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Steam Reforming

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24.1

Introduction

A rapidly increasing number of publications deal with steam reforming of fossil and renewable fuels in microstructured reactors. In most cases, the application standing behind this work is the generation of hydrogen for portable, mobile and small-scale stationary fuel cell systems as future distributed source of electrical energy.

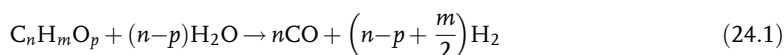
A small-scale steam reforming reactor may work as a single device named a pre-reformer positioned upstream of high-temperature fuel cells such as solid oxide fuel cells (SOFCs). However, most mobile fuel cell systems rely on proton exchange membrane (PEM) technology and in this case the reformer is the core part of a more complex hydrogen generation device, which is generally named a fuel processor [1].

Research activities in the field of steam reforming in microchannels are concerned with the development of specific catalyst coatings, with reactor development and with integration of such reactors into complete fuel processors. After a brief overview of the chemistry of steam reforming, these aspects are discussed in the sections below.

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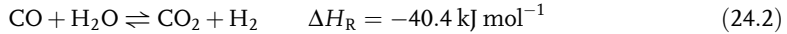
Reaction System

Steam reforming is the gas-phase conversion of energy carriers such as hydrocarbons and alcohols described by the general formula $C_nH_mO_p$ with steam to a mixture of carbon monoxide and hydrogen according to the reaction



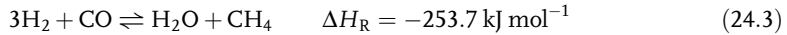
The ratio $(n-p)/n$ is called the steam-to-carbon (S/C) ratio of the feed. The product mixture of the endothermic reaction is named the reformat. Usually it contains, in addition to hydrogen and carbon monoxide, significant amounts of unconverted

steam and to a lesser extent some unconverted fuel and carbon dioxide, the latter being formed by the consecutive water gas shift reaction:



The water gas shift reaction increases the hydrogen concentration in the reformat. Owing to its exothermic character, higher reaction temperatures favor the reverse reaction.

Methane is frequently formed in significant amounts. Higher reaction temperatures decrease methane formation according to the equilibrium of the methanation reaction:



However, methane may be tolerated by most fuel cell systems up to 5 vol.% without damage.

Numerous other byproducts may be formed, such as light hydrocarbons and decomposition species in the case of alcohol fuels [1], which are all undesirable because they reduce the formation of the desired hydrogen.

Most systems working at the smallest scale work at ambient pressure and therefore the effect of pressure on the thermodynamics [1] will not be discussed here.

24.3

Catalyst Coatings for Steam Reforming in Microchannels

Because conditions are less well defined in a small-scale energy generation devices during shut-down and start-up, suitable steam reforming catalysts for small fuel processors need to be more robust against exposure to air and moisture compared with steam reforming catalysts for large-scale industry running under constant conditions for several years. For example, during start-up of a small system, reduction of the catalyst with hydrogen, which is frequently applied in industrial systems, is not possible at all, because no hydrogen is available. On the contrary, it might be required to heat up the reactor by hot air or combustion gases, before the reforming process is started, and the catalyst activity must not suffer from this treatment in a practical system. All these aspects require consideration when selecting a catalyst formulation for a steam reformer smaller than the industrial scale.

The reactors applied for catalyst evaluation are usually laboratory-type devices, which allow the removal of the microstructured plates after testing [2–9]. They are operated with electric power for heating and therefore are still far away from practical application. Therefore, the design of these reactors will not be discussed in detail here, bearing in mind that they are useful tools for catalyst screening and characterization.

24.3.1

Catalyst Development and Characterization for Alcohol Steam Reforming in Microchannels

Methanol is an attractive fuel for low-power applications, because the reaction temperature required for steam reforming is limited to values below 300 °C, which

in turn minimizes heat losses from a small-scale system. Hence numerous research groups working on microchannel steam reforming are focusing on methanol as fuel.

The carbon monoxide content present in reformat produced by methanol steam reforming is the lowest of all fuels compared at the same molar steam-to-carbon (S/C) ratio. Assuming an S/C ratio of >2 and a reaction temperature of $300\text{ }^{\circ}\text{C}$, not more than 1.2% of CO will be present in the feed [10]. This is related to the water gas shift equilibrium and reduces the workload of the subsequent gas purification steps.

Catalyst coatings under development for methanol steam reforming may be divided into copper-based systems and precious metal systems, namely Pd/ZnO.

The main advantage of commercial Cu/ZnO catalysts is their relatively high activity at operating temperatures below $300\text{ }^{\circ}\text{C}$. The catalysts are usually sensitive to temperatures exceeding $300\text{ }^{\circ}\text{C}$, which is a drawback when start-up procedures with hot combustion gases may result in temporary temperature excursions above $300\text{ }^{\circ}\text{C}$. In other words, it is difficult to heat a reactor to an operating temperature close to $300\text{ }^{\circ}\text{C}$ within a few minutes without locally exceeding this temperature. Furthermore, Cu/ZnO catalysts are pyrophoric, which means they show temperature excursions when exposed to air. On top of that, Cu/ZnO catalysts require pretreatment in hydrogen to gain full activity right after start-up.

Bravo *et al.* [11] coated commercial CuO/ZnO/Al₂O₃ catalyst in capillaries and gained 97% conversion at 97% carbon dioxide selectivity at a weight hourly space velocity (WHSV) of $3.9\text{ L h}^{-1}\text{ g}_{\text{cat}}^{-1}$. The WHSV obtained by Bravo *et al.* is low compared with hydrocarbon reforming, where the WHSV is usually in the order of several hundred $\text{L h}^{-1}\text{ g}_{\text{cat}}^{-1}$. This originates from the low reaction temperature of methanol steam reforming and thus the advantage mentioned above has another drawback, which is obviously not remotely compensated by the improved mass transfer in microchannels.

Men and coworkers investigated methanol steam reforming over Cu/CeO₂/Al₂O₃ catalysts [12–14] in a 10-fold screening reactor developed by Kolb *et al.* [3]. At a reaction temperature of $250\text{ }^{\circ}\text{C}$ and an S/C ratio of 0.9, the atomic ratio of copper to ceria was varied from 0 to 0.9, revealing the lowest conversion for pure ceria and a sharp maximum for a ratio of 0.1. The carbon monoxide selectivity was lower than 2% for all samples. As byproduct, substantial amounts of dimethyl ether were observed for all samples; the highest selectivity of 23% was detected for pure ceria. The dimethyl ether formation was attributed to separate dehydration of methanol on the alumina surface.

Dimethyl ether formation was also observed by Men *et al.* for Cu/ZnO/Al₂O₃ catalysts [15]. Lowering the WHSV to $10\text{ L h}^{-1}\text{ g}_{\text{cat}}^{-1}$ was required at an S/C ratio of 2 to achieve full conversion of the methanol without byproduct formation. Under these conditions, around 1 vol.% of carbon monoxide was detected in the reformat.

Reuse *et al.* [16] applied a self-developed reactor carrying microstructured plates for the determination of methanol steam reforming kinetics over a commercial copper-based low-temperature water gas shift catalyst from Süd-Chemie. Kinetic expressions were determined for both a tubular fixed-bed reactor containing 30 mg of catalyst particles and the microreactor coated with the catalyst particles. A power law

Table 24.1 Reaction order of fixed bed and microreactor determined by Reuse *et al.* [17] for methanol steam reforming.

Parameter	Fixed bed	Microchannels
m	0.70 ± 0.02	0.70 ± 0.1
n	0.1 ± 0.04	0.0 ± 0.1
o	-0.1 ± 0.1	-0.2 ± 0.1
k	$7.8 \times 10^{-5} \pm 0.9 \times 10^{-5}$	$4.8 \times 10^{-5} \pm 0.6 \times 10^{-5}$

kinetic expression of the following form was determined for methanol steam reforming:

$$-R_{\text{CH}_3\text{OH}} = k_0 e^{-\frac{E_a}{RT}} p_{\text{CH}_3\text{OH}}^m p_{\text{H}_2\text{O}}^n p_{\text{H}_2}^o \quad (24.4)$$

Similar values were determined for the reaction order in both systems at a lower rate of reaction for the microchannels, as shown in Table 24.1.

The inhibition by hydrogen was obviously more pronounced in the microchannels. Without hydrogen in the feed, the reaction rate was on average 34% higher for the coated catalysts.

Pfeifer *et al.* investigated several CuO/ZnO and CuO/ZnO/TiO₂ catalysts, which were either prepared from sintered nanoparticles or from titania nanoparticles impregnated with Cu/ZnNO₃ [18]. They compared the performance of these catalysts with that of a Pd/ZnO catalyst, which was obtained by impregnating zinc oxide nanoparticles with palladium acetate. The noble metal catalyst was more active, but all samples showed rapid deactivation, which was attributed to coke formation. Another drawback of the palladium catalyst was its higher carbon monoxide selectivity. The authors then focused on Pd/PdZn/ZnO systems [19]. The formation of a Pd/Zn alloy at higher reduction temperatures was identified as crucial to achieve lower carbon monoxide selectivity. Similar results were obtained by Chin and coworkers [20, 21]. The Pd/Zn alloy was assumed to be not only formed during reduction by pure hydrogen but also *in situ* in the hydrogen-rich reaction mixture of methanol steam reforming [22].

Later, Pfeifer *et al.* [23] prepared Pd/Zn catalysts by both pre- and post-impregnation of zinc oxide washcoats with palladium. The origin of the high amounts of carbon monoxide was finally attributed to an interaction of palladium with the metal foils specifically during the post-impregnation procedure, which was proven by the preparation of powder catalyst (no coating). These samples showed carbon monoxide concentrations below the equilibrium of water gas shift. Isolated Pd(0) was assumed to form the carbon monoxide excess. For both preparation routes, the highest activity was determined for the samples containing 10 wt.% palladium, which were also the most stable against deactivation. The WHSV amounted to $18 \text{ L h}^{-1} \text{ g}_{\text{cat}}^{-1}$ for the activity tests, which is more than four times higher than the results achieved by Bravo *et al.* [11], which were discussed above. Dimethyl ether was detected only at trace levels of a few hundred ppm by Pfeifer *et al.* over their Pd/ZnO catalyst [4].

Ethanol steam reforming catalysts were developed by Men *et al.* [24]. Nickel, rhodium and ruthenium catalysts on different carrier materials such as alumina, silica, magnesia and zinc oxide were tested at a S/C ratio of 1.5 and WHSV $90 \text{ L h}^{-1} \text{ g}_{\text{cat}}^{-1}$ in the temperature range $400\text{--}600^\circ\text{C}$. All the monometallic catalysts were mainly selective for acetaldehyde and ethylene. Over the rhodium catalyst, a reaction temperature of 600°C was required to achieve 80% hydrogen selectivity. A rhodium/nickel/ceria catalyst containing 5 wt.% rhodium, 10 wt.% nickel and 15 wt.% ceria on alumina performed even better. Full conversion was achieved at 500°C with only methane and carbon oxides as carbon products. This catalyst showed full conversion at 650°C for more than 100 h [24].

24.3.2

Development of Catalyst Coatings for Hydrocarbon Steam Reforming in Microchannels

Find *et al.* [25] developed a nickel-based catalyst for methane steam reforming. As material for the microstructured plates, AluchromY steel, which is an FeCrAl alloy, was applied. This alloy forms a thin layer of alumina on its surface, which is less than $1 \mu\text{m}$ thick. This layer was used as an adhesion interface for the catalyst, a method which is also used in automotive exhaust systems based on metallic monoliths. Its formation was achieved by thermal treatment of microstructured plates for 4 h at 1000°C . The catalyst itself was based on a nickel spinel (NiAl_2O_4), which stabilizes the catalyst structure. The sol-gel technique was then used to coat the plates with the catalyst slurry. Good catalyst adhesion was proven by mechanical stress and thermal shock tests. Catalyst testing was performed in packed beds at a S/C ratio of 3 and reaction temperatures between 527 and 750°C . The feed was composed of 12.5 vol.% methane and 37.5 vol.% steam balance argon. At a reaction temperature of 700°C and 32 h^{-1} space velocity, conversion close to the thermodynamic equilibrium could be achieved. During 96 h of operation the catalyst showed no detectable deactivation, which was not the case for a commercial nickel catalyst serving as a base for comparison.

Kolb *et al.* [26] applied small externally heated sandwich-type reactors sealed by laser-welding for catalyst screening on propane steam reforming. Steam and propane were fed to the reactors at a low S/C ratio of 1.4 at reaction temperatures between 450 and 750°C . Catalyst coatings containing 5 wt.% rhodium, platinum and palladium were tested. The platinum sample was calcined after impregnation at a lower temperature of 450°C to avoid sintering, and all other samples at 800°C . A commercial nickel steam reforming catalyst coated on the microchannels showed low activity even at 750°C . On the other hand, activity of the noble metal-based catalysts was already significant at 450°C . The rhodium sample was exclusively selective for propane steam reforming at 550°C . The platinum and palladium catalysts had inferior selectivity and deactivated significantly within 1 h even at 650°C , which was attributed to coke formation. Then ceria-containing bimetallic samples were prepared, which showed lower coke formation. For the most active and stable sample, an Rh/Pt/ CeO_2 catalyst, the effect of S/C ratio was determined at reaction temperatures between 650 and 750°C at a WHSV of about $300 \text{ L min}^{-1} \text{ g}_{\text{cat}}^{-1}$.

The sample showed stable conversion for a 6 h test duration. Later, 1000 h durability could be achieved over an improved proprietary catalyst formulation [27].

Thormann *et al.* [9] investigated the performance of Rh/Al₂O₃ and Rh/CeO₂ catalysts in hexadecane steam reforming in the low-temperature range from 400 to 700 °C. Full conversion of hexadecane, which served as surrogate for diesel fuel, was achieved at a S/C ratio of 4.0 and 700 °C reaction temperature only over the CeO₂-supported sample, which also showed short-term stability for 16 h, and the alumina-supported sample suffered from rapid deactivation.

24.4

System Design and Integrated Microstructured Reactors

24.4.1

Design Concepts of Microstructured Fuel Processors for Fuel Cells

Because steam reforming is endothermic, it requires energy input, which is performed by external firing of tubular steam reforming reactors on the industrial scale. For stationary fuel cell systems on the scale of power plants, this technology is applicable, of course. However, the smaller the energy supply system becomes, the more stringent are heat losses, integration and space demand. An alternative is to add air to the reformer feed, which leads to autothermal reforming, a combination of partial oxidation and steam reforming.

Fuel cells running on reformat do not convert the hydrogen contained in the reformat completely. Thus a significant amount, usually about 20% of the hydrogen, leaves the fuel cell anode unconverted. It may be fed back to the fuel processor and provide energy to the reforming process as an alternative to autothermal reforming. Integrated heat exchangers/reactors open the door to such integrated processing concepts. The endothermic steam reforming reaction may be coupled to an exothermic catalytic combustion in such reactors. This idea was proposed for the macro-scale as a so-called catalytic plate reactor (CPR) by Reay [28]. Later, Eigenberger and coworkers [29–32] investigated theoretically and practically heat exchanger/reactors for methane steam reforming on the meso-scale. The reactors were made from specially prepared ceramic monoliths and from structured and welded steel foils.

Zanfir and Gavriilidis [33] studied the combination of methane oxidation and methane steam reforming in an integrated heat exchanger with micro- and meso-scale reaction channels by a two-dimensional model. Co-current flow of reformer and combustor gases was chosen for the reactor model. Pressure was close to ambient, a S/C ratio of 3.4 and a feed temperature of 520 °C were assumed for the process. An almost 260 K temperature rise was calculated for the reactor wall temperature along the feed flow path owing to the slower kinetics of the steam reforming reaction. The axial temperature gradient increased when the half-height of the channels was decreased from 0.5 to 2 mm at constant inlet velocity (Figure 24.1). Larger channel dimensions made the heat transfer less efficient and less catalyse was available at

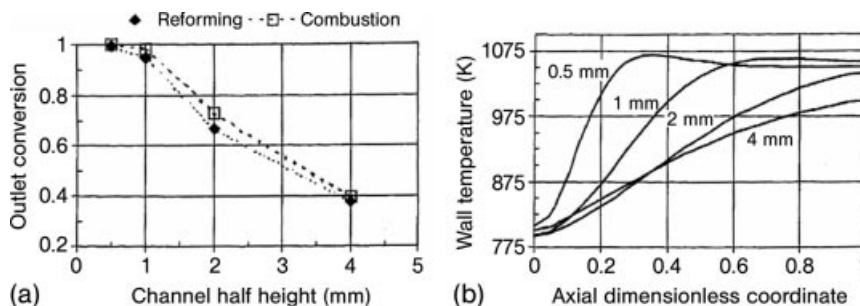


Figure 24.1 Numerical calculations of combined methane combustion and steam reforming. (a) Outlet conversion versus channel half-height; (b) wall temperature as a function of dimensionless reactor length; calculation results determined at constant inlet velocity [33].

higher flowrate of reactands. Mass transfer limitations occurred in the large channels and the catalyst mass was not sufficient under the conditions assumed. In a third case study, the thickness of the catalyst layer was increased at constant WHSV by increasing the inlet flow rate. Increasing the catalyst layer thickness from 10 to 60 μm decreased the conversion from 100% to below 70% for both reaction paths.

Simulation work performed by Cuttillo *et al.* for diesel fuel processing [34] revealed that steam reforming has a higher system efficiency than autothermal reforming when the anode off-gas is utilized.

For a methane steam reforming fuel processor, more than 15% higher fuel processor efficiency was determined experimentally by Heinzl and coworkers [35] when utilizing fuel cell anode off-gas compared with combustion of extra methane fuel.

Delsman *et al.* investigated the advantages of a microstructured methanol reformer coupled with a catalytic burner for anode off-gas over a conventional fixed-bed system [36]. Two ranges of electrical power output of the corresponding fuel processor–fuel cell system were considered, namely 100 W and 5 kW. The calculations revealed a more than 50% lower reactor size and more than 30% less catalyst mass required for the microreactor in case of the 100 W system. For the 5 kW system, the reactor volume was only 30% lower, but the catalyst savings were up to 50%.

The above theoretical and practical investigations demonstrate the potential improvements achievable with microreactor technology, especially in the case of steam reforming.

24.4.2

Reactors for Alcohol Steam Reforming

Similarly to catalyst development, activities dealing with integrated reactors and complete systems for steam reforming in microreactors are dominated by systems applying methanol as fuel, ethanol steam reformers being the exception.

24.4.2.1 Reactors for Methanol Steam Reforming in the Low and Sub-watt Power Range

Some work has been done on methanol steam reformers in the low power range of a few watts and less, which are dedicated to the power supply for electronic devices such as mobile phones. Consequently, production techniques are applied that are known from micro electro mechanical systems (MEMS) and silicon is the construction material chosen. Applying these techniques, electrical heaters for start-up and temperature sensors may be integrated into the devices. In some cases, sputtered catalysts are used, which usually suffer from low surface area and activity [37]. When fixed catalyst beds are applied [38], the pressure drops are consequently high, which would increase the power demand of the dosing equipment of future systems. If electrical heating is chosen as the energy source of steam reforming, about 30% of the electrical energy produced by the fuel cell would be required for running the reformer [39]. This is rather a conservative value and such simplified systems suffer from poor efficiency.

Jones *et al.* [40] presented an integrated and miniaturized device for methanol steam reforming consisting of two evaporators/preheaters, a steam reformer and a combustor with a total volume of less than 0.2 cm^3 for the power range between 50 and 500 mW. The energy for the steam reforming reaction was transferred from the combustor device having 3 W power, which was fed by an $\text{H}_2\text{-O}_2$ mixture for start-up and later by methanol and air. More than 99% conversion was achieved for the steam reforming reaction [21] at a S/C ratio of 1.8 and 325°C reaction temperature over palladium/zinc oxide catalyst [41]. Selective methanation served for CO removal downstream of the reformer. The porous disk burner temperature exceeded 400°C . The thermal power of the device was 200 mW at 9% efficiency. Assuming 60% fuel cell efficiency and 80% hydrogen conversion, the net efficiency of the system amounted to 4.5% and the power output was calculated to be 100 mW. Such an efficiency would still outperform a lithium ion battery [42]. Later the efficiency was increased by decreasing the reaction temperature of the reformer [43].

Numerical calculations demonstrated the dominant effect of heat losses of such a small-scale system [41]. About 40% heat losses were also determined experimentally in a slightly bigger system [44].

Park *et al.* developed components for a methanol fuel processor [45], which consisted of a combustion chamber for hydrogen oxidation filled with platinum catalyst supported on carbon nanotubes and a combined evaporator–steam reformer, which was merged in a single device by two intertwined, spiral-shaped channels for evaporation and steam reforming, as shown in Figure 24.2. The burner heated the device to the operating temperature within 5 min. However, the system showed excessive temperature gradients and the hydrogen flow rate required for the combustion reaction exceeded the hydrogen flow rate produced by the reformer. This originated from incomplete methanol conversion below 25%.

Kim and Kwon described a microreactor, heated by electricity, which carried a copper/zinc oxide catalyst [46]. About 4 mL min^{-1} of hydrogen was produced by the reactor. At a reaction temperature of 300°C and an S/C ratio of 1.1, full methanol conversion was achieved. Subsequently the same group developed a chip-like

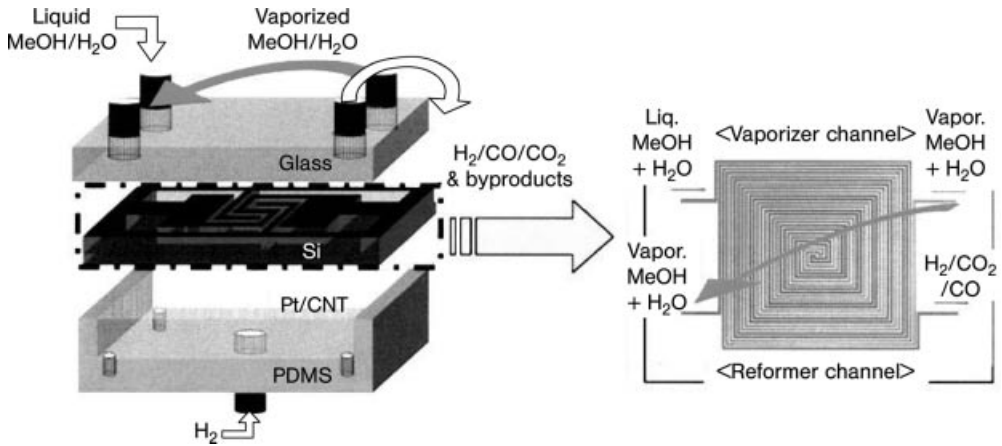


Figure 24.2 Combined evaporator, methanol steam reformer and hydrogen burner [45].

glass reactor, supplied with energy by decomposition of hydrogen peroxide over a platinum/alumina/silica catalyst [47]. More than 90% methanol conversion could be achieved over a copper/zinc oxide/alumina/silica catalyst at 270 °C. However, the conversion of hydrogen peroxide was incomplete. The electrical power equivalent of the reformat hydrogen corresponded to 1.5 W_{el}.

Kwon *et al.* described a miniaturized methanol fuel processor–fuel cell system [48]. The reformer, a preferential oxidation reactor and the fuel cell were fabricated separately from silicon wafers by photolithographic methods. The wafers were sealed by anodic bonding of a Pyrex glass cover. Commercial copper/zinc oxide catalyst was used for methanol steam reforming, and a commercial platinum catalyst served as the catalyst for the carbon monoxide clean-up. The fuel cell membrane electrode assembly carried carbon monoxide-tolerant platinum/ruthenium catalyst. The devices were heated by electrical thin-film resistance heaters. The size of the reformer was 1 cm³ and it converted the methanol feed completely at a reaction temperature of 280 °C and a low S/C ratio of 1.0. The hydrogen production of the fuel processor corresponded to a thermal power of 3.2 W, and the carbon monoxide concentration of the reformat was reduced from 0.3 vol.% to almost 0 ppm at a reaction temperature of 220 °C by the preferential oxidation reactor, which had a size of only 0.57 cm³. The fuel cell performance with reformat hydrogen was comparable to operation with pure hydrogen and degradation of the fuel cell performance was not observed for a duration of 20 h.

Yoshida *et al.* [44] designed an integrated methanol fuel processor from silicon and Pyrex glass substrates for a power equivalent of 10 W. It comprised steam reforming, evaporation and combustion functional layers (Figure 24.3). A commercial Cu/ZnO catalyst served for reforming, and the Pt/TiO₂ combustion catalyst was prepared by a sol–gel method. A high power density of 2.1 W cm⁻³ was determined for the device.

Little information is available on the status of fuel processor development in industry. A silicon wafer methanol reformer was developed by Casio's research division [49]. The catalyst achieved 98% methanol conversion and supplied a

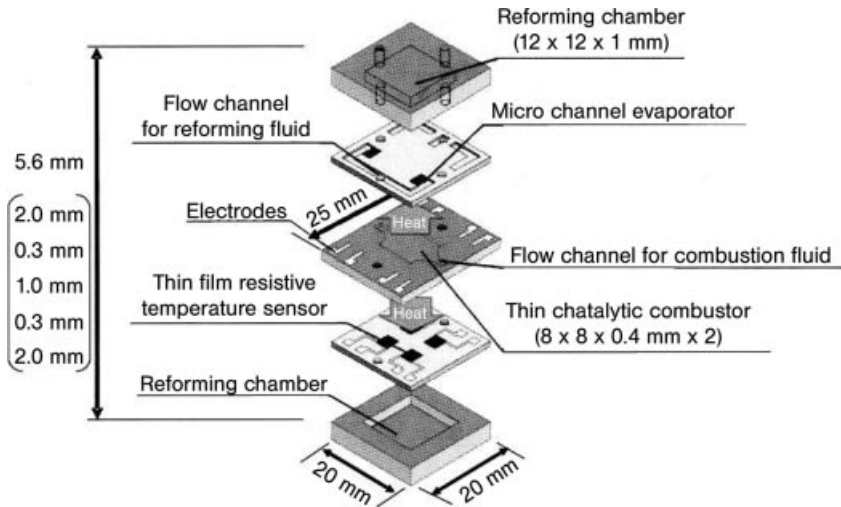


Figure 24.3 Small-scale methanol reformer–evaporator–burner system with 4 W electrical power equivalent [44].

hand-held computer with energy for 20 h. Later, Terazaki *et al.* at Casio [50] developed a fuel processor made of 13 glass plates comprising evaporators, a steam reformer, a hydrogen off-gas burner and CO clean-up functionalities (Figure 24.4). The device was insulated by vacuum packaging and radiation losses were minimized by a thin Au layer. Sealing was realized by anodic bonding. The fuel processor was tested in connection with a miniaturized fuel cell [51]. It achieved 98% methanol conversion. About 2.5 W of electrical energy was produced. A similar methanol reformer with integrated heating functionalities was presented later by Kawamura *et al.* at Casio [52], which was developed in cooperation with the University of Japan. Similarly to the device developed by Kim and coworkers, described above, the reformer carried only one single meandering channel, which was 600 μm wide, 400 μm deep and 333 mm long. The Cu/ZnO catalyst required reduction under hydrogen. Full methanol conversion could be achieved at 250 $^{\circ}\text{C}$ and the thermal power equivalent of the hydrogen product was in the region of 3.3 W. Subsequently a complete fuel processor was developed [53], containing an anode off-gas burner, which supplied the methanol reformer with energy. Palladium-based catalyst was used for reforming. The preferential oxidation reactor was operated between 110 and 130 $^{\circ}\text{C}$. The fuel processor had a volume of 19 cm^3 and a weight of 30 g, including vacuum layer insulation and radiation shields, which reduced the heat losses of the system to 1.2 W. The electrical power consumption was in the region of 70 mW. The fuel processor was combined with a fuel cell and balance-of-plant as shown in Figure 24.4. The system was operated at the Fuel Cell Seminar 2006 for demonstration purposes.

Kundu *et al.* at Samsung [54] developed a microreactor for methanol steam reforming in the power range 5–10 W. The microreactor was 30 mm wide and long and comprised evaporation and steam reforming zones. Parallel and serpentine channels for steam reforming were tested alternatively; the serpentine arrangement

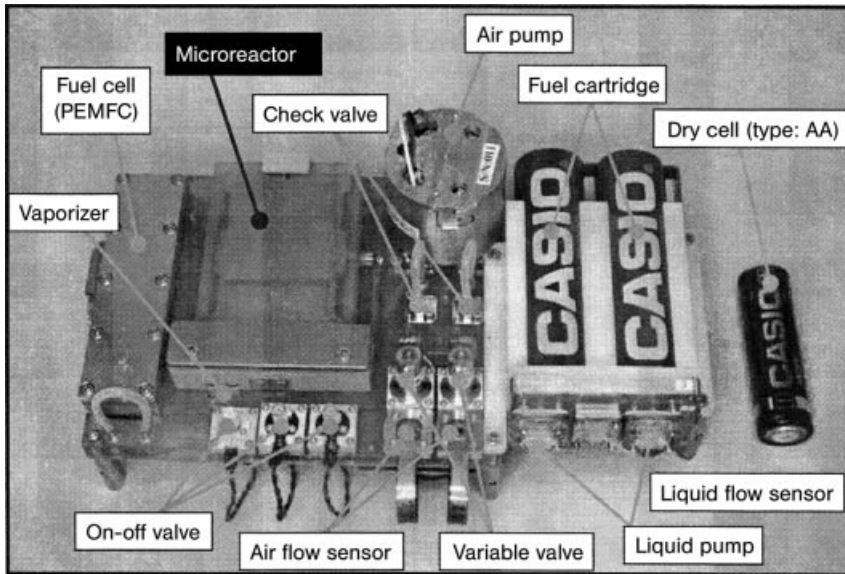


Figure 24.4 2.5 W methanol fuel processor–fuel cell system developed by Casio [53].

showed superior results [54]. A 140 mg amount of commercial Cu/ZnO catalyst from Johnson-Matthey was introduced into the channels and kept in the system by filters. A methanol–water mixture was fed into the reactor at $0.01\text{--}0.02\text{ mL min}^{-1}$ at a S/C ratio of 1.2, which corresponded to a gas hourly space velocity between 6000 and $13\,000\text{ h}^{-1}$. The catalyst was activated by the water–methanol mixture itself. It required about 30 min to achieve maximum activity by these means. The reformat contained 75 vol.% hydrogen, 24 vol.% carbon dioxide and 1.5 vol.% carbon monoxide. Up to 90% methanol conversion could be achieved at a reaction temperature of $260\text{ }^{\circ}\text{C}$. The system suffered from catalyst durability issues owing to sintering of the copper oxide particles [8].

Motorola cooperated with Engelhard and the University of Michigan to develop a microstructured steam reformer in a project funded by the US Department of Commerce’s Technology Administration [55]. The integrated fuel processor–fuel cell system consisted of an evaporator, a combustor, a reformer, heat exchangers, insulation layers and the fuel cell. Ceramic technology was used. The device had a maximum power output of 1 W [56].

Other microscale methanol steam reformers were developed, either heated by electricity [57] or coupled with a catalytic burner [58].

24.4.2.2 Alcohol Steam Reforming in Microstructured Plate Heat Exchangers

One critical issue especially related to methanol steam reforming is the narrow operating temperature window required for the reactors, which is related to the catalyst technology applied. Both reactor design and reactor material may help to achieve this goal. Highly heat conductive reactor material such as aluminum or

copper assists the heat distribution over the length axis [4]. Components and systems ordered by their increasing power equivalent are presented below.

A combined evaporator and methanol reformer was developed by Park *et al.* [5] to power a 5 W fuel cell. The device was heated by electrical heating cartridges. Prior to coating the channels with a commercial CuO/ZnO/Al₂O₃ catalyst (Synetix 33-5 from ICI), an alumina sol was coated on the channel surface as an interface. The catalyst was reduced in 10% hydrogen in nitrogen at 280 °C prior to exposing it to the reaction mixture. At a reaction temperature of 260 °C, 90% methanol conversion was achieved and the carbon monoxide concentration in the reformat was lower than 2 vol.%. Later, Park *et al.* [59] developed a combined afterburner–methanol reformer with an electric power equivalent of 28 W, which was sealed by brazing. Methanol conversion of 99% could be achieved at a reaction temperature of 240 °C.

Reuse *et al.* [16] combined endothermic methanol steam reforming with exothermic methanol combustion in a plate heat exchanger reactor, which was composed of a stack of 40 foils (Figure 24.5). Each foil carried 34 S-shaped channels. Cu/ZnO catalyst from Süd-Chemie (G-66MR) was coated into the channel system for the steam reforming reaction. Cobalt oxide catalyst served for the combustion reaction. The reactor was operated in co-current mode. The steam reformer was operated at a S/C ratio of 1.2. At reaction temperatures between 250 and 260 °C, more than 95% conversion and more than 95% carbon dioxide selectivity were achieved.

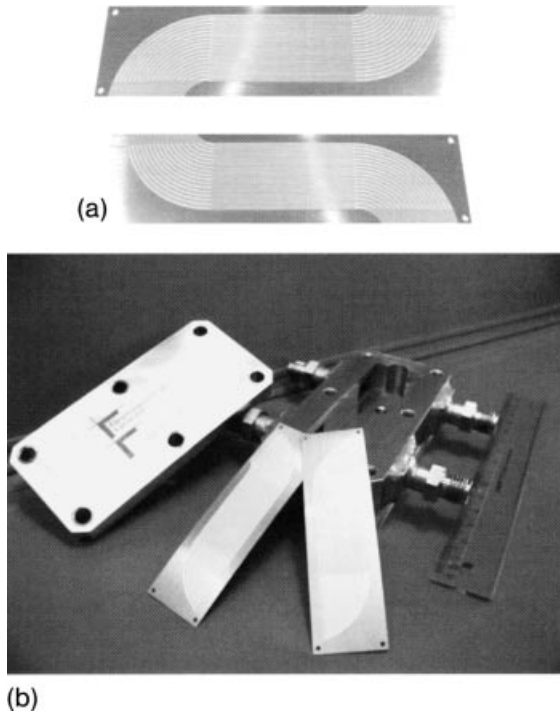


Figure 24.5 Integrated reformer–combustor for methanol steam reforming [16].

Men *et al.* reported the operation of a small-scale bread-board methanol fuel processor composed of electrically heated reactors [15]. A methanol steam reformer, two-stage preferential oxidation reactors and a catalytic afterburner were switched in series. A fuel cell equipped with a reformate-tolerant membrane, which had a 20 W nominal power output, was connected to the fuel processor and operated for about 100 h.

Palo *et al.* [60] presented the concept of an integrated fuel processor for portable military applications with 15 W power output. System specifications were a weight of less than 1 kg and a volume of less than 100 cm³, which translates to a targeted power density of more than 0.15 kW dm⁻³. A methanol–air mixture was vaporized and superheated and then combusted in a separate burner, which fed the methanol steam reforming reaction with energy. Light-off of the combustion gases occurred at 70 °C [61]. The hot combustion gases were used to supply the fuel preheater–evaporator of the combustor and the fuel preheater–evaporator of the reformer with energy. Full conversion was achieved in the steam reformer, when tested separately. At a reaction temperature of 350 °C, a contact time of 140 ms and a S/C ratio of 1.8, full conversion of the methanol was achieved. The carbon monoxide concentration of 0.8 vol.% was low owing to the catalyst technology applied. The fuel processor efficiency was calculated to be 45%, which is a competitive value for a small-scale device.

Schouten *et al.* [62] designed a methanol fuel processor for an electrical power output of 100 W. In contrast to the concepts presented above, the fuel processor was composed of three separate devices. The methanol–water mixture was evaporated by the hot off-gases of the catalytic burner and fed to the integrated steam reformer–burner reactor. Cu/ZnO catalyst supported by alumina was applied for the steam reforming reaction. The reformate was then fed to a reactor for CO removal, not shown here. The residual hydrogen contained in the anode off-gas was combusted in the burner over platinum/alumina catalyst. Start-up was effected by feeding methanol directly to the burner. The integrated reformer–burner reactor fabricated at IMM is shown in Figure 24.6.

A complete methanol fuel processor for the electrical power equivalent range 60–170 W was reported by Holladay *et al.* [63]. The device, which is shown in Figure 24.7, had a volume of less than 30 cm³, a mass lower than 200 g and a

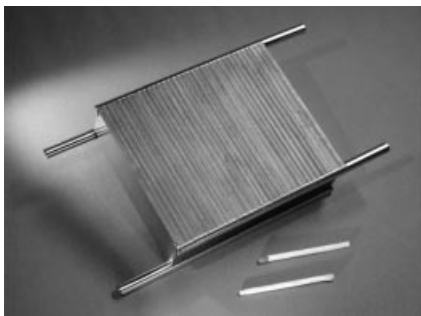


Figure 24.6 Integrated methanol reformer–burner for a 100 W fuel processor. Source: IMM.

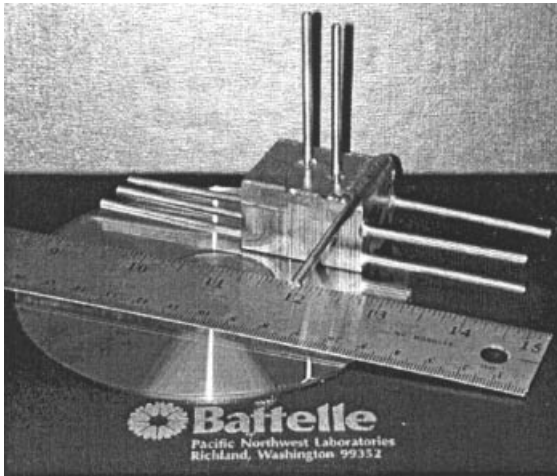


Figure 24.7 Integrated methanol fuel processor with 100 W power equivalent [63].

thermal efficiency of more than 80%. The reformer was operated at a reaction temperature of 350 °C.

Catalysts from Süd-Chemie were applied for methanol steam reforming by Cremers *et al.* [64]. Because the catalyst activity was too low compared with the design criterion, a fixed-bed microreactor was built with integrated heat-exchange capabilities. The reactor contained 60 micro fixed-bed passages taking up 15.9 g of catalyst and 62 heating passages and was designed to supply a fuel cell of 500 W electrical power. Heating oil, which was preheated by an external burner, served as the heating fluid in this case. More than 90% conversion was achieved at the design point at a reaction temperature of 250 °C. During the first 4 h of operation, 15% of the initial activity of the catalyst was lost, but then the activity remained stable for another 4 h. The catalyst could be regenerated by oxidation and subsequent reduction. The microstructured reactor had a start-up time demand of 18 s after being heated to the operating temperature, which was considered as an improvement on conventional fixed-bed technology. A turn-down ratio of 1:5 could be realized without significant changes in product composition.

An integrated heat exchanger–reactor for methanol steam reforming was developed by Hermann *et al.* [65] at GM/OPEL for a 50 kW methanol fuel processor. The system specifications included a volumetric power density of more than 5 kW dm⁻³, a gravimetric power density of more than 2.5 kW kg⁻¹ and a transient response to load changes from 10 to 90% in milliseconds.

First a 5 kW combined methanol steam reformer–catalytic combustor was built. The reactor was composed of modules of three types of plates forming a stack. Instead of microchannels, fins served as mechanical support and improved heat transfer. A total of 225 plates were incorporated into the reactor. The reactor was designed for a maximum operating pressure of 4 bar and 350 °C maximum reaction temperature. The experimental results presented were determined at a partial load of the device [1–2 kW for the lower heating value (LHV) of the hydrogen produced]. At a S/C ratio of

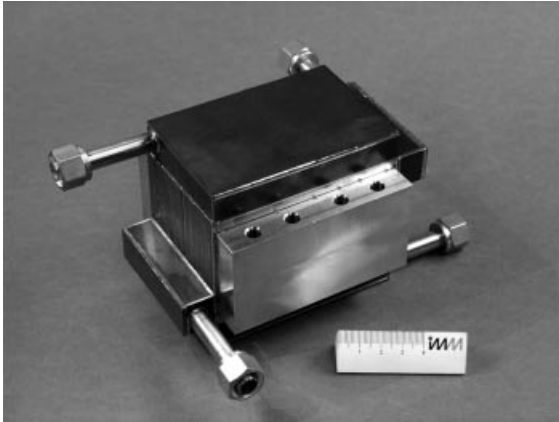


Figure 24.8 Combined ethanol steam reformer–anode off-gas burner with 250 W power equivalent. Source: IMM.

1.5 and a pressure of 3 bar, full conversion of the methanol was achieved and $0.9 \text{ m}^{-3} \text{ h}^{-1}$ of hydrogen was produced. The hydrogen production rate was regarded as competitive with literature data.

Shah and Besser presented results from their development work targeted at a 20 W_{el} methanol fuel processor–fuel cell system [66]. The layout of the system consisted of a methanol steam reformer, preferential oxidation, a catalytic afterburner and an evaporator. Vacuum packaging was the insulation strategy for the device, which is in line with other small-scale systems described above. A micro fixed-bed steam reformer coupled to a preferential oxidation reactor was then developed by the same group with a theoretical power output of 0.65 W.

Figure 24.8 shows a microstructured ethanol steam reformer combined with a catalytic afterburner by plate heat exchanger technology. A Co/ZnO catalyst coating was applied for ethanol steam reforming at temperatures in the region of $600 \text{ }^\circ\text{C}$, and a noble metal catalyst coated on the second flow path of the heat exchanger served for the catalytic hydrogen combustion reaction. Both reactions were operated in a co-current flow arrangement. Electric heating cartridges served for start-up. The reactor, which had a power equivalent of about 250 W, showed up to 90% ethanol conversion at a S/C ratio of 3.0.

24.4.2.3 Hydrocarbon Steam Reforming in Microstructured Plate Heat Exchangers

Hydrocarbon steam reforming generally requires higher operating temperatures and therefore construction material such as stainless steel and nickel-based alloys are the preferred choice. Microstructured steam reforming reactors and fuel processors based on steam reforming technology will be discussed below in order of increasing electrical power equivalent.

A combined methane steam reformer–catalytic hydrogen burner was developed by Ryi *et al.* [67] for a thermal power equivalent of 67 W. Rh/Mg/Al₂O₃ was applied as the steam reforming catalyst and Pt/Sn/Al₂O₃ served as the hydrogen combustion

catalyst. The reactor was sealed by brazing and operated as a co-current heat exchanger at a reformer temperature of 700 °C and a S/C ratio of 3; 95% methane conversion was achieved in the reactor. Homogeneous hydrogen combustion upstream of the reactor was avoided by mixing the combustion gases within the reactor, utilizing the flame-arresting properties of microchannels. Subsequently, Ryi *et al.* [68] added microstructured heat exchangers for preheating the air fed to the combustor and evaporating the water and preheating the steam and methane feed of the reformer part of the reactor. These modifications allowed the thermal power output of the hydrogen present in the reformat to be increased to 220 W. However, the thermal power equivalent of the hydrogen feed, which was required to keep the reactor in operation, was still higher at about 310 W and therefore the system would not be able to run in a self-sustaining manner in the state presented by Ryi *et al.*. This emphasizes the need for efficient insulation strategies.

Because of the existing distribution grid for LPG and its widespread application in caravans and trailers, it is an attractive fuel for the electrical power supply of such vehicles. The German company Truma, Europe's largest manufacturer of heating systems for caravans and trailers, has developed a fuel processor–fuel cell system together with IMM (Institut für Mikrotechnik Mainz). The utilization of microstructured plate heat exchanger technology made a compact design of the fuel processor possible. The proprietary fully integrated system is shown in Figure 24.9.

Fitzgerald *et al.* [69] presented a microstructured isooctane heat-exchanger steam reformer heated by combustion gas with a total volume of 30 cm³, which produced enough hydrogen for a 0.5 kW PEM fuel cell. At ambient pressure, a temperature of 650 °C, a residence time of 2.3 ms and a high S/C ratio of 6, up to 95% conversion were achieved at 90% hydrogen selectivity. Decreasing the S/C ratio at constant residence time decreased the isooctane conversion, but not the hydrogen selectivity.

Cremers *et al.* [70] and Pfeifer *et al.* [71] presented a reactor combining endothermic methane steam reforming with the exothermic combustion of hydrogen stemming from the fuel cell anode off-gas (Figure 24.10). NiCroFer 3220H was



Figure 24.9 The 250 W_{e1} fuel cell–fuel processor system VEGA developed by cooperation between Truma and IMM. Photograph courtesy of TRUMA.

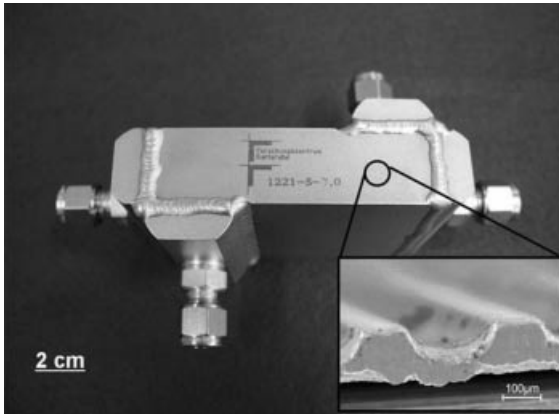


Figure 24.10 Combined methane reformer–combustor designed for 500 W electrical power output [72].

applied as the reactor material. The reactor was designed to power a fuel cell with 500 W electrical power output. The steam reforming side of the reactor was operated at an S/C ratio of 3 and temperatures exceeding 750°C . A nickel spinel catalyst developed earlier [25] was applied for the steam reforming reaction.

Figure 24.11 shows a microstructured coupled diesel steam reformer/catalytic afterburner developed by Kolb *et al.* [27], which was operated at temperatures exceeding 800°C . The reactor, which was coated with catalyst from Johnson-Matthey Fuel Cells, had separate inlets for anode off-gas and for air supply to the burner. Full conversion of the diesel fuel was achieved for a total operation time of 40 h with this reactor, which had a power equivalent of 2 kW thermal energy of the hydrogen produced.

Whyatt *et al.* [73] developed a combined system of independent evaporators, heat exchangers and reformers for isooctane steam reforming. Four integrated

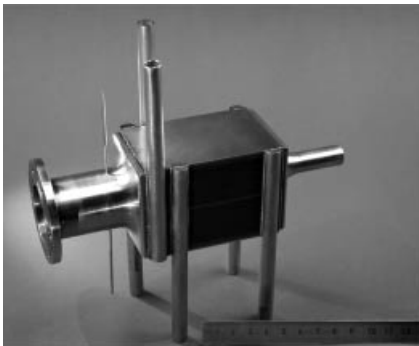


Figure 24.11 Combined diesel steam reformer–anode off-gas burner designed for 2000 W thermal power output of the hydrogen product [27].

reformers—cross-flow heat exchangers switched in series were fed by four independent water vaporizers which were supplied with energy from anode off-gas combustion performed in an independent burner. The combustion gases supplied the cross-flow heat exchanger—reformers and the water vaporizer units with energy. The machining of microstructured components was done by photochemical etching and sealing by diffusion bonding. The reformers achieved up to 98.6% conversion at 750 °C reaction temperature a S/C ratio of 3 and a product composition of 70.6% H₂, 14.6% CO, 13.7% CO₂ and 0.9% CH₄. Sufficient reformat was generated to feed a 13.7 kW PEM fuel cell.

To decrease the start-up time and the electrical power demand of the air supply system, Whyatt *et al.* [74] redesigned completely the system described above. The objective was to meet the US Department of Energy ambient temperature start-up time demand targets, which amounted to <1 min by 2005 and <30 s by 2010.

Figure 24.12 shows the prototype system. The energy for start-up and continuous operation was provided by homogeneous fuel combustion rather than catalytic combustion to decrease the time demand of start-up. The power was supplied to the reformer and the evaporator, which was placed behind the reformer in a duct. After mixing the fuel with the combustion air, the combustion gases were passed through this duct and heated the devices by a cross-flow arrangement. The steam reformer was designed to operate at an outlet temperature of 650 °C and a S/C ratio of 3. It was composed of reforming reaction channels of small height, which were as wide as the whole device. The combustion gases passed around these single channels. The target start-up time demand of 60 s could be achieved with this device; however, CO clean-up reactors were not incorporated into this system.

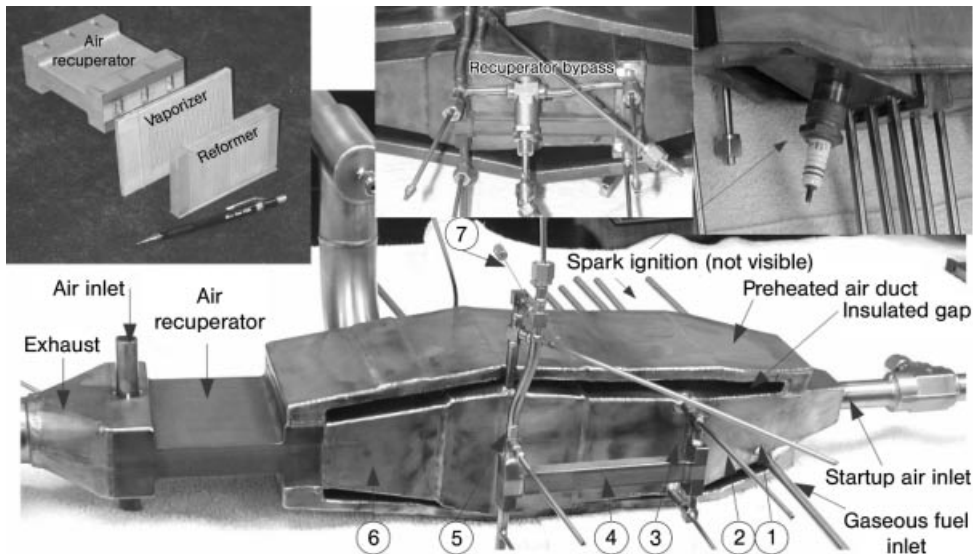


Figure 24.12 Prototype rapid start-up octane steam reformer.

24.5

Conclusion

The last system described above is an impressive demonstration of how the application of microtechnology along with novel design concepts bears great potential for technology advances in the field of future distributed and sustainable energy generation. However, not only the technical feasibility needs to be proven but also cost issues and production techniques addressed adequately to introduce the novel concepts onto their future marketplaces.

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