Chemical Engineering Journal 142 (2008) 309–317

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Assessing the adaptability to varying fuel supply of an autothermal reformer

Marita Nilsson[a,*], Xanthias Karatzas[a], Bård Lindström[b],
Lars J. Pettersson[a]

[a] *KTH – Royal Institute of Technology, Department of Chemical Engineering and Technology, Teknikringen 42, SE-100 44 Stockholm, Sweden*
[b] *PowerCell, Sven Hultins Gata 9D, SE-412 88 Göteborg, Sweden*

ARTICLE INFO

Article history:
Received 20 January 2008
Received in revised form 26 February 2008
Accepted 29 February 2008

Keywords:
Hydrogen
Multifuel autothermal reformer
Auxiliary power unit
Rh catalyst

ABSTRACT

The present paper describes the study of an autothermal reformer and its fuel-flexible capabilities. Experiments have been performed in a reactor designed to generate hydrogen by autothermal reforming for a 1–5 kW_e polymer electrolyte fuel cell. Both logistic fuels (diesel, gasoline, and E85) and alternative fuel candidates (methanol, ethanol, and dimethyl ether) were tested in the reformer. The same catalyst composition, Rh supported on Ce/La-doped γ-Al_2O_3 and deposited on cordierite monoliths, was used for all fuels. The practical feasibility of reforming each fuel in the present reactor design was tested and evaluated in terms of fuel conversion and selectivity to hydrogen and carbon dioxide. Temperature profiles were studied both in the axial and radial direction of the reformer. It was concluded from the experiments that the reformer design was most suitable for use with hydrocarbon mixtures such as diesel, gasoline, and E85, where it represents a good basis for an optimized multifuel-reformer design.

1. Introduction

Fuel cells offer an energy efficient and clean technology for the future transport sector. One of the first market penetration opportunities for fuel cells is likely to be realized by implementation in heavy-duty truck auxiliary power units (APUs). APUs are systems providing electricity to trucks at standstill, operating independently of the main engine. The hydrogen required for the fuel cell can be generated by reforming the existing truck fuel. Among the technologies for reforming of fuels into hydrogen, autothermal reforming (ATR) is considered to be the most feasible alternative in automotive applications due to its high thermal efficiency and dynamics during transient operation as well as its lower system complexity [1]. The general reaction formula for ATR, using air as the oxygen source and assuming that the products are only CO_2 and H_2, can be expressed as follows:

$$C_nH_mO_p + x(O_2 + 3.76\,N_2) + (2n - 2x - p)H_2O \rightarrow nCO_2 + \left(2n - 2x - p + \frac{m}{2}\right) H_2 + 3.76xN_2 \quad (1)$$

Today, no alternative transportation fuel has been agreed on as generally preferable to others, and it is likely that we are heading towards an even broader mix of fuels and vehicle propulsion technologies. In Sweden, the Commission on Oil Independence has proposed a 40–50% reduction of petroleum-based fuels by 2020 [2]. Still, substantial measures to promote the transition to alternative technologies are lacking at the political level. Upcoming emission legislations worldwide will, however, accelerate the transition of the transportation-related energy system [3,4]. Regional differences in fuel supply will then impose requirements on the trucks and an APU system that can run on several fuels will be a big advantage. From a manufacturer's perspective, the development of one APU package that can fit every type of truck and that can be the same in the short term as in the phasing over to alternative fuels, would allow them to effectively keep pace with the growing demands. These factors stress the need for a fuel-flexible solution.

Optimal reactor design is essential to ensure efficient reforming resulting in complete fuel conversion, maximum hydrogen selectivity, and low amounts of carbon monoxide [5]. This makes the development of multifuel reformers challenging. Reforming for automotive fuel cell systems has been extensively studied during the last decades, focusing on single transportation fuels [6]. However, few studies show results for systems with fuel-flexible capabilities. One example is Renault together with Nuvera, who are developing an onboard fuel processor that can convert a variety of fuels into hydrogen for powering of fuel cell vehicles [7,8].

The present paper describes the possibilities of running an autothermal reformer, designed for a 1–5 kW_e fuel cell auxiliary

---

[*] Corresponding author. Tel.: +46 8 7909150; fax: +46 8 108579.
E-mail address: marita@ket.kth.se (M. Nilsson).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.02.026

Table 1
Comparison of properties for the fuels tested in the study [9–12]

	Diesel	Gasoline	DME	Ethanol	E85	Methanol
Chemical formula	$\sim C_{14}H_{26}$	$\sim C_8H_{18}$	CH_3OCH_3	C_2H_5OH	$\sim C_{2.9}H_{7.7}O$	CH_3OH
Molecular weight (g mol^{-1})	~194	~114	46.1	46.1	~58.6	32
Boiling point @ 1 bar (°C)	180–320[a]	25–205	−24.8	78.5	40–170	64.6
Vapor pressure @ 38 °C (bar)	negl.	0.48–1.08	$5.1_{(20\,°C)}$	0.16	0.35–0.70	0.32
Liq. density @ 15 °C (kg m^{-3})	800–820	721–785	$666_{(20\,°C)}$	789	785	791
Rel. density, gaseous (air = 1)	–	–	1.59	–	–	–
Liq. viscosity @ 25 °C (mPa s)	2–4	~0.5	0.12–0.15	1.1	n.a.	0.54
Heat of vaporization (MJ/kg)	0.27	0.30	–	0.84	n.a.	1.1
Lower heating value (MJ/kg)	43	44	29	27	29	20
Autoignition temperature (°C)	206[b]	260–460	235–350	365	n.a.	470
Flammability limits in air (vol%)	1–5	1.4–7.6	3–17	3–19	n.a.	6–50
Sulfur content max (wt ppm)	10	10	0	0	10	0
Aromatic content max (vol%)	5	35	0	0	n.a.	0
Cetane number min (*n*-cetane)	50	–	55–68	8	–	~5
Octane number min (research)	–	95	–	107	101–104	106

[a] T^{95}.

[b] *n*-Cetane.

power unit, using various transportation fuels. Both logistic fuels (diesel, gasoline, and E85) and alternative fuel candidates (dimethyl ether, ethanol, and methanol) have been tested. The fuels and their properties are outlined in Table 1. The overall aim of the study was to evaluate the flexibility of the ATR reactor and the capability of the specific reactor design to operate on various fuels, particularly for use in PEFC-APU systems up to 5 kW$_e$. The same catalyst composition, Rh supported on Ce/La-doped γ-Al_2O_3, was used for all fuels. Rh/Al_2O_3 has proven to be an effective catalyst for ATR of hydrocarbon mixtures, such as diesel and gasoline [13–15], as well as of ethanol [16,17] and methanol [18].

2. Experimental

2.1. Autothermal reformer

The experiments were performed in a reactor designed to generate hydrogen by catalytic autothermal reforming for a 1–5 kW$_e$ polymer electrolyte fuel cell. The reformer consists of a stainless steel horizontally mounted tubular reactor with a length of 220 mm, 80 mm inner diameter and 2 mm wall thickness, shown in Fig. 1 as a schematic drawing. The design of the reformer has been developed to satisfy performance targets such as efficiency, reliability and durability, and makes use of internal heat exchange for control of the reaction conditions. The walls of the reactor were insulated with alumina–silica blanket insulation to minimize heat losses. The liquid fuels were delivered to the reformer using an electronically controlled piston pump (0–65 cm^3/min, 6.9 bar maximum pressure, Fluid Metering Inc.) and injected through a stainless steel spray nozzle generating a hollow-cone spray of fuel with a spread angle of approximately 70° (0.51 mm diameter, Spraying Systems Co). Following injection, the fuel was vaporized in a mixture of superheated steam (110 °C) and air that had been heated to a temperature enabling fuel vaporization. This injection system was chosen in order to be robust and simple, and without the need for cooling of the nozzle. Air-assisted nozzles typically give finer sprays, but can result in the formation of coke on the tip of the nozzle during reforming [19] and were therefore discarded for use in this system. The air/steam mixture is delivered through an 8 mm wide mantle around the reactor, enabling indirect heat exchange with the reformer, and enters a non-catalytic prereforming section through 33 holes, each with 2 mm diameter, positioned 40 mm upstream of the prereforming section (see Fig. 1). The size of the holes was chosen to achieve high linear velocity of the air/steam mixture to improve the turbulence, while avoiding

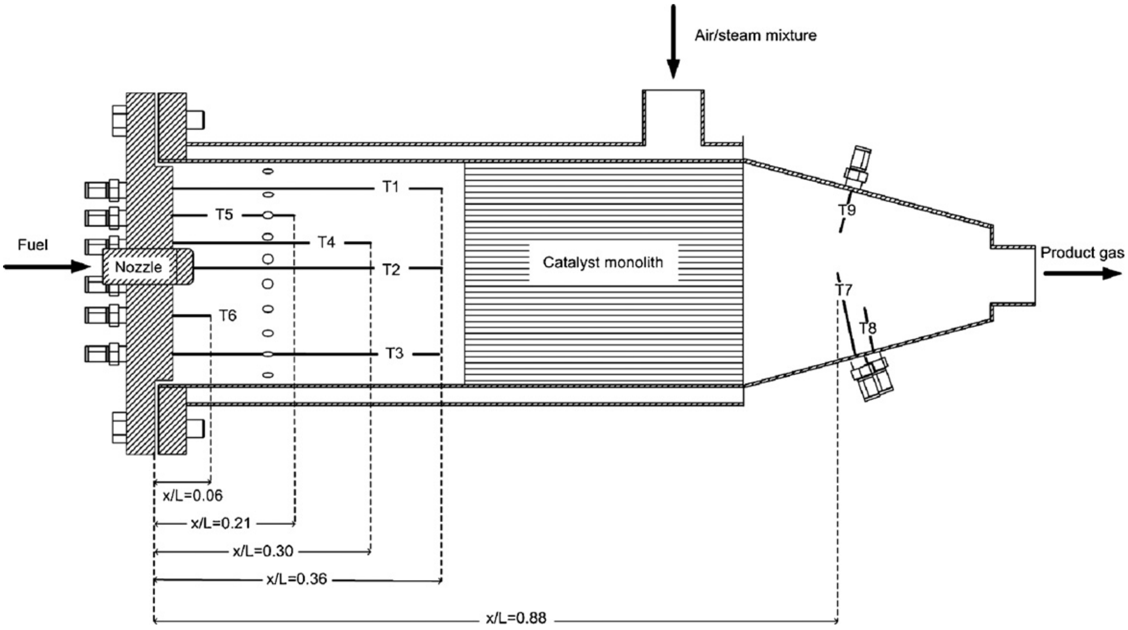

Fig. 1. Schematic drawing of the reformer (T#–thermocouple, *L*–length of reformer).

too large a pressure drop. The superheating was performed in a separate unit by means of tubular heating elements. Gases were fed to the reformer using mass flow controllers (Bronckhorst High-Tech EL-Flow models). Dimethyl ether, the only gaseous fuel tested, was added through a tube from the flange at the inlet of the reformer after removal of the nozzle. The reformer is divided into a mixing/prereforming section and an autothermal reforming section. The uniform reactant mixture from the prereforming section enters a monolithic reforming catalyst (78 mm diameter, 100 mm length), fixed in the second part of the reactor using high-temperature insulation tape (Dalfratex).

The catalysts used in the experiments were prepared in-house by means of incipient-wetness impregnation of γ-Al_2O_3 powder (initial surface area 150 m^2/g, Sasol Germany) using aqueous solutions of nitrate salts followed by calcination (700 °C/3 h) and dip-coating of the monolith. The monoliths were cut out from cordierite blocks with a cell density of 400 cells per square inch, which were acquired from Corning Inc. The catalytically active material was composed of rhodium (1 wt%), cerium dioxide (10 wt%), and lanthanum oxide (5 wt%). Catalysts for autothermal reforming need to be active both for steam reforming and partial oxidation. Further, they have to be mechanically robust during reaction conditions and resistant to coke formation and sulfur in the fuel (in the case of diesel, E85, and gasoline reforming). It is believed that the oxygen-binding capacity of Rh/γ-Al_2O_3 is improved by adding oxygen-transporting additives, in this case ceria, thereby assisting the mechanism of carbon removal from the metal surface [20]. Besides storing and releasing oxygen, ceria is known to stabilize noble metal dispersion [21] and to promote the activity of reforming reactions by enhancing the adsorption and dissociation of water molecules [22]. Lanthanum is commonly used to stabilize γ-alumina, thus avoiding transitions to undesired alumina phases induced by high reaction temperatures [23]. Due to these effects, ceria and lanthanum were used as dopants for the Rh/γ-Al_2O_3 system to be evaluated in the screening of different fuels for autothermal reforming. This catalyst composition has previously been shown to be active and stable during autothermal reforming of commercial diesel fuel [15].

2.2. Operational considerations

Each fuel tested in the ATR study has its own optimal operating conditions (O_2:C, H_2O:C, and temperature). The chosen starting parameters were either based on earlier experience within the research group or collected from literature data [15,16,24–26]. The parameters were chosen with the aim of avoiding coke formation and minimizing the methane and carbon monoxide concentration in the product gas. Guidelines for which operating conditions that will result in the desired conditions can be obtained by means of thermodynamic calculations. Choosing the right operating conditions is, however, more difficult when using fuels consisting of complex mixtures of hydrocarbons with varying composition, such as diesel, E85, and gasoline. Considering the oxygen-to-carbon ratio, too much oxygen will result in an unstable reaction as well as loss of efficiency due to total combustion. However, sufficient oxygen is needed for generation of heat to maintain the steam reforming reaction. A surplus of steam is advantageous for suppression of carbon monoxide and coke but at the expense of the cost to superheat a large amount of steam. Considering the volume and weight of the vaporizer and the condenser recovering water from the fuel cell, a low steam-to-carbon ratio is favorable. In many studies, the reforming reactions are controlled by an external heat supply in order to study the reaction behavior at varying temperatures and operating parameters without considering heat losses from the reactor. In practice, a process more exothermic than predicted will generally be necessary. The heat integration is unique for every reactor setup and the operating parameters chosen for the experiments in this study were adjusted during the experiments to be able to control the reforming reactions in the present reformer. In Table 2, the operating parameters for the various fuels are shown. An amount of fuel was used that theoretically would give an amount of hydrogen resulting in 3 kW electricity in a PEFC. Due to varying properties of the different fuels and varying O_2:C and H_2O:C used, this resulted in different space velocities over the catalyst.

Experiments were run until stable and reproducible results were obtained. Each fuel was tested repeatedly during a week. During shutdown of the reformer, the air was shut off first, followed by fuel and steam. Air was then flushed through the reformer to burn off potential coke on the catalyst surface. Coke could then be detected by increases in temperature after the monolith. An ocular inspection of the catalyst and the inside of the reactor walls was also performed after each experiment.

2.3. Collection of data for evaluation

Temperatures were measured using K-type thermocouples, placed in the mixing section (T1–T6 in Fig. 1) and after the catalyst (T7–T9 in Fig. 1), and the temperature profiles were collected in LabVIEW. The reactor effluent product compositions were studied by gas chromatography (GC), using a Varian CP-3800

Table 2
Operating parameters for the different fuels used in the multifuel study

	Fuel used	Flow rate (g fuel min^{-1})	O_2:C[h] (mol:mol)	λ[i]	H_2O:C (mol:mol)	GHSV (h^{-1})
Diesel[a]	Commercial fuel[f]	12.0	0.40	0.27	2	8700
Gasoline[b]	Commercial fuel[f]	14.4	0.40	0.26	2	10900
Dimethyl Ether[c]	Gerling Holz & Co. 99.9%	20.4 (l)	0.25	0.17	2	8800
Ethanol[d]	Altia Oyj 95%	15.8	0.35	0.24	3	9500
E85	Commercial fuel[g]	18.6	0.40	0.27	3	12900
Methanol[e]	VWR International 98.5%	22.7	0.20	0.13	1.7	6900

Operating parameters obtained from:

[a] Reference [15].

[b] Reference [24].

[c] Reference [25].

[d] Reference [16].

[e] Reference [26].

[f] Swedish Environmental Class 1 (MK1).

[g] 85 vol% bio-ethanol/15 vol % MK1 gasoline.

[h] Comment: oxygen in the fuel not included in the ratio.

[i] λ = actual-to-stoichiometric air/fuel ratio.

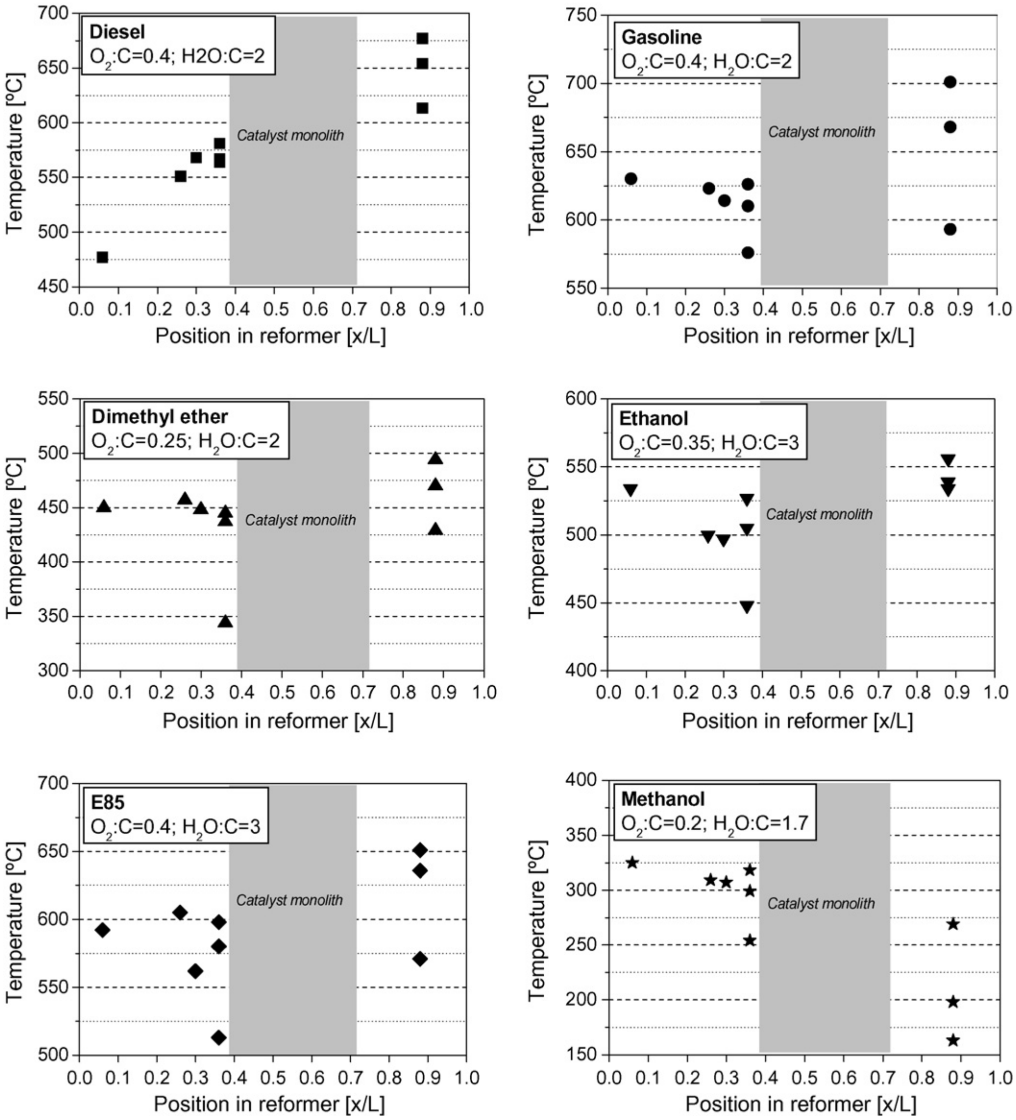

Fig. 2. Temperature profiles in the reactor during autothermal reforming of the various fuels, $P = 3\ \mathrm{kW_e}$ (L–length of reformer, positions of the thermocouples are shown in Fig. 1).

and a Varian 3400CX. The CP-3800 is equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) and two packed columns, a Porapak Q and an MS 5A where CH_3OH, CH_4, CO, CO_2, dimethyl ether (DME), H_2, N_2, and O_2 can be quantitatively analyzed. The 3400CX is equipped with two capillary columns, a VF-1 ms and a GS-Q and two FIDs. This GC was used for detection of the higher molecular-weight hydrocarbons in diesel and gasoline, as well as of C_2H_5OH. The reformate was passed through a condenser at ca. 10 °C prior to the gas analysis.

2.4. Results analysis

The key criterion in evaluating the various fuels in the present study was the practical feasibility of the ATR process. By this, it was meant that the reaction should be self-sustaining and stable and convert the main part of the fuel into a hydrogen-rich gas. Together with the temperature profiles, the following equations were used for evaluation of the data, with F corresponding to molar flows:

$$\mathrm{H_2\ selectivity\,(\%)} = \frac{F_{\mathrm{H_2+CO}}}{F_{\mathrm{H_2,max}}} \times 100 \tag{2}$$

$$\mathrm{Conversion\,(\%)} = \frac{F_{\mathrm{fuel,in}} - F_{\mathrm{fuel,out}}}{F_{\mathrm{fuel,in}}} \times 100 \tag{3}$$

$$\mathrm{CO_2\ selectivity\ parameter\,(\%)} = \frac{F_{\mathrm{CO_2}}}{F_{\mathrm{CO_2}} + F_{\mathrm{CO}}} \times 100 \tag{4}$$

The hydrogen selectivity (Eq. (2)) was defined as the moles of hydrogen plus carbon monoxide in the product gas obtained per mole of fuel divided by the theoretical maximum ratio at the specific condition (assuming all carbon reacts to CO_2). In the experiments with diesel, gasoline, and E85, the amount of unconverted hydrocarbons was estimated by means of atomic carbon balances. Diesel fuel was then assumed to consist solely of $C_{14}H_{26}$ and gasoline of C_8H_{18}. The $CO_2/(CO_2 + CO)$ product ratio (Eq. (4)) was used as a parameter to evaluate the selectivity to CO_2 relative to CO, not including other carbon-containing components such as CH_4 and unconverted hydrocarbons. The efficiency of the reformer was cal-

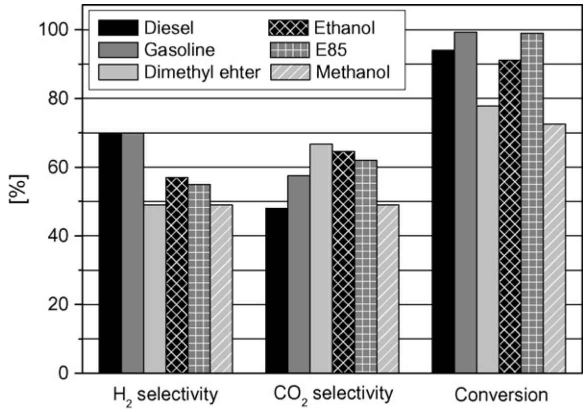

Fig. 3. Comparison of the different fuels in terms of H_2 selectivity, CO_2 selectivity, and conversion during autothermal reforming.

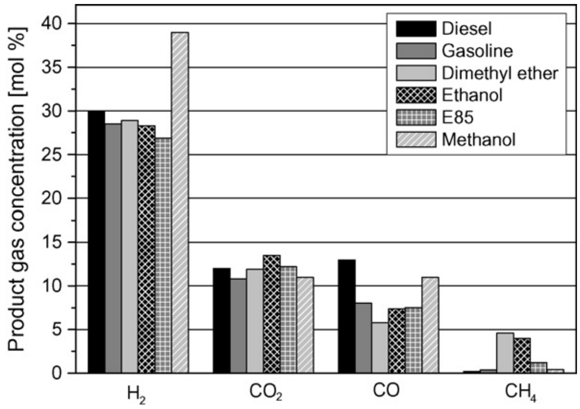

Fig. 4. Product gas concentrations of H_2, CO_2, CO, and CH_4 during autothermal reforming of the various fuels.

culated according to Eq. (5), where LHV corresponds to the lower heating values.

$$\eta_{\mathrm{ref}} = \frac{(F_{H_2} + F_{CO})\mathrm{LHV}_{H_2}}{F_{\mathrm{fuel}}\mathrm{LHV}_{\mathrm{fuel}}} \times 100 \qquad (5)$$

3. Results and discussion

It is essential to emphasize that the main focus of this study not has been to optimize the reformer performance for each fuel, but to evaluate the flexibility of the reformer using different fuels. Even though the commercial hydrocarbon fuels (diesel, gasoline, and E85) pose difficulties due to their complex composition, the authors of this paper find importance in experimentally evaluating the feasibility of reforming real fuels, since those impossibly can be represented with a single hydrocarbon. In addition, the commercial fuels contain sulfur and additives for improvement of fuel properties and combustion engine characteristics, which may affect the reforming process and catalyst negatively. We would also like to call attention to the differences in diesel and gasoline composition in different countries of the world. The Swedish fuels used in this study contain comparatively low amounts of sulfur and the aromatics content in Swedish diesel is very low compared to diesel fuels in other countries, which makes the reforming process less complex. It is considered likely though, that the fuel quality in other countries will approach the Swedish standard in the near future.

Fig. 2 shows representative examples of the reactor temperature profiles after stabilization of the autothermal reforming reactions during experiments with the various fuels. The temperature profiles were used to indicate what reactions are occurring and to what extent. The profiles show exotherms in the mixing zone and whether the resulting reaction enthalpy over the catalyst is negative or positive. The temperature distribution is evaluated both in the axial and radial direction (T1–T9 in Fig. 1). In Fig. 3, the fuels are compared in terms of fuel conversion and selectivity to hydrogen and carbon dioxide, respectively. Fig. 4 shows typical product gas compositions obtained and Fig. 5 values of hydrogen selectivities vs. time on stream during 100 min. In the following paragraphs, the results are used to discuss the practical potential of each fuel for use in the current reformer design with the Rh-based catalyst.

3.1. Diesel reforming

In a previous study by the authors, varying operating conditions have been evaluated for the current reformer using Swedish commercial diesel fuel [15]. The oxygen-to-carbon ratio (O_2:C) was then varied between 0.3 and 0.45, corresponding to λ values between 0.2 and 0.3 (λ = actual-to-stoichiometric air/fuel ratio). Maximum performance was obtained at O_2:C = 0.4. The steam-to-carbon (H_2O:C) was varied between 2 and 3, without significant difference in performance and without any observed coke on the catalyst surface. An apparent issue with a multifuel reformer is that the design and catalyst composition will not be optimized for any particular fuel. The reactor and catalyst used in the present study have initially been designed for use with diesel fuel. In the mixing/prereforming zone of the reformer, the long-chain hydrocarbons in diesel fuel are broken down into shorter molecules. Exothermic low-temperature reactions generate heat to sustain the reactions and will also facilitate the subsequent catalytic reforming. With an efficient mixing/prereforming, the risk for coke deposition on the catalyst surface can be minimized. Mixture preparation by cool flames is one method of prereforming the fuel [27]. Cool flames can be attained only in a narrow temperature and pressure interval. In order to stay in this interval, avoiding the risk of igniting the fuel, a balancing of the heats of reactions and heat losses is essential. Regardless of the method of prereforming, cool flames or homogeneous partial oxidation, a partial breakdown of the long-chain hydrocarbons improves the mixing of the reactants by increasing the temperature and the turbulence. As can be seen in Fig. 2, the temperatures in the mixing section range from 475 °C before the air/steam inlet holes (T6) to 585 °C at the catalyst inlet (T1). The relatively low temperature difference in the radial direction at the catalyst inlet (T1 – T3) indicates efficient reactant mixing. In contrast, the radial temperature difference after the monolith and

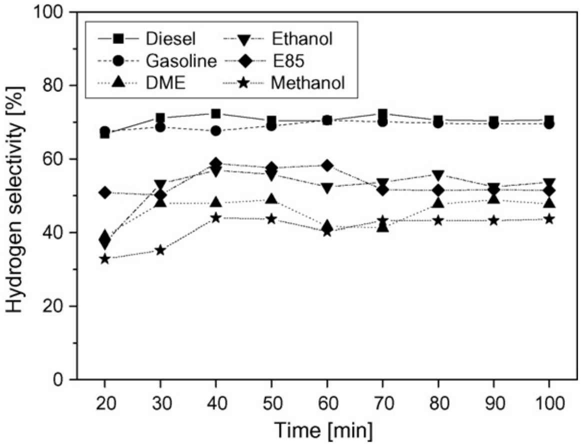

Fig. 5. Hydrogen selectivity vs. time for autothermal reforming of the respective fuels.

incomplete conversion (96%) suggest unsatisfactory mixing of the reactants leading to local differences in operating parameters. A problem is that there are no dedicated components for these systems, such as nozzles giving a fine spray of fuel at low pressure and over a wide range of flow rates. The issue of achieving good mixing of the fuel spray with the air/steam mixture is therefore considered in need for improvement. The achievable reforming temperature was limited by the reactor design (such as thermal insulation and geometry) and it could therefore not be concluded if the incomplete conversion was a result of a too low temperature or if it is a matter of design. Nevertheless, the results show that the current reformer design is a good starting point in the development of an optimized reforming process for commercial diesel fuel. The CO_2 selectivity parameter was close to 50% and the selectivity to hydrogen 70% (21 mol H_2/mol $C_{14}H_{26}$), the highest obtained for all fuels tested in this study (Fig. 3).

The catalyst composition has initially been chosen for minimization of coke and methane formation during autothermal reforming of diesel fuel. No coke was observed during the experiments, either during purging with air at shutdown or on the surface of the catalyst after reaction. Trace amounts of carbonaceous material were found in the condensate from the reactor effluent. Methane concentrations were relatively low, typically around 2000 ppm (Fig. 4). Thermodynamic equilibrium calculations of $(CH_2)_x$ reforming indicate a methane concentration of 3600 ppm at 650 °C and 1800 ppm at 675 °C.

3.2. Gasoline reforming

The reformer was found to perform satisfactorily using gasoline as the fuel. This was not unexpected, since gasoline, like diesel, is a hydrocarbon mixture that can be effectively prereformed by means of cool flames or homogeneous partial oxidation without large losses in efficiency prior to the catalyst [28]. Gasoline contains a high portion of aromatics though, a maximum of 35% in Swedish MK1 gasoline, in contrast to diesel that mainly consists of long straight-chain hydrocarbons (50–70% paraffins [9]). Aromatics are more stable during reforming and have a higher tendency to form coke than do paraffins [24]. Palm et al. [29] have shown that the addition of aromatics during ATR of paraffins (C_{13}–C_{15}) has a strong negative impact on the fuel conversion.

Due to a higher thermal load of gasoline in the experiments compared to the diesel reforming experiments, a higher reforming temperature was obtained. Even though the temperature was unevenly distributed in the radial direction of the reformer (Fig. 2), with a temperature difference of almost 100 °C at the catalyst outlet, a high fuel conversion of 99% was achieved (Fig. 3). This could be due to a number of reasons. Firstly, gasoline is more easily evaporated than diesel, since the vapor pressure is higher (Table 1). Further, the olefin and oxygenate fractions in gasoline are more reactive compared to the paraffins in diesel, which may be difficult to crack. This is also the case considering the aromatics in gasoline, which typically are more reactive than the aromatic fraction in diesel (generally consisting of polyaromatics), even if the total aromatic concentration is higher in gasoline.

The CO_2 selectivity parameter was higher for gasoline compared to diesel (Fig. 3), despite the higher temperature. This is, however, in line with values from thermodynamic equilibrium calculations at 700 °C, with calculated ratios of 53 and 41% for C_8H_{18} and $(CH_2)_x$, respectively. The hydrogen selectivity was 70% (13 mol H_2/mol C_8H_{18}), comparable to the results obtained during diesel reforming. The methane concentration was relatively low during the experiments, but higher compared to diesel reforming, between 3000 and 4000 ppm (Fig. 4). No coke was observed during shutdown or on the catalyst surface. Small amounts of coke were, however, found on one of the thermocouples (T2) in the mixing section of the reformer. This effect could be caused by nickel on the surface of the thermocouple, promoting the formation of coke.

3.3. Dimethyl ether (DME) reforming

The autothermal reforming of dimethyl ether has previously been tested in a small-scale reactor using Pd-based monolithic catalysts [25]. It was found that high selectivities to hydrogen and carbon dioxide could be obtained using $PdZn/Al_2O_3$ catalysts during autothermal reforming of DME. The optimal operating parameters for this catalyst were found to be an O_2:C of 0.35 ($\lambda = 0.23$) and a H_2O:C of 1.3 or higher at 350–400 °C.

In the tests described here, the startup of the reformer was performed by igniting the air/fuel mixture in the partial oxidation mode, then switching to the autothermal mode. In this way, the desired reforming temperature could be reached. It was found that the formerly optimized parameters could not be used in the present reactor design, because the temperature increase in the mixing zone could not be controlled due to gas phase reactions. The parameters were adjusted stepwise and the reaction could be stabilized at an O_2:C of 0.25 ($\lambda = 0.17$) and a H_2O:C of 2. This resulted in a catalyst inlet temperature of 450 °C and a maximum outlet temperature of 500 °C (Fig. 2). Oxidation reactions were needed to sustain the reforming reaction over the catalyst but led to losses in efficiency. It will be difficult to reach very high efficiencies with the present reactor design using DME, because a reforming temperature higher than the ignition temperature is needed. The efficiency loss is also shown by the hydrogen selectivity being less than 50% (2.4 mol H_2/mol DME).

Rh has been shown to be active for the direct decomposition of DME [30], according to Eq. (6). The significance of the direct decomposition reaction was indicated by a high concentration of CO together with a high concentration of CH_4 (Fig. 4). The importance of this reaction was also demonstrated by turning off the steam and air while still obtaining relatively high hydrogen and carbon monoxide concentrations in the product gas.

$$CH_3OCH_3 \rightarrow CH_4 + CO + H_2 \quad \Delta H_R^0 = -1\,\mathrm{kJ\,mol^{-1}} \tag{6}$$

Hydrogen not originating from Eq. (6) will most likely be a result of steam reforming of DME (Eq. (7)). Due to this reaction, as well as oxidation reactions, a fairly high CO_2 selectivity parameter of 67% was achieved. This was the highest value of CO_2 selectivity obtained for the different fuels in this study (Fig. 3). However, the conversion was low, likely a result of the injected fuel penetrating the monolith before being properly mixed with the air/steam mixture. The molar flow of DME was considerably larger than the flow of fuel during gasoline reforming, which means that the mixing will be an issue if the electrical load is to be kept at 3 kW.

$$CH_3OCH_3 + 3H_2O(g) \rightarrow 2CO_2 + 6H_2 \quad \Delta H_R^0 = 122\,\mathrm{kJ\,mol^{-1}} \tag{7}$$

Coke deposition was observed on the catalyst surface after reaction. The coke was concentrated in the first part of the monolith and was burnt off in air prior to the following experiment. No decline in activity resulting from coke deposition could be observed with time during the experiments.

The main conclusion is that DME is probably not suited for autothermal reforming in fuel cell auxiliary power units with this reactor design and using Rh as the reforming catalyst.

3.4. Ethanol reforming

Ethanol steam reforming is often performed at comparatively high steam-to-carbon ratios. This is partly due to the high steam-to-carbon ratio resulting from the fermentation process where ethanol is produced. By removing the distillation unit required to produce pure ethanol, the production process becomes more economical. In contrast, the cost of heating water in the reformer inlet gas will increase. High steam-to-carbon ratios are favorable when considering that ethanol reforming typically produces large amounts of coke, deactivating the catalyst. This is especially the case when using Ni catalysts, and can be suppressed by running the process in excess of steam [31]. In the experiments described herein, no coke was observed either during purging with air or on the surface of the Rh catalyst, but was found in the condensate from the reactor effluent. This feature has been explained by Cavallaro et al. [16] as a process where the Rh/Al_2O_3 catalyst surface is automatically regenerated by oxygen in the feed, producing CO_2. It has been proposed that coke is produced through the polymerization of ethylene over Rh/Al_2O_3 catalysts [16].

Relatively high concentrations of methane were formed during the reaction (Fig. 4). Methane can originate from ethanol decomposition (Eq. (8)), methanation (Eq. (9)), or decarbonylation of acetaldehyde (Eq. (10)).

$$C_2H_5OH(g) \rightarrow CH_4 + CO + H_2 \quad \Delta H_R^0 = 50\,\mathrm{kJ\,mol^{-1}} \tag{8}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O(g) \quad \Delta H_R^0 = -205\,\mathrm{kJ\,mol^{-1}} \tag{9}$$

$$CH_3CHO(g) \rightarrow CH_4 + CO \quad \Delta H_R^0 = -19\,\mathrm{kJ\,mol^{-1}} \tag{10}$$

Methane formation has been shown to increase at insufficient Rh loading, which decreases hydrogen yield and leads to deactivation of the catalyst [32]. Efforts were made to identify the byproducts formed during ethanol reforming. Acetaldehyde, ethylene, ethane, and acetic acid were injected into the GC, but could not be separated adequately to enable identification of the samples from the experiments.

Ethanol conversion was not satisfactory, just above 90% (Fig. 3). This aspect together with the byproducts formed brings us to the conclusion that this reactor setup is not optimal for ethanol reforming. A higher Rh loading (>1 wt%) might be needed to increase conversion and avoid the formation of byproducts. Nevertheless, considering the incomplete conversion, fairly high hydrogen selectivity, 57% (2.6 mol H_2/mol C_2H_5OH), was obtained during ethanol reforming (Fig. 3). A reformer that can perform well with both hydrocarbon mixtures and ethanol does therefore not seem to be unattainable.

3.5. E85 reforming

E85 was chosen as a fuel in this study, because it is a commercially available fuel, intended for fuel-flexible vehicles, widely used in Sweden but becoming more common in the United States as well [33]. The gasoline content of the fuel (at least 15%) is used to improve the cold start performance of the vehicles. Hydrogen generation from ethanol has been thoroughly reported in the literature, while extensive results from reforming of E85 are lacking. The reformer performance and catalyst will be affected by the gasoline content of the fuel and it is therefore considered important to experimentally evaluate the feasibility of reforming E85 fuel.

The experiments were initiated at the same operating parameters that were used during ethanol reforming, and were then adjusted stepwise. An oxygen-to-carbon ratio of 0.4 ($\lambda = 0.27$) was found to be needed to achieve high conversion and a stable temperature profile. The higher thermal load of E85 compared to pure ethanol resulted in a higher reforming temperature. Consequently, the conversion of the fuel was higher too (99%). After approximately 30 min of operation, there was a shift in temperature and the temperatures in the prereforming zone suddenly increased by 100–150 °C. By comparing the gas chromatograms before and after this rise, it was found that it was the gasoline components in the fuel, with retention times between 3 and 15 min that started to be converted (or partially broken down) prior to the monolith. Interestingly, the temperature profile during E85 reforming closely reflects the one obtained during gasoline reforming but at a lower temperature level (see Fig. 2).

The selectivity to CO_2 was somewhat lower during E85 reforming than for reforming of pure ethanol (Fig. 3). The higher portion of CO may be a result of the higher temperature required to reform the gasoline fraction of the fuel. The hydrogen selectivity was also lower during E85 reforming, 55% (3.6 mol H_2/mol fuel), likely due to a larger part of the fuel being oxidized prior to the catalyst. It was also found that the methane concentration in the product gas was lowered from 4% during pure ethanol reforming to 1.2% during E85 reforming (Fig. 4). The explanation for this is probably that the endothermic decomposition reaction (Eq. (8)) is less favored at the higher temperature. To study the effects of the gasoline fraction in the fuel on the long-term stability of the process and catalyst, more thorough experiments are needed. Still, the results presented here show that E85 has large potential to be used in diesel and gasoline reformers.

3.6. Methanol reforming

The methanol reforming experiments were started by first preheating the reactor and catalyst bed to about 200 °C, then introducing steam and methanol followed by a stepwise addition of air. This procedure was used because it was found that the dynamic response of introducing air was very fast and would influence the balancing of the exothermic oxidation and endothermic reforming reactions negatively during initiation of the reactants to the reactor. Problems with large efficiency losses due to complete combustion that were observed during reforming of DME and ethanol were not considered important since methanol can be reformed at a lower temperature, where there is no risk of igniting the fuel.

Initially, temperature increases resulting from oxidation reactions were observed in the mixing zone. However, the temperatures prior to the catalyst were fluctuating and decreased slightly with time. This was explained by insufficient vaporization of methanol causing condensation of methanol droplets on the thermocouples. Since the electrical load (theoretical) was kept constant in all experiments, the volumetric flow of fuel was about twice compared to the diesel experiments. The spray of fuel may therefore have penetrated the monolith without being properly mixed with the air/steam mixture. Furthermore, the heat of vaporization is about five times higher for methanol than for diesel (Table 1). The temperatures both at the catalyst inlet (T1–T3 in Fig. 1) and at the outlet (T7–T9 in Fig. 1) differed in the radial direction, suggesting unsatisfactory mixing of the reactants as well. The poor fuel vaporization and/or reactant mixing resulted in a low activity for methanol reforming over the catalyst. This was shown by the relatively low hydrogen selectivity obtained (H_2 selectivity: 49%; 1.3 mol H_2/mol CH_3OH).

The temperatures after the catalyst were lower than the catalyst inlet temperatures indicating endothermic reactions over the catalyst (Fig. 2). A high concentration of CO in the product gas (Fig. 4) implies a mechanism where methanol is decomposed into CO and H_2 (Eq. (11)). This reaction pathway has been shown to occur preferentially over group VIII metals, such as Rh [34]. Lyubovsky and Roychoudhury [18] suggest that oxidative reforming of methanol consists of several overlapping steps: methanol oxidation (Eq. (12)), methanol decomposition and water–gas shift (Eq. (13)). CO_2 in the product gas most likely originates from the water–gas shift reaction, where water reacts with CO to form CO_2 and additional hydrogen but could also be due to methanol steam reforming (Eq. (14)). The reactivity of Rh towards methanol decomposition has been shown to be promoted by oxygen adsorption, which can also oxidize the products [35]. Around 4000 ppm of methane was also observed in the product gas (Fig. 4).

$$CH_3OH \rightarrow CO + 2H_2 \quad \Delta H_R^0 = 90\,\mathrm{kJ\,mol^{-1}} \tag{11}$$

$$CH_3OH(g) + 1.5O_2 \rightarrow CO_2 + 2H_2O(g) \quad \Delta H_R^0 = -677\,\mathrm{kJ\,mol^{-1}} \tag{12}$$

$$CO + H_2O(g) \leftrightarrow CO_2 + H_2 \quad \Delta H_R^0 = -41\,\mathrm{kJ\,smol^{-1}} \tag{13}$$

$$CH_3OH(g) + H_2O(g) \rightarrow CO_2 + 3H_2 \quad \Delta H_R^0 = 49\,\mathrm{kJ\,mol^{-1}} \tag{14}$$

The present reformer does not seem to be suitable for methanol reforming in a truck fuel cell auxiliary power unit. Due to difficulties with vaporization of the fuel, electrical loads up to 5 kW cannot be obtained. The reactor design could presumably be used with smaller flows since the autoignition temperature of methanol is high relative to the reforming temperature. Alternatively, a configured system, with the possibility to preheat the fuel, could be an option. However, Rh is selective for the decomposition of methanol and if a high CO_2 selectivity from the reformer is desirable, another catalyst composition should be considered. A 5 kW methanol reformer prototype has been developed earlier in our research group, using CuZn-based reforming catalysts [36]. Cu-based catalysts, however, are not suitable in multifuel reformers due to their poor thermal stability.

4. Summary and final remarks

The main purpose of this study was to evaluate the feasibility of reforming different fuels in a reactor making use of closely integrated prereforming (by means of homogeneous partial oxidation) and reforming (catalytic) processes. More specifically, the same reformer and catalyst composition was used for all fuels. It was found that the reformer worked successfully with diesel, gasoline, and E85 but less satisfactorily with DME, ethanol, and methanol. The hydrocarbon fuels need higher temperatures for conversion compared to the oxygenated fuels, but can be effectively reformed into hydrogen-rich gases in the present reactor without large losses in efficiency in the mixing section. Oxygenates are generally easier to reform but have lower energy densities, which means larger flows of fuel are needed. This led to difficulties in the present reactor design, where part of the fuel penetrated the monolith without being accurately mixed with the air/steam mixture.

Reproducible results could be obtained for all fuels; the hydrogen selectivities during 100 min on stream are shown in Fig. 5. The reformer efficiencies amounted to 61% (diesel), 62% (gasoline), 45% (DME), 51% (ethanol), 59% (E85), and 43% (methanol). In the reformer used in this study, all of the heat needed for the steam reforming reaction is supplied by oxidation of the fuel in order to keep the reactions self-sustaining. In a reformer making use of an external heat source, the amount of hydrogen obtainable from the fuel, and hence the reformer efficiency, will be higher. The reforming process needs to be coupled with a cleanup strategy to achieve low enough CO concentrations for the PEFC to tolerate. A well-designed heat integration of the entire fuel processor will make the system more efficient. The results are also expected to improve with further optimization of the reaction conditions (O_2:C, H_2O:C, and temperature) for each fuel.

This study has shown that commercial fuels can be used to experimentally evaluate the adaptability of a specific reactor design for different fuels, even if all reactants and products from reforming mixtures of hydrocarbons cannot be identified. The reactor design presented herein was found to be an excellent basis for an optimized reforming process that can easily be adapted for (at least) diesel, gasoline, and E85.

Rh was found to be a suitable catalyst material for use in multifuel reformers. The catalyst performed well with diesel, gasoline, ethanol, and E85 but was not selective for hydrogen generation by autothermal reforming of DME and methanol. It will be a problem in a multifuel reformer that the reforming catalyst cannot be optimized for the complex reaction network in the ATR system for every fuel, but Rh-based catalysts, even though expensive, appear very promising candidates. Local differences in operating conditions caused by insufficient reactant mixing resulted in large temperature differences in some experiments. Therefore, the risk for hot-spot formation in the catalyst monolith will be high and can result in gradual deactivation of the catalyst over time due to sintering. A closer coupling of the exothermic oxidation reactions and the endothermic steam reforming reactions in the monolith could be obtained using metallic substrates with higher thermal conductivity.

The experience gained from the study has resulted in a new, improved hydrocarbon fuel reformer design that is currently being tested. Choosing the right nozzle is considered fundamental; the new design includes a nozzle yielding a spray with very fine droplets (<10 μm) to accelerate vaporization and mixture blending. The system also allows preheating of the liquid fuel prior to injection, enhancing the vaporization even further. Numerical simulations have shown that the holes where the air/steam mixture enters the reformer are positioned too high upstream of the prereforming section, resulting in unfavorable flow profiles. In order to improve the turbulence, the holes have been repositioned in the new design.

A successful diffusion of fuel cell-based APUs into the market could advance the development of the fuel cell technology in the transport sector. The choice of technology for hydrogen generation will likely be of large importance in establishing a market. Fuel-flexible reformers are regarded as advantageous from several perspectives and could offer simplicity and robustness to the APU systems.

Acknowledgements

The Swedish Energy Agency and the Foundation for Strategic Environmental Research are gratefully acknowledged for financial support. Thanks also to Corning Inc. for supplying cordierite substrate and to Sasol Germany GmbH for providing the alumina.

References

[1] S. Specchia, A. Cutillo, G. Saracco, V. Specchia, Ind. Eng. Chem. Res. 45 (2006) 5298–5307.

[2] Swedish Commission on Oil Independence, Making Sweden an Oil-free Society, Report 21 June 2006.

[3] California Air Resources Board, Assembly Bill (AB) 32 Fact Sheet–California Global Warming Solutions Act of 2006, Sacramento, California.

[4] The European Commission, Euro VI proposal, http://ec.europa.eu/enterprise/automotive/mveg_meetings/meeting98/euro_vi_proposal.pdf, last visited 2008-01-10.

[5] T. Aicher, L. Griesser, J. Power Sources 165 (2007) 210–216.

[6] P. Ferreira-Aparicio, M.J. Benito, J.L. Sanz, Catal. Rev. 47 (2005) 491–588.

[7] B.J. Bowers, J.L. Zhao, M. Ruffo, R. Khan, D. Dattatraya, N. Dushman, J.-C. Beziat, F. Boudjemaa, Int. J. Hydrogen Energy 32 (2007) 1437–1442.

[8] Y. Shi, J. van Pelt, R. Khan, M. Ruffo, J. Zhao, B. Bowers, J. Cross III, ECS Trans. 5 (2007) 645–654.

[9] The Swedish Petroleum Institute, SPI, www.spi.se, last visited 2008-01-09, last updated 2008-01-09.

[10] D. Lide (Ed.), Handbook of Chemistry and Physics, 80th ed., CRC Press, Boca Raton, 1999.

[11] Dieselnet, www.dieselnet.com, last visited 2008-01-08.

[12] H.F. Mark, D.F. Othmer, C.G. Overberger, G.T. Seaborg, Kirk-Othmer Encyclopedia of Chemical Technology, fourth ed., Wiley-Interscience Publication, New York, 1992.

[13] G. Kolb, T. Baier, J. Schürer, D. Tiemann, A. Ziogas, H. Ehwald, P. Alphonse, Chem. Eng. J. 137 (2008) 653–663.

[14] M. Ferrandon, T. Krause, Appl. Catal. A 311 (2006) 135–145.

[15] M. Nilsson, L.J. Pettersson, B. Lindström, P. Ekdunge, F. Von Corswant, C. Villa, 2006, Fuel Cell Seminar Abstracts, 238–241, November 13–17, 2006, Honolulu.
[16] S. Cavallaro, V. Chiodo, A. Vita, S. Freni, J. Power Sources 123 (2003) 10–16.
[17] V. Fierro, O. Akdim, C. Mirodatos, Green Chem. 5 (2003) 20–24.
[18] M. Lyubovsky, S. Roychoudhury, Appl. Catal. B 54 (2004) 203–215.
[19] M. Sgroi, G. Bollito, G. Saracco, S. Specchia, J. Power Sources 149 (2005) 8–14.
[20] X. Wang, R.J. Gorte, Catal. Lett. 73 (2001) 15–19.
[21] A.F. Diwell, R.R. Rajaram, H.A. Shaw, T.J. Truex, Stud. Surf. Sci. Catal. 71 (1991) 139–152.
[22] J.R. Rostrup-Nielsen, Catal. Today 18 (1993) 305–324.
[23] H. Schaper, E.B.M. Doesburg, L.L. van Reijen, Appl. Catal. 7 (1983) 211–220.
[24] A. Qi, S. Wang, C. Ni, D. Wu, Int. J. Hydrogen Energy 32 (2007) 981–991.
[25] M. Nilsson, P. Jozsa, L.J. Pettersson, Appl. Catal. B 76 (2007) 41–49.
[26] B. Lindström, Development of a methanol reformer for fuel cell vehicles, PhD thesis, KTH, Department of Chemical Engineering and Technology, TRITA-KET R172, ISBN 91-7283-406-4, 2003.
[27] L. Hartmann, K. Lucka, H. Köhne, J. Power Sources 118 (2003) 286–297.
[28] J. Matos da Silva, I. Hermann, C. Mengel, K. Lucka, H. Köhne, AIChE J. 50 (2004) 1042–1050.
[29] C. Palm, P. Cremer, R. Peters, D. Stolten, J. Power Sources 106 (2002) 231–237.
[30] F. Solymosi, J. Cserényi, L. Ovári, J. Catal. 171 (1997) 476–484.
[31] P. Vaidya, A.E. Rodrigues, Chem. Eng. J. 117 (2006) 39–49.
[32] S. Cavallaro, Energ. Fuel. 14 (2000) 1195–1199.
[33] US Department of Energy, Alternative Fuels & Advanced Vehicles Data Center, www.eere.energy.gov/afdc, last visited 2008-01-08, last updated 2007-09-25.
[34] Y. Matsumura, M. Okumura, Y. Usami, K. Kagawa, H. Yamashita, M. Anpo, M. Haruta, Catal. Lett. 44 (1997) 189–191.
[35] Y. Li, M. Bowker, Catal. Today 10 (1991) 421–424.
[36] B. Lindström, L.J. Pettersson, J. Power Sources 118 (2003) 71–78.