Performance Comparison between Autothermal and Steam Reforming in a Diesel Fuel Processor for a PEM Fuel Cell

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GENERAL ASPECTS

Hydrogen and fuel cells are widely seen as key solutions for the power demand of the 21st century, enabling clean and efficient production of power and heat from a range of primary energy sources. Hydrogen based energy system can build bridges to the future, through a cost-effective planning and efficient transition. In the long term hydrogen-based economy fossil fuels energy sources will be reduced to a minimum and substituted by renewable energy sources. To govern the transition, in the short term hydrogen will be produced using existing energy systems based on different conventional primary energy sources by forcing the transformation processes with higher and higher energy efficiency. Following this pathway, there are, for example, large efforts in exploring the on-board reforming technologies, which would thus avoid the actual lack of hydrogen infrastructure and related safety issues. From this viewpoint, the present work deals with the comparison between two different 10 kW_e Fuel Processors (FP) systems for hydrogen-rich fuel gas production starting from diesel oil, based respectively on Autothermal (ATR) and Steam Reforming (SR) process and related CO clean-up technologies; the obtained hydrogen rich gas is fed to the PEMFC stack of an Auxiliary Power Unit (APU). Based on a series of simulations with Matlab/Simulink, the two systems models were compared in terms of efficiency, heat recovery capability, water balance and process scheme complexity. For sake of simplicity, cetane was assumed in this work as the representative compound for the diesel fuel oil.

THE FUEL PROCESSOR

The Fuel Processor (FP) is the hydrogen production system directly on board of the vehicle: the diesel oil reforming primary step is followed by a series of other catalytic steps suitable for both increasing the H_2 amount in the reformate gas and CO removal. Hydrogen production by diesel oil can be carried out mainly by two reactions: steam reforming (SR: C_{16}H_{34} + 16H_2O \rightarrow 16CO + 33H_2) [1] and partial oxidation (POX: C_{16}H_{34} + 8O_2 \rightarrow 16CO + 17H_2) [2]. The SR reaction is endothermic, thus it needs external heat addiction; conversely, the POX reaction is exothermic but it produces a gas containing less hydrogen. The third possibility is to combine in several ratios the two SR and POX reactions, in order to perform an autothermal reforming (ATR) process. In this particular case, a suitable O_2/H_2O ratio makes the reaction isothermal and self-sustaining.

The main reactor of a FP system is the reformer, which produces a hydrogen rich gas. Most studies on ATR catalyst suggest the contemporary use of steam-reforming [3] and oxidation reactions [4, 5]. The commercial steam-reforming (SR) catalysts are supported on Al_2O_3 and MgAl_2O_4, but also other supports have been proposed [5]. The two reactions take place at high temperature (700-800°C). In both cases (ATR and SR), the reformate gas mixture contains large CO quantities, a poison for the electro-catalysts of actual PEMFCs anode, able to operate with no more than 10 ppm of CO. For this purpose it is necessary to adopt,
immediately after the hydrogen production unit (ATR or SR reformer), a CO clean-up system. This unit generally consists of two water-gas shift reactors (WGS: \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \)) which reduce the CO concentration down to 3,000 ppm [6] thanks to water addiction; moreover, they simultaneously produce further hydrogen. A final reactor of CO preferential oxidation (CO-PROX: \( \text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2 \)) is capable to completely remove the CO under the limit of 10 ppm [7] thanks to the addiction of a small air flow rate, but reduces a bit the total amount of hydrogen due to its concomitant unavoidable direct oxidation. The WGS reaction is commonly carried out in two stages: the first one operating at high temperature (HTWGS: 350-450°C) with iron-based catalyst, the second one working with a copper-zinc catalyst at lower temperature (LTWGS: 200-250°C). The CO-PROX temperature operating range is 80-270°C.

In the performance study of a diesel FP and in particular to reach large efficiency, heat recovery assumes large importance: its maximization in fact, is mandatory to achieve top system efficiency. As a PEMFC can exploit about 80% of the hydrogen produced, the remaining part can be burned to recover thermal energy: this is a very important heat source of the system, but not the only one. The series of cascade reactors work at different decreasing temperatures: the excess heat from one reactor outlet to the subsequent reactor inlet might also be recovered. Moreover, in the FP analysis, particular attention has been paid to the water balance: water is required in the reforming reactor and for injections before the CO clean-up reactors; therefore, water needs to be recovered from the FP itself to render its balance self-sustaining.

The FP efficiency is defined as the ratio between the power of the produced hydrogen flow rate based on its lower heating value (LHV) and that of the fed fuel flow rate based on its LHV. The total system APU efficiency is indeed defined as the ratio between the electric power generated and that of the used fuel based on its LHV. For a PEMFC the FC efficiency could be considered equal to 50% (anode efficiency equal to 80%).

**Autothermal Fuel Processor Model**

![Scheme of the diesel FP based on ATR.](image)
The scheme of FP based on ATR is shown in Figure 1. The FP model consist of a diesel-reforming unit, a HTWGS unit, a LTWGS and a CO-PROX unit. Moreover, between the Reformer/HTWGS units and HTWGS/ LTWGS units there are a water injection (WI) and a heat exchanger (HX) unit, whereas between LTWGS/CO-PROX units there is only a WI. The model is completed by the afterburner (AFB) unit and the HX units for the thermal energy recovery. Molar and energy balances are solved in each block as well as in the overall system. For the diesel oil reforming, the basic assumption considers that the ATR unit converts a mixture of water, air and diesel into a hydrogen-rich stream containing H2, H2O, CO, CO2 and N2. The model assumes that the POX reaction runs to complete oxygen consumption and the SR reaction runs to complete diesel consumption. The reformer outlet gases are supposed to reach the thermodynamic equilibrium and the model evaluates their outlet temperature and equilibrium composition. Subsequently, the WGS reaction runs to the equilibrium conditions as well; the model used a typical WGS equilibrium constant [8]. The hydrogen-rich reformer outlet gas, before entering the HTWGS unit, transfers its heat to the reformer air inlet flow (the HTWGS inlet temperature is controlled by WI). The stream coming out from the HTWGS unit is cooled by the diesel fuel oil; the latter evaporates and is afterwards mixed with the steam and the air coming into the reforming section. Both the WGS reactors are modeled supposing they work isothermally and reach the thermodynamic equilibrium. The flow generated by the LTWGS must be cooled down to 150°C before entering the CO-PROX unit: a water injection in this case allows a easier and better control of the inlet temperature. The model considers a CO selectivity value in the CO-PROX block of 33% [9]. The stream coming out from the CO-PROX unit must be cooled down to 80°C before entering the FC anode side: to avoid temperature pinch points in the recovery heat exchanger, only part of the recoverable heat is used to pre-heat the ATR feed water. This one, before being completely evaporated with the hot exhaust gases from the AFB, is employed to maintain the CO-PROX reactor isothermal. The hydrogen unused at the anode side of the FC is recovered as fuel for the AFB. Summarizing, water is necessary for the ATR reactor, the two WGS reactors (in both cases to thermodynamically favor the reactions and to better control the reactor inlet temperature) and before the CO-PROX reactor (to reduce the reactor inlet temperature). For a proper overall water management, the condensed water before and after the FC anode side, and that after the FC cathode side must be collected. As the amount of these three water streams is less than the needed one, it is necessary to cool down the AFB exhaust gases with an air radiator to recover an additional water amount. A conservative temperature value of 70°C for the radiator outlet AFB exhaust gases allows to easily satisfy the overall water balance. The whole system is considered to be operated at 2 bar.

Steam Reforming Fuel Processor Model
The scheme of FP based on SR is shown in Figure 2. The SR model is similar to the ATR one, but only the steam reforming reaction takes places in this case. The SR outlet gas is in thermodynamic equilibrium. The main difference between the two situations is represented, obviously, by the reforming unit. As the SR reaction is endothermic, heat must be supplied. Since the thermal power generated by the combustion of hydrogen off-gas from the FC anode is not sufficient, a limited diesel fuel flow rate has to be burnt in the AFB, to assure the required heat to the SR unit. The best technological configuration so far available on the market allows to integrate in a single multifunctional item the catalytic AFB and the catalytic SR reactor, to maximize the heat exchange efficiency: thanks to a progressive fuel feeding along the AFB, the risk of hot spot formation is greatly reduced. Two main advantages can be thus reached: (i) the temperature profile through the AFB is almost constant; (ii) the AFB catalyst is preserved from sintering effects, due to hot spots. The remaining part of the system (HTWGS, LTWGS and CO-PROX units) has been kept very similar to the ATR one, in order to draw a comparison of the two FPs in contexts as similar as possible.
RESULTS AND DISCUSSION

Two FP models have been developed and coded in Matlab/Simulink so as to compare them in terms of efficiency, hydrogen concentration fed to FC, water balance and process scheme complexity. All the presented results refer to steady state conditions simulations.

The comparison of the total inlet molar flows (diesel fuel, air and water) is shown in Figure 3: it can be noticed that the diesel fuel demand for the ATR scheme is 2.85 mmol/s, as opposed to 2.62 mmol/s for the SR scheme. The FP scheme based on SR reactor requires less diesel fuel (-8%) and water (-11%) to generate 10 kW_e, but a higher amount of air (+21.8%). The air flow to the FC cathode has been determined assuming a cathode stoichiometry equal to 2.

![Figure 3](image-url)  
Fig. 3 Comparison of the total inlet flows for ATR (yellow) and SR (green) FPs.
The comparison of the gas flows composition (H₂, CO, H₂O, CO₂ and N₂ at the reformer outlet and FC anode inlet) is shown in Figure 4: it can be noticed that the anode side PEMFC inlet flow from the ATR system contains 36.4% vol. H₂, against 55.9% vol. H₂ from the SR one. From the FC point of view, such higher H₂ volume percentage is an advantage, allowing a performance improvement, e.g. the MEA voltage increases and therefore the number of MEAs in the PEMFC stack decreases.

![Composition comparison between ATR (yellow) and SR (green) FPs at the Reformer outlet and FC inlet.](image)

**Fig. 4** Composition comparison between ATR (yellow) and SR (green) FPs at the Reformer outlet and FC inlet.

The water recovery is easier for the ATR system (+12.2%) than for the SR one (+6.1%). The AFB of the SR system, in fact, works with very high air excess to better control the maximum allowed temperature, which can not exceed 850-900°C. As a consequence, due to the high amount of nitrogen coming out from AFB, the water molar fraction in the AFB flue gases is lower and the water recovery at the radiator outlet temperature of 70°C is therefore less.

![APU and FP efficiency comparison for between ATR (yellow) and SR (green).](image)

**Fig. 5** APU and FP efficiency comparison for between ATR (yellow) and SR (green).
The efficiency comparison is shown in Figure 5: the SR system enables a slightly higher APU efficiency, 38.7%, versus the 35.5% of the ATR one. Also the FP efficiency of the SR system results higher, 96.6%, in comparison with the 88.8% of the ATR one. On the other hand, taking into consideration the system complexity, the APU with ATR reforming would be preferable since it does not make use of the integrated reactor SR + AFB.

CONCLUSIONS

Figure 6 shows a summary of pros and cons of the two ATR and SR systems qualitatively weighted. The FP based on the SR scheme appears superior in terms of FP and APU efficiency and hydrogen FC inlet concentration, notwithstanding a slightly higher plant complexity.

![Fig. 6 Pros and cons of PF based on ATR (yellow) and SR (green).](image)

REFERENCES