Compact methanol reformer test for fuel-cell powered light-duty vehicles

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Abstract

On-board production of hydrogen from methanol based on a steam reformer in connection with the use of low-temperature fuel-cells (PEMFC) is an attractive option as energy conversion unit for light-duty vehicles. A steam reforming process at higher pressures with an external burner offers advantages in comparison to a steam reformer with integrated partial oxidation in terms of total efficiency for electricity production. The main aim of a common project carried out by the Forschungszentrum Jülich (FZJ), Haldor Topsøe A/S (HTAS) and Siemens AG is to design, to construct and to test a steam reformer reactor concept (HTAS) with external catalytic burner (FZJ) as heat source as well as catalysts for heterogeneously catalyzed hydrogen production (HTAS), concepts for gas treatment (HTAS, FZJ) and a low-temperature fuel cell (Siemens). Based on the experimental results obtained so far concerning methanol reformers, catalytic burners and gas conditioning units, our report describes the total system, a test unit and preliminary test results related to a hydrogen production capacity of 50 kW (LHV) and dynamic operating conditions. This hydrogen production system is aimed at reducing the specific weight (<2 kg/kW_{th} or 4 kg/kW_{el}) combined with high efficiency for net electricity generation from methanol (about 50%) and low specific emissions. The application of Pd-membranes as gas cleaning unit fulfill the requirements with high hydrogen permeability and low cost of the noble metal. © 1998 Elsevier Science S.A.

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1. Introduction

Drive systems for cars using a polymer electrolyte membrane fuel cell (PEMFC) can lead to increased energy usage efficiency and, especially, substantially reduced emissions compared with the best foreseeable drive system based on the internal combustion engine. Methanol is the best energy carrier for such systems, when taking availability, costs and safety aspects into account.

Objectives of a common project are the design and construction of the units of the passenger car drive system, i.e. the compact methanol reformer (CMR) including a catalytic burner, gas cleaning unit(s) and PEMFC. Further objectives are assembly and operation of the complete test system, the description of the dynamic behaviour of this test system and calculation of the energy and emission balances for the full fuel cycle. On completion of the research the design and

construction of a compact unit comprising methanol reformer, gas cleaning step and PEMFC stack on a mass production basis should be possible. The total unit should have the following characteristics:

1. total weight less than 4 kg/kW_{el};
2. total volume less than 5 l/kW_{el};
3. start-up time less than a few minutes;
4. price less than 100 ECU/kW_{el} if mass produced;
5. emissions of CO, NO_X and VOC are lower than EURO 2005 standard.

The detailed design of the CMR, including the catalytic burner and gas cleaner will mainly be done by HTAS. The operation under both stationary and transient conditions will mainly take place at FZJ. In parallel with the above, improved membrane gas cleaning systems will be developed by HTAS and tested in connection with the CMR prototype at FZJ. Siemens will provide know-how about the reformer/fuel cell interface and will deliver a prototype
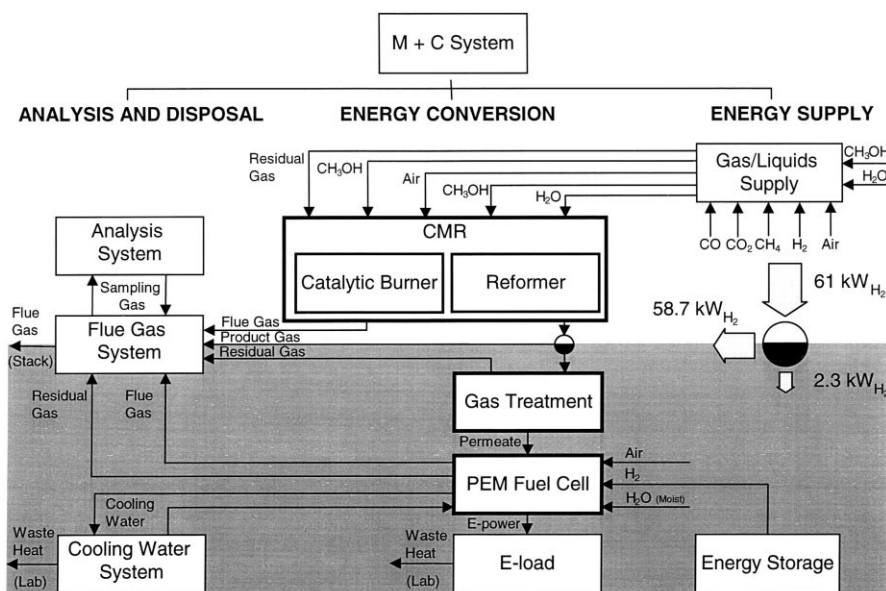
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Fig. 1. Test drive system.

PEMFC stack to be tested in integration with the CMR prototype. The fuel cell stack will be examined after use.

The test drive system in Fig. 1 consists basically of a methanol reformer; a catalytic burner supplying heat to the methanol reformer; a gas clean-up system and a PEMFC stack plus assorted pumps, blowers and heat exchangers. In addition, a quite elaborate control, a data acquisition system and analysis system is included. The CMR consisting of the reformer and the catalytic burner including the necessary heat transfer system will be constructed for the full, projected electric power generated, i.e. 25 kW, whereas the gas clean-up unit and the PEMFC stack will be limited to 1 kW due to the present state of the technical development and economic considerations. Mass and energy balances have been calculated and a flowsheet prepared which forms the basis of the final design of the test drive system.

2. CMR for hydrogen from methanol

The steam reforming of methanol is catalyzed by Cu/ZnO-type catalysts and can be performed in integral fixed bed reactors [1]. The methanol/water (CH_3OH/H_2O) mixture is converted into hydrogen (H_2) and carbon dioxide (CO_2) according to the following, heterogeneously catalyzed reforming reaction:

$$CH_3OH + H_2O \Leftrightarrow CO_2 + 3H_2 \qquad (1)$$

In addition to this reforming reaction, the reverse shift reaction also proceeds. Thus, the product gas also contains carbon monoxide (CO).

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \qquad (2)$$

The heterogeneously catalyzed reforming of methanol with

water produces a hydrogen-rich gas at low pressures in the operating temperature range of 200 to 300°C. The actual gas composition will depend on the approach to the chemical equilibrium, which is a function of catalyst activity and space velocity [2]. The combination of the gas cleaning with the methanol reformer requires the hydrogen production unit to operate at a high pressure level of 20 bar. Equilibrium calculations and experimental data of methanol steam reforming at high pressures indicate a slight decline in the rate of methanol conversion at high pressures.

As part of the completed JOULE II project, experiments were carried out for methanol steam reforming under test conditions similar to those described here, but using long fixed beds (1.5 m ⇔ 150%) [3]. Since much shorter beds are used in constructing the compact methanol reformer, additional experiments were carried out in the JOULE II test rig, see Fig. 2. Fig. 3 shows measurement series at temperatures of 260 and 280°C using a catalyst bed with
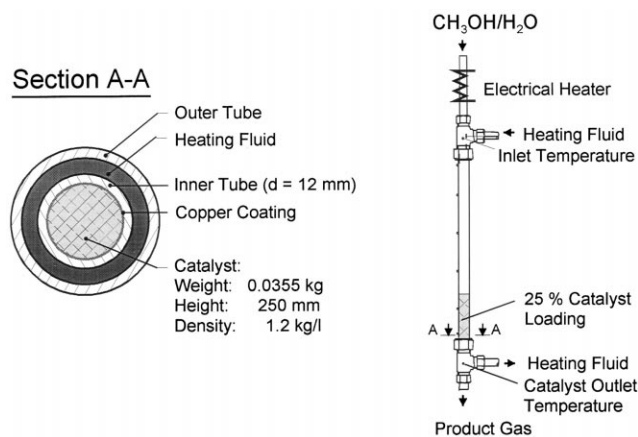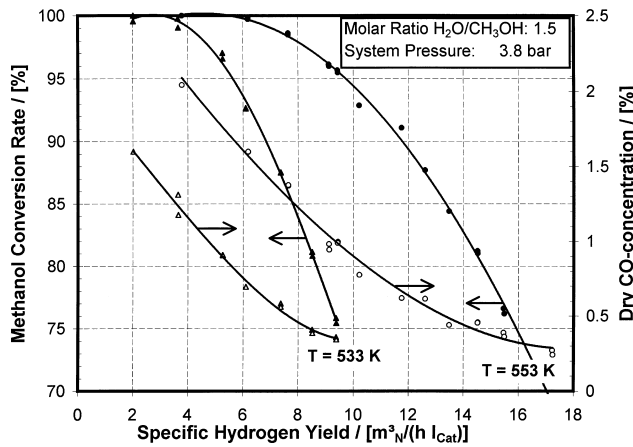

Fig. 2. Reformer test rig.

Fig. 3. Experimental reformer results.

35.5 g (25.5%) of catalyst at 3.8 bar. The catalyst used is a methanol reforming catalyst in the form of pellets called MDK-20 and produced by HTAS.

Fig. 3 shows measurements of the methanol conversion rate as a function of hydrogen yield. The hydrogen yield covers the amount of hydrogen produced under standard conditions (1.013 bar, 273.15 K) per hour and per litre catalyst. It can be seen that the conversion rate is 100% for low educt mixture loads, i.e. low hydrogen yields. At higher loads or hydrogen yields, the methanol conversion rate decreases with increasing load. A possible operating point for a reformer may be 10 $m^3/(h \; l_{cat})$ for a conversion rate of 95% at 280°C. Operating conditions with conversion rates below 95% are not of interest for operating a compact reformer. In comparison, the measurements by Colsman [3] for conversion rates up to 95% at 280°C show 13 $m^3/(h \; l_{cat})$. It can also be seen that the hydrogen yields increases 1.7-fold in a temperature interval from 260 to 280°C at constant conversion rate, whereas a further temperature increase to 300°C in the range of high methanol conversion rates does not involve any further increases.

In addition, Fig. 3 shows the CO content (dry state) in the reformer product gas as a function of hydrogen yield for both temperatures, i.e. 260 and 280°C. It can be seen that, starting from equilibrium, the CO content decreases with increasing hydrogen yield. Due to the CO content in equilibrium, the CO contents are at a higher level with rising temperature. For a conversion rate of 95% and a hydrogen yield of 10 $m^3/(h \; l_{cat})$ a CO content of 0.8% CO is shown for a 25% bed at 280°C.

3. Catalytic burner for heat generation

The catalytic burner in the compact reformer has the function of providing the thermal energy required for the reforming reaction, on the one hand, and of quantitatively converting all gases from the system, which still contain burnable fractions, into carbon dioxide and water. This gives the following requirement profile:

1. the emissions of CO, nitrogen oxides and hydrocarbons must be below the EZEV standard due to appropriate burner design;
2. the operating range is to be selected so as to prevent flashbacks, since these lead to a disconnection of fuel supply and thus interrupt operation;
3. different fuels of various composition are supplied to the burner. Moreover, inert admixtures also leave the drive system through the burner. Attention must be paid to the influence on the emission balance;
4. furthermore, the burner should not change its properties throughout the service life of the drive system, i.e. it must have adequate long-term stability.

The basic burner structure is a ceramic hollow cylinder to which fuel gas premixed with air is internally supplied, see Fig. 4. On the outer cylinder surface, a wire mesh coated with noble metal is provided on which the combustion reaction takes place in a catalyzed manner. In order to control the combustion process, the temperature is measured both on the outer side, i.e. on the catalyst, and on the inner side of the hollow cylinder using thermocouples.

Investigations have already been carried out concerning the flashback and conversion behaviour of the burner. The
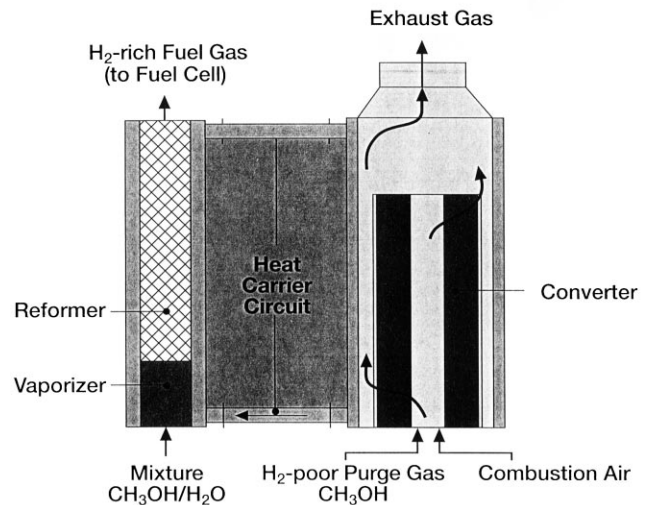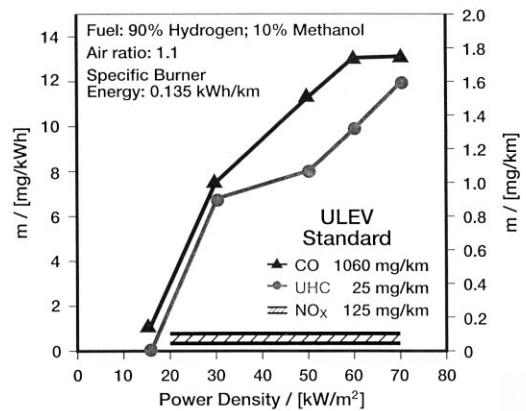

Fig. 4. Catalytic burner with methanol reformer.

following burner properties are derived from experience gained in these experiments. The burner has a density of 311 kg/m^3, the amount of catalyst on the wire mesh is 20 g/m^2 for an active layer thickness of 0.26 mm. The system parameters thus selected ensure both optimum heat extraction and the minimum requirement of retention time in the catalyst layer for the maximum possible isolation effect of the fibrous structure. The experimental catalytic burner is cooled by a water jacket and a flue gas heat exchanger [4].

Use in a vehicle defines two basically different operating modes for the catalytic burner. For start-up purposes pure methanol from the tank is used as fuel for the burner. For continuous operation the catalytic burner uses methanol from the tank mixed with the retentate from the membrane separation unit and also anode off-gas, depending on the operating mode of the PEMFC.

As an example, the CO, UHC and NO$_X$ emissions were mapped with a hydrogen/methanol mixture as a function of the power density, see Fig. 4. The fuel composition was 90% hydrogen and 10% methanol. The air ratio was 1.1. These low CO emissions of the catalytic burner as a unit of a fuel-cell-driven vehicle – responsible for the exhaust emissions of a vehicle – result in CO specific vehicle emissions of a passenger car much lower than the California EZEV (equivalent zero emissions vehicle) standard which is 1/10 of the ULEV (ultra low emission vehicle) standard; the situation is similar for the emissions of NO$_X$ and unburned hydrocarbons (UHC). More detailed information is given in [4–7].

4. Hydrogen permeable membrane for gas treatment

However, state-of-the-art low-temperature fuel cells – PEMFC – are sensitive to traces of carbon monoxide and the byproducts of fuel gas production from reforming methanol to hydrogen. A maximum concentration of 10 ppmv CO is permitted in the fuel gas on the anode side (Pt anode). Additionally, one has to recognize that CH$_3$OH could be a poison for the PEMFC anode, too. For a reversible performance loss Amphlett et al. [8] specify a permissible CH$_3$OH content in the anode feed gas of 5000 ppm. Besides this, it is desirable to avoid any performance loss including that caused by poisoning with methanol or other byproducts of methanol reforming. In the final analysis, the fuel gas produced from methanol on board must have a gas composition ensuring a sufficient service life of the novel fuel cell at high efficiency.

In order to satisfy the fuel gas requirements of the PEMFC with respect to a low CO content, several processes of integrated or separated gas conditioning are available and have been investigated within the JOULE II project [3]: (i) CO shift conversion; (ii) selective CO methanation; (iii) selective CO oxidation; (iv) adsorption process and (v) membrane process. The different gas cleaning processes are discussed in more detail by Colsman [3]. As a result

Table 1

Operating conditions of the gas cleaning unit based on supported Pd-membranes

	Operating conditions
Inlet gas	66.8% H$_2$
	2.6% CO
	20.5% CO$_2$
	9.9% H$_2$0
	0.2% MeOH
Pressure	20 bar g (feed-side)
	0.5 bar g (sweep-side)
Temperature	350°C
Demands	H$_2$ delivery: 17 m^3/h
	H$_2$ yield: 85%

of the experimental work, FZJ and HTAS intend to pursue a cleaning process based on a Pd-membrane which will be tested together with a compact methanol reformer within their JOULE III project.

In Table 1 the expected operating conditions of the membrane unit are listed. The inlet gas to the membrane unit contains 2.6% CO. As CO readily chemisorbs on Pd at low temperatures, precautions must be taken to avoid a reduction of the hydrogen permeability due to the presence of CO. The hydrogen permeability of a commercially available 100 μm thick Pd/23% Ag membrane in the presence of CO has been studied in a series of experiments. The results clearly indicate that the minimum operating temperature of the membrane in the presence of CO must be 350°C. This is in agreement with Chabot et al. [9] who have shown that the hydrogen permeability of a Pd/23% Ag membrane is reduced at temperatures below 300°C in the presence of CO.

A general drawback to the use of Pd-membranes for hydrogen separation is the high price of the Pd metal. The energy requirement of a small, fuel cell driven passenger car (1100 kg) corresponds to approx. 17 m^3/h delivered by the gas cleaning unit. Assuming the steady state key figures summarised in Table 1, the required diffusion capacity of the membrane has been estimated to 8.7 m^3/h/bar$^{0.5}$. Based on a diffusion capacity of 8.7 m^3/h/bar$^{0.5}$, the calculated effect of reduced membrane thickness on the investment in Pd metal (based on the price of raw material) is presented in Table 2. The application of conventional membrane technology (80–100 μm) is obviously very costly and far beyond the acceptable price of the total compact unit (reformer, gas cleaning step and PEMFC stack) which is 2500 ECU. Moreover, besides the raw material price of the Pd metal additional manufacture costs also have to be included before a final price of the total membrane unit can be estimated. Altogether, Table 2 clearly emphasizes the need for development of very thin, if possible less than 1–5 μm, Pd-membranes.

As the very thin Pd-membranes suffer from mechanical weakness and are unable to withstand high pressure differences, the membranes have to be mechanically supported. Within the frames of the JOULE III project, it was therefore

Table 2

Cost of Pd-membrane, hydrogen equivalent to 25 kW electricity

Membrane thickness (μm)	D/L ($m^3/m^2/h/bar^{0.5}$)	Area (m^2)	Mass of Pd (g)	Price of Pd (ECU)	Mass of ceramic (kg)	H_2/N_2 selectivity (–)
100	6	1.45	1740.00	5911	–	–
80	7.5	1.16	1113.60	3783	–	–
50	12	0.73	435.0	1478	4.0	–
10	60	0.15	17.40	59	0.8	–
5	120	0.07	4.35	15	0.4	–
4*	150	0.05	2.51	9	0.3	128
2	300	0.03	0.70	2	0.2	–
1	600	0.01	0.17	1	0.1	–

*HTAS today.

decided to focus on the development of 1–5 μm thin Pd membranes supported on a ceramic tube.

The developed membranes have been tested in the diffusion unit at HTAS. The nitrogen and hydrogen permeability are measured at 350°C. On the assumption that the rate-determining step is the diffusion of atomic hydrogen through the Pd-metal, the permeation rate of hydrogen $\dot{V}_{H_2}$ can be expressed as

$$\dot{V}_{H_2} = \frac{D}{L} A \left(\sqrt{p_{H_2,\,1}} - \sqrt{p_{H_2,\,2}} \right) \ [m^3/h] \tag{3}$$

where $p_{H_2,\,1}$ and $p_{H_2,\,2}$ are the partial pressures of hydrogen on the feed (1) and permeate (2) side respectively: A is the membrane area, L is the membrane thickness; and D is the hydrogen permeation coefficient. The estimated hydrogen permeability (D/L) through the Pd-layer is corrected by subtracting the estimated hydrogen permeability through the small leaks from the overall measured hydrogen permeability.

The present status of the developed membranes is shown in Table 2 marked by an asterisk. It is seen that due to the high hydrogen permeability of 150 $m^3/m^2/h/bar^{0.5}$, the required investment in noble metal has reached a reasonably low level. The measured H_2/N_2 selectivity is 128.

A severe demand on the gas cleaning unit in a fuel-cell powered vehicle will be that the supported membrane has to be mechanically resistant to start-ups and shutdowns, i.e. temperature cycling in hydrogen or in an inert atmosphere. It can be adduced that the differences in the thermal expansion coefficients between the ceramic support and the Pd-membrane could result in peeling of the Pd layer. Moreover, the Pd metal is sensitive to hydrogen embrittlement at temperatures below 300°C because the high solution of hydrogen atoms in the Pd metal causes an expansion of the metal lattice.

The supported Pd-membranes have been temperature cycled in nitrogen between 350 and 100°C. During the temperature cycling of the supported membrane, the nitrogen flow through the small leaks was measured. The results indicate that the temperature treatment is not increasing the already existing leaks. It is noted that the leak flow is highest at the lowest temperature and vice versa. This beha-

viour is ascribed to the thermal expansion and contraction of the Pd metal that closes and opens the small leaks, respectively. The present results do indicate that the developed supported Pd-membranes are capable of withstanding the temperature cycling in an inert gas. The leakage could transport some CO into the permeate, which would poison the PEMFC anode. In order to avoid the negative influence of residual CO on the electrochemical process a methanation unit converts the CO and part of the CO_2 into methane (CH_4), which is expected to be inert with regard to a Pt anode. This second cleaning step is necessary since no completely tight ceramic-based membrane is available.

5. Balance calculations for different powertrains and fuel cycles

Medium-term options for vehicle fuel-supply based on a PEMFC-system and an electric motor are methanol, ethanol or gasoline. All of these provide high-energy density for the storage systems and include proved handling and infrastructure. A long-term option for PEMFC-powered vehicles of the future could be hydrogen produced on a non-fossil basis. Methanol, ethanol and gasoline as energy carriers have to be converted to hydrogen or a hydrogen-rich synthesis gas in front of the fuel-cell systems by means of a reformer before chemically-bound energy can be converted to electricity and mechanical energy required for driving the vehicle. Methanol could also be directly converted in the fuel cell.

Passenger cars with fuel-cell powertrains may show in comparison with a 5-l-gasoline/100 km passenger car of the next generation advantages in terms of energy consumption and carbon-dioxide emissions, especially for hydrogen-powered fuel cell vehicles (hydrogen in the storage of the vehicle). These advantages are smaller as soon as fuel production and fuel transport are considered in calculation of full fuel-cycle balances. Fuel-cell powered vehicles, however present considerable advantages in terms of limited specific emissions and ozone formation potentials in comparison with ICE (internal combustion engine)-powered vehicles, with natural-gas powered ICE promising a very low emission potential.

Table 3

Balance calculations

	LDV (ICE = 100%, %)	FFC (ICE = 100%, %)
Energy consumption	57	79
CO_2 (best case)	56	60
CO	0.1	1
NO_X	<1	10*
VOC	1	10 (w/o CH_4)

*Assumption: methanol transport with non-diesel fueled HDV (heavy-duty vehicle).

Based on our experiences and balance calculations for the discussed powertrain the net electricity production with a heated steam reformer (HSR) and a PEMFC based on methanol and air offers for a light-duty vehicle (LDV) of about 1000 kg advantages with respect to system efficiency (42% with a fuel cell efficiency of 55%, 48% with a fuel cell efficiency of 62%) and operational procedures in comparison to a system with an autothermal partial oxidation reformer (POX) or a HSR based on gasoline (33% (POX) or 38% (HSR) with a PEMFC efficiency of 55%).

Available results in the framework of our contribution to the JOULE III project show for a full fuel cycle (FFC) with natural gas based methanol as energy carrier and a reformer/catalytic burner/gas cleaner combined with a PEMFC and electric motor in the light-duty vehicle (methanol consumption 91 MJ/l00 km) compared with a gasoline fueled light-duty vehicle (LDV-ICE: 1000 kg, 31 MJ/100 km at the wheels and 155 MJ/100 km for the MVEG (New European) driving cycle, fulfilling EU standard 2005 for CO, VOC, NO_X) in percentages of the LDV-ICE (100%) (Table 3).

6. Conclusions

For mobile applications, attention is directed towards the integration of polymer electrolyte membrane fuel cells (PEMFC) in electric drives for road vehicles based on hydrogen or on methanol with integrated on-board hydrogen production. The concept presented here combines the components of the hydrogen production system, i.e. a methanol reformer, a catalytic burner and a gas cleaning unit, with a PEMFC and an electric motor.

Vehicles with methanol as the energy carrier, a PEMFC and an electric motor have advantages with respect to efficiency and, in particular, with respect to limited emissions as compared with conventional propulsion systems using internal combustion engines. Based on the experimental results obtained so far concerning methanol reformers, catalytic burners and gas conditioning units, our report describes the total system, a test unit and preliminary test results related to a hydrogen production capacity of 50 kW (LHV) and dynamic operating conditions. This hydrogen production system is aimed at reducing the specific weight (<2 kg/kW$_{th}$ or 4 kg/kW$_{el}$) combined with high efficiency for net electricity generation from methanol (about 50%) and low specific emissions. Experimental results and calculations clearly show that the CO, nitrogen oxides (NO_X) and volatile organic compounds (VOC) for the total fuel cycle could be reduced by a factor of 100 for CO (1000 for the car only), of about 10 for NO_X—including non-diesel fueled methanol transport—(>100 for the car only) and of about 10 for VOC—without methane—(100 for the car only). The application of Pd-membranes as gas cleaning unit fulfils the requirements with high hydrogen permeability and low cost of the noble metal.

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