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Introduction – R&D methanol reformer for onsite H₂ supply

The objectives of this work package are the R&D of a methanol reforming system with higher outlet pressure, capacity and purity as well as reduced costs providing low cost hydrogen fuel suitable for LT-PEM fuel cells in the addressed markets. This is to be verified by conducting of laboratory testing of the developed components and complete system. In order to reach these objectives we have been through the following tasks:

Task 3.1
Definition of suitable catalyst with improved performance & reduced costs

Concerning the active material within the catalyst formulation there are two catalyst types which are considered for the methanol steam reforming, namely copper-based (Cu) and precious metal-based (PM) catalysts. Main issues for the selection are efficiency, lifetime and costs.

Copper-based catalysts are state of the art for steady state methanol steam reforming systems on an industrial scale. The main advantages are the high activity at moderate temperatures of around 250 – 300 °C and the relatively low costs. The main disadvantages of copper-based catalysts are their high sensitivity for deviations in the operating conditions, their low cycle stability and the high degradation rate. Copper based catalysts can lose about 1/3 of their activity within 1.000 h of operation even under ideal operating conditions. The small temperature range in which the catalyst shows high activity (250 °C - 300 °C) is followed by a range in which the catalyst has a highly accelerated degradation rate (300 °C - 320 °C) and above 320 °C the life expectancy of the catalyst is reduced to a few hundred ours. Another major disadvantage for small- and medium sized units is that Cu-based catalysts are oxidised (CuO) as delivered from the supplier and have to be activated at reducing conditions within a temperature range of about 200 - 250 °C requiring a reducing agent, e.g. H₂. Once the catalyst is activated for the methanol reforming it is pyrophoric (sensitive for O₂). To keep air or oxygen out of the catalyst zone of the reforming reactor an inert purge gas is needed for start-up, shutdown, standby or down-time of the reformer system. Due to these effects much effort has to be taken to precisely adjust the temperature in the complete reactor not only during steady state operation but also especially during transition states (e.g. heat-up).

Precious metal methanol reforming catalysts can be used for various applications especially if high power densities and frequent cycling is required. They show high temperature stability in a range of 200 °C - 1.000 °C and also very high activity for methanol steam reforming without any treatment before utilization. The often-discussed disadvantage of precious metal catalysts is the high and volatile price of precious metals. On the other hand the higher activity and therefore higher space velocity (GHSV) reduces reactor size and the required total amount of precious metal compared to copper-based catalysts. Additionally it has to be taken into account that precious metal catalysts can be recycled after use. More than 98 % of the remaining precious metals can be recovered from catalysts for chemical processes and over the entire product lifetime.

Considering the above stated advantages and disadvantages for the two types of catalysts, precious metal catalysts are the preferred type for developing the methanol steam reformer system for the given application in this project. Especially the required pre-treatment with the resulting sensitivity to oxygen and the small available temperature range argue against copper-based catalysts.

Samples of the suggested precious metal catalyst formulation, provided by Catator, have been tested under defined conditions including steady state operation and cycling operation in a special catalyst test rig at ZBT. As can be seen in Figure 1, stable results could be obtained. Even after about 750 hours of operation no significant degradation or drop in performance could be detected.
Results and conclusions

The choice of a precious metal (PM) catalyst simplifies the design and operation conditions of the developed reformer system. The PM catalyst shows high activity and stability during the performed cycling and life time tests of the catalyst.

Task 3.2
R&D of a pressurized reformer system for onsite H₂ supply

There are a number of reactions to take into consideration in fuel processing. The highest hydrogen yield is obtained when using pure Steam Reforming (SREF) where a mixture of the hydrocarbon feed stock and steam is reacted over a suitable catalyst. The hydrogen concentration is much higher in SREF processes (about 70%) whereas processes including Auto Thermal Reformation (ATR) or Catalytic Partial Oxidation (CPOx) (exothermal steam reforming conditions with addition of oxygen/air) give a lower hydrogen yield. The developed reformer system in this project is based on a SREF-process.

Cator has during the last two decades been heavily engaged in the development of novel catalyst-and reactor systems. The main focuses have been directed to process intensification, i.e. to increase the output of a chemical reactor system per unit volume. The design solutions are especially favorable in cases where the reaction is performed under simultaneous heat transfer, like in combustion and fuel processing.

A cutting edge design must be described by three characteristics in general: low cost, high durability and top performance. The focus of the development work for a pressurized reformer system, called Optiformer, has been on following items:

- It is essential to use ordinary construction materials in order to converge to a realistic price level.
- It is of great importance to avoid thermo-mechanical issues often found in too rigid structures comprising stiff building blocks.
- It is important to provide a highly integrated unit comprising all balance-of-plant components like heat exchangers, evaporators, recuperator, etc. in a compact and lightweight architecture.
The Optiformer concept is based on a coil-concept, where a SREF catalyst is inserted into a coiled/helix shaped tube. The basic idea is that there should be a close coupling between the exothermic and the endothermic reactions from a heat-transfer point of view. The Optiformer consists of a number of individual parts tied together in an integral design, as shown in Figure 2 (left).

- Helix shaped coil containing the SREF-catalyst (SREF=steam reforming)
- Central catalytic burner with internal mixer, 2nd cylindrical mesh, diversion plate and ignitor
- Helix shaped tubular arrangement for steam generation
- Exhaust gas recuperation
- Water-gas-shift section (WGS)
- Air cooled and insulated reactor vessel

The commissioned reformer system including all balance of plant components is presented in Figure 2 (right).

**Results and conclusions**

The capacity of the reformer unit is 10 Nm³/h of H₂ at an operation pressure of 9 bar (g). The overall dimension of the SREF reactor is ca. ø 312 x l 415 (mm) and its weight is ca. 50 kg. The reformate gas composition is: CO = 3.1%; CO₂ = 22.6%; CH₄ = 1.26%; H₂ = 72%. The reformer system fulfils the main technical targets set in the project.

**Task 3.3**

**R&D of suitable reformate purification unit**

State of the art pressure swing adsorption plants (PSA) have typically industrial scale with high outputs up to several 100,000 m³/h of pure hydrogen and operation pressures in the range of 10 – 30 bar. Medium to small hydrogen production plants as addressed within LiquidPower (10 m³/h) commonly apply alternative purification technologies like catalytic preferential oxidation or membrane separation which either can only convert single undesired components like CO in the reformate or have to employ very costly materials like Pd/Ag-membranes. Furthermore smaller plants especially small reformers commonly do not operate at elevated pressures. Pressurized
reforming as described above now enables the application of the pressure swing adsorption as purification unit.

The main challenge for the PSA development within LiquidPower was to demonstrate a downscale of the PSA technology to the defined output range of about 10 m³/h (30 kW) and simultaneously to gain the required purity within the given parameter range namely the relatively low pressure in the range of < 10 bar which is limited by the maximum pressure for the pressurized reformer. In order to meet the economic requirements the development focused on the use of commercially available adsorbents, materials and components. Therefore common standard molecular sieves and activated carbon materials have been applied for adsorption. However the functionality had to be confirmed for the non-industrial scale application.

H₂-purity will be evaluated by measurement of carbon monoxide CO as the leading component within the expected products. Further performance indicators are the recovery rate as well as the productivity.

The consortium agreed to add the development of a small scale stand-alone PSA-system with comparable settings in the range of 0.35 kW (H₂ output) to the original project plan. Based on this small scale PSA-system required components have been identified, initial laboratory tests have been performed and the PSA-process steps have been validated. The characterization took place with predefined synthetic reformate gas at this stage of development.

The PSA utilizes a four bed set-up according to the so called Lofin PSA process. Combining the four separate batch operations in an appropriate adsorption cycle comprising up to 9 discrete steps like pressurization, adsorption purge and regeneration enables a continuous hydrogen production. The steps, a typical pressure curve for one adsorber as well as the resulting gas composition for the complete small scale PSA are presented in Figure 3. It can be noted that within one full cycle (about 12 minutes) a stable H₂-purity with CO < 3 ppm can be achieved at 7 bar adsorption pressure (step 3).

![Figure 3: Adsorption cycle for one column, gas composition and pressure as a function of time](image)

Summarizing the results from the small scale PSA system shows that parameter changes of pressure, load and cycle time affect the performance of the PSA-system. Increased pressure is advantageous.

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1 According to ISO 14687-2 „Hydrogen fuel – product specification, Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles“ CO serves as leading component (canary species) for the evaluation of the purity of H₂ derived by steam reforming and PSA
for the purity and the productivity. Increasing the load results in a downgraded purity but has advantages for the recovery and productivity. Whereas cycle time elongation affects the purity negatively, the recovery positively and has no impact on the productivity. System optimization is therefore mainly a trade-off between high purity and high recovery.

The main findings from the small-scale test unit were used as input for the design of the full scale PSA unit. The general dimensions as well as the proportions of the adsorbent layers have been transferred. The P&I-diagram has been fixed and balance of plant component specifications have been determined. An accompanying work package was the detailed elaboration and documentation of a possible path of a CE conformity assessment which has to be performed by a third party on the way to commercialization.

Results and conclusions

The resulting main design specifications of the PSA system are presented below and in Figure 4.

- Nominal output: \( P_{\text{H}_2} \sim 30 \text{ kW}, V_{\text{H}_2} \sim 10 \text{ m}^3/\text{h} \)
- Design pressure: \( p_{\text{max}} = 12 \text{ bar} \)
- Volume: \( 4 \times 110 \text{ l} = 440 \text{ l} \)
- Weight adsorber columns: \( 4 \times 240 \text{ kg} = 960 \text{ kg} \)
- \( h \times w \times d \) of the rack: \( 3.0 \text{ m} \times 1.8 \text{ m} \times 1.2 \text{ m} \)

![Figure 4: PSA set-up, adsorbent layers and column-arrangement](image)

The PSA-system has been assembled at the ZBT laboratory and mounted into a designated housing. The set-up is dominated by the four adsorption columns (flange design, stainless steel tubes). Furthermore numerous industry standard valves and instruments have been installed at the top and the bottom of the columns to facilitate the cycling operation, see Figure 5.
**Task 3.4**  
**Construction of laboratory test system and conduction of tests**

The two developed sub-systems have been integrated to a complete fuel processor system as presented in Figure 6. Main efforts of this integration work have been the preparation of the infrastructure, the implementation of all mechanical and electrical interfaces, the development of the system control, the development and implementation of an appropriate safety concept with focus on explosion protection at the designated site as well as the stepwise functionality test of all safety devices, components and subsystems. The fuel processor system is approved to be in operation according to the German industrial safety regulations including ATEX directive, pressure equipment directive, gas appliance directive et cetera. The semi-automated sequence control enables systematic characterization especially of the PSA operation in order to check the system performance against the idealized small scale PSA results and overall targets.
Results and conclusions

Characterization of the fuel processor system included the determination of the start-up time, check of the reformate gas (composition, volume flow, stability) and finally the performance of the purification unit indicated by the hydrogen purity, recovery and productivity. As the degree of freedom for the coupled system is restricted in some points the described trade-off between high purity and high recovery has been addressed mainly by varying the adsorption cycle time. Figure 7 shows typical cycling operation of the PSA in combination with the methanol reformer. In contrast to the idealized small scale measurements it could be seen that operation and result parameters like pressure, gas-composition and flow were subject to significant fluctuations. Additionally the pressure drop in the process chain has been higher than predicted thus the outlet pressure of the PSA is in the range of 4 to 5 bar and the adsorbent capacity could not be fully utilized. Nevertheless a CO fraction of 25 - 50 ppm and an average H\textsubscript{2}-volume flow of 110 l/min corresponding to around 20 kW could be measured in the purity-recovery-optimum operation which leads to a recovery of about 57 % and a productivity of 0.26 l\textsubscript{H2}/(min * l\textsubscript{ads}).
The reformer operation revealed optimization potential with regard to pressure and temperature fluctuations. An optimized temperature control would enable an independent stable long term operation of the reformer. Reducing the pressure drop in the process chain by eliminating and redesigning components enables the utilization of the adsorbent capacity which finally enhances the hydrogen purity. In order to enhance the hydrogen recovery the inevitable H₂ losses caused during pressurization and purge steps have to be minimized. Therefore the alignment of the subsystem-capacities seems to be a key factor. As the absolute volume of the PSA is too high for the maximum reformate production rate either the reformer capacity can be increased by a factor of around 1.2 or the PSA has to be downsized vice versa. Finally continuous hydrogen flow and stable PSA outlet pressure can be obtained by the use of a suitable hydrogen buffer tank as a source for hydrogen in the steps pressurization and purge.

**Task 3.5**

**Continuous manufacturing & cost evaluation**

The target in the project was an outlet price for produced H₂ of around 4 €/kg. The subsystems have been evaluated separately by means of cost groups. Numbers have been added for the complete fuel processor system with the result that at the current state of development and assuming that up to 10 units will be produced per year the specific capital expenditure (CAPEX) will be in the range of 4000 €/(m³*h). The economy of scale has been evaluated which leads to a price reduction of about 40 % for a volume of 1000 units per year. Though the cost estimations show that the CAPEX is quite high it is yet possible to produce pure hydrogen with a competitive price. It could be found that CAPEX only corresponds to about 20-30 % of the outlet price for H₂. The dominating share is the price of the fuel methanol as main operational expenditure (OPEX) which varied from 0.24 to 0.45 €/kg in the last 3 years. The target can be reached if the price for methanol is in the range of 0.25 €/kg even for a high CAPEX as can be observed in Figure 8.
Conclusion WP3

The technical target in the project was the development of a fuel processor system that can operate at a high pressure (target 7-9 bar) and with a high capacity (target 30 kW H₂) and with a production of pure hydrogen (target 99.9 % H₂). The functionality of the full scale laboratory test system has been demonstrated. The evaluation of the results shows plausibility with theory and with idealized small scale PSA system tests. Although the defined targets could not be reached in every point especially pressure and capacity this work package terminates with a successful demonstration of a methanol fuel processor system of the 20 - 30 kW class. Significant optimization potential has been described in order to reach the defined targets with a next generation fuel processor.

Finally the cost evaluation shows that the operational expenditure has the dominant influence on the hydrogen price and that a target of 4 €/kg can be reached with the current system set-up assuming that the methanol price is in the range of 0.25 €/kg even with relatively high capital expenditure.