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Increasing the electric efficiency of a fuel cell system by recirculating the anodic offgas

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Abstract

The University of Duisburg-Essen and the Center for Fuel Cell Technology (ZBT Duisburg GmbH) have developed a compact multi-fuel steam reformer suitable for natural gas, propane and butane. Fuel processor prototypes based on this concept were built up in the power range from 2.5 to 12.5 kW thermal hydrogen power for different applications and different industrial partners. The fuel processor concept contains all the necessary elements, a prereformer step, a primary reformer, water gas shift reactors, a steam generator, internal heat exchangers, in order to achieve an optimised heat integration and an external burner for heat supply as well as a preferential oxidation step (PrOx) as CO purification. One of the built fuel processors is designed to deliver a thermal hydrogen power output of 2.5 kW according to a PEM fuel cell stack providing about 1 kW electrical power and achieves a thermal efficiency of about 75% (LHV basis after PrOx), while the CO content of the product gas is below 20 ppm. This steam reformer has been combined with a 1 kW PEM fuel cell. Recirculating the anodic offgas results in a significant efficiency increase for the fuel processor. The gross efficiency of the combined system was already clearly above 30% during the first tests. Further improvements are currently investigated and developed at the ZBT.

Keywords: Steam reformer; Selective oxidation; Residential power supply; Efficiency; Anodic offgas; Recirculation

1. Introduction

Polymer electrolyte membrane fuel cells (PEM FC) are well qualified for household applications because of the high power density and the operating temperature level of about 60–80 °C to supply heat for hot water for domestic use or to support the room heating system of the building. The hydrogen rich steam reformat gas from natural gas is a suitable fuel for polymer electrolyte membrane fuel cells for residential power supply. Mainly autothermal reforming has been employed as hydrogen production process for these small scale processes in the power range of a few kilowatt. However, autothermal fuel processors generate gas qualities containing less than 50% hydrogen because of a high nitrogen content while the reaction heat is supplied by internal combustion of a part of the fuel gas with air. Fuel processors based on the autothermal concept appear to show advantages, transferring the necessary heat for the endothermic reforming reaction into the catalyst bed, during start-up and during load changes compared to fuel processors based on steam reforming. But with respect to product gas quality the steam reforming process shows benefits, because the endothermic reaction heat is provided by an external burner leading to hydrogen concentrations above 75% in the dry product gas. Furthermore, a higher overall system efficiency of the complete fuel cell system can be expected in case of steam reforming because the energy content of the anodic offgas, mainly unconverted hydrogen from the fuel cell stack, can be recovered in the reformer burner in order to supply heat for the reforming reaction.

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2. Experimental results of the fuel processor

The University Duisburg-Essen and the ZBT Duisburg GmbH have developed a compact multi-fuel steam reformer concept for residential power supply suitable for natural gas, propane and butane. One of the built fuel processors is designed to produce 2.5 kW_{th} hydrogen power, based on the lower heating value of hydrogen of 241 $kJ\,mol^{-1}$, which may lead to an electrical power output of about 1 kW, which is typical and suitable for a one-family household [1–3]. For reformer measurements introduced in the following methane was used as fuel gas in order to have exactly defined inlet parameters for the evaluation of product gas quality and reformer efficiency. In case of natural gas the fuel gas additionally has to be desulphurised in a bed of impregnated activated charcoal at room temperature from natural sulphur compound and odorants. After adding liquid water to the methane gas stream, evaporating the water and preheating of the mixture, the reactants are converted with the aid of a catalyst at temperatures of about 750 °C to form a mixture of gases consisting of H_2, CO_2, CO, residual CH_4 and residual steam. In the subsequent water gas shift conversion, the CO content can be reduced to less than 1% while the residual CO is removed in a fine purification unit, the preferential oxidation or PrOx. After passing through a particle filter the reformat gas can now be ducted to the PEM fuel cell, where electrical power and heat are generated.

The developed steam reforming based fuel processor concept is composed of low cost subunits that incorporate mainly standard components in order get a highly modular, compact and inexpensive system. A gas processing module forms a unit, consisting of a prereformer, a primary reformer, water gas shift conversion, steam generator, internal heat exchangers in order to achieve an optimised heat integration and an external burner for heat supply. All these components are housed in a well-insulated metal cylinder as shown in Fig. 1. A separate PrOx reactor is added to the fuel processor outside the insulated cylinder in order to achieve a less elaborate temperature control of the exothermic reaction of the CO purification. During steady-state operation the CO concentration of the product gas is below 20 ppm in the complete power range.

The presented fuel processor is designed to deliver a thermal hydrogen power output from 500 W as part load (according to 170 $l_{s.t.p.}$ H_2 per hour) to 2.5 kW (according to about 850 $l_{s.t.p.}$ H_2 per hour) at rated power. Several of these modules may be combined to meet higher power demands. The compact design of such a module facilitates the integration in a conventional heating system. Using commercially available burner systems and inexpensive catalyst materials can lead to an economically competitive fuel processor. The estimated target costs for the fuel processor are less than US\$ 350 kW_{el}^{-1} (as estimated based on mass production figures).

The reformer efficiency $\eta_{Reformer}$ may be defined as the lower heating value (LHV) of the produced hydrogen referred to the lower heating value of the used methane for reformer educt and for the burner heat supply.

Fig. 1. Photograph of the 2.5 kW_{th} compact steam reformer with separate PrOx as CO purification step in the test rig height: 600 mm, diameter: 280 mm.

$$\eta_{Reformer} = \frac{\Delta H_{u,H_2}}{\Delta H_{u,CH_4}} \frac{\dot{n}_{H_2,\,Product}}{\dot{n}_{CH_4,\,Reformer} + \dot{n}_{CH_4,\,Burner}}. \qquad (1)$$

This equation is one possible method to calculate the efficiency of the reformer and is suitable to characterise and to evaluate a stand-alone reformer system without recirculation of the anodic offgas. Only the produced hydrogen is defined as benefit and the methane for the burner and for the reformer is defined as effort. Using the higher heating value (HHV) of 285 $kJ\,mol^{-1}$ instead of LHV is also possible and usual.

Fig. 2 presents the main results of experimental tests to characterise the steady-state behaviour of the reformer as a function of the load, firstly without combining the reformer with the PrOx reactor. The gas composition (on dry basis) measured with an online gas analysis shows a high hydrogen content of the product gas, typical for steam reforming, which is slightly decreasing from 79.5 vol.% at 20% part load (corresponding to 0.5 kW_{th}) to 78 vol.% at rated power (corresponding to 2.5 kW_{th}). According to the hydrogen decrease, the CO content of the product gas and the content of residual methane is slightly increasing with respect to the load of the single reactors and the catalysts employed. The pre-

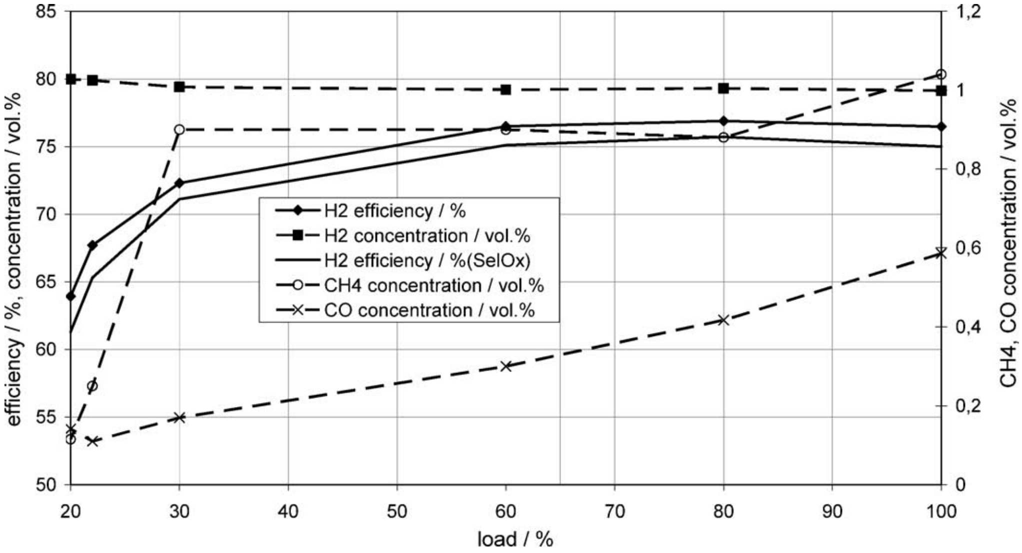

Fig. 2. Gas quality and efficiencies of the reformer as a function of load for steady-state operation.

sented thermal reformer efficiency η_{Reformer} as defined above shows a maximum value of about 77% at rated power. The efficiency decrease to 64% at 20% part load is mainly caused by a modulation limit of the burner used (only 50% part load possible) and a less effective heat transfer of the flue gas to the reformer walls, which results in a rising flue gas temperature and hence, increasing heat losses.

Additionally, tests were performed combining the reformer with a PrOx step in order to evaluate the quality of the product gas as fuel for a fuel cell. It could be observed that the CO content was mainly lower than 20 ppm in all steady-state operation measurements. The efficiency of the combined reformer/PrOx system is also presented in Fig. 2 showing a slight lower efficiency due to the fact that air with an air ratio of about 3.0 (corresponding to the CO content downstream the low temperature shift reactor) is added to the gas stream in order to oxidise the carbon monoxide and hence, a small amount of hydrogen is also oxidised resulting in a somewhat lower thermal efficiency.

It has to be kept in mind that for a complete fuel cell system the most important criterion is not the efficiency of a single component like fuel processor or fuel cell stack, but the efficiency of the total system resulting from the interaction of all relevant components. Considering the gross efficiency of a combined system containing fuel processor and fuel cell stack, but firstly neglecting the losses caused by the electrical converter and the power demand of the peripheral components like pumps, valves and system controls, the total efficiency η_{total} may be defined as gross electrical power output of the fuel cell related to the thermal input of methane power for burner and reformer feed stream

$$\eta_{\mathrm{total}} = \frac{P_{\mathrm{el}}}{P_{\mathrm{CH_4,Reformer}} + P_{\mathrm{CH_4,Burner}}} \tag{2}$$

where the methane input $P_{\mathrm{CH_4,Reformer}}$ and $P_{\mathrm{CH_4,Burner}}$ can be calculated with $\Delta H_{\mathrm{u,CH_4}} = 801\,\mathrm{kJ\,mol^{-1}}$ by

$$P_{\mathrm{CH_4,Reformer}} = \dot{n}_{\mathrm{Reformer}}\,\Delta H_{\mathrm{u,CH_4}} \quad \text{and}$$
$$P_{\mathrm{CH_4,Burner}} = \dot{n}_{\mathrm{Burner}}\,\Delta H_{\mathrm{u,CH_4}}. \tag{3}$$

The electric efficiency of the fuel cell stack η_{FC} may be defined as electrical power output P_{el} related to the hydrogen power input $P_{\mathrm{H_2}}$

$$\eta_{\mathrm{FC}} = \frac{P_{\mathrm{el}}}{P_{\mathrm{H_2}}} = f_{\mathrm{U}}\eta_{\mathrm{V}}. \tag{4}$$

This expression for the stack efficiency shall include the conversion efficiency of the stack, which is nearly equivalent to the voltage efficiency η_{V} and should be defined as average cell voltage referred to the free enthalpie $\Delta G_0 = -237.3\,\mathrm{kJ\,mol^{-1}}$ resulting in a reversible cell voltage of 1.23 V, but also containing the fuel utilisation f_{U} of the fuel cell stack. These definitions lead to a simple expression for calculating the total gross efficiency of a combined system, including fuel processor, fuel cell stack and recirculation of the unused anodic offgas, characterised by the fuel utilisation, f_{U}, by

$$\eta_{\mathrm{total}} = \eta_{\mathrm{FC}}\eta_{\mathrm{Reformer}} \tag{5}$$

The efficiency of the reformer η_{Reformer} is calculated according to the equation given above including hydrogen losses caused by the PrOx reactor. The proposed calculating procedure may lead to high reformer efficiency figures because the positive effect of the anodic off gas recirculation is added to the fuel processor. Hence, numerical values of the efficiency of the fuel processor may exceed 100%, while the figure for the fuel cell stack is relatively low because of the included fuel utilisation.

The principle favourable effect of recirculating the anodic offgas on the efficiency of the complete system is demon-

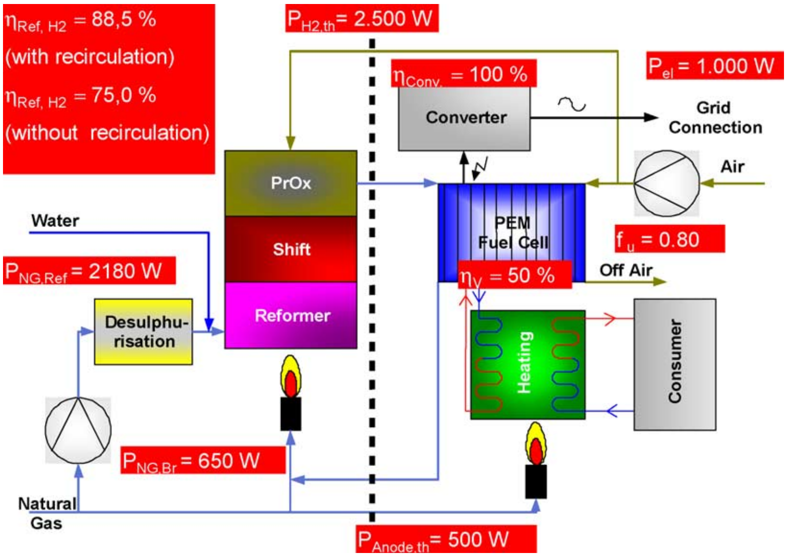

Fig. 3. Numerical example for the efficiency increase caused by recirculating the anodic offgas.

strated in a numerical example presented in Fig. 3. Assuming a fuel utilisation of the fuel cell stack of 80% and a conversion or voltage efficiency of the stack η_V of 50% leading to a fuel cell efficiency η_{FC} according to Eq. (4) of 40% the recirculation of the anodic offgas results in a fuel processor efficiency of about 88.5% according to the efficiency $\eta_{Reformer}$ given in Eq. (1). Compared to the fuel processor efficiency of about 75% at rated power after the CO purification in Fig. 2, which was measured with methane as fuel for reformer and burner, a significant efficiency increase of about 13.5% can be determined. In the numerical example, given the gross efficiency η_{total} of the combined system, including anodic offgas recirculation, achieves

$$\eta_{total} = \frac{1000\,\mathrm{W}}{2180\,\mathrm{W} + 650\,\mathrm{W}} = 35\%. \quad (6)$$

This value has to be compared to simple process chain of fuel processor and fuel cell stack without internal usage of the anodic offgas

$$\eta_{total} = \frac{1000\,\mathrm{W}}{2180\,\mathrm{W} + 650\,\mathrm{W} + 500\,\mathrm{W}} = 30\%. \quad (7)$$

The numerical example given shows impressively the effectiveness of recirculating the anodic offgas and clarifies the benefit of the method for the total system efficiency. The influence of the unconverted methane in the reformer product gas, which increases the heating value of the anodic offgas, is neglected in the estimation given. The unconverted methane, present in the anodic offgas, is used in the reformer burner and hence, reduces the necessary amount of additional methane.

Currently, the 2.5 $\mathrm{kW_{th}}$ steam reformer system includes a commercial burner with a thermal power range from 0.4 to 1.3 kW. Some modifications of the burner had to be realized in order to enable the simultaneous use of methane, representing the natural gas and the anodic offgas. Then the modified fuel processor was experimentally tested again. Fig. 4 presents the experimental investigation of the fuel processor operated with methane and synthetic anodic offgas. The experimental evaluation procedure is equivalent to that shown in Fig. 2. In the example given a fuel utilisation f_U of 66% was assumed. Hence, the thermal burner power consists of the heating value of the supplied methane and also of the heating value of the anodic offgas. Because of the carbon dioxide content of the anodic offgas the burner temperature is decreased, which results also in somewhat lower reforming temperatures. The conversion of the methane is reduced and the methane content in the product gas caused by unconverted methane increases. But also a significant increase of the reformer efficiency of about 95% according to the given efficiency Eq. (1) can be determined, because of using anodic offgas a noticeable lower amount of methane is necessary and has to be supplied to the reformer burner. This efficiency increase of the fuel processor will directly increase the overall efficiency of the total system also.

A very important aspect of a fuel cell based residential power supply systems is the positive environmental impact with respect to the low fuel consumption caused by the combined heat and power production, the low carbon dioxide emissions and the possible low emission of pollutants. At the time being there is no actual law in force limiting the emissions of a fuel cell system. Hence, Table 1 summarises the actual laws and regulations for gas heating boilers as possible benchmark.

At the moment it is not yet clear, what the exact regulations and emission limits for fuel cell systems will be in the future. It can be assumed that these regulations will be comparable to those already existing for heating boilers. In Germany, the most restrictive regulation is the environmental protection emblem called “Blauer Engel”, which is an ambitious but

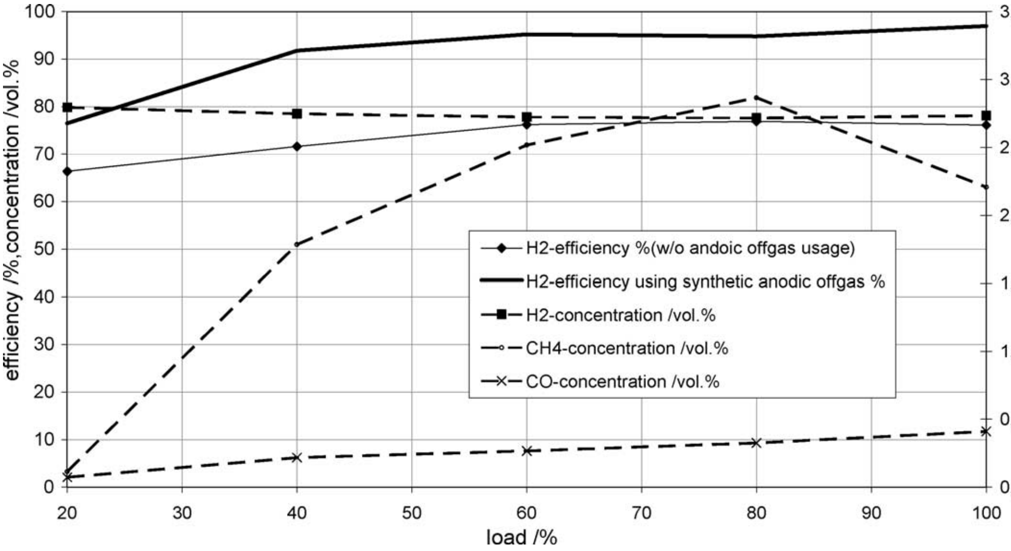

Fig. 4. Gas quality and efficiency of the reformer (without PrOx) using methane and anodic offgas.

Table 1

Summary of actual laws and regulations for exhaust gas limits of gas heating boilers

Gas component (mg kWh^{-1})	German enviromental protection emblem “Blauer Engel”	German emission control prescription “BimSchV”	German technical standard “DIN 4702/1”	Directive of the European Union (Europ. gas-geräterichtlinie (90/396/EWG)
NO_X	60	80	150	200
CO	50	60	100	100

desirable goal for a fuel cell based residential power supply systems. Firstly, it is an essential and necessary task to keep the emissions within the boundaries of the emission control prescription “BImSchV”.

Measurements of the pollutant content of the flue gas were performed while operating the burner with a mixture of anodic off gas and methane. A flue gas analysing device for exhaust gas qualities was used to measure the pollutant content of the exhaust gas. The NO_X and the CO concentrations of the burner flue gas as a function of the load are shown in Fig. 5. The measured emission figures are referred to the thermal burner power for each load point in order to get the burner emissions directly comparable with the considered regulations. Hence, the limits given by the German BImSchV are

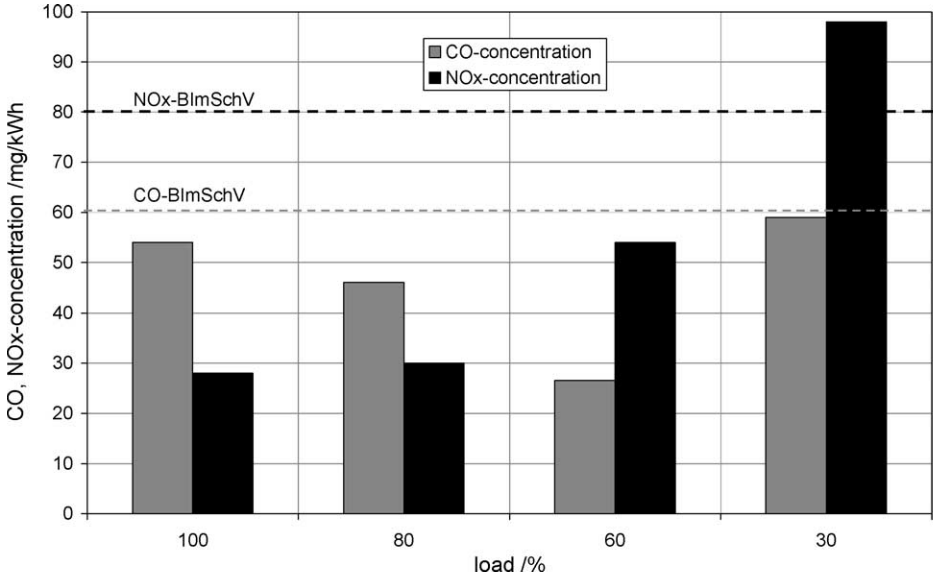

Fig. 5. NO_X- and CO-emissions of the fuel processor applying recirculation of anodic offgas.

also depicted in Fig. 5 in order to have a reference line. In most cases, the commercial burner is already able to keep the flue gas emissions within the given boundaries. Only at 30% part load the NO_X concentration lies above the limits given in the German emission control prescription (BimSchV). Nevertheless, current investigations at the ZBT are performed modifying and improving the burner in order to reduce the emissions further.

3. Experimental investigation of the combined system

A prototype fuel cell stack from Proton Motor, Starnberg, Germany, built 2001, suitable for reformat gas and operating at nearly ambient pressure was selected for the combination of fuel processor and fuel cell stack. The chosen fuel cell meets a lot of typical requirements with respect to residential power supply applications. Particularly a low pressure drop at anode and cathode side, a low air to fuel ratio and the feature of internal humidification of the cathode air are remarkable stack issues in order to achieve an efficient and less complex system.

Hence, the steam reformer was combined with a PEM fuel cell and the anodic offgas was recirculated in order to provide reaction heat for the fuel processor. The feed is controlled by mass flow controllers, the gas composition can be measured downstream the LT-shift as well as downstream the PrOx in order to protect the stack against intolerable product gas qualities and CO peaks. Fig. 6 shows the test stand with gas supply, fuel processor with PrOx and fuel cell stack. First experimental results of the process chain without recirculation of the anodic offgas have been published recently [4,5].

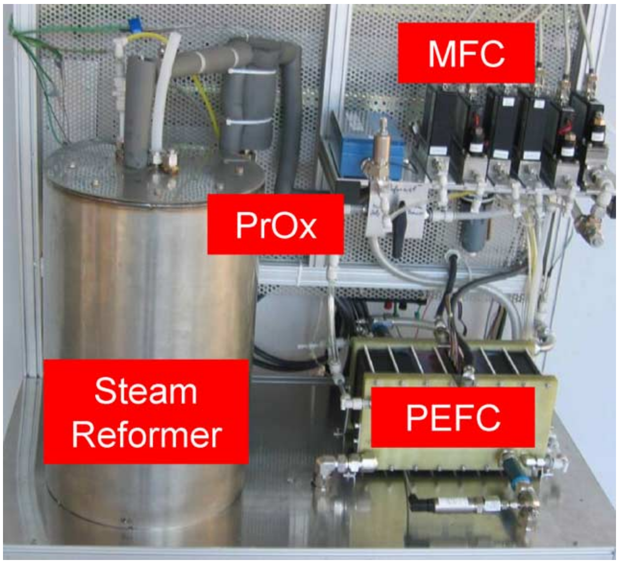

Fig. 6. Combined system consisting of fuel processor, fuel cell and recirculation of anodic offgas.

The system was characterised in steady-state operation trying to keep the fuel utilization of the PID-controlled PEM fuel cell to be nearly constant at about 70%. Fig. 7 represents the efficiency of the reformer η_{Reformer} including anodic offgas recirculation, the efficiency of the fuel cell including fuel utilization η_{FC} and the gross total system efficiency η_{total}.

The efficiency of the reformer is calculated according to Eq. (1) including hydrogen losses caused by the PrOx reactor. The gross total efficiency of the laboratory system is always higher than 30% for the whole load range from 30 to 100% during these first measurements. A system ef-

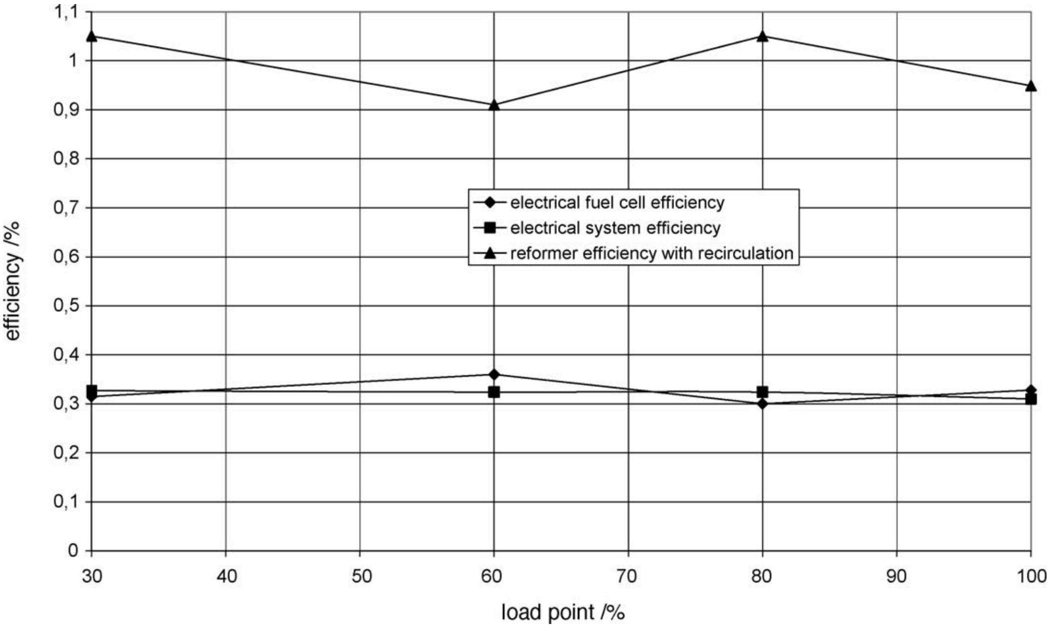

Fig. 7. Efficiencies of total system, fuel processor and fuel cell stack at steady-state operation at a fuel utilization f_U of about 0.7.

ficiency of about 35% should be possible by further improvements and optimisations. Depending on the peripheral components used like inverter, pumps, valves, sensors and control unit, an overall net efficiency close to 30%, depending on the selected peripheral components, could be achieved.

4. Summary and conclusion

The University of Duisburg-Essen and the Center for Fuel Cell Technology (ZBT Duisburg GmbH) have developed a compact multi-fuel steam reformer suitable for natural gas, propane and butane. Fuel processor prototypes based on this concept were built up in the power range from 2.5 to 12.5 kW thermal hydrogen power for different applications and different industrial partners. One of the fuel processors designed to deliver a thermal hydrogen power output of 2.5 kW was combined with a 1 kW PEM fuel cell. Recirculating the anodic offgas leads to a significant efficiency increase for the fuel processor. The gross efficiency of the combined system was clearly above 30% during the first tests; further improvements are currently investigated and developed at the ZBT.

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