combustion engines are noisy.

• *Sustainability.* FCs are power sources that use methanol or ethanol and hydrogen, which can be produced as renewable fuels. Methanol and hydrogen can be produced by gasification of biomass or municipal solid waste, providing a pathway to a sustainable energy future.

Generally, the criteria used in comparing the three electricity-generating systems are complex and difficult to evaluate and sometimes contradictory (e.g. "safety" sometimes means more expensive). More complex sustainability criteria such as extended exergy accounting or life cycle analysis [13] should be applied for more exact comparisons for all considered systems.

Table 15.5 Exergetic efficiency for rechargeable batteries.

	Chemical energy (W h L^{-1})	Electrical energy (W h L^{-1})	Chemical energy (W h kg^{-1})	Electrical energy (W h kg^{-1})
Methanol	4300		5300	
Methanol–water (1:1)	2150		2650	
Methanol–water tank + fuel cell	~2100	800[a]	~2300	900[a]
Li ion battery		210		100

[a] 40% conversion efficiency is assumed for the direct methanol FC.

**15.5
Conclusion**

The promising applications of integrated FP–FC systems are portable power supplies in electronic and electrical devices and also in residential and recreational sectors. The maximum amount of work produced in an FP–FC system is different for various fuels, but is approximately the same for each fuel when expressed per mole of H_2 generated via steam reforming. The application of exergy analysis to micropower systems permits a high level of energy integration of the FP, which what contributes to miniaturization of the system. The overall exergetic efficiency of the system is about 37% and the largest exergy losses occur in the FC, the burner, the vaporizer and the reformer. The overall exergetic efficiency of the fuel-to-electricity conversion is higher for the FP–FC system than for rechargeable batteries and combustion engines.

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