

Future aspects of energy technology

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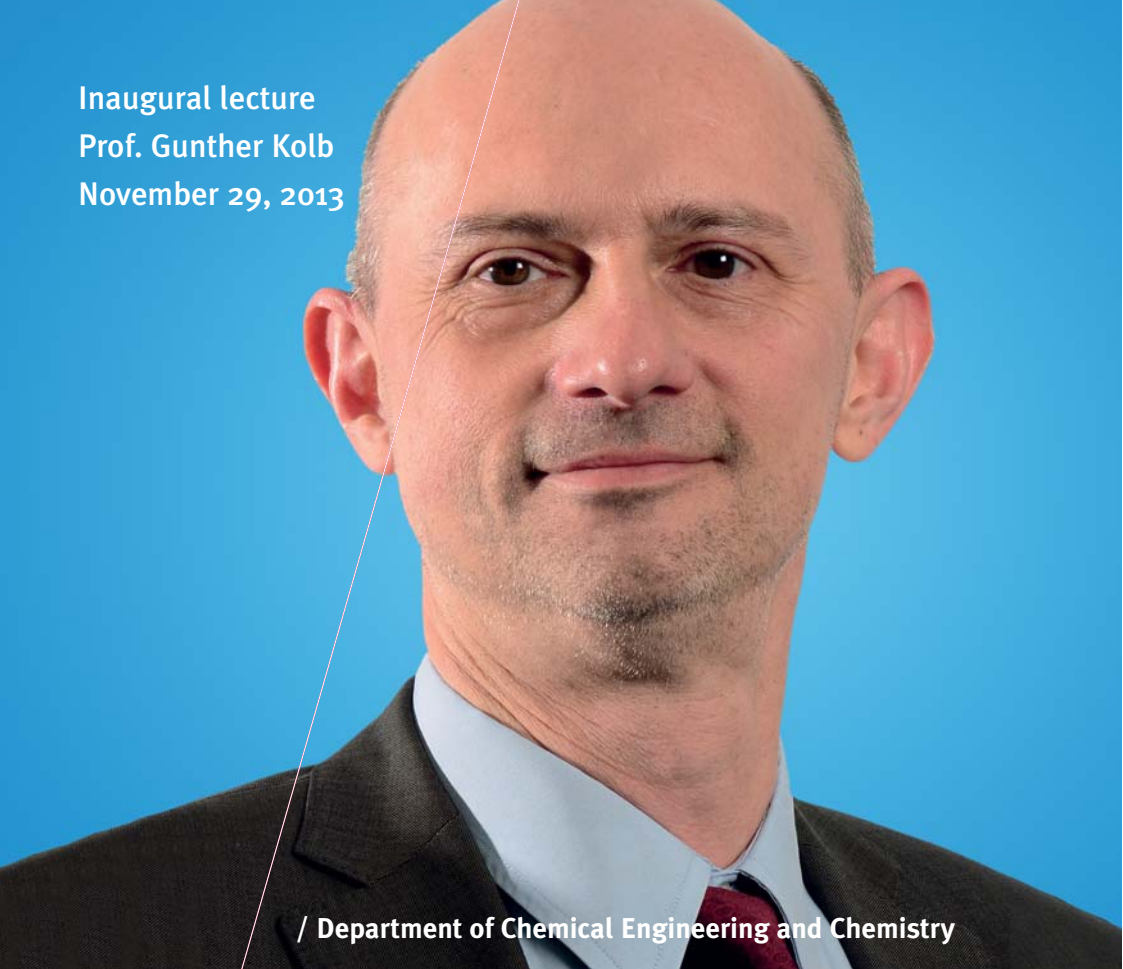
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Inaugural lecture
Prof. Gunther Kolb
November 29, 2013



/ Department of Chemical Engineering and Chemistry

TU e Technische Universiteit
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Future Aspects of Energy Technology

Where innovation starts

Inaugural lecture prof. Gunther Kolb

Future Aspects of Energy Technology

Presented on November 29, 2013
at Eindhoven University of Technology

Intro - From coal genesis towards methanation

The ongoing exponential growth of the human population on Earth creates enormous stress on the natural environment. However, contact with nature, its beauty and its slow-moving processes have always been a font of power and reflection for me. Losing this contact bears the danger not only of fast-forwarding into our increasingly technology-driven society but also of forgetting the rules of a limited environment – and the resources of our planet are limited without doubt.

Nowadays the vast majority of human energy consumption relies on fossil fuels, which were created through distributed, green and sustainable processes (plant growth) followed by sub-optimal but intensified transformation processes (heat and pressure impact). The low quality of the products of this procedure has led, in some cases (crude oil), to the formation of centralized purification plants, which

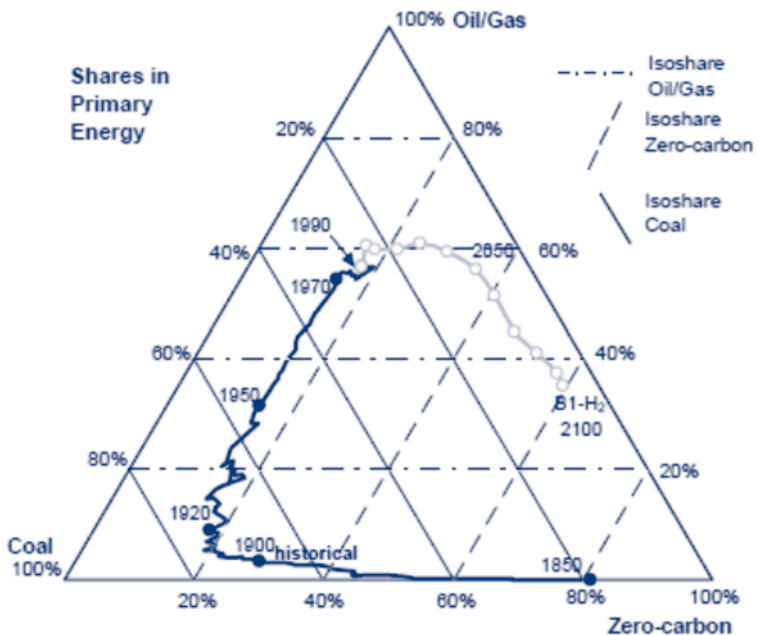


Figure 1

Global shares in primary energy use (1) (source: Elsevier)

create a certain monopoly of access to fuel. Our re-transformation processes are still mainly based upon homogeneous reactions, not so different to what our ancestors started when discovering the advantages of burning organic material. However, the main fuel used has changed rapidly in the last 200 years from wood through coal to natural gas and crude oil as shown in figure 1, which proves that a movement back to a zero-carbon society is feasible, though certainly not straightforward.

Future sustainable generation of energy and energy carriers should necessarily apply distributed utilization ('harvesting') of energy from wind, solar and biomass sources. Optimized transformation processes towards novel energy carriers such as methane or methanol through catalytic conversion and process intensification are required to achieve efficient process chains as well as novel catalytic re-transformation by fuel cells or their alternatives.

The investigation of novel routes of renewable fuel synthesis and power generation should not be driven by short-term consideration of current and near-term fuel prices and availability, but rather consider the foreseeable fact that the demand of fossil fuels will exceed its supply in future, which will change price scenarios completely. Unless the technology is readily available to supplement the fossils at this point in time, energy supply problems will rapidly develop into the central issue for mankind.

Microstructured reactors for energy related applications

Parallel to the growing interest in microreactors for organic synthesis, gas phase reactions have become the subject of an increasing number of investigations. This has quickly led to the introduction of heterogeneous catalysts as coatings or fixed beds into the microreactors.

On this basis the process intensification potential of microstructured reactors has attracted attention in the field of energy technology, where compact, decentralized solutions are required. Meanwhile, the entire field from portable and mobile power generation to stationary and decentralized production of fuels and electrical energy is subject to worldwide research in the field of microtechnology. An overview of sustainable routes from bio-sources towards fuels and electric energy is provided in figure 2.

While ceramic and metallic monoliths, developed initially for automotive exhaust treatment, carry microscale channels and are actually 'microreactors' by definition, the microreactors discussed here represent plate-heat-exchanger technology with microscale channels coated with catalyst or bearing fixed beds of catalyst where appropriate.

Prominent applications of such reactors are auxiliary power units (APU) based upon fuel-cell technology for aircraft, trucks, recreational and other vehicles. To meet the stringent size and cost demands of such applications the step towards microstructured plate heat-exchanger technology was an obvious one. The number of customers addressed by mobile power generation systems creates a mass market, ranging from hundreds of units per year to tens of thousands and more.

Another application field of microreactors under current investigation is the distributed production of fuels such as biodiesel, bio-alcohols and, via Fischer-Tropsch synthesis or methanol, of synthetic fuels, a concept which revolutionizes the current centralized and monopolistic supply of fuel.

The technical feasibility of microstructured fuel processors and fuel synthesis plants has been proven, the required durability of the processes has been achieved in many cases, even the cost savings are obvious when compared to conventional reactor technology and the first systems have been introduced into the market, but the last hurdle still needs to be taken: to penetrate the market and make the novel processes cost competitive against established technologies.

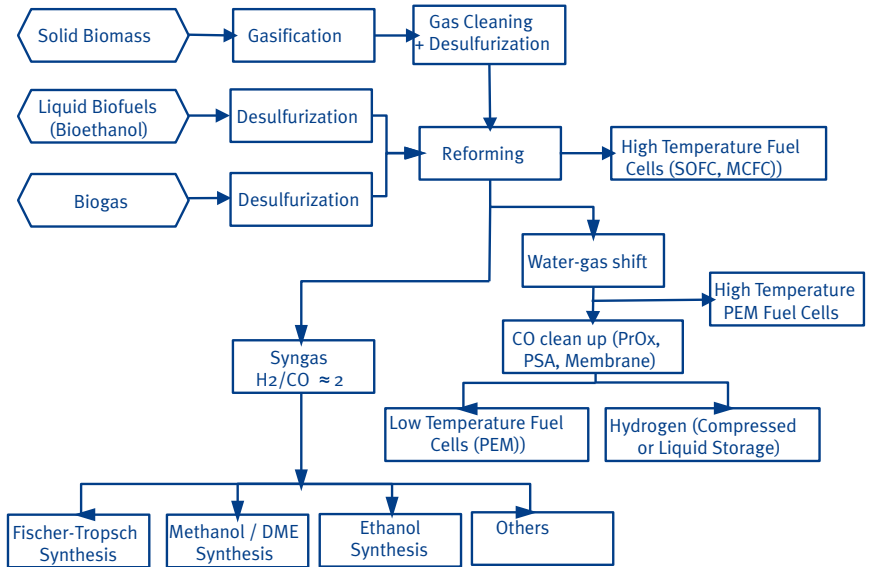


Figure 2

Renewable routes for energy and fuel production based on chemical synthesis routes; modified from (1) (source: IMM)

Future concepts of de-centralized sustainable fuel production and centralized integrated bio-refineries need to combine several or even a multitude of process steps to fully utilize the potential of the novel processing routes and become competitive, just as has been the case in the past century for chemical and petrochemical plants. Figure 3 shows the concept developed in the scope of the European project BIOGO, which aims to produce gasoline-grade hydrocarbons from biogas and bio-oil. The simplified process scheme comprises the co-generation of synthesis gas by partial oxidation of biogas combined with the steam reforming of bio-oil applying microchannel plate heat-exchanger reactor technology. Synthesis gas with an H_2/CO ratio slightly above 2 is achieved at elevated pressure while simultaneously avoiding coke formation at minimum methane formation. The subsequent methanol synthesis requires a recycle loop

and is followed by the methanol to gasoline (MTG) stage. Preliminary calculations revealed that the overall process is energy self-sufficient at a carbon efficiency of 50%.

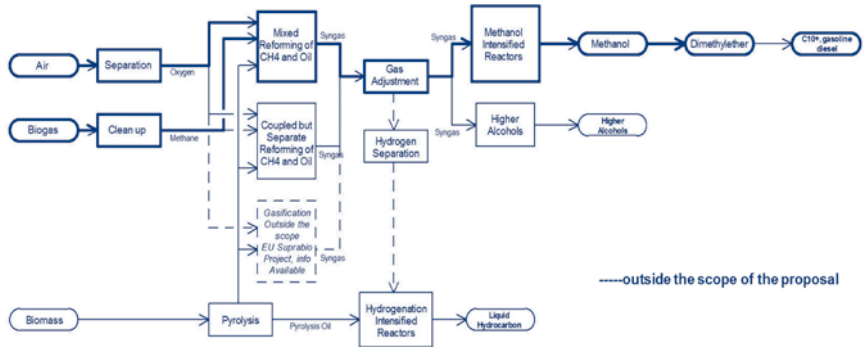
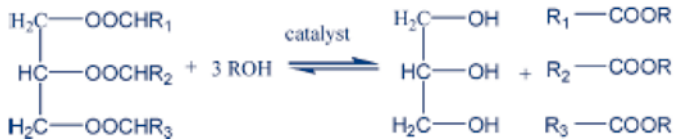


Figure 3

R&D pathways of the European project BIOGO (source: IMM)

Biodiesel is another example of a widely accepted alternative and renewable fuel. The production of biodiesel, which is a transesterification of tryglycerides from sources such as vegetable oils or animal grease to fatty methyl esters (FAME),



(36)

is performed according to the conventional process at moderate conditions (60–70°C at atmospheric pressure) with homogeneous catalysts (NaOH, KOH) and a surplus of methanol. The process is strongly limited by mass transport (2). To reduce the residence times, high operating costs and energy consumption and low production efficiency of biodiesel production, studies have focused on process intensification (3), and microtechnology offers obvious advantages here (4). Basically, different possibilities do exist to introduce microtechnology, or at least smaller reactor dimensions, into the biodiesel production process, namely:

- The application of micromixers to improve the contacting of liquid feed components, which form different phases.
- Improving the mass transfer of the homogeneously catalyzed reaction through operation in small channels or tubes after the mixing.

- Operation under supercritical conditions in microreactors to further intensify the process.
- Operation with immobilized heterogeneous catalysts coated onto the channel walls.

The small diffusion times in microchannels will improve the performance of heterogeneous catalysts, while separation problems and related waste water generation are minimized. By these means it is possible to reduce the residence time necessary to achieve complete conversion from several to tens of hours to a few seconds (4). Currently, a complete mobile pilot plant under construction by the author's group at IMM applies supercritical conditions and heterogeneous catalysts immobilized in microchannels for the conversion of non-edible animal grease, waste and frying oils into biodiesel.

Design considerations

Practical microreactors consist of a multitude of channels, normally thousands or tens of thousands with at least one dimension in the sub-millimeter scale.

In contrast to liquid phase chemistry, pressure drop is a considerably more crucial issue when gases are transported through a chemical reactor. The specific applications in the field of energy technology require a further minimization of parasitic power losses because fuel prices need to compete with options the currently available. Therefore microchannels or microstructures for practical applications need to create minimum pressure drop at maximum heat transfer but also at minimum fabrication costs.

A dimensionless plot of the Stanton number vs. the Fanning friction factor reveals that lowest pressure drop in a practical system is achieved through two parallel plates not contacting each other as shown in figure 4a. Disordered structures such as foams enhance the pressure drop to a much higher degree than the improved heat transfer would justify.

We performed CFD simulations of a multitude of geometries of microchannels, microfins and other geometries with the result that a three-dimensional

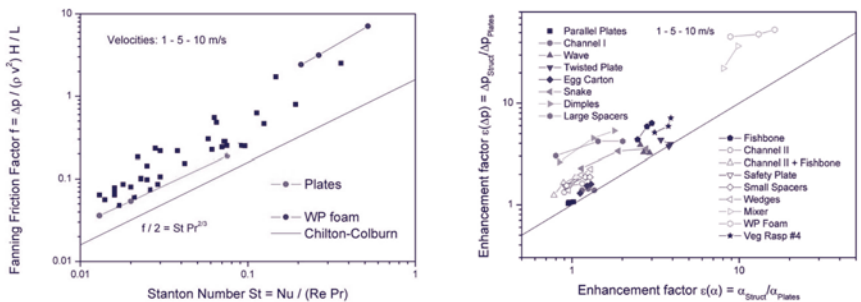


Figure 4

a (left): Dimensionless plot of the Fanning Friction Factor vs. Stanton Number for a variety of microstructured geometries; the Chilton-Colburn Equation is represented as a solid line

b (right): Dimensionless plot of the enhancement factors of pressure drop and heat transfer for a variety of microchannel and microstructured geometries (source: IMM)

arrangement of plates in an egg-carton like arrangement provides the best results, also taking the practical aspects of fabrication into account. Figure 4b shows the enhancement factor of pressure drop (normalized by the pressure drop of parallel plates) vs. the enhancement factor of heat transfer calculated in an analogous manner for different flow velocities. Plates corrugated to such an egg-carton shape also have advantages when the heat exchange process involves the condensation of liquids from permanent gases because the geometry is more open and allows the liquid to leave the system while sufficient surface area of the heat exchanger remains for the heat transfer between the gases. The disadvantages of liquid hold-up in channel-like geometries are known from water formation in the flow fields of low-temperature PEM fuel cells.

The arrangement of a multitude of microstructured heat-exchangers optimized for low pressure drop in an open-flow field is shown in figure 5. It is a CFD simulation of the tail cone of an airplane with heat-exchangers at the bottom of the cone skin and a blower positioned at the back of the cone. The vessel in the center of the cone is a liquid hydrogen tank. The simulation revealed acceptable equipartition of the flow through all heat-exchangers. In many cases flow equipartition is also a crucial issue inside the individual heat-exchanger.

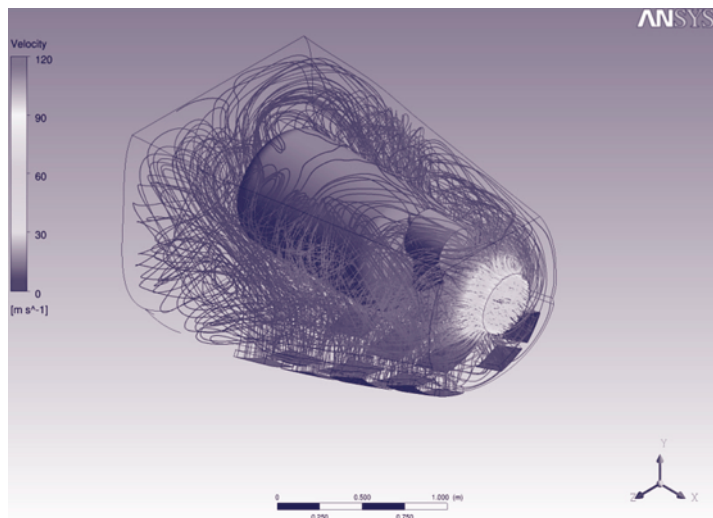


Figure 5

CFD simulation of the air flow through an array of heat-exchangers and inside an aircraft tail cone; the air movement is achieved through a blower positioned at the rear of the cone (source: IMM)

Similar to the problematic condensation of liquids from permanent gases in microchannels, the evaporation of liquids in parallel, ordered microchannels remains an issue in practical systems because impurities may enter and deposit inside the evaporator causing blockage while smooth and constant evaporation is required. Though we initially developed an evaporator concept based upon a large multitude (tens of thousands) of channels of smallest dimensions in the range below $50\mu\text{m}$ as fabricated by laser ablation, practical problems with this technology forced us to move towards less ordered structures and even foam-like structures, especially because pressure drop is less of an issue for such geometries.

Three possible flow arrangements exist for heat-exchangers:

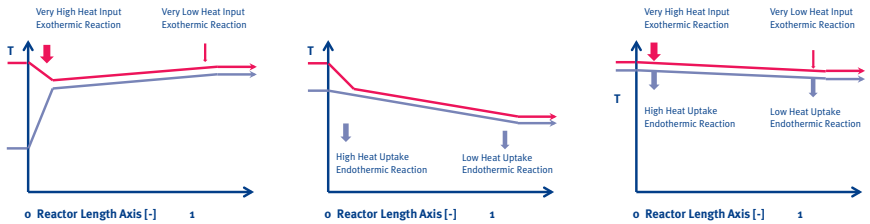
1. Counter-current flow, which allows highest efficiency as far as the heat-exchange is concerned
2. Co-current flow
3. Cross-flow

For plate heat-exchanger (micro)reactors the heat supply originates not only from the fluids entering the heat-exchanger but also from the heat consumption or heat supply of the chemical reactions taking place. From the viewpoint of the practical application of such reactors, the reactions performed therein may be classified in three groups:

1. Reactions requiring the isothermal behavior of the reactor
2. Equilibrium reactions requiring a declining temperature profile over the reactor length axis
3. Equilibrium reactions requiring an increasing temperature profile over the reactor length axis

Reactions of type 1 include exothermic reactions such as combustion, partial or preferential oxidation or Fischer-Tropsch synthesis, which require heat removal from the reactor to avoid temperature runaway beyond the durability of the reactor wall material. The second group belonging to type A are endothermic reactions that require heat supply such as steam reforming. Obviously the combination of endothermic with exothermic reactions is feasible in such a heat-exchanger. The graphs below show the principal temperature profiles achieved in such reactors, which have to be operated as co-current heat-exchangers to achieve conditions as close to isothermicity as possible (5-8). They can be operated as (a) co-currently cooled reactors for exothermic reactions, leading to an increasing temperature profile, (b) co-currently heated reactors for endothermic

reactions, leading to a decreasing temperature profile or (c) co-currently operated reactors coupling an exothermic with an endothermic reaction, which also leads to decreasing temperature profiles in most cases because the exothermic reactions are normally faster. However the temperature drop is usually less than in case (b):



Type 1 Reactions

(a) cooled exothermic reaction

(b) heated endothermic reaction

(c) coupled endothermic/
exothermic reactions

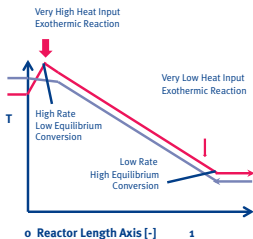
The extent of the temperature gradients inside the reactors obviously depends on the heat capacity flows of both gas streams, while the excellent heat transfer in microchannels enable the quick equalization of large temperature gradients between the fluid and the wall. However, a slightly declining temperature profile is not a practical problem in a hydrocarbon reformer especially when higher hydrocarbons are the feedstock because the feedstock is almost completely converted to light hydrocarbons, carbon oxides and hydrogen close to the reactor inlet. Therefore a slightly lower reaction temperature towards the reactor outlet does not affect catalyst activity and stability because conversion of light hydrocarbons is less demanding for the catalyst. A lower temperature towards the reactor outlet even reduces the carbon monoxide content in the product through the equilibrium conversion of the water-gas shift reaction. A lower reaction temperature, however, favors methane formation owing to the equilibrium of the methanation reaction.

Efficient cooling of exothermic reactions can also be achieved through evaporating and superheating liquids. The reactor then shows a similar temperature profile compared to the coupling with an endothermic reaction (1c), so long as heat supply and demand are well balanced.

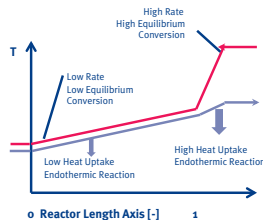
As far as the equilibrium reactions of type 2 are concerned, the water-gas shift reaction is a prominent example, and the focus of a number of numerical investigations in the past. Another case is the methanation reaction, which is the reverse reaction of methane steam reforming. This reaction type requires

a counter-current operation because low reactor temperature is desired at the reactor outlet to shift the equilibrium of the reactions in a favorable direction. In many cases the heat of reaction leads to a temperature crossing of coolant and hot gas flow, but only in cases where the coolant heat capacity stream does not significantly exceed the heat capacity stream of the hot (reactive) gas flow. Alternatively, an endothermic reaction could be operated on the cooling gas side, but this has never been realized to date according to the knowledge of the author.

Equilibrium reactions of type 3, such as reverse water-gas shift, require an increasing temperature profile, which is achievable by countercurrent operation of a heating flow. Alternatively, an exothermic reaction could supply the heat in counter-current flow.



Type 2 reactions; declining profile



Type 3 reactions; increasing temperature profile

It is obvious from theory that cross-flow arrangements result in a less efficient heat-exchange process. However, requirements such as low pressure drop might lead to such a heat-exchanger design for practical applications, as is realized in the cooling system of every automobile. However, there are other reasons for choosing the cross-flow design in other applications.

Few examples are published in open literature dealing with the dynamic simulation of (microstructured) fuel processors. Most of this work deals with the development of suitable start-up strategies. It is difficult to achieve short start-up time with a chain of reactors heated with hot gas from the inlet of the chain. The small channel dimensions of ceramic or metallic monoliths or plate heat-exchangers create excellent heat transfer and consequently all heat is removed from the heating gas by the cold reactor. It therefore takes a long time until the next component downstream in the chain substantially increases its temperature. This apparently is a time-consuming procedure, which bears the danger of overheating the first reactors to temperatures exceeding the stability of the catalysts inside. More sophisticated start-up procedures rely on in-situ production of heat in

each component of the chain or on distributed parallel heating, which is feasible when plate heat-exchanger technology is applied. Pre-heating of plate heat-exchanger reactors in a short time requires large volume flows through the device, which is not feasible in the 'regular' flow paths but requires a third cross-flow path that carries open ducts for pre-heating (9). Figure 6 shows a LPG fuel processor composed of steam reformer, water-gas shift reactor and evaporator, all of them carrying open cross-flow paths for pre-heating.

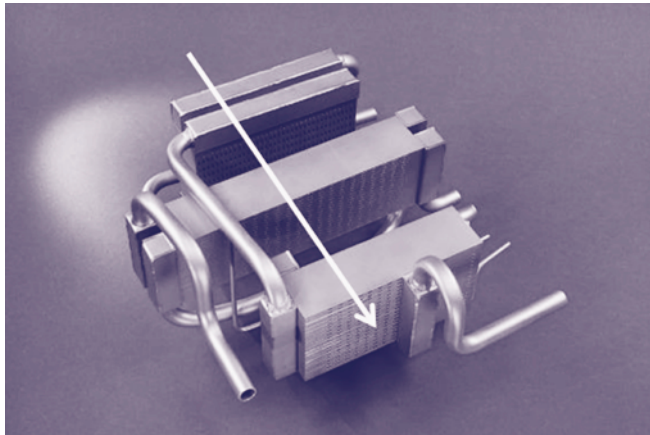


Figure 6

LPG fuel processor for a 250 W fuel cell based upon microchannel plate heat-exchanger technology; the reactors carry cross-flow channels as a third flow path for pre-heating; the flow direction of the heating gas is indicated by the white arrow (source: IMM)

The practical design of plate heat-exchanger reactors requires not only the consideration of the specific behavior of the reactor and of the catalyst under conditions of full and partial load but also their dynamic behavior.

While the reduction of the flow rates (turn-down) obviously improves the performance of a water-gas shift heat-exchanger reactor (10), the opposite is the case for reactions such as methanol steam reforming over conventional Cu/ZnO catalysts and preferential oxidation of carbon monoxide over Pt-type catalysts. Methanol is preferably adsorbed at the catalyst surface and converted. As soon as the conversion is almost complete, the catalyst promotes another reaction, namely reverse water-gas shift, which leads to the excessive formation of carbon monoxide under conditions of partial load for this catalyst type.

A similar phenomenon is observed in preferential oxidation reactors in an oxygen deficient atmosphere, especially under conditions of partial load, because most catalysts for preferential oxidation of carbon monoxide have at least some activity for water-gas shift and its reverse reaction. Therefore over-sizing the reactor incurs the danger of impaired conversion and, unfortunately, the same applies for partial load of the reactor. Because the concentration of carbon monoxide tolerated by low-temperature fuel cells is usually 100 ppm or less, even low catalytic activity for reverse water-gas shift becomes an issue. In this case improved heat management through integrated cooling helps to improve the reactor performance.

Another important parameter of the design of microstructured reactors is the proper choice of channel/ structure dimensions so as to gain optimum pressure drop and catalyst utilization. Baier et al. calculated the optimum channel size for water-gas shift reactors needed to avoid diffusion limitations. Under realistic flow conditions (Volume Hourly Space Velocity, VHSV) for a channel height of 200 μm no diffusion limitations were found, while severe diffusion limitations were observed for a channel height of 800 μm , which corresponds with the experimental observations of other authors (11). However, a trade-off is required between catalyst utilization and pressure drop in a practical system (12). Increasing the channel height from 200 μm to 800 μm doubles the reactor length required to achieve the same carbon monoxide conversion.

Reforming all kinds of fuel is carried out with either steam (endothermic steam reforming), air (exothermic partial oxidation) or both gases (oxidative steam reforming). In the latter case the feed composition can be chosen in such a manner that energy consumption and generation are balanced and the reactor becomes self-sustaining (autothermal reforming). Consequently, autothermal conditions are usually chosen in the event that ceramic or metallic monoliths are applied. A drawback of autothermal reforming is the hot spot formation at the reactor inlet, which causes catalyst stability problems that emanate from sintering of the active species and loss of specific surface area of the catalyst carrier. Simulations (13-15) confirmed, that steam reforming has higher system efficiency compared to autothermal reforming, when the hydrogen contained in the anode off-gas is combusted in an integrated heat-exchanger reactor and the heat is utilized to raise the steam required for the process. For a methane steam reforming fuel processor more than 15% higher fuel processor efficiency was gained by these means as verified by experiments (16). Other numerical simulations revealed more than 80% savings of reactor volume and more than 99% savings of catalyst mass when comparing tubular fixed bed technology to

catalyst coated plate heat-exchangers (17), which seems to be rather optimistic when compared to similar calculations of other authors (18). However, all the calculations promise benefits for small fuel processor technology through the application of plate heat-exchanger and microreactor technology.

Dynamic simulations of complete systems of microstructured reactors and heat-exchangers are rare in public literature (19). We investigated an ethanol fuel processor with a thermal output of 65 kW, which is comprised of a microchannel ethanol steam reformer operated at 10 bar, a microstructured water-gas-shift and several heat-exchangers and coupled evaporators/catalytic burners as balance-of-plant. The development work included static and dynamic simulations applying ASPEN plus and ASPEN Dynamics and the development of a control strategy for the fuel processor. The dynamic interplay of the different components in the system is determined by the thermal mass of the components and the effects of changing feed flow rates through load changes. It took about 1 h to return to stable operation after such load changes. The time response of the system was determined by (a) small time constants for the species flows (instantaneous in the model) and (b) large time constants by storing and releasing heat into and from the components respectively. The temperature of the process streams did not change significantly during the load changes, a maximum deviation of ± 10 K being observed. The mass flow rates of the new operating points were achieved practically without any delay while the volume fraction of hydrogen in the process streams was affected to only a small degree.

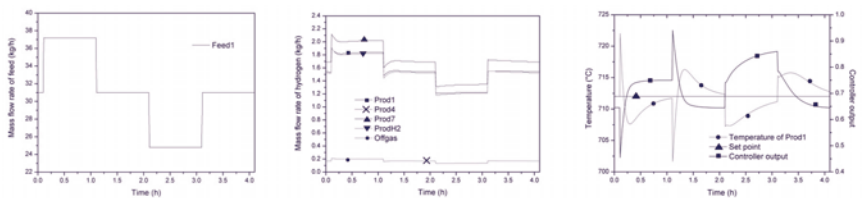


Figure 7

Mass flows (left) and temperatures of the gas flows (right) of a 65 kW_{th} ethanol fuel processor investigated by dynamic simulations of Kolb et al. (19)

Fuel cell systems operated with reformat instead of pure hydrogen do not completely consume the hydrogen contained in the reformat. A significant amount of hydrogen, usually about 20%, leaves the fuel cell anode unconverted. The fuel processor efficiency is improved if this hydrogen is fed back to the fuel processor to provide energy for the reforming process or to raise the steam required. This energy demand does not exist in the case of autothermal reforming.

Figure 7 shows the system design of a diesel fuel processor based upon steam reforming developed within the scope of a European project. As described above, the anode and cathode off-gases were fed to the catalytic afterburner, which was integrated into the steam reformer reactor in this case. Both gas flows were utilized as coolants before they entered the afterburner, the anode off-gas as coolant for the reformer off-gas before it entered the water-gas shift reactor, the cathode off-gas for cooling the water-gas shift reactor itself in a counter-current flow arrangement as described above. Another back-coupling implemented in the system is the evaporation of the steam required for the reformer feed, which is mainly supplied with heat by the off-gas of the afterburner integrated in the steam reformer. After individual component tests, we assembled and operated the system as shown in figure 7. The cathode off-gas flow could not be set to sufficiently high values because the water-gas shift reactor was then cooled too much. This created high AFB temperatures. Consequently the AFB off-gas flow was too small and insufficient to raise enough steam in the evaporator, requiring higher steam addition from the PrOx reactor, which decreased the temperature of the reformer feed. So more air had to be introduced into the reformer feed to regain a higher temperature. However, this did not completely solve the problem and left the reformer temperature too low, causing a release of unconverted HC, which damaged the downstream components, namely the PrOx reactor. The high degree of back coupling of the current system design created a situation whereby the system could not be operated at the design points, which was not obvious from the beginning but rather originated from factors that were difficult to precisely predict, such as heat losses to the environment, by calculations or simulations.

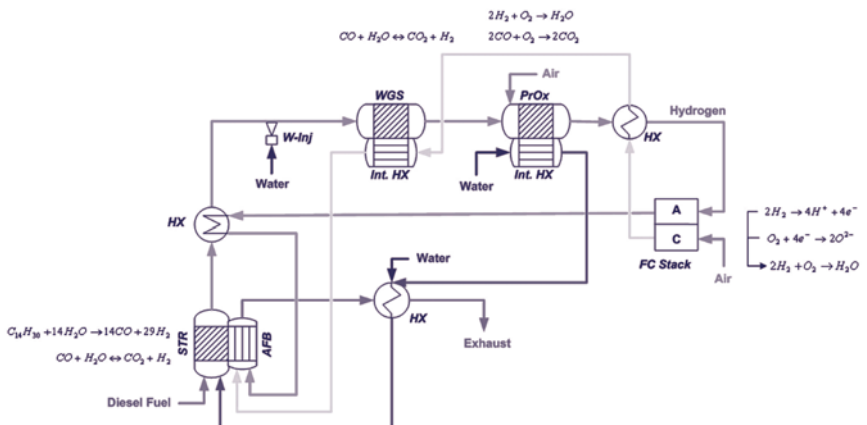


Figure 8

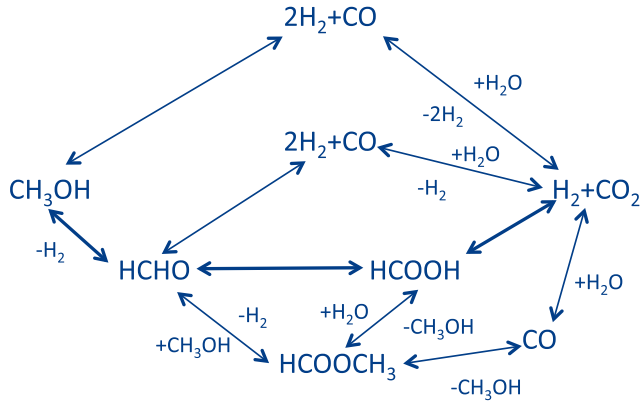
Simplified flow scheme of a diesel fuel processor/ fuel cell system (source: IMM)

Aspects of catalyst design and durability

Operating conditions are less well defined in small-scale power generation devices and de-centralized fuel production plants compared to industrial-scale plants, especially during start-up and shut-down. Therefore catalyst technology suited for smaller-scale systems needs to be more robust against exposure to air and moisture compared to catalysts designed for large-scale industrial plants that tend to be operated under constant conditions for several years. For example, during the start-up of a small system, reduction of the catalyst with hydrogen, which is frequently applied on an industrial scale, is not feasible because no hydrogen is available. Indeed, it might even be required to expose the catalyst to an oxidizing atmosphere in order to pre-heat the reactor internally through hot-air or combustion gases without impairing catalyst activity. The catalyst formulation and the reactor design determine the start-up strategy of fuel processors of smaller than industrial scale.

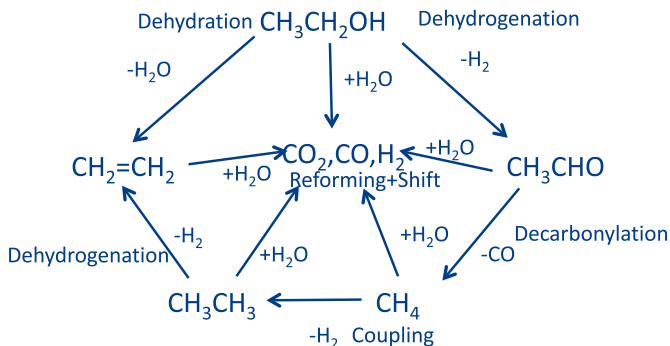
Another specific feature of microstructured plate heat exchanger reactor technology is the low catalyst mass per reactor volume, which can be introduced into it. This drawback is counter-balanced by a much better utilization of the catalyst owing to the improved heat and mass transfer in the thin catalyst layers coated onto the channel walls. Consequently catalysts of higher activity are required to compensate the lower catalyst mass. The catalyst costs are less of an issue compared to fixed bed reactors, for example, owing to the improved utilization. Therefore formulations of higher activity such as precious metals have advantages despite their higher cost. Automotive exhaust systems, which rely on precious metal catalyst technology, are a widespread application with similar requirements and technical solutions.

Methanol is an attractive fuel for low-power applications because the reaction temperature required for steam reforming is limited to values below 400°C, which in turn minimizes heat losses from smaller-scale systems. The reaction, though fairly simple at a first glance, is part of a complex network of reactions (20), and it is not yet clear which reaction pathway is followed, especially when novel catalyst formulations (21) are concerned:



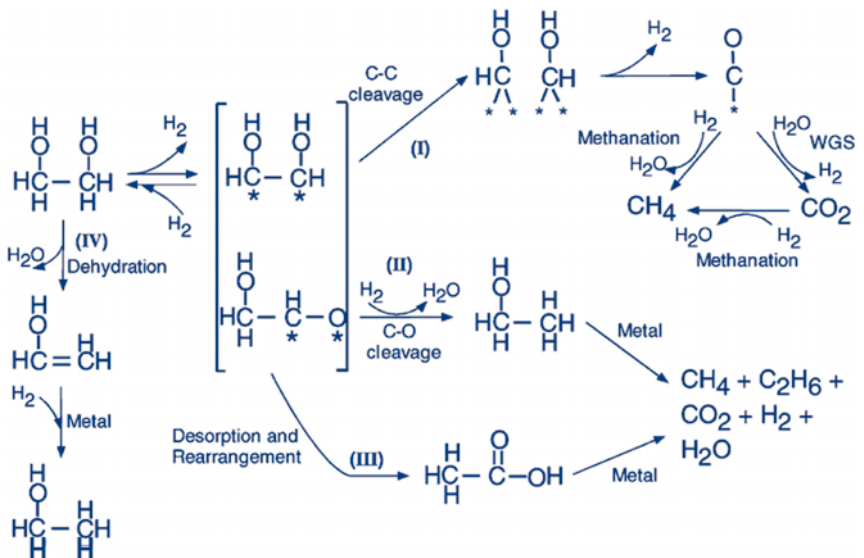
However, recent investigations (22) support the assumption that the reaction follows the pathway indicated by the bold arrows at least for $\text{Pd}_2\text{Ga}/\text{Ga}_2\text{O}_3$ catalyst. The presence of a few ppm of formic acid in the product of a methanol reformer larger than laboratory scale under certain operating conditions when operated with $\text{Pt}/\text{In}_2\text{O}_3$ encourages us to assume that a similar pathway might be followed by this catalyst type. The formation of byproducts is a critical issue in the reaction system because the operating temperature is limited (300°C over Cu/ZnO catalysts and about 400°C for Pd/ZnO and $\text{Pt}/\text{In}_2\text{O}_3$ to maintain the catalyst durability and to minimize carbon monoxide selectivity, respectively).

Another renewable fuel is bio-ethanol. Its conversion by steam reforming has a reaction scheme of similar complexity leading to numerous byproducts all impairing the efficiency of the reforming process and the durability of a fuel cell connected to the reformer (23):



The situation is different for ethanol reforming compared to methanol, because the byproducts such as ethylene and acetaldehyde are formed in parallel at least over noble metal (rhodium) catalysts especially at lower reaction temperature, while the decomposition of these byproducts can be easily achieved at higher reaction temperature. However, higher reaction temperature is required anyway to suppress the methane formation through the methanation reaction.

Higher alcohols are interesting as both sustainable fuels and potential hydrogen sources. Glycerol is readily available from biodiesel production in a quality less suited for pharmaceutical and cosmetic applications without further cost-intensive purification, which creates the need for other applications. Ethylene glycol can be produced directly and efficiently via catalytic hydrogenation of cellulose or cellulosic biomass derived oxygenated compounds (24). Cellulose, as the most abundant component of biomass (accounting for 35-50%), is considered a promising alternative to fossil resources. In addition, ethylene glycol is the most abundant molecule of compounds derived from the catalytic conversion of cellulose, accounting for more than 70% of cellulose derivatives, making ethylene glycol a renewable energy carrier readily available when cellulose is converted in substantial amounts. Compared to the schemes discussed above, the reaction network of the ethylene glycol steam reforming is even more complex:



Its catalytic conversion is limited to a narrow temperature window. At lower temperatures coke formation deactivates the catalyst while at higher temperatures the homogeneous decomposition creates coke as well, which makes the operation of the reforming process challenging and requires high oxygen mobility on the catalyst surface.

The impurities contained in renewable fuel sources such as cellulose, biomass and biogas, all of which have potential as future hydrogen sources, require novel, poison resistant catalytic formulations. Another novel process route under current investigation is the utilization of carbon dioxide from biogas through its conversion to natural gas (methane) by methanation. In particular, the heat management of the exothermic methanation reaction has considerable potential for improvement through the application of microstructured plate heat-exchangers, which promise compact solutions at moderate catalyst cost. The same demand for poison resistant catalysts applies consequently for downstream processes in the reformer, e.g. water-gas shift.

The determination of kinetic expressions to quantify the behavior of such novel catalyst formulations is preferably performed in gradient-free (differential) reactors. Gradient-free recycle reactors allow the determination of kinetics at higher conversion, i.e. closer to the practical operating conditions of the process. The introduction of catalyst coatings into microreactors removes intraparticle diffusional resistance from the reaction.

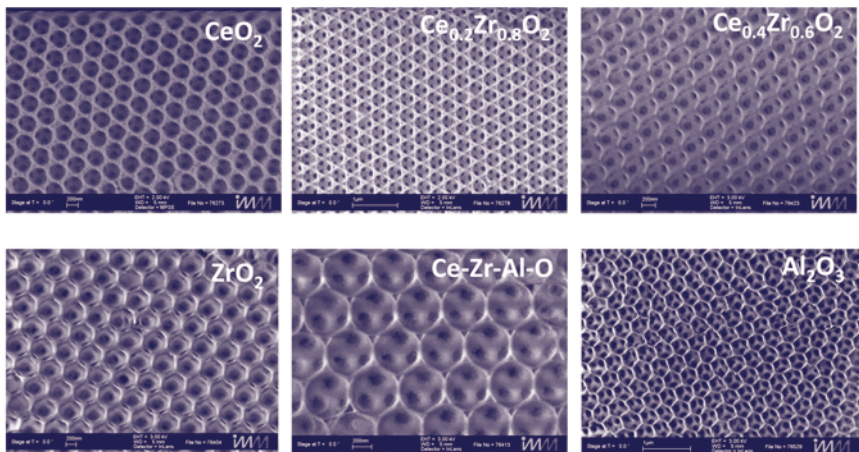


Figure 9

Catalyst carrier material synthesized as inverse opal structure (source: IMM)

Efforts to further increase the catalyst's accessibility through synthesis of open geometries such as inverse opals (25) (see figure 9) suffer from the obvious drawback of the low mechanical durability of such coatings.

The advantages of concentration-controlled operation of a recycle reactor for the investigation of complex reaction networks and the determination of deactivation kinetics of catalytic systems (see figure 9) (26), a technique abandoned for a long time, in conjunction with the utilization of microchannels and novel, fast analysis instruments of higher precision, promises to create novel insights into the behavior of catalytic systems.

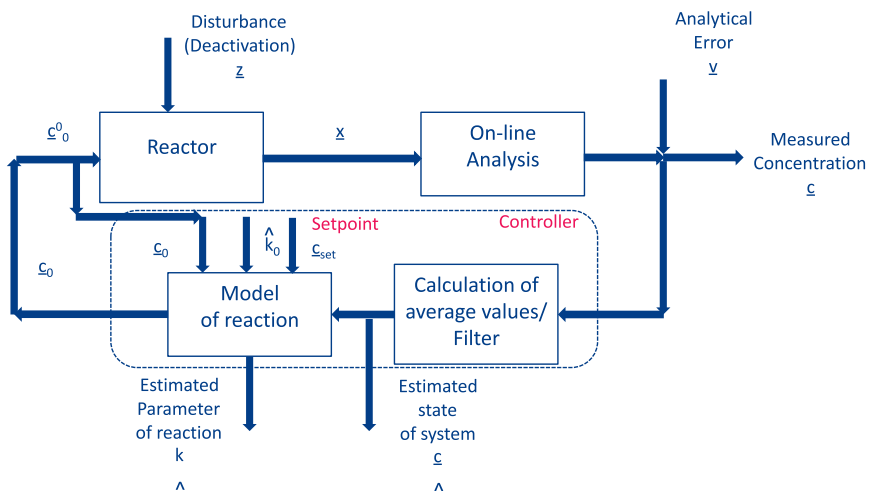


Figure 10

Principle of the concentration-controlled recycle reactor (26) (source: Elsevier)

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