

Review of an energy and exergy analysis of a fuel cell system

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Abstract

A review of an energy and exergy analysis of the KTI 25 kW fuel cell system is described. This system consists of a fuel cell and a fuel processor. An examination of the system's integration concept is done with the aim of pinpointing the existing losses. The exergy calculations are performed with the Aspen Plus programme using a Fortran extension. Energy and exergy calculations are presented in a Sankey and Grassmann diagram, respectively. The system's major energy losses are involved with off-gases, while the system's major exergy losses are associated with internal process irreversibilities. It is concluded that the exergy calculations pinpoint the losses accurately and that the exergy analysis gives a better insight of the system's process.

Introduction

Highly efficient energy production systems with low emissions to the environment will be of increasing importance in the near future [1–5]. Optimization of efficiency and process operation is therefore a major issue in system development. The conventional approach is based on the first law of thermodynamics, yielding an energy analysis of a particular system. A more powerful approach is based on the first and second law of thermodynamics, the exergy analysis. Exergy analysis takes the quality of energy into account and pinpoints irreversibilities present in a system.

In this paper the results of an energy and exergy analysis of the first European fuel cell plant, namely the 25 kW fuel cell demonstration system of Kinetics Technology International (KTI), Zoetermeer, will be presented.

The fuel cell system

The fuel cell system on which the analysis is based consists of a phosphoric acid fuel cell integrated with a hydrogen manufacturing unit. The global scheme as shown in Fig. 1 [2] divides the fuel cell system in four relevant subsystems.

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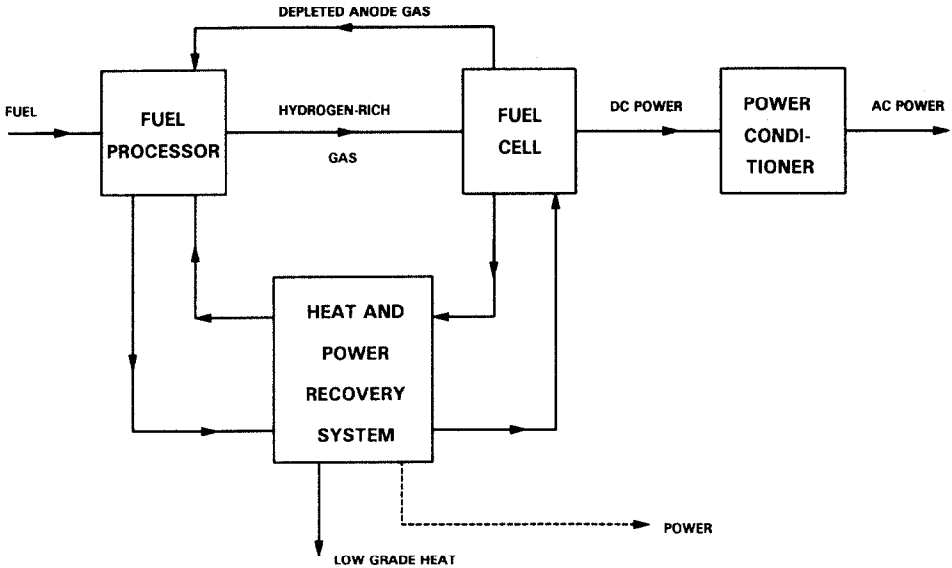


Fig. 1. Block scheme fuel cell system [2].

The first main subsystem is the fuel cell, which converts chemical energy of a hydrogen-rich fuel and an oxidant-rich gas, usually air, directly into electrical energy. It is the reverse process of water electrolysis; therefore, the reaction product is water. Like all other processes, it is subject to certain irreversibilities. The energy, not converted into electric power, is partly available as heat with a temperature of about 180 °C and partly as chemical energy in the unreacted gases as well as sensible heat in the gas leaving the anode compartment.

For the production of a hydrogen-rich gas for the fuel cell the conversion of the fuel (in this case natural gas) is required. This is achieved in the second subsystem. The fuel processor converts natural gas into a hydrogen-rich gas by a conventional steam-methane reforming process followed by shift conversion.

The fuel cell and the fuel processor are closely integrated in order to achieve an optimum heat and power recovery. The level of integration has the largest influence on the overall system performance, together with some key process variables, such as reformer temperature and pressure and the ratio of steam to hydrocarbons in the reformer feed inlet stream.

The power conditioner finally converts the d.c. power produced by the fuel cell into a.c. power. The power conditioner has typically an efficiency of 0.90 to 0.98, largely dependent on the size of the conditioner. For the system under consideration, the power efficiency was 0.90. Since the power conditioner transfers d.c. electricity to a.c. electricity, the energy efficiency is the same as the exergy efficiency. The power conditioner was not optimized for the system under consideration (for cost reasons) and therefore not included in the system evaluation.

A flowsheet, which shows the steam ejector, the reformer, the CO shift converter, the dewatering unit, the heat exchanger network, the reboiler and the fuel cell stack, is presented in Fig. 2 [3].

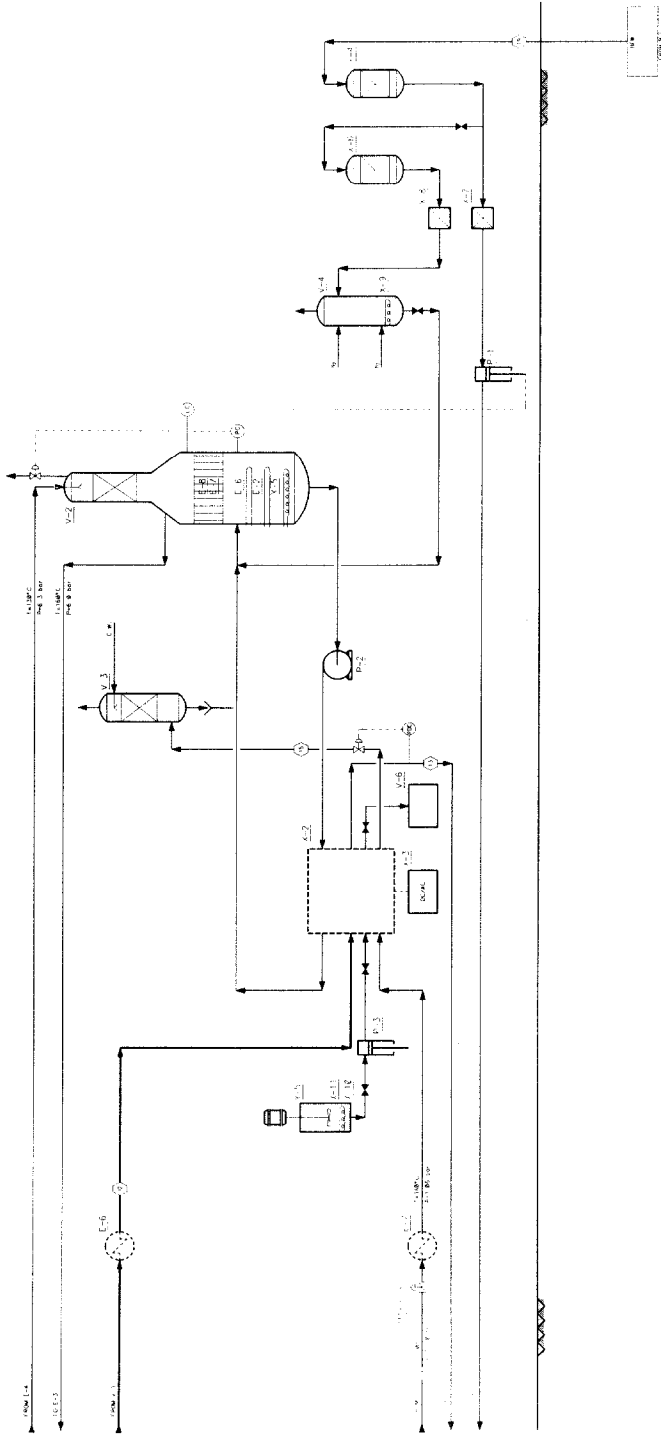


Fig. 2. Flowsheet 25 kW fuel cell system [3].

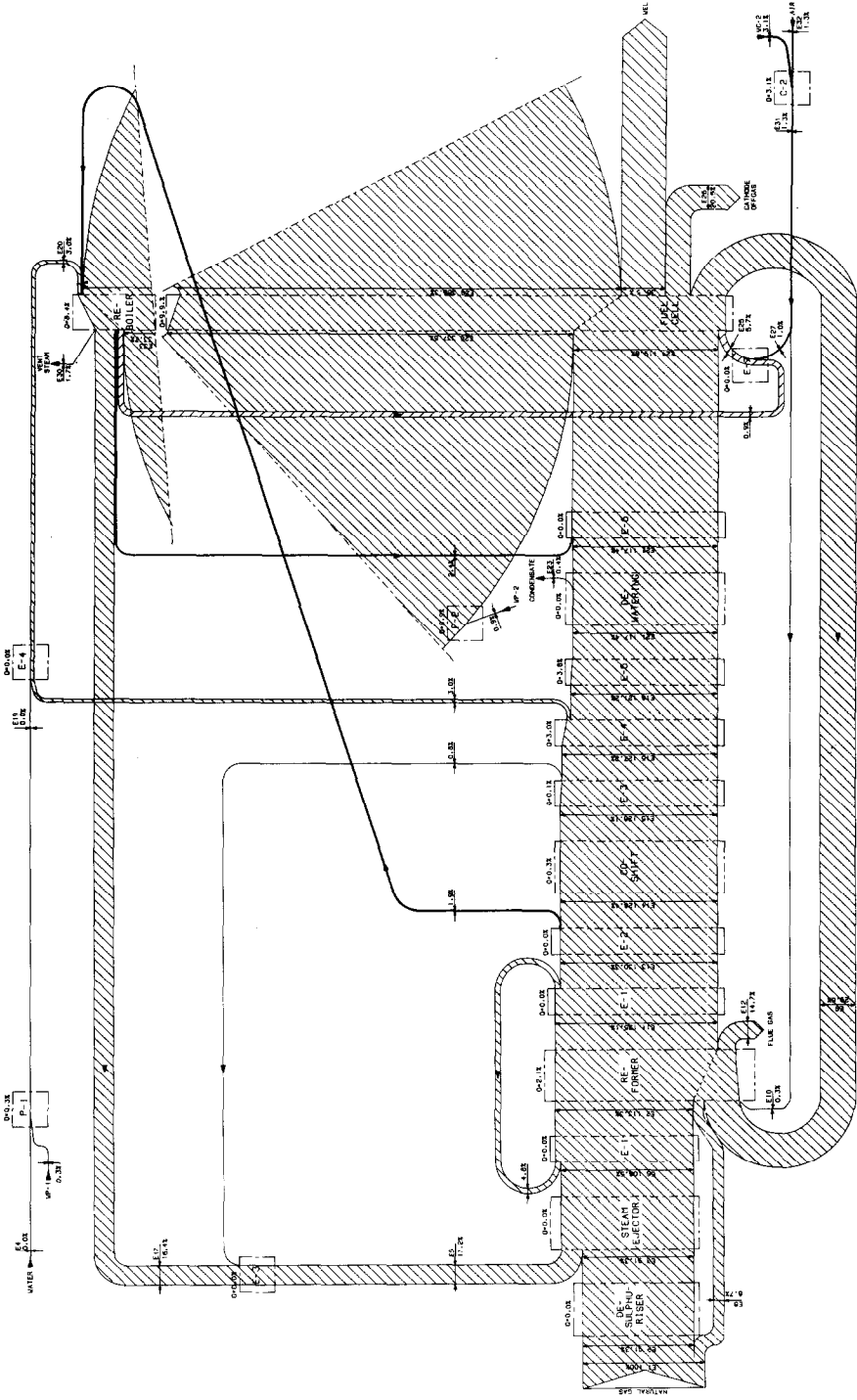


Fig. 3. Sankey diagram fuel cell system.

Natural gas is first desulfurized (R-1A/B). The gas is then compressed and mixed with a steam venturi ejector (X-1). The compressor (C-1) is only used for start-up purposes. During steady-state operation this compressor is shut down. The gas/steam mixture passes to the reformer (H-1) via a preheat exchanger (E-1). The reformer heats the gas mixture and brings it into contact with a catalyst so that a reaction occurs giving a process gas containing H_2 , CO, CO_2 , H_2O (vapour) and a little residual CH_4 . The reformer is so arranged that the reformed process gas gives some heat to the incoming steam/natural gas mixture inside the reformer. The cooling process is completed in the preheater (E-1). The process gas passes to the low temperature shift reactor (R-2) where further H_2 is produced in the presence of a catalyst. The process gas then passes to another heat exchanger (E-3) where it is cooled, while process steam is superheated. Further cooling of the process gas in another heat exchanger (E-4) preheats boiler feed water. The next heat exchanger/condenser (E-5) continues this process using cooling water. The condensate is separated out in a knock-out drum (V-1). The dried process gas is then heated (E-6) before being fed into the fuel cell stack (X-2) at the anode. The fuel cell uses part of the hydrogen in the gas. The flue gases are vented up the flue gas stack, after giving up some of its residual energy to the reformer.

The air for combustion is provided by a blower (C-2). This same blower supplies air to the cathode of the fuel cell via a preheater (E-7) in the steam drum.

The demineralization units and filters (X-4, 6, 7, 8) provide boiler feed water for making process steam and ultrapure water for the cell cooling circuit. The boiler feed water is provided by a pump (P-1) and is then vaporized by an internal heat exchanger (E-8) present in the steam drum (V-2). The process steam generated passes to another heat exchanger (E-3) where it is superheated prior to mixing with natural gas.

In order to design the most synergic system, optimum system integration especially between fuel cell and fuel processor is important. Evaluation of the energy and exergy losses in the system are a helpful tool to achieve this optimum integration.

The conventional approach: the energy analysis

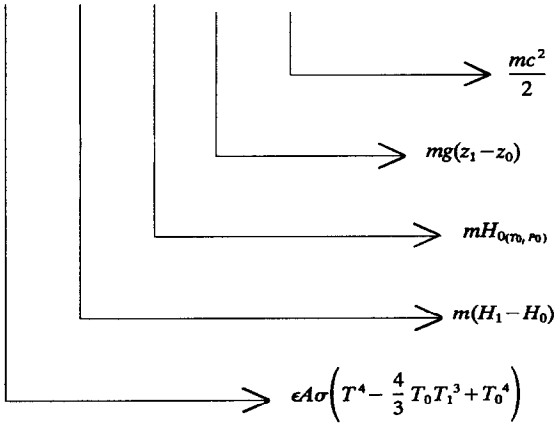
For the subject fuel cell system, a conventional thermodynamic analysis was used to provide information for the improvement of the design. The conventional approach is based on the first law of thermodynamics, which governs the conservation of energy.

An energy analysis of the relevant process streams was done using the general eqn. (1), which contains energy terms for radiation, thermal, chemical, potential and kinetics and may contain additional energy terms (e.g., magnetism) as well.

Substitution of the necessary process data in eqn. (1) gives the energy content of every stream. The energy terms for momentum, radiation emission and gravity are assumed to be negligible. Before carrying out the calculations the parameters T_0 , P_0 , H_0 and Z_0 of the reference environment have to be defined, which are the reference ambient temperature, reference ambient pressure, the reference enthalpy at ambient conditions and the reference height level. The chosen reference values are arbitrary since the reference environment is due to continuing changes. Therefore it is very important to mention the chosen reference parameters. The chosen reference parameters used in this paper are $T_0=298$ K, $P_0=10^5$ Pa (1 bar). The reference enthalpy values are, by convention, based on the heat of formation (at reference conditions of T_0 , P_0) and the C_p value of the respective components.

The results of the calculations of the fuel cell system can conveniently be represented in a Sankey diagram (Fig. 3). The width of a stream in the Sankey diagram is proportional

$$\text{Energy} = En_r + En_{th} + En_{ch} + En_p + En_k + \dots \quad (1)$$



to the amount of energy. The most important streams are the incoming natural gas, which has been defined as 100% and the produced electrical power W_{elec} , being 36.5% of the energy available in the incoming natural gas. The heat produced by the fuel cell is transported to the reboiler to produce steam. The hydrogen-rich anode off-gas is used as a main fuel for the reformer burner. In the Sankey diagram, the energy losses (relative to the energy of the system inlet stream (E-1)) due to compressor (C-2) and pumps (P-1) and (P-2) are also mentioned.

From the diagram one can conclude that the largest energy losses occur in the outlet streams, viz. 20.5% (cathode off-gas) and 14.7% (flue gas from reformer), followed by smaller energy losses of 9.9% in the fuel cell and 8.4% in the reboiler.

A more powerful approach: the exergy analysis

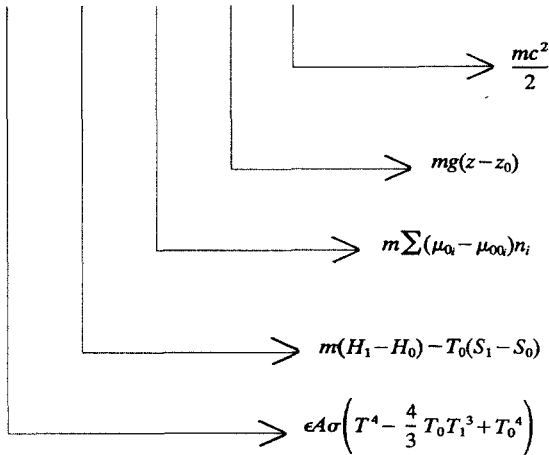
Energy exists in many different forms like work, heat, electrical energy, enthalpy, etc. The second law of thermodynamics indicates the restriction of the transformation of energy from one form into another in a very distinct way.

Exergy is defined as the maximum amount of work that is available in a gas, fluid or mass as a result of its nonequilibrium condition relative to an environment reference point. More precisely, exergy is the maximum work potential of a system, stream or matter or a heat interaction in relation to a reference environment as the datum state. The reference environment, the so-called dead state [6], is characterized by a perfect state of equilibrium, i.e., absence of any gradients or differences involving pressure, temperature, chemical potential, kinetic energy and potential energy. The environment constitutes a natural reference medium with respect to which the exergy of different systems is evaluated. Unlike energy and mass, exergy is not subject to a conservation law.

The different exergy terms are presented in eqn. (2), which contains exergy terms for radiation, thermal, chemical, potential and kinetics (again additional terms for exergy may be added).

Comparing eqns. (1) and (2) important differences are found in the thermal and chemical terms. The major difference is the presence of the entropy parameter, S ,

$$\text{Exergy} = Ex_r + Ex_{th} + Ex_{ch} + Ex_p + Ex_k + \tag{2}$$



which is a consequence of the second law of thermodynamics [7]. The exergy terms for momentum, radiation emission and gravity are again assumed to be negligible. Another difference between the two equations is the added parameter μ_{00} , the chemical potential of the dead state. The chemical potential has to be defined for each individual chemical component. Although there is no standard definition available of the reference environment, the differences between the various proposed reference environments are not substantial for the system under evaluation. In this paper the reference environment according to Gaggioli [8] has been chosen for practical reasons. The differences between these reference environments are marginal for most of the components used in the fuel cell system [9–11]. The component ‘water’ is, however, subject to large differences in the different reference environments. An explanation for the differences is the huge variation of water in our surroundings [12], dependent on time and location. The Gaggioli standard has been chosen for calculation of the exergy values of water and its vapour.

The exergy data can conveniently be presented by an equivalent method as the energy data in a so-called Grassmann diagram [6] (Fig. 4). Since the produced electrical energy is equal to the amount of exergy (as electrical energy can be nearly completely converted into work) the scalable width of ‘ W_{elec} exergy’ is defined in the same manner as the width of W_{elec} energy. The exergy of the incoming natural gas is in this case also defined as 100%. The produced electrical exergy W_{elec} is 39.1% of the exergy available in the inlet feed+fuel stream. The amount of exergy produced as heat in the fuel cell is about 7% of the exergy in the system inlet stream.

From the exergy analysis it can be concluded that the largest irreversibilities occur in the reformer and the fuel cell and to a lesser extent in the reboiler and the steam ejector.

Engineering tool for exergy analysis

In order to carry out energy and exergy analyses, it is mandatory to have a programme integrated with a widely-used engineering design package. Aspen Plus has

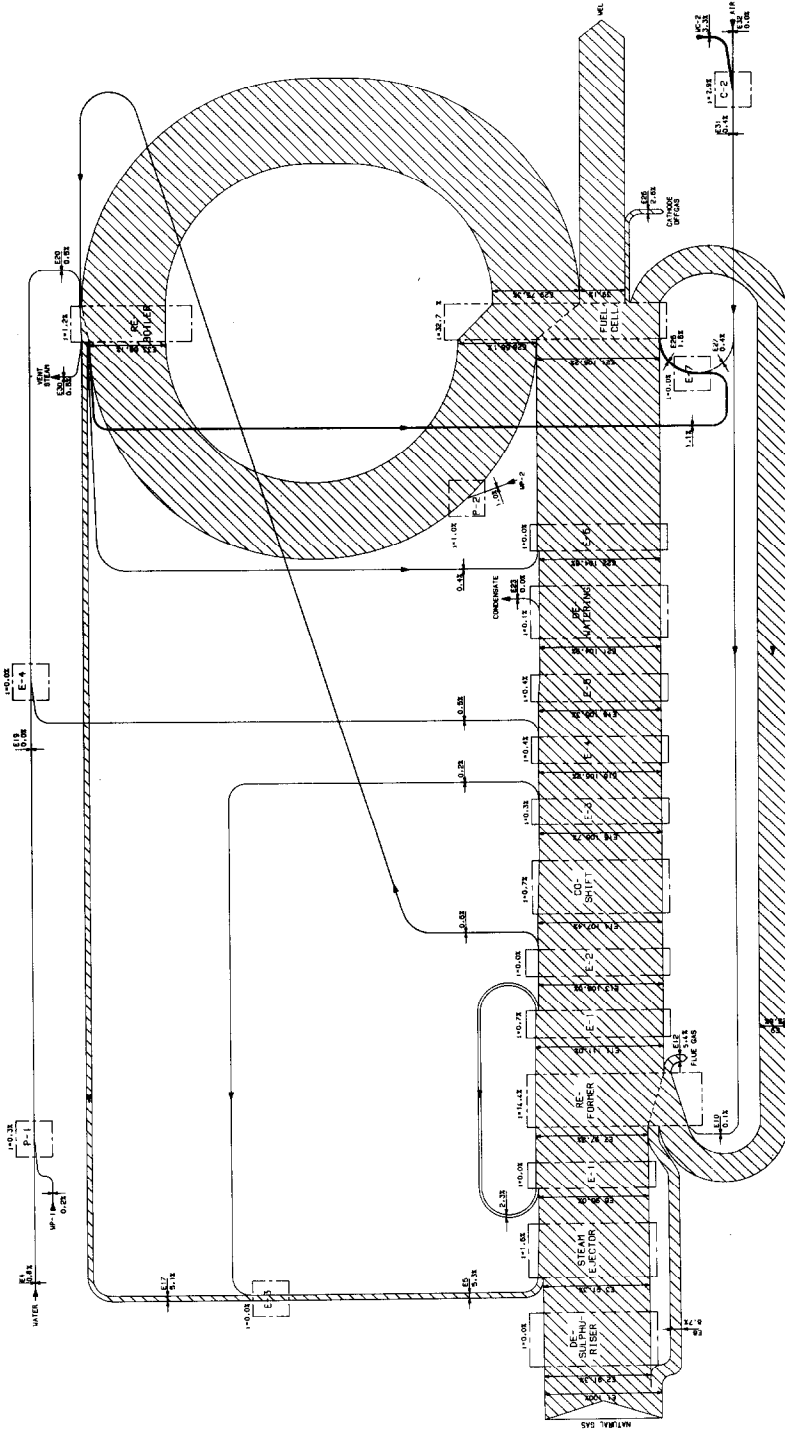


Fig. 4. Grassman diagram fuel cell system.

been used as the tool for the calculations presented in this article. The standard Aspen Plus programme, however, does not offer the possibility to perform exergy calculations. By expanding the standard Aspen Plus process simulation programme with a suitable Fortran extension programme [13] exergy calculations are possible. Such an exergy Fortran code has been developed by Rosen [9, 14–17]. Although the Fortran exergy code is still in a development phase state, satisfactory exergy calculations could nevertheless be obtained.

Results and discussion

The main results are presented in Fig. 5, showing the overall energy and exergy losses of the most important process units. Figure 5 shows the different loss percentages of the system's feed and fuel by the energy and exergy method.

The losses associated with waste emissions, for example the 'flue gas reformer' and the 'cathode off-gas' are significant on an energy basis, but they are relatively insignificant on an exergy basis. These off-gases, which have mainly low-grade heat, primarily consist of combustion gases. The potential usefulness for further system integration of these off-gases is therefore limited (unless for cogeneration if low-grade heat can be employed, e.g., in city heating).

The exergy losses, which occur in the reformer and in the fuel cell, are due to irreversibilities associated with combustion *casu quo* oxidation processes and heat transfer across large temperature differences. Besides electrical energy the fuel cell also produces heat. The energy and exergy values of the produced electrical energy and low-temperature heat are compared in Table 1.

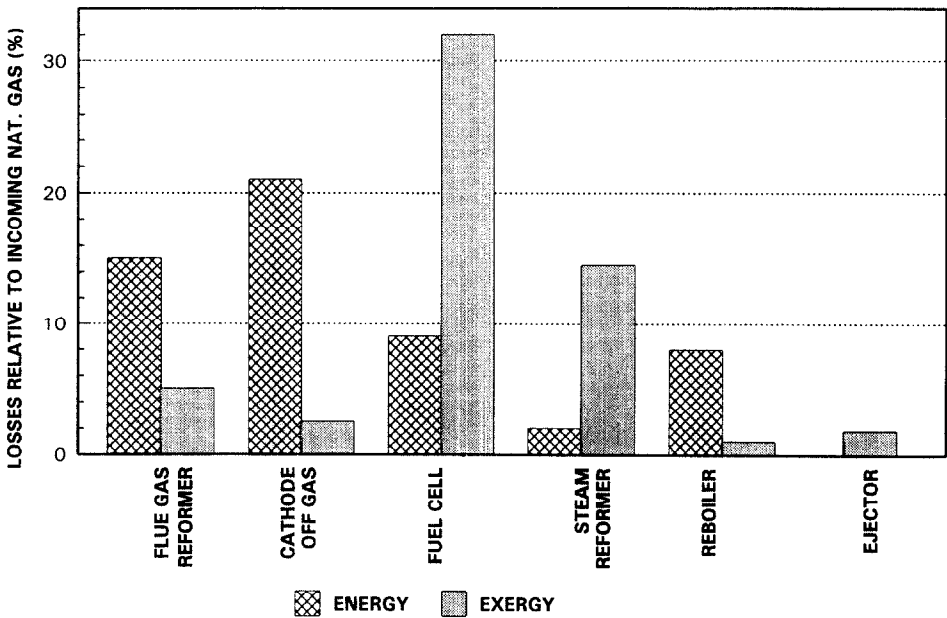


Fig. 5. Energy and exergy losses.

TABLE 1
Produced electrical energy and heat by the fuel cell

	W_{el}	Q
Energy (kJ/h)	90000	84000
Exergy (kJ/h)	90000	27000

The large differences, being a factor 3, between energy and exergy content of Q can be explained with the Carnot efficiency [18, 19]. Equation (3) shows the relation between the amount of heat and the available work, which is equivalent to the exergy content, that can be obtained from a heat source:

$$\text{Work} = Ex_Q = \eta_{\text{Carnot}} Q = \frac{T_1 - T_0}{T_1} Q \quad (3)$$

Increasing the working temperature of the fuel cell would reduce the exergy loss, but this is restricted due to material limitations. Further improvements of the units can be studied by making an exergy balance [6].

The significant exergy losses are due to the evaporation of the reboiler water, which is a consequence of the involved entropy increase.

The relatively high exergy losses in the steam ejector are a result of the increase in entropy due to the mixing of the two gases.

The significant exergy loss in the fuel cell stack (Fig. 5) is related to the two-phase (water/steam) cooling system. A single phase cooling system would reduce the exergy losses in the fuel cell stack significantly.

The most important energy losses are associated with the off-gases and waste emissions, while the most important exergy losses are due to internal irreversibilities in the process. The energy analysis does not take into consideration the degradation of energy during the transformation, but the exergy analysis does. The explanation is found in the extra term in eqn. (2), the entropy S , which always increases due to the process irreversibilities.

The fuel cell system's concept of integration [20] with respect to the process limitations is principally correct, because internal irreversibilities and operation limitations are mainly responsible for the occurred exergy losses. Further system efficiency improvement can only be achieved through optimization of the single process units themselves.

Conclusions

The exergy analysis is superior to the energy analysis as it gives a better insight into the irreversibilities of the process. Unlike exergy analysis, the energy analysis does not take into consideration the degradation of the transformed energy. The insights gained with the exergy analysis are the accurately pinpointed locations, where the irreversibilities do occur.

For the fuel cell system significant exergy losses are associated with the reformer and the fuel cell. The overall system design is principally correct, improvements can only be achieved by upgrading the physical limitations of the process units themselves.

Using the Aspen Plus programme with the Fortran extension it is possible to determine the exergy and energy losses of a process in a systematic way and thus optimize designs with respect to exergy and energy losses.

Acknowledgements

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List of symbols

En	energy flow, J s^{-1}
Ex	exergy flow, J s^{-1}
H	enthalpy, J kg^{-1}
T	temperature, K
c	velocity, m s^{-1}
z	height level, m
m	mass flow, kg s^{-1}
P	pressure, Pa
σ	Stefan Boltzman constant, $\text{J s}^{-1} \text{m}^{-2} \text{K}^{-4}$
μ	chemical potential, J mol^{-1}
n	mol per mass, mol kg^{-1}
ϵ	emissivity, -
W_{elec}	electrical power, J s^{-1}
Q	heat flow, J s^{-1}
A	surface area, m^2
C_p	specific heat, $\text{J kg}^{-1} \text{K}^{-1}$
S	entropy, $\text{J K}^{-1} \text{kg}^{-1}$

List of subscripts

r	radiation
th	thermal
p	potential
k	kinetic
ph	physical
ch	chemical
i	chemical component
1	actual state
0	standard environmental state
00	dead state

Terminology

Environmental state [9]

The state of a system when it is in *thermal* and *mechanical* equilibrium with the reference environment, i.e., at pressure P_0 and temperature T_0 of the reference environment.

Dead state

The state of a system when it is in *thermal, mechanical and chemical* equilibrium with a conceptual environment (having intensive properties pressure P_0 , temperature T_0 , and chemical potential μ_{i00} for each of the reference substances in their respective dead states).

Reference environment

An idealization of the natural environment which is characterized by a perfect state of equilibrium, i.e., absence of any gradients or differences involving pressure, temperature, chemical potential, kinetic energy and potential energy. The environment constitutes a natural reference medium with respect to which the exergy of different systems is evaluated.

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