Microstructured reactors for diesel steam reforming, water-gas shift and preferential oxidation in the kiloWatt power range

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ABSTRACT

The paper reports from development and testing of three microstructured reactors of the kW scale, namely an oxidative diesel steam reformer, a water-gas shift reactor and a preferential oxidation reactor as first prototypes of a future fuel processor system. The reformer (cubic shape, edge length 80 mm) had a co-current flow arrangement. While oxidative diesel steam reforming was performed in one flow path, the energy supply for this endothermic reaction originated from the combustion of hydrogen in an integrated afterburner. The reactor was operated in the temperature range between 850 °C and 900 °C at S/C ratios between 3.2 and 4.6 and O/C ratios of 0.15–0.2. Full conversion of the diesel fuel could be achieved under all test conditions, however, formation of light hydrocarbons started after some hours of operation at lower S/C ratios.

At this stage of the development, the clean-up reactors were tested separately applying reformate surrogate as feed. The water-gas shift reactor was operated as a counter-current heat-exchanger, which utilized the cathode off-gas of the fuel cell as coolant. This further converted the CO towards the reactor outlet exceeding the equilibrium conversion achievable at the inlet. The reactor was operated at temperatures of up to 400 °C at the inlet and 250 °C at the outlet. Over 90% conversion could be achieved in this single stage water-gas shift reactor.

The second clean-up stage, namely the preferential oxidation reactor, was designed as a co-current heat-exchanger. Water evaporation was chosen as the cooling source. The CO could be reduced under most operating conditions to levels below 100 ppm, which is sufficient to operate a CO-tolerant low temperature PEM fuel cell with the purified reformate.

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1. Introduction

Idling of trucks for the generation of power when the truck is not in motion has been a common practice especially in the US, where the driver cabins are large and require excessive amounts of electrical power. Because the main engine of the truck is very inefficient when idling and generates about twice as much NO_x compared with driving at 90 km h^{-1} [1,2] this gives rise to a pollution problem. The average idling time amounts to more than 1800 h per vehicle per annum and 3.8 billion L of diesel had been consumed in this manner every year in the US. Consequently, legislation prevents truck idling in most states of the US since the beginning of 2008. Therefore alternative power generation systems or auxiliary power units (APUs) are required. Fuel cell technology promises advantages concerning efficiency, emissions and noise for this application. In case the fuel cell is linked to a diesel fuel processor, the existing fuel infrastructure could be utilized avoiding the distribution issues of alternatives such as compressed hydrogen. Such an application is regarded as niche market with significant potential [3]. Other applications of diesel fuel processor/fuel cell systems are naval systems and, in the case of kerosene, aircrafts [4].

To-date, relatively few diesel reformer reactors and fuel processors have been reported in the open literature. While some applications are based upon partial oxidation of the diesel fuel [5–7], most of them rely on autothermal reforming (ATR) [8–13]. While ATR has the potential for low system complexity and could utilize ceramic or metallic monolithic reactors readily available from automotive exhaust clean-up technology, it suffers from lower efficiency when compared to steam reforming [4,14]. However, the thermal mass of the system, the number of start-up procedures per day, the duration of the system operation and many other factors affect the overall system efficiency as well.

To-date only few diesel fuel processors are known from the open literature, which have worked with steam reforming. Krummrich et al. reported about a diesel 25 kW fuel processor for future application in naval systems [15]. An adiabatic pre-reformer was switched upstream the steam reformer in this

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particular case. Irving et al. presented a multi-fuel processor based upon microstructured reactor technology [16], which was also capable of converting diesel fuel. However, not many details of the reactor design had been disclosed.

The current paper presents results from a microstructured plate-heat-exchanger operating under conditions of oxidative steam reforming, which are still far away from autothermal operation, while the heat was supplied to the reactor by integrated hydrogen combustion as is described in Section 3.

In case PEM fuel cell technology is coupled to the fuel processor, the reformate requires purification from the carbon monoxide formed during the reforming process owing to the limited CO tolerance of the PEM fuel cell anode catalyst. This is usually done by means of catalytic processes, namely water-gas shift (WGS) and preferential oxidation (PrOx) reactions (see also Section 2).

The literature regarding the performance of water-gas shift reactors in the kW scale is rather limited to-date and mostly deals with adiabatic monoliths [17–19] and membrane reactors [20–22].

Apart from an earlier publication of the authors group [23] results from water-gas shift in microchannels were mostly generated in isothermal testing reactors to-date concentrating on catalyst development rather than on a system [24,25].

Similar to water-gas shift, the preferential oxidation reaction requires at least two stages or multiple points of oxygen addition to achieve stable and sufficiently high conversion of the remaining carbon monoxide to levels below 100 ppm as required by the low temperature PEM fuel cell. This applies both for fixed bed reactors [26,27] and monolithic reactors [17,28–31] and increases system complexity and cost.

Plate-heat-exchanger technology has the potential for efficient removal of the heat of the PrOx reaction, which then allows for the utilization of a single stage approach [32,33].
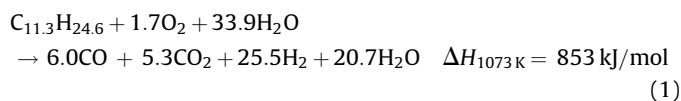
2. Reaction system

Diesel fuel is more difficult to reform compared to alcohols and lighter hydrocarbon mixtures owing to coke formation issues, which may occur during its injection into the feed mixture or over the catalyst downstream. To prevent the latter, reaction temperatures exceeding 800 °C should be envisaged, which needs to be taken into consideration when choosing the catalyst formulations. The catalyst itself needs to be resistant to sintering at these elevated temperatures.

To generate hydrogen from fossil hydrogen carriers, steam and/or air can be added to the reformer feed, which corresponds then to steam reforming, partial oxidation and autothermal reforming processes. Only in the case that the reformer works in a thermally neutral manner should oxidative steam reforming be named autothermal reforming and corresponds to an atomic O/C ratio between 0.7 and 0.9 depending on the diesel feedstock and the experimental factors such as quality of insulation, which determines the heat losses of the system of course. In the event of lower oxygen addition than is required for autothermal conditions, the oxidative steam reforming is still endothermic and requires external energy input. Such conditions were chosen for the reactor here and the additional energy was generated by an integrated afterburner as described in Section 3.

The diesel fuel applied for the experiments presented in the current paper was pseudo Euro V diesel supplied from Shell, which could be described by the simplified overall formula $C_{11.3}H_{24.6}$. However, analyses confirmed the presence of a significant amount of aromatics in this feedstock and therefore the hydrogen number is in fact lower.

Calculations from Aspen® modelling software revealed the following scheme for oxidative diesel steam reforming, performed at S/C 3, O/C 0.3 and 800 °C:

$$C_{11.3}H_{24.6} + 1.7O_2 + 33.9H_2O$$
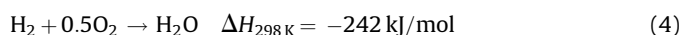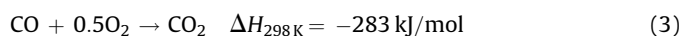$$\rightarrow 6.0CO + 5.3CO_2 + 25.5H_2 + 20.7H_2O \quad \Delta H_{1073\,K} = 853\,kJ/mol \tag{1}$$

In Eq. (1) the equilibrium of the water-gas shift reaction is taken into consideration, while the methanation reaction is not included. However, owing to the thermodynamic equilibrium, formation of methane is only minor according to thermodynamics at temperatures exceeding 800 °C [4]. Nevertheless methane might be formed depending on the catalyst formulation.

The carbon monoxide clean-up reactions will be discussed only briefly below. Water-gas shift is usually performed in two stages at temperatures around 375–450 °C in the first stage and between 200 °C and 300 °C in the second [4]:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \; \Delta H_{298\,K} = -41\,kJ/mol \tag{2}$$
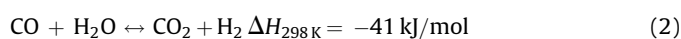
The reactor presented here was rather a medium temperature shift reactor coated with suitable catalyst and operated between 420 °C at the temperature maximum and 250 °C at the outlet.

The preferential oxidation of carbon monoxide is highly exothermic and accompanied with unselective and parasitic hydrogen oxidation:

$$CO + 0.5O_2 \rightarrow CO_2 \quad \Delta H_{298\,K} = -283\,kJ/mol \tag{3}$$

$$H_2 + 0.5O_2 \rightarrow H_2O \quad \Delta H_{298\,K} = -242\,kJ/mol \tag{4}$$

Usually an excess of oxygen is required to achieve the desired high degree of conversion.

3. Fuel processor concept and design of the reactors

3.1. Flow scheme of the planned fuel processor

The concept of the auxiliary power unit, for which the reactors discussed here were designed as first stage prototypes is shown in Fig. 1. A low temperature PEM fuel cell with reformate tolerant anode catalyst is supplied with purified reformate from the microstructured fuel processor.

The fuel processor is composed of an oxidative steam reformer (STR) which gains the energy for the steam reforming reaction mainly from combustion of the anode off-gas in an integrated afterburner (AFB). This anode off-gas is pre-heated in a heat-exchanger (HX-1), which cools the reformate downstream the reformer at the same time. Part of the cathode off-gas, pre-heated firstly in heat-exchanger HX-04 and then in the water-gas shift reactor, is utilized as the oxygen source for the combustion reaction in the afterburner. The steam for the reforming reaction is raised mainly in the evaporator, which is supplied with energy from an integrated heat-exchanger utilising the afterburner off-gas heat.

The catalytic carbon monoxide clean-up is performed in a single stage water-gas shift reactor (WGS), designed as a counter-current heat-exchanger and in a preferential oxidation reactor (PrOx) cooled in a co-current flow arrangement by water evaporation. The steam generated in the PrOx reactor is added to the steam reformer feed. On top of diesel and steam feed, a small amount of air is fed to the oxidative steam reformer, which is well beyond the air required to achieve conditions of autothermal reforming.