

Modelling of Soot Oxidation by NO₂ in a Diesel Particulate Filter

Mehrdad Ahmadijad

Johnson Matthey Technology Centre / University of Birmingham, UK

Athanasios Tsolakis

University of Birmingham, UK

Jan M. Becker, Claus F. Goersmann, Andrew D. Newman

Johnson Matthey Emission Control Technologies

Timothy C. Watling

Johnson Matthey Technology Centre

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ABSTRACT

Two approaches were adopted to study soot oxidation by NO₂; firstly microreactor tests were performed on soot produced by a soot generator over a range of NO₂ concentrations and temperatures. This enabled measurement to be made under well-controlled conditions. Secondly, soot oxidation measurements were made on an engine bench to obtain data under more realistic, if less controlled, conditions. In the microreactor work NO₂ consumption by soot oxidation and the selectivity of the soot oxidation to CO and CO₂ were measured. The latter was found to vary only slightly with temperature and to be independent of NO₂ concentration. By modelling this data using a 1-dimensional model, rate equations for the soot-NO₂ reaction were determined. These were then tested against the engine data. The soot used in this study was characterised by thermogravimetric analysis, N₂ physisorption and transmission electron microscopy.

1. INTRODUCTION

As a result of increasing public concern over air quality and the harmful affects of exhaust emissions, many countries including the US, Japan and those in the EU, have limited the harmful emissions from diesel exhaust by enforcing tighter emissions legislation. These harmful emissions include gaseous emissions such as NO_x, carbon monoxide (CO) and hydrocarbons (HC), as well as Particulate Matter (PM). PM is composed of carbonaceous soot particles, soluble organic fraction (SOF), and sulphates. The volatile content is highly dependent on engine combustion conditions and is difficult to quantify.

Figure 1 shows an example of PM composition from a post-1994 US heavy-duty diesel engine [1]. Most researchers have used the accumulated literature [2-4] on graphite combustion as the starting point for understanding the mechanism of soot combustion, since graphite offers a model with a simple and ordered structure. However, actual engine soot has a more complex structure and contains absorbed hydrocarbons and impurities, which originate from fuel and lubricating oil [5].

Diesel Particulate Filters (DPF) are an important technology for controlling PM. Collected soot may be removed from the DPF by oxidation with NO₂ or O₂. Reaction of soot with NO₂ is possible at temperatures above 200°C. In favourable cases DPF regeneration occurs continuously during normal vehicle operation.

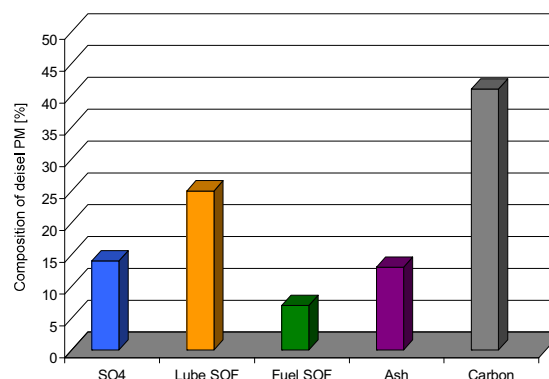


Figure 1 Composition of diesel PM collected from a diesel engine over the heavy-duty FTP transient cycle [1].

A Diesel Oxidation Catalyst (DOC) may be placed in front of a DPF to produce the required NO_2 by oxidation of NO from the engine. As no intervention by the engine is required, this is often referred to as passive regeneration [6]. Reaction of soot with O_2 , on the other hand, requires higher temperatures ($>500^\circ\text{C}$) not encountered during normal vehicle operation. Hence DPF regeneration with O_2 requires the exhaust gas temperature to be considerably increased, typically through engine management or injection of fuel before a DOC placed in front of the DPF to generate an exotherm; this is known as active regeneration [7].

Several studies have been carried out to investigate the interaction of NO_2 with carbon in the temperature range of $100\text{--}500^\circ\text{C}$ [8,9]. Many researchers [2,3,8] have highlighted the different nitrogen and oxygen surface complexes such as C- NO_2 , C-ONO, C- ONO_2 , and C-O, formed during the interaction of carbon with NO_2 or NO/O_2 at low temperature. Jeguirim *et al.* [10] investigated the oxidation of carbon by automotive exhaust gases such as O_2 , H_2O , and NO_2 in the temperature range of $300\text{--}400^\circ\text{C}$. They found that two distinct carbon oxidation reactions occur in the presence of NO_2 and O_2 , a direct reaction between NO_2 and the carbon surface, and a cooperative reaction involving O_2 and NO_2 simultaneously. In the later case, NO_2 promoted the decomposition of the intermediate C(O) complexes. They also conducted a study on the promotional effect of water, which explained how water vapour increases the overall oxidation rate without appearing in the chemical equation for the reaction.

The modelling of DPF systems has been described in several papers [11-16]. It is not the intention of this paper to provide a comprehensive review of the past modelling papers on this topic. The purpose of this work is to develop an accurate 1-dimensional mathematical model capable of predicting soot oxidation over the DPF. The primary emphasis is on improving the description of soot oxidation by NO_2 . For this purpose a series of microreactor experiments were conducted to understand the rate of soot oxidation with NO_2 , and its selectivity to CO and CO_2 , and hence to determine a rate equation for the soot- NO_2 reaction. This model was then tested against real engine data. Characterisation techniques such as N_2 physisorption, Thermogravimetric Analysis (TGA) and transmission electron microscopy (TEM), were employed, to help with understanding these complex soot structures and compositions better. The developed DPF model in this study can be used as a powerful tool for designing of aftertreatment systems.

2. WALL-FLOW FILTER MODEL

DPF simulations were run using a 1-dimensional model that has been previously described [11-13]. The model is based on the classical Bissett model [17], but incorporates recent advances [14-15]. The model treats the gas and solid (filter wall and soot) phases separately and includes equations for the mass, momentum and energy balances of the gas in

the inlet and outlet channels, together with the solid energy balance and a soot mass balance. Since this work was concerned with passive regeneration, significant exotherms were not expected. The following assumptions were made:

- 1) Negligible radial temperature and concentration gradients.
- 2) Inlet channel narrowing due to soot deposition on the wall was taken into account.
- 3) Soot was deposited on the filter wall in accord with the velocity profile, *i.e.* the higher momentum due to the greater mass of PM was not considered.
- 4) No radiative heat losses.
- 5) Inertial contributions to the pressure drop, due to expansion/contraction at the filter exit/entrance, was included.
- 6) All the soot was assumed to be in the form of cake in the inlet channel, *i.e.* deep bed filtration was not considered.
- 7) Reactants reach the soot by convection with the bulk gas flow through the wall; diffusion was not considered.
- 8) The pressure drop across the filter wall and soot cake can be determined by Darcy's law.

3. EXPERIMENTAL

3.1 CHARACTERISATION

3.1.1 Soot collection

Two types of soot were used in this study *viz.* synthetic soot, from a soot generator (SG), and soot from an engine. Synthetic soot was made using a Combustion Diesel Particulate Generator Solution system. BS EN590 Ultra Low Sulphur Diesel (USLD) was used as the fuel source. Tight control of the primary air/fuel ratio ensured a constant soot production rate. Secondary air (not directly involved in combustion) prevented the flame contacting the walls of the burner housing, resulting in very stable combustion. The soot was collected with a DPF. The gas flow rate was 180kg h^{-1} and the soot loading rate was approximately 10g h^{-1} . The DPF inlet temperature was 250°C . The gas was sucked through the DPF using a vacuum blower located downstream of the DPF. The system incorporated an air-to-air heat exchanger to protect the vacuum blowers from high temperature. Engine soot was collected using the same procedure as used for loading DPFs in the engine bench tests (section 3.3); in this case the fuel was ASTM D 975 USLD.

3.1.2 TGA

A Perkin Elmer Pyris Diamond TG/DTA Thermogravimetric / Differential Thermal Analysis module was used. About 6mg of sample was weighed and placed in the ceramic sample holder and loaded into the TGA machine. The sample was ramped at $5^{\circ}\text{C min}^{-1}$ to 630°C in either N_2 or a combination of N_2 and air flowing at 200ml min^{-1} . In the latter case, the gas was switched from N_2 to air at 400°C . The sample was held at 630°C for 10min at the end of the experiment.

3.1.3 N_2 Physisorption

The surface area of the soot was determined by N_2 physisorption using a Quantachrome Autosorb-1. 50mg of soot was used for the analysis.

3.1.4 TEM

TEM images were obtained using a Tecnai F20 transmission electron microscope. The sample was mounted by crushing and dusting a small portion of the sample onto a holey carbon film on a copper TEM grid.

3.2 MICROREACTOR EXPERIMENTS

Microreactor experiments were used to study the kinetics of the soot- NO_2 reaction under well-controlled conditions. The soot was produced using a soot generator described in section 3.1.1. The soot (0.1g) was mixed with 0.6g of crushed cordierite monolith (sieved to $250\text{--}355\mu\text{m}$) by shaking in a closed glass bottle. This mixture was then placed in a stainless steel reactor. The reactor was then heated to the required temperature in flowing N_2 (2.0L min^{-1}). To start the experiment, NO_2 and 4.5% H_2O in N_2 were switched into the feed. The reactor outlet was analysed by FTIR. Experiments were performed at series of NO_2 concentrations (100-400ppm) and temperatures ($200\text{--}400^{\circ}\text{C}$).

Soot is oxidised by NO_2 to a mixture of CO and CO_2 . The selectivity of soot oxidation to CO formation is defined as:

$$\text{CO selectivity} = \frac{[\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{out}} + [\text{CO}_2]_{\text{out}}} \quad (1)$$

where $[\text{CO}]_{\text{out}}$ and $[\text{CO}_2]_{\text{out}}$ are the reactor outlet concentration of CO and CO_2 . However, the measurement of CO_2 concentration by FTIR was found not to be sufficiently accurate. Therefore the CO_2 conversion was calculated from the oxygen and nitrogen balance. From the oxygen balance:

$$2[\text{NO}_2]_{\text{in}} + [\text{NO}]_{\text{in}} = 2[\text{NO}_2]_{\text{out}} + [\text{NO}]_{\text{out}} + [\text{CO}]_{\text{out}} + 2[\text{CO}_2]_{\text{out}} \quad (2)$$

From the nitrogen balance:

$$[\text{NO}_2]_{\text{in}} + [\text{NO}]_{\text{in}} = [\text{NO}_2]_{\text{out}} + [\text{NO}]_{\text{out}} \quad (3)$$

Combining Eq. 2 and 3 and knowing that $[\text{NO}]_{\text{in}} = 0$ gives:

$$[\text{CO}_2]_{\text{out}} = \frac{[\text{NO}_2]_{\text{in}} - [\text{NO}_2]_{\text{out}} - [\text{CO}]_{\text{out}}}{2} \quad (4)$$

Substituting this into Eq. 1 gives:

$$\text{CO selectivity} = \frac{2[\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{out}} + [\text{NO}_2]_{\text{in}} - [\text{NO}_2]_{\text{out}}} \quad (5)$$

This equation was used to calculate the CO selectivity of soot oxidation by NO_2 in this work.

3.3 ENGINE BENCH EXPERIMENTS

The engine testing was conducted using a 5.9L ISB-215 Tier 2/3, 6 cylinder engine which gave $3.3\text{g kWh}^{-1} \text{NO}_x$ and $0.13\text{g kWh}^{-1} \text{PM}$ over the Non-Road Transient Cycle (NRTC). A $9.5 \times 12\text{in}$ ($0.2413 \times 0.3048\text{m}$), 200/12 ($310\,000\text{cells/m}^2$, 0.30mm wall thickness) cordierite DPF was used. Each experiment consisted of two stages, soot loading and regeneration. Soot loading was carried out using the set up shown in **Fig. 2a**. A Pd DOC upstream of the DPF was used to remove CO, HC and VOF without producing significant NO_2 , which would react with the soot. Filters were loaded at 200°C to approximately 3g L^{-1} . Regeneration was carried out over a range of temperatures ($200\text{--}400^{\circ}\text{C}$) using a slightly different set up (**Fig. 2b**). A CSF and Pt DOC were placed upstream of the DPF. The CSF served to prevent any further soot reaching the DPF. The CSF allows the regeneration to be modelled without needing to know how much soot was coming from the engine.

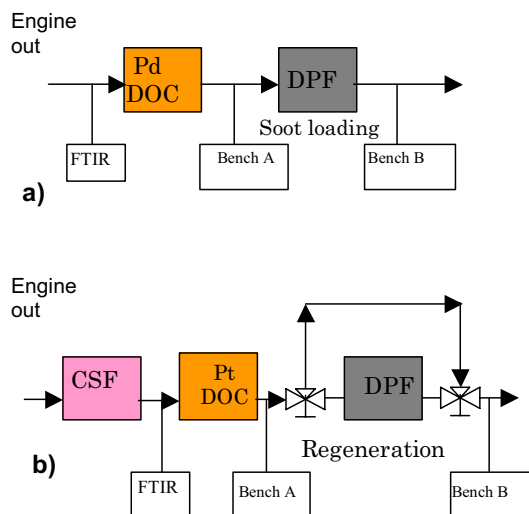


Figure 2 Schematic representation of the set up for DPF, soot loading (a) and regeneration (b).

The Pt DOC was used to oxidise NO to NO₂, which then reacts with the soot. The gas composition before and after the DPF was analysed using two bench analysers (Horiba Mexa 7500D) for CO, HC, NO, NO₂ and O₂. An FTIR (MKS 2030HS) bench was used to measure the DOC inlet gas composition. The regeneration was periodically interrupted to enable the DPF to be removed for weighing to determine the soot loading. All the weights were recorded at 200°C. The frequency of weighing was increased as the regeneration temperature increased to allow for the faster rate of soot removal, e.g. every hour at 200°C and every 15min at 450°C. A bypass around the DPF was used to enable the removal of the DPF for weighing with minimum disruption to the engine.

To understand the contribution of the soot-O₂ reaction on regeneration a couple of tests were run with a Pd DOC in front of the DPF. The Pd DOC produces minimal NO₂, so any regeneration will be predominantly due to the soot-O₂ reaction. These tests were run at higher temperature (375 and 450°C), where the soot-O₂ reaction was expected to be important. A balance point test was also conducted using a similar set up to **Fig. 2b**, except that the CSF in front of the DOC was removed and the DPF was initially clean. The DPF was removed for weighing at an hourly interval. During DPF weighing, the exhaust flow was sent through the bypass loop to ensure that the exhaust gas only passed through the DPF when the engine had stabilised at steady state operating point, to make sure the soot entering the DPF was (reasonably) well defined

4. RESULTS AND DISCUSSION

4.1 SOOT CHARACTERISATION

The two types of soot used in this study, i.e. from a soot generator and from an engine, were characterised by TGA to give more insight into soot composition, by N₂ physisorption to determine the surface area and by electron microscopy to understand the morphology of the soot. It was not the intention of this paper to carry out a comprehensive characterisation on these soot samples but simply to shed a little more light to the compositions and differences between these two soot samples with these available techniques. Since the composition of soot depends on many factors such as fuel, engine type, etc., these characterisation techniques helped us to make a comparison between the two soot samples when comparing microreactor and engine data.

4.1.1 TGA

TGA is a useful method for determining the relative amount of volatile/desorbable material in the soot and the reactivity of the soot. The weight loss when the sample was under N₂ can be taken to be due to desorption of volatile components such as H₂O and VOF, whilst weight loss under air was assumed to be due to soot oxidation, as well as desorption. Any

residual weight at the end of an experiment with air is attributed to ash.

Figure 3 shows TGA results for the two soot samples under both gas regimes. Both samples show weight loss under N₂ till 400°C, which indicates the desorption of water and volatile fractions, however no clear distinction can be made between desorption of water and HCs. Closer comparison of these results indicates that the soot sample from the engine shows slightly more rapid weight loss compared to the sample from the soot generator, indicating that the engine soot contains a slightly higher fraction of volatile components. However, the relative weight loss at 400°C for both samples are very small and similar (about 5wt%). As part of this likely to be due to H₂O desorption, this suggests the amount of VOF is small in both soot samples. In the experiments with the N₂-air combination, the weight trace starts to diverge from the N₂ only weight trace after 450°C and shows rapid weight loss due to soot oxidation by O₂ after about 500°C for both soot samples. Note that the TGA work was done on soot only; no corderite was present.

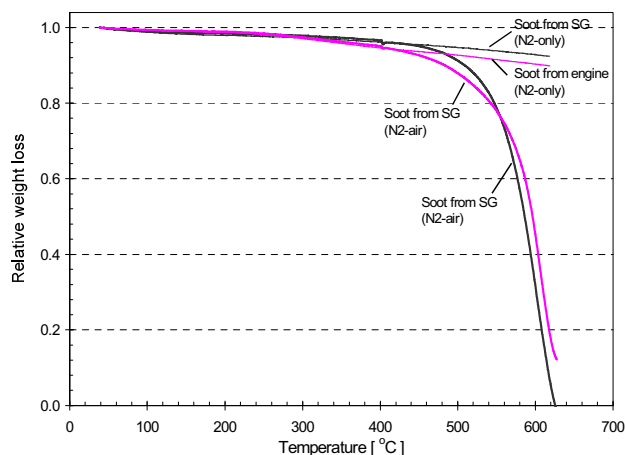


Figure 3 TGA of SG and engine soot. The sample was either in a stream of N₂ (N₂ only in the legend) or a combination of N₂ (T<400°C) and air (T>400°C) (N₂-air in the legend).

4.1.2 Surface Area Measurement

N₂ physisorption was employed to determine the surface areas of the two samples. To look at the effect of VOF desorption on surface area, these samples were outgassed under two different conditions, 100°C for 24h and 350°C for 60h. The results are presented in **Table 1**. As can be seen from the results there is a relatively small difference between the surface area of the soot from the engine and from the soot generator.

The increase in surface area from the 100°C to 350°C outgassing is larger for the engine soot, perhaps indicating that this has a slightly higher VOF content. When this is compared with TGA results at 350°C, it can be seen that there is an observable difference in the weight loss between the two samples at this temperature. However, this difference was not more than 2%.