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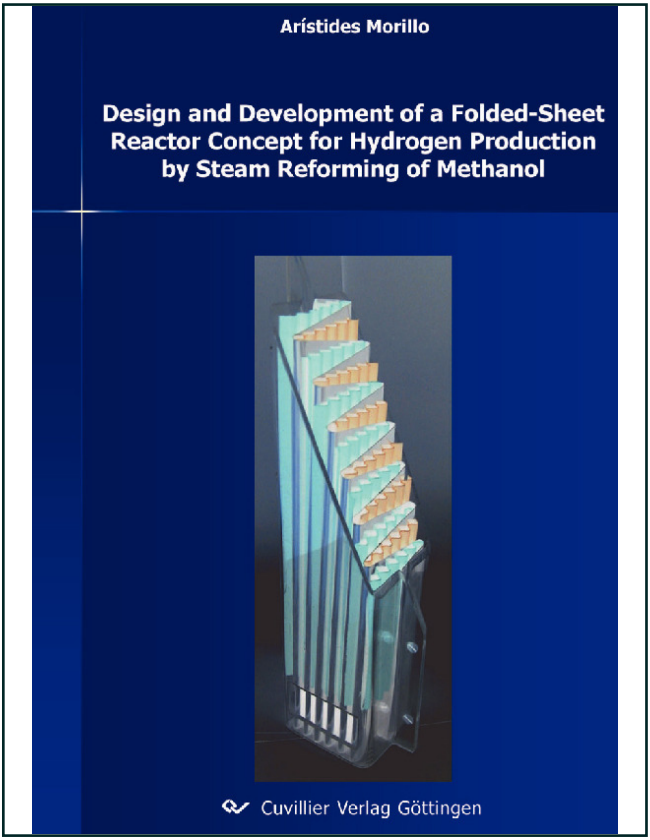
"Design and Development of a Folded-Sheet Reactor Concept for Hydrogen Production by Steam Reforming of Methanol



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Design and Development of a Folded-Sheet Reactor Concept for Hydrogen Production by Steam Reforming of Methanol

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Chapter 1

Introduction

1.1 The Way to the Fuel Cells

Over the past years, the constant demographic growth has caused an accelerated increase of the general demand of energy, specially but not only in the automotive sector.

In addition, the constant increase of the prices of the primary sources of energy, as a result of a predictable scarcity of the crude-oil and its derivatives, has motivated the intensive search for alternative sources of clean energy, to guarantee an optimal balance between efficient generation of energy, environmental protection and low costs. Several primary energy sources like solar, eolic, chemical, and electrochemical are in competition for producing energy with low- or non-pollutant emissions and high system efficiency.

The use of the so-called Proton Exchange Membrane Fuel Cells (PEMFC), also known as Polymer Electrolyte Membrane Fuel Cell, has been introduced and well accepted for mobile applications, because of their important benefits, in particular:

- high efficiency: fuel cells can theoretically convert up to 90 % of the energy contained in its fuel into usable electric power and heat. Fuel cell efficiency is not limited by the Carnot limit, because they convert directly chemical energy into electrical energy,
- high power density: depending of the nature of the electrolyte used, fuel cells can operate in a wide power density range, and - contrary to internal combustion engines - can operate at low load with high efficiency,
- fuel cells are friendly to the environment: substitution of conventional internal combustion engines by fuel cells should improve air quality, reduce green-house emissions, and even for power-plants could also reduce cooling water consumption and waste water discharge,
- fuel cells contain no moving parts and eliminate several of the sources of noise associated with conventional transportation systems,
- fuel cells have their highest theoretical efficiency at low temperatures, favoring PEM fuel cells,

- flexible size: depending of the application, fuel cells can be assembled for example in centimeter to meter ranges.

Today it is assumed that fuel cell technology may play a pivotal role in a new technological renaissance - just as the internal combustion engine revolutionized life at the beginning of the 20th century [8]. Such an innovation could have a global environmental and economic impact. Therefore major automobile manufacturers in the world are developing fuel cell vehicles and almost every energy supplying company is thinking seriously about the future application of fuel cells.

1.2 Fuel Cell Process Optimization

In recent decades there has been a significant increase in the energy efficiency of the process industry by optimization of unit operations. To maintain the trend of increasing energy efficiency, it will be necessary to concentrate some physical steps and chemical reactions into a single process step to achieve the desired product with the desired specifications at high efficiency. This combination of unit operations is called ***Process Intensification*** - Figure 1.1.

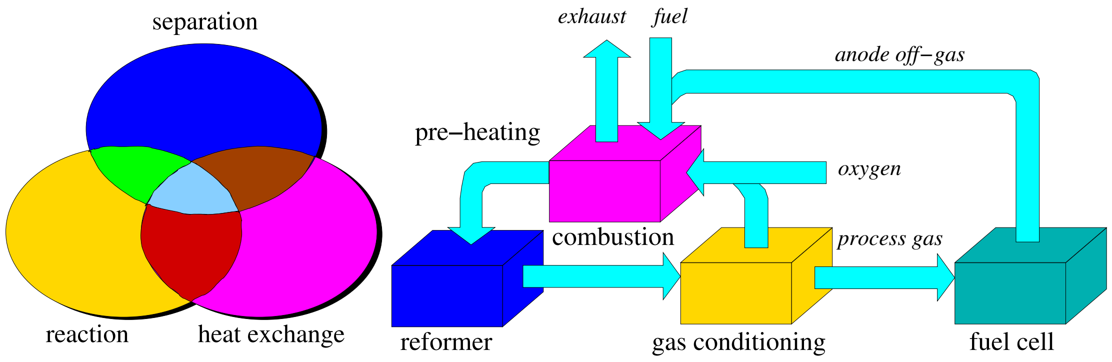

Figure 1.1: Examples for process intensification (*left*) and process integration (*right*)

Process intensification involves making fundamental changes to processing technologies aiming at the development of new compact devices and techniques that lead to substantial improvements in the production processes, reductions in the size of production equipment, lower investment costs, lower energy use and waste production, and finally to more sustainable technologies. In particular, process intensification aims at new and compact designs in which two or more classical unit operations are combined into one hybrid unit.

The process intensification concept is highly related to ***Process Integration*** . Process integration is an established technology for continuous processes in the chemical industry. It involves, for example, the use of heat exchanger networks to optimize heat energy by linking hot and cold process streams in the most thermodynamically advantageous way. While process integration provides valuable incremental improvements, process intensification offers the potential of substantial savings. Both techniques also offer opportunities for higher product quality and yields.

More specifically, fuel cell process optimization requires provision of a suitable fuel, in general hydrogen which at the present will be predominantly generated by reforming of a fossil or renewable organic feedstock. Since reforming requires energy at elevated temperatures the energy integration, using all available energy sources of the process and recovering heat from all hot process streams, is of prime importance. This is shown in Figure 1.1-right, where fuel is fed to a reforming reaction in order to produce a hydrogen rich gas and after, impurities are removed in a conditioning step and mixed with the anode off-gas coming from the fuel cell. This ”fuel cell off-gas” is catalytically burned with oxygen (from air) and the heat released is used to preheat the initial fuel feed up to reforming temperature.

1.3 Hydrogen Production for Fuel Cells

For long time multitubular catalytic fixed-bed reactors filled with catalyst pellets and heated by flame burners from the top or the side walls (see Figure 1.2) were the state of the art for hydrogen generation via endothermic steam reforming of fossil fuels [9, 10, 11, 12].

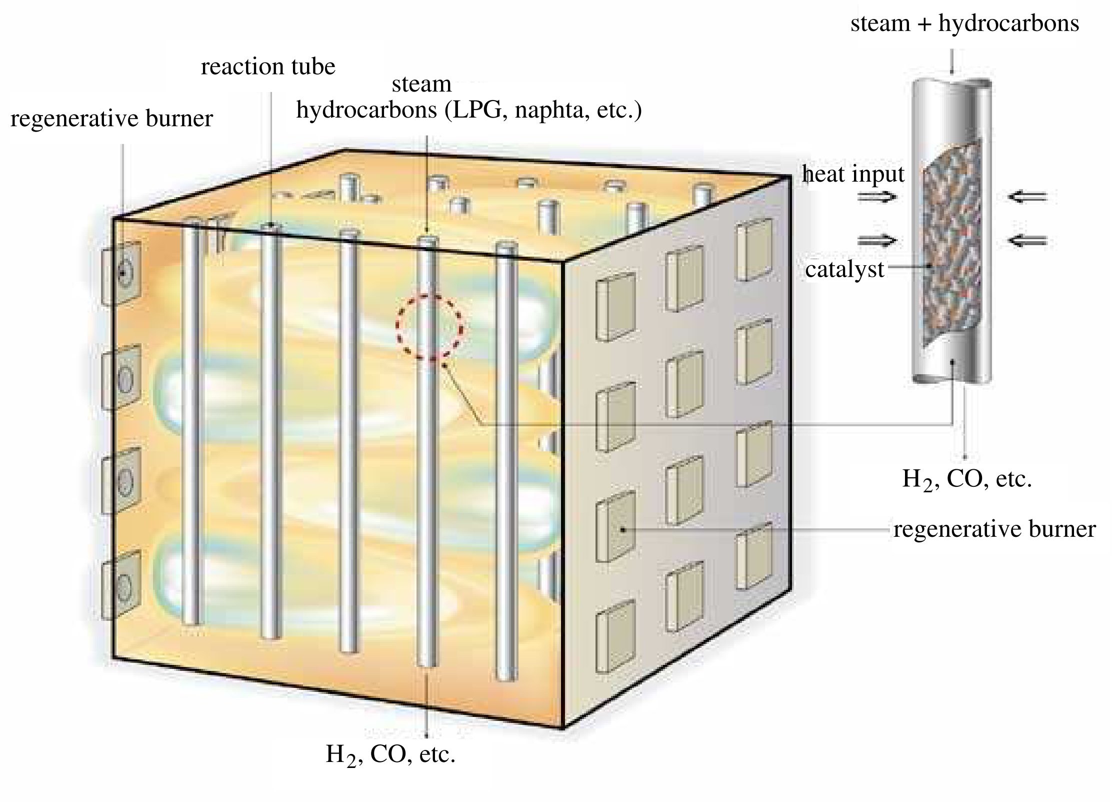

Figure 1.2: Conventional large scale steam reformer [13].

Here, the major problem was faced when attempting to implement this principle for decentralized small scale or mobile on-board production processes. Large scale reformer systems feature severe limitations regarding heat integration [2]. The heat transfer from the heat carrier (e.g., flame burner, thermo oil, electrical heating, etc.) to the catalyst bulk is hampered by the low thermal conductivities within the catalyst bed (around 1 $\frac{W}{m \cdot K}$), resulting in inefficient catalyst utilization. Substantially improved heat transfer and an efficient heat recovery are therefore crucial for an enhanced process performance.

A way to achieve these goals is to replace the multitubular arrangement by a parallel-plate reactor design where the catalyst of the reforming reaction is coated at one side of a plate and the required heat of reaction is supplied by a catalytic combustion which takes place at the catalyst deposited at the other side of the wall. Then a sequence of parallel reforming and combustion channels are combined into one parallel-plate reactor.

In the past, microchannel devices in form of monolith honeycomb reactors were widely used to help reducing the heat transfer limitations [14, 15, 16, 17]. Ceramic monolith substrates can carry a bigger amount of coating than metallic supports, which gives ceramics the advantage in applications where catalyst deactivators are present or where very high levels of precious metal are needed to reach the desired performance. However, problems with respect to the hermetic seal of the ceramic monolith ends, and in general to the reactor handling (e.g. catalyst interchangeability) were a strong drawback for this class of devices.

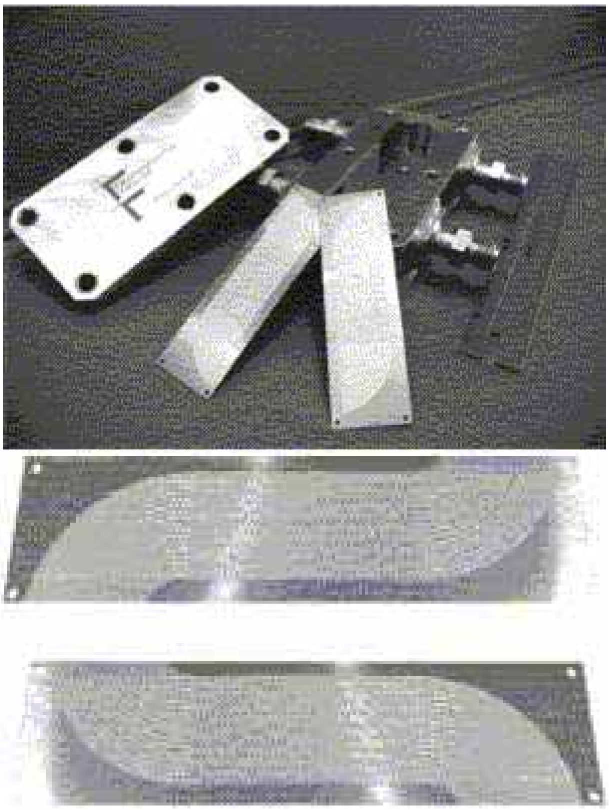

Figure 1.3: Two-passage microstructured reactor with 2500 micro-channels arranged on 25 plates. The channels are 40 mm long, 100 μm deep, and 200 μm large. *Top:* Housing of the reactor; *bottom:* Microstructured plates. (Research Center of Karlsruhe) [18].

Parallel-plate devices were considered as alternative to the monolith reactors. Parallel-plate based apparatuses with an associate large volume-related exchange area have been widely studied and implemented as an alternative for overcoming problems regarding efficient heat transfer. Hydrogen production for fuel cell applications was one of the main targets for this reactor concept. For small scales, some research facilities worked intensively in order to overcome typical construction difficulties. The *IHI* institute proposed a plate-based reformer for hydrogen generation which involves the autothermal heat integration between the endothermic reforming reaction and the exothermic combustion of a fuel gas [19]. A further version of this autothermal parallel-plate reformer was developed by *BG/Advantica* for steam reforming of methane coupled with total combustion of a fuel gas [20]. Here, production equivalents up to 40 $\frac{kW_e}{l}$ have been demonstrated at 650 °C under laboratory conditions. A first microchannel natural gas reformer was achieved by *A. Dicks* in the University of Queensland (Australia) in 2001 [21, 22, 23]. *X. Zhang et al.* studied several catalyst formulations for steam reforming of methanol in microchannel reactors [24]. *Zanfir et al.* performed detailed calculations on plate reformers for hydrogen production by methane steam reforming, pointing out the benefits of the reactor principle regarding heat transfer [25, 26]. A series of very compact microchannel reactors has been successfully constructed by *The Pacific Northwest National Laboratories* and proven for hydrogen production [27]. Hereby important efforts have been carry out by *Reuse et al.* in developing microstructured apparatuses for hydrogen production by methanol steam reforming and partial oxidation [18]. The reactor (Figure 1.3-top) consists of stacked plates (Figure 1.3-bottom) in which steam reforming and partial oxidation can be performed separately. For steam-reforming, the microstructured channels are coated with a suspension of a commercial copper based catalyst (G-66MR, Südchemie). Recently *Whyatt et al.* reported further progress in the steam reforming of natural gas in microchannel hydrogen processors for fuel cell applications (Figure 1.4) [28]. Finally the benefits of plate-based devices have been also proven in the practice in other application fields, like photocatalytical processes [29, 30], reactive etching [31] and classical heat-exchange.

All around the world, companies are working on the development of on-board hydrogen processors for fuel cell applications. Some prototypes have been experimentally validated and put into operation under realistic conditions. In Table 1.1 a list with the most popular companies that are actually working in hydrogen production for mobile applications is given. It can be seen that the majority of the developers are working on processors that are based on gasoline fuels. This responds mainly to the fact that gasoline infrastructure is already available. Methanol and natural gas are even alternative fuels that have been also strongly considered.