

Engine bench and road testing of an engine oil containing MoS₂ particles as nano-additive for friction reduction



M.F. Sgroi^{a,*}, M. Asti^a, F. Gili^a, F.A. Deorsola^b, S. Bensaid^b, D. Fino^b, G. Kraft^c, I. Garcia^d, F. Dassenoy^e

^a Group Materials Labs, Centro Ricerche FIAT, Strada Torino 50, 10043 Orbassano, Italy

^b Politecnico di Torino, Department of Applied Science and Technology, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

^c FUCHS Schmierstoffe, Friesenheimerstr. 19, 68169 Mannheim, Germany

^d Materials Division, IK4-CIDETEC Research Centre, Paseo Miramn 196, 20009 Donostia-San Sebastián, Spain

^e Ecole Centrale de Lyon, LTDS, bt H10, 36 avenue Guy de Collongue 69134, Ecully, France

ARTICLE INFO

Keywords:

Nano-lubricants
Inorganic fullerenes
Nano-particles
Engine tests

ABSTRACT

The development of new advanced lubricants is a key factor for the production of cleaner and more durable internal combustion engines. New improved anti-friction and anti-wear additives are required to improve the fuel economy and reduce the greenhouse gases emission. The inclusion of nanoparticles known as solid lubricants (MoS₂ and WS₂ inorganic fullerenes) in engine oils could help to improve the performance of internal combustion engines. This paper describes the results of the testing activities performed on a fully formulated engine oil incorporating MoS₂ nanoparticles. The nano-lubricant allowed demonstrating on the New European Driving Cycle (NEDC) a reduction of 0.9% of fuel consumption with respect to the reference lubricant without nanoparticles.

1. Introduction

The development of new advanced lubricants is a key factor for the production of cleaner and more durable internal combustion engines. As a matter of fact, the improvement of performance and efficiency of modern engines is mainly related to optimization of the combustion process but this requires in parallel materials able to sustain extreme working conditions. In this scenario new lubricants and coatings for engine components are of fundamental importance. The engine oil has an important role in the reduction of fuel consumption as a consequence of minimization of friction losses and has a strong impact on both the durability of mechanical components and on the behavior of the emission after-treatment systems. The roadmap on the development of new engine oils, shared between lubricant suppliers and engine manufacturers, foresees the progressive reduction of the viscosity of the lubricants, in order to reduce the losses in elasto-hydrodynamic regime. As a consequence, new improved anti-friction and anti-wear additives are required to protect the mechanical components during cold start-up when boundary lubrication regime may occur. Moreover exhaust catalysts can be poisoned by some components of additive package of the lubricant and the diesel particulate filter (DPF) durability can be reduced by the ashes generated by the burning of

the engine oil. The main contributors to the formation of ashes are zinc, sulphur and phosphorus, commonly found in anti-wear additives known as ZDDP (Zinc dialkyl-dithio-phosphates) and in anti-friction additives based on organic molybdenum and sulphur compounds. For reducing the impact on the DPF, zinc-free low and ultra-low SAPS (Sulphated Ash, Phosphors and Sulphur) oils are being developed for modern diesel engines. In this scenario the inclusion of MoS₂ and WS₂ solid lubricant nanoparticles, known as *inorganic fullerenes* (IF), in a fully formulated engine oil could help to improve the performances of the lubricant and of the engine [1,2]. Inorganic fullerenes were first synthesized by Tenne and his research group at the Weizmann Institute of Science [3,4] and were proposed for different applications including lubrication, electronics, data storage and electron microscopy (as microscope tips) [5]. The lubrication mechanism of inorganic fullerenes was debated for a long time and recently it was described as a combination of sliding/exfoliation and rolling of the nanoparticles between the surfaces of the tribological contact [6–13]. Moreover, alternative routes for the synthesis of MoS₂ nanoparticles have recently been explored [14,15] in the framework of the AddNano project. More recently other experimental works were devoted to the exploration of performances of MoS₂ nanoparticles in lubrication [16–19]. A general review on the use of nanoparticles as lubricant additives was recently

* Corresponding author.

E-mail address: mauro.sgroi@crf.it (M.F. Sgroi).

published by Gulzar et al. [20].

The AddNano Consortium, partially funded by the European Commission, investigated the possibility to include inorganic fullerenes and similar particles in the formulation of engine oils and greases. MoS₂ nanoparticles integrated in the additive package of a FUCHS 5W30 engine oil showed a 50% reduction of the coefficient of friction in tribological lab scale experiments [2]. The nano-oil was formulated modifying the additive content in order to disperse in a stable way the nanoparticles and avoiding counter productive interactions with the other components of the formulation (anti-foam, anti-oxidant, detergents, anti-wear and anti-friction additives). In the present work, the characterization of the nano-lubricant on an engine test bench simulating the real working conditions of a modern diesel engine is reported. Moreover the lubricant was tested on a vehicle and aged for 20,000 km. The evolution of oil ageing during the mileage accumulation was evaluated by periodic chemical analysis and by measurement of the fuel consumption and emissions of the engine.

2. Experimental

2.1. Nano-particles and lubricating oils

The MoS₂ nanoparticles were synthesized by IK4-CIDETEC using a low cost wet chemistry route (patent application EP15382166.5) that can be easily scaled up for industrial production. Prior to mixing nanoparticles with the oil, MoS₂ nanoparticles were characterized using High Resolution Transmission Electron Microscopy (HR-TEM). Experiments were performed on a JEOL 2010F electron microscope operating with 200 kV accelerating voltage. The characterization of the nanoparticles was made by depositing a drop of highly diluted nanoparticle dispersion in heptane onto a standard holey-carbon copper grid. The morphology of the MoS₂ nanoparticles, reported in Fig. 1, is of nearly spherical IF-type with concentric nested layers showing a considerable amount of point defects and grain boundaries. According to Dassenoy et al. [11], this type of defective structure leads to the exfoliation of the particles and to the formation of a lubricating tribolayer formed by MoS₂ on the mating surfaces. In contrast, the lubrication mechanism for not defective particles is based on the rolling of the nano-sphere between the surfaces of the tribological contact. Fig. 2 shows the size distribution of the particles: their mean diameter is about 52 nm.

The selected reference lubricant was the zinc-free 5W30 multi-grade engine oil produced by FUCHS Schmierstoffe. The nanoparticles were pre-dispersed by a combination of mechanical stirring and ultrasound irradiation in a reference oil containing dispersants able to avoid aggregation and settling of the solid phase. Then this pre-

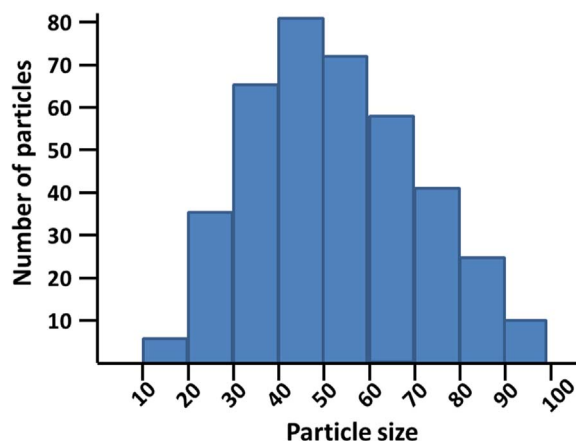


Fig. 2. Size distribution of IF-MoS₂ nanoparticles: the data were obtained sampling a relevant number of particles and measuring the dimensions by HR-TEM.

concentrate was diluted in partially formulated engine oils to obtain the nano-lubricant. The concentration of nanoparticles was investigated between 0.1 and 2 wt%, the optimal concentration in terms of tribological performances being 0.5 wt%. The additives of the nano-lubricant were adapted to obtain a stable dispersion and to avoid negative interaction between different components. Moreover the composition of the nano-lubricant was maintained as similar as possible to that of the reference oil. The tested samples and their characteristics are reported in Table 1. As expected the presence of nanoparticles, due to the low concentration, does not modify the viscosity and rheological properties of the fluids.

2.2. Experimental setup for engine tests

A possible interaction between the MoS₂ nanoparticles and commercial catalysts, representative of EURO V-compliant catalytic converters used in the diesel passenger cars after-treatment systems, was investigated. The test bench included a diesel engine (OPEL 1900 cm³ JTD common Rail) connected to a dynamo-meter (AVL Alpha 240 KW) with a maximum rpm/torque of 10,000 rpm /600 Nm. The experimental campaign was performed as follows: initially, the engine was conditioned with the reference oil, through a standardized procedure for internal oil circulation before the test was started. Then the tests were run at five different engine points, defined by two parameters, the engine speed (rpm, revolutions per minute) and the brake mean effective pressure (BMEP), expressed respectively in rpm and in bar. In order to reproduce the most representative operating conditions, the selected engine points were: 1500×1, 2000×2, 2500×3, 3000×4 and

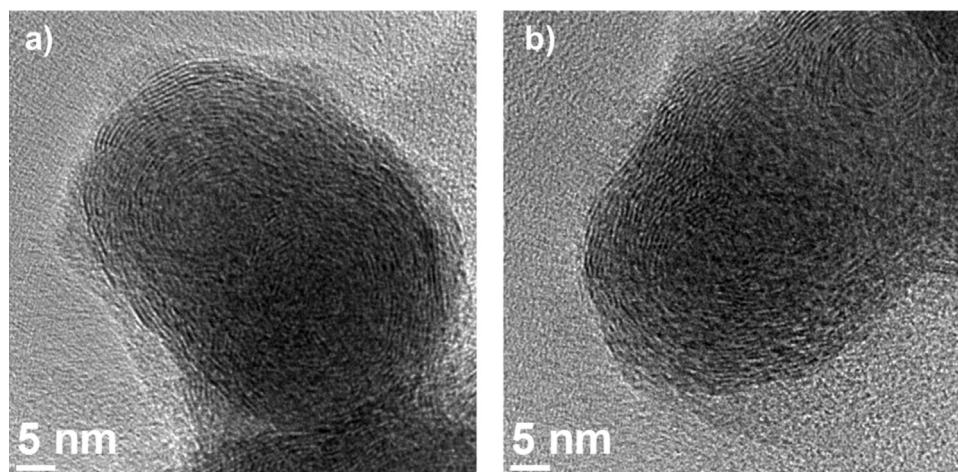


Fig. 1. HR-TEM images of two different (a and b) IF-MoS₂ nanoparticles.

Table 1
Denomination and properties of tested nano-lubricants samples.

Sample	Viscosity grade	Kinematic viscosity
FUCHS 5W30	5W30	60.04 @ 40 °C, 10.18 @ 100 °C
FUCHS 5W30+MoS ₂	5W30	60.11 @ 40 °C, 10.18 @ 100 °C

3500×5. For each engine point, four different temperatures of the cooling water of the engine were identified and examined (40, 60, 80 and 95 °C). The exhaust gas recirculation (EGR) was fixed to zero in all operating conditions. These settings were operated through the dedicated AVL PUMA program, by monitoring all engine conditions with INCA software connected to the Electronic Control Unit (ECU) integrated with ETAS and BOSCH instrumentation: the temperature of the cooling water, of the engine outlet exhaust gases and of the lubricant oil were measured by means of K-type thermocouples. An AVL 733S Dynamic Fuel Meter balance was integrated to the AVL PUMA system in order to measure the fuel consumption. The same procedure was adopted for the nano-lubricant. The tests consisted in monitoring and measuring the exhaust gas composition, the size distribution of emitted particulate matter, the temperature and pressure, for each engine point and for each cooling water temperature. In particular, the gas composition was continuously detected before and after both the Diesel Oxidation Catalyst (DOC) and the Diesel Particulate Filter (DPF), by an ABB gas analyser, equipped with two Uras26 analysers for N₂O, NO, CO₂, CO and SO₂, and a Magnos 206 analyser to measure O₂. The unburned hydrocarbons (HCs) were measured by a Hartmann & Braun Multifid14 analyser. The soot particle size distribution was recorded using a Scanning Mobility Particle Sizer 3080 (SMPS), whose detailed description is given in previous works [21,22]. The engine exhaust gases were sampled using a heated pipe (1 m long, 6 mm diameter, kept at a temperature of 150 °C), followed by two ejector pump diluters in series (Dekati Ltd.): each stage provided a dilution factor of about 8, resulting a 64-fold overall dilution, which was calibrated measuring the carbon dioxide concentrations in the exhaust and in the sample flow, and then the exiting gas was transported to the SMPS system through a 4 m long tube with an internal diameter of 4 mm.

2.3. Experimental set-up for road tests

The vehicle selected for road tests of the lubricants was an Euro 5 Lancia Delta, with a weight of 1.430 kg and equipped with 2.0 dm³ diesel engine. Table 2 reports the main characteristics of the engine.

The emission after-treatment system included a DOC (Diesel Oxidation Catalysts) and a catalysed SiC DPF (Diesel Particulate Filter) positioned in the exhaust line in the so-called CC (Closed Coupled) configuration, i.e. close to engine, downstream to the turbocharger. Since the DPF is gradually clogged by ashes produced by the combustion of the engine oils, the main objective in this study was to clarify if the use of a nano-lubricant containing solid particles can increase the amount of ashes damaging the particulate filter.

2.4. Mileage accumulation program

To evaluate the effects of the ageing of the lubricant and of the

Table 2
Main characteristics of the engine of the Lancia Delta 2000 16 V MJT.

Engine characteristics	
Stroke number	4
Displacement	2.0 dm ³
Max. power @ 4000 rpm	165 HP
Max. torque @ 2000 rpm	360 Nm

nanoparticles, mileage accumulation was carried out through two different paths, urban and extra-urban. The ratio of accumulated distance between urban and extra-urban/highway was about 1:5. This corresponds to a common usage profile of a diesel engine. Chemical analysis of the lubricants was performed at the beginning of the road tests sampling the oil from the engine reservoir. This procedure allows determining the degree of contamination of the fresh oil due to residuals of the lubricant used immediately before. The testing with the reference FUCHS 5W30 lubricant lasted for 5000 km. The performance, in terms of fuel economy, of FUCHS 5W30+MoS₂ were compared with the reference after 5000 km of ageing. After that the nano-lubricant was aged up to 20,000 km and the performance of the engine were evaluated thanks to roller bench tests every 5000 km.

2.5. Chemical analysis

The lubricants were characterized from a physico-chemical point of view through standard analytical techniques. The presence of wear elements in the used oils was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) according to the norm D5185. Kinematic viscosities were measured according to the standard D445 and viscosity index according to D2270. Water content was determined according to D1744. Finally total acid number (TAN) and total base number (TBN) were measured according to D4739 and D664 respectively. The reference norms can be found on the ASTM's website [23].

2.6. Roller bench facility

Fuel consumption tests were carried out on a roller chassis dynamometer facility equipped with temperature and humidity controls, gas analysers for pollutants and CO₂ evaluation and systems for particulate matter monitoring. Fuel consumption was estimated on the basis of CO₂ emissions. Fig. 3 reports the scheme of the bench with the main features.

The expected fuel economy benefit of using the nano-lubricant, evaluated on the basis of previous tribological studies, is about 1–2% [2]. On the other hand, the experimental error for the measurement of fuel consumption on standard driving cycles (like the NEDC, New European Driving Cycle) is about 1%. For this reason a constant velocity method was implemented to reduce the measurement uncertainty and appreciate the effect of the nano-lubricant on the fuel consumption of the car. CO₂ emissions were measured for the following velocities and gear speeds:

- 3rd gear speed at 50 km/h corresponding to about 2000 rpm
- 4th gear speed at 50 km/h corresponding to about 1500 rpm
- 5th gear speed at 120 km/h corresponding to about 2800 rpm

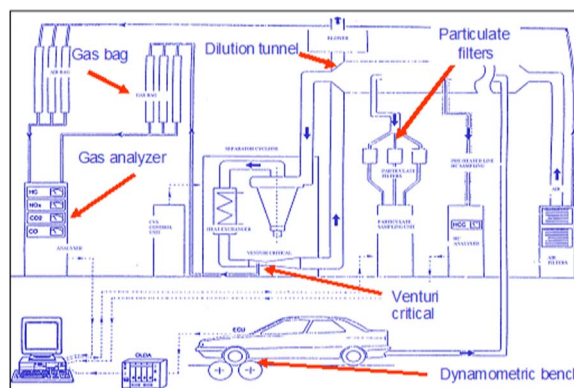


Fig. 3. Roller chassis dynamometric and emissions analysis system.

The above conditions correspond to three representative stationary engine points included in the NEDC cycle. Moreover collected engine emissions and electronic board data were analysed at different accumulated mileage to check the impact of oil ageing on the performance of the engine (4 cycles were acquired for each mileage accumulation step).

3. Results and discussion

3.1. Engine bench tests

The particulate emissions measured by the SMPS measured at two different engine points (couples of RPM and BMEP in bar: 1500×1 and 2000×2) and cooling water temperature (40, 60, 80 and 95 °C) are illustrated in Figs. 4 and 5. Particulate emissions were monitored at the engine outlet (i.e. the DOC inlet), at the DOC outlet (i.e. the DPF inlet) and at the DPF outlet. By these measurements it was possible to estimate the impact of the nano-additive on the generation of particulate matter during the combustion process. The mass concentrations of the carbonaceous particles are reported in Tables 3 and 4 for the reference and nano-lubricant respectively. The use of the MoS₂ nanoparticles affected the particulate distribution in the exhaust gases. Focusing on the engine point 1500×1 (see Fig. 4) it can be observed that the particulate distribution at the DOC inlet as well as at the DPF inlet showed a Gaussian trend at all cooling temperatures, as described by Kittelson et al. [24,25]. At the DOC inlet, the particulate emissions measured with the reference and the nano-lubricant showed a very similar behavior at 40 °C and 80 °C, whereas at 60 °C and 95 °C the peak of the particle size distribution with the nano-lubricant was

shifted at lower particles diameters with respect to the reference oil. Concerning the DPF inlet, the curves for the two samples were almost equivalent: the particles with dimension lower than 50 nm (nuclei mode) were significantly decreased, while the particles with size over 50 nm (accumulation mode) remained substantially unchanged. Finally, the DPF outlet emissions at 1500×1 never exhibited, at all cooling water temperatures, significant amounts of particulate. For the engine point 2000×2 (Fig. 5), the trend of the curves at the DOC inlet is very similar to the engine point 1500×1: the particulate emissions for the reference and the nano-lubricant were almost overlapped at 40 °C as well as 80 °C. At 60 °C and 95 °C the concentration of the particles with low diameter was higher by using the MoS₂ nanoparticles as additive.

The curves of particulate distribution for the other engine points (2500×3, 3000×4, 3500×5) showed a trend similar to the one described previously for 1500×1 and 2000×2; for the sake of brevity, they are reported in the Supplementary material (Figures S1–S3). In general, the DOC was able to nullify the small variations arising in the distribution profiles at different engine points, demonstrating a high efficiency in the oxidation of the finest fraction of particles generated by the nano-lubricant, presumably being constituted by aerosol instead of solid particles [26]. The distribution curves at the DPF inlet are very similar for both lubricants and they showed a substantial flattening of their profile. Furthermore, the concentration of the finest fraction of particulate at the DOC outlet was even decreased at 40 °C by employing the nano-additivated oil, meaning a lower content of volatile and sulphur-based compounds in the exhaust gases. Also the efficiency of the DPF was not affected by the nanoparticles, with a complete abatement of the soot. At the DPF outlet, the concentration of soot

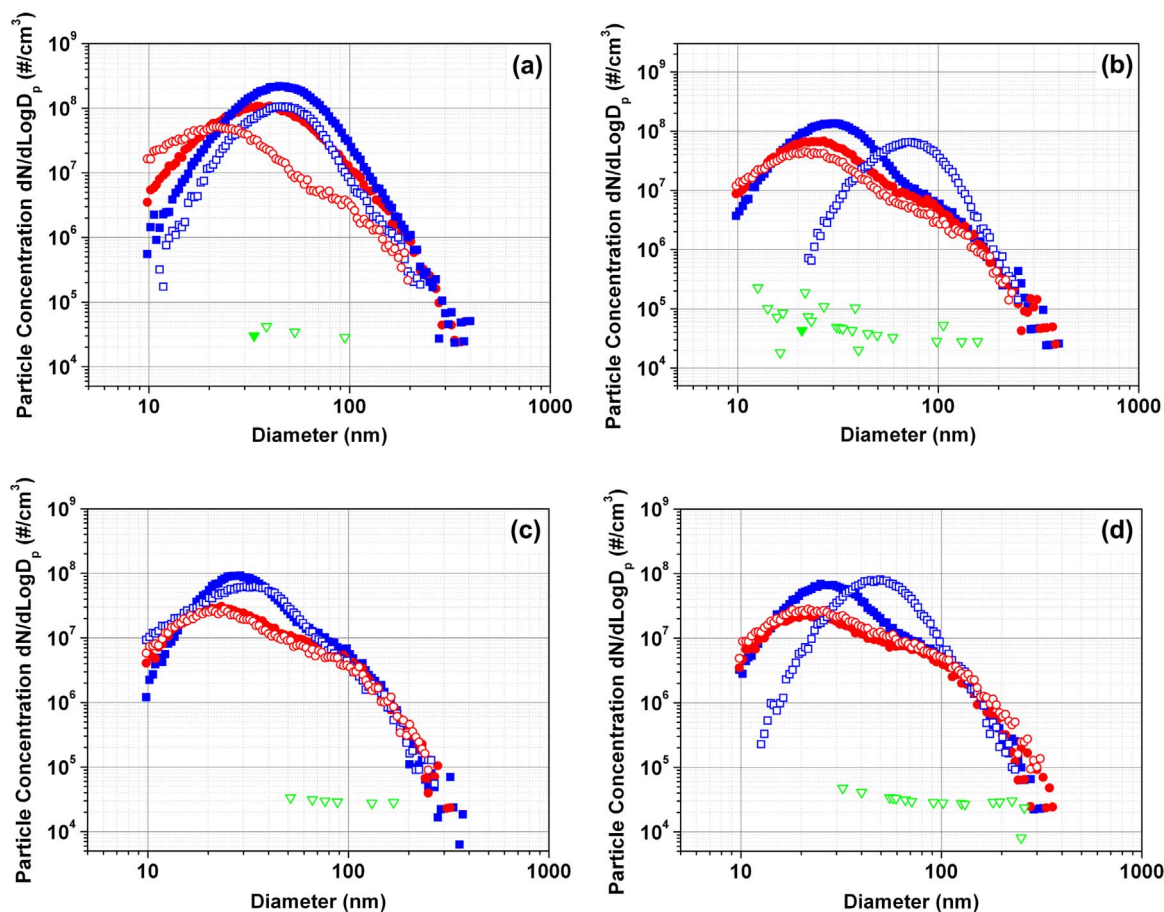


Fig. 4. Soot particle concentration versus particles diameter for the engine point 1500×1 before the DOC (squares), before the DPF (circles), after the DPF (triangles), for the reference oil (open symbols) and nano-lubricant (closed symbols) at four cooling water temperatures: (a) 40 °C, (b) 60 °C, (c) 80 °C, (d) 95 °C. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

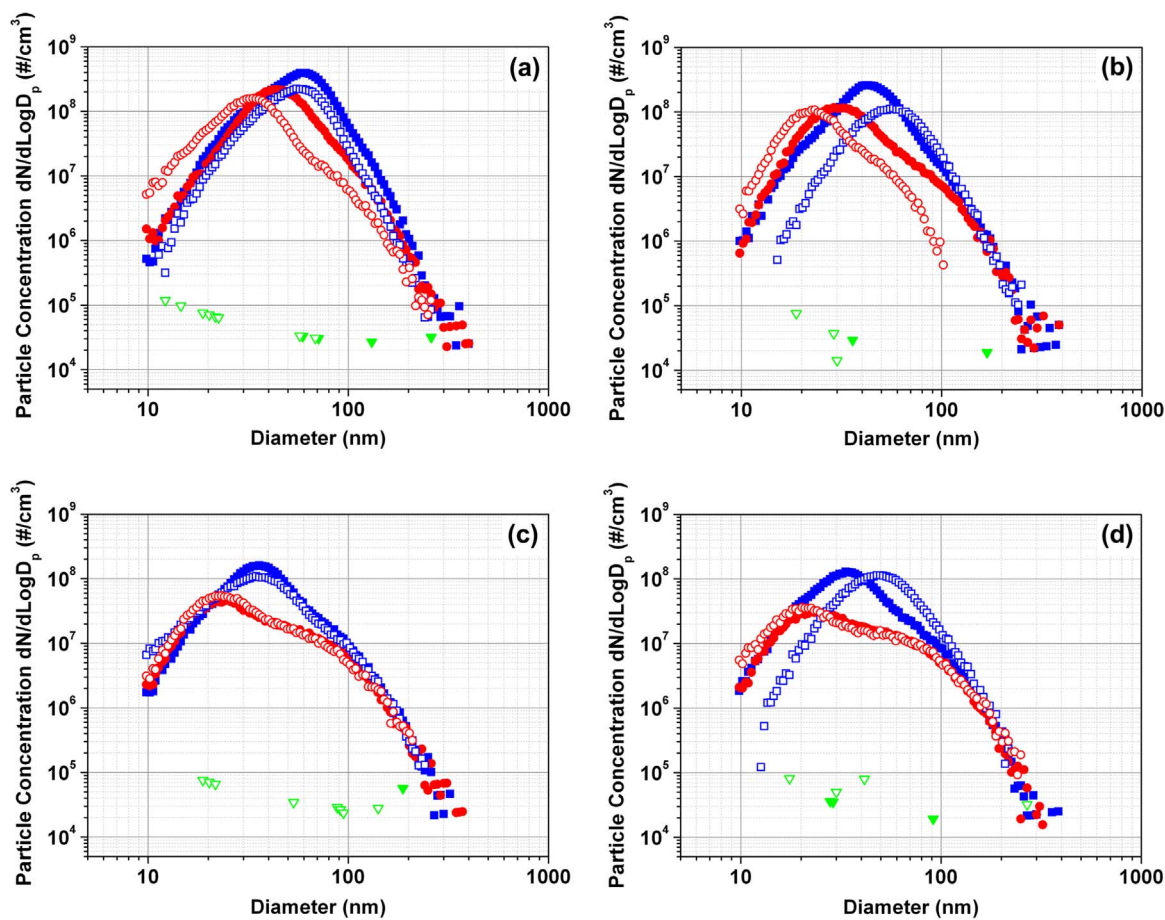


Fig. 5. Soot particle concentration versus particles diameter for the engine point 2000x2 before the DOC (squares), before the DPF (circles), after the DPF (triangles), for the reference oil (open symbols) and nano-lubricant (closed symbols) at four cooling water temperatures: (a) 40 °C, (b) 60 °C, (c) 80 °C, (d) 95 °C. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

Table 3

Mass concentration ($\mu\text{g}/\text{m}^3$) of soot particles before the DOC, before the DPF and after the DPF, for the FUCHS 5 W30 reference oil.

Temperature	Engine point	in DOC	in DPF	out DPF
40 °C	1500x1	6677	2403	0
	2000x2	18,474	5062	0
	2500x3	21,205	7936	17
	3000x4	18,517	7264	1
	3500x5	20,202	6374	15
60 °C	1500x1	15,850	2483	4
	2000x2	11,221	2246	0
	2500x3	12,181	5459	6
	3000x4	19,904	6912	3
	3500x5	19,882	6496	33
80 °C	1500x1	3050	2362	4
	2000x2	5734	3085	2
	2500x3	7637	4413	3
	3000x4	12,202	5088	2
	3500x5	13,461	5434	21
95 °C	1500x1	6054	3722	22
	2000x2	9322	3219	9
	2500x3	7850	4518	13
	3000x4	11,946	5030	4
	3500x5	14,698	4976	25

with the nano-lubricant was always equal or lower to that with the reference oil, for all the engine points and the cooling temperatures considered, as can be appreciated in Tables 3 and 4. The analysis of the

Table 4

Mass concentration ($\mu\text{g}/\text{m}^3$) of soot particles before the DOC, before the DPF and after the DPF, for the FUCHS 5W30+MoS₂ oil.

Temperature	Engine point	in DOC	in DPF	out DPF
40 °C	1500x1	18,121	8655	0
	2000x2	37,126	13,101	6
	2500x3	34,466	13,557	10
	3000x4	40,636	12,073	7
	3500x5	28,328	10,121	18
60 °C	1500x1	5037	3558	0
	2000x2	12,128	4862	1
	2500x3	15,189	7196	3
	3000x4	22,957	8026	0
	3500x5	19,061	9602	8
80 °C	1500x1	3637	2526	0
	2000x2	6534	3266	2
	2500x3	9065	5163	1
	3000x4	10,295	6114	0
	3500x5	14,703	6611	8
95 °C	1500x1	3200	1831	0
	2000x2	5453	2041	3
	2500x3	6899	3227	0
	3000x4	8864	3811	0
	3500x5	8903	4004	3

distribution of the particulate size showed at the engine outlet an evident increase of the concentration of the ultra-fine particles for some engine points and cooling temperatures by using the nano-lubricant.

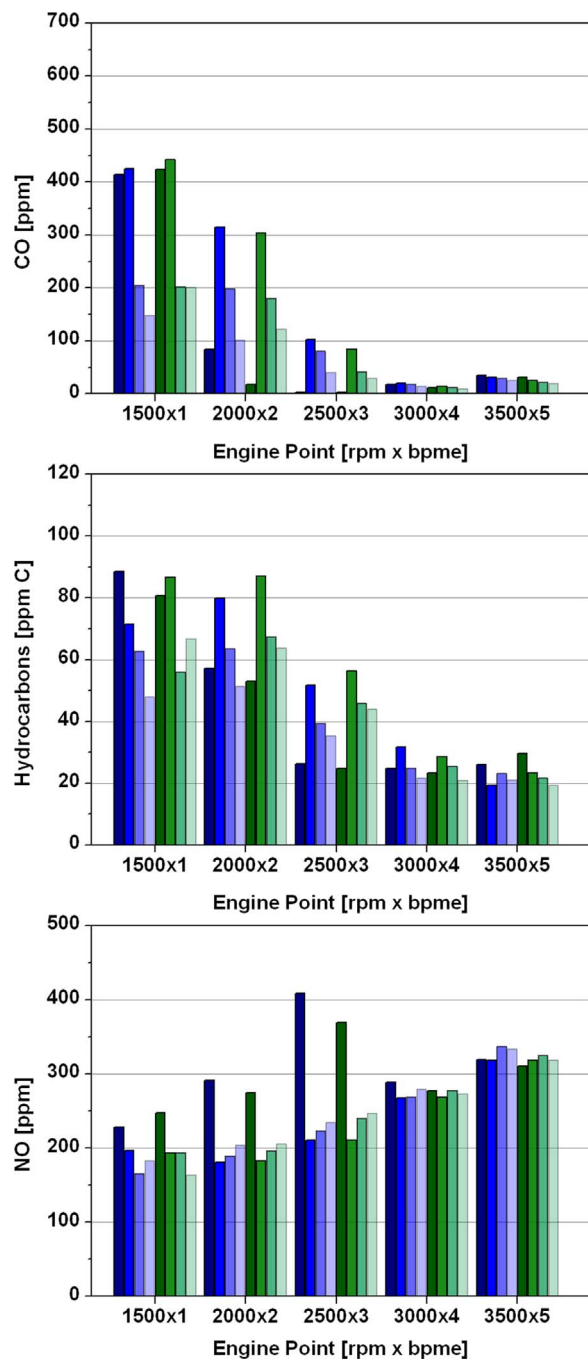
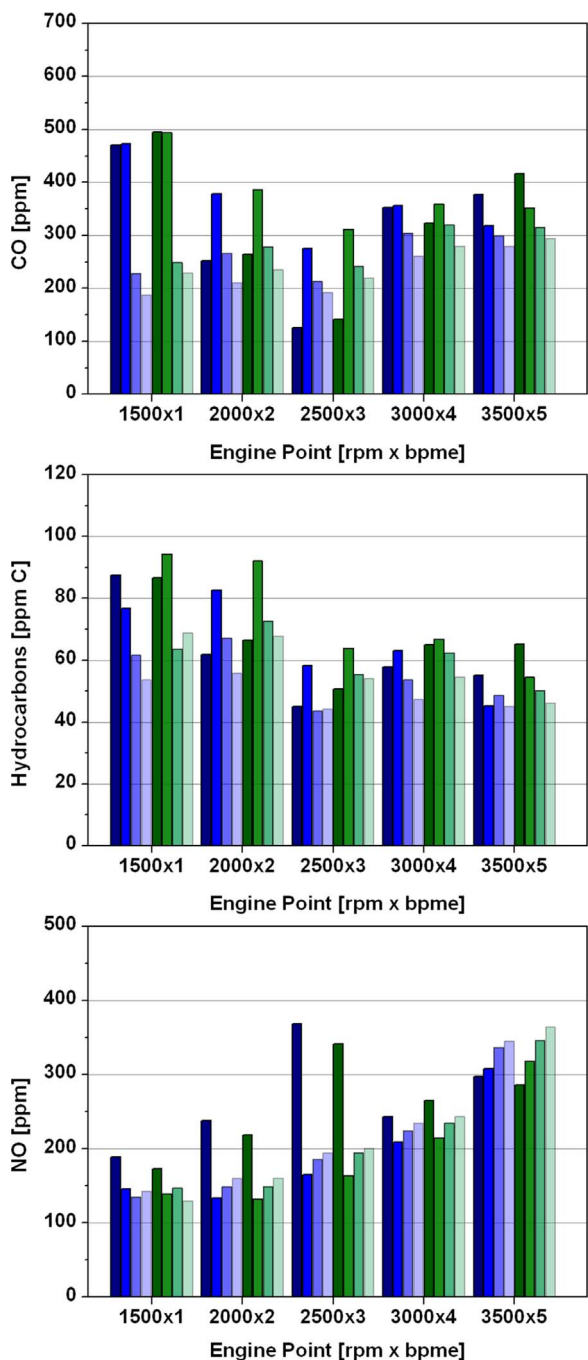


Fig. 6. CO, HC and NO concentration at the engine outlet at different engine points for the reference oil FUCHS 5W30 (filled white) and the FUCHS 5W30+MoS₂ oil (grey) at various cooling water temperatures (40 °C, 60 °C, 80 °C and 95 °C, from left to right).

Fig. 7. CO, HC and NO concentration at the DOC outlet at different engine points for the FUCHS 5W30 reference oil (filled white) and the FUCHS 5W30+MoS₂ oil (grey) at various cooling water temperatures (40 °C, 60 °C, 80 °C and 95 °C, from left to right).

This fraction of particles belongs to the nuclei mode including, besides soot particles, also soluble organic fraction (SOF) and sulphur-based compounds that can be formed during dilution and cooling of the exhaust gases [26]. These species can likely cause the increase of the nuclei mode when the nano-additivated oil is employed. Even if these compounds are precursors of the nucleation of the soot particles, the total mass concentration of soot particle for the nano-lubricant was however lower with respect to the reference oil at the considered engine points and cooling temperatures. The shift of the peak towards smaller size for the oil additivated with MoS₂ nanoparticles was substantially eliminated at the DOC outlet and the curves resulted quite identical, because the carbonaceous soot, which belongs to the latter class, is poorly oxidized at the DOC operating temperature, whereas the volatile

and sulphur-based compounds, belonging to the nuclei mode, are oxidized in the DOC.

The effect of the addition of the MoS₂ nanoparticles to the reference oil was also evaluated by the analysis of the CO, HC and NO_x concentrations in the gaseous emissions at the engine outlet (i.e. DOC inlet), DOC outlet (i.e. DPF inlet) and DPF outlet, illustrated in Figs. 6, 7 and 8 respectively. It is worth pointing out that the nano-additivated oil showed slight variations in the concentrations for some scattered engine points and cooling temperatures with respect to the reference oil. In particular, the CO and HC values presented a not negligible but not pronounced increase at the engine and DPF outlets, whereas in most cases NO_x were decreased, especially at low engine points (1500×1, 2000×2 and 2500×3) and low cooling temperatures. A

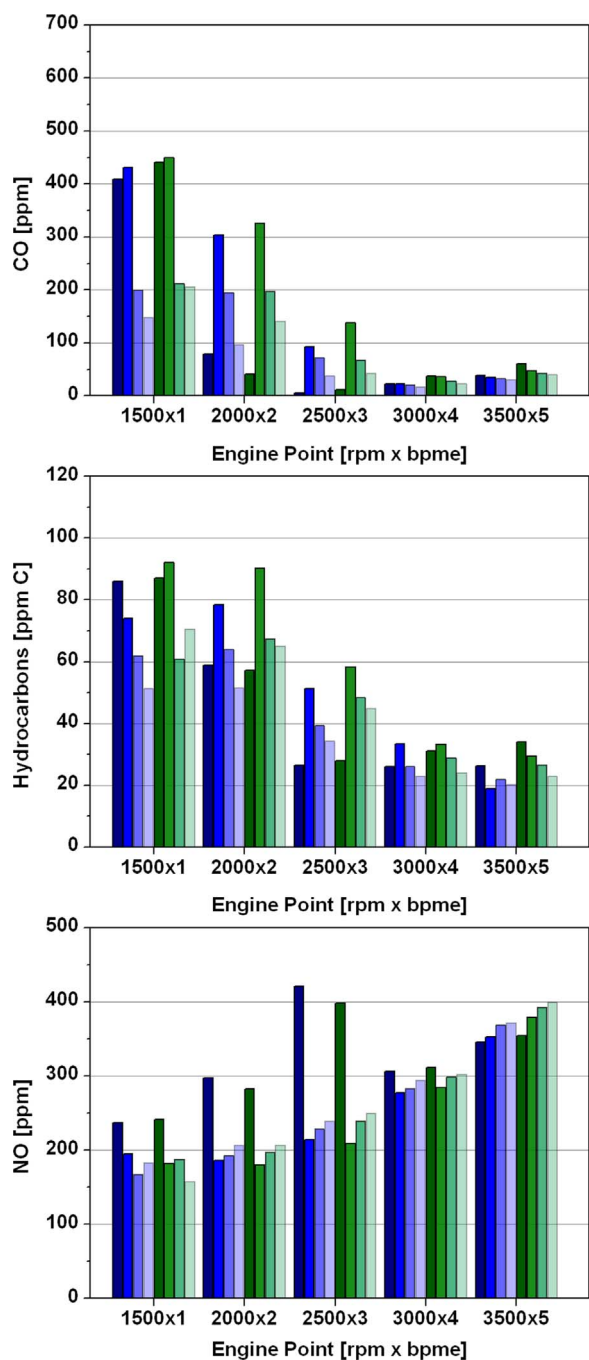


Fig. 8. CO, HC and NO concentration at the DPF outlet at different engine points for the FUCHS 5W30 reference oil (filled white) and the FUCHS 5W30+MoS₂ oil (grey) at various cooling water temperatures (40 °C, 60 °C, 80 °C and 95 °C, from left to right).

systematic trend can be hardly identified, and the largest part of these variations can be substantially considered inside the experimental error. Finally, we observed a general improvement of the fuel economy at almost every engine point, with a maximum effect (5%) at the engine point 3500×5 (see Fig. 9). This result proved to be systematic and was within the range of fluctuating values of fuel consumption measured at steady state conditions (1–2%).

As described, the addition of the MoS₂ nanoparticles to the reference oil allowed obtaining a behavior that can be considered generally better with respect to the reference oil, with very similar gaseous emissions, lower particulate emissions and the absence of additional SO₂ emissions arising from the possible combustion of MoS₂. This suggested that a better combustion regime was reached

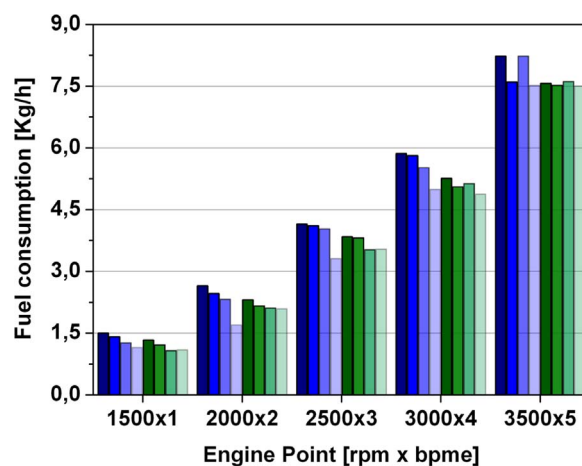


Fig. 9. Fuel consumption at different engine points for the FUCHS 5W30 reference oil (filled white) and the FUCHS 5W30+MoS₂ oil (grey) at various cooling water temperatures (40 °C, 60 °C, 80 °C and 95 °C, from left to right).

with the MoS₂ additive, i.e. with no interference of the nanoparticles during the fuel combustion. A further demonstration of this enhanced behavior was achieved by the measurement of the fuel consumption reported in Fig. 9. MoS₂ nanoparticles reduced the fuel consumption at almost every engine conditions, with a more remarkable improvement in absolute terms at low and intermediate water (and thus oil) temperatures, and severe engine points (2500×3, 3000×4, 3500×5).

3.2. Road tests

The Lancia Delta oil sump was filled with the 5 W30 reference oil and the vehicle was operated for 5000 km to stabilize all tribological contacts. After this conditioning procedure, the fuel consumption and emissions were measured on the roller chassis dynamo-metric bench. Four fuel consumption tests were carried out with the 5W30 reference oil. After the preliminary conditioning with the reference lubricant, the engine was flushed out three times with the nano-lubricant. Then mileage accumulation started and the car was driven along the two selected routes (urban and extra-urban) for a total of 20,000 km, performing chassis dynamometric characterization (fuel consumption and emissions) at 5000, 10,000 and 20,000 km and comparing the results with those obtained with the reference oil. The lubricants were analysed during the mileage accumulation program to monitor the ageing in term of variation of viscosity, water content and modification of total base and acid numbers. An increased water content can indicate a contamination of the oil due to water generated by the combustion process: an excessive contamination can lead to a decrement of lubrication performance. The total acid number (TAN) is crucial to maintain the mechanical integrity of equipment and to prevent internal damage of components. TAN is related to the oxidation of the oil, so it increases overtime or if the oil is exposed to high temperature. Oxidation severely reduces the oil ability to protect internal components and can also affect the viscosity. The TAN is defined as the weight (in milligrams) of a standard base (e.g. potassium hydroxide, KOH) that is required to neutralize all of the acidic components within the oil. To balance the increase of acidity of the crankcase lubricants during their service life, manufacturers add to the formulation basic compound. The total base number (TBN) determines how effective is the oil in protecting the engine components from corrosion. The unit of measurement for both TAN and TBN is mg of KOH per gram of oil sample. The results of physico-chemical analysis of the oils during the mileage accumulation program are reported in Table 5.

The CO₂ emission data for the reference 5 W30 oil annealed for 5000 km and the those obtained with the nano-lubricant during the

Table 5

Results obtained from chemical analysis on the lubricants during the mileage accumulation.

Parameter	Unit	FUCHS 5W30		FUCHS 5W30+MoS ₂			
Mileage	km	0	5000	0	5000	10,000	20,000
Viscosity (40 °C)	cSt	60.04	58.59	60.00	58.27	57.04	56.08
Viscosity (100 °C)		10.18	10.05	10.23	10.09	9.59	9.7
Viscosity Index	–	158	159	159	161	159	159
TAN	mg KOH /g	1.59	1.91	1.67	1.70	2.93	3.29
TBN	mg KOH /g	10	7.80	9.35	8.50	7.60	6.4
Water content	ppm	–	525	823	492	381	598
Cr content	ppm	0	1	1	1	1	3
Cu content	ppm	0	2	1	3	5	7
Fe content	ppm	0	24	0	16	39	96
Mn content	ppm	0	2	1	1	2	5

Table 6

Comparison of CO₂ emission factors (EF) derived from bag analysis at different constant speeds. At each kilometric value, the measurement was repeated 4 times and the reported data are the medium values. δCO₂ are the percentage variations of the emission factors with respect to the reference.

Sample	50 km/h		50 km/h		120 km/h	
	3rd gear		4th gear		5th gear	
	EF (g/ km)	δCO ₂	EF (g/ km)	δCO ₂	EF (g/ km)	δCO ₂
Reference 5000 km	112.2	0.0	86.2	0.0	155.8	0.0
Nanolubricant 0 km	108.6	-3.2	84.2	-2.3	157.7	1.2
Nanolubricant 5000 km	109.3	-2.6	84.4	-2.1	161.6	3.7
Nano-lubricant 10,000 km	109.4	-2.5	84.3	-2.2	162.1	4.0
Nano-lubricant 20,000 km	109.3	-2.6	83.3	-3.3	159.3	2.2

mileage accumulation program are reported in Table 6.

The results obtained on chassis dynamo-metric test bench during the mileage accumulation program can be commented as follows:

- On the basis of CO₂ emissions at 5000 km (i.e. direct comparison between the two oils aged in the same way) at low speed, a lower fuel consumption is observed using the nano-lubricant, while at high speed the trend is reversed. The advantage of using the nano-lubricant at low speed is about 2–3% but this is compensated by an opposite result at higher speed.
- The mileage accumulation does not modify the performances of the nano-lubricant and the degradation of the oil and nanoparticles has a minimal impact on fuel consumption.
- During the use of the nano-lubricant no signs of accelerated wear processes are evident since the content of wear elements, especially iron, remains very low (see Table 5).
- The viscosity and the viscosity index of the nano-lubricant are essentially equal to those of the reference fluid. The presence of nanoparticles, as expected, does not alter the rheologic behavior of the oil. Moreover the viscosities do not change during the mileage accumulation.
- Even at 20,000 km the nano-lubricants shows a moderate water content (sign of no contamination) and acceptable values of TAN and TBN. It is hence possible to exclude uncontrolled degradation of the fluid during the tests.

The most interesting result is related to the reduction of friction at



Fig. 10. Engine rotational speed versus CO₂ emission factor curves obtained from constant speed cycle data.

low engine speed: this is expected because in those conditions the engine is working in mixed regime (near boundary conditions) and the presence of nanoparticles can help to reduce the coefficient of friction between moving parts. On the other hand the presence of nanoparticles should be negligible at high engine regimes where hydrodynamic conditions occur. On the contrary a negative effect on fuel consumption is observed: this behavior is still unclear and deserves further studies. To better interpret the results, it is possible to calculate the CO₂ emissions reduction that the nano-lubricant can yield during a standard NEDC cycle. The reference oil FUCHS 5W30 was aged up to 5000 km, so the following analysis is based on the comparison of the two lubricants at that point of the mileage accumulation program. The basic assumptions and the calculation method can be summarized as follows:

- An interpolation function, correlating the CO₂ emission to the revolutions per minute (rpm) of the engine, was built on the basis of the CO₂ emission data measured at the three constant speeds (see Fig. 10).
- The revolutions per minute measured during the NEDC cycles were used to obtain, through the interpolation function, the CO₂ emission as a function of time.
- The CO₂ emissions were integrated over the cycle duration, obtaining in this way the CO₂ emission factors on the NEDC cycle.

On the basis of the above mentioned data processing scheme, the CO₂ emission factors of FUCHS 5W30+MoS₂ resulted to be 0.9% lower than those obtained with the reference FUCHS 5W30.

4. Conclusions

The aim of the present job was the assessment, at engine and vehicle level, of the behavior of a nano-lubricant based on MoS₂ nanoparticles in terms of fuel consumption and noxious emission. The engine bench tests allowed verifying the compatibility of the nano-lubricant with the after-treatment system and its influence on the pollutant emissions. They showed a general improvement of the emission abatement with respect to the reference oil, with lower particulate emissions, very similar concentrations of the gaseous emissions (mainly CO, HCs and NO) and no additional SO₂ emissions deriving from the possible decomposition of the molybdenum disulphide nanoparticles. For some engine points and cooling temperatures, an increase of the ultra-fine soot particles was measured at the engine outlet, although the DOC efficiently burned this fraction and at the DPF inlet the differences resulted to be nullified. Furthermore, the measured fuel consumption on engine test bench highlighted increased fuel savings for almost every engine points and cooling temperatures, with values reaching even 5% at some specific operative conditions. Finally,

the inclusion of MoS₂ nanoparticles in the reference oil resulted to be fully compatible with the after-treatment system of current passenger vehicles, showing a reduction of all the pollutant emissions to levels lower than those reached with the reference oil and a remarkable performance in terms of fuel consumption, demonstrating an improvement with respect to the current unmodified lubricant oil. The evaluation on the vehicle allowed to test and age the nano-lubricant in real working conditions with a special emphasis on the possible benefits on fuel consumption. The reduction on fuel consumption measured during the roller bench tests entails a fuel economy of about 1% at the vehicle level (extrapolated on the NEDC). The difference with respect to the better results observed at engine level can be explained considering the impact of the energy losses present on vehicle, as the friction in the transmission system and tyre/road contact and the aerodynamics. The ageing of the lubricant does not alter the performance of the nano-additive. According to the experimental results the formulated nano-lubricant appear a good low cost solution to reduce the fuel consumption with no modification of the engine. A further research is recommended to assess the behavior of the additive based on MoS₂ nanoparticles in order to understand the impact on the very long term durability of the after-treatment components and the possible emissions of ultra-fine nanoparticles containing molybdenum (with dimensions not filtered by the DPF).

Acknowledgments

The ADDNANO Project (Grant no. 229284), funded by the European Commission as part of the 7th Framework Programme, is gratefully acknowledged for the financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.triboint.2016.10.013>.

References

- [1] B. Gullac, O. Akalin, Frictional characteristics of IF-WS₂ nanoparticles in simulated engine conditions, *Tribol Trans* 53 (6) (2010) 939–947. <http://dx.doi.org/10.1080/10402004.2010.511761>.
- [2] M. Sgroi, F. Gili, D. Mangherini, I. Lahouij, F. Dassenoy, I. Garcia, et al., Friction reduction benefits in valve-train system using IF-MoS₂ added engine oil, *Tribol Trans* 58 (2015) 207–214. <http://dx.doi.org/10.1080/10402004.2014.960540>.
- [3] L. Cizaire, B. Vacher, T.L. Mogne, J. Martin, L. Rapoport, A. Margolin, et al., Mechanisms of ultra-low friction by hollow inorganic fullerene-like MoS₂ nanoparticles, *Surf Coat Technol* 60 (2002) 282–287. [http://dx.doi.org/10.1016/S0257-8972\(02\)00420-6](http://dx.doi.org/10.1016/S0257-8972(02)00420-6).
- [4] L. Yadgarov, V. Petrone, R. Rosentsveig, Y. Feldman, R. Tenne, A. Senatore, Tribological studies of rhenium doped fullerene-like MoS₂ nanoparticles in boundary, mixed and elasto-hydrodynamic lubrication conditions, *Wear* 297 (2013) 1103–1110. <http://dx.doi.org/10.1016/j.wear.2012.11.084>.
- [5] A.P.E. York, Inorganic fullerenes, onions, and tubes, *J Chem Educ* 81 (5) (2004) 673–676. <http://dx.doi.org/10.1021/ed081p673>.
- [6] L. Joly-Pottuz, F. Dassenoy, M. Belin, B. Vacher, J. Martin, N. Fleischer, Ultralow-friction and wear properties of IF-WS₂ under boundary lubrication, *Tribol Lett* 18 (2005) 477–485. <http://dx.doi.org/10.1007/s11249-005-3607-8>.
- [7] I. Lahouij, B. Vacher, J. Martin, F. Dassenoy, IF-MoS₂ based lubricants: influence of size, shape and crystal structure, *Wear* 296 (2012) 558–567. <http://dx.doi.org/10.1016/j.wear.2012.07.016>.
- [8] I. Lahouij, F. Dassenoy, L. de Knoop, J. Martin, B. Vacher, In situ tem observation of the behavior of an individual fullerene-like mos₂ nanoparticle in a dynamic contact, *Tribol Lett* 42 (2) (2011) 133–140. <http://dx.doi.org/10.1007/s11249-011-9755-0>.
- [9] I. Lahouij, E. Bucholz, B. Vacher, S. Sinnott, J. Martin, F. Dassenoy, Lubrication mechanisms of hollow-core inorganic fullerene-like nanoparticles: coupling experimental and computational works, *Nanotechnology* 23 (37) (2012) 375701. <http://dx.doi.org/10.1088/0957-4484/23/37/375701>.
- [10] I. Lahouij, F. Dassenoy, B. Vacher, J. Martin, Real time tem imaging of compression and shear of single fullerene-like MoS₂ nanoparticle, *Tribol Lett* 45 (1) (2012) 131–141. <http://dx.doi.org/10.1007/s11249-011-9873-8>.
- [11] I. Lahouij, B. Vacher, F. Dassenoy, Direct observation by in situ transmission electron microscopy of the behaviour of IF-MoS₂ nanoparticles during sliding tests: influence of the crystal structure, *Lubric Sci* 26 (3) (2014) 163–173. <http://dx.doi.org/10.1002/ls.1241>.
- [12] P. Rabaso, F. Ville, F. Dassenoy, M. Diaby, P. Afanasiev, J. Cavoret, et al., Boundary lubrication: influence of the size and structure of inorganic fullerene-like mos₂ nanoparticles on friction and wear reduction, *Wear* 320 (2014) 161–178. <http://dx.doi.org/10.1016/j.wear.2014.09.001>.
- [13] J. Tannous, F. Dassenoy, I. Lahouij, T.L. Mogne, B. Vacher, A. Bruhács, et al., Understanding the tribochemical mechanisms of IF-MoS₂ nanoparticles under boundary lubrication, *Tribol Lett* 41 (1) (2011) 55–64. <http://dx.doi.org/10.1007/s11249-010-9678-1>.
- [14] G. Santillo, F. Deorsola, S. Bensaid, N. Russo, D. Fino, Mos₂ nanoparticle precipitation in turbulent micromixers, *Chem Eng J* 207–208 (2012) 322–328. <http://dx.doi.org/10.1016/j.cej.2012.06.127>.
- [15] S. Bensaid, F. Deorsola, D. Marchisio, N. Russo, D. Fino, Flow field simulation and mixing efficiency assessment of the multi-inlet vortex mixer for molybdenum sulfide nanoparticle precipitation, *Chem Eng J* 238 (2014) 66–77. <http://dx.doi.org/10.1016/j.cej.2013.09.065>.
- [16] A. Sedova, R. Ron, O. Goldbart, O. Elianov, L. Yadgarov, N. Kampf, et al., Re-doped fullerene-like MoS₂ nanoparticles in relationship with soft lubrication, *Nanomater Energy* 4 (2015) 30–38. <http://dx.doi.org/10.1680/nme.14.00020>.
- [17] H. Wu, L. Qin, Q. Zeng, G. Dong, Understanding the physical adsorption action mechanism of MoS₂ nanoparticles in boundary lubrication with different polyisobutyleneamine succinimide (PIBS) concentrations, *Tribol Lett* 60 (2015) 1–12. <http://dx.doi.org/10.1007/s11249-015-0604-4>.
- [18] A. Tomala, B. Vengudusamy, M. Rodríguez Ripoll, A.N. Suarez, M. Remškar, R. Rosentsveig, Interaction between selected MoS₂ nanoparticles and ZDDP tribofilms, *Tribol Lett* 59 (2015) 1–18. <http://dx.doi.org/10.1007/s11249-015-0552-z>.
- [19] M.S. Charoo, M.F. Wani, Tribological properties of IF-MoS₂ nanoparticles as lubricant additive on cylinder liner and piston ring tribo-pair, *Tribol Ind* 38 (2016) 156–162.
- [20] M. Gulzar, H.H. Masjuki, M. Kalam, M. Varman, N.W.M. Zulkifli, R.A. Mufti, et al., Tribological performance of nanoparticles as lubricating oil additives, *J Nanopart Res* 18 (2016) 1–25. <http://dx.doi.org/10.1007/s11051-016-3537-4>.
- [21] J.C. Caroca, F. Millo, D. Vezza, T. Vlachos, A.D. Filippo, S. Bensaid, et al., Detailed investigation on soot particle size distribution during DPF regeneration using standard and bio-diesel fuels, *Ind Eng Chem Res* 50 (2011) 2650–2658. <http://dx.doi.org/10.1021/ie1006799>.
- [22] S.C. Marcano, S. Bensaid, F. Deorsola, N. Russo, D. Fino, Nanolubricants for diesel engines: related emissions and compatibility with the after-treatment catalysts, *Tribol Int* 72 (2014) 198–207. <http://dx.doi.org/10.1016/j.triboint.2013.10.018>.
- [23] (<http://www.astm.org>).
- [24] D.B. Kittelson, Engines and nanoparticles: a review, *J Aerosol Sci* 29 (5/6) (1998) 575–588.
- [25] Abdul-Khalek I, Kittelson D, Brear F. The influence of dilution conditions on diesel exhaust size distribution measurements. SAE Paper 1999-01-1142; 1999. p. 103–111.
- [26] (<https://www.dieselnet.com/gl-s.html>); 2016.