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Hydrogen from methanol for fuel cells in mobile systems: development of a compact reformer

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Abstract

On-board generation of hydrogen from methanol with a reformer in connection with the use of a proton-exchange membrane fuel cell (PEMFC) is an attractive option for a passenger car drive. Special considerations are required to obtain low weight and volume. Furthermore, the PEMFC of today cannot tolerate more than 10 ppm of carbon monoxide in the fuel. Therefore a gas conditioning step is needed after the methanol reformer. Our main research activities focus on the conceptual design of a drive system for a passenger car with methanol reformer and PEMFC: engineering studies with regard to different aspects of this design including reformer, catalytic burner, gas conditioning, balances of the fuel cycles and basic design of a compact methanol reformer. The work described here was carried out within the framework of a JOULE II project of the European Union (1993–1995). Extensive experimental studies have been carried out at the Forschungszentrum Jülich GmbH (KFA) in Germany and at Haldor Topsøe A/S in Denmark.

Keywords: Fuel cells; Hydrogen; Methanol; Mobile systems; Compact reformer

1. Introduction

In the field of low-temperature fuel cells for mobile systems, there are advanced development programs worldwide concerning proton-exchange menbrane fuel cells (PEMFCs) for pure hydrogen on the anode side and oxygen or air on the cathode side. Such demonstration projects for hydrogen/air as the feedstock are a bus (Ballard Power Systems) in Canada and a transporter (Mercedes) in Germany both equipped with Ballard fuel cells.

In American projects as well as in the European Union's JOULE II/III projects and in a German pilot project, however, developments have been initiated using methanol in vehicles with fuel cells. The use of methanol as an on-board hydrogen source is advantageous when considering distribution infrastructure, safety aspects and driving range of the vehicles. Accordingly a drive system must be developed permitting: (i) hydrogen-rich fuel gas to be produced in the vehicle on the basis of methanol, and (ii) hydrogen-rich synthesis gas to be converted by the fuel cell.

However, state-of-the-art low-temperature fuel cells are sensitive to traces of carbon monoxide (CO) and other byproducts of the fuel gas production from methanol. A maximum concentration of 10 ppm CO is permitted in the fuel gas on the anode side [1]. For this reason, the above-mentioned projects focus on development of the production of a hydrogen-rich synthesis gas from methanol with small fractions of side products and for the fabrication of novel electrode materials for the fuel cell. 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.

The main tasks of the programme [2] deal with:

- investigating the production of a hydrogen-rich gas with a low CO content based on a heterogeneous catalytic system with a high stability for dynamic stress in a mobile system;
- developing a catalytic burner to utilize off-gas as a heat source for the endothermic methanol reforming process, and
- design and basic engineering for a compact reformer system with catalytic burner for a passenger car with a PEMFC delivering 25 kW electricity.

2. Production of a synthesis gas from methanol

In order to minimize the total expenditure of energy and total emissions for the full fuel cycle from the primary source

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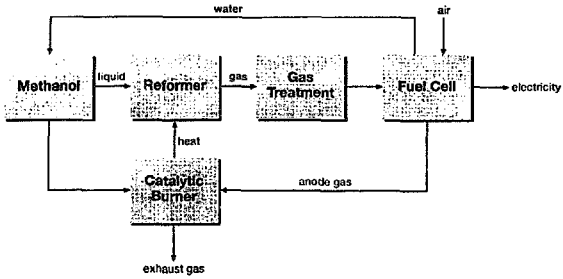

Fig. 1. Methanol-based fuel cell powered vehicle.

carrier to the car wheel, methanol must first of all be produced from natural gas [3]. The physical properties of methanol are similar to those of conventional fuels under ambient conditions. Therefore methanol can be stored in a tank like gasoline. A mixture of methanol (tank) and water (product of the fuel cell) is delivered by a feed pump to a unit where it is heated, evaporated and superheated. The superheated mixture then enters a reformer in which methanol and water are reformed to produce a hydrogen-rich synthesis gas. The energy for the endothermic reforming process will be delivered by the integrated catalytic burner fed with off-gas from the anode and/or the gas treatment unit and/or methanol from the storage tank. The reformer product gas has to be treated in a separate unit in order to adapt it to the fuel cell requirements. In order to provide fuel and power for start-up and peak load purposes, both gas and electricity buffer systems are foreseen. The concept is shown in Fig. 1.

The configuration with methanol storage, methanol reformer combined with a catalytic burner for heat supply, gas treatment, low-temperature fuel cell PEMFC and electric drive results in a drive system for passenger cars which will provide considerable emission advantages as compared with conventional vehicles with respect to both energy consumption and emission of harmful compounds [3].

3. Methanol reforming

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:

$$CH_3OH + H_2O = CO_2 + 3H_2 \quad \Delta H_{200\,^\circ C} = +58.4\ \text{kJ/mol} \qquad (1)$$

In addition to this reforming reaction, the reverse shift reaction also proceeds. Thus, the product gas also contains CO:

$$CO_2 + H_2 = CO + H_2O \quad \Delta H_{200\,^\circ C} = +39.4\ \text{kJ/mol} \qquad (2)$$

The endothermic reforming reaction takes place at temperatures above 150 °C on copper/zinc catalysts. The heterogeneously catalyzed reforming of methanol with water produces a hydrogen-rich gas. The gas composition in the preferred operating temperature 200–300 °C range and low pressures are shown in the example in Fig. 2 as a function of the water/methanol ratio at the reformer inlet with the composition of the product gas after reforming at a pressure of 5 bar and a temperature of 200 °C in equilibrium. The actual gas composition will depend on the approach to the chemical equilibrium, which is a function of catalyst activity and space velocity. Autothermal reforming of methanol with steam and oxygen results in very similar fuel gas compositions.

In the framework of this common project of Forschungszentrum Jülich GmbH and H. Topsoe A/S, different concepts of a methanol reforming reactors, catalytic converters and catalysts (Haldor Topsøe A/S) have been tested, experimentally, in the laboratory. These experiments show that the hydrogen yield obtainable and the CO concentration in the product gas depend on the mode of heat supply during the endothermic reaction or on the temperature profile in the methanol reformer. Under quasi-isothermal operating conditions, up to 12 m^3 (STP) of hydrogen per hour and dm^3 of catalyst were obtained (methanol conversion >95%), see Fig. 3. The maximum hydrogen yield corresponds to about 36 kW (hydrogen lower heating value) or an electric power of 22 kW per dm^3 of catalyst in a fuel cell with an electric

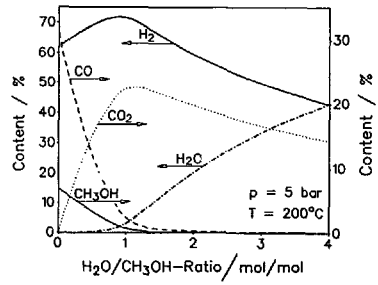

Fig. 2. Equilibrium gas compositions for methanol reforming.

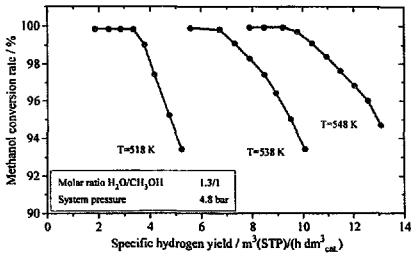

Fig. 3. Methanol reformer performance.

efficiency of 62%. These experiments and other considerations have led to a new design of a methanol reformer and test facility, which has been constructed and started up in the laboratory in a scale of about 0.1 $dm^3 - 1\ dm^3$ of catalyst.

In order to satisfy the fuel gas requirements of the PEMFC with respect to a low CO content, several processes of integrated or separate gas conditioning are available and have been investigated within the JOULE II project [4]: (i) CO shift conversion; (ii) selective CO methanation; (iii) selective CO oxidation; (iv) adsorption process, and (v) membrane process.

The chemical conversion processes (ii) and (iii) basically permit the production of a fuel gas with a CO content below 100 ppm at equilibrium. The separation processes (iv) and (v) permit the production of very pure hydrogen (>99.99 vol.% of hydrogen).

With the chosen water/methanol ratio of 1.3 the resulting CO content in the reformer gas is about 2%. It is impossible to obtain CO concentrations below 6000 ppm in a subsequent water gas shift step at a temperature of approximately 200 °C due to equilibrium limitations. Lower temperatures will lead to an unacceptably high volume of the catalyst with the presently available shift catalysts. This option was therefore abandoned early in the project.

Methanation is thermodynamically feasible, even if the undesirable side reaction of CO_2 methanation should take place. A CO content of less than 10 ppm in the fuel gas can theoretically be obtained at temperatures below 240 °C. For CO methanation to be technically feasible, however, a reasonable selectivity is imperative. If significant CO_2 methanation occurs, this will lead to temperature runaway and significant hydrogen loss.

Selective CO oxidation is another possibility for gas conditioning. Oxygen must be fed to the unit in a very well-controlled manner in the form of air and the oxidation catalyst should be selective with respect to CO oxidation. The oxidation of hydrogen must be suppressed. Thus, the temperature of this process can be controlled. This must also be the case in the dynamic driving mode. Assuming the establishment of an equilibrium, a CO content of less than 100 ppm can only be obtained in the fuel gas at temperatures below 120 °C.

Similarly to adsorption processes, which are too cumbersome to be used in a car, membrane processes with suitable materials can separate pure hydrogen from the product gas of the reformer. The possible hydrogen yield is in the range of 90%. A pressure difference across the membrane is required as the driving potential. Calculations, when low cost polymer membranes are used, have shown a trade-off between hydrogen yield and CO content in the permeate. Another possibility is to use Pd/Ag membranes available on the market, although their cost is prohibitive. Such a membrane has been purchased and tested in the framework of this project in a separate unit behind the reformer. Hydrogen purities above 99.999 vol.% and a permeate flow of about 4 m^3 (STP)/($h\ m^2$) at a high hydrogen yield can be realized.

4. Catalytic burner

In the drive system which methanol reformer, fuel cell and electric motor, the catalytic burner serves to supply the endothermic methanol reforming with heat, see Fig. 4. The catalytic burner consists of a fibrous support structure, which is surrounded with wire meshs. The catalyst (platinum on a carrier of aluminum oxide) is placed on the wires of these nets. The fibrous support structure equalizes the speed of the fuel/air mixture inside the burner. Moreover, it is used as a thermal insulation between the hot reaction zone and the cool feed gas. The experimental catalytic burner is cooled by a water jacket and a flue gas heat exchanger [4].

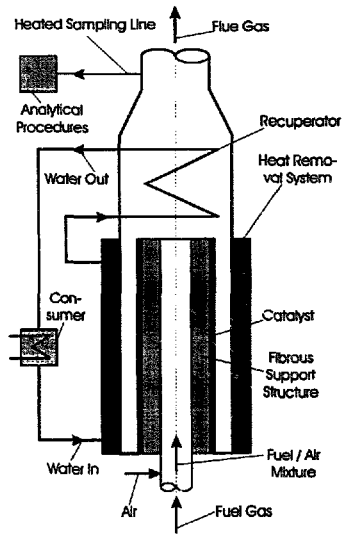

Fig. 4. Catalytic burner.

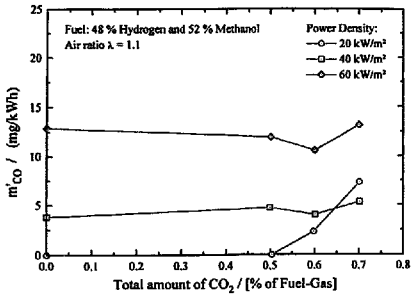

Fig. 5. Emissions of carbon monoxide.

The 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 the 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 the anode off-gas, depending on the operating mode of the PEMFC.

In order to investigate the behaviour of the catalytic burner in different parts of the driving cycle, a series of experiments has been carried out simulating the situations in the reformer. Methanol/water mixtures were used as the feedstock as well as simulated membrane and anode off gases with methanol added in sufficient quantities to satisfy the overall heat demand of the system. The following operating parameters have been varied systematically: (i) air ratio for stationary operation; (ii) amount of hydrogen in the fuel; (iii) CO_2 content in the fuel; (iv) power density (Burner load related to the outer surface of the support structure), and (v) start-up procedures.

As an example, the CO emissions have been mapped with hydrogen/methanol/CO_2 mixtures with power densities from 20–60 kW/m^2 as a function of the CO_2 content, see Fig. 5. The fuel composition was 48% hydrogen and 52% methanol. The air ratio was 1.1. These low CO emissions of the catalytic burner as 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, which are much lower than the California ULEV (ultra low-emissions vehicle) standard; the situation is similar for the emission of NO_x and volatile organic compounds (VOCs).

5. Engineering of the compact methanol reformer

Based on the experimental results obtained in the project concerning methanol reforming, catalytic burner and gas conditioning, the engineering division of Haldor Topsøe A/S has carried out a basic engineering design of a compact methanol reformer (CMR).

The design is based on the optimized methanol reforming catalyst from Haldor Topsøe A/S and the catalytic burner from Forschungszentrum Jülich GmbH.

We have prepared: (i) process flow diagrams at a load of 30 and 100%, respectively, showing heat and mass balances of the units and pressures, temperatures and compositions of the main streams, and (ii) equipment duties. The special operation procedures concerning start-up and shutdown, and rapid load variations have been considered.

The main results are that the weight of the unit will be approximately 75 kg for a 25 kW electricity fuel cell output and its volume will be 73 dm^3. These numbers are thus close to 2 kg(dm^3)/kW, the goals of the car industry. The start-up and load following characteristics are, however, still considered to be somewhat slower than one would expect.

The capacity of the CMR is determined by a fuel cell output of 25 kW electric power. At about 50% efficiency this corresponds to 16.7 m^3 (STP)/h pure hydrogen to be delivered from the membrane unit. The output from the CMR upstream the membrane unit is 19.7 m^3 (STP)/h hydrogen (membrane hydrogen efficiency 85%).

6. Balance of the total system

The balance of all energy flows, including reformer, catalytic burner, hydrogen separation and pumps as well as turbines, has been calculated both at Haldor Topsøe A/S using their proprietary GHEMB (general heat and mass balance) as well as at KFA using their SIMSCI-PRO-II program. The results are shown in Fig. 6.

The SIMSCI-PRO-II program demonstrates that on the basis of the project boundary conditions an overall efficiency of 48% (net electricity for electric drive/LH methanol) can

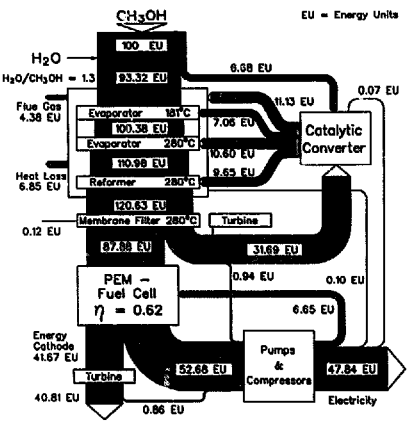

Fig. 6. Balance of energy flows.

be obtained, assuming a fuel cell efficiency of 62%. Taking a small (1100 kg) passenger car operating at the European ECE-R-15 driving cycle as the basis for the calculations, 9 kWh/100 km are required at the wheels. Taking into consideration the energy transformations at the motor shaft, electric motor, converter, the internal consumption and the recovery of braking energy results in an energy demand of 12 kWh/100 km to be covered by the fuel cell. This translates into a methanol requirement of 25 kWh/100 km or 5.7 dm^3 methanol/100 km or 37.3 kWh/100 km, if the energy conversion efficiency of transforming natural gas into methanol is taken into account. Compared with a conventional drive system, such a passenger car drive with a reformer, PEMFC and electric motor offers a reduction in primary energy consumption of approximately 50% [3]. Catalyst development and tests, optimization of methanol reformer, catalytic converter and different gas conditioning led to the following key results: high hydrogen yield of the reformer, low emissions from the converter, design of a compact reformer, clean hydrogen as the fuel for PEMFCs by using membranes, low-energy consumption (33%), low CO_2 emissions (33%), very low CO and NO_x emissions ($\ll 1\%$), low specific VOC emissions (30%). (These data account for a fuel cell powered passenger car based on methanol in comparison to a conventional car fullfilling the ULEV standards.)

7. Summary

Vehicles with methanol as the energy carrier, a polymer electrolyte fuel cell (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. The experimental results have led to a new design of a methanol reformer including a catalytic burner as the heat source for the reforming process and a membrane as gas treatment in order to reduce the H_2O, CO_2, CH_3OH and CO contents of the fuel. Experimental results and calculations clearly show that the emission of CO, NO_x and VOCs during the total fuel cycle could be reduced by a factor of 100 for CO, 6 for NO_x and 8 for VOCs compared with a total fuel cycle including a passenger car with a gasoline internal combustion engine fulfilling the 1997 California ULEV emission standard [3].

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