

Analysis of energy and water management in terms of fuel-cell electricity generation

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Abstract

Hydrogen-powered low-temperature fuel cells (PEFCs) are the energy conversion units in vehicles with methanol as the energy carrier and a power train consisting of the following main units: methanol reformer (H₂ production) including catalytic converter, gas treatment, PEFC with peripheral units, electric motor with electric controllers and gearbox. The process engineering analysis is based on a simulation model and describes the energy and water management as a function of different assumptions as well as operating and ambient conditions for net electricity generation in a PEFC-powered power train. In particular, it presents an approach for balancing both water recovery (PEFC) and the use of water for the methanol reforming process as well as for the humidification of the PEFC. The overall balances present an optimised energy management including peripheral air compression for the PEFC. © 1998 Elsevier Science S.A.

Keywords: PEFC; Fuel cell; Electricity generation; Power train; Methanol reformer; Water management

1. Process analysis of the drive system

The drive system conceived at the Research Centre Jülich (FZJ) with methanol as the energy carrier, fuel gas production with subsequent gas treatment (Pd/Ag separation membrane) and low-temperature fuel cell (PEFC) including peripheral components will be presented and analysed using a commercial program system. This selected drive system is subjected to a process analysis; the major points of interest are fuel gas production, energy balance, cathode air supply and water regime.

2. Program system

The commercial program system applied here contains a large number of different components, such as heat exchangers, chemical reactors, blowers and tubes, which can thus be balanced as process engineering steps. By a meaningful combination of these components it is possible to describe complete systems in terms of process engineering without having to know the structural design of the individual components.

The computer program considers, in particular, material

and energy flows using an integrated physical property library. The physical properties available in this library are internally processed by means of selectable thermodynamic methods. The selection of the method is governed by the problem; in the present case, for example, the gas equation after Soave-Redlich-Kwong is used; the Wilson equation and Henry's law are essentially used for the description of gas-liquid equilibria.

3. Fuel gas production

Within the overall process under consideration (Fig. 1) the production of hydrogen fuel gas from methanol fuel is of particular significance. The investigation of the different possibilities makes methanol-steam reforming appear particularly promising.

Methanol and water are pressurised to operating pressure, evaporated in heat exchanger E1 and superheated in heat exchanger E2, as well as converted into a hydrogen-rich gas in reformer R1 (Fig. 1).

The boiling temperatures of the water/methanol mixture (Fig. 2) are clearly dependent on mixture quality and pressure and are considered in the heating procedure (see Section 5, Fig. 4).

The catalytic reforming of methanol with steam – in

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comparison with hydrocarbon reforming – already offers the possibility of hydrogen recovery, i.e. fuel gas production for the fuel cell, at low temperatures.

With the conditions selected in the computer model

- water/methanol ratio; $M = 1.3$
- reforming temperature; $\vartheta = 250^{\circ}\text{C}$
- reformer pressure; $p = 20$ bar.

A specific yield of up to $450 \text{ mol H}_2/\text{h dm}^3_{\text{cat}}$ is achieved at a Cu/Zn contact. In the model under consideration, equilibrium is assumed (Table 1, BL 4). For the currently available anode catalysts of the PEFC, CO in concentrations of >10 ppm constitutes a temporary catalyst poison. In the reformer product, the fraction is always in the % range so that gas treatment becomes necessary. The high reformer pressure (20 bar) leads to a sufficiently high H_2 partial pressure (13.2 bar), as is required for treating the fuel gas with a Pd/Ag membrane as a filter for achieving high hydrogen permeation rates [2].

Behind the permeation filter, the hydrogen is directly cooled with water in the quench cooler B2, so that the fuel gas is simultaneously humidified before entering the fuel cell on the anode side.

The respective balancing location can be seen from the flow chart (Fig. 1) and the energy flow diagram (Fig. 10)

4. Low-temperature fuel cell

The fuel cell in the process model uses a proton exchanger membrane as the electrolyte [12] whose working temperature is below 100°C . It is currently regarded as particularly promising for use in motor vehicles.

Due to the cell reaction the necessary water is generated in the cell itself. However, as will be shown in the following, the usability of this product water depends on the operating data of the cell and on external conditions. Water entrained with hydrogen into the anode compartment tends to migrate as a solvating envelope to the cathode where the water of the cell reaction is produced. In order to use this water for membrane humidification, adequate pressure conditions must be ensured. The absorptive capacity of a gas for water at different temperatures and pressures, as shown in Fig. 3, initially appears to be trivial, but is indicative of the comparatively small working window. If the dew-point temperature applicable to the respective pressure (Fig. 3) is exceeded or the value falls below the condensation pressure for a temperature, water can be evaporated from the membrane so that the latter becomes dry. Proper humidification of the membrane is a prerequisite for its high proton conductivity and thus also for a high power density. The resistivity increases with progressing desiccation so that a failure may ultimately arise [10]. Desiccation of the membrane also

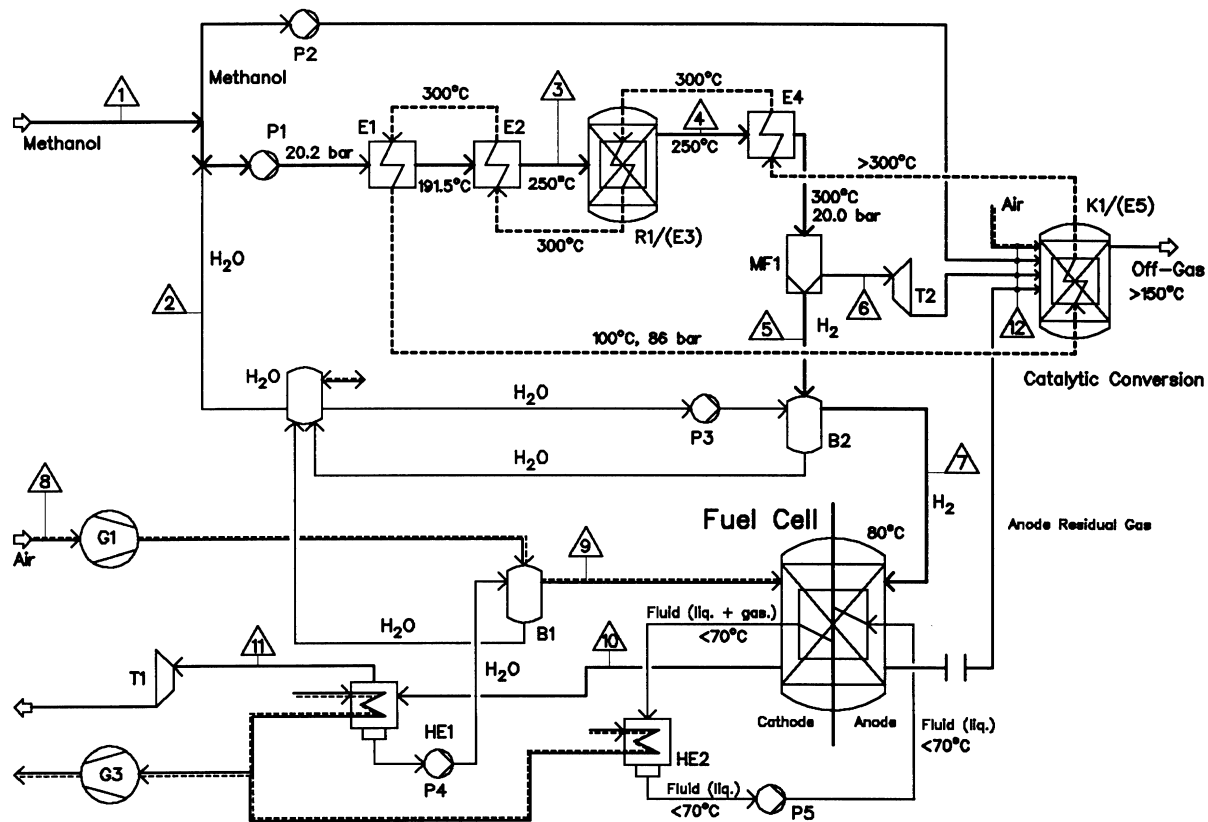


Fig. 1. Overall process. Triangles = balancing locations (BL), see Table 1; P, pump; E, heater; R1, reformer; MF1, membrane filter; K1, catalytic converter; B, humidifier/quench cooler; T, expansion turbine; G, blower; HE, cooler.

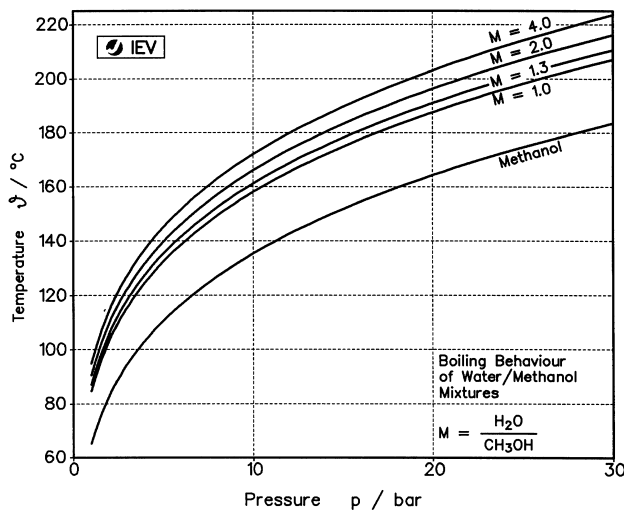


Fig. 2. Boiling behaviour of water/methanol mixtures.

involves shrinkage, i.e. the occurrence of mechanical stresses, the permeability for permanent gases increases, and both contributes to a possible failure.

5. Process heat and off-gas

In the proposed system with hydrogen purification by a Pd/Ag permeation filter, the residual gas from the filter, the retentate, can be converted with air into a low-pollution off-gas in the catalytic converter K1, a catalytic burner [4,11]. The heat released is used for evaporating the water/methanol mixture and for methanol reforming through a heat transfer system (Fig. 4) [5]; the heat production required for evaporating and superheating the water/methanol mixture and for reforming and superheating the reformat to the filter operating temperature is supplemented by the conversion of additional methanol in this catalytic converter, producing superheated steam at a pressure of 86 bar ($\vartheta \approx 330^\circ\text{C}$). Fig. 4 shows the temperature profile of the heat transfer system and, in particular, how heat is first given off to the Pd/Ag filter with decreasing temperature of the heat transfer medium, then for isothermal reforming, superheating and evaporation of the water/methanol mixture at the condensation temperature of $\vartheta \approx 300^\circ\text{C}$, and finally for warming the water/methanol mixture to about 190°C while the heat transfer medium is further cooled (water $< 300^\circ\text{C}$).

6. Cathode air supply

The cathode air is compressed and then humidified and cooled in the quench cooler B1 (Fig. 1) before giving off oxygen for the cell reaction at the cathode in the cell, taking up product water and heating up to cell temperature. After leaving the cell, condensable water is cooled and separated in the cooler and condenser HE1, and finally expanded.

For cell operation with air as the oxidation gas, a significantly higher excess of oxygen is necessary compared to operation with pure oxygen. Fig. 5 shows the general trend, i.e. an increase in cell voltage by increasing the excess air, described here by the air ratio (λ), is limited. Changes in the pore structure of the cathode can influence the transport mechanism and lead to different results; according to the measurements, ($\lambda = 2.5$ is the maximum value to be used and also the nominal value for calculating the water regime of the system; see Section 7).

At a pressure on the cathode side clearly above the anode pressure, advantages are achieved for the cell voltage, but also a greater stability of the I/U characteristic. There is then a permeation possibility for the product water towards the anode [10]. This at least in part eliminates the need for evaporation of the product water produced in liquid form in the pore system of the cathode and leading to Poiseuille flow.

7. Water management

Methanol reforming and the humidification of process gases requires water which should not be additionally provided, but produced in the system itself. The recovery of product water for these purposes influences the apparatus expenditure for cathode air management, but also clearly depends on external conditions such as air temperature and relative air humidity.

The Pd/Ag permeation filter for hydrogen separation from the synthesis gas provides a hydrogen quality which permits cell operation almost without anode off-gas. Actually occurring impurities can leave the cells with a continuous or discontinuous off-gas stream. In the example examined, these impurities are so small that they are within computational error and are neglected. This permits calculations with a fuel utilisation of 100%. Based on this

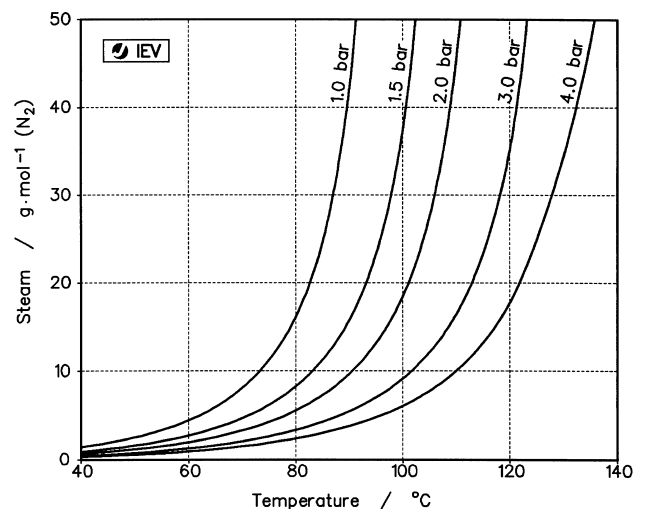


Fig. 3. Absorptive capacity of gases for water vapour at different overall pressures.

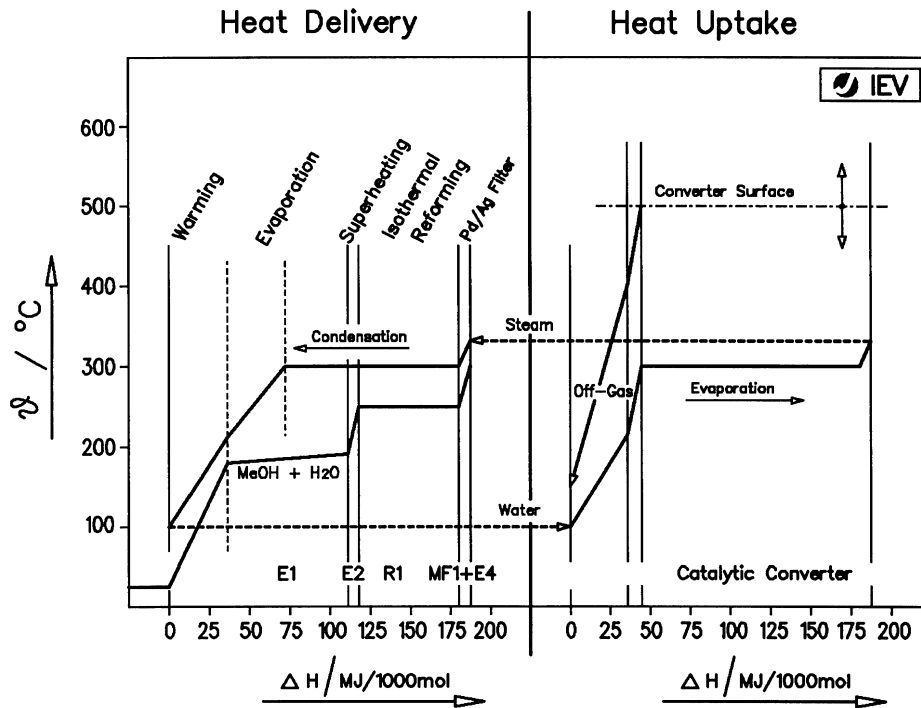


Fig. 4. Temperature profile of the heat transfer system.

assumption and on a corresponding pressure control between cathode and anode, ($\Delta P \leq 0.3$ bar), not only the product water but also the water introduced by humidifying the fuel cell gas stream will exclusively arise on the cathode side, as does the adhering water from natural humidity and humidification of the fresh cathode air.

If the cell is operated with markedly higher pressure differences, $\Delta P > 0.5$ bar, part of the water migrating towards the anode due to hydraulic pressure will arise on the anode side. In this case, water separation must take place on both operating sides. If, however, the cathodic dew point is below the membrane temperature, i.e. the cell temperature, no hydraulic exchange will take place since the water on the membrane surface is already transformed into the vapour phase.

The total amount of water remains the same and will be regarded in the following as if it were produced exclusively on the cathode side, on which the main amount of water is left even in the case of very large pressure differences, $\Delta P \geq 1.5$ bar. The objective of examining the water management is to determine the amount of condensable water as a function of:

- the partial pressure of water vapour; and
- the temperature of the cathode exhaust air.

This correlation is shown in Fig. 3 at elevated temperatures.

The partial water vapour pressure is influenced by:

- the amount of fresh air;
- the fresh air temperature;

- the relative air humidity; and
- the working pressure.

The temperature of the cathode exhaust air after leaving the cell, and thus the temperature at which the water vapour contained in the air can be condensed, is determined by:

- ambient temperature; and
- apparatus conditions (here HE1 (Fig. 1)).

Figs. 6–8 show the excess water of the entire PEFC system according to Fig. 3. The amounts of water to be provided for reformation and humidification in the quench

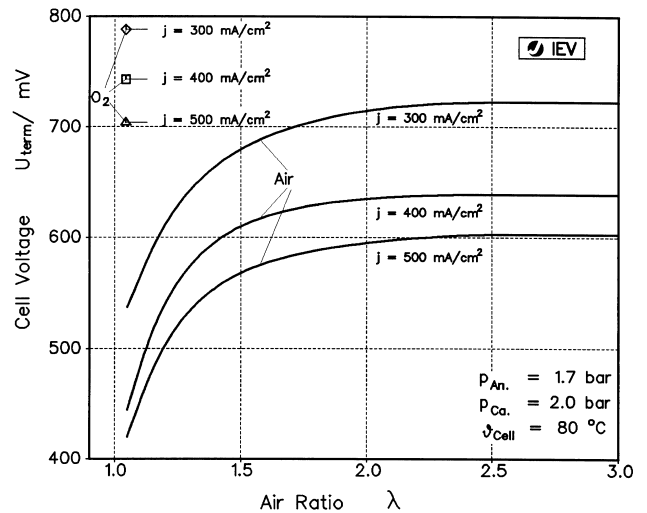


Fig. 5. Influence of the air ratio λ on the current/voltage characteristic of the PEFC (membrane electrode assembly: Giner, series no. 454-31-2).

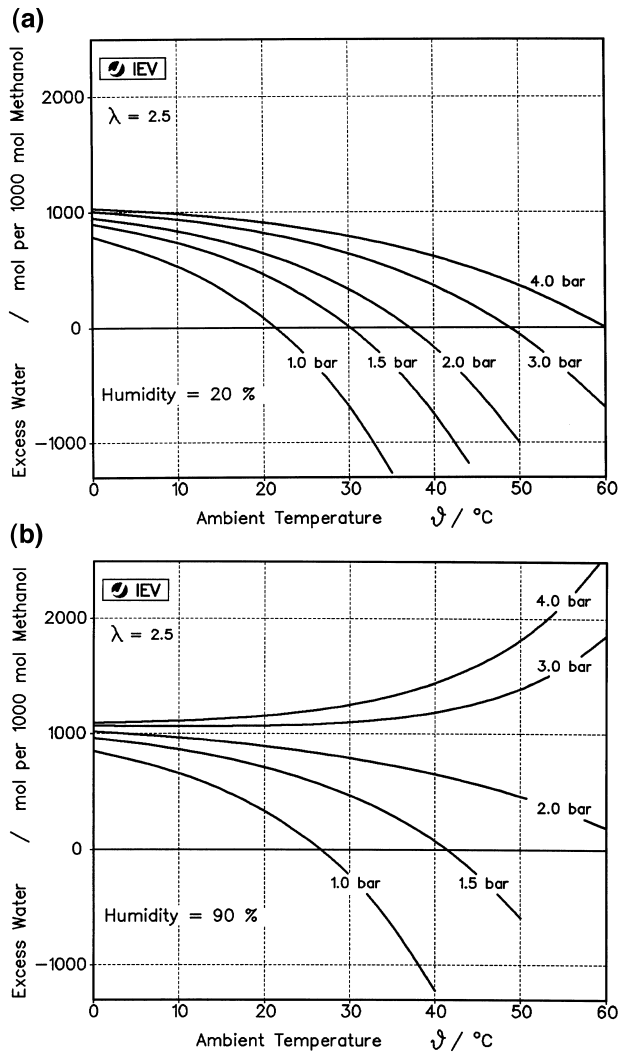


Fig. 6. Influence of ambient temperature and relative humidity on the water regime of a PEFC system at different cathode pressures.

coolers are already included. The negative region of excess water (y-axis) always indicates the additional demand to be covered from outside in the concrete case.

The reference point of 1000 mol methanol represents the amount of methanol in front of the reformer; for heating and reaction enthalpy it will be necessary to additionally provide heat from methanol by conversion in the catalytic converter (see Sections 5 and 8).

If a temperature difference of 20 K (cathode exhaust air versus coolant fluid temperature) achievable at HE1 is used with an air ratio of $\lambda = 2.5$, Fig. 6a,b shows the pronounced dependence of the recoverable amount of water as excess water on:

- ambient temperature;
- relative humidity of the fresh cathode air; and
- working pressure on the cathode side.

The influence of the air ratio on the amount of condensable water becomes apparent in Fig. 7a,b. With a small air ratio it is possible to recover the amount of water necessary

for operating the system even at low cathode pressure and under unfavourable ambient conditions (example: $\lambda = 1.1$, ambient temperature = 50°C, $p = 1.5$ bar, rel. humidity = 60%, excess water = 200 mol/1000 mol MeOH); elevated pressure permits higher air ratios, always for 60% relative humidity of the ambient air.

The data presented up to now apply to a heat exchanger (Fig. 1, HE1) at which a temperature difference $\Delta T = 20$ K versus ambient temperature can be reached. The influence of cooler and condenser quality is shown in Fig. 8a,b. Poor heat exchange considerably restricts the working range of the PEFC system with respect to the utilisation of the self-produced water, especially at low cathode pressure.

Fig. 9 provides an insight into the conditions in the cathode compartment with respect to the water regime. This calculation is based on the fact that all the water concerning the cell is exclusively seen in this part. Moreover, the results are only applicable to the process flow proposed in Fig. 1. As long as the temperature remains below the dew point

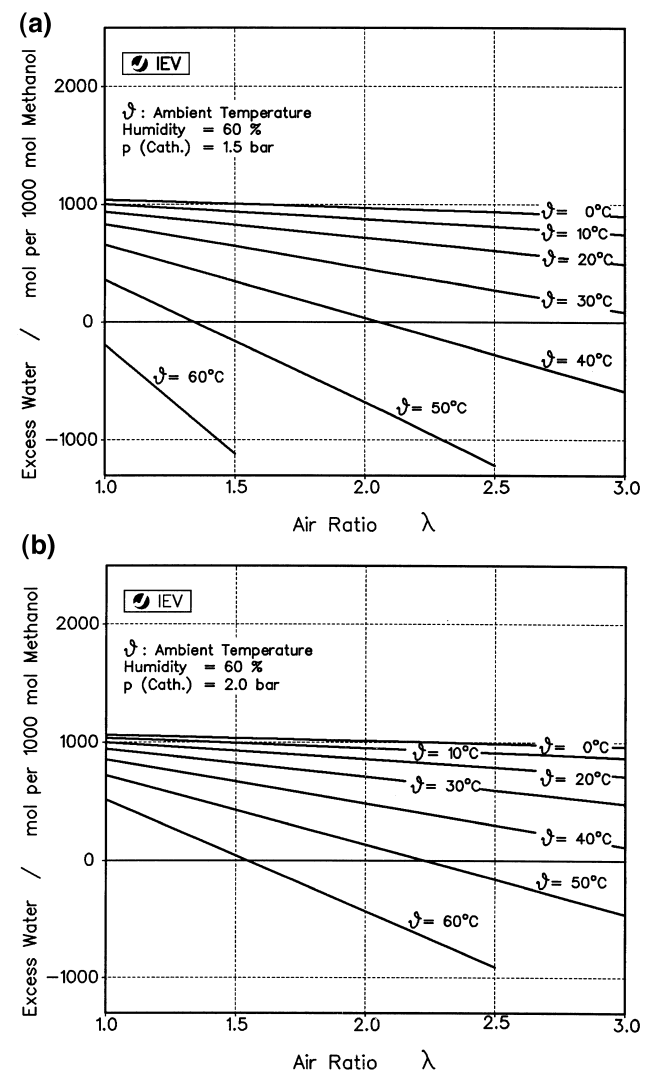


Fig. 7. Influence of air ratio and cathode pressure on the water regime of a PEFC system including ambient temperature and relative humidity.

immediately on the electrolyte membrane, the humidification necessary for proton conductivity is ensured. Above the dew point desiccation may occur; a temperature far below the dew point restricts transport in the porous supporting layer of the electrode catalyst.

8. Energy balance

The energy flow diagram in Fig. 10 can be regarded as a consistent result. It shows the energy consumption for vaporisation, superheating and reformation of the water-methanol mixture for the production of the cell fuel gas.

The major portion of the heat required for vaporisation, superheating and reformation can be recovered by the catalytic converter from the flue gas of hydrogen purification in this process configuration; a smaller portion originates from methanol additionally converted there. The methanol conversion rate relevant for the energy balance can be com-

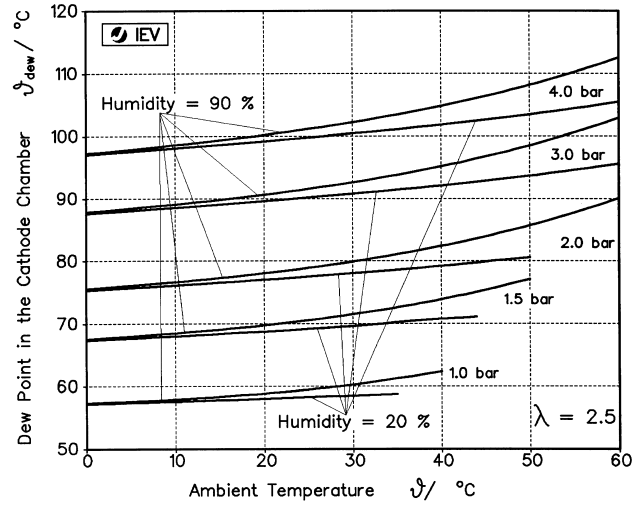


Fig. 9. Dew point in the cathode compartment including relative humidity and cathode pressure.

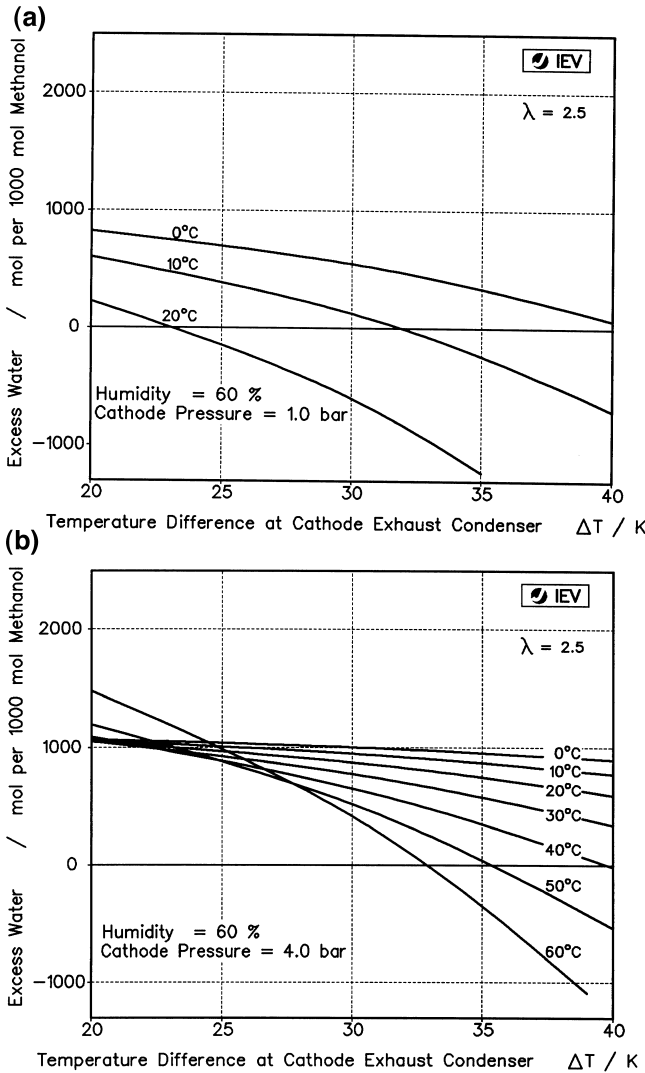


Fig. 8. Influence of cooler efficiency and cathode pressure on the water regime of a PEFC system at different ambient temperatures.

pletely observed by a comparison of the material flows at the individual balancing locations (BL) for this exemplary operating case, (see Table 1, Figs. 1, and 10).

Heat losses at the devices are left out of the balance calculation; they are particularly dependent on the design. A compact design can minimise losses at this point and, together with the cathode exhaust air, can serve for heat supply at a low temperature level.

The power for compressing the cathode air is particularly dependent on the necessary operating parameters. For the case described, the following boundary conditions are applicable:

- rel. humidity = 65%
- ambient temperature = 25°C

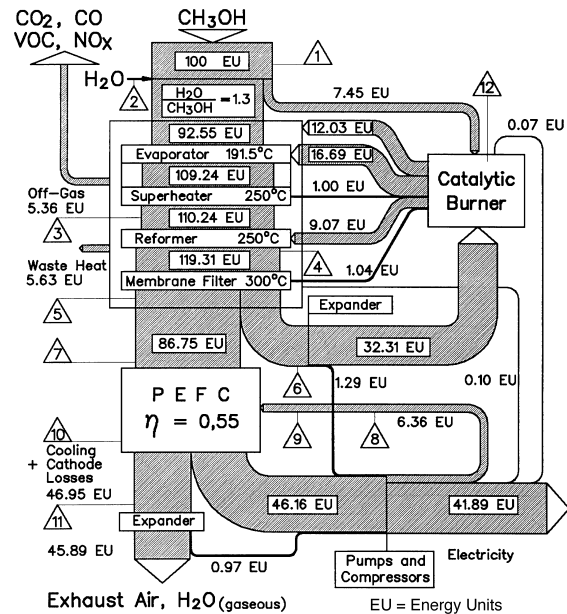


Fig. 10. Energy flow in a PEFC system with reformer and catalytic converter. EU, energy units.

Table 1

Gas stream according to the balance example

BL	1	2	3	4	5	6	7	8	9	10	11	12
Gas (<i>n</i>)												
CH ₃ OH	1080.5	–	1000	27.8	–	27.8	–	–	–	–	–	108.3
H ₂ O	<0.2	1300	1300	404.4	–	404.4	376.1	316.6	1121.3	3914.9	688.7	451.9
H ₂	–	–	–	2839.9	2417.2	422.6	2417.2	–	–	–	–	422.6
CO	–	–	–	76.5	–	76.5	–	–	–	–	–	76.5
CO ₂	<0.2	<0.2	<0.2	895.6	–	895.6	–	5.2	5.2	5.2	5.2	896.4
O ₂	<0.2	<0.2	<0.2	–	–	–	<0.2	3021.6	3021.6	1812.9	1812.9	453.3
N ₂	<0.2	<0.2	<0.2	<0.2	–	<0.2	<0.2	11719.0	11719.0	11719.0	11718.9	1758.2
Ar	<0.2	<0.2	<0.2	<0.2	–	<0.2	–	135.1	135.1	135.1	135.1	20.3
Σ <i>n</i>	1081	1300	2300.1	4244.4	2417.2	1827.1	2793.4	15202.7	16002.3	17665.6	14610.7	4187.5
ϑ (°C)	25	25	250	250	300	300	63	25	53	80	45	53
p (bar)	1.0	1.0	20.1	20.0	1.7	20.0	1.7	1.0	2.0	2.0	2.0	1.0

BL, balancing locations according to Figs. 1 and 10. The respective balancing location can be seen from the flow chart (Fig. 1) and the energy flow diagram (Fig. 10).

- air pressure = 1000 hPa
- cathode pressure = 2.0 bar
- air ratio $\lambda = 2.5$
- compressor efficiency = 0.6

A particularly important variable concerning the energy yield of the system is the necessary power of the cathode air compressor. The power of the compressor drive, neglecting a performance chart which includes the efficiency applicable in the concrete case, is directly proportional to the amount.

Attention must be additionally paid to the change in volume of the amount of air to be compressed due to air humidity. Elevated humidity also means an additional gas (as steam) for the same amount of oxygen, which requires more power for compression. Fig. 11 shows the small influence of air humidity at low temperatures, i.e. in absolute terms, low water vapour fraction, and the increase of the necessary power at higher temperature and higher air humidity. The data were calculated for an air ratio of $\lambda = 2.5$ for an adiabatic efficiency of compression of $\eta = 0.6$; the reference here is the input of 1000 mol of methanol/h in front of the reformer, i.e. 177.5 kW relative to the lower heating value.

9. Discussion

The operation of an electricity generating system with PEFC involves a great number of process engineering steps so that many facts and changing parameters must be considered for its optimisation.

- As long as only a very low CO concentration is permitted in the fuel gas, a filter, here the Pd/Ag membrane, remains justified; this requires high pressure for steam-methanol reformation. The high purity of hydrogen enables almost complete fuel utilisation.

- Residual gas (retentate from the filter) and minor amounts of residual anode gas are quantitatively converted at the catalytic converter and used for heat supply of the system.

The water requirement of the system is linearly dependent on the power requirement of the entire drive system as a reaction partner in methanol reforming; added to this is water for the necessary humidification of the PEFC membrane. The water needed can be produced in the system itself.

- Low relative air humidity and high ambient temperatures reduce the possibility of water separation.
- A decrease in the amount of cathode air and high cathode pressure improve water separation.
- A deterioration in the efficiency of the condenser for cathode exhaust air reduces the possibility of water separation.

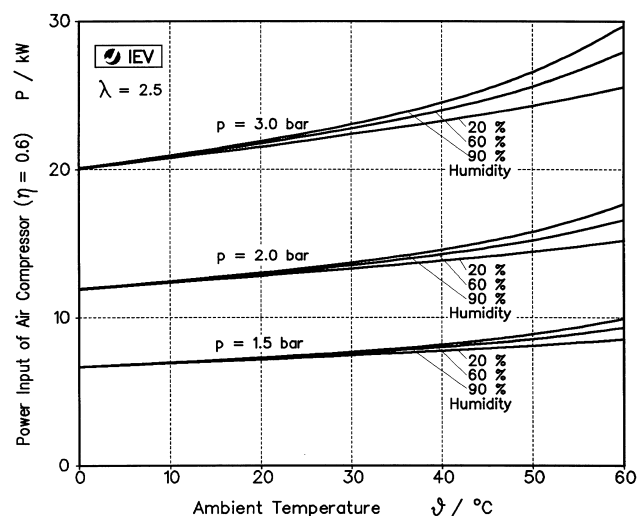


Fig. 11. Influence of air temperature, relative humidity and cathode pressure on the power input of an air compressor in the PEFC system (1000 mol MeOH/h = 177.5 kW lower heating value).

The water formed in the PEFC, however, cannot be recovered within the balance limits under all conceivable operating and ambient conditions (ambient air temperature and humidity, air ratio, cathode pressure) to such an amount that sufficient water is available for the reformer. Any modification of the water separation potential must take account of the direct influence on the cell and the (parasitic) power input of the cathode air compressor, which amounts to approx. 13.8% in the example given (Table 1, Fig. 10, Section 8).

- Decreasing the amount of cathode air (air ratio λ) below a cell-specific limit value deteriorates the current/voltage characteristic of the fuel cell.
- Increasing the cathode pressure increases the required power input of the air compressor.
- Decreasing the amount of cathode air reduces the power input required at the air compressor.
- High atmospheric humidity at high ambient temperature requires a markedly increased compressor power for the same amount of oxygen.

The force necessary for operating a vehicle, and thus ultimately also the necessary propulsion power, is largely determined by the total mass of the vehicles, which is distinctly influenced by the mass of the electricity generating system. This influence will therefore have to be taken into account when optimising the complete driving system. In regions with extreme climatic conditions (high ambient temperatures and low air humidity) an additional water tank, for example, could therefore be more appropriate than a particularly high cell pressure, a large condenser (HE1, Fig. 1) and low cathode excess air.

Advantages of fuel cell electric drives with methanol as the fuel over conventional drive systems with internal combustion engines are also attributable to the fact that very low specific emissions per kilometre can be achieved for the

vehicle [8] as well as for the entire energy conversion chain with methanol production from natural gas [7].

Comparable drive systems are under development worldwide [1,3,6,9], priority being given to the technical feasibility of methanol reformers including catalytic converter, fuel cell and cathode air compressor. The present analysis shows that particular attention in component development must also be given to process engineering units such as mixture evaporators (methanol/water) and condensers for the cathode exhaust air.

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