ELSEVIER

Catalysis Today 47 (1999) 407–414

CATALYSIS TODAY

Catalytic radiant burner for stationary and mobile applications

B. Emonts*

Institut für Energieverfahrenstechnik (IEV), Forschungszentrum Jülich GmbH (FZ), D-52425 Jülich, Germany

Abstract

In present discussions on energy conversion processes aimed at producing both thermal and process heat, catalytic burners provide an alternative approach for future applications. Catalytic burners are advantageous in that they cause only low pollutant emissions during the process of converting chemical energy into heat. In addition, novel engineering concepts require the complete combustion of a variety of fuels and fuel mixtures. Against this background, a novel catalytic radiant burner was developed at the Research Centre Jülich. Under near-stoichiometric conditions, this catalytic burner burns both natural gas with hydrogen admixture in a heat recovery boiler for stationary heat production and methanol with hydrogen admixture in a reformer producing process heat to be used in a fuel cell drive system. The emission data of the catalytic heater were recorded at a nominal power of 11.5 kW, a nominal air/fuel ratio of 1.15 and different hydrogen ratios between 0% and 50% and were 7–3 mg/kW h for carbon monoxide and 3.3–3.9 mg/kW h for nitrogen oxides. The test runs for a catalytic burner to be used for heating a compact reformer in a fuel cell vehicle were carried out at a power density of 15–60 kW/m^2, a nominal air/fuel ratio of 1.1 and different hydrogen, carbon dioxide and water ratios. For nitrogen oxides emissions of less than 0.4 mg/kW h, the measured carbon monoxide amount ranges between 0 and 13 mg/kW h.

Keywords: Catalytic combustion; Catalytic radiant burner; Catalytic heater; Fuel cell drive system

1. Introduction

In the past few years, great efforts have been devoted to the development of catalytic combustion systems. Main emphasis was placed on the application of heterogeneous catalysis for infrared emitters as well as stationary gas turbines and aircraft engines. However, market introduction has only been reached for a few concepts omitting complete premixing of air and fuel.

The concept developed at the FZ Institute of Energy Process Engineering is schematically shown in Fig. 1. It is also described in detail in [1,2]. All gases are admixed to the preheated combustion air in a mixer. The fuel gas/air mixture enters a carburettor where the liquids are added. The mixture then flows radially through a cylindrical support structure of ceramic fibres. The reaction takes place on the outer surface coated with noble metal catalysts. Most of the heat is transferred by radiation to the heat removal system facing the burner. The fibrous support structure is intended to ensure as far as possible that no flashbacks occur. Furthermore, its function is to homogeneously distribute the mixture so that uniform reaction conditions with reduced emissions can be established. In the subsequent recuperator, further heat is extracted from the flue gas. The analytical procedures enable the determination of carbon monoxide and carbon dioxide

---

*Tel.: +49-2461-61-3525; fax: +49-2461-61-6695.

0920-5861/99/$ – see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S0920-5861(98)00323-X

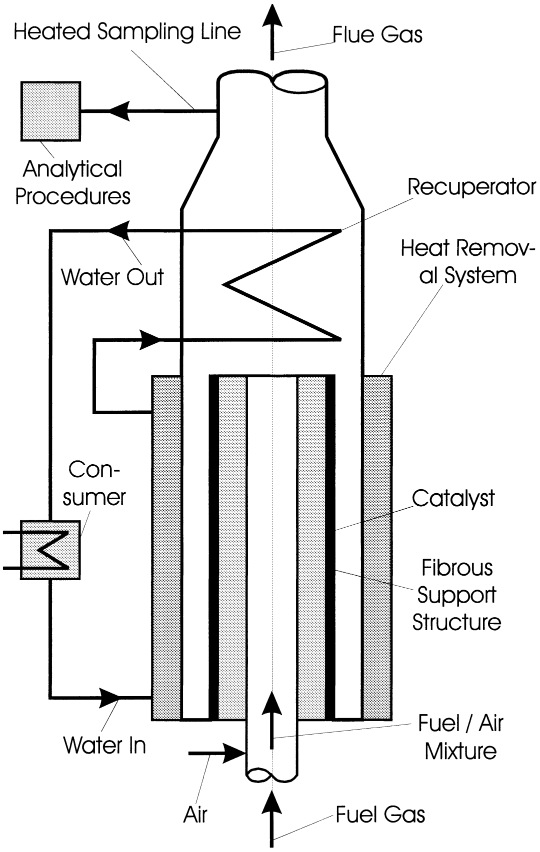

Fig. 1. Catalytic radiant burner.

(CO and CO_2), oxygen (O_2), nitrogen oxides (NO, NO_x) and unburned hydrocarbons (UHC). These can be further analysed for aldehydes, ketones, alkanes and hydrogen using discontinuous measuring techniques – gas chromatography (GC) and high-pressure liquid chromatography (HPLC). The outside and inside diameters for the burner are generally 100 and 40 mm, respectively. Its height is kept constant at 300 mm in all experiments. The fibre densities range approximately between 250 and 320 kg/m^3. Several fibrous structures with different coating density were available for the experiments. The catalyst material was platinum. In some test series, palladium was also used. The coating density is the amount of catalyst relative to the outer surface of the fibrous structure. It was between 0.5 and 5.0 g/m^2 in numerous measurement series.

2. Stationary application

The efficient use of energy represents an important potential for conserving our resources. In addition to these economic aspects, ecological aspects are currently gaining particular significance. Higher efficiencies in energy conversion and economical consumption also mean less environmental pollution due to emissions. Lowering of the prescribed limits in power plants or for heat generation forces the manufacturers to apply new techniques and modern methods of conversion. This paper presents such a technique, which has apparently gained increasing significance in the recent past, i.e. heat production by means of catalytic combustion.

2.1. *Description of the catalytic heater*

Within the framework of a development contract a catalytic heating system is to be developed and tested for Solar Wasserstoff Bayern. This device is to be operated with either natural gas or mixtures of natural gas and hydrogen and air as the oxidant at a maximum thermal load of 11.5 kW [3]. The highest volume fraction of hydrogen in the fuel gas should be 50%. The air/fuel ratio is varied between 1.05 and 1.6. Fig. 2 shows the main components of the catalytic heating system setup at the Institute of Energy Process Engineering (IEV) of the FZ Jülich [4]. A software-assisted process control system from Siemens (S5) records all measuring signals, controls and monitors the combustion process and regulates both the gas and cooling water supply. For failsafe control and monitoring, an automated firing unit is installed behind the heater control S5. It acts directly on the ignition system. The two fuel gases and the combustion air are proportioned and their volume flows measured by special armatures of the gas supply before they enter the cross-flow mixer of the burner. The fuel gas/air mixture then flows through a cylindrical porous ceramic fibre structure in the radial direction from the interior outwards, as can be seen in Fig. 3. This fibrous support structure coated with a catalyst material on its outer surface is suspended in a heat recovery boiler equipped with a heat removal system to which most of the heat produced in the reaction zone is transferred by thermal radiation. Further heat is extracted from the flue gas by a subsequent tube bundle recuperator. The

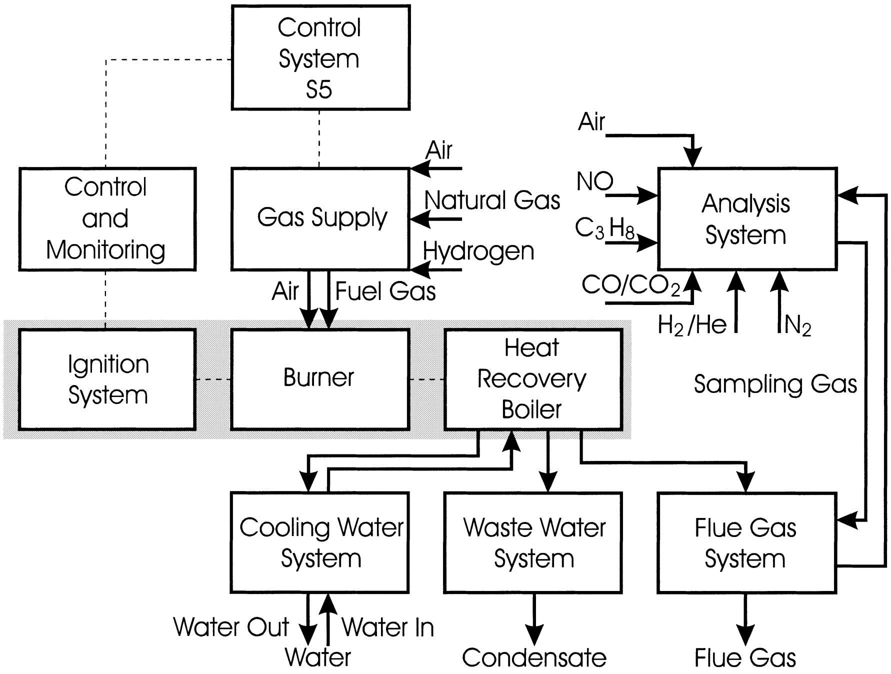

Fig. 2. Block diagram of the catalytic heater.

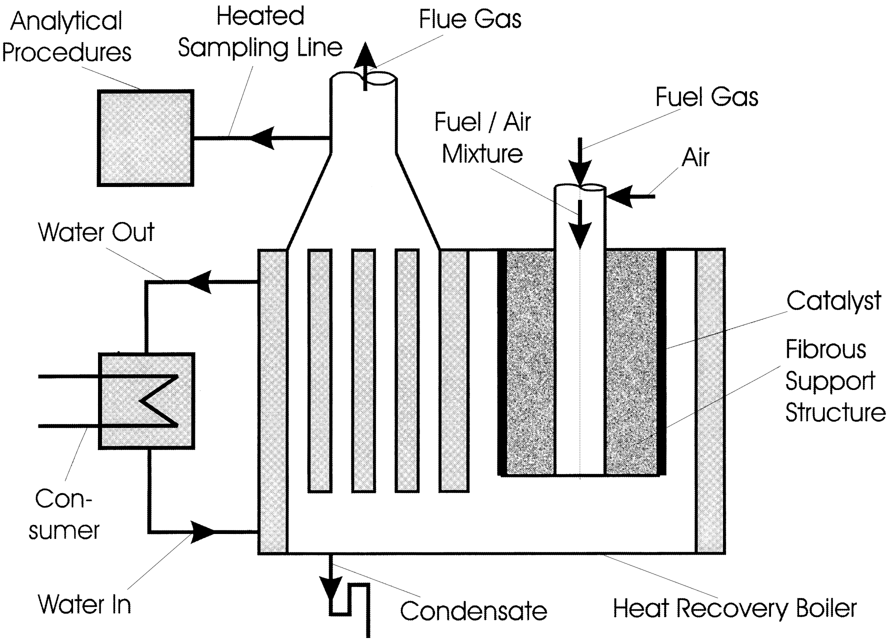

Fig. 3. Catalytic heater.

flue gas is cooled below the respective dew point so that part of the entrained water is condensed out and can be discharged through the waste water system. Before leaving the heat recovery boiler through the flue gas system, a small amount of gas is fed to the flue gas analysis system through a heated sampling line. The flue gas analysis system permits the continuous determination of oxygen (O_2), carbon monoxide and carbon dioxide (CO, CO_2), nitrogen oxides (NO, NO_x) and unburned hydrocarbons (UHC). The cooling water system consists of two circuits. In a closed circuit the water flows through the heat recovery boiler and gives the heat absorbed off to a second open water circuit through a heat exchanger referred to as the consumer.

The heat recovery unit permits the modes of operation designated 1 and 2. Mode 1 serves to keep the boiler water return temperature constant. This can be achieved by mixer adjustment. Load control ensures the constant inlet temperatures required for mode 2.

2.2. *Operating results and discussion*

In the following, only results obtained with the system shown in Fig. 3 will be presented. Experimental results from measurements on the unit in Fig. 1 have already been discussed elsewhere, see e.g. [2,5]. The data specified below refer to operating mode 1 with a return temperature of 50°C. Water supply was set to an inlet temperature of 70°C for the highest thermal load of 11.5 kW. The thermal load was determined from the energy content of the fuel gas on the basis of the higher heating value. The density of the fibrous support structure was 317 kg/m^3. The catalyst material was palladium with a coating density of 5 g/m^2, i.e. the absolute palladium quantity was 0.5 g.

The most important result is the fact that all required operating regimes were possible without flashback using the burner and heater described. Fig. 4 shows the carbon monoxide emissions as a function of thermal load for four hydrogen ratios and the operating air ratio of 1.15. The hydrogen ratio is the ratio of hydrogen to fuel gas supply. The guaranteed design value of 100 mg/kW h was fixed as the limit on the ordinate. Actual values remained below this limit in all cases with pure natural gas operation. Hydrogen admixture leads to far higher emission values, at least in the lowest power range. The values only drop below the guaranteed limit from a thermal load of 7.5 kW upwards. The drop in CO emissions with load is attributable to the higher reaction temperatures. In the case of maximum burner load, the emissions range between 3 and 7 mg/kW h and are thus very low even for the highest hydrogen admixture. However, they are markedly higher at partial load. In this range, catalytic burners do not currently offer any advantage over conventional systems.

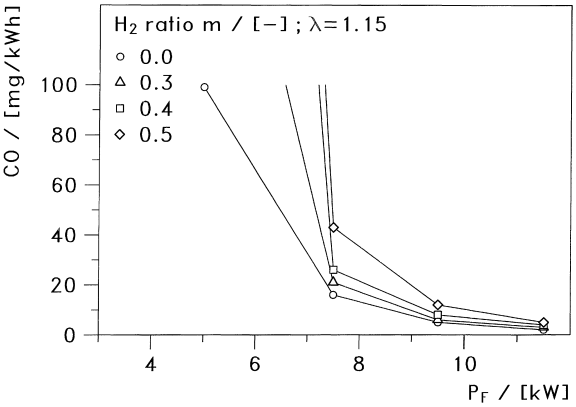

Fig. 4. CO emissions.

Fig. 5 shows the specific NO_x emissions as a function of the air ratio and H_2 ratio for 11.5 kW nominal power. Except for the near-stoichiometric range, they are within a narrow band of about 0.8 mg/kW h. In comparison with the values specified in [6], however,

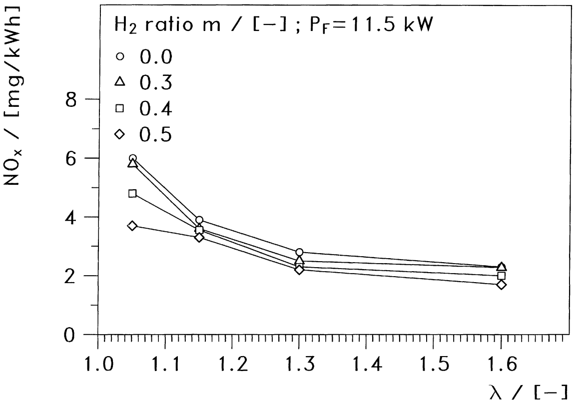

Fig. 5. NO_x emissions.

the emission factors presented here are higher than that known from earlier studies at the Institute. The highest values were measured for pure natural gas operation. The NO_x values decrease with increasing hydrogen amount. This seems to be inconsistent with the reaction temperatures measured in the catalyst layer, which rise with increasing hydrogen fraction. Hydrogen is converted preferentially in the immediate vicinity of the reaction zone, i.e. on palladium. The reaction temperatures are therefore highest for this case. The high emission values for the combustion of pure natural gas suggest that high temperatures prevail in the secondary reaction zone, but these could not be measured. The absolute level of NO_x emissions also suggests temperatures in the secondary reaction zone above those in heterogeneously catalysed conversion, i.e. on the catalyst.

3. Mobile application

In the field of low-temperature fuel cells for mobile systems, there are advanced development programmes worldwide concerning proton-exchange membrane 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, a transporter and a van (Mercedes-Benz) in Germany, all 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 the distribution infrastructure, safety aspects and driving range of the vehicles. Accordingly, a drive system must be developed permitting hydrogen-rich fuel gas to be produced in the vehicle on the basis of methanol, and 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 produced from methanol. A maximum concentration of 10 ppm CO is permitted in the fuel gas on the anode side [7]. For this reason, the above-mentioned projects focus on developments concerning 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 [8] 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 residual 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.

3.1. *Fuel cell drive system*

In a fuel cell drive system with reformer, catalytic burner, gas treatment, fuel cell, energy storage and electric motor for mobile application (Fig. 6) methanol is stored in a tank, exhibiting physical properties similar to those of conventional fuels under ambient conditions. The water for methanol reforming is not tanked, but condensed behind the fuel cell as a hydrogen oxidation product and admixed to the methanol. A fuel pump delivers this mixture to an evaporator where it is heated up, vaporized and superheated. The superheated mixture then flows into a reformer where the reforming of methanol and water into a hydrogen-rich synthesis gas takes place as a heterogeneously catalysed reaction with heat supply.

Since a fuel cell with conventional catalyst can only be supplied with low CO contents in the fuel gas and since, at the same time, the water fraction in the educt mixture should not be too high, so that the energy balance is not deteriorated, a water/methanol ratio of 1.3–1.5 mol/mol is chosen. Methanol is then largely converted and the CO contents are 1–3 vol%, so that the hydrogen-rich synthesis gas from the reformer must be subjected to a subsequent gas treatment. The reaction heat is passed to the reformer by external heating of the reaction tubes through a heat transfer system, the heat being generated in a catalytic burner where the methanol and/or unconverted gas from the anode is catalytically oxidized with air so that, on the whole, the specific emissions produced are very low.

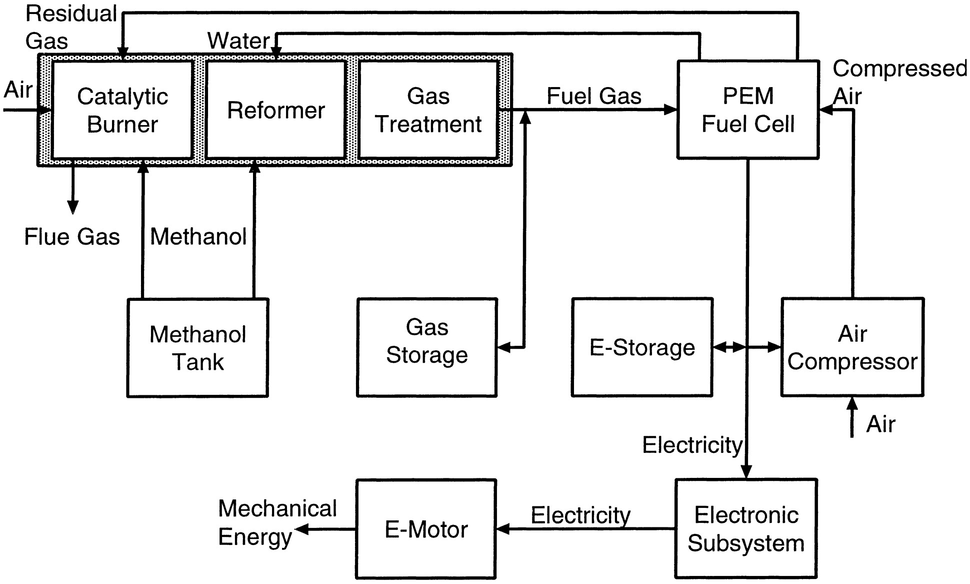

Fig. 6. Block diagram of the fuel cell drive system.

The catalytic burner consists of a fibrous support structure, which is surrounded with wire mesh. The catalyst (platinum on a carrier of aluminium 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 cold feed gas. The experimental catalytic burner is cooled by a water jacket and a flue gas heat exchanger [9], see Fig. 1.

3.2. *Test results and discussion*

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 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 conditions in the reformer. Methanol/water mixtures were used as the feedstock as well as simulated membrane and anode residual gases with methanol added in sufficient quantities to satisfy the overall heat demand of the system. The following operating parameters have been varied systematically: air/fuel ratio for stationary operation, amount of hydrogen in the fuel, CO_2 content in the fuel, power density (burner load relative to the outer surface of the support structure) and start-up procedures.

As an example, the CO emissions have been mapped with hydrogen/methanol/CO_2 mixtures with power densities from 20 to 60 kW/m^2 as a function of the CO_2 content, see Fig. 7. The fuel composition was 48% hydrogen and 52% methanol. The air/fuel ratio was 1.1. Except for the lowest power density, the emission values are approximately constant. They amount to about 13 mg/kW h at q=60 kW/m^2. Since carbon dioxide like other inert substances reduces the flame velocity, it also has a favourable effect on flashback protection. It was therefore even possible to carry out experiments with pure hydrogen as the fuel.

With respect to future anode residual gas operation with various high water fractions, the operating characteristics of the burner should be indicated with different water contents in the methanol. At 15, 30 and 45 kW/m^2 the water fraction was varied between 0 and 1.3 relative to 1 mol of methanol. The air/fuel ratio amounted to 1.1 for the entire experimental series. The nitrogen oxides NO_x represented in

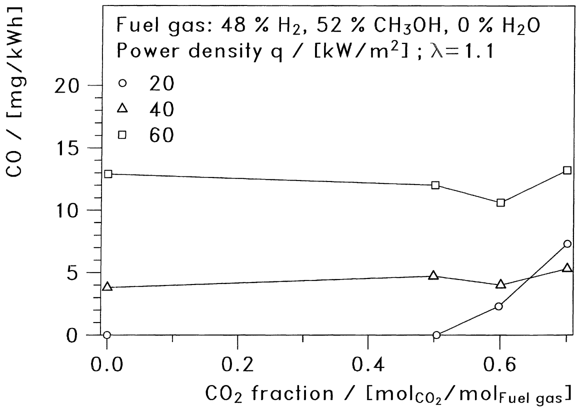

Fig. 7. CO emissions.

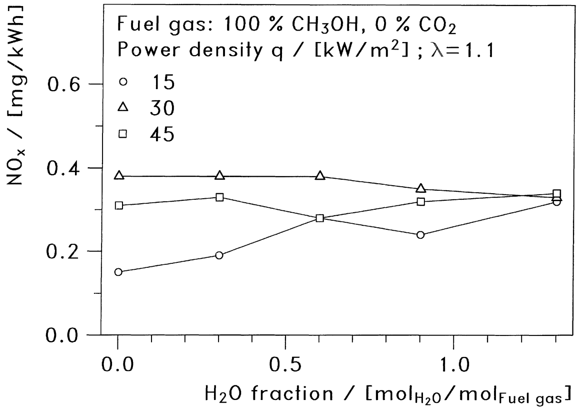

Fig. 8. NO_x emissions.

Fig. 8 are not clearly influenced by the power density or the air/fuel ratio. At less than 0.4 mg/kW h the NO_x emissions are very low.

These low CO and NO_x emissions of the catalytic burner as unit in a fuel cell driven vehicle – responsible for the exhaust emissions of a vehicle – result in CO and NO_x 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 volatile organic compounds (VOCs) [10].

4. Conclusions

Catalytic combustion is a promising energy conversion technique eliminating or reducing the conflicting combination of NO_x formation and CO release known from conventional flame burners. In addition, the achievable efficiency is particularly high for all applications requiring low- and medium-temperature heat. Classical fields of application are water heaters and domestic heating systems. For this purpose, the catalytic heater shown in Fig. 3 was conceived as a novel heat recovery boiler with a cylindrical, cooled combustion chamber and a subsequent tube-bundle recuperator which, due to its basic design, only causes insignificant radiation losses. As far as the pollutant concentrations emitted from the catalytic heater described are concerned, the greatest reduction potential is to be found for NO_x emission. The values are below 6 mg/kW h throughout the range examined. Although CO emission increases at partial load due to excessively low reaction temperatures, a low value of 3 mg/kW h can be achieved for the design case. A compact design with high energy yield and low pollutant emissions is characteristic of a future-oriented heater which can also comply with more stringent emission standards if equipped with a catalytic radiant burner.

Vehicles with methanol as the energy carrier, a proton-exchange membrane 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 methanol reformer including a catalytic burner as the heat source for the reforming process and a membrane for 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 [11].

References

[1] B. Emonts, FZ Report Jül-2275 (1989).
[2] P. Bröckerhoff, B. Emonts, in: A. Holmen, K.-J. Jens, S. Kolboe (Eds.), Natural Gas Conversion, vol. 61, Chapter IV, Elsevier, Amsterdam, 1991, p. 557.

[3] H. Blank, A. Szyszka, Proceedings of the Nineth World Hydrogen Energy Conference, Paris, vol. 2, 22–25 June 1992, p. 677.
[4] B. Emonts, P. Bröckerhoff, VDI Report 1182 (1995) 359.
[5] P. Bröckerhoff, B. Emonts, Proceedings of the 10th World Hydrogen Energy Conference, Cocoa Beach, vol. 3, 20–24 June 1994, p. 1581.
[6] K. Hoelzner, A. Szyszka, Energie 45 (1993) 38.
[7] V.M. Schmidt, P. Bröckerhoff, B. Höhlein, R. Menzer, U. Stimming, J. Power Sources 49 (1994) 299.
[8] J.B. Hansen, K. Aasberg-Petersen, B. Höhlein, Proceedings of the Fuel Cells for Traction Applications Symposium, Stockholm, 8 February 1994, p. 90.
[9] B. Höhlein, G. Colsman, R. Menzer, P. Bröckerhoff, E. Riedel, J.B. Hansen, I.I. Primdahl, Proceedings of the 10th World Hydrogen Energy Conference, Cocoa Beach, vol. 2, 20–24 June 1994, p. 1461.
[10] P. Bröckerhoff, B. Emonts, Proceedings of the 10th International Symposium on Alcohol Fuels, Colorado Springs, 7–10 November 1993, p. 1045.
[11] P. Biedermann, H.G. Düsterwald, B. Höhlein, U. Stimming, S. Birkle, R. Kircher, C. Nölscher, H. Voigt, W. Drenckhahn, Presented at the 27th International Symposium on Automotive Technology and Automation, Aachen, 31 October–4 November 1994.