

# Compact hydrogen production systems for solid polymer fuel cells

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## Abstract

Generally there are several ways to produce hydrogen gas from carbonaceous fuels like natural gas, oil or alcohols. Most of these processes are designed for large-scale industrial production and are not suitable for a compact hydrogen production system (CHYPS) in the power range of 1 kW. In order to supply solid polymer fuel cells (SPFC) with hydrogen, a compact fuel processor is required for mobile applications. The produced hydrogen-rich gas has to have a low level of harmful impurities; in particular the carbon monoxide content has to be lower than 20 ppmv. Integrating the reaction step, the gas purification and the heat supply leads to small-scale hydrogen production systems. The steam reforming of methanol is feasible at copper catalysts in a low temperature range of 200–350°C. The combination of a small-scale methanol reformer and a metal membrane as purification step forms a compact system producing high-purity hydrogen. The generation of a SPFC hydrogen fuel gas can also be performed by thermal or catalytic cracking of liquid hydrocarbons such as propane. At a temperature of 900°C the decomposition of propane into carbon and hydrogen takes place. A fuel processor based on this simple concept produces a gas stream with a hydrogen content of more than 90 vol.% and without CO and CO<sub>2</sub>. © 1998 Elsevier Science S.A.

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## 1. Introduction

Fuel cells are electrochemical systems converting chemical energy directly into electrical energy. Heat and water are by-products. These systems work very efficiently and produce low emissions. Therefore they are very interesting for future applications such as central and decentral production of electricity and heat, and use for traction purposes. Different fuel cell types, characterised by the used electrolyte, are currently being developed and have typical requirements for the system design such as operating temperature or fuel gas quality. The fuel cell type which has the greatest potential for mobile applications, given by the highest power density, is the low-temperature fuel cell with a polymer electrolyte membrane as electrolyte (SPFC). As the anode catalyst of a solid polymer fuel cell (SPFC) is usually based on platinum being easily poisoned by carbon monoxide, the conditioned feed gas should contain less than 20 ppmv CO.

In general there are several ways to produce hydrogen from carbonaceous fuels. For example, natural gas, liquid petrol gas, gasoline, diesel fuel, coal, biomass or different alcohols can be used for hydrogen production. The main

processes are steam reforming, partial oxidation, gasification, and thermal or catalytic cracking as presented in Fig. 1. The industrial production of hydrogen is mainly based on the steam reforming of natural gas followed by pressure swing adsorption as a purification step. This process is designed for large-scale processes and is not suitable for compact and mobile hydrogen production systems in a power range of 1.0 kW.

The design of a simple and compact hydrogen production system (CHYPS) for supplying a SPFC is the main target of the presented systems. They represent the integration of reaction step, gas purification and heat supply in a compact way, which is suitable for mobile and stationary applications. The fuel input for the two different systems is on the one hand a liquid mixture of methanol and water and on the other, propane gas, which is usually stored in liquid form in pressure vessels.

## 2. Production of pure hydrogen via methanol steam reforming

### 2.1. Fundamentals

The generation of hydrogen by catalytic steam reforming

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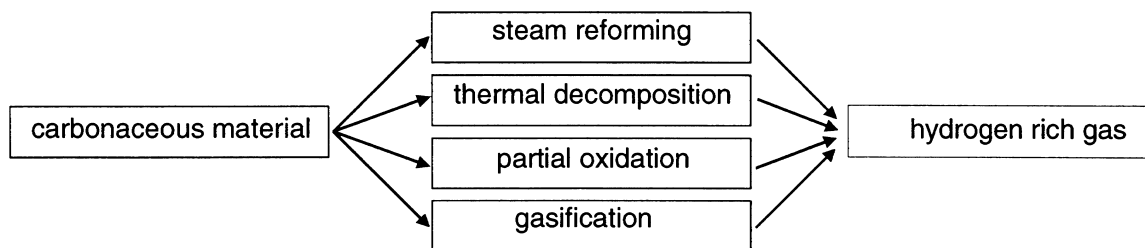
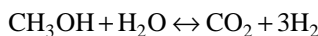
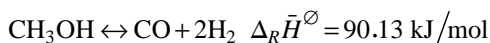


Fig. 1. Main processes for the production of hydrogen.

of methanol has been studied as a means of supplying polymer electrolyte membrane (PEFC) fuel cells. In particular the transport properties of methanol with high energy density, high energy storage capacity and a fairly simple convertibility into hydrogen-rich fuel gas at low temperatures make methanol interesting for mobile applications within a small power range. To produce a hydrogen-rich gas under higher pressure with a low energy demand, the use of a liquid mixture of methanol and water as feed for the process is quite practical. The methanol steam reforming is feasible at solid catalysts with copper as active compound in a temperature range from 200 to 350°C. An increasing system pressure improves the activity of the catalyst but also reduces the methanol conversion. The methanol reforming can be described by the following main reactions [6,7]:



$$\Delta_R \bar{H}^\ominus = 48.97 \text{ kJ/mol}$$



The gas composition and especially the CO content of the product gas of the methanol steam reforming is strongly influenced by the steam-to-carbon ratio (S/C) of the feed

mixture. In Fig. 2 the product gas composition in the thermodynamic equilibrium is given as a function of the steam to carbon ratio. The calculation has been performed for a system pressure of 5 bar and a conversion temperature of 310°C.

The equilibrium data show a rapid decrease of the carbon monoxide content in the product reformat gas with increasing steam-to-carbon ratio in the feed. Also, the conversion temperature has an important influence on the CO rate in the reformat gas, caused by the water gas shift reaction, which is also catalysed by the copper catalyst.

The gas separation using membranes is based on the selective gas transport through the membrane. In particular, the usage of metal membranes offers an effective and simple possibility to purify hydrogen gas. The most popular metal used for hydrogen separation has been palladium or its alloys. Indeed, the palladium/hydrogen system has been studied intensely, beginning with the early work of Graham Well over a hundred years ago.

The basic mechanism of the gas transport through metals is illustrated in Fig. 3. The first step is the gas transport from the gas phase to the membrane surface (1), which is followed by the dissociation of the hydrogen molecules (2). The actual gas transport through the metal (3) is only

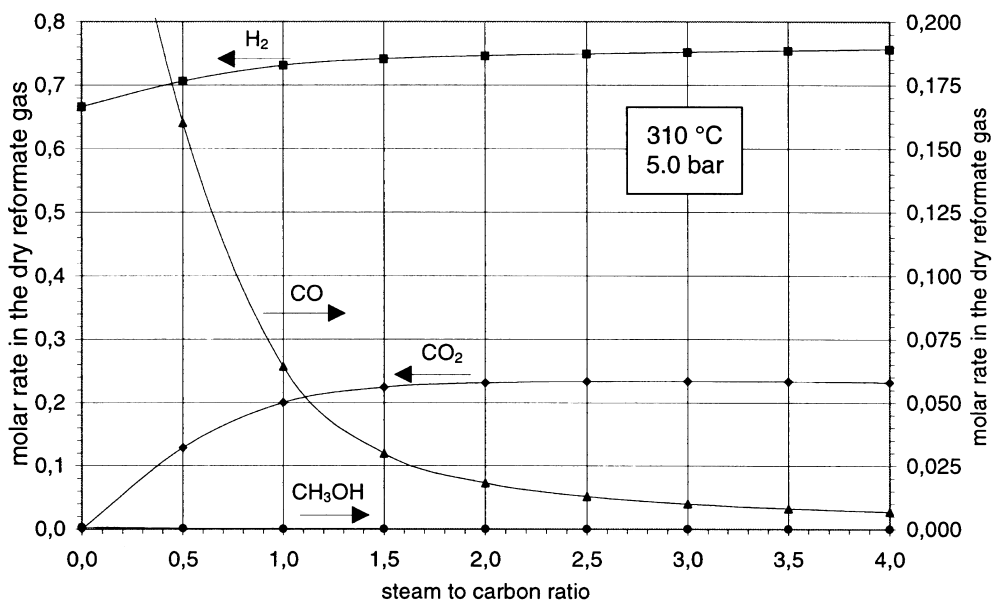


Fig. 2. Gas composition in the thermodynamic equilibrium as a function of steam-to-carbon ratio.

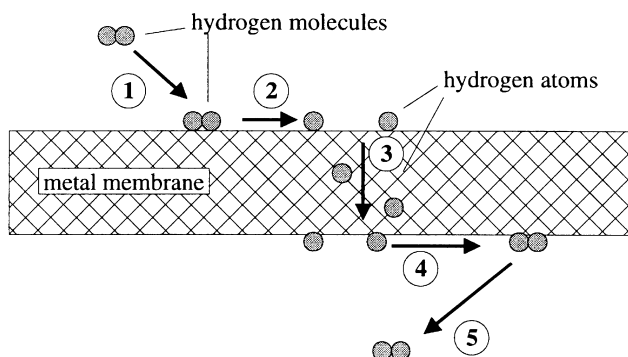


Fig. 3. Hydrogen diffusion through metal membranes.

possible for hydrogen atoms, therefore a recombination (4) is necessary on the pure gas side. The desorption of the hydrogen molecules (5) is the final interim step of this process [2].

While palladium is an attractive membrane material, several operation problems remain. First, palladium has an  $\alpha$ - $\beta$  phase transition which is dependent upon hydrogen concentration in the metal at temperatures below 300°C. Expansion and contraction of the lattice with varying hydrogen concentrations lead to embrittlement and fracture of the metal. Some control of this problem can be obtained by alloying with silver. Inclusions of silver into the palladium significantly reduce the critical temperature and pressure of the  $\alpha$ - $\beta$  phase transition [3–5]. While this does increase the longevity of the membranes, these materials are expensive. Further, it is recommended that all heating and cooling of the membrane between working temperatures or during start-up or shut-down should be accomplished either in a purge gas or vacuum. Very rapid temperature and pressure changes have to be avoided. Known poisons for palladium such as hydrogen sulfide, chlorine, bromine and some unsaturated hydrocarbons should be avoided in the gas stream.

## 2.2. System description (Fig. 4)

The system consists of a feedpump, a vaporiser for the liquid feed mixture of methanol and water, a steam reformer containing the copper catalyst and a catalytic burner to provide the necessary heat input. For solid polymer fuel cells the gas quality is an important criteria. Therefore a gas purification step behind the methanol reformer is necessary for a compact hydrogen production system. The vaporiser, the steam reformer, the gas purification and the catalytic burner are placed in a cylindrical case with a diameter of 140 mm and a length of 600 mm. The total weight of this laboratory hydrogen production system is 15.5 kg. With further improvements of system parameters and design a power density of about 0.3 kW<sub>H<sub>2</sub></sub>/dm<sup>3</sup> (0.25 kW<sub>H<sub>2</sub></sub>/kg) is possible.

Neglecting expanded adsorption processes, the highest gas quality is reachable with metal membrane systems as a purification step. The permeation rate of hydrogen through a dense metal membrane mainly depends on the pressure

difference between the feed gas and the pure gas, the system temperature, the feed gas composition, the effective membrane surface and the membrane thickness.

A palladium/silver alloy is the most common material for hydrogen separation membranes. For the presented system a palladium membrane with 24 wt.% silver is used for the gas purification. The implemented membrane is a product of Johnson Matthey, Royston, UK, and offers a surface of 140 cm<sup>2</sup> for the hydrogen permeation with a membrane thickness of 7.5 mm. The catalytic burner is supplied by the bleed gas of the metal membrane gas purification, which contains the residual hydrogen and carbon monoxide of the reformat gas, and by additional fuel.

## 2.3. Experimental and results

The experimental investigations on the compact hydrogen production system via methanol reforming have been performed with a test stand as shown in Fig. 5. The methanol/water feed is pre-mixed in a separate fuel container. A membrane pump compresses the liquid mixture up to the system pressure and is used to control the volumetric flow. The gas composition of the pure gas, the bleed gas and the reformat gas can be analysed, and flowmeters determine the volumetric flow.

The variable operation parameters for the experimental investigations are the system pressure in the range from 3.0 and 7.0 bar, the methanol flow, the steam to carbon ratio of the feed, and the system temperature. The limits of the temperature are given by the required working temperature of the membrane (over 250°C) and the thermal stability of the used catalysts (maximum 350°C). Therefore experimen-

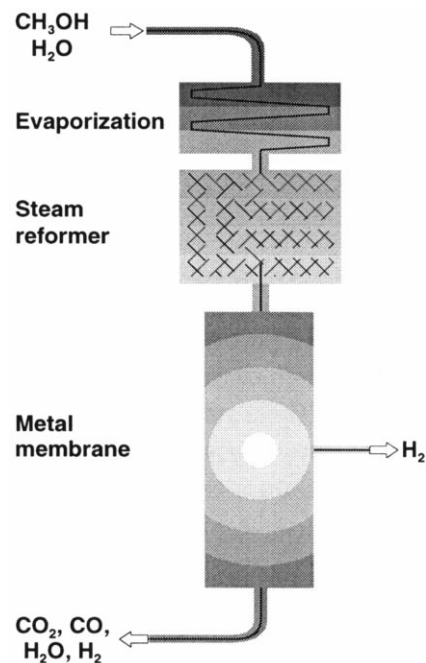


Fig. 4. Scheme of process principle of the compact methanol reformer system for pure hydrogen production.

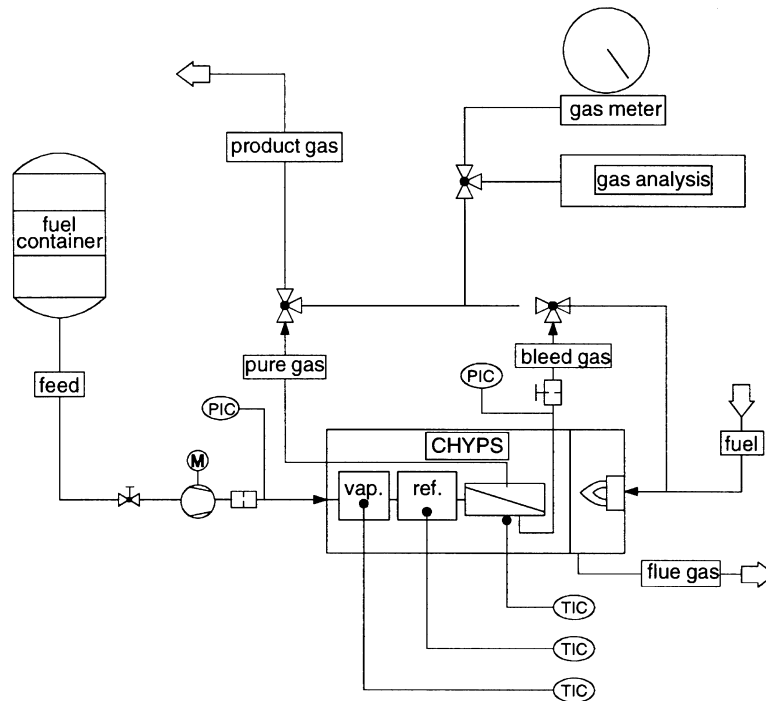


Fig. 5. Flowsheet of the test device of the compact hydrogen production system via methanol reforming.

tal investigations were carried out at operation temperatures between 285 and 320°C.

For the system parameters of 5 bar system pressure, a steam-to-carbon ratio in the reformer feed gas  $S/C = 2.0$ , a methanol system input equivalent to 1.1 kW and a variable system temperature, the hydrogen power content of reformat gas, bleed gas and pure gas is shown in Fig. 6. The efficiency of the total system is strongly dependent on the hydrogen recovery rate of the purification step. The recovery rate of the metal membrane is described by the ratio of the pure hydrogen flow through the membrane to the hydrogen content in the reformat gas. During these experiments, represented in Fig. 6, the hydrogen recovery rates range between 40% to 62%. With increasing system temperature the reformat hydrogen flow stays nearly constant, but the hydrogen separation process in the metal membrane is favoured by increasing the temperature. The permeation rate of hydrogen through the metal membrane is strongly influenced by the membrane temperature. Furthermore the recovery rate can be improved significantly, increasing the system pressure as shown in Fig. 7.

By increasing the system pressure from 5 bar up to 7 bar, the pure hydrogen pure gas output rises by about 30%. The maximum of hydrogen flow equivalent to 1.17 kW is produced at 7 bar absolute system pressure, with 1.38 kW methanol as feed, a steam-to-carbon ratio  $S/C = 2.0$ , and a system temperature of 320°C.

This is equivalent to an overall system efficiency  $\eta$  of about 54% calculated by the ratio of produced pure hydrogen gas of 1.17 kW to the methanol input of 1.38 kW, the power of the membrane pump to compress the liquid methanol water mixture  $P_{\text{comp}}$  of 10 W and the measured addi-

tional heat input  $\dot{Q}_{\text{heat}}$  of 780 W for heat losses, endothermal reaction heat and vaporisation heat. The efficiency is described by the following equation:

$$\eta = \frac{\Delta_R \bar{H}_{\text{H}_2}^\ominus \cdot \dot{N}_{\text{H}_2, \text{ pure}}}{\Delta_R \bar{H}_{\text{CH}_3\text{OH}}^\ominus \cdot \dot{N}_{\text{CH}_3\text{OH}, \text{ input}} + P_{\text{comp}} + \dot{Q}_{\text{heat}}}$$

The determined value of the total efficiency of 54% might be acceptable for such a laboratory system. The effectiveness is mainly influenced by the heat losses of the system chamber. By improving the thermal insulation of the casing of the system an efficiency of about 70% should be possible.

The gas quality of the produced hydrogen gas is decreasing with increasing system pressure due to higher leakage through the sealing of the Palladium membrane. This effect could be minimised by design improvements [1]. The impurities of the produced hydrogen are traces of carbon monoxide and carbon dioxide. For the operating parameters of a steam-to-carbon ratio of 2.0, an absolute system pressure of 5 bar, a methanol input of 1.1 kW and a system temperature in the range from 285 to 320°C, the impurities of CO and CO<sub>2</sub> in the pure gas compared to their content in the reformat gas are shown in Fig. 8.

Depending on the application of the produced hydrogen, the gas impurities are more important. Especially for supplying a low temperature fuel cell, the carbon monoxide content is the characterising value of the gas quality. The produced hydrogen gas of the compact hydrogen production system containing a CO rate in the range of 40 to 60 ppmv depending on the operation parameters. This gas quality might be suitable for low-temperature fuel cells. Usual

gas qualities for the hydrogen gas are below 10 ppmv CO. Therefore an additional hydrogenation step such as a methanation could be necessary for this special application. But the used palladium membrane is a prototype; the design and the performance of the metal membrane will be improved by Johnson Matthey to achieve an acceptable CO level for PEM fuel cells.

### 3. Production of a hydrogen-rich gas via thermal and catalytic cracking of propane

#### 3.1. Fundamentals

The generation of a hydrogen-rich gas suitable for SPFC applications can easily be carried out by thermal or catalytic decomposition of light hydrocarbons, in particular methane and propane. Such a system can be built much smaller, simpler and less expensive than existing ones, based on steam reforming technology. Because there is no oxygen in the feedgas, the produced hydrogen-rich gas contains no CO or CO<sub>2</sub> which could harm the fuel cell or decrease the efficiency of a fuel cell stack. So the expense for a complex gas purification is not necessary. Purities of more than 95% hydrogen, dependent on the operating conditions, are possible. Furthermore, systems based on thermal or catalytic decomposition of hydrocarbons can be built on the small scale of a few hundred watts so that portable applications are imaginable.

The production of hydrogen-rich gases by thermal or catalytic decomposition of methane or natural gas is a well-known process and is described in the literature by several authors [8–10]. Propane as feedstock for hydrogen production offers a new way towards a cheap fuel for fuel cells.

The decomposition of propane is mentioned only with respect to the production of olefins for the chemical industry but not for hydrogen production. Thus our investigations are concentrated on the thermal and catalytic cracking of propane, which can be described by the following main reaction:



The cracking process of propane offers some advantages. Firstly, propane is a widespread and cheap fuel with a high power density. It can be stored in liquid form in pressure vessels and can be transported easily. Furthermore, the endothermic cracking process itself needs only about 7% of the heat of combustion of propane to dissociate the propane molecules into carbon and hydrogen. It is known from many pyrolysis experiments with propane that the major products are hydrogen, methane, ethylene and propylene. By increasing the residence time or the temperature of the pyrolysis gas, ethylene and propylene are likewise cracked into hydrogen, methane and carbon. Under accurate experimental conditions, the produced gas consists only of hydrogen with a few percent of methane, which does not harm the membrane of an SPFC. Methane can be considered as an inert gas for the stack of a fuel cell working in the temperature range of 80–100°C [10].

In Fig. 9 the product gas composition in the thermodynamic equilibrium of the propane cracking process is shown. The calculations are made for different pressures in a temperature range from 500 to 1200°C.

The equilibrium calculations show a strong dependence of the product gas composition of temperature and pressure. Propane decomposition is endothermic and the process is more efficient at higher temperatures. Due to the increase of volume during propane decomposition, the decomposition

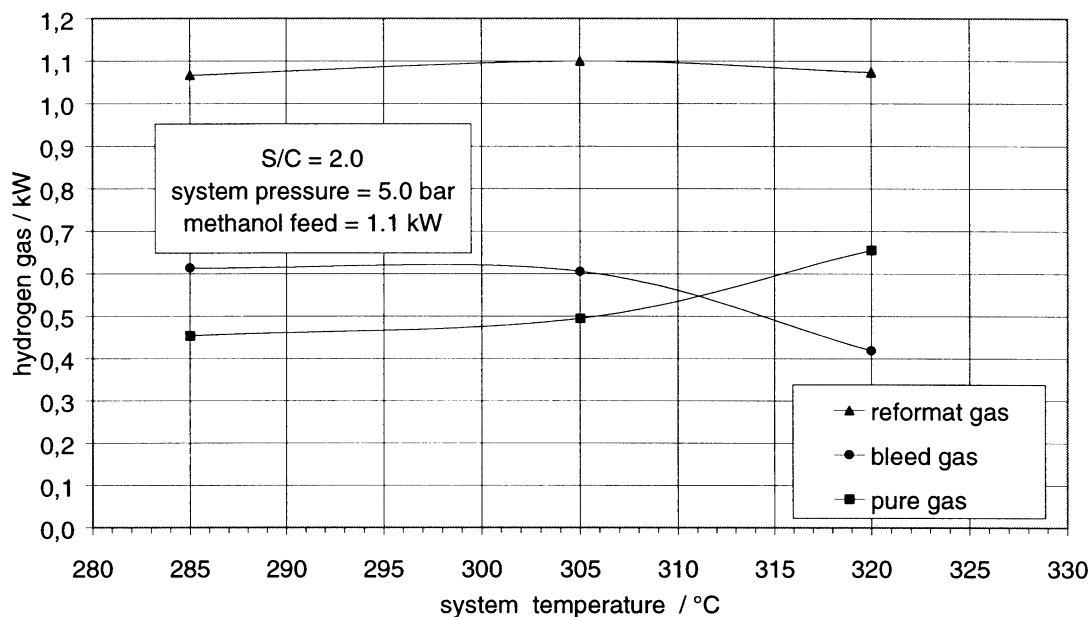


Fig. 6. Hydrogen power of reformat gas, bleed gas and pure gas at a system pressure of 5 bar.

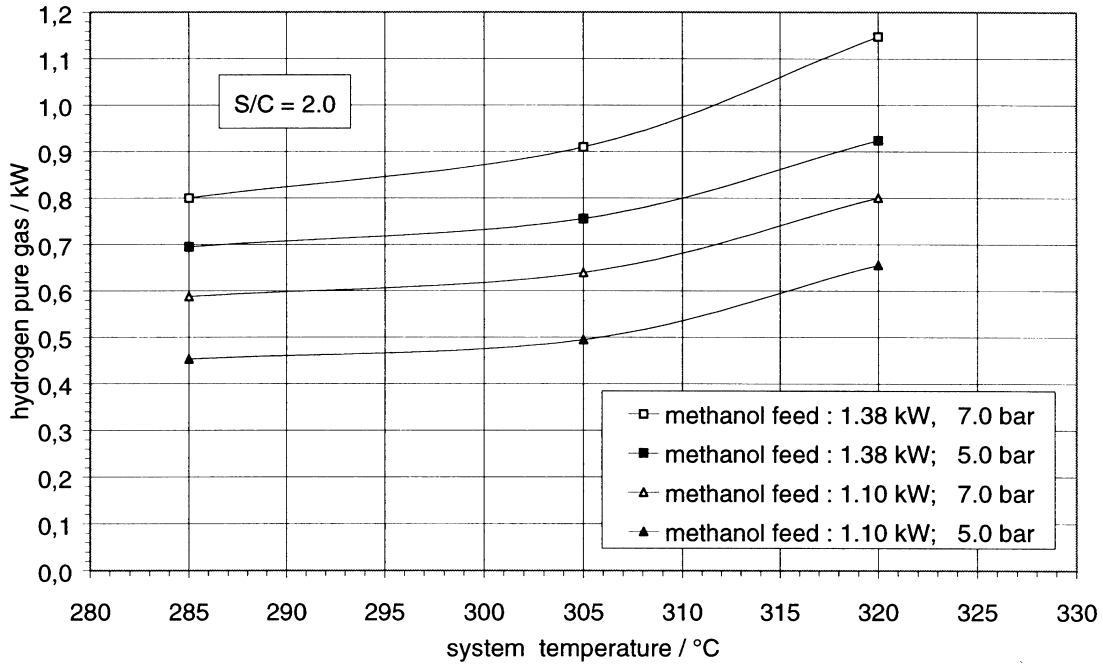


Fig. 7. Hydrogen power at different methanol feeds and at different system pressures.

is favoured by decreasing pressure. Therefore the process works better at low pressures and reduced system temperatures.

Higher reaction rates of the process can be achieved by the use of catalysts for the cracking process. Several studies investigated the decomposition of light hydrocarbons, mainly methane, with the help of catalysts in the last years. The tested catalysts included Pd, Pt, Rh, Ru, Ir, Re Co, Ni, W, Fe, Mn, Mo, Ta, Cu, Ag, Cr, Ti and V<sub>2</sub>O<sub>5</sub>. The studies agreed that the most suitable catalysts for this application are Pd, Rh, Ru, Ni, Co and Fe [8–12].

Some of the elements, especially Ni, Cr and Fe, are often used in high alloyed steels so that the walls of the reactors itself catalyse the crack process. The reaction rates in such reactors are significantly higher and, depending on the experimental conditions, the hydrogen content of the product gas reaches the values of hydrogen in the equilibrium calculations.

3.2. System description

The construction principle of the small cracking reactor is

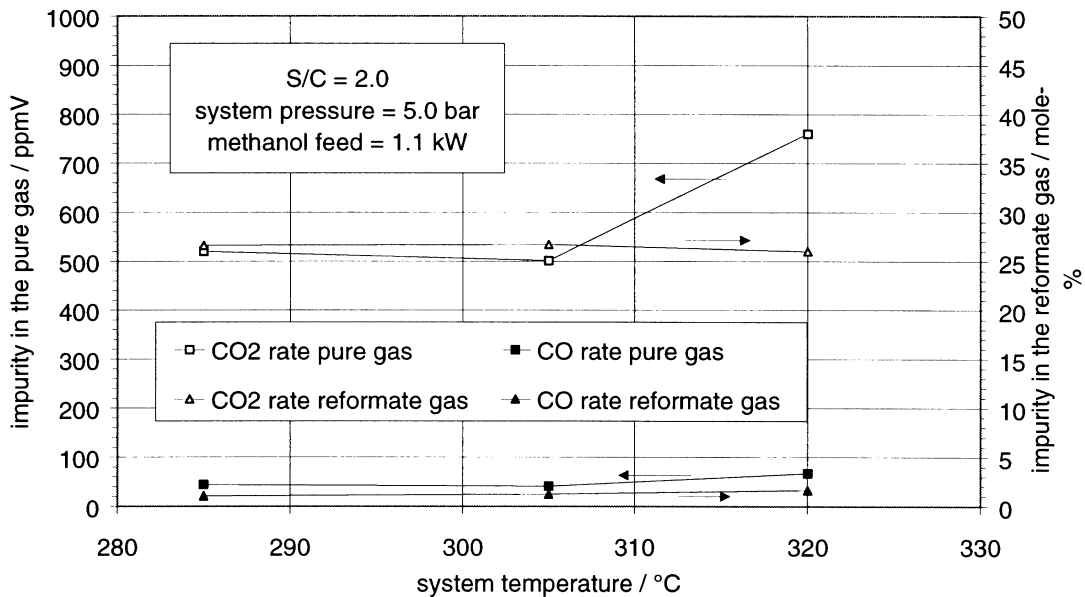


Fig. 8. CO and CO<sub>2</sub> impurities of the produced hydrogen gas.

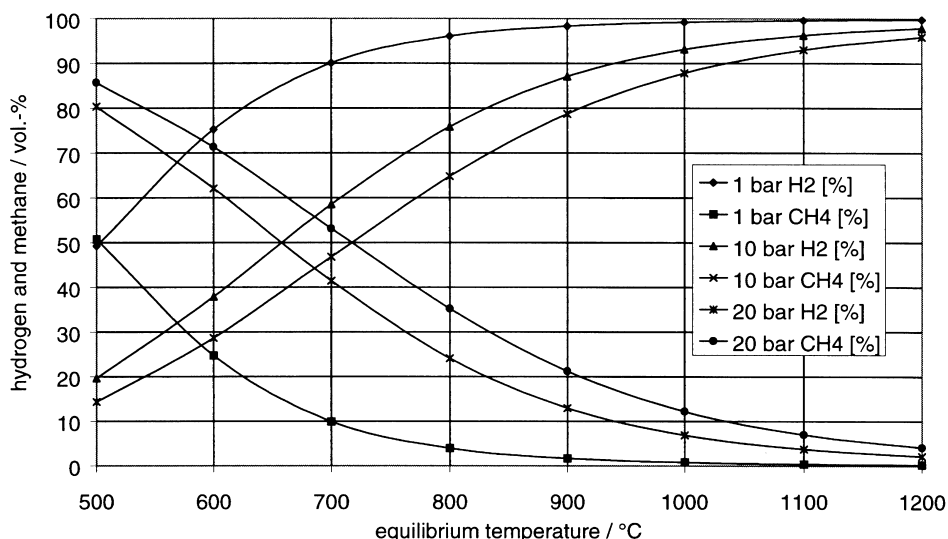


Fig. 9. Gas composition in thermodynamic equilibrium of the propane cracking process.

shown in Fig. 10. The propane feed is preheated by the exhaust gas of two external propane burners supplying the necessary heat input to the system. The preheated gas enters the cracking reactor with a gas temperature of about 600°C. Inside the reactor the overall cracking reaction of the propane takes place. At temperatures in the range of 700–900°C and at atmospheric pressure, the feed decomposes into hydrogen, methane and solid carbon. The carbon produced in the cracking process adheres at the reactor walls, covers the surface, and reduces the heat exchange between the reactor walls and the gas flow within operation time. Some of the carbon particles are transported by the gas stream to the reactor exit and have to be removed before the gas can be used in a fuel cell. Therefore two filters are placed at the reactor exit.

### 3.3. Experimental and results

The investigations of the thermal cracking process of propane were performed in a test stand shown in Fig. 11. The experimental equipment consists mainly of the two-reactor, two pre-heater system, and a gas-chromatograph to determine the output gas composition. The reactor is fed with propane (purity 99.5%) which is stored in liquid form in a tank and then ducted by two mass flow controllers into the two pre-heaters of the reactor unit. The cracking reactor is made of two chambers separated by each other through a common wall. In this two-reactor system, one reactor is used for hydrogen production while the other one is being regenerated.

About 55% of the energy of propane is stored in the carbon, therefore its burning can be used to supply the heat for the cracking reaction in the second chamber. The energy released from the burning of carbon is 7 times greater than the energy needed for the thermal decomposition. It may be possible to sustain the process by burning off the carbon in one chamber to run the process in the second

one. In the presented system, the reactors are heated by two external propane burners. Carbon is burned off by introducing air into the reactor. The produced heat supports the decomposition reaction in the other chamber. Most of the carbon remains in the reactor; only small particles are transported by the gas to the reactor exit where they are removed by filter elements. The gas leaving the reactor can now be used without further purification in fuel cell systems. The hydrogen-rich gas is analysed by a Chrompack Micro GC CP2002 with a Poraplot Q and a Molsieve 5 Å column for the detection of H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, N<sub>2</sub> and O<sub>2</sub>.

The variable operation parameter for the investigation is the volumetric flow of the propane feed which characterises different residence times of the gas in the reactor. Wall

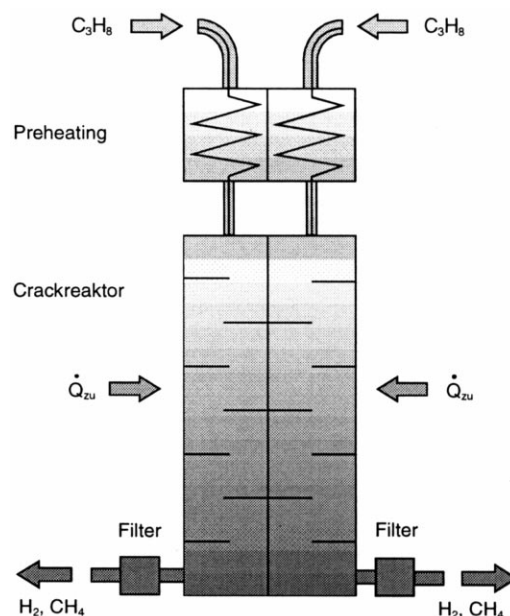


Fig. 10. Construction principle of the compact propane cracking reactor for the production of a hydrogen-rich gas.

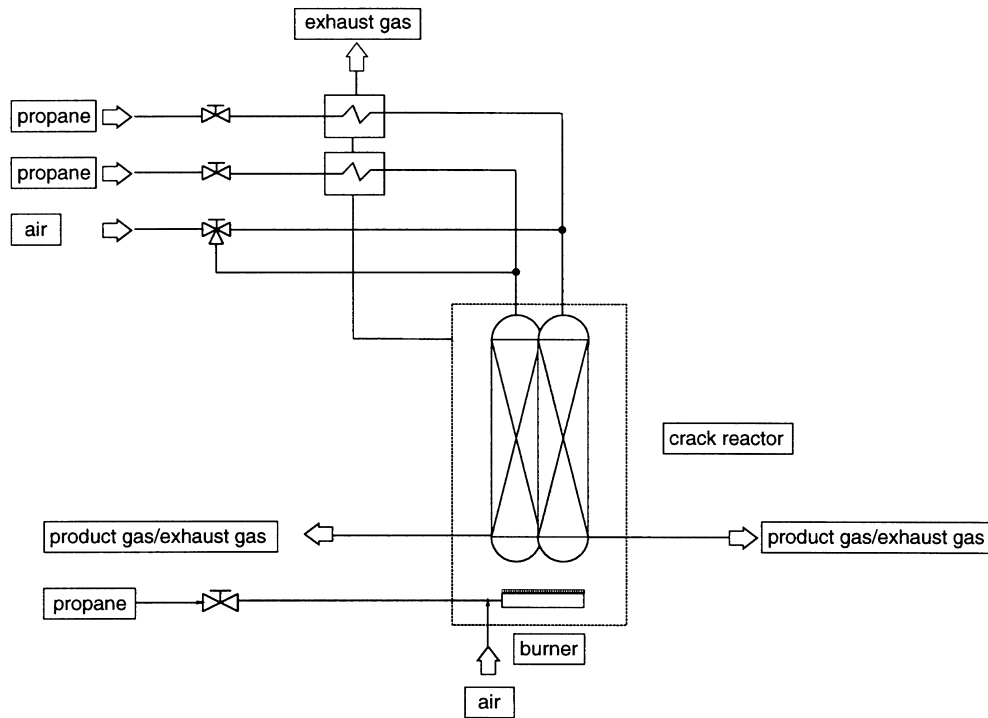


Fig. 11. Test stand flowsheet of the compact propane cracking reactor system.

temperature was held at 900°C and system pressure at 1 bar. Fig. 12 shows the gas composition of the product gas during experimental time.

The hydrogen content in the product gas decreases slowly with experimental time. The following reasons for this performance have to be taken into account. First, the carbon deposition at the reactor walls covers the active catalytic components of the wall material. Furthermore, the reactor volume decreases slowly by the deposited carbon and there-

fore the residence time of the gas in the reactor decreases. These reasons lead to a slight decrease of the hydrogen content in the product gas. The experiment with the highest hydrogen output was the one with a volumetric flow of 1800 sccm propane feed. At this flow the residence time of the cold gas was 100 s and the hydrogen content of the effluent gas 84%. In this case equilibrium concentration of hydrogen is 98.3%. Compared to the two other feed flows, the power output related to the produced hydrogen reached a maxi-

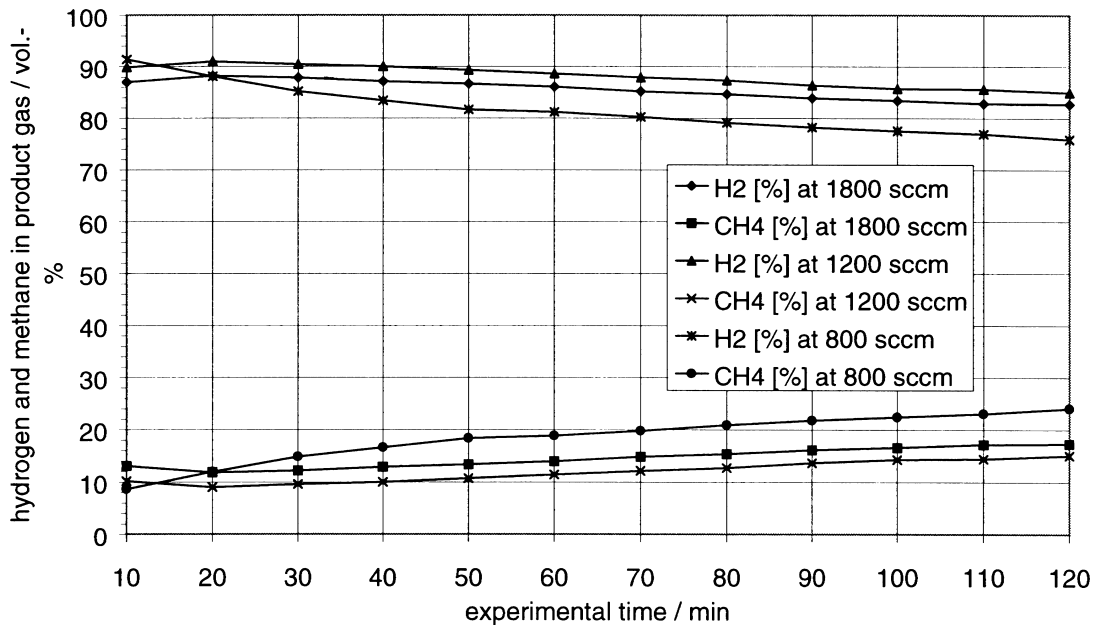


Fig. 12. Product gas composition at a wall temperature of 900°C and atmospheric pressure.



mum. So far the hydrogen output of this laboratory-scale reactor amounts to 1.04 kW.

Another product of the decomposition process is solid carbon buildup in the reactor in three different forms. Dependent upon operating conditions, carbon is either obtained in the form of amorphous carbon, soot or graphite. They are formed in the gas phase by coke precursors such as acetylene, diolefins and aromatics which produce polycyclic hydrocarbons. Several growth mechanisms are surmised, such as agglomeration of small carbon particles, polymerisation of hydrocarbons, or decomposition of hydrocarbons on carbon particles. Soot particles taken from the gas phase are of spherical form and have nearly the same diameter of about 0.8  $\mu\text{m}$ . The carbon particles from the reactor walls have a cobblestone structure. They are probably formed from drops of tar deposited on the reactor wall. This type of coke made up the main part of the carbon build in the cracking process. The third form is filamentous carbon formed by catalytic material on the reactor walls.

#### 4. Conclusions

Methanol reforming is a convenient way to produce pure hydrogen for SPFC applications. The integration of reaction and purification step in a small and compact system makes mobile and decentral power generation systems based on carbonaceous fuels interesting.

The other suitable way to produce a hydrogen-rich gas for SPFCs is the decomposition of light hydrocarbons. Such

systems can be built very small, simple and inexpensive because further gas purification is not necessary. Furthermore, the process itself has the lowest energy consumption [8] compared to other hydrogen production technologies. The process can be carried out without release of carbon dioxide if the produced carbon is not burned off but stored or used for other applications.

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