

Reforming of natural gas—hydrogen generation for small scale stationary fuel cell systems

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Abstract

The reforming of natural gas to produce hydrogen for fuel cells is described, including the basic concepts (steam reforming or autothermal reforming) and the mechanisms of the chemical reactions. Experimental work has been done with a compact steam reformer, and a prototype of an experimental reactor for autothermal reforming was tested, both containing a Pt-catalyst on metallic substrate. Experimental results on the steam reforming system and a comparison of the steam reforming process with the autothermal process are given. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Efficient use of energy in combined heat and power systems is one of the most attractive research fields in energy technology. As energy conversion devices, fuel cells are interesting due to their low emissions, low noise level and good efficiency even in the low power range and at partial load.

For application in residential areas natural gas is the best fuel. The high temperature solid oxide fuel cell¹ (SOFC) and the proton exchange membrane fuel cell² (PEMFC) are considered good candidates for this application. For the low temperature membrane fuel cells, a fuel with a high content of hydrogen and a very low level of CO is required. Therefore, development of compact reformer systems including the required gas clean-up is being carried out.

In principle, there are three reforming processes [1]:

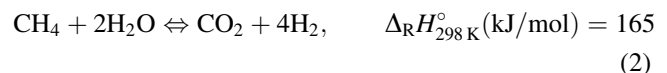
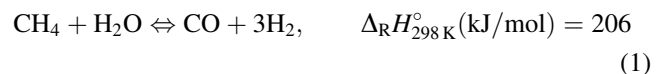
- partial oxidation;
- autothermal reforming (ATR);
- steam reforming.

The steam reforming process was used for early prototypes because it leads to the best gas quality. The shift conversion of CO and the selective oxidation of CO have

been investigated as further steps for the gas clean-up. A typical composition of reformed gas is as follows: 75–78% hydrogen, 30% CO₂, traces of methane and 10–20 ppm of CO. This can be used as a suitable fuel for membrane fuel cells. The power density of the fuel cell is almost unaffected by inert gas components. Nevertheless, the overall system efficiency is a matter of further intensive development, because the fuel utilisation of the fuel cells and the thermal characteristics of complete systems still require improvement. Strategies for quick start-up, shut-down and load changes are also subjects of the on going investigation.

2. Theoretical considerations

The steam reforming reactions for natural gas (assuming pure methane) are



Since these reactions are highly endothermic, an external heat source (e.g. a radiation burner) is required. For complete conversion of methane high temperatures in the catalyst system are essential. Therefore, effective heat transfer from the burner surface to the reactor wall has to be provided.

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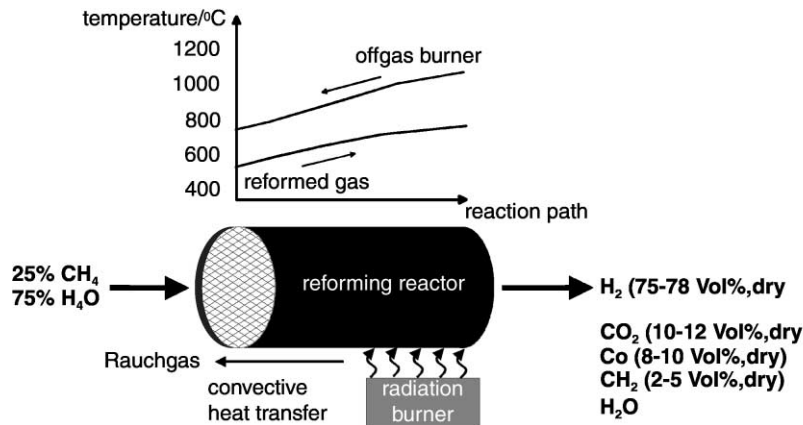
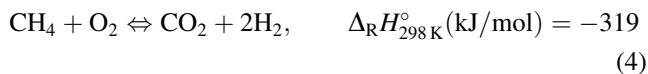
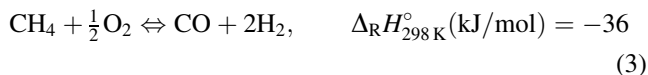


Fig. 1. Features of a steam reformer for methane [2].

Fig. 1 shows typical features of a steam reformer for methane. The product gas composition and the corresponding temperature profiles have been investigated experimentally at Fraunhofer ISE in the low power range up to 15 kW_{th} (LHV, H₂) [2,3]. Steam reforming of methane yields the best hydrogen content of all the reforming processes with 75–78 vol.% (referring to dry product gas). The basic process parameters of steam reforming are

- *S/C*, the ratio of steam to carbon at the reformer inlet.
- *R/B*, the ratio of reformer methane flow *R* to burner methane flow *B*.
- *p_{ref}*, the overall reforming pressure.

In addition to Eqs (1) and (2), partial oxidation occurs for autothermal reforming according to



The oxidation reactions are exothermic and self-sustaining. Thus, heat is released directly in the catalyst supporting the endothermic reforming reactions.

Characteristic features of an autothermal methane reformer as presented in [4] are shown in Fig. 2. The main process parameters are

- *S/C*, the ratio of steam to carbon (as for steam-reforming).
- *λ*, the air ratio, defined as inlet oxygen stream to stoichiometric combustion oxygen stream.
- *p_{ref}*, the overall reforming pressure.

In general, the temperature profile of autothermal reformers is characterised by a sharp rise at the inlet zone with the fast oxidation reaction. Following the reaction path the temperature decreases because of the endothermic reforming reactions. Since no sub-system for heat management is required, start-up and response characteristics are favourable compared to steam reformers. However, it should be pointed out that the hydrogen content is much lower due to the dilution with nitrogen from the reactant air. This is a negative aspect for fuel cell systems involving parasitic

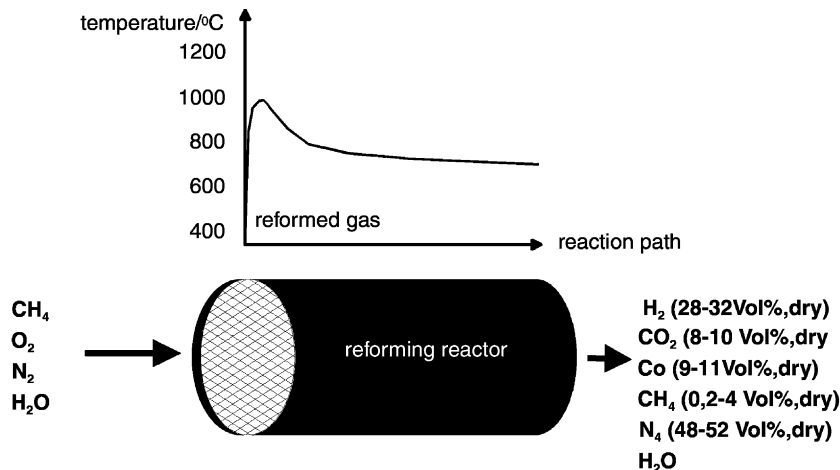


Fig. 2. Features of an autothermal reformer for methane [6].

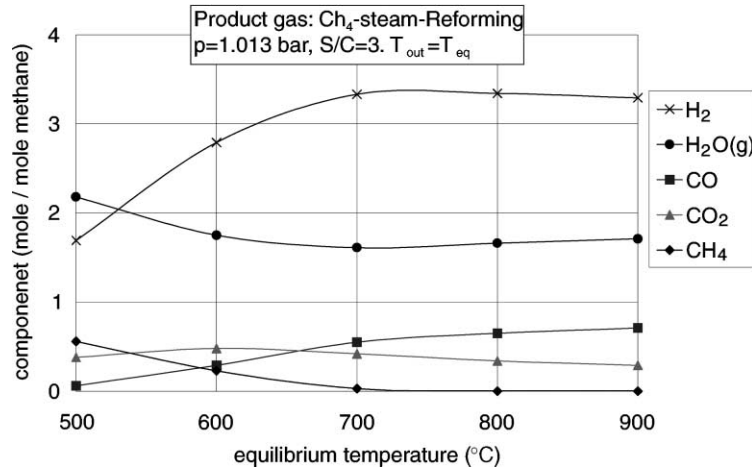


Fig. 3. Product gas composition as a function of temperature at thermodynamic equilibrium for steam reforming, pressure: $p = 1.013$ bar, $S/C = 3$.

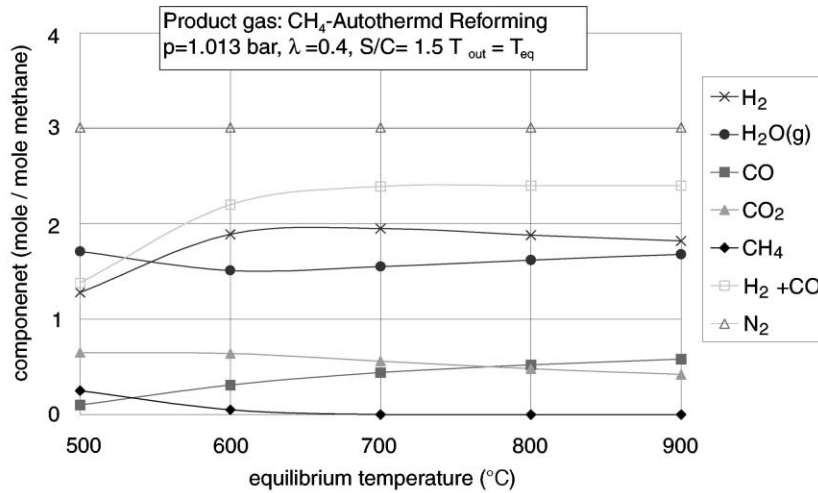


Fig. 4. Product gas composition as a function of temperature at thermodynamic equilibrium for autothermal reforming, pressure: $p = 1.013$ bar, $\lambda = 0.4$, $S/C = 1.5$.

losses arising from air compression (ATR and PEMFC) and the mass transfer conditions for the hydrogen at the anode side in the fuel cell.

Calculated product gas compositions (in vol.%, including water) at thermodynamic equilibrium of steam reforming and autothermal reforming are plotted over the reaction temperature in Figs. 3 and 4. The thermodynamic calculations have been carried out for ambient pressure (1.013 bar). For both processes the maximum content of H₂ and CO is reached at approximately 700 °C. In this case, there is no methane in the product gas. At the outlet of well-designed reforming reactors gas concentrations are not far away from the calculated equilibrium values.

3. Experimental studies

Fig. 5 shows a compact steam reformer including a heat-exchanger, a two-part reforming reactor and a radiation

burner which has been developed at the ISE and successfully installed in a hydrogen producing plant, see [4]. First, methane and water pass a heat-exchanger where the water is vaporised and heated to the reformer inlet temperature (450–600 °C). The first section of the reactor is heated convectively by fuel gas. The second section is heated by direct radiation from a low-NO_x ceramic burner.

Then, the product gas of the steam reformer passes two fixed bed reactors filled with two commercial catalysts for high and low temperature shift reactions (G-3C for HTS and G-66A for LTS, both Südchemie). The heat from exothermic CO-conversion is removed by an internal heat-exchanger. Typical results for the product gas of the three units SR, HTS and LTS are given in Table 1.

The performance of the hydrogen generation systems was evaluated in terms of gas process efficiency, see Fig. 6.

$$\eta_{\text{ref},1} = \frac{\dot{n}_{\text{H}_2} \cdot \text{HHV}_{\text{H}_2}}{(\dot{n}_{\text{CH}_4,\text{ref}} + \dot{n}_{\text{CH}_4,\text{burn}}) \cdot \text{HHV}_{\text{CH}_4}} \quad (5)$$

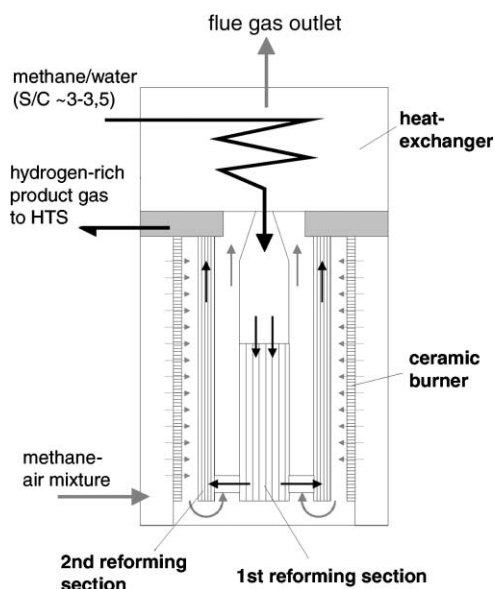


Fig. 5. Design of the compact steam reformer [4].

Table 1

Product gas compositions (dry basis) of the hydrogen generation (SR, HTS and LTS) in experiments at $p_{ref} = 1.5$ bar abs, $S/C = 3-3.5$, $\dot{V}_{CH_4,ref} = 1$ m³ (STP)/h, $R/B = 1.35$

	Outlet reformer	Outlet HTS	Outlet LTS
CH ₄ (mole%, dry)	3.0	2.7	2.6
CO ₂ (mole%, dry)	12.2	15.9	19.0
CO (mole%, dry)	9.0	3.6	0.3
H ₂ (mole%, dry)	75.8	77.8	78.1

$$\eta_{ref,2} = \frac{\dot{n}_{H_2} \cdot HHV_{H_2}}{(\dot{n}_{CH_4,ref} + \dot{n}_{CH_4,burn} - \dot{n}_{CH_4,Offgas}) \cdot HHV_{CH_4}} \quad (6)$$

According to Eq. (5), the efficiency $\eta_{ref,1}$ is calculated from the total molar flow of hydrogen output after LTS and the total methane flow input to the reformer and the burner, based on the higher heating values (HHV), respectively. Efficiency $\eta_{ref,2}$ is based on the ratio of the total hydrogen output after LTS and the net methane flow to the reformer and the burner. Net methane flow means that the unconverted methane in the product gas, and thus in the offgas of fuel cells, is assumed to be recycled to the burner.

The range of hydrogen generation is shown in Fig. 7 for experiments at $S/C = 3-3.5$ and $R/B = 1.3$, both at atmospheric pressure and at $p_{ref} = 6$ bar abs. The highest hydrogen production was 4.94 m³ (STP)/h for $\dot{V}_{CH_4,ref} = 1.33$ m³ (STP)/h, $R/B = 1.33$ and $S/C = 3.18$ at a gaseous hourly space velocity of about 3540 l (STP)/l_{kat}/h at the reformer inlet and 1640 l (STP)/l_{kat}/h at HTS and LTS inlet, respectively. The steam reforming process is also limited by stable operation of the ceramic radiation burner. The value $\dot{V}_{CH_4,burn} = 0.48$ m³ (STP)/h was determined as lower limit of continuous operation.

For operation with natural gas an activated carbon bed is used to desulphurise the feed before it enters the reformer. As the dry product gas after LTS still contains 2000–4000 ppmv CO, a fixed bed reactor with a noble metal catalyst is used for selective oxidation of the carbon monoxide. Tests with the gas processing plant showed a gas quality suitable for the Energy Partners PEM fuel cell: <10 vol.% CO, 20 vol.% CO₂, 77 vol.% H₂, 1 vol.% N₂, and 2 vol.% CH₄, respectively. At plant operation the refor-

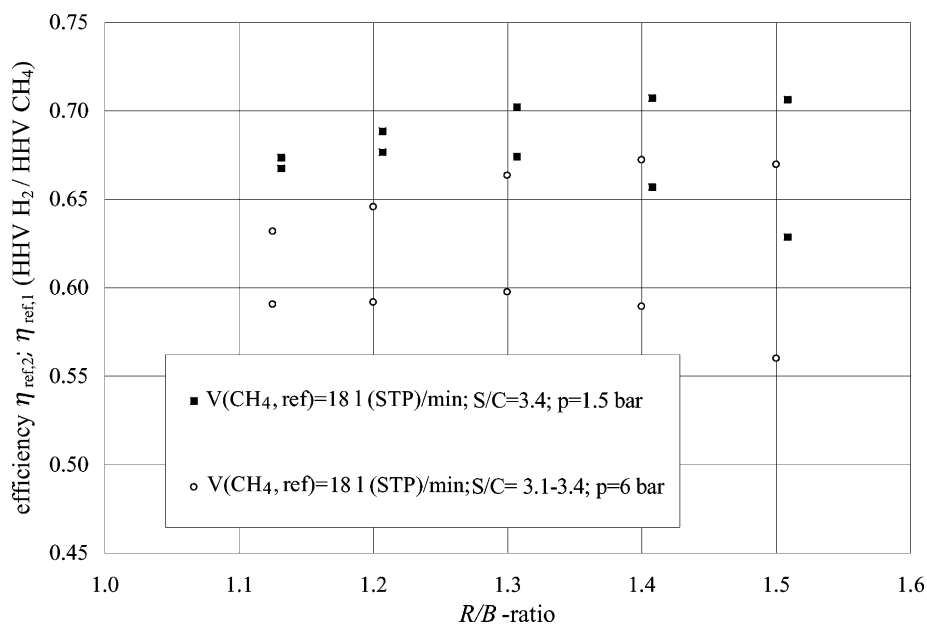


Fig. 6. Hydrogen generation (SR, HTS and LTS) efficiencies according to Eqs (5) and (6), based on higher heating values of hydrogen and methane, respectively, for experiments at $p_{ref} = 1.5$ and 6 bar abs.

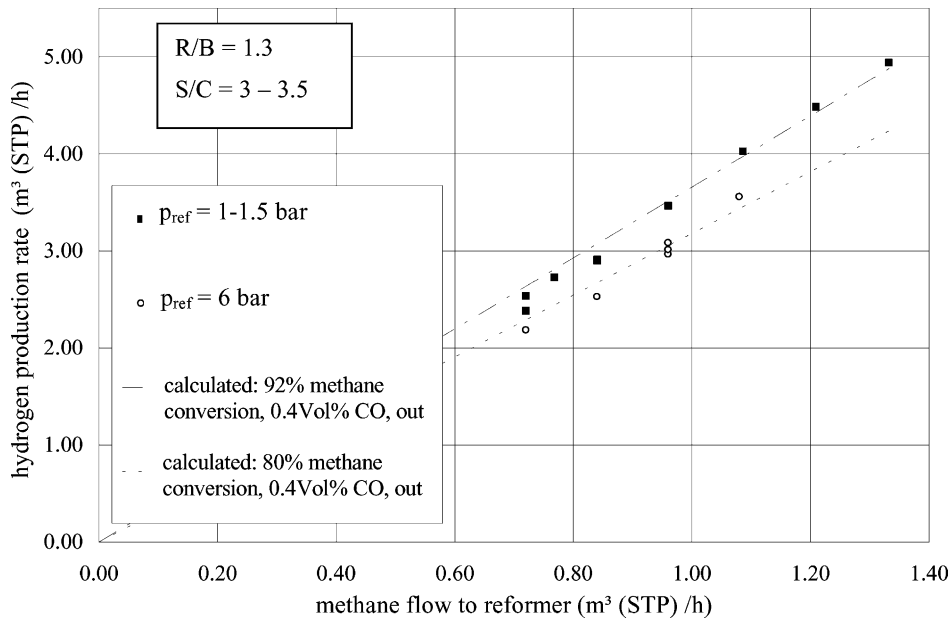


Fig. 7. Hydrogen production rate of the compact steam reformer (including HTS and LTS).

mate after the selective oxidation unit is compressed and stored at high pressure (200 bar). Future work will aim at direct supply of the fuel cell by the gas processing plant without intermediate storage.

ATR technology has also been tested at the department of Energy Technology at the Fraunhofer ISE as an alternative to steam reforming. Since there is significant interest to establish fuel cell technology for mobile applications, recent experimental work focused on testing liquid fossil fuels as the hydrogen source, e.g. gasoline or ethanol.

For stationary applications natural gas is preferred. As a first prototype an experimental reactor was designed containing a Pt-catalyst on a metallic substrate followed by a fixed bed of Pt-catalyst. For the starting period of the ATR, the metallic substrate is heated electrically until the catalytic combustion of a stoichiometric methane/air-mixture is reached. The apparatus is warmed up by the heat of the combustion reaction and later on water is added to limit the temperature rise in the catalyst while the air flow is reduced to sub-stoichiometric settings. Typical experimental conditions were $\lambda = 0.3\text{--}0.5$, $S/C = 0.25\text{--}1$ at atmospheric pressure and a methane inlet flow of $0.2\text{--}2\text{ m}^3$ (STP)/h. An example for product gas composition at maximum methane conversion is presented in Table 2. The highest efficiency of hydrogen and carbon monoxide production according to

Eq. (7) was 78.4%. As CO can be converted almost totally into hydrogen in subsequent shift reactors and a final purification step (see [5]), the CO flow is added to the hydrogen yield

$$\eta_{\text{ATR}} = \frac{(\dot{n}_{\text{H}_2} + \dot{n}_{\text{CO}}) \cdot \text{HHV}_{\text{H}_2}}{\dot{n}_{\text{CH}_4, \text{in}} \cdot \text{HHV}_{\text{CH}_4}} \quad (7)$$

The ATR showed a more flexible load change characteristic and a shorter start-up time compared to the compact steam reformer described above. The design is simple so that investment costs can be saved. As new generation PEM fuel cells are able to convert feed gas with typical hydrogen concentrations for autothermal reforming of about 30 vol.% the autothermal process should be promoted further.

4. Conclusions

1. For hydrogen generation natural gas can be reformed either by steam reforming alone or by simultaneous partial oxidation combined with steam reforming (autothermal reforming).
2. Both of the processes have been investigated experimentally at the Fraunhofer ISE. Thermodynamic equilibrium is nearly reached in both cases. That means that the hydrogen content is approximately 80% for steam reforming and 30% for the autothermal process. Therefore, the gas quality of either alternative is suitable for new generation fuel cells.
3. For stationary residential applications natural gas is proposed as the hydrogen generating fuel. The autothermal process is more flexible than the steam reformer regarding the start-up time and the load change

Table 2

Product gas compositions (dry basis) of the ATR in an experiment at $\lambda = 0.44$, $S/C = 0.5$, $p = 1$ bar abs and methane flow of 0.5 m^3 (STP)/h

N ₂ (mole%, dry)	CH ₄ (mole%, dry)	CO ₂ (mole%, dry)	CO (mole%, dry)	H ₂ (mole%, dry)
53.3	0.2	7.1	8.9	30.5

characteristic so that the drawback of the lower hydrogen content might eventually be tolerate.

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