

Part V
Fuel Processing

23

Application and Operation of Microreactors for Fuel Conversion

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The production of hydrogen is a well-established process in industry [1, 2]. However, industrial-scale hydrogen production does not meet the requirements of on-site hydrogen production for small stationary and portable applications using fuel cells. There is a need for small-scale fuel processors that are compact, light weight, highly dynamic and achieve a high efficiency by combining hydrogen production, heat transfer and gas clean-up. The three major approaches for the on-site conversion of various hydrocarbon fuels to hydrogen are steam reforming, catalytic partial oxidation and oxidative steam reforming, the latter often operated as catalytic autothermal reforming. For the production of hydrogen for fuel cells, microchannel reactors have been extensively studied.

23.1

Applications of Fuel Conversion

23.1.1

Power Range

For different applications, the power needed from the fuel cells varies from less than 1 W for small applications such as sensors and mobile phones to over 100 kW for automobiles and stationary applications. With microreactors, hydrogen flows capable of producing power in the range from 0.01 W to 50 kW have been achieved [3]. Numerous applications of fuel conversion in microstructured devices have dealt with the combination with fuel cells to yield a power supply for microelectric devices and microsensors and as an alternative to a conventional battery. Thus, the resulting power output of the fuel cell has been in the low watts area, from 0.01 W to a few watts, as in the integrated methanol fuel processors built by companies such as Casio and Motorola [4]. PNNL has developed various low-power portable fuel processor systems, from lower than 1 W [5–7] to systems that could provide 15 W, such as a portable and lightweight system for a soldier portable fuel cell [8, 9]. In the range of



Figure 23.1 Prototype of a 5 kW reformer with integrated flue gas heating for gasoline steam reforming developed at the Forschungszentrum Karlsruhe, Germany (by courtesy of Forschungszentrum Karlsruhe).

systems generating 1–10 W, the MIT suspended tube reactor (1.6 W) was a novelty, as the thermal cracking of ammonia was applied to produce hydrogen [10]. Another reactor in the power range of 1–10 W has been developed by Lehigh University [11, 12] for portable electronic devices such as laptop computers and cell phones. This reactor included a membrane for the water gas shift reaction and hydrogen separation.

For automobile or small stationary applications, hydrogen production creating higher power outputs from several hundred watts to more than 100 kW is needed. A scalable reaction system with a proposed maximum output of $10 \text{ m}^3 \text{ s}^{-1}$ of hydrogen was presented by Velocys [13]. The projected dimensions of the reactor were in the region of several meters and it was designed for small stationary applications and could also have been used for synthesis gas production on offshore platforms. A methanol steam reforming system for 5 kW has been fabricated by GM/Opel [14]; the final target was a system for a 50 kW car engine/traction system. The Forschungszentrum Karlsruhe also presented a 5 kW microchannel steam reformer for gasoline (Figure 23.1) and additional micro-heat exchangers including evaporation for energy recovery for application in auxiliary power unit (APU) systems [15]. Ballard Power Systems [16] presented a monolithic integrated methanol fuel processor capable of producing 20 L min^{-1} of hydrogen. Truma and IMM more recently presented a complete system for 250 W of electricity for caravanning based on LPG reforming [17].

23.1.2

Demands from Applications

Depending on the application type, there are several determining factors that influence the design of a fuel processor, such as maximum power output, response

time demand to load changes, small volume, low weight and, as a crucial factor for mass production, low fabrication costs. The last is the most serious for automotive applications, whereas for applications on yachts, caravans or even for stationary applications (co-generation of electricity in houses), the fabrication costs may be higher. One of the first projects demonstrating low-cost fabrication of the microstructure by embossing was Micromotiv [15]–Forschungszentrum Karlsruhe and Gräbener Pressensysteme were therefore funded by the Federal Ministry for Education and Research in Germany. The response time and the volume and weight often influence the fuel conversion route. In general, routes of utilizing oxygen for hydrogen production possess faster reaction kinetics and could result in faster dynamics or a lower reactor volume. However, higher efficiencies can be obtained by steam reforming (see Section 24.2) and for this route microstructured reactors are superior to conventional reactors due to their heat transfer capabilities.

23.1.3

Fuels

The availability and properties of the fuel could also be design criteria for the fuel processing system since there can be different regulations for handling in different areas of the world or the regulations could depend on the application. Propane, methane, methanol, ethanol and higher hydrocarbons such as gasoline and diesel have been used as fuels. Methanol is a fuel that is widely used: it is cheap, easy to produce from natural gas and has the highest hydrogen to carbon ratio. Its steam reforming also takes place at relatively low temperatures of about 250 °C. Due to the toxicity of methanol, methane and LPG, diesel and gasoline are widely used alternatives, although the reforming temperatures are in the region of 700 °C. In recent years, ethanol made from renewable materials has become more attractive.

23.2

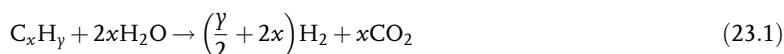
Operation of Microreactors for Fuel Conversion

23.2.1

Routes for Fuel Conversion

The main part of the fuel processing system is the reformer that produces the hydrogen needed for the fuel cells, no matter what power is needed. Generally, there are three routes for the fuel conversion in microreactors: steam reforming, catalytic partial oxidation and oxidative steam reforming.

The first route is steam reforming (SR), an endothermic reaction where the fuel reacts with steam over a heterogeneous catalyst at temperatures depending on the hydrocarbon used:

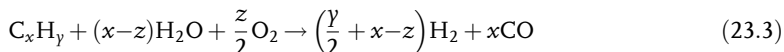


Steam reforming has the highest hydrogen yield, but due to the endothermic nature of the reaction, special care to guarantee sufficient heat transfer is needed.

The catalytic partial oxidation (CPO) of hydrocarbons is exothermic, so no external heat source is required. Disadvantages include high temperatures, difficult control and challenges to the construction materials. Additionally, this route has the lowest hydrogen yield of the three reforming reactions:



Alternatively, oxidative steam (OSR) or catalytic autothermal reforming (CAR) can be applied in microreactors. This is slightly different to autothermal reforming (ATR), widely used in industry to produce syngas, since it is fully catalytic. Oxygen is introduced into the fuel–steam feed in the same reactor microstructure. Some portion of the fuel undergoes oxidation, generating heat to drive the steam reforming of the remaining fuel. Oxidative steam reforming has an intermediate hydrogen yield and the heat of reaction may also be adjusted for heat losses to obtain the autothermal mode by varying the steam to carbon ratio (H_2O/C) and the oxygen to carbon ratio (O/C):



Due to the excellent heat transfer capabilities of microreactors, most studies utilizing them for hydrogen production have dealt with the steam reforming of various hydrocarbons, including gaseous and liquid fuels such as methane, methanol, ethanol, natural gas, gasoline and diesel.

The operating temperature of the reforming process is determined more by the fuel used rather than by the conversion route. The material and construction of the equipment used, however, are dependent on the reaction temperature and the reactant composition. The reforming of methanol takes place at temperatures as low as 250–300 °C, ethanol at about 600–650 °C and methane steam reforming needs temperatures up to 900 °C; higher hydrocarbons such as gasoline and diesel can be reformed at 700–750 °C. During steam reforming, a reducing atmosphere is always present, whereas in conversion routes applying oxygen, both reducing and oxidative atmospheres can vary. Another aspect is coke formation, which is favored at high temperatures with low steam concentration. This might be extremely demanding for the microreactor design due to the high volumetric surface area increasing the possibility of coke formation and the low channel diameter leading to rapid blocking. Also, the small wall thickness between microchannels could lead to rapid breakdown of the system due to corrosion. Moreover, special care has to be taken with appropriate heat generation and dissipation in the reformer to avoid catalyst deactivation and to yield a high thermal efficiency. Thermal efficiency based on the lower heating value (LHV) can be defined according to Equation 23.4 based on the amounts and combustion energies (ΔH) of hydrogen produced, of fuels reformed, of fuel combusted and of byproducts (methane, CO) combusted or oxidized (in purification steps or sepa-

rated), and also of the fuel cell anode off-gas contents, which could be/have been burned in the whole fuel processor.

$$\eta(\text{LHV}) = \frac{n(\text{H}_2) \times \Delta H(\text{H}_2)}{n(\text{fuel}_{\text{reformed}}) \times \Delta H(\text{fuel}_{\text{reformed}}) + n(\text{fuel}_{\text{burned}}) \times \Delta H(\text{fuel}_{\text{burned}}) + \sum_{\substack{i=\text{byproducts,} \\ \text{off-gas (fuel cell)}}} n_i \Delta H_i} \quad (23.4)$$

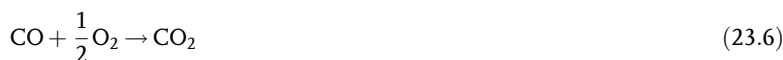
where η = efficiency, n = amount (moles), ΔH = heat of combustion (J mol^{-1}) and byproducts, off-gas (fuel cell) = burnable byproducts in the off-gas of the fuel cell if not combusted.

The superiority of microreactors for reduced deactivation due to less thermal load on the catalyst has been proven several times (e.g. [47]), even benchmarked to a fixed bed [18] or to a foam [19]. However, one should be careful when operating the catalyst in a microreactor at its kinetic limit. The deactivation behavior of a specific catalyst could be more visible than in a conventional fixed bed or even coated foam. The mass of thin wall-coated catalysts operated free from mass transfer limitations could be much less for reaching 100% conversion. However, there is no backup catalyst mass. Hence additional catalyst mass has to be considered for process layout [20]. Also, leaks and the parallelizing of microstructures (concerning their feed distribution and heat distribution) are a challenge that can influence the catalyst stability and thus the operation of a microreactor [40].

23.2.2

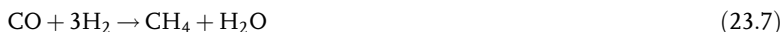
Gas Clean-up

The output of the reformer is typically fed to PEM fuel cells with operation temperatures of about 80°C , hence the PEM feed needs special attention. The carbon monoxide content must be kept below ~ 50 ppm so as not to adsorb on the PEM catalyst and lower the fuel cell efficiency. Therefore, a gas clean-up is needed at the exit of the fuel processor. Depending on the conversion route and the fuel – or in most cases the conversion temperature, which determines the water gas shift equilibrium between CO_2 and CO – a complete fuel cell system needs a gas clean-up like a water gas shift reactor (reaction: Equation 23.5) or a preferential oxidation reactor, i.e. selective oxidation of CO in the presence of H_2 (reaction: Equation 23.6) [21, 22].



Another purification method is the selective methanation of carbon monoxide where no additional air is required; however, the yield of hydrogen is decreased as three molecules of hydrogen are consumed per molecule of CO . Furthermore, it is

possible for CO₂ to react with hydrogen as the temperature increases, so careful temperature control is needed [23].



Methanation and preferential oxidation serve in both cases for obtaining ultra-low CO contents, whereas the water gas shift reaction is mainly applied for conversion routes applying oxygen or for high-temperature processes where a water gas shift at temperatures around 300–400 °C can lead to a considerable increase in hydrogen yield.

Membrane separation is also used to separate hydrogen selectively from the rest of the reformat gases. Palladium membranes provide excellent permeation selectivity to hydrogen. A disadvantage is the low long-term stability of thin membranes in pressurized systems – the lowering of the amount of Pd being a prerequisite for low-cost clean-up.

A microscale preferential oxidation reactor (PrOx) was developed by researchers at the Stevens Institute of Technology [24] and also at the TU Eindhoven [22] to decrease the carbon monoxide level in the reformat stream to below 100 ppm.

A palladium-based micromembrane was reported by Karnik *et al.*, [12, 25]. The novelty of the structure proposed was that it integrated hydrogen separation and water gas shift reaction capabilities in the same structure. The membrane was a composite of four layers: copper, aluminum, spin-on-glass (SOG) and palladium. The copper, aluminum and SOG layers served as a structural support and the copper was intended to catalyze the water gas shift reaction to increase the hydrogen yield. The membrane was tested for hydrogen permeation with a hydrogen–nitrogen mixture (80% N₂); it was capable of withstanding a pressure gradient of only 10 psi without breaking, so it needed further improvement for application in a reforming system.

When hydrocarbon distillate fuels such as gasoline, diesel or jet fuels are used, it is also necessary to include a desulfurization unit in the fuel processor system. Hence Shaaban and Campbell [26] patented a system with an effective sulfur removal process that was able to operate with various hydrocarbons. It consisted of a reformer with membrane purifier and water recovery, a catalytic combustor for fuel to provide the energy for the reforming process and the desulfurization unit.

23.2.3

Heat Generation

Heat generation for the endothermic steam reforming process is accomplished in several ways. The most common way is the catalytic or homogeneous combustion of fuel cell off-gas containing ~20% hydrogen with the addition of the initial fuel to deliver the heat required for stationary operation. The heat required, including steam generation, is in the region of one-third of the chemical energy of the fuel. Catalytic combustion is mainly carried out in microchannels adjacent to the reforming microchannels and is superior to homogeneous combustion, implying high compression and heat losses. These losses result from the addition of an inert gas when trying to adjust flame temperatures to the temperature levels of reforming. An

alternative of applying an intermediate heating fluid implies even higher heat losses. With catalytic combustion, the heat flux can be easily adapted to the reforming demand by sequential dosage of fuel to air [27]. The reforming gas itself is also often preheated by counter-current flow with reformat in front of the reactor to guarantee optimized reaction conditions. Initial heating up of the whole system is often achieved by the homogeneous combustion of fuel. Most fuels do not ignite catalytically at room temperature.

23.2.4

Development Stages

To design an efficient and compact fuel processor system, one must pass through several developmental stages, which differ in terms of the operation of the microreactor. So-called test reactors are normally used for catalyst testing and include the option to change the catalyst. Often, the catalyst foils are stacked and clamped [28] or a simple one-foil system can be laser welded [29]. The heating is done electrically in these systems; there are seldom two separate fluid flows – reactant flow and heating/cooling fluid – as leak tightness between the microstructured elements is a problem. However, even if there is no integrated second fluid, there is still an advantage of the microstructure for the operation of the reaction since heat transfer from or to the catalyst is still high. The housings of these test reactors are relatively large compared with the microstructure inside. From the concept of these test reactors, it is clear that these cannot be operated either in a real dynamic mode or in a way to produce power output, since a large mass must be heated and heat losses to the environment dominate the overall efficiency. Before a fully engineered prototype is built, an intermediate step can often be used experimentally, which could also be used to verify modeling of the reactor behavior. It could be called a feasibility reactor, which allows different modes of cooling/heating to be obtained by the counter- or co-current flow of reactants and heating/cooling fluid or variations in temperature profile along the reactor by electrical heating (e.g. [30]). Subsequently, a prototype, i.e. a fully engineered reactor capable of dealing with reaction heat by cooling (for CPO) or heat supply by integrated fuel (e.g. fuel cell anode off-gas) burning (for SR), can be integrated into peripheral equipment and be further optimized together with the equipment to obtain an integrated plant concept.

23.2.5

Integrated Plant Concepts

An integrated plant concept for the conversion of fuel to hydrogen for a PEM fuel cell means that several steps are incorporated in the system. These steps are (1) vaporization and/or preheating of fuel and water/air, (2) reforming reaction, (3) gas-clean up and (4) cooling of the reformat gas before feeding the PEM fuel cell. Heat at an appropriate temperature level for the different steps must also be produced initially or during hydrogen generation. Hence the heat flow in the process units must be tightly controlled according to the load changes.

23.2.6

Examples of Different Approaches and Integration Levels

This section gives an overview of several studies reported in the literature at different levels of integration and their approaches. The list is not intended to cover fully all work done so far in this research area.

A prototype for a methanol reforming silicon reactor was designed at Lehigh University [11, 12, 31]. Their microreaction system, made of silicon wafers, consisted of four main components: a mixer/vaporizer of methanol and water, a catalytic steam reformer with a copper catalyst, the combined water gas shift reactor–membrane (as mentioned before) and integrated resistive heaters, sensors and control electronics. The reformer was tested with a stainless-steel housing. The authors reported a conversion of 90% for methanol, which corresponds to a power output of 15 W.

Another prototype of an integrated reactor was set up by Reuse *et al.* [28]. In the laboratory reactor, foils for the steam reforming of methanol and the combustion of methanol for heat generation were stacked in an alternating pattern. A special foil in the middle of the reactor allowed for temperature measurements along the channel. A commercial Cu/Zn catalyst from Süd-Chemie was used (G-66MR). First the kinetics of both reactions were studied independently in an isothermal microstructured reactor and subsequently the reactions were coupled in the developed two-passage reactor under co-current conditions (Figure 23.2). The axial temperature gradients never exceeded 2.5 K. Therefore, the kinetic models could be used to predict the steady-state and dynamic reactor behavior. Based on this prototype reactor, an integrated system with a fixed-bed reactor was designed [32, 33].

The most highly integrated methanol reforming system was designed for use in sub-watt power supplies (0.01–0.1 W) by Holladay's group at Batelle [5, 6]. The complete system incorporated two vaporizers/preheaters, a heat exchanger, a



Figure 23.2 Prototype of an integrated reformer and combustor for methanol steam reforming (built at the Forschungszentrum Karlsruhe) [28].

catalytic combustor and a catalytic methanol reformer in a very small volume ($<0.25 \text{ cm}^3$). The system was built from stainless steel with conventional milling techniques.

Another sub-watt power system was also developed by researchers from Batelle [34] as an alternative to conventional battery technology. The microscale fuel processor system for liquid fuels such as methanol and butane consisted of an integrated vaporizer, steam reformer and combustor. The system generated 10–500 mW_e power output with a reactor volume of less than 5 mm^3 . The energy density of the system operated with methanol was stated to be at least an order of magnitude greater than that of lithium ion batteries.

A packed-bed microreactor system built from borosilicate glass consisting of an evaporator, a heater, reactor bed and a gas collector was reported by Giorecki *et al.* [35]. Methanol fuel was used and reformed with a commercial Cu/ZnO catalyst provided by Süd-Chemie.

Researchers at the Korean Institute of Energy Research developed a methanol fuel reformer [36]. The system included a vaporizer and reformer based on sheet architecture with etched microchannels. The microreactor consisted of a vaporizer and a reformer connected serially. The prototype generated sufficient hydrogen for a power output of 15 W.

Irving *et al.* developed a fuel processor system that could provide hydrogen without further purification for 1–5 kW power output of the PEM fuel cell [37]. The Innova-Gen fuel processor could reform fuels of multiple types including natural gas, gasoline and diesel (see Figure 23.8).

In contrast to most other appliances, the Ballard reaction system [16] was not based on metallic sheet architecture but was made with technologies from powder metallurgy such as pressing and sintering, which fix the catalyst powder and shape complex functional structures. Therefore, with that approach any sealing was omitted. They integrated all process steps that are on a similar temperature level in one monolith. Important advantages were similar start-up and dynamic control of the system, lower cost and easy replacement of the catalytic section. Hence, all steps such as vaporization, reforming or autothermal reforming and selective oxidation of carbon monoxide accompanied by the burning of hydrogen were included in the system.

A reaction system with an integrated catalytic combustor for the steam reforming of methane was built at the Forschungszentrum Karlsruhe [38]. The reactor (Figure 23.3), designed for 500 W power output, was operated autonomously without an external heat supply. Furthermore, the system was operated under static and dynamic load conditions. Start-up tests showed good performance and a stable product composition in less than 20 s after admission of methane to the system with a reaction temperature of 750–800 °C. To cope with these high temperatures, the core of the reactor was built from high-temperature-stable steel, Nicrofer 3220 HT (Krupp VDM).

A combined system composed of a methanol reformer, a preferential oxidation reactor and a fuel cell was set up by Kwon *et al.* [39]. All three components were made using silicon and MEMS technology. At a methanol feed rate of $1 \text{ cm}^3 \text{ h}^{-1}$, 100%

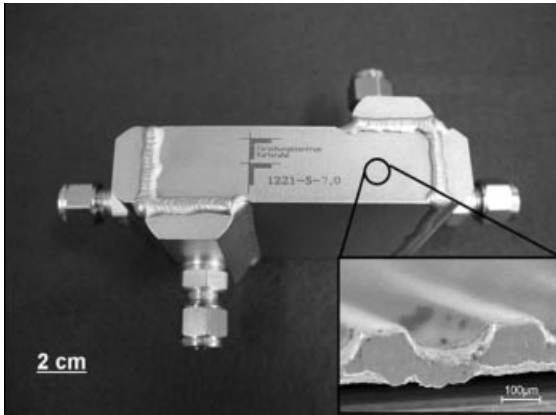


Figure 23.3 Methane steam reformer (built at the Forschungszentrum Karlsruhe) made of high-temperature steel and SEM of microstructure [38].

conversion was obtained, and with a PrOx reactor in series, CO was reduced to below the detection limit. Heating, however, was supplied electrically.

A system for application in a cell phone also based on MEMS technology was designed by Samsung [40] (Figure 23.4). Aspects such as the start-up time for the reaction temperature and the hydrogen flow, catalyst durability and volume of the total system were considered. The catalyst was introduced as small particles (50–100 μm) and a uniform packing was obtained. Maximum power output was 2.4 W, sufficient for a cell phone.

A microchannel reactor for high-temperature steam reforming of methane, isooctane and a benchmark fuel was developed by Whyatt *et al.* [41]. The main

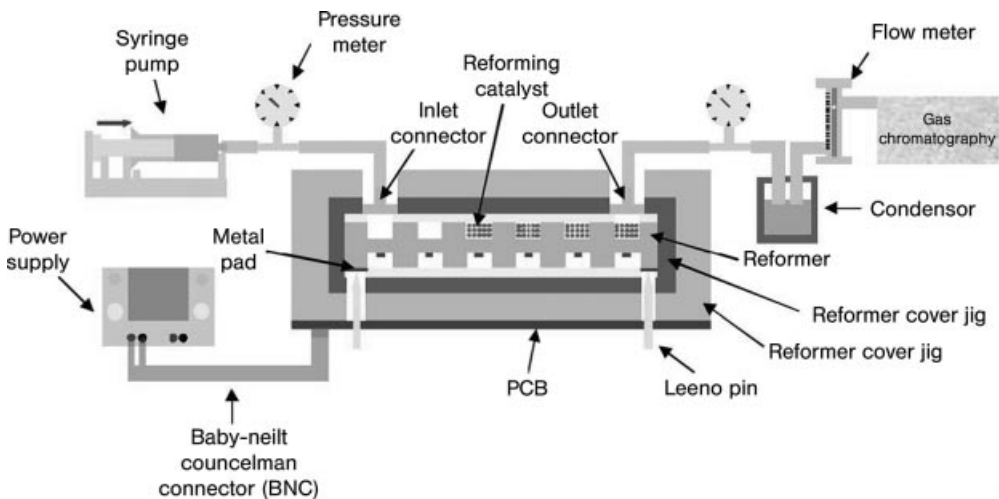


Figure 23.4 Experimental setup of MEMS-based micro-fuel processor by Samsung [40].

focus of their investigation was the fast start-up of the reaction system. The system design consisted of a low-pressure drop reactor, vaporizer and air recuperator. The microchannel reactor yielded approximately 0.5 kW_e at 650°C and was capable of producing 2 kW_e power output if operated at 850°C . The reactor was made of Inconel 625 and was of the same weight as the vaporizer (400 g), which was able to supply steam for a 2 kW_e reforming capacity. In a further progress report, the development of a thermally efficient and low capital cost system for the distributed hydrogen production from natural gas for stationary vehicle refueling was described [42]. A prototype was designed and tested at a 5 kg day^{-1} scale of hydrogen output.

The system designed by Thompson at the University of Michigan was initially also set up for on-board fuel processing. After their decision to discontinue on-board fuel processing research, the conversion of natural gas into a hydrogen-rich gas for stationary PEM fuel cells was attempted [43]. An integrated gasoline fuel processor prototype was developed, focusing on efficient thermal coupling, improved catalyst performance due to optimal reactor temperatures profiles and better cold-start and transient responses. A gas clean-up of the effluents of the autothermal process was included by means of a high- and a low-temperature water gas shift reactor and subsequently a PrOx reactor. The catalysts were supported on FeCrAlY metallic foam incorporated in the microreactors. For the use of reformulated gasoline, a high-performance desulfurizer was proposed to be included in the future. A concept for a thermally integrated natural gas fuel processor was also evaluated.

An integrated fuel processing system for different fuels for mobile and small-scale stationary power units up to a range of 5 kW_e was developed by the IMM [44]. A complete fuel processor for 5 kW (Figure 23.5) was set up for use of isooctane as fuel. It is under development for various fuels such as methanol, ethanol, LPG and gasoline. The complete fuel processor was composed of a catalytic autothermal reformer reactor, a heat exchanger for cooling the reformat downstream of the CAR,



Figure 23.5 5 kW catalytic autothermal reformer built by IMM [44].

a cross-flow cooled high-temperature water gas shift reactor (HT-WGS), a low-temperature water gas shift reactor (LT-WGS) and a PrOx reactor again cooled by a cross-flow arrangement. Additionally, a microstructured heat exchanger with a capacity of 2 kW was incorporated between the CAR and the HT-WGS reactor to cool the reformat from the exit temperature of the CAR to the desired feed temperature of the HT-WGS. As catalyst for the high- and low-temperature water gas shift reactions, a 1 wt.% Pt/CeO₂ catalyst on alumina was used. The low-temperature water gas shift reactor was not designed as a heat exchanger because of the minor heat generation by the low-temperature water gas shift reaction.

Park *et al.* developed a methanol steam reformer as a compact hydrogen supplier for small fuel cells [45]. Two designs of sheet type reactors, each comprising a fuel vaporizer, heat exchangers, a catalytic combustor and a steam reformer were built and evaluated. The two designs differed mainly in microchannel geometry and reactor assembly. One reactor contained microchannels 500 μm wide and 200 μm deep; the other reactor channels were 300 μm wide and 200 μm deep. These reactors were bonded by a brazing process. The reactors were heated electrically at the start. When the temperature reached 250 °C, methanol was combusted to supply the heat for the reactor operation, including fuel vaporization and methanol steam reforming. The second reactor produced three times more hydrogen at a similar reactor volume, yielding a power output of 59 W. The authors concluded that reactor fabrication processes such as microchannel patterning, catalyst coating and microchannel bonding can significantly affect the reactor performance.

A study of a ceramic reactor for on-site hydrogen production from propane at temperatures between 800 and 1000 °C was reported by Mitchell and Kenis [46]. They showed that the ceramic microreactor can be used with an S : C ratio as low as 1.095 without coking or deactivation of the ruthenium catalyst deposited on the SiC porous monoliths.

One of the systems with the highest output of hydrogen to be built up from units (Figure 23.6) was the fuel processor proposed by Velocys. Tonkovich *et al.* [13] designed a microchannel steam reformer with integrated methane partial oxidation and subsequent combustion to create the required energy for the endothermic methane steam reforming in the adjacent channels. The integrated reactors could be further numbered-up to achieve any desired large-scale plant capacity, where a full-scale unit (3.9 × 5.8 × 3.9 m) produced 10 m³ s⁻¹ of hydrogen by placing 30 commercial-scale microchannel reactors in six reactor assemblies (Figure 23.7).

Most reaction systems are at the stage of a test system or prototype; there are few fuel processor systems commercially available. One of the commercially available systems is the highly integrated InnovaGen fuel processor (Figure 23.8). This system integrates a microreactor and a micro-heat exchanger with advanced sulfur-tolerant catalysts and gas purification by membrane technology. A fuel injector atomizes the liquid fuels and mixes them thoroughly with steam. The off-gas of the membrane gas purification is combusted in cross-flowing channels to supply the heat for the endothermic steam reforming reaction. Irving and coworkers have also developed a proprietary catalyst formulation tolerant to a low sulfur content consisting of a bimetallic compound on Al₂O₃ [47]. Three different heat exchangers provided the

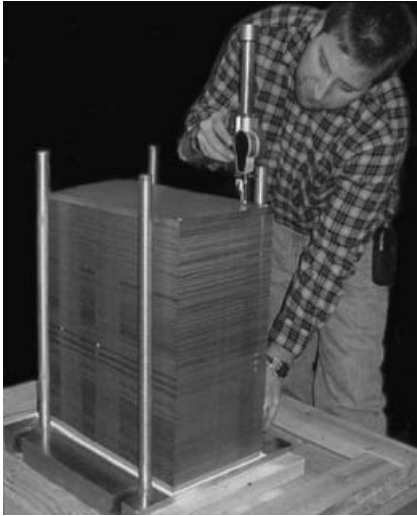


Figure 23.6 One reactor element (out of 30) for a proposed hydrogen production reactor skid ($10 \text{ m}^3 \text{ s}^{-1}$) built by Velocys [13].

temperatures for various zones within the system. With methane as fuel the prototype produced hydrogen for a 2.5 kW_e fuel cell; with diesel the output was sufficient for a 1 kW_e fuel cell.

23.2.7

Influences on Efficiency

Heat loss from the fuel processor has a significant effect on device performance. Thus the pure CPO process is unfavorable for high process efficiency in comparison with SR and OSR. However, there are more effects that should be considered. Microreactors that are operated autothermally with lower environmental losses achieve lower reaction light-off temperatures. For high-temperature reactions, the consider-

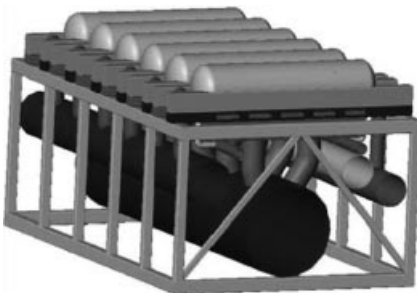


Figure 23.7 Schematic of a full-scale hydrogen production reactor skid ($10 \text{ m}^3 \text{ s}^{-1}$) designed by Velocys [13].

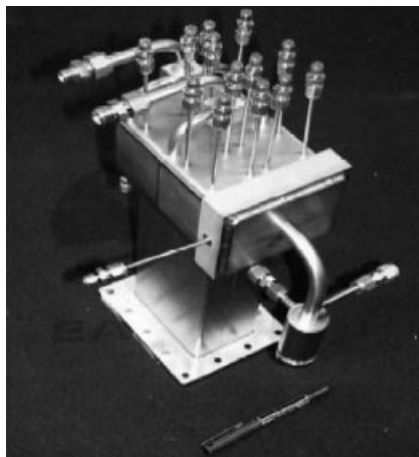


Figure 23.8 InnovaGen fuel processor including microchannel steam reformer, fuel injector and burner [37].

ation of the thermal isolation, either through design or materials selection, of a microreactor plays an important role in achieving the desired performance. A large increase in efficiency can be achieved by thermal integration due to optimized process design. However, this is strongly limited by the size of the hydrogen production unit. The thermal efficiency on an LHV basis could vary from 19% in the sub-watt power region [6] to 28% and around 80% for 20 and 100 W, respectively [3]. Values of 78% have also been reached in a 1 kW system; the theoretical maximum of efficiency there was calculated to be 82% [39], which depends on the system design, i.e. the heat recovery concept.

23.3

Conclusion and Outlook

From the variety of applications, fuel types converted and number of publications, it is clear that considerable operational knowledge about fuel conversion in microreactors is available, although thermal efficiency is still improvable in the sub- to low-watt power regions.

Some companies have started to announce the commercial availability of microreactor-based fuel processors in the past and present. Additionally, as more and more companies have the intention to explore the potential of microreaction technology for fuel conversion and small-scale electricity production, a commercial breakthrough may therefore be feasible in the future. Fast and efficient heat and mass transfer in microreactors and their operating strategies are prerequisites for such success. However, to obtain commercial breakthrough, a proof of principle in everyday life, i.e. long-term stability of catalysts under operation with “real” fuel and also of microreactor performance and material over several thousand hours, is still lacking – as for conventional fuel processors also.

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