

Performance of Particle Oxidation Catalyst and Particle Formation Studies with Sulphur Containing Fuels

Piotr Bielaczyc

BOSMAL Automotive R&D Institute

Jorma Keskinen

Tampere Univ of Technology

Jakub Dzida and Rafal Sala

BOSMAL Automotive R&D Institute

Topi Ronkko

Tampere Univ of Technology

Toni Kinnunen and Pekka Matilainen

Ecocat Oy

Panu Karjalainen

Tampere Univ of Technology

Matti Juhani Happonen

Tampere Univ. of Technology

ABSTRACT

The aim of this paper is to analyse the quantitative impact of fuel sulphur content on particulate oxidation catalyst (POC) functionality, focusing on soot emission reduction and the ability to regenerate. Studies were conducted on fuels containing three different levels of sulphur, covering the range of 6 to 340 parts per million, for a light-duty application. The data presented in this paper provide further insights into the specific issues associated with usage of a POC with fuels of higher sulphur content. A 48-hour loading phase was performed for each fuel, during which filter smoke number, temperature and back-pressure were all observed to vary depending on the fuel sulphur level. The Fuel Sulphur Content (FSC) affected also soot particle size distributions (particle number and size) so that with FSC 6 ppm the soot particle concentration was lower than with FSC 65 and 340, both upstream and downstream of the POC. Conversely, FSC did not have major effects on the soot particle number reduction efficiency of the POC. Soot and other exhaust compounds accumulated within the POC during this phase, gradually built a pressure drop across the POC. The final mass of collected matter in the POC differed significantly according to the sulphur content. The efficiency of removal of gaseous pollutants by the POC was found to be markedly worse for the fuels with higher sulphur content, although this deterioration was observed to be non-linear. Following the accumulation phase, a duty cycle was applied that caused the POC to commence passive regeneration. The time taken for the POC to cleanse itself of accumulated matter and thereby eliminate the pressure drop was observed to increase with increasing fuel sulphur content. The proportion of NO_x leaving the POC in the form of NO₂ was also found to vary as a strong function of fuel sulphur content.

CITATION: Bielaczyc, P., Keskinen, J., Dzida, J., Sala, R. et al., "Performance of Particle Oxidation Catalyst and Particle Formation Studies with Sulphur Containing Fuels," *SAE Int. J. Fuels Lubr.* 5(2):2012, doi:10.4271/2012-01-0366.

INTRODUCTION

Particulate matter in ambient air, including the pollutants emitted from internal combustion engines, can adversely affect human health [1,2,3,4,5] and the environment by interfering with the climate and ecosystems. Among others, the particulate matter (PM) present in diesel exhaust is of special concern because, due to their respirable size, they can penetrate deep into human lungs affecting health; see e.g. [6,7,8]. On the other hand, the vehicle particle emissions are generated in our immediate environment meaning that millions of people get exposed daily to these emissions. However, harmful characteristics and affecting mechanisms of the pollutants are unclear. Fuel composition, its physical and chemical parameters have very important influences on the quantity and constitution of emissions. Fuel characteristics can affect emissions in three key areas [9,10,11]:

- by influencing injection parameters,
- by connection with the creation of pollutant matter in the engine or in the atmosphere,
- by influencing the efficiency of emission control systems.

Particulate matter emitted in diesel exhaust is a complex internally and/or externally mixed mixture of carbonaceous soot, unburned fuel and lubricants and perhaps fuel pyrolysis products. Particulate matter can be solid and liquid; typically PM includes four fractions of diesel particulates: (1) solid soot, (2) SOF (heavy hydrocarbons), (3) sulphur compounds and (4) ash. Sulphur content is one of the fuel properties which has the most influence on particulates, for modern engines [9,12]. The particulate emissions of diesel engine exhaust are a function of number of parameters, for example: engine type, engine operating conditions, fuel and lubricant oil composition [9]. The size distribution of submicron diesel exhaust particles can be divided typically into two separate modes called *accumulation mode* (AM) and *nucleation mode* (NM) [13]. The accumulation mode consists of solid agglomerated soot particles which can carry volatile or semivolatile components (e.g. sulfur compounds, water, hydrocarbons) on the surface [14]. Nucleation mode particles have been commonly reported to consist of water, sulfuric acid and hydrocarbons. Several studies have indicated that the nucleation mode particles are semi-volatile and the particle formation occurs when the exhaust gas is cooled and diluted in the atmosphere [10,15,16]. In addition, the studies have indicated that the sulphur from fuel and lubricant oil have a driving role in the particle formation process. However, some of recent studies [17,18] have indicated that the nucleation mode particle formation can take place also without the sulphur driven process so that the nuclei of nucleation mode are formed already at high temperature conditions.

Diesel vehicles are typically equipped with oxidative exhaust aftertreatment like diesel oxidation catalysts (DOCs) or diesel particle filters (DPFs) in order to reduce

hydrocarbon, carbon monoxide and soot emissions. The oxidative aftertreatment can affect the semivolatile exhaust particle fraction both because of hydrocarbon oxidation and because usually it promotes the conversion of SO_2 to SO_3 . SO_3 reacts with water molecules, forming sulfuric acid. Further, based on modeling studies [19,20], the sulfuric acid and water can nucleate when exhaust gas cools and dilutes in the atmosphere or it can condensate on the surfaces of soot particles. With the DOC the semi-volatile nucleation mode exists at high load and high FSC even though no nucleation mode was measured without after-treatment [10,16,21,22].

Developing countries with growing economies, such as China or India, have become significant and growing contributors to sulphur containing particulate emissions as there are many high-FSC (high fuel sulphur content) fuels in use. It is well-known that normal, high-efficiency Diesel Particulate Filter (DPF) with a wall flow design, cannot be used in conditions with high sulphur level fuels. Moreover, its application is less cost efficient than a Particulate Oxidation Catalyst's (POC) [23,24]. A POC, combined with a Diesel Oxidation Catalyst (DOC) placed upstream, is a significant emissions control technology used to reduce the PM in those applications, and also typically to meet Euro 3 and Euro 4 emission limits. The POC system is a flow-through passive self-regenerating and maintenance-free partial Diesel particulate filter.

In the worst case scenario, there is a high sulphur fuel in use and the engine is running at low load (low exhaust temperature) for a long time without phases allowing the passive system to work. This scenario was targeted for simulation in this study, illustrating the differences between three fuel sulphur content levels and low driving speeds, like city driving conditions in major cities in India and China with rural high-FSC fuels (as high as 2500 ppm).

TEST BED FACILITIES

The experimental setup is shown in [Figure 1](#) (photos [Figure 2](#)). Studies were performed on an engine test bed with an eddy-current dynamometer, equipped with a number of measuring channels with a 1 Hz acquisition rate. Pressure sensors installed both upstream and downstream of the POC system permitted determination of the soot loading as well as the rate of POC regeneration during the test. In turn, the temperature sensors, installed close to the pressure sensors, were very closely observed for any gas temperatures fluctuation which could strongly interrupt soot collection inside the POC system. Also embedded into the test stand was a Horiba gas analyser to measure gaseous compounds, and AVL Smoke Meter for particulate emission monitoring.

In particle size distribution measurements the exhaust sample was diluted in two different ways. In order to measure soot particle size distributions and particle reduction efficiency of the POC system, the sample, taken upstream or downstream of the aftertreatment system, was diluted using two stage dilution (ejector diluters). In the first stage the

dilution air temperature was 250 °C and the dilution ratio (DR) was around 10. In the second stage the dilution air temperature was equal to room temperature (25 °C) and the DR was around 8. To study the effects of FSC on volatile particle formation [25], the exhaust sample was diluted using a porous tube diluter (PTD) [26,27]. The PTD dilution system has been used widely in nucleation mode particle studies [10,17,25,27]. In the PTD, the dilution air temperature was 30 °C, the DR was set to 12 and the relative humidity of the dilution air was below 5%. After the PTD, the diluted sample was led into an ageing chamber and secondary dilution conducted by an ejector (DR 8, room temperature). The carbon dioxide concentration was measured in the raw exhaust and at two other locations in the sampling setup. Final dilution ratio corrections were performed according to the measured CO₂ concentrations.

been corrected with particle losses in the TD [31] and with the dilution ratio.

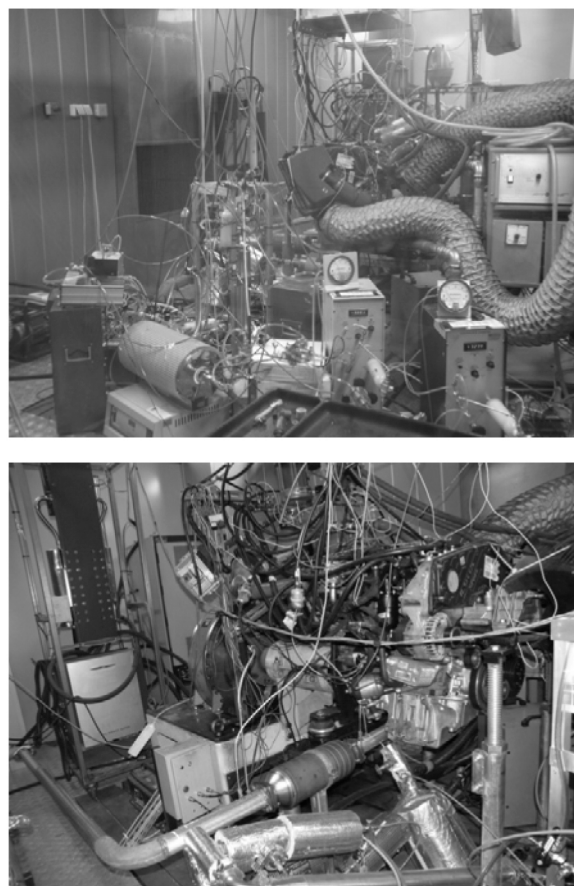


Figure 2. Test bed layout.

DESCRIPTION OF MEASUREMENTS

Separate DOC+POC systems were used to test three different fuels containing 6 ppm, 65 ppm and 340 ppm of sulphur, respectively named as follows: S6, S65 and S340. The engine chosen was a passenger car diesel engine complying with the Euro 4 emission standard with 1.9 l of displacement and maximum output power of 150 hp. The test profile used for the comparison study lasted 49 h and consisted of two phases, determined according to the smoke number [FSN] and the inlet DOC+POC exhaust gas temperature as crucial factors:

- Soot loading phase - 48 h of engine running at a low load point with a maximum exhaust temperature of 250 °C (to simulate city-driving conditions in major cities of India and China)
- Regeneration phase - 1 h of engine running at a medium load point with a maximum exhaust temperature of 400°C (to simulate conditions where regeneration initiates after a long loading period)

The test cycle was run for each fuel of various sulphur content. The loading phase was performed in order to

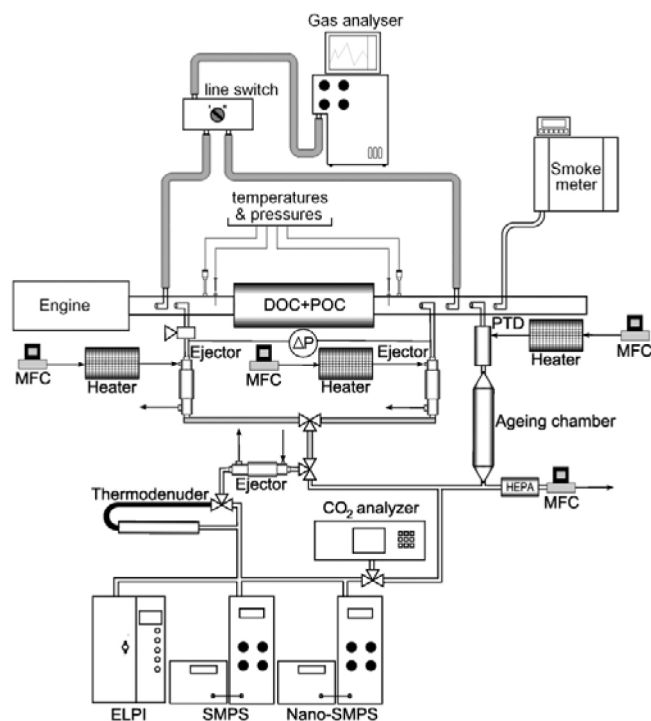


Figure 1. Experimental setup for the test bed measurements.

Particle size distributions were measured with a SMPS (Scanning Mobility Particle Sizer, DMA 3081 and CPC 3025, TSI inc.) [28] Nano-SMPS (DMA 3085 and CPC 3025, TSI inc.) [29] and ELPI (Electrical Low Pressure Impactor, Dekati Ltd.) [30] equipped with a filter stage. The measurement ranges of the Nano-SMPS, the SMPS and the ELPI were 3-60 nm, 10-420 nm and 7 nm-10 µm, respectively. In all the particle measurements there was an option to use a thermodenuder (TD) with low nanoparticle losses to study particle volatility characteristics. The particles downstream of the TD (operating at 265 °C) are regarded as nonvolatile. All size distributions presented in this paper have