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Microstructured Fuel Processors for Fuel-Cell Applications

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Microstructured reactors are being developed at IMM for the processing of various fuels to provide hydrogen for mobile and portable fuel-cell systems. The key feature of the systems is the integrated-plate heat-exchanger technology, which allows for thermal integration of several functions in a single device. For example, steam reforming may be coupled with exothermic reactions in separate flow-paths of a heat exchanger. Catalyst coatings are also under development for numerous reactions, such as propane steam reforming, methanol steam reforming, catalytic combustion, water-gas shift, and preferential oxidation of carbon monoxide. These catalysts are being investigated in specially developed testing reactors. Reactors and complete fuel processors are being tested up to 5 kW power output of the corresponding fuel cell.

Keywords fuel processing, microstructured reactors, plate heat-exchanger reactors

1. Introduction

Within the scope of hydrogen generation for fuel-cell systems, space demand and weight are critical issues for small- and medium-sized applications that range from a few watts to tens of kilowatts. Thus, the process intensification benefits of microtechnology (Ref 1) are currently within the focus of the worldwide research in fuel processing.

Generally, a fuel reformer is composed of a reformer reactor and, in most cases, catalytic gas-purification reactors that remove carbon monoxide from the reformate because it is harmful, at least in polymer electrolyte membrane (PEM) fuel cells, the most common fuel cells used in small-scale applications (Fig. 1). In addition, fuel and/or water evaporators and heat exchangers are required, the latter to adjust the temperatures of the feed of the individual reactors and to improve system efficiency.

The operation temperature of the reforming process is dictated by the fuel that is used. Methanol reforming is performed in microreactors at temperatures not exceeding 300 °C, whereas hydrocarbon reforming takes place at much higher temperatures (700 °C for iso-octane, 750 °C for propane, and even higher for methane).

The unique advantages of microstructured devices for fuel processing are manifold. In addition to the space demands and weight benefits mentioned above, integrated microstructured heat exchangers/reactors open the door to novel processing concepts.

The endothermic steam reforming reaction may be coupled to exothermic catalytic combustion in an integrated heat exchanger. However, this approach, although often claimed, has hardly been applied so far. One application on methanol steam reforming was recently published by Reuse et al. (Ref 2), and power for the endothermic steam reforming was generated by the exothermic combustion of hydrogen stemming from the off-gas of the fuel-cell anode, which still contains ~10% or more hydrogen.

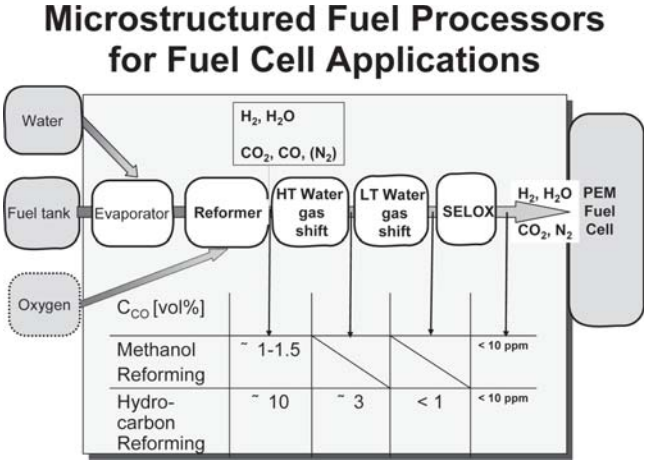

Fig. 1 Principal flow scheme of a fuel processor based upon catalytic CO clean-up

An exothermic partial oxidation reaction may be operated in an integrated heat exchanger to remove the heat of reaction, which prevents hot-spot formation and may improve catalyst performance.

Furthermore, known catalytic gas-purification processes are all exothermic, and removal of heat from these reactors improves their performance. The water-gas shift (WGS) reaction operates close to its thermodynamic equilibrium. Thus, the process is performed in conventional systems with an intermediate cooling step applying two separate reactors [high-temperature (HT) and low-temperature (LT) WGS]. On the other hand, the space demand of the shift reactors is a crucial problem in fuel processors that rely on conventional technology. Here, microtechnology may well bring substantial benefit,

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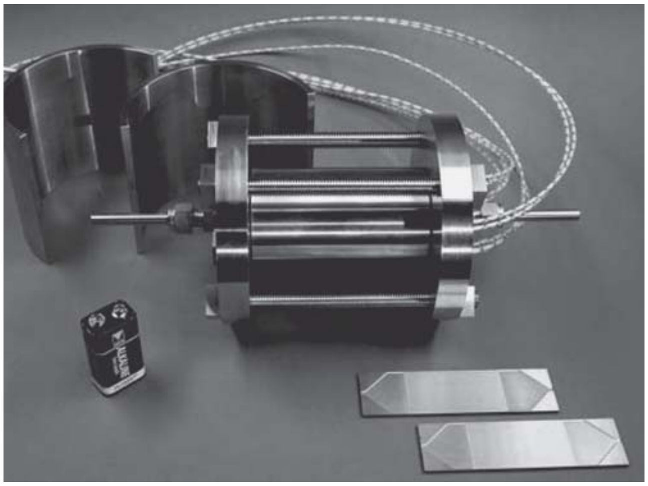


Fig. 2 Reforming reactor for high-temperature operation

Fig. 3 Stacklike testing reactor for catalytic combustion of methanol

as integrated microstructured heat exchangers/reactors offer the possibility of functioning within a single device and with an internal temperature gradient that moves the thermodynamic equilibrium in the desired direction. This results in a drastic reduction of reactor size (Ref 3).

Finally, the selective oxidation of carbon monoxide is an exothermic reaction as well, where the operation temperature of the catalyst needs to be kept in a narrow range to achieve optimum conversion. Thus, removing the heat generated gives potential for improving the reactor performance and decreasing its size.

2. Experimental Procedures

2.1 Reactors for Catalyst Testing

At Instit für mikrotechnik mainz (IMM), many different testing reactors have been developed within the last few years for the different applications discussed above. Figure 2 shows a high-temperature testing reactor developed for hydrocarbon reforming reactions. It carries two testing plates, which are removable and compressed in the reactor body to achieve metallic sealing. This allows for operation at temperatures exceeding 800 °C.

To test catalysts in low-temperature reactions, more catalyst mass may be required. Thus, stacks of microstructured plates mounted into a housing and sealed by screws and gaskets are another type of reactor that has been developed. Figure 3 shows a stacklike testing reactor developed at IMM for catalytic combustion of methanol. A total of 16 plates may be introduced into the reactor, and then the heat generated by combustion amounts to 300 W.

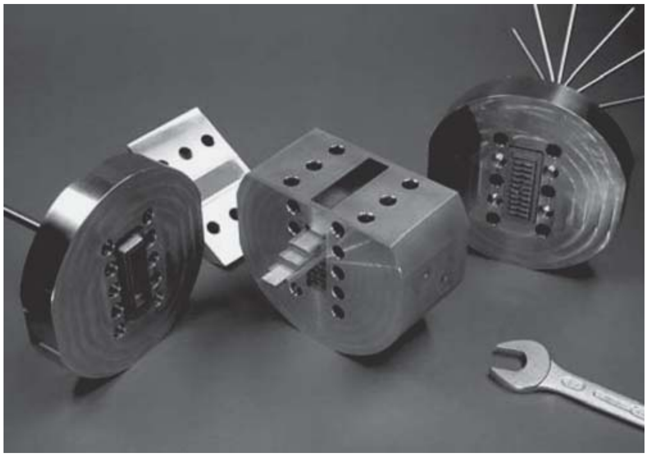


Fig. 4 Parallel screening reactor for high-temperature and high-pressure reactions

Catalyst screening may be performed in screening reactors that carry parallel channel systems and that have separate exits to allow for separate analysis of the product of each individual plate. Such devices were developed at IMM for ambient pressure and moderate temperatures up to 500 °C and, in an upgraded version, for pressures up to 100 bar and temperatures up to 800 °C (Fig. 4).

2.2 Catalyst Development

Catalyst development at IMM covers methanol and propane reforming, WGS reactions, selective oxidation, and catalytic combustion of hydrogen and various fuels, such as hydrocarbons and alcohols. Recent results described below provide an overview of this work. Basically, the wash-coating procedure is currently the main deposition method used at IMM (Ref 4). Both laboratory-prepared and commercial catalysts were used to coat the microchannels. Much effort has been spent in dedicated research projects to achieve mechanically and thermally durable coatings that are evenly distributed both from channel to channel and over the channel length. The distribution of the active species on the wash-coats is shown using SEM and in-depth SIMS (Fig. 5).

The species concentration found for a Cu/Cr catalyst is shown. Surface enrichment and decreasing concentrations of copper were found in this special case, which proves that there is potential for further improvement.

A home-made Rh/Pt/CeO_2 catalyst on alumina wash-coat basis was identified as a good candidate for propane steam reforming (Ref 5). The combination of Rh-generating stability and high activity toward reforming, Pt improving the dispersion of Rh and catalyst stability against coking, CeO_2 supplying oxygen to the noble metals and improving the WGS functionality, thus reducing the CO content of the products revealed an excellent performance of the catalyst (Fig. 6). Full conversion was achieved for a steam/carbon ratio of 3.2 at a temperature of 750 °C and residence time of 10 ms. Under these conditions, only CO and CO_2 were found in the product as

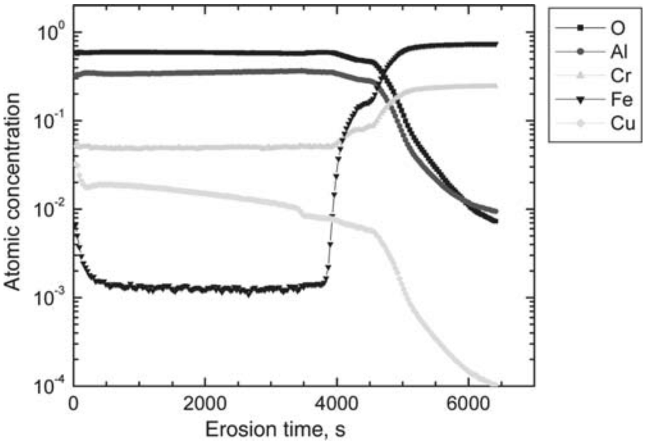


Fig. 5 In-depth species concentration of a Cu/Cr catalyst introduced as wash-coat into a microchannel

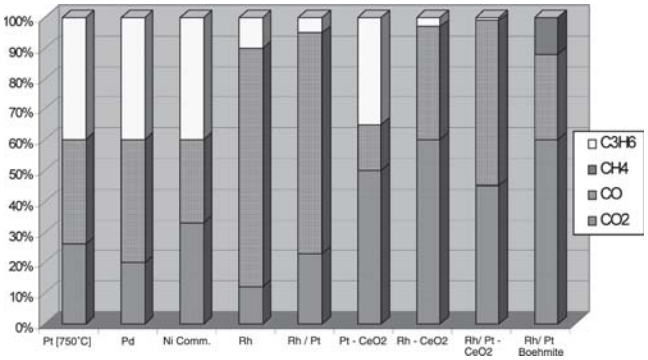


Fig. 6 Selectivity pattern of catalyst coatings applied for propane steam reforming

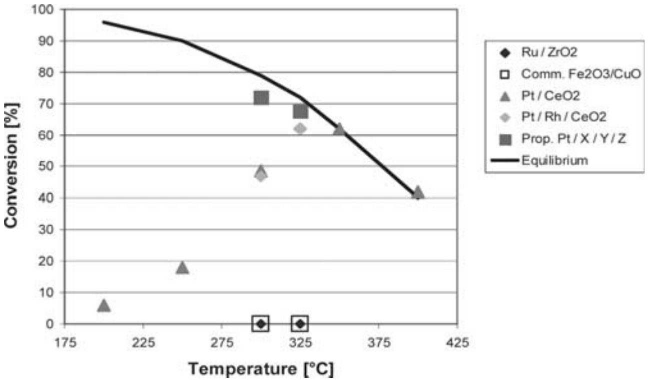


Fig. 7 Activity pattern of different catalysts in low-temperature WGS

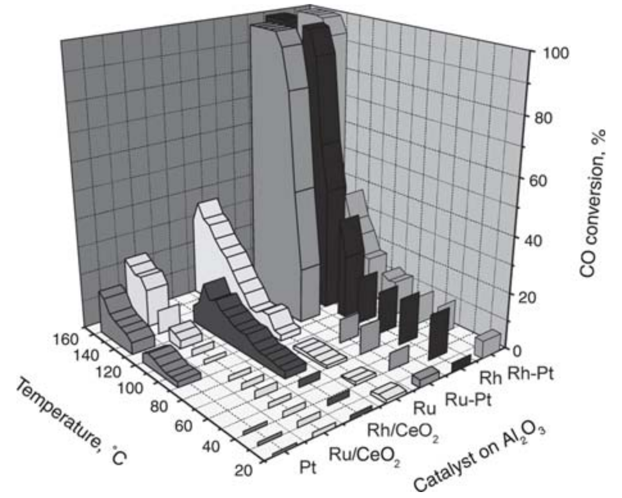


Fig. 8 Results from catalyst screening for selective oxidation of CO

carbon species. A GHSV of 62,000 h^{-1} was achieved at full conversion for the reformer reactor.

If a fuel-cell efficiency of 55% and a fuel-cell hydrogen utilization of 90% are assumed, a power density of ~40 kW/dm^3 could be calculated for the microstructured steam reforming reactor. In other words, a reformer reactor of volume 1 dm^3 would generate enough hydrogen for a fuel cell with an electric output of 40 kW.

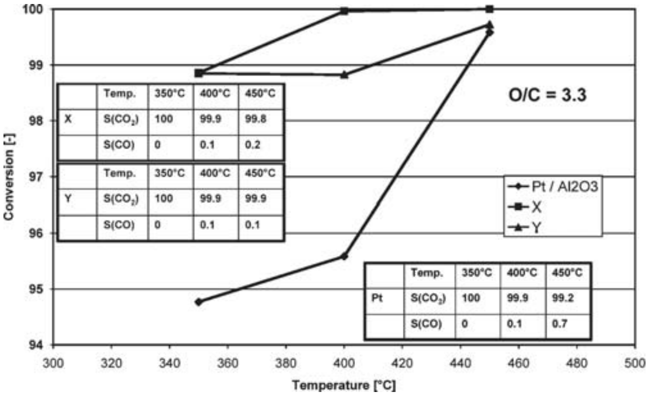
Short-term stability could be proven for this catalyst. However, long-term stability testing remains a future task currently addressed by 1000 h tests.

Numerous catalyst systems have been under investigation at IMM to achieve the novel demands of fuel processing in microstructured reactors. For example, reformer concepts exist wherein air is used for heating the reactors during start-up, which deteriorates the performance of Cu/Zn low-temperature WGS catalysts dramatically. Systems based on noble metals might be proper alternatives in such a design.

The WGS catalyst should be capable of covering the entire operation range from the high-temperature WGS (~10% CO in feed) to the low-temperature WGS (~3% CO in feed). This is important when running an integrated heat exchanger/reactor that covers both stages. Figure 7 shows several selected catalysts. Commercial Fe/Cr catalysts, as usually applied in the high-temperature WGS, are not active at the reaction temperature applied. Pt/CeO_2 catalysts made from commercial, Pt-based catalysts show significant activity (Ref 6). Introduction of a second noble metal species, such as Rh or Ru (the latter not shown here), did not improve catalyst activity. On the contrary, the catalysts were selective toward the undesired methanation reaction. An IMM laboratory-prepared Pt-based catalyst outperformed all other catalysts discussed herein regarding activity and selectivity towards WGS (Fig. 7).

Selective oxidation of carbon monoxide, which is the last step of catalytic CO clean-up, is also under investigation at IMM (Ref 7). Ru/Pt, Rh, and Rh/Pt catalysts proved to be the most active species investigated (Fig. 8). However, short-term (20 h) stability could be demonstrated only for the Rh/Pt system. Further investigations on stability and alternative catalyst formulations are underway.

Total oxidation of fuels is an important reaction when steam reforming is applied, because both the evaporation process and steam reforming require energy supplies. The oxidation process needs to be complete (ideally, achieving 100% conversion), robust against air surplus, which is necessary for adjustment of the appropriate operation temperature, and stable over the long term. At IMM, various commercial catalyst systems, such as Pt- and Pd-containing catalysts, were performance-tested in total propane oxidation. Pt is known to be sensitive to inhibition mechanisms that involve oxygen, and these prevent full conversion at air surplus. This is not the case for Pd, however, which has lower activity. Therefore, novel catalyst



	Temp.	350°C	400°C	450°C
X	S(CO_2)	100	99.9	99.8
	S(CO)	0	0.1	0.2

	Temp.	350°C	400°C	450°C
Y	S(CO_2)	100	99.9	99.9
	S(CO)	0	0.1	0.1

	Temp.	350°C	400°C	450°C
Pt	S(CO_2)	100	99.9	99.2
	S(CO)	0	0.1	0.7

Fig. 9 Conversion versus reaction temperature for homemade catalysts compared with commercial Pt catalyst

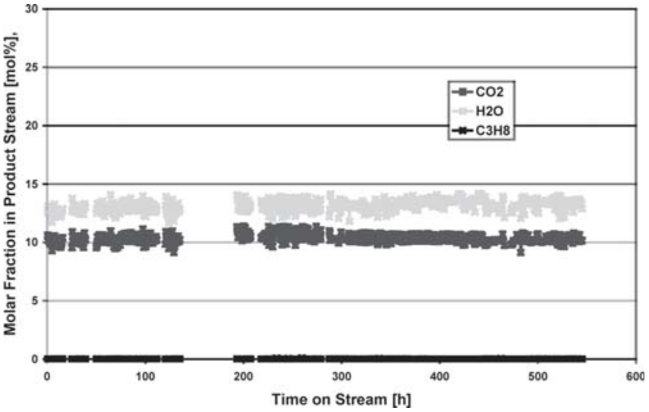


Fig. 10 Long-term stability test for total oxidation of propane

formulations have been developed at IMM that do not suffer from either drawbacks (Fig. 9). The long-term stability of one of these formulations was recently proven in 1000 h stability tests (Fig. 10).

Further development is underway, especially in high-temperature applications such as hydrocarbon reforming. Here, thin catalyst layers may well be sufficient to achieve high activities, and thus completely new catalyst types manufactured by sol-gel processes or CVD become a feasible option. For coatings as thin as a few micrometers, the content of the active species becomes negligible, which makes possible the application of costly noble metals without financial drawbacks.

3. Results and Discussion

3.1 Integrated Reactor Concepts

The design concepts of microstructured reactors need to be adopted for their applications. Testing devices normally have the option to exchange catalyst carrier plates, and most of these are electrically heated. Thus, gaskets are applied, and heating may be done by heating cartridges. This makes the reactors relatively bulky compared with the size of the microstructured plates that are incorporated. As a first step toward size reduction, IMM has developed a testing reactor for preferential oxidation, which is a hybrid of testing and processing devices (Ref 7). The reactor itself is an integrated counter-flow heat exchanger and designed for a 100 W methanol reformer. It is coupled with two counter-flow heat exchangers (Fig. 11). This highly integrated device still contains graphite gaskets to allow for changing of the microstructured plates. A laser-welded device was built as a prototype later, and it was considerably smaller as it did not require sealing or screws. At IMM, an integrated reactor for similar use compared with the device presented by Reuse et al. (Ref 2) (see also above) has been realized. It is a 100 W methanol reformer combined with a catalytic afterburner, which combusts the anode off-gas of the fuel cell (Fig. 12). However, the energy supply of the anode off-gas of the fuel cell is generally not sufficient for hydrocarbon steam reforming. Thus, either additional fuel needs to be burned in a separate burner or the reforming itself needs to be carried out in the presence of oxygen (partial oxidation or autothermal reforming). At IMM, current projects deal both with autothermal reforming and combined steam reforming/catalytic combustion of hydrocarbons.

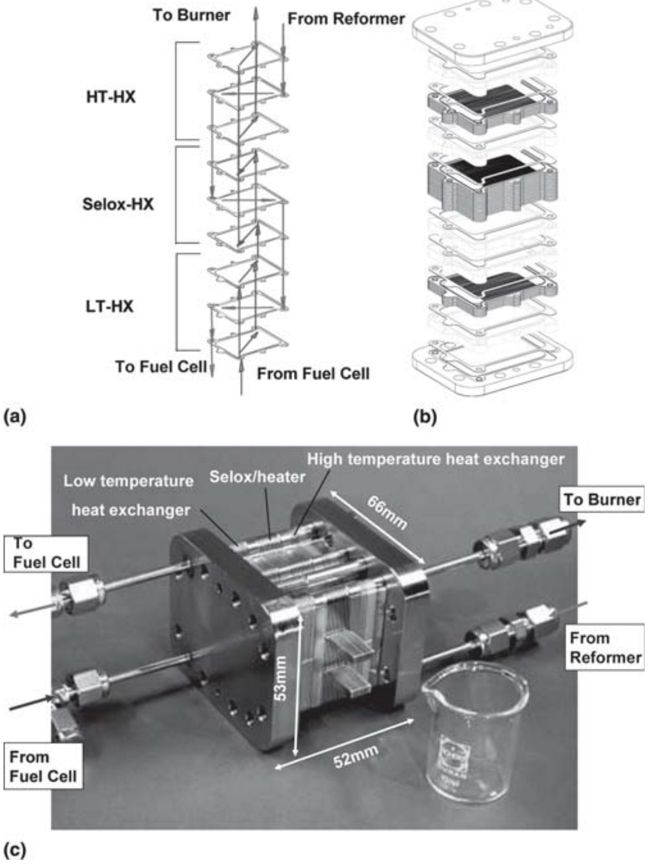


Fig. 11 Testing reactor designed for the selective oxidation of CO: (a) flow paths; (b) explosion view; (c) mounted device

In processing devices, the amount of wall material must be minimized to reduce their start-up times. For these applications, different sealing concepts are required, such as laser welding or diffusion bonding. IMM has developed a laser-welded 10 kW counter-flow heat exchanger, which may be applied as an integrated heat exchanger/reactor (Fig. 13). Currently, 5 kW laser-welded reforming reactors, WGS reactors, and PrOX reactors are being tested at IMM within the scope of a project aiming to achieve a complete fuel processor operating with autothermal iso-octane reforming.

Heat exchangers and evaporators are essential balances in the plant components of fuel processors. Again, microstruc-

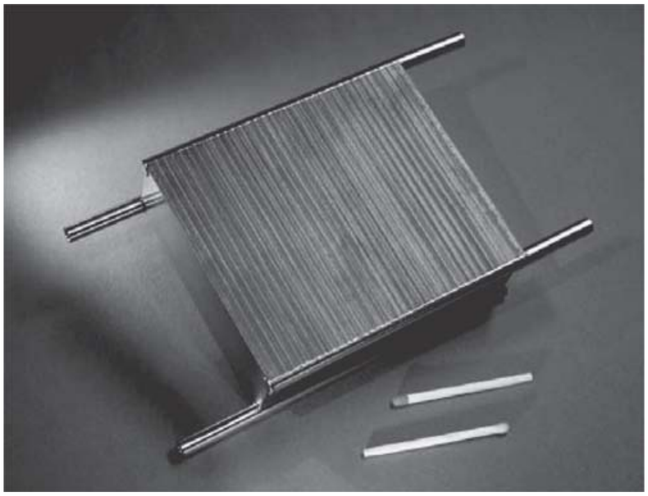


Fig. 12 Combined steam reformer/catalytic burner for methanol and fuel-cell anode off-gas, respectively

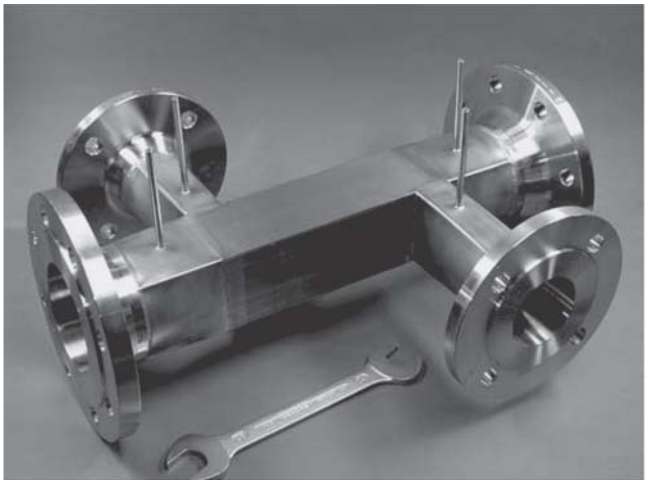


Fig. 13 10 kW microstructured heat-exchanger developed at IMM

tured devices offer great potential for improved performance and reduced dimensions. Figure 14 shows a prototype of a 5 kW hot-gas-driven evaporator developed at IMM which allows for complete evaporation of water and organic liquids in a single step. The energy supplied by the hot gas drives the reaction forward toward improved overall system efficiency, especially for fuel-processing systems.

3.2 System Testing

Finally, laboratory and pilot-plant test rigs are required for testing catalyst and reactor performance. At IMM, five laboratory-scale test rigs are available. One is dedicated to catalyst testing, one for long-term stability tests, and one for small-scale fuel processor testing; the remaining two rigs are dedicated for heat-exchanger and evaporator performance testing.

Corresponding with the increasing size of microstructured devices in the kW range, the test rigs consequently can surpass laboratory scale. IMM has recently put into operation a pilot-scale test rig that includes an 8 kW conventional evaporator and processes 180 Ndm^3/min gas (Fig. 15).

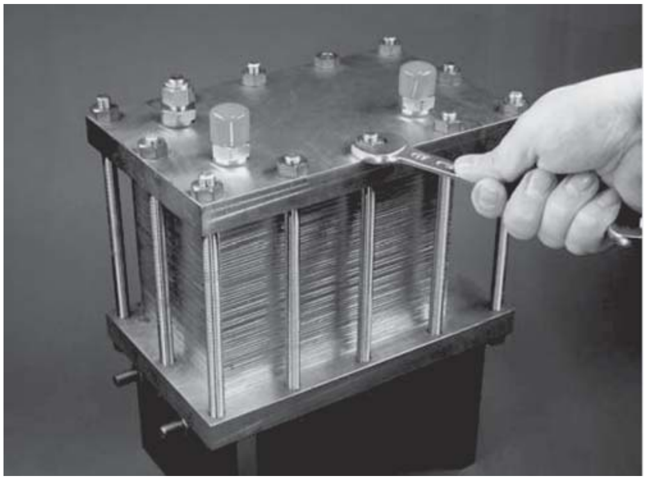


Fig. 14 5 kW integrated heat exchanger/evaporator developed at IMM

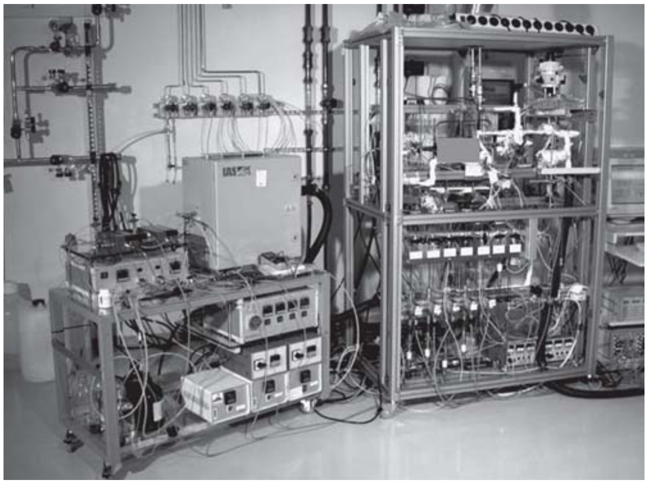


Fig. 15 Pilot-plant test rig for 5 kW fuel processor component testing

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