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# Direct steam reforming of diesel and diesel–biodiesel blends for distributed hydrogen generation

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## ABSTRACT

Distributed hydrogen generation from liquid fuels has attracted increasing attention in the past years. Petroleum-derived fuels with already existing infrastructure benefit from high volumetric and gravimetric energy densities, making them an interesting option for cost competitive decentralized hydrogen production.

In the present study, direct steam reforming of diesel and diesel blends (7 vol.% biodiesel) is investigated at various operating conditions using a proprietary precious metal catalyst. The experimental results show a detrimental effect of low catalyst inlet temperatures and high feed mass flow rates on catalyst activity. Moreover, tests with a desulfurized diesel–biodiesel blend indicate improved long-term performance of the precious metal catalyst. By using deeply desulfurized diesel (1.6 ppmw sulfur), applying a high catalyst inlet temperature (>800 °C), a high steam-to-carbon ratio ( $S/C = 5$ ) and a low feed mass flow per open area of catalyst (11 g/h cm<sup>2</sup>), a stable product gas composition close to chemical equilibrium was achieved over 100 h on stream. Catalyst deactivation was not observed.

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## Introduction

The lack of an existing hydrogen production and distribution infrastructure is widely considered an obstacle to an increased deployment of stationary and mobile fuel cell systems in the

market [1–3]. In the transition phase towards sustainable hydrogen production (for instance by making use of excess wind energy and subsequent water electrolysis), it can be reasonable to produce hydrogen from liquid fuels with readily available infrastructure. Furthermore, liquid fuels offer the advantage of high gravimetric and volumetric energy densities.

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Today, the prevalent hydrogen production technology is steam reforming of natural gas [4]. However, centralized production suffers from additional hydrogen distribution costs. In contrast, on-board hydrogen production from liquid fuels for auxiliary power units (APUs) in heavy duty vehicles, which generally is regarded as an important early market for fuel cells in the transport sector [2], avoids the additional distribution-related costs, but suffers from a high level of system complexity. Therefore, several authors consider distributed hydrogen generation (DHG) from liquid fuels (diesel, biodiesel, methanol, ethanol etc.) to be a promising mid-term option for hydrogen production [3,5–9]. Hulteberg et al. [5] hypothesize that DHG systems will provide hydrogen at the lowest cost by 2020. DHG is currently being investigated in the framework of the FP7 project NEMESIS2+. Within this project a novel hydrogen generator (50 Nm<sup>3</sup>/h) based on diesel and biodiesel is being developed for the purpose of integrating it into an existing refueling station. Apart from integrating such a system into refueling stations, on-site hydrogen generation from diesel is potentially applicable to the chemical industry, in particular for blanketing, hydrogenation and chemical synthesis.

Conversion of hydrocarbons into a hydrogen rich gas can be achieved via partial oxidation (POX), autothermal reforming (ATR) or steam reforming (SR). Among these three options, SR is currently the most established hydrogen production technology [10]. The product gas of SR is characterized by a high partial pressure of hydrogen (70–80 vol.% on a dry basis) compared to 40–50 vol.% for ATR and POX [11]. Drawbacks of the SR technology are a poor dynamic behavior and a comparatively high level of system complexity. Taking this into account, SR is widely considered as the preferred hydrogen production method for stationary applications [4,12].

While successful pre-reforming of diesel in the low temperature range (400–500 °C) using Ni-based catalysts has been demonstrated by several working groups [13,3,14], direct SR of diesel at high temperatures (~800 °C) is still at a relatively early research and development stage and needs further improvement [8]. Typically, diesel SR catalysts become deactivated within a few hours of on-stream exposure [15], which is mainly attributed to coking, sulfur poisoning and sintering of the catalyst [16].

Ming et al. carried out SR of diesel surrogate hexadecane using a proprietary catalyst formulation in a packed-bed reactor. Stable catalyst performance was shown for 73 h on stream without observing deactivation or carbon deposition [17]. Goud et al. conducted SR of hexadecane using a Pd/ZrO<sub>2</sub> catalyst coated on metal foils at steam-to-carbon ratios (S/C) of 3–6 and  $T = 750\text{--}850\text{ °C}$ . A first-order kinetic model with a first-order deactivation rate was obtained. The catalyst deactivation rate was found to be accelerated by the presence of sulfur, at low S/C and at low temperatures [18].

In recent years, research groups have propagated the use of microstructured reactors for SR of diesel-like fuels, thereby circumventing problems related to heat and mass transfer limitations. Thormann et al. investigated hexadecane SR over a Rh/CeO<sub>2</sub> catalyst using microstructured devices [19,20]. The experiments revealed a fast transient response, thereby making it an interesting option for mobile APU applications.

However, the reformer system suffered from high heat losses. Kolb et al. [21] developed a microstructured plate heat exchanger composed of stainless steel metal foils. Oxidative diesel steam reforming (molar O/C-ratio: 0.12–0.2) was performed using Euro V diesel supplied by Shell and using commercial catalysts provided by Johnson Matthey. Although a diesel conversion of 99.9% was achieved, formation of light hydrocarbons started after only a few hours of operation at  $S/C < 4$  indicating the onset of catalyst deactivation. In a follow-up study, Grote et al. [22] carried out further steam reforming tests (4–10 kW thermal input) using a diesel surrogate mixture, accompanied by computational fluid dynamics modeling. The results show an increase of residual hydrocarbons (caused by deactivation of catalyst activity) with decreasing temperature. In order to prevent the formation of higher hydrocarbons, a reformer outlet temperature in excess of 1013 K was required. Long-term performance data was not presented by the authors. In a second follow-up study, Maximini et al. [23] tested four downscaled microchannel diesel steam reformers (1 kW<sub>th</sub>) with different precious metal coatings at S/C ratios of 3 and 4. Increased carbon formation was observed when reducing the temperature from 800 °C to 700 °C. This was accompanied by the formation of higher hydrocarbons like C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>. The same group of authors presented experimental results of a microstructured diesel SR fuel processor coupled with a PEM fuel cell [24]. The 10 kW<sub>th</sub> reformer consisted of 35 reformer channels with a channel height of 0.6 mm and 34 combustion channels being operated at  $S/C = 5$  and 6 and a reactor outlet temperature of 765–800 °C. The results indicated a clear trend toward increasing residual hydrocarbon formation for higher feed mass flow rates. Furthermore, the stack voltage was observed to be highly sensitive to the residual hydrocarbon concentration in the reformat gas.

Other research groups used Ni-based catalysts for SR of diesel as Nickel is less expensive and more readily available than precious metals [6,15,25–27]. Fauteux-Lefebvre et al. [6] tested an Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub>-supported nickel–alumina spinel catalyst in a lab-scale isothermal packed-bed reactor at various operating conditions. Mixing of fuel and water was achieved by feeding in a stabilized hydrocarbon–water emulsion, which successfully prevented undesired pre-cracking. Product concentrations close to equilibrium for up to 20 h on-stream exposure were reported at severe operating conditions ( $T < 720\text{ °C}$ ,  $S/C < 2.5$ ). Steam reforming of commercial diesel was carried out for more than 15 h at  $S/C < 2$ . Carbon formation on the catalyst surface was not observed, although measured diesel conversion was lower than 90% [15].

Boon et al. were the first to report stable diesel steam reforming at temperatures of 800 °C using commercial precious metal catalysts [3]. The experiments were carried out in a packed-bed reactor at low gas hourly space velocities (GHSV) of 1000–2000 h<sup>-1</sup>. Diesel evaporation was achieved by spraying diesel in a hot gas phase, thereby preventing self-pyrolysis during the evaporation step. Stable conditions with no sign of deactivation were reported for 143 h on stream at 1.2 bar, 800 °C and  $S/C = 4.6$  and 2.6 using Aral Ultimate diesel with an added 6.5 ppm sulfur. Similar experiments with commercial BP Ultimate diesel containing 6 ppm sulfur turned out to be more challenging due to problems with blocking of

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