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Portable PEFC generator with propane as fuel

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Abstract

Propane is a typical widespread fuel, which is often used for camping applications, because it can be transported easily and be stored in liquid form in pressure vessels for mobile and portable use. Propane as feedstock for hydrogen production offers a new way to a cheap fuel for fuel cells. The generation of a PEFC hydrogen fuel gas can be perfomed by catalytic cracking of propane. The decomposition of the liquified hydrocarbon takes place at temperatures above 800°C at atmospheric pressure. A fuel processor based on this simple concept can be built much smaller and less expensive than existing ones using steam reforming technology. A propane cracking system works without shift-conversion, gas purification for removal of CO and without a steam generator. The removal of small amounts of CO from the hydrogen rich gas produced is possible by using a simple methanation step. A low cost portable fuel cell device is under development consisting of a polymer electrolyte fuel cell, a hydrogen production system based on catalytic cracking of propane, a propane storage container and an electronic control unit. Combined with a fuel cell providing 200 W gross electric power, a net power output of about 130 to 160 W can be achieved. The PEFC used will contain low cost bipolar plates made of carbon–polymer composite materials. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Hydrogen; Thermal cracking of propane; Catalytic cracking of propane PEFC; Bipolar plates; Carbon-polymer; Composite materials

1. Introduction

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 literature by several authors [1,2]. Propane as feedstock for hydrogen production offers a new way to a cheap fuel for fuel cells. The generation of a PEFC hydrogen fuel gas can be perfomed by catalytic cracking of propane. The decomposition of the liquified hydrocarbon takes place at temperatures above 800°C. A fuel processor based on this simple concept can be built much smaller and less expensive than existing ones which use steam reforming technology.

Propane is a typical widespread fuel, which is often used for camping applications. So this might be a promising market for small portable fuel cell systems using propane as fuel. Propane is an important byproduct of oil exploration and of crude oil processing in refineries. In general, the sulphur content of propane is very low, so it is an environmentally beneficial fuel. Propane is a cheap fuel with a high power density. It can be transported easily and

can be stored in liquid form in pressure vessels with typical contents ranging from 425 g for very small gas canisters up to 33 kg for mobile and portable use. The propane molecule C_3H_8 has a high hydrogen content. Commercial propane is a mixture of at least 95 mass% propane and propene, the residual fraction consists of ethane, ethene, butane and butene.

2. Fundamentals

The cracking of propane in order to produce hydrogen as fuel for fuel cells offers some advantages due to the simple process design. Hence, these investigations are concerned with thermal and catalytic cracking of propane, which can be described by the following main reaction [1]:

$$C_3H_8 \Leftrightarrow 3C + 4H_2, \qquad \Delta_R\overline{H}^\emptyset = 103.8 \text{ kJ/mol.}$$
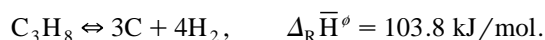
The endothermic cracking process itself needs only about 5% of the lower heating value of propane to dissociate the propane molecules into carbon and hydrogen. A disadvantage is the ratio of hydrogen to propane of four compared to a ratio of about 10 for steam reforming. This drawback should be compensated by the advantages of the

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Autothermal reforming process

Propane

Water

Air

| Autothermal Reformer | → | HT-Shift | → | NT-Shift | → | Fine Purification | → | PEFC |

Catalytic cracking of propane

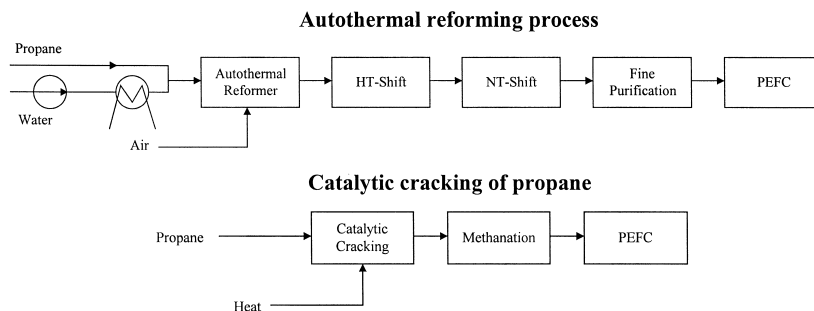Propane → | Catalytic Cracking | → | Methanation | → | PEFC |

Heat

Fig. 1. Process schemes of autothermal reforming and thermal cracking of propane.

simple system design. The catalytic decomposition produces a hydrogen-rich gas stream with residues of methane and traces of carbon monoxide and carbon dioxide. A propane cracking system works without shift-conversion, gas purification for removal of CO and without a steam generator, therefore, the reactor can be built much cheaper and less complex than systems based on steam reforming. The removal of small amounts of CO caused by oxygen impurities in the propane feed or the reduction of the oxidized catalyst is possible by using a simple methanation step as shown in Fig. 1.

A calculation of the gas composition in a thermodynamic equilibrium of an autothermal reforming process of propane as a function of temperature with a steam to carbon ratio S/C = 1 and a stoichiometric value $\lambda = 0.4$ is presented in Fig. 2. At a temperature of 700°C, the calculations show a maximum hydrogen content of about 25 vol.%. Most of the gas consists of nitrogen and water as steam. Carbon monoxide and carbon dioxide amounts to about 8 vol.% each. Therefore, a further gas treatment to purify the hydrogen rich gas is necessary if the gas is to be used in PEFC applications. As the anode catalyst of a polymer electrolyte membrane fuel cell is usually based on platinum, which is easily poisoned by carbon monoxide, the conditioned feed gas should contain less than 100

ppmv CO and preferably less than 10 ppmv. A carbon monoxide management system is required to lower the CO concentration to acceptable levels. In many cases, the CO purification system consists of a combination of physical or chemical processes to achieve the necessary reduction in CO content, which makes the overall hydrogen production process more complex and expensive.

In Fig. 3, the product gas composition in the thermodynamical equilibrium of the propane cracking process is depicted. The calculations are made for different pressures in a temperature range of 500–1200°C. The equilibrium calculations show a strong dependence of the product gas composition on temperature and pressure. The endothermic propane decomposition is more efficient at higher temperatures. Due to the increase of volume during propane cracking, the decomposition is favoured by decreasing pressure. The figure demonstrates that this process yields high hydrogen concentrations at ambient pressure and temperatures of 800°C or higher.

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 precise experimental conditions, the gas
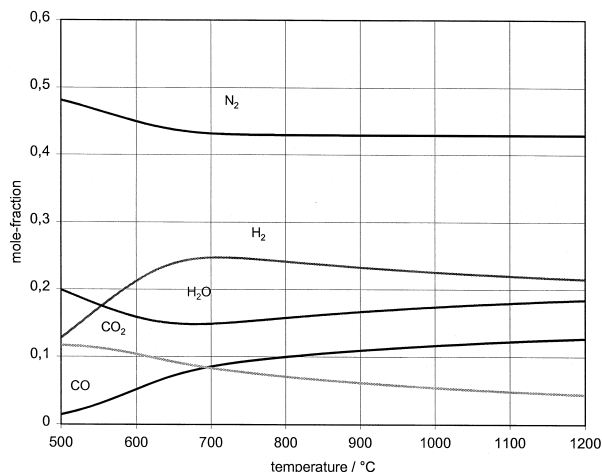
Fig. 2. Gas composition in the thermodynamic equilibrium of autothermal reforming of propane (S/C = 1, $\lambda = 0.4$).
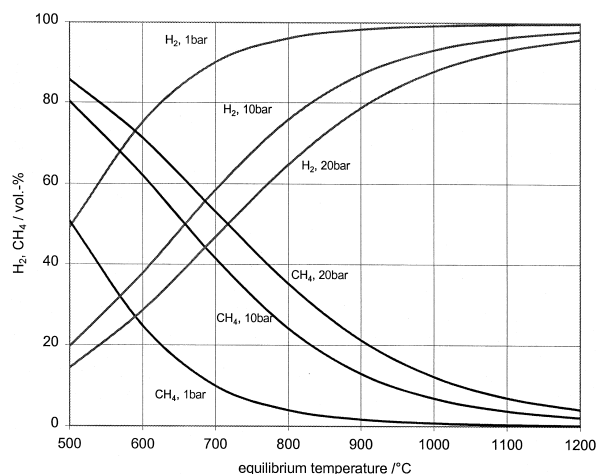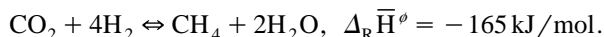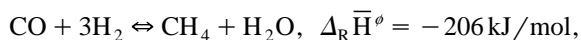
Fig. 3. Gas composition in thermodynamical equilibrium of propane cracking.

produced only consists of hydrogen with a few percent of methane, which does not harm the PEFC. Methane can be considered as an inert gas for the stack of a PEFC working in the typical temperature range of 60–80°C [2].

High reaction rates for the process can be achieved by using appropriate catalysts for cracking. In recent years, several studies investigated the decomposition of light hydrocarbons, mainly methane, with supported catalysts. The studies agreed that the most suitable catalysts for this application are Pd, Rh, Ru, Ni, Co and Fe [2]. Furthermore, carbon particles formed during the cracking reaction have catalytic activity for the decomposition process [2]. Therefore, the hydrogen content of the product gas can nearly approach the amount of hydrogen in the calculation of thermodynamic equilibrium. The deposited carbon accumulates on the surface of the catalyst and the hydrogen rich gas exits from the reactor. After a certain time, the catalyst is covered with carbon and must be regenerated. This can be done by passing air over the catalyst to burn off the carbon.

A small amount of carbon monoxide and carbon dioxide is produced at the beginning of the cracking step resulting from the reaction of propane feed and residual oxygen from the regenerating step and also from the reduction of the catalyst, which has been oxidized during regeneration. All the catalysts which have been tested so far produced some carbon monoxide caused by catalyst reduction. The CO content is higher at the beginning of a decomposition step and decreases rapidly. The cracking gas mixture must be ducted to the burner for a few minutes until the CO content decreases to less than about 1 vol.%. The CO concentration can be reduced further to a suitable level for PEFC of 20 ppmv by a methanation step over a catalyst. The carbon monoxide and the traces of carbon dioxide react as follows:

$$CO + 3H_2 \Leftrightarrow CH_4 + H_2O, \ \ \Delta_R \overline{H}^{\phi} = -206 \, kJ/mol,$$

$$CO_2 + 4H_2 \Leftrightarrow CH_4 + 2H_2O, \ \ \Delta_R \overline{H}^{\phi} = -165 \, kJ/mol.$$

Fuel processors operating on steam reforming cannot be combined with a methanation reactor, because of the presence of carbon dioxide which would react with hydrogen to form methane. The removal of CO from a hydrogen-rich gas by methanation is a well known technology that leads to a CO content of less than 10 ppmv. Using such a simple methanation step to remove CO is a very important advantage of a propane cracking fuel processor.

3. Portable fuel cell system concept

The key elements of the proposed system are an appropriate catalyst and a suitable reactor design. The overall portable fuel cell system consists of a propane cracking batch reactor, a methanation reactor, a burner, an air blower, a propane container, eight magnetic valves, a control unit, a polymer electrolyte fuel cell (PEFC), an accumulator and a charge controller and is shown in Fig. 4.

The basic reactor concept consists of a two-reactor system, in which one reactor is used for hydrogen production while the other one is being regenerated; hence, the cracking reactor is constructed of two chambers for batch operation. The catalytic bed has to accept the deposition of greater amounts of solid carbon without showing greater changes in flow resistance. The reactor material has to withstand high thermal loading with temperatures in excess of 1200°C during regeneration by burning off the deposited carbon. Furthermore, the gas quality inside the reactor chamber changes from a reducing atmosphere during the cracking step with deposition of carbon, which can lead to a carbonization of the wall material, to an oxidizing atmosphere during regeneration. Therefore, a high-temperature alloy with a high Ni-content has been chosen as reactor material.

A propane gas flow in the range of about 0.7 Nl/min is fed to the cracking system. In the two-reactor system, one reactor is used for about 30 min for hydrogen production of 2.25 Nl/min equivalent to a hydrogen power content of
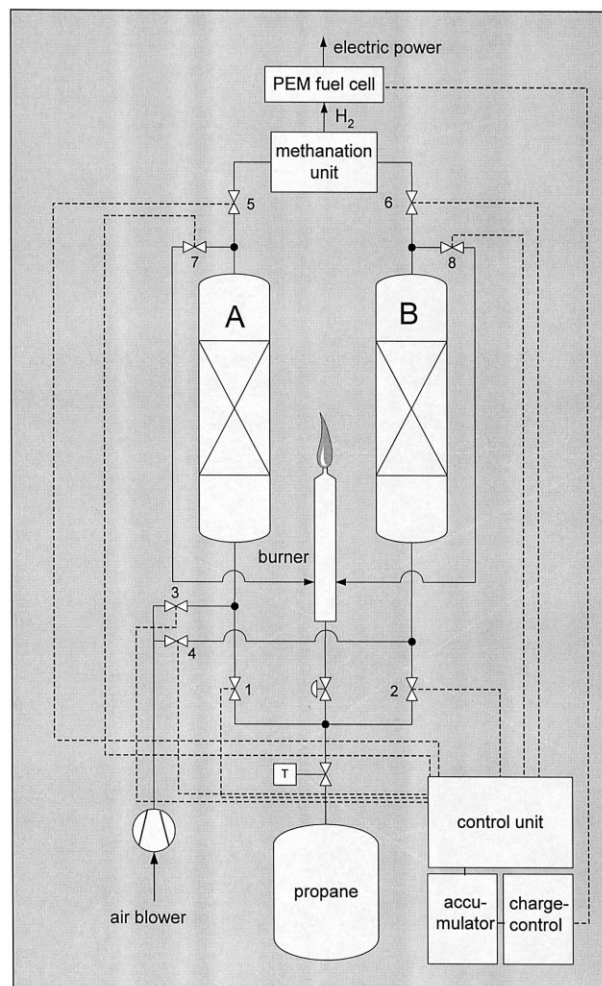

Fig. 4. Scheme of a portable fuel cell system with propane cracker.

400 W, while the other one is being regenerated by an air flow of about 15 Nl/min. The calculated power output of hydrogen is based on a lower heating value of 3 kWh/Nm^3.

In the system described, the reactors are heated by a central propane burner to a temperature of about 900°C, where the propane feed decomposes into hydrogen, methane and solid carbon. The commercial propane burner used in this system has a maximum power output of 1.5 kW$_{th}$. This maximum power is necessary for a quick start up of the system. During cracking and regeneration, the burner has only to compensate for the heat of start up and cracking of propane and thermal losses access the surface of the system.

About 55% of the lower heating value of the cracked products are stored in the deposited carbon. At 900°C, the energy released from the burning of the carbon is seven times higher than the energy needed for thermal decomposition. Thus, neglecting heat losses, a maximum conversion efficiency, defined as lower heating value of the produced hydrogen in relation to that of the cracking propane feed, is given by $\eta_{conv.} = 47\%$. Assuming that the fuel cell has an electric power output of 200 W$_{el}$ and with a maximum demand of electrical power for the peripheral components of about 70 W$_{el}$, a propane feedgas stream corresponding to 1000 W, a power demand of 400 W$_{th}$ to heat up the feed gas to cracking temperature and to compensate the necessary cracking energy and heat losses, the overall net electrical efficiency of the laboratory system described amounts to $\eta_{net} = 9\%$, for a fuel cell efficiency of 50%.

Most of the carbon remains in the catalyst bed; only small particles are transported by the gas flow to the reactor exit where they can be removed by filter elements. The product gas leaving the cracking reactor can now be ducted to the methanation step, which consists of a small chamber of 50 ml volume filled with a precious metal catalyst. At a temperature of 300°C, the methanation step reduces the carbon monoxide content of the gas to a level lower than 10 ppm. This gas can now be used as fuel for a PEFC without any further purification. Besides the advantage of CO removal the steam produced during the methanation serves as a humidifier for the hydrogen-rich gas.

A typical operating cycle of the system starts with hydrogen production by propane cracking in chamber A, while chamber B is regenerated by blowing air through the catalyst bed burning off the deposited carbon. The combustion air of 15 Nl/min is fed into the system by a membrane pump which needs 24 W$_{el}$ at an operating voltage of 12 V. This pump is double ended and also serves as air supply for the PEFC.

After about 30 min, both reactors crack propane for about 2 min simultaneously, but the product gas of chamber B is ducted to the burner because of the high concentrations of CO and CO$_2$. When the content of carbon monoxide in chamber B is lower than 1 vol.% chamber A will be regenerated and chamber B starts to produce the

gas mixture. This is fed via the methanation reactor to the PEFC. In this way a continuous fuel supply for a PEFC can be provided [3,4].

There are several peripheral components necessary to sustain a continuous hydrogen supply for the fuel cell system. The time control unit, the relays for the magnetic valves, the magnetic valves and the membrane pump have an electric power demand, which lies between 40 and 70 W.

4. Experimental results

The catalyst should be able to sustain a few hundred cycles. Several different catalysts have been tested, most of them were supported on porous ceramic. To avoid the formation of carbon in the bulk of the catalyst, which would otherwise lead to early deactivation or destruction, the ceramic should have a low porosity and therefore can only provide a small active surface. Furthermore, the catalyst and its support structure should be resistant to temperatures of up to 1200°C. The first investigations included the testing of catalysts made of Ni, Fe Co, Pd, Pt and Ru to search for an appropriate catalyst. The objective of such catalyst screening is to determine the hydrogen production rate and the stability as a function of the number of cycles.

Figs. 5 and 6 show typical experimental results of long-term testing of a commercial Ni- and a commercial Fe-catalyst. Fig. 7 represents an in-house self developed and stabilized precious metal catalyst. The diagrams show the gas composition as a function of cycle time during six cycles of a typical long-term test for the different catalysts. In this test procedure, to evaluate lifetime and stability of the catalysts a cracking step lasted 15 or 30 min. The hydrogen production step was followed by 15 or 30 min of regenerating the catalyst, burning off the deposited carbon
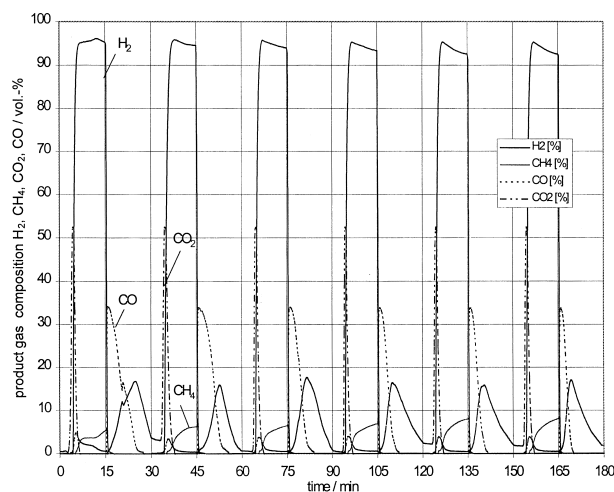

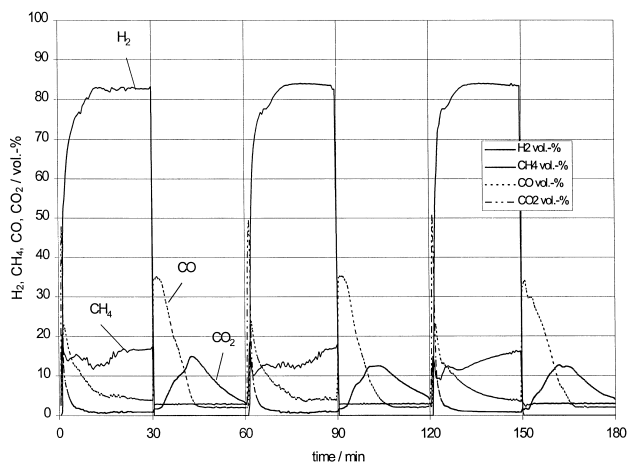Fig. 5. Gas composition during cracking and regeneration cycles of a Ni-catalyst at 900°C and 1 bar.

Fig. 6. Gas composition during cracking and regeneration cycles of a Fe-catalyst at 900°C and 1 bar.

by blowing air through the catalyst bed. The long-term test included 240 cycles. Each cycle consisted of 15–30 min of propane cracking and regeneration. The catalyst bed had a temperature of 900°C during the propane cracking and a maximum temperature of about 1200°C during the regeneration of the catalyst bed.

The product gas composition of the Ni-catalyst, as shown in Fig. 5, is characteristic for metal catalysts like Ni-, Fe- and Co-catalysts. At the beginning of each cracking step the carbon dioxide content of the gas produced increases to about 50 vol.% and higher for a very short time. Simultaneously, the carbon monoxide content increases also. The reason for such high concentrations of carbon dioxide and carbon monoxide is due to the reduction of the catalyst which has been oxidized during the regeneration step. The propane feedgas is now cracked to form carbon and hydrogen, which reduces the metal oxide during formation of CO_2, CO and steam. In case of Ni catalysts, the CO_2 content drops after about 2 min to a few hundred ppm and the CO content decreases to about 0.7 vol.%, while the H_2 content increases rapidly to nearly 97 vol.% with residual methane. The deposited carbon starts to cover the surface of the catalyst and leads to a slight decrease of its activity. While the hydrogen content is decreasing with time, the methane content increases continuously to about 7 vol.% within 15 min. The reaction rate of the cracking process decreases because of the carbon covering the catalyst surface. The desired cycle time of about 30 min can easily be achieved, as shown in Fig. 6 for the iron catalyst. Iron catalysts produce CO and CO_2 for a longer period because the oxygen uptake of iron during the regeneration process is higher than that of nickel.

After 15 min the propane feed was shut down and air was blown into the catalyst bed to regenerate the reactor. Now, combustion gas leaves the exit of the catalyst bed. The carbon burns off and the CO concentration rises rapidly to 35 vol.% during the first 3 min of regeneration.

While the carbon monoxide is decreasing the carbon dioxide content increases. At the end of the regeneration step, the CO and the CO_2 content of the flue gas become depressed because of the complete burning of the carbon. The regeneration air flows through the reactor without a chemical reaction. Only a small amount of the air oxidizes the surface of the catalyst to form metal oxide. Therefore, the regeneration air flow is a useful optimization point.

In contrast to the metal catalysts Ni, Fe and Co, precious metals yield a very different gas composition during the cracking and regeneration cycles. Precious metals are much more active in catalyzing chemical reactions and, therefore the metal loading of this catalysts can be kept to a minimum. As an example, the gas composition from a precious metal catalyst is shown in Fig. 7. This figure shows the product gas composition of a proprietary catalyst with a special stabilized support to prevent the active metal surface layer from sintering.

At the beginning of each cracking cycle, the CO and CO_2 content is much lower than in cracking with Ni or Fe catalysts. Almost no carbon dioxide is produced during the cracking cycle and the carbon monoxide content decreases rapidly after about 2 min. The minimum hydrogen content at the end of the cracking cycle is always in the range of 68–70 vol.%. Burning off the deposited carbon from a commercial, non-stabilized catalyst leads to about 20 vol.% of carbon dioxide in the combustion gas, whereas the stabilized catalyst produces larger amounts of carbon monoxide during regeneration. This effect may be a characteristic of the higher activity of the stabilized catalyst surface.

The CO content of the hydrogen gas during the cracking step can easily be reduced with a methanation reactor. A variety of suitable catalysts for methanation were tested, the catalyst temperature was chosen between 250°C and 400°C. The best results were achieved by a commercial Ru-catalyst, which was selected for the portable hydrogen production system. The hydrogen rich gas containing only
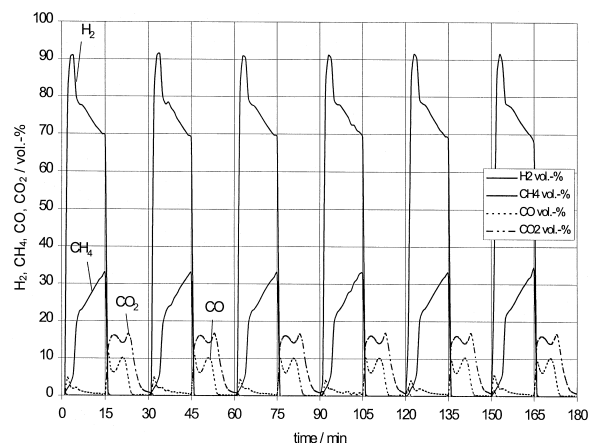

Fig. 7. Gas composition during cracking and regeneration cycles of a self developed stabilized precious metal catalyst at 900°C and 1 bar.

steam, methane and carbon dioxide is suitable for a PEFC. This hydrogen gas can now be ducted to a PEFC.

5. Portable cracking system

From these catalyst investigations, a portable hydrogen production system based on catalytic cracking of propane as feedstock was developed. Fig. 8 shows a photograph of the propane cracker. The laboratory model has a volume of about 72 l without the tank and fuel cell and a weight of 15 kg. The hydrogen power output amounts to 500 W. In the start up phase the external propane burner consumes 1.2 kW of propane. During normal operation the system requires about 400 W to sustain the cracking process and to compensate for heat losses. The cracking reactors require 0,8 Nl/min propane for a hydrogen production of 500 W power output. The gas produced consists of about 90 vol.% of hydrogen and residual methane. The peripheral components such as magnetic valves, membrane pump, charge control and control unit need an electric power supply of nearly 80 W. With further development and optimization the efficiency of the whole system including fuel cell can be increased by 15-20%. Due to the simple concept, the projected costs for such a hydrogen production system without fuel cell are in a range of 800-1000 DM (US$400–500).

The hydrogen content of the product gas of the laboratory system is dependent on the type of catalyst. The two batch reactors of the cracker were filled with different
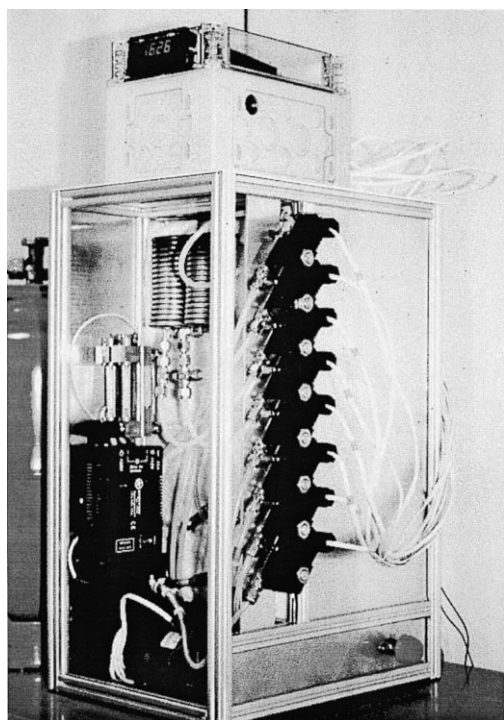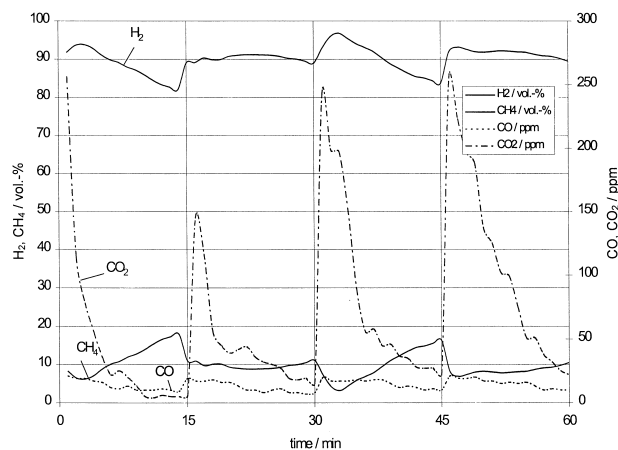
Fig. 9. Product gas composition of the catalytic cracking system with methanation.

catalysts for testing purposes. In chamber A the propane feed was cracked over a commercial precious metal catalyst while chamber B were filled with a proprietary stabilized precious metal catalyst. Both catalysts have the same metallic loading a support of γ-Al_2O_3; the catalyst in chamber B was stabilized with a rare earth metal to prevent the catalytic component from sintering. Fig. 9 shows the difference in activity between these two catalysts. The commercial catalyst in Reactor A loss its activity during the first 15 min of hydrogen production rapidly. After switching to the second chamber B containing the stabilized catalyst, the activity stayed almost constant for 15 min. The product gas showed a continuous gas flow with a hydrogen content of 90 vol.%. The carbon monoxide content in the hydrogen-rich produced gas can be reduced to about 20 ppmv or below with a simple methanation unit filled with a ruthenium catalyst.

6. Fuel cell stack with low cost bipolar plates

A completely portable PEFC generator with propane as fuel a 200 W/12 V PEFC stack is under development. The special feature of the stack will be the use of low cost bipolar plates. The bipolar plates employed in the PEFC

Fig. 8. Laboratory model of the catalytic cracking system.

Table 1
Material costs of low cost composites

Composite	Carbon–polymer	Carbon black polymer
Volume Resistivity	0.05 Ω cm	0.2 Ω cm
Density	1.61 g/cm^3	1.01 g/cm^3
Costs per kg	5.8 DM/kg	3.3 DM/kg
	3.1 US$/kg	1.8 US$/kg
Costs per kW[a]	13 DM/kW	5 DM/kW
	7.0 US$/kW	2.7 US$/kW

[a]At very moderate current densities (cell voltage: 0.7 V, currrent density: 0.2 A/cm^2).
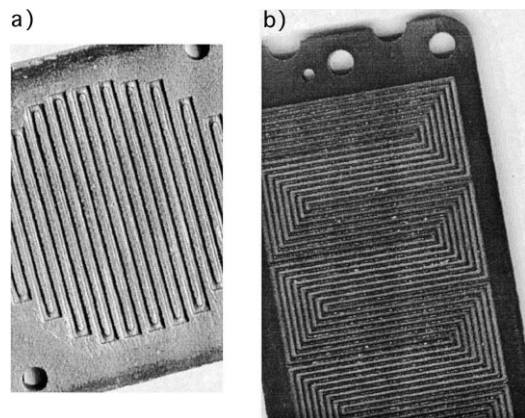
Fig. 10. Low-cost bipolar plates.

stack will consist of a recently developed low cost carbon–polymer composite. Volume resistivity, density, material costs and costs per kW of two development lines of low-cost composites are shown in Table 1.

Standard composite mixtures consisted of a thermoplastic polymer and a carbon compound with additional additives [5]. The mixtures were prepared in a kneader at 230°C. The product was then transferred to a heated press and was manufactured into bipolar plates of high mechanical strength. Carbon–polymer bipolar plates up to 30 cm × 30 cm are under development with this processing technique.

Two examples of experimental bipolar plates of carbon–polymer composite material are shown in Fig. 10.

Cell performance of the carbon–polymer bipolar plates was evaluated at 60°C and ambient air pressure in a 2 cell PEFC-stack (active area = 17.36 cm^2) with stainless steel end plates. The 2 cell PEFC-stack with carbon–polymer bipolar plate of 6 mm thickness exhibited, at 500 mA/cm^2, a 30 mV lower cell voltage than with stainless steel bipolar plates of 5 mm thickness. Besides low cost and electrical conductivity, the corrosion resistance in the fuel cell environment is another important design criteria for bipolar plates. Therefore, extended corrosion tests and lifetime tests are currently underway with a number of partners.

7. Summary and outlook

The generation of a PEFC hydrogen fuel gas can be performed by catalytic cracking of propane. A fuel processor based on this simple concept can be built much smaller and less expensive than existing ones using steam reforming technology, because the reactor design is possible without shift-conversion, gas purification for removal of CO or a steam generator. The removal of CO from the hydrogen-rich gas produced is possible by using a simple methanation step.

The process steps and the chemical reactions of propane cracking and methanation have been intensively investigated, a number of different commercial catalysts were tested and a two stage catalyst system has been developed. Now, a portable fuel cell device for demonstration purposes with a net power output of about 130 W is under development, consisting of a polymer electrolyte fuel cell (PEFC), a hydrogen production system based on catalytic cracking of propane, a propane storage container and an electronic control unit.

The main points for further development and optimization will be the use of magnetic valves with less energy consumption and using the exothermic combustion energy of carbon during regeneration for the cracking process. In this way, a theoretical maximum electrical efficiency of about 23% can be achieved assuming a fuel cell efficiency of 50%. Increasing the power output of such a system for stationary applications would require the energy content of the carbon to be recovered as high quality heat from burning the CO-rich gas outside the chambers or by integrating heat exchangers into the reactors. This could lead to a higher fuel utilization of the propane.

For the portable PEFC generator with propane as fuel, a 200 W/12 V- PEFC stack is under development at the University of Duisburg. The special feature of the stack will be the use of low cost bipolar plates made of a carbon-polymer composite. Hence, an overall portable electric power generator consisting of a hydrogen production system based on catalytic cracking with simple process design and a fuel cell with low cost bipolar plates will become available.

References

[1] M. Steinberg, Production of Hydrogen and Methanol From Natural Gas with Reduced CO_2-Emissions Hydrogen Energy Progress XI, Proc. Of the 11th World Hydrogen Energy Conference, Stuttgart Germany 1996.
[2] M.G. Poirier, C. Sapundzhiev, Catalytic decomposition of natural gas to hydrogen for fuel cell applications, Int. J. Hydrogen Energy 22 (4) (1997) .
[3] K. Ledjeff-Hey, V. Formanski, Th. Kalk, J. Roes, Compact hydrogen production systems for solid polymer fuel cells, J. Power Sources 71 (1998) .
[4] K. Ledjeff-Hey, Th. Kalk, J. Roes, Catalytic cracking of propane for hydrogen production for PEM fuel cells, 1998 Fuel Cell Seminar, Proceedings, Palm Springs, CA, 1998.
[5] K. Ledjeff-Hey, F. Mahlendorf, O. Niemzig, A. Trautmann, Electonically conducting composite materials as bipolar plates for PEM Fuel Cells, 1998 Fuel Cell Seminar, Proceedings, Palm Springs, CA, 1998.