Steam reforming of commercial ultra-low sulphur diesel

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ABSTRACT

Two main routes for small-scale diesel steam reforming exist: low-temperature pre-reforming followed by well-established methane steam reforming on the one hand and direct steam reforming on the other hand. Tests with commercial catalysts and commercially obtained diesel fuels are presented for both processes. The fuels contained up to 6.5 ppmw sulphur and up to 4.5 vol.% of biomass-derived fatty acid methyl ester (FAME). Pre-reforming sulphur-free diesel at around 475 °C has been tested with a commercial nickel catalyst for 118 h without observing catalyst deactivation, at steam-to-carbon ratios as low as 2.6. Direct steam reforming at temperatures up to 800 °C has been tested with a commercial precious metal catalyst for a total of 1190 h with two catalyst batches at steam-to-carbon ratios as low as 2.5. Deactivation was neither observed with lower steam-to-carbon ratios nor for increasing sulphur concentration. The importance of good fuel evaporation and mixing for correct testing of catalysts is illustrated. Diesel containing biodiesel components resulted in poor spray quality, hence poor mixing and evaporation upstream, eventually causing decreasing catalyst performance. The feasibility of direct high temperature steam reforming of commercial low-sulphur diesel has been demonstrated.
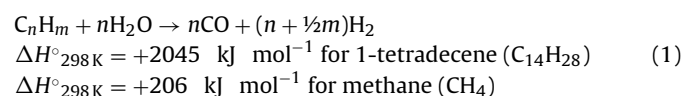
1. Introduction

The increasing deployment of proton-exchange membrane fuel cells (PEMFC) in residential applications as well as in transport creates a small scale demand for hydrogen in absence of an infrastructure for local hydrogen distribution. While sustainability will eventually stipulate hydrogen from renewable energy sources, an economically efficient phase in the transition towards sustainability will make use of the available infrastructure for fossil fuels and locally generate a suitable fuel cell feed through fuel processing [1–4]. By fuel processing, conventional fossil fuels are converted into pure hydrogen, or reformate low in carbon monoxide (<10 ppm) and sulphur (<0.1 ppm as H_2S), as required by PEMFC [1]. Natural gas and LPG are readily converted, but this is not yet the case with liquid fuels. Still, liquid fuels such as diesel are attractive because of existing infrastructure, potentially higher well-to-wheel

efficiencies, safe fuel handling and storage, and high energy densities [5].

Diesel is a complex mixture of hydrocarbon compounds containing saturates, olefins, and aromatics as well as a wide variety of brand specific additives [9,10]. Present-day commercial ultra-low sulphur diesel (ULSD) contains up to about 10 ppmw of sulphur, largely in the form of refractory organic sulphur molecules, e.g., dimethyldibenzothiophenes [6,7]. As of 2010, 5.75% by energy content of fatty acid methyl ester (FAME) can be present in the EU [8]. The process for converting diesel into hydrogen-rich PEMFC feed gas consists of the following steps [1]: (a) fuel reforming into synthesis gas (hydrogen, carbon monoxide), (b) sulphur removal, (c) water–gas shift (WGS) to convert carbon monoxide into hydrogen and carbon dioxide, and (d) gas cleanup/CO removal. Oxygen is the reactant to convert diesel via exothermic partial oxidation (CPO), while steam is used in the endothermic steam reforming (SR), and both oxygen and steam in the thermoneutral autothermal reforming (ATR). Steam reforming theoretically offers the highest system efficiency, albeit at the expense of complex start-up and slower transients [5]. Steam reforming (1) has been selected as the preferred reforming process:

$$C_nH_m + nH_2O \rightarrow nCO + (n + \frac{1}{2}m)H_2$$
$$\Delta H°_{298\,K} = +2045 \quad kJ \quad mol^{-1} \text{ for 1-tetradecene } (C_{14}H_{28}) \qquad (1)$$
$$\Delta H°_{298\,K} = +206 \quad kJ \quad mol^{-1} \text{ for methane } (CH_4)$$

The boiling range of the constituents makes fuel introduction, evaporation, and mixing of reactants difficult [11,20,26,41,42]. Direct vaporisation via e.g., a heat exchanger or electric heater is

I. Desulphurisation, pre-reforming, steam reforming

diesel → | organic sulphur removal | → | adiabatic pre-reforming | → | steam reforming | → | water-gas shift (high, low temperature) | → | gas cleanup | → hydrogen-rich gas

II. Desulphurisation, direct steam reforming

diesel → | organic sulphur removal | → | steam reforming | → | water-gas shift (high, low temperature) | → | gas cleanup | → hydrogen-rich gas

III. Direct sulphur-tolerant steam reforming H₂S removal

diesel → | steam reforming | → | H₂S removal | → | water-gas shift (high, low temperature) | → | gas cleanup | → hydrogen-rich gas
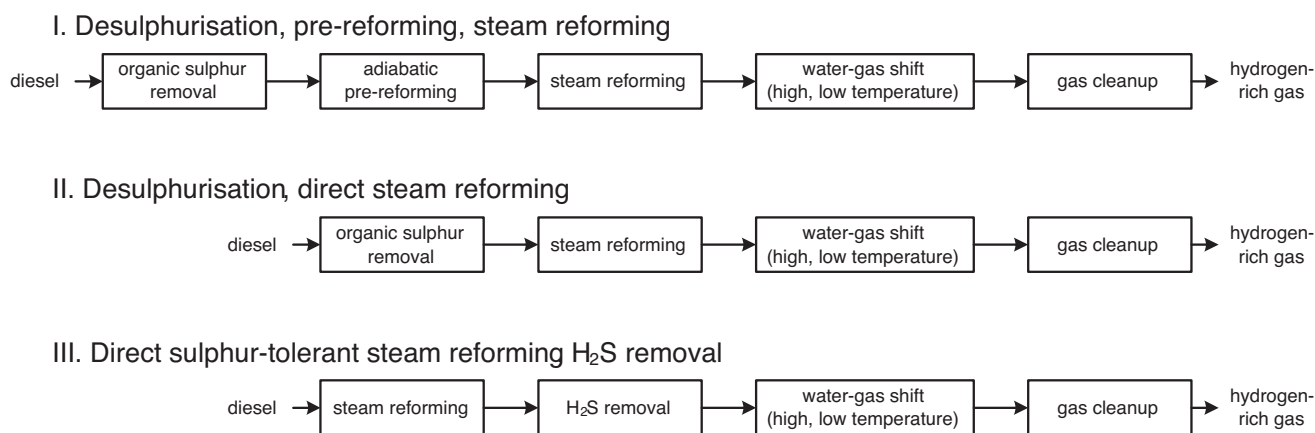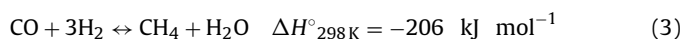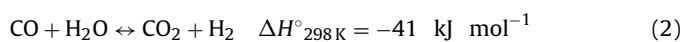
Fig. 1. Process routes for production of hydrogen-rich gas from diesel via steam reforming and desulphurisation.

troublesome because of the risk of pyrolysis and coking at elevated temperatures [11,12]. Alternatively, hot gas assisted diesel evaporation by spaying cold diesel into a hot gas feed is a feasible technology for diesel evaporation and mixing [13,14].

Three main process alternatives for diesel fuel processing via steam reforming are shown in Fig. 1. Direct high-temperature steam reforming of heavy fuels (Fig. 1, options II and III) is most efficient, but technically challenging because of the risk of coking on the catalyst [5,15,16]. Adiabatic pre-reforming is a well established preconditioning step, converting all hydrocarbons to CH_4, CO, CO_2, and H_2 by combination of low-temperature steam reforming (1), WGS (2) and methanation (3):

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^\circ_{298\,K} = -41 \quad kJ \; mol^{-1} \tag{2}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H^\circ_{298\,K} = -206 \quad kJ \; mol^{-1} \tag{3}$$

Pre-reforming is done at a relatively low temperature of around 500 °C and it produces a gas mixture that can be safely heated in a steam reformer (Fig. 1, option I) [17–21]. While steam reforming (1) is strongly endothermic, WGS (2) and methanation (3) are exothermic. For heavy fuels such as diesel, adiabatic operation results in a characteristic temperature profile [22], schematically depicted in Fig. 2, depending on fuel composition and on the operating pressure that affects the thermodynamic equilibrium for methanation (3). The axial temperature profile shifts because of catalyst deactivation. The temperature minimum moves along the reactor axis in the direction of flow, and the width of the profile broadens as is illustrated in Fig. 2. Several reports of liquid fuel pre-reforming over nickel catalysts are available. Piwetz et al. of Haldor Topsøe developed a fuel processor, based on HDS and pre-reforming over a nickel catalyst, reporting up to 1918 h of testing with diesel fuel [23]. Deac-
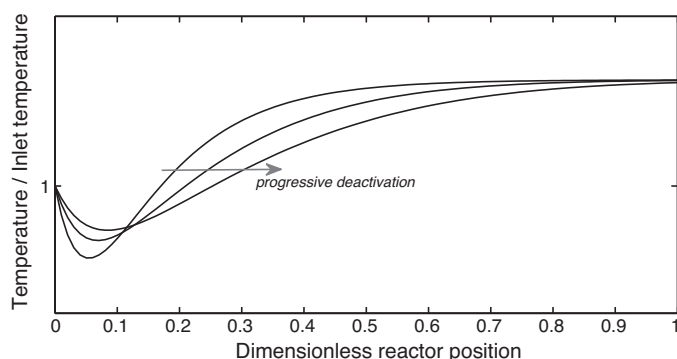
tivation was caused by both gum formation and sulphur poisoning. Improved sulphur tolerance is sometimes claimed for precious metal catalysts although coke deposition problems appear to persist. A series of rhodium-based low-temperature pre-reforming catalysts has been developed and tested by Zheng, Strohm, and Song [24–26], demonstrating sulphur tolerance up to 22 ppm for up to 72 h and separately stability in an accumulated 10 days test, all with jet fuel and S/C = 3. In the same conditions, a commercial nickel catalyst deactivated dramatically in only a few hours due to coke formation. Little literature data is available on the reforming of FAME containing fuels. Steam reforming of biomass-derived organic oxygenates may proceed mechanistically very similar to steam reforming of fossil hydrocarbons [27]. However, oxygenates are generally less stable than their mineral counterparts and can therefore increase the risk of pyrolysis before the fuel is fully evaporated and well-mixed with steam. Chiodo et al. [28] have found pronounced decomposition of glycerol and coke formation starting at 450 °C and formation of encapsulating carbon at 650 °C and above. In addition, oxygenates may form carbonaceous deposits through condensation/dehydration reactions [29–32]. Reforming of oxygenates over nickel catalysts has been reported to give significant amounts of coke [27,28] whereas noble metal catalysts appear to be somewhat better suited for reforming oxygenates [28,31,32].

Apart from the presence or absence of a pre-reformer, the process routes shown in Fig. 1 differ in desulphurisation. Sulphur can be removed either as organic sulphur before the reformer (Fig. 1, options I and II), or as H_2S after conversion in the reformer (Fig. 1, option III). Organic sulphur can be removed either by selective adsorption or by hydrodesulphurisation (HDS). Both techniques suffer from the fact that the organic sulphur components in diesel consist of refractory substituted dibenzothiophenes that are very difficult to adsorb or convert selectively, particularly in presence of diesel additives [1,6,7,33–37]. The presence of FAME further adds to the complexity of desulphurisation by reactive adsorption as recently shown by Pieterse et al. [7]. Philippe et al. [38] have shown that oxygenates can be detrimental in deep HDS over conventional CoMo-based catalyst. In spite of the challenges, Haldor Topsøe have presented a combined HDS/ZnO and pre-reforming system for logistic fuels in fuel cell applications [21,23]. HDS was capable of reducing 0.2 wt.% S to below 1 ppmw, which still harmed the adiabatic pre-reformer downstream [23]. As an alternative to diesel desulphurisation, it is possible to capture sulphur with a properly designed ZnO sulphur trap, if the organic sulphur molecules can be converted into H_2S in the reforming process [39,40]. Muradov et al. [39] have followed this approach, applying low-temperature hydrocracking of high-sulphur diesel followed by an iron-based
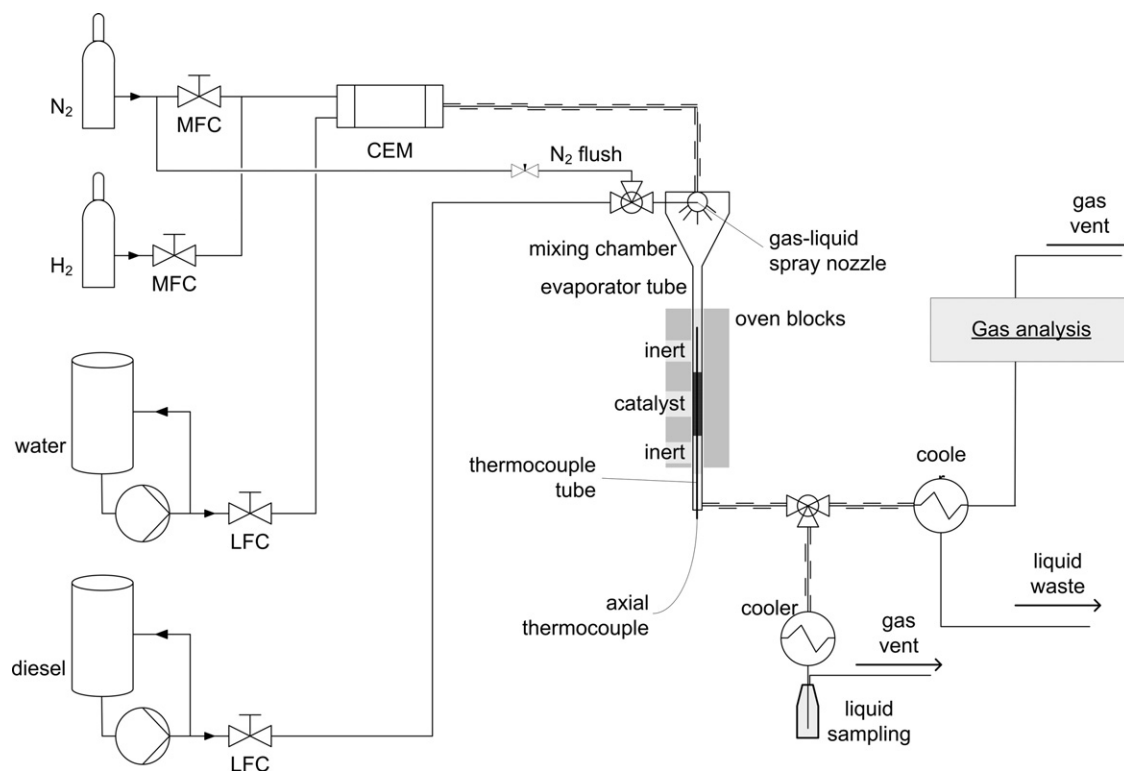

Fig. 2. Typical axial temperature profiles in an adiabatic diesel pre-reformer.

Fig. 3. Diesel reforming setup, processing $6 \, g \, h^{-1}$ of liquid fuel.

redox system for removal of H_2S and high-temperature steam reforming.

Scale-up of pre-reforming and direct steam reforming technology towards commercial application requires confidence that can be gained from long-term experiments. A few long-term experiments have been reported in the literature. This paper reports a series of bench-scale experiments of diesel reforming over a nickel-based catalyst and a precious metal-based catalyst, both commercially available. The process routes envisioned are desulphurisation – pre-reforming – steam reforming (Fig. 1, option I) and direct steam reforming – desulphurisation (Fig. 1, option III). It serves to demonstrate low-temperature pre-reforming as well as direct high-temperature steam reforming of diesel, culminating in a total time on stream with a single catalyst batch for pre-reforming of 118 h, and for direct steam reforming for 590 h.

2. Experimental

Two different commercial diesel fuels have been utilised (Table 1). Because the fuels were obtained from commercial refuelling stations, they contained additives that are normally present in commercial diesel fuels. In order to increase the content of sulphur, 0.9 ppmw and 6.5 ppmw S were added to sulphur-free Aral

Table 1
Diesel fuels as obtained.

Fuel	Sulphur[a] (ppmw)	FAME[b] (vol.%)
Aral Ultimate[c]	0	<0.1
BP Ultimate[d]	6	4.5

[a] Sulphur content in mg of sulphur atoms per kg of fuel, ASTM D3120 by Intertek Caleb Brett, Hoogvliet (NL).
[b] FAME content, EN 14078 by Intertek Caleb Brett, Hoogvliet (NL).
[c] Aral Ultimate obtained from Aral Tankstelle Reiner Lenkeit in Isselburg (D), May 2008.
[d] BP Ultimate obtained from BP Hoefplan in Alkmaar (NL), October 2008.

Ultimate by dissolving dibenzothiophene ($C_{12}H_8S$), obtained in 98% purity from Sigma–Aldrich, The Netherlands. BP Ultimate contains a wide variety of sulphur components (measured with GC–PFPD as described elsewhere [7]), of which 4,6-dimethyl dibenzothiophene is most abundant. The BP diesel also contained 4.5 vol.% of biodiesel as FAME. Sulphur was added to Aral Ultimate in high-temperature steam reforming tests only.

A nickel catalyst and a noble metal catalyst have been investigated in pre-reforming and steam reforming tests (Table 2). In the first case, the reactor was loaded with 20 g of Ni catalyst particles that had been crushed and sieved to 0.2–0.4 mm size and then diluted with an equal amount of SiC (0.2–0.5 mm, Gimex, The Netherlands). In the second case, 15 g of PM catalyst powder was diluted with an equal amount of high-purity α-alumina powder (99.99% metals basis, Alfa Aesar, Germany) and then pressed, crushed, and sieved to 0.85–2 mm. Before each experiment, catalysts were heated with a typical rate of 0.5–1 °C min^{-1} in 20% H_2/N_2 before addition of steam and subsequently diesel.

The schematic layout of the reforming setup is shown in Fig. 3. The reactor tube has an internal diameter of 15.75 mm, where the catalyst is placed in an annulus surrounding the axially placed thermocouple tube (3 mm outer diameter). The reactor was packed with a catalyst bed of 150–200 mm height, preceded and followed by SiC sieve fraction packing.

Assessment of catalyst performance was based upon gas analysis, liquid sampling (interpreted visually and based on the characteristic smell of organics), and the temperature profile (Fig. 3). Gas analysis included ABB Advance Optima online analysis (NDIR for CO, CO_2, CH_4 and TCD for H_2) and an Interscience TraceGC with a Porabond Q/Molsieve plot column and TCD for H_2, N_2, CH_4, CO and a Capillary Al_2O_3/KCl column and FID for C_xH_y up to toluene, with a detection limit of 10 ppmv. For liquid sampling, the gas flow was cooled down to 5 °C while collecting the condensate – visual inspection could be used to qualitatively assess whether or not unconverted hydrocarbons were present on top of the aqueous condensate. Gas analysis has been used to quan-

Table 2
Commercial diesel reforming catalyst samples used.

Code	Vendor	Catalyst	Shape	Type
Ni	CRI Kataleuna Houston, TX, USA	KL6629 Pre-reforming	Tablets, 4 mm × 4.5 mm	Nickel
PM	Umicore Hanau, Germany	S-Type Pre-reforming	Powder	Precious metal

tify diesel conversion, which is defined here as the molar flow of CO, CO_2, and CH_4 products divided by the molar flow of carbon atoms in the feed stream. However, it is difficult to quantify the onset of deactivation by analysis of the product spectrum alone. Instead, it was decided to focus upon the axial temperature profile. The catalysts were operated at sufficiently low space velocities ($1000–2000\,h^{-1}$) to make sure that the sequential reactions and therefore also the axial temperature profile are well within the catalyst bed. Catalyst deactivation may then be observed through a shift in the temperature profile as explained above.

Fuel introduction, as explained, is preferably done by spraying diesel in a hot gas phase. The very low diesel feed flow of $6\,g\,h^{-1}$ was introduced in the gas stream by a nozzle that consisted of a diesel feed capillary placed perpendicular to the gas flow. The two feed channels were designed such that the high momentum of the gas feed results in a continuous fine spray of diesel (see Fig. 4). Despite careful consideration of the configuration, nozzle plugging could not always be prevented.

The pre-reforming experiments, at temperatures up to 525 °C, have been performed with aluminium oven blocks (Fig. 3). All catalysts were heated with a typical rate of 0.5–1 °C min^{-1} in 20% H_2/N_2 before addition of steam and subsequently diesel. The temperature gradient over the catalyst bed in absence of reaction was always less than 5 °C. For direct steam reforming, the aluminium oven blocks were replaced by stainless steel. The lower thermal conductivity of steel caused a somewhat larger temperature gradient of about 30 °C over the reactor in absence of reaction. Nevertheless, the position of the reaction zone having a temperature gradient in the order of 40 °C could be accurately determined. Over the length of the catalyst bed, the temperature was measured at seven fixed positions. Since the position and value of the temperature minimum is important to assess catalyst stability, these were actively determined by axially shifting of the thermocouple until the temperature minimum was located.

3. Results

3.1. Diesel pre-reforming

The result of the first 116 h stability test at 475 °C is shown in Fig. 5. Throughout the entire test, the outlet concentrations were at the predicted thermodynamic equilibrium values (HSC Chemistry [43]). GC analysis showed all non-methane hydrocarbons
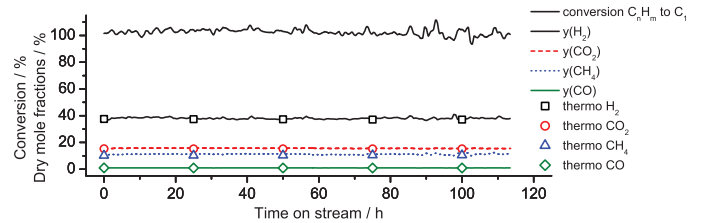

Fig. 5. Diesel conversion and product composition during pre-reforming stability test: Ni catalyst, $6\,g\,h^{-1}$ Aral Ultimate, oven temperature 475 °C, S/C 4.6, GHSV $2000\,h^{-1}$.
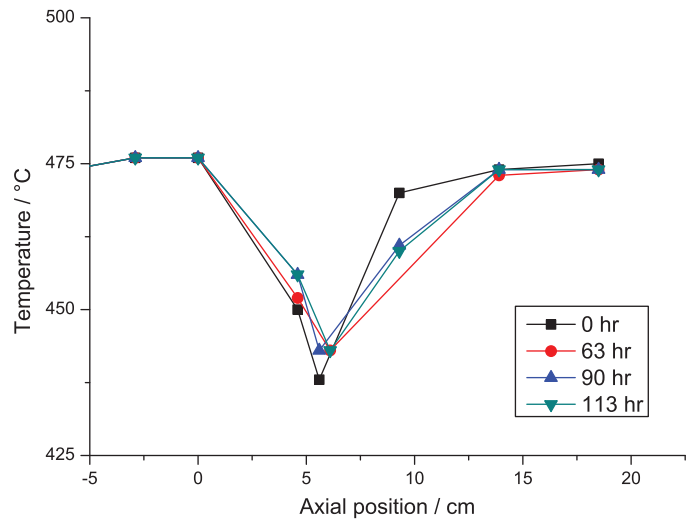

Fig. 6. Temperature profiles during diesel pre-reforming stability test. Settings see Fig. 5.

below detection limit, indicating full diesel conversion. The measured temperature versus the axial position in the bed is shown in Fig. 6 for a number of times. The typical pre-reforming temperature profile (cf. Fig. 2) is observed. In time, the profile does not significantly broaden after the initial 63 h on stream, and especially the temperature minimum maintains its axial position. This indicates that the catalyst performance is rather stable under the applied conditions.
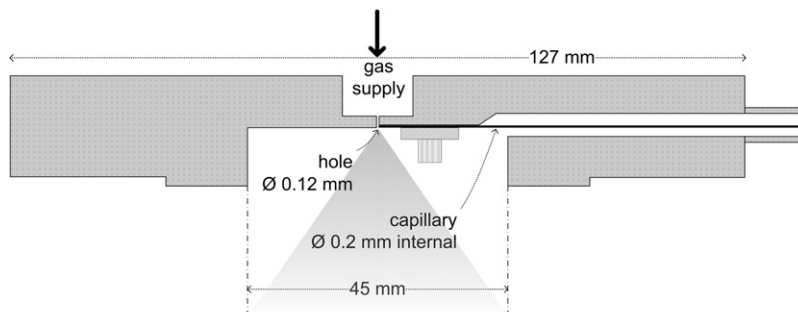

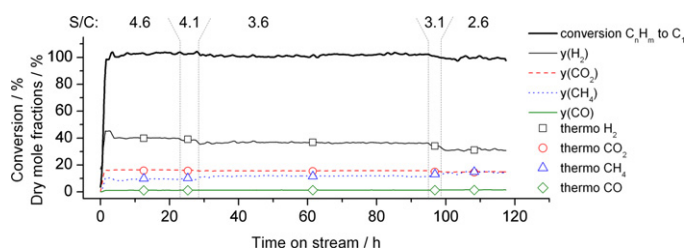**Fig. 4.** In-house developed diesel spray nozzle.

Fig. 7. Diesel conversion and product composition during pre-reforming stability test with reduced steam feed: Ni catalyst, $6\,g\,h^{-1}$ Aral Ultimate, reactor 475 °C, S/C 4.6–2.6, GHSV 2000–1000 h^{-1}.
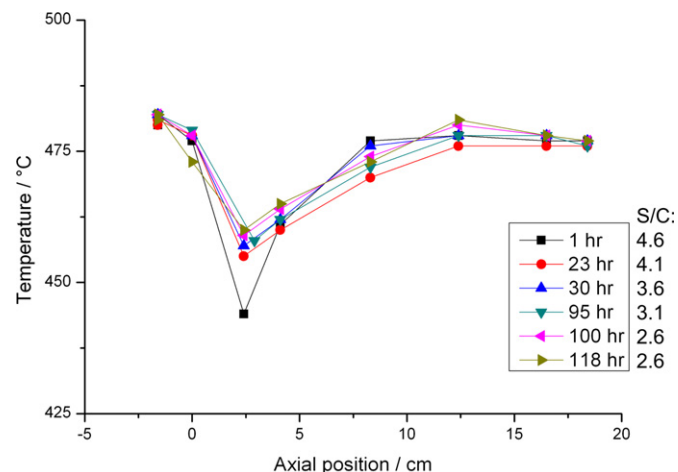

Fig. 8. Temperature profiles during diesel pre-reforming stability test with reduced steam feed. Conditions see Fig. 7.

In a subsequent test with fresh catalyst, the possibility to lower the S/C ratio was investigated. In a test of 118 h in total, the ratio was reduced from standard 4.6 down to 2.6, see Fig. 7. Packing of the fresh catalyst bed caused a deviation in the original temperature profile (Fig. 8, S/C = 4.6) compared to the previous test (Fig. 6) with the same operating conditions. A S/C ratio of 3.6 had no impact upon catalyst stability, as confirmed by the temperature profiles in Fig. 8. With S/C = 2.6 there was no indication of catalyst deactivation for the duration of 20 h.

3.2. Diesel steam reforming

The Umicore S-Type Pre-reforming catalyst showed insufficient activity at pre-reforming temperatures below 550 °C and was tested for direct high-temperature steam reforming at higher
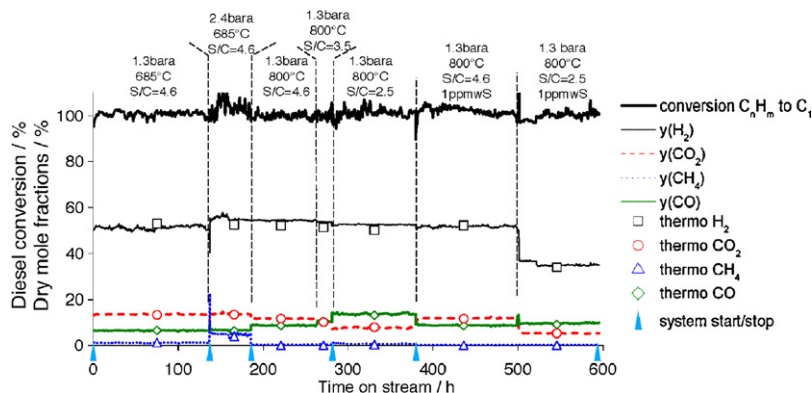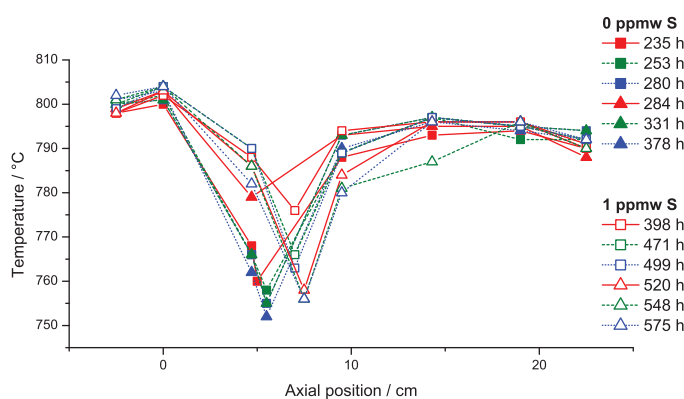

Fig. 10. Temperature profiles with first batch of Umicore S-Type Pre-reforming catalyst, conditions in Fig. 9. Data comprises measurements at 800 °C, without sulphur (closed symbols) and with 0.9 ppmw sulphur (open symbols), with S/C 4.6 (squares) and S/C 2.5 (triangles).

temperatures, not only converting higher hydrocarbons, but also converting methane to carbon oxides and hydrogen. Initial tests at 685 °C using commercial sulphur-free Aral Ultimate diesel showed full diesel conversion, a gas composition at thermodynamic equilibrium and no significant catalyst deactivation over a period of 180 h, see Fig. 9. Further testing using the same catalyst sample was done at 800 °C. The methane concentration at the outlet was below 0.1 vol.% throughout the test (thermodynamics: 0.04%). Apart from the product composition being at equilibrium, the stability at S/C = 4.6 and 2.5 was confirmed by the temperature profiles shown in Fig. 10. At 379 h on stream, 0.9 ppmw of S was added to the fuel in the form of dibenzothiophene (DBT). Subsequently, during both the 122 h operation at S/C = 4.6 and 95 h of operation at S/C = 2.5, i.e., for 217 h in total, the temperature profile is pushed further into the catalyst bed due to the presence of sulphur. However, the profile remains located at the same axial position and does not significantly broaden, see Fig. 10, indicating no sign of progressive deactivation. At 596 h time on stream, the steam supply failed and the reactor was exposed to diesel/nitrogen only at elevated temperature, causing complete reactor blockage by coke.

In the subsequent experiment a fresh catalyst batch was exposed for 143 h to steam reforming of Aral Ultimate diesel with an increased sulphur content of 6.5 ppmw by addition of DBT, see Fig. 11. The temperature profiles again show no indication of significant progressive catalyst deactivation (Fig. 12, 0–143 h). Finally, the Umicore S-Type Pre-reforming catalyst was tested for direct steam-reforming of commercial BP Ultimate diesel, the results of which are shown in Figs. 11 and 12 from 150 h time on stream onwards. The latter figure showed a slightly lower minimum tem-

Fig. 9. Cumulative time on stream with first batch of Umicore S-Type Pre-reforming catalyst, Aral Ultimate fuel (after 501 h, with lowering the S/C additional N_2 was supplied to improve the diesel spray, leading to lower concentrations of products).
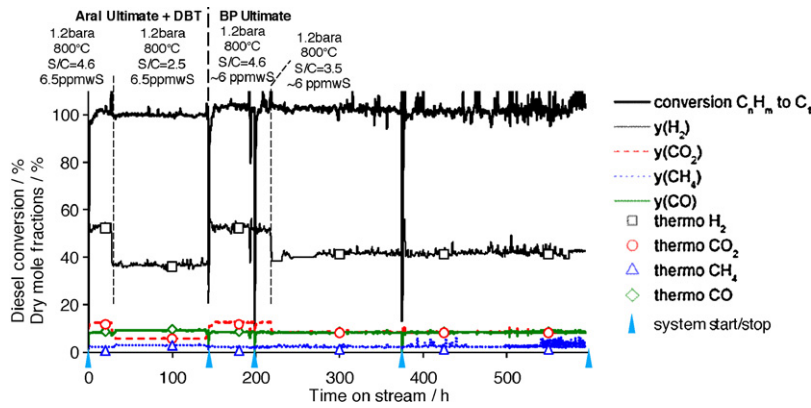
Fig. 11. Cumulative time on stream with second batch of Umicore S-Type Pre-reforming catalyst, Aral Ultimate and BP Ultimate fuels (with S/C 2.5 and S/C 3.5, additional N_2 is supplied to improve the diesel spray, leading to lower concentrations of products).

perature with Aral Ultimate as compared to the results with BP Ultimate, indicating somewhat lower rates of reaction for the latter. The experiments with this diesel were very demanding for the nozzle configuration. The Umicore S-Type Pre-reforming catalyst was found to be stable with high S/C with the standard configuration (diesel feed capillary of 0.2 mm internal diameter) for 55 h, before blocking of the diesel capillary occurred at 198 h on stream, see Fig. 11. Then the test was continued with a larger diesel capillary (0.25 mm internal diameter) in order to increase the operation time. Indeed, the nozzle could be operated for almost 180 h before it was plugged again at 374 h on stream, see Fig. 11. The nozzle was again replaced, allowing for a final test that lasted for 220 h (Fig. 11, 374–594 h). However, the instability of the diesel conversion values after 198 h in Fig. 11 already indicated that the larger capillary gives a poorer spray. Poor spray quality, as discussed above, may

easily result in coking of the reactor. Locally, a rather harmful combination of low steam concentrations and high temperatures may have resulted, leading to enhanced risk of coke formation [12,26]. The temperature profile in Fig. 12 shows stable operation up till 380 h on stream and the onset of catalyst deactivation coinciding with placement of the last nozzle. The conclusion that the observed deactivation of the catalyst was caused by the poorer spray, rather than the catalyst itself, is further supported by the observed coke deposition in the reactor spray chamber. Fig. 13 shows that coke deposition occurred in the mixing chamber and the pre-heating section of the reactor, i.e., upstream of the catalyst bed, rather than near the catalyst itself.

In total, the Umicore S-Type Pre-reforming catalyst has been operated in 2 batches: the first for 596 h at the various conditions, shown in Fig. 9; the second for 594 h with high sulphur, and for the final 451 h with 4.5 vol.% FAME, shown in Fig. 11. The first and second batch of catalyst experienced six and five start-ups and shutdowns, respectively. The liquid condensate contained no visi-
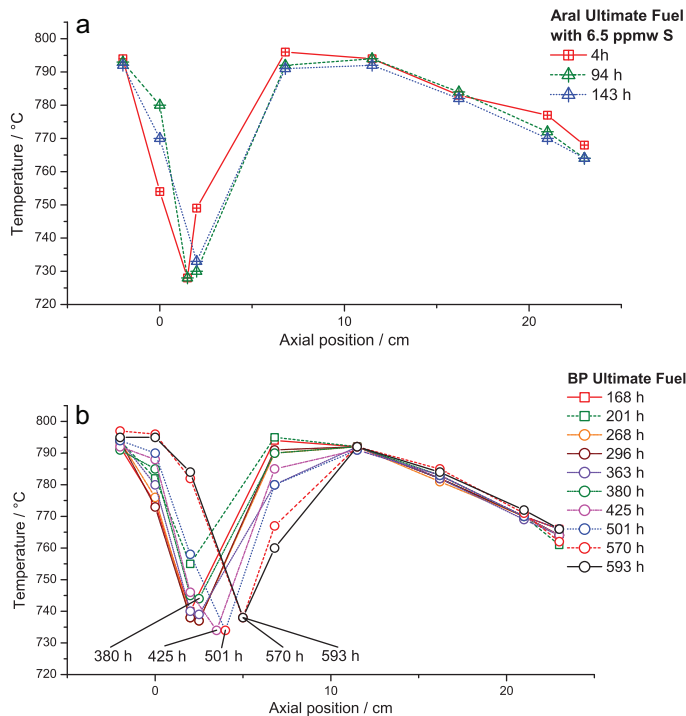

Fig. 12. Temperature profiles with first batch of Umicore S-Type Pre-reforming catalyst, conditions in Fig. 11. Data includes (a) measurements with Aral Ultimate with 6.5 ppmw S (open symbols with crossmark) and (b) with BP Ultimate (open symbols), at S/C 4.6 (squares), S/C 3.5 (circles), and S/C 2.5 (triangles). Deactivation starts after 380 h on stream, for which temperature minima are indicated.
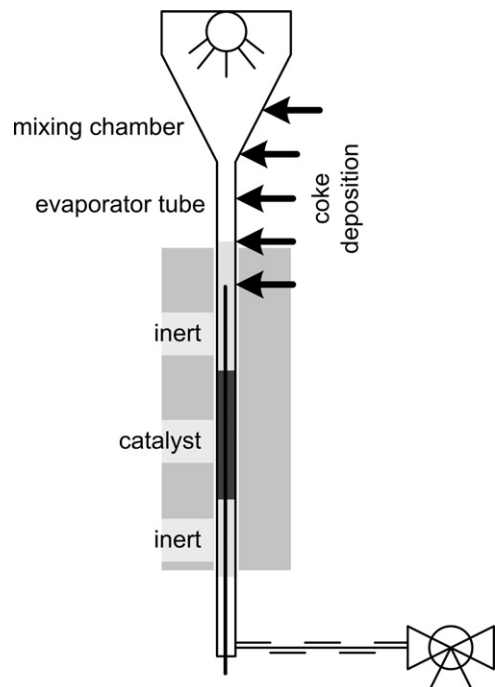

Fig. 13. Coke deposition in ULSD direct steam-reforming with 0.25 mm diesel capillary.

ble organic layer or smell of organic constituents. Full conversion in operation was also confirmed by GC analysis, showing by-products only during incomplete conversion, i.e., start-up and shutdown.

4. Discussion

Both for diesel pre-reforming operating conditions and for direct steam-reforming operating conditions, experiments have demonstrated suitable commercially available catalysts, i.e., without rapid deactivation, for commercially obtained diesel fuels, including common additives. Both processes have been demonstrated in 100+ h stability tests at space velocities of 1000–2000 h^{-1}. Such a low space velocity is partly due to the excess amount of catalyst required for an adequate measurement of the temperature profile (see above), and partly typical for the reforming of heavy feedstock at low temperatures (in case of pre-reforming) or in presence of sulphur (in case of direct steam reforming) [5,15,17]. Comparable values are indeed reported in the literature [24,26,45].

The Ni-based catalyst was tested for over 100 h in order to confirm catalyst stability at S/C 4.6. In a later test, the catalyst was subjected to S/C 3.5 for 70 h and S/C 2.6 for 20 h. Based on the measured axial temperature profiles as a function of time on stream it was concluded that at both conditions the catalyst appeared stable. It is thereby confirmed that sulphur free diesel can be pre-reformed over a nickel-based catalyst without rapid deactivation. In reforming gasoline and kerosene over Ni/La$_2$O$_3$–Al$_2$O$_3$, similar stabilities have been reported in a 100 h stability test by the Dalian Institute of Chemical Physics [44,45]. In order to be able to operate in the envisaged process configuration, the catalyst stability must therefore be confirmed with ULSD and a desulphurisation process upstream. No by-products were detected in pre-reforming: there was no organic layer in the condensate and the GC analysis revealed no C$_{1+}$ hydrocarbons.

For the PM catalyst, stability was successfully demonstrated for 138 h at 685 °C reactor temperature and S/C 4.6. Then the temperature was further increased and stability tests are aimed at gradually approaching conditions of direct steam reforming of commercial ULSD. At these conditions, there was no visual evidence of coke deposits and in contrast to what has been concluded by Zheng et al. [26], it was possible to perform direct high-temperature steam reforming of diesel. The sulphur content was then increased from sulphur-free Aral Ultimate to 0.9 ppmw S and 6.5 ppmw S by addition of DBT. Sulphur does cause a decrease in catalyst activity as indicated by a shift of the temperature profile further downstream (but still well within the catalyst bed). Still the temperature profile in the presence of sulphur remained stable in time and no sulphur related progressive deactivation has been observed up to 6.5 ppmw S. In the current tests it was indeed confirmed that high-temperature steam reforming is possible in presence of sulphur with a precious metal catalyst, but now at the sulphur level encountered in ULSD in Western-Europe nowadays, and with diesel fuel. In the final test with commercially obtained Aral Ultimate, the catalyst was stable for 113 h with 6.5 ppmw S and S/C 2.5. Then, a final test run was done with BP Ultimate as commercially obtained ULSD. Apart from the sulphur content of 6 ppmw S, 4.5 vol.% of FAME is now present as well. The constructed nozzle was not suitable for processing this fuel, as the diesel capillary rapidly plugged. This plugging may be related to the presence of oxygenates. Usage of a larger capillary presumably led to poor diesel atomisation and relatively large droplets, yet it was still possible to operate the catalyst for 376 h with ULSD at a S/C ratio of 3.5. The experiment was stopped when large coke deposits were found upstream of the catalyst bed. Some catalyst deactivation had occurred, shown in the temperature profile, but it was likely induced by the coking upstream of the catalyst, forming coke precursors that lead to coke deposition on the catalyst. Before the onset of deactivation, the catalyst had been stable for 162 h.

5. Conclusion

Pre-reforming of diesel has been investigated with CRI Kataleuna KL6629 (Ni) catalyst and high-temperature diesel steam reforming with Umicore S-Type Pre-reforming (PM) catalyst. For adiabatic pre-reforming of desulphurised diesel, it was found that the CRI catalyst was stable and showed no by-products for up to 118 h and S/C as low as 2.6.

Umicore S-Type Pre-reforming catalyst was found to be capable of direct steam-reforming of commercial ULSD (without preceding desulphurisation) at 685–800 °C, with S/C 2.5–4.6, without H$_2$ in the feed, for a total time on stream of 1190 h with two catalyst batches. In a final test, the catalyst was operated for 376 h with ULSD, S/C 3.5. Deactivation was observed in this test through the recorded temperature profile, but this appears to be due to coke precursors formed on the wall of the mixing chamber, in turn caused by the poor quality of spray. The nozzle of the injector was suitable for spraying automotive grade diesel but not ULSD. Most importantly, direct steam reforming of commercial ULSD without prior desulphurisation or pre-reforming is technically feasible, thereby creating a smaller, more efficient, and less complex reformer.

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