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Bench-scale demonstration of an integrated deSoot–deNO$_x$ system

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Abstract

A catalytic deSoot–deNO$_x$ system, comprising Pt and Ce fuel additives, a Pt-impregnated wall-flow monolith soot filter and a vanadia-type monolithic NH$_3$-SCR catalyst, was tested with a two-cylinder DI diesel engine. The soot removal efficiency of the filter was 98–99 mass% with a balance temperature (stationary pressure drop) of 315 °C at an engine load of 55%. The NO$_x$ conversion ranged from 40 to 73%, at a NH$_3$/NO$_x$ molar ratio of 0.9. Both systems were measured at a GHSV of 52 000 l/(l h). The maximum NO$_x$ conversion was obtained at 400 °C. The reason for the moderate deNO$_x$ performance is discussed. No deactivation was observed after 380 h time on stream. The NO$_x$ emission at high engine loads is around 15% lower than that of engines running without fuel additives. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: NO$_x$ reduction; Diesel soot oxidation; Diesel fuel additives

1. Introduction

The diesel engine owes its popularity to its fuel efficiency, reliability, durability and relatively low fuel price. Its further development should be focused on the adverse effects on environment and health caused by NO$_x$- and soot emissions. Soot particles are formed in the cylinder of the engine, due to local shortages of oxygen. Nitrogen oxides are formed in an oxygen-rich atmosphere at high temperatures and pressures. Measures to reduce particulate mass emission will result in an increase in NO$_x$ emissions and visa versa. This phenomenon is known as the NO$_x$-PM trade-off. Only a few primary techniques, such as fuel–water emulsions and direct water injection into the cylinder, are available that are able to reduce PM formation with a simultaneous reduction of the NO$_x$ emission. This integrated abatement of both soot and NO$_x$ is, however, insufficient to comply with future emission legislation. Therefore, an after-treatment process for the simultaneous reduction of the diesel engine's emissions has to be aimed for.

In earlier work, Jelles et al. [1,2] developed a catalytic deSoot system. They showed that the Pt/Ce fuel additives combined with a Pt-impregnated wall-flow monolith gave optimal soot removal results at a balance temperature of 310–320 °C. Recently, it was found that a balance point around 275 °C was obtained by optimalisation of the filter design [3]. Krijnsen et al. [4] developed a catalytic deNO$_x$ system, using a commercial Frauenthal, consisting of V$_2$O$_5$–WO$_3$–TiO$_2$ catalyst and NH$_3$ as a reducing agent. Integration of these systems is then a logical step.

The goal of the integration of the deSoot and deNO$_x$ system is to investigate the effect of the Pt wall-flow monolith and Pt/Ce fuel-borne additive on the deNO$_x$ performance of the V$_2$O$_5$–WO$_3$–TiO$_2$ Frauenthal catalyst downstream of a genuine diesel engine. Within

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this scope, the temperature of the deSoot filter and the deNO$_x$ catalyst were varied, as well as the NH$_3$/NO$_x$ ratio and the engine load.

2. Experimental

As soot abatement technology, a platinum-impregnated cordierite wall-flow monolith was used in combination with platinum and cerium fuel-borne additives. The platinum additive (Platinum Plus 3100) was a gift from Clean Diesel Technologies and the cerium (DPX9) was a gift from Rhodia. For the NO$_x$ removal, an SCR (vanadia-type) honeycomb catalyst was applied downstream of the deSoot catalyst. Ammonia was used as NO$_x$ reductant. Ammonia was obtained from Hoek Loos (The Netherlands) in 20 vol.% in nitrogen and added to the desired concentration in the exhaust gas stream by means of a mass-flow controller. A flow sheet of the experimental set-up is given in Fig. 1.

An LPW2, Lister–Petter water-cooled, 6.6 kW, two-cylinder diesel engine fitted with a Stamford generator, 5.3 kW, was used, running on a commercially available summer diesel fuel was used containing 400–500 ppm sulphur. The engine power was dissipated using a variable resistance bank that allowed engine loads of 15, 20, 30 or 55% of the rated engine power. During the measurements, the additive concentrations were kept at 2 ppm Pt and 30 ppm Ce. These additives were blended with the diesel fuel. The fuel consumption was measured gravimetrically. The intake air temperature was controlled at 30 °C. A constant exhaust gas-flow rate was maintained by a pump downstream of the integrated system, independently on the pressure over the system and was set at a GHSV of 52 000 l/(l h). The remainder was vented directly.

The deSoot system consisted of a cylindrical 20 mm × 40 mm (diameter × length) cordierite wall-flow monolith (Corning, EX80) impregnated with 0.6 wt.% platinum. The monolith was dipped into a Pt solution (8 mg/g tetra-amineplatinum(II)chloride hydrate (Aldrich 27,920) in water) for impregnation and subsequently dried at 100 °C (at 10 °C/min) for 1 h and calcined at 750 °C (at 5 °C/min) for 1 h. After drying, ceramic paste was used to plug the endings of the monoliths in a checkerboard fashion. Finally, the plugged monolith was dried again at 90 °C, followed by calcination at 450 °C for 4 h (5 °C/min). After this treatment, Pt clusters of 50–100 nm can be observed [1]. These clusters have shown to be essential for converting NO to NO$_2$, which enhances the soot combustion [1]. The filter housing was heated and the temperature within the deSoot section was controlled.

The NO$_x$ reducing agent was found to be partially oxidised when injecting it upstream of the deSoot filter. Therefore, it had to be dosed downstream of the deSoot filter. Downstream of the NH$_3$ injection location, a static mixer and a temperature-controlled deNO$_x$ catalyst were located. For the deNO$_x$ section, a cylindrical 20 mm × 40 mm (diameter × length) monolith was cut from a commercial Frauenthal monolith, consisting of V$_2$O$_5$–WO$_3$–TiO$_2$.

After leaving the deNO$_x$ catalyst, the exhaust gas passed a paper (check) filter, which served to incidentally detect the deSoot filter leaking. Finally,

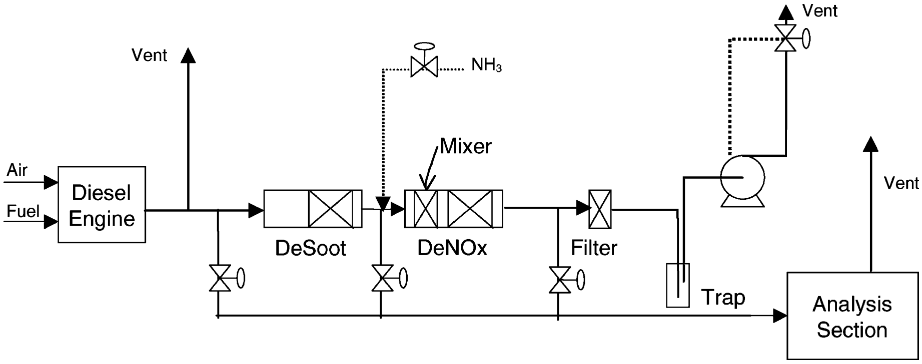

Fig. 1. Schematic flow sheet of the deSoot–deNO$_x$ reactor set-up.

the gas was vented via a condensate trap, an exhaust membrane pump and a flow controller. As a result of pumping the exhaust gas through the system, the pressure in the system was slightly below atmospheric pressure.

The NO, NO_2 and NO_x emissions were measured by an Eco Physics CLD 700 EL ht NO_x analyser based on the chemiluminescence principle. The gas was sampled upstream or downstream of the deSoot filter or downstream of the deNO_x catalyst. The sample lines were all heat traced at a temperature of about 120 °C. Washing bottles containing 35 wt.% sulphuric acid and 85 wt.% phosphoric acid removed ammonia and water from the sample streams and as a consequence no ammonia slippage could be measured.

To investigate the effect of both deSoot filter temperature and deNO_x temperature, the temperatures of both catalysts were varied independently. The effect of the engine load (i.e. NO_x concentration) on the NO_x conversion was investigated while keeping the deSoot filter at standard conditions. The deNO_x temperature was varied between 250 and 450 °C. In addition, the NH_3/NO_x molar ratio was varied between 0.25 and 1.4 to estimate its effect on the NO_x conversion.

The effect of fuel-borne additives on the NO_x emission from the LPW2 engine was investigated by measuring the NO_x emission and NO_2/NO_x ratio at: (1) the exhaust pipe, (2) the deSoot system, and (3) the deNO_x system as indicated in Fig. 1. The NO_2/NO_x ratios were measured at standard catalyst conditions. During these measurements, no NH_3 was injected into the exhaust gas. In addition to these measurements, the temperature of the deSoot section was varied between 50 and 600 °C to investigate its effect on the NO_2/NO_x ratio.

In the discussion, the results of the fuel-borne fuelled LPW2 engine will be compared to a similar LPW3 engine running on the same diesel fuel, but without additives.

3. Results and discussion

Not only the Pt clusters affect the soot combustion, but also the fuel additives play an important role in the mechanism of filter regeneration [1–3]. The cerium additive catalyses the particulate oxidation by the NO_2 formed over the Pt clusters. The platinum additive is thought to continuously reactivate the Pt clusters, since the system was stable without lost of activity (no change in balance temperature) over the time interval of 380 h in the presence of commercially available diesel fuel, containing 400–500 ppm sulphur. It is known that SO_3 can deactivated platinum catalysts under these applied conditions. The result is an equilibrium temperature of 315 °C at a GHSV of 52 000 l/(l h). The soot production rate (g/s) of the engine (at 3.7 kW, i.e. 55% of rated power; 35 mg soot/m_n^3 exhaust gas) will equal the soot oxidation rate (g/s) at this temperature by the catalytic system. This temperature is called the balance point temperature and is in agreement with earlier work. The filter efficiency of the Pt-impregnated wall-flow monoliths lies at 98–99%. For more details on this deSoot system, the reader is referred to Jelles et al. [1–3].

The NO_x emission and NO_2/NO_x ratio as a function of the engine load are given in Table 1. The NO_2/NO_x ratios as a function of the sampling locations are given in Table 2. It can be seen that the NO_2/NO_x ratio is highest upstream of the deSoot filter and decreases further downstream. The NO_2/NO_x ratio was also measured downstream of the deSoot filter as a function of filter temperature (50–600 °C). Neither the ratio nor the NO_x emission were significantly affected

Table 1
NO_x emissions as a function of engine load

Rated power (%)	LPW2 (additives)		LPW3 (no additives)	
	NO_x emission (ppm)[a]	NO_2/NO_x	NO_x emission (ppm)[a]	NO_2/NO_x
15	580	0.17	540	0.07
20	645	0.17	650	0.07
30	810	0.17	950	0.07
55	1200	0.17	1450	0.07

[a] NO_x emission expected when using dry combustion air of 30 °C; correction based on data of the LPW3 engine.

Table 2
Average NO_2/NO_x ratios and standard deviations as a function of the sample location at a GHSV of 52 000 l/(l h)

Location	NO_2/NO_x ratio
Upstream of deSoot filter (100 °C)	0.17 ± 0.02
Downstream of deSoot filter (50–600 °C)	0.12 ± 0.02
Downstream of $deNO_x$ catalyst (350 °C)	0.10 ± 0.01[a]

[a] Without NH_3 injection into the exhaust.

by the filter temperature. The NO_2/NO_x fraction was significantly increased in the LPW2 deSoot section in comparison to the LPW3 ($NO_2/NO_x = 0.17$ and 0.07, respectively) that ran without fuel-borne additives. Also this relatively high ratio was found in the exhaust manifold of the LPW2 diesel engine. The phenomenon behind this effect remains unclear and is beyond the scope of the paper. The NO_2/NO_x ratio drops over both the deSoot filter section and the $deNO_x$ section when no NH_3 is injected into the exhaust. Measurement results were also compared to the engine NO_x and NO emissions of a similar LPW3 engine (three cylinders instead of two) running on the same fuel, but without fuel additives, as displayed in Table 1. It can be seen that the NO_x emission is equal for the LPW2 engine at engine loads below 2.2 kW and significantly lower (up to 15%) than the LPW3 engine at higher engine load and are in agreement with earlier field-tests observations [5]. The phenomenon behind this effect remains unclear and is also beyond the scope of this paper.

The effects of the deSoot filter temperature and the $deNO_x$ catalyst temperature are displayed in Fig. 2. NO_x conversions range from 40 to 73% at a GHSV of 52 000 l/(l h) at a NH_3/NO_x ratio of 0.9, dependent on deSoot (200–600 °C) and $deNO_x$ temperature (250–450 °C).

As can be seen in Fig. 2, the NO_x conversion over the SCR catalyst increased with increasing deSoot temperature. These results seem to be contradictory to other recent publications [6,7]. The difference in results is attributed to the fact that the NO_2/NO_x ratio over the deSoot catalyst did not change as function of temperature. In general, the NO conversion into NO_2 is a function of temperature and the kinetics of the applied catalyst. The lower the temperature, the higher is the NO_2 concentration. Due to the effect of the (trapped) soot oxidation by NO_2, in which NO is dominantly is formed, the apparent NO_x/NO ratio over the deSoot system is constant, as shown in Table 2.

The effect of the NH_3/NO_x ratio on the NO_x conversion is given in Fig. 3. The more reactant is dosed to the exhaust gas, the more NO_x is converted. In the absence of a deSoot system, the NH_3 conversion up

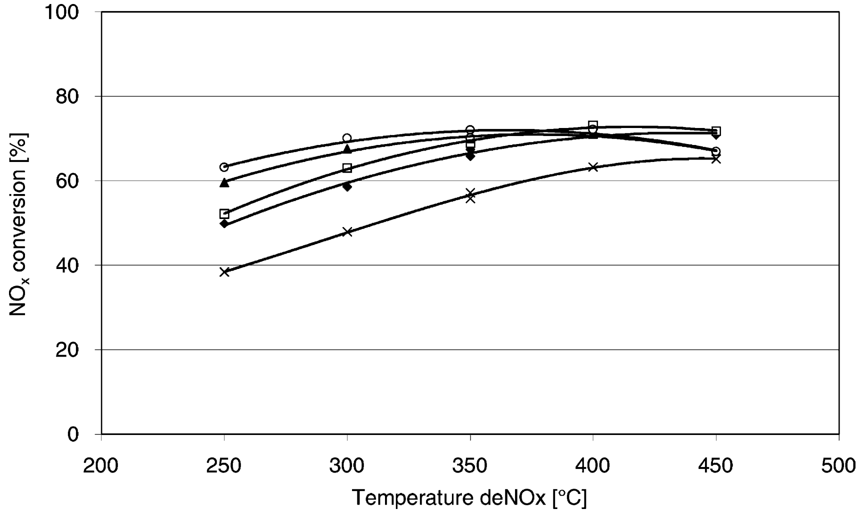

Fig. 2. NO_x conversion as a function of the $deNO_x$ catalyst temperature and deSoot temperature at NH_3/NO_x molar ratio of 0.9, at a GHSV of 52 000 l/(l h), engine load of 1.4 kW; deSoot temperature: (×) 200 °C; (◆) 350 °C; (□) 400 °C; (▲) 500 °C; (○) 600 °C.

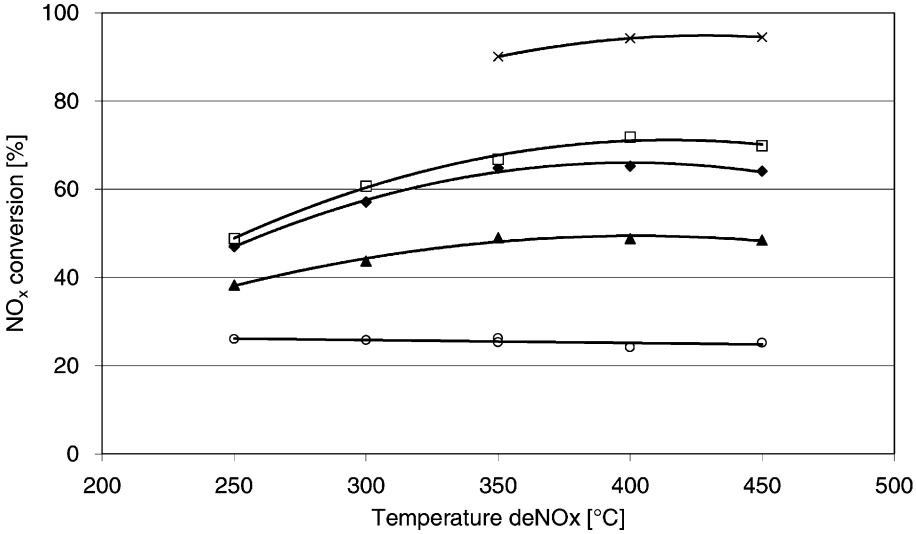

Fig. 3. NO_x conversion as a function of the $deNO_x$ catalyst temperature and NH_3/NO_x ratio, at a GHSV of 52 000 l/(l h), deSoot system presence, 1.4 kW (620 ppm NO_x); NH_3/NO_x: (○) 0.25; (▲) 0.51; (◆) 0.87; (☐) 1.08; NH_3/NO_x: (×) 1.4 at 3.7 kW (1200 ppm NO_x).

to a NH_3–NO_x ratio of 1 is almost quantitative [4]. In the presence of a deSoot system, the NH_3 conversion is suppressed to a large extent (up to 40%). This suppression of the Frauenthal catalyst in the NO_x abatement has to be attributed to SO_3 in the gas phase. The deSoot system contains platinum, which is known to be the best SO_2 into SO_3 catalyst. Apparently, the formed SO_3 will preferentially adsorb onto the active SCR-$deNO_x$ sites on the Frauenthal catalyst and, thereby, inhibits the NO_x reduction to some extent. The same observation was recently made for a large shipment diesel engine [8]. If upstream of an SCR system, a deSoot system was installed which is capable to convert SO_2/SO_3 the NO_x reduction will be suppressed.

No significant amounts of Pt, Ce or carbonaceous material were found on the Frauenthal catalyst after being on stream for about 380 h. After this time on stream, NO_x conversions were still reproducible, whereas the deSoot filter kept its balance point temperature of 315 °C.

It can be concluded from these investigations on the deSoot–$deNO_x$ system downstream of the LPW2 engine that the $deNO_x$ performance of the Frauenthal catalyst was high and of practical importance. This integrated combination opens the possibility of the simultaneous removal of both soot and NO_x for future diesel emission legislation certifications.

4. Conclusions

When combining the catalytic Pt-impregnated soot filter system with an SCR Frauenthal catalyst at a GHSV of 52 000 l/(l h) and fuelling the engine with Pt/Ce additive containing diesel fuel, soot removal efficiencies of 98–99% and NO_x conversions ranging from 40 to 73% are achieved. At these conditions, the balance point temperature of the soot filter was 315 °C. The maximum observed NO_x conversion was 95% at a NO_x catalyst temperature of 400 °C, a NH_3/NO_x ratio of 1.4, a Soot filter temperature of 315 °C and a GHSV of 52 000 l/(l h). NH_3 slip cannot, however, be excluded. This diminished NO_x conversion is attributed to the presence of SO_3 in the gas phase. This SO_3 is generated by the deSoot system. No significant amounts of Pt, Ce or carbonaceous material were found on the Frauenthal catalyst after being on stream for about 380 h. No deactivation of the deSoot and the $deNO_x$ catalytic systems was observed after this time interval. A 15% reduction of NO_x emission was determined for an engine running at Pt and Ce additives at engine loads higher than 30%.

References

[1] S.J. Jelles, M. Makkee, J.A. Moulijn, G.J.K. Acres, J.D. Peter-Hoblyn, Application of an activated trap in combination with fuel additives at an ultra-low dose rate, SAE 990113, 1999.

[2] S.J. Jelles, R.R. Krul, M. Makkee, J.A. Moulijn, The influence of NO_x on the oxidation of metal activated diesel soot, Catal. Today 53 (1999) 623–630.

[3] S.J. Jelles, M. Makkee, J.A. Moulijn, Ultra-low dosage of platinum and cerium fuel additives as diesel particulate control, Topics Catal. 16/17 (1–4) (2001) 269–273.

[4] H.C. Krijnsen, J.C.M. Van Leeuwen, R. Bakker, H.P.A. Calis, C.M. Van den Bleek, Optimum deNO_x performance using feedforward reductant control, Fuel 80 (7) (2001) 1001–1009.

[5] E.R. Fanick, J.M. Valetine, Emissions reduction performance of a bimetallic platinum/cerium fuel-borne catalyst with several diesel particulate filters on different sulfur fuels, SAE P-2001-01-0904, 2001.

[6] G.R. Chandler, B.J. Cooper, J.P. Harris, J.E. Thoss, A. Uusimäki, A.P. Walker, J.P. Warren, An integrated SCR and continuously regenerating trap system to meet future NO_x and PM legislation, SAE P-2000-01-0188, 2000.

[7] J. Gieshoff, A. Schäfer-Sindlinger, P.C. Spurk, J.A.A. van den Tillaart, G. Garr, Improved SCR systems for heavy duty applications, SAE P-2000-01-0189, 2000.

[8] H. Jansma, M. Makkee, J.A. Moulijn, Testing downstream of shipment diesel engine, Unpublished results, March 2001.