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Effect of oxygenated and paraffinic alternative diesel fuels on soot reactivity and implications on DPF regeneration

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A R T I C L E   I N F O

A B S T R A C T

A wide range of alternative fuels has recently emerged worldwide, as a means to reduce the dependence on fossil resources and to meet the stringent energy and emissions legislations. In the diesel market, oxygenated biofuels such as biodiesel and e-diesel (low content ethanol-diesel blends) and paraffinic fuels such as those derived from Fischer-Tropsch processes (GTL) or hydro-treatment of vegetable oils (HVO) stand out as the most promising ones. A current challenge that these fuels face is their effect on loading and regeneration performance in diesel particle filters –DPFs–, an aftertreatment technique commonly adopted to abate particulate emissions. This work analyses the oxidative behavior of soot under controlled temperature-atmosphere conditions. Five fuels (conventional diesel fuel, e-diesel, HVO, GTL and conventional biodiesel) were tested in a Euro 5 automotive engine. The effect of the oxidant gas composition (oxygen content and NO_2 presence) and the engine injection strategy (small modifications around the original manufacturer setting) were analyzed. Results revealed a greater ability of soot from paraffinic and, especially, oxygenated biofuels to be oxidized under lower temperature conditions. In particular, e-diesel soot needed the lowest temperature and its oxidation pattern was the fastest and the least sensitive to the oxygen concentration in the exhaust gas, which makes feasible the use of exhaust gas recirculation during active regeneration. From the original injection strategy, small advances/delays and/or the presence of a fuel post-injection did not significantly alter the reactivity of soot. NO_2 concentration in the exhaust gas showed no significant effect on the soot oxidation process at temperatures higher than 300 °C.

1. Introduction

Alternative fuels will play a prominent role for achieving the EU objectives of substituting fossil fuels and reducing the GHG emissions as recently agreed in the 2015 United Nations Climate Change Conference, though under non-binding commitments and with no enforcement mechanism. In the case of diesel market, a mix of fuels derived from a large variety of feedstock will be available in the future to confront climate, technology and renewability challenges. Paraffinic fuels (including hydro-treated vegetable oils –HVO– and Fischer-Tropsch –FT– fuels), conventional biodiesel or alcohol-blended fuels (which presently show poor cold stability in the case of ethanol) are candidates for the diesel mix, among others.

Prior work has extensively reviewed the effects of these and other alternative fuels on engine/vehicle performance and emissions [1–4]. Concisely, a reduction of those emissions that benefit

from the presence of oxygen and/or the lack of aromatic compounds in the fuel (i.e. PM, CO, THC) has been reported, together with no loss in thermal efficiency and a fuel consumption that is inversely proportional to the heating value of the fuel. However, the effect of these fuels on the after-treatment device performance is a more recent issue and the available information is still scarce.

The fuel composition and the engine operating parameters (injection, exhaust gas recirculation) affect the combustion and therefore the oxidative reactivity of soot and the ability to regenerate the DPF. For example, in a Cummins engine retrofitted with a catalyzed filter the use of biodiesel decreased the regeneration temperature by 110 °C when compared to diesel operation [5], which is in agreement with TGA [6], temperature-programmed oxidation [7], surface area [8] and primary particle size [9] results obtained under controlled lab conditions. In addition, the soot generated running a single-cylinder diesel engine with different ethanol percentages showed a similar nanostructure than diesel soot but a higher concentration of oxygenated moieties that could increase the soot reactivity [10]. A higher active surface area for ethanol-derived soot has been found [11]. Paraffinic fuels-derived

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soot has been analyzed as well, reporting a similar surface structure and no significant differences during oxidation when HVO soot was compared to diesel soot [12].

Regarding the effect of the engine operating parameters, it is generally agreed that increasing the injection pressure enhances the reactivity of soot [6,13,14]. The effect of the EGR ratio [15,16] and the engine speed/torque [17] have been analyzed as well. The injection timing [18], as in the present work, has also been studied, concluding that small changes on the injection from the original timing baseline significantly modified the soot oxidation rate (i.e. the soot reactivity). However, the combined effect of injection timing and fuels was not included in the test plan, and the experimental design did not include tests with injection initiated after top dead center, as it is common nowadays in diesel vehicles to reduce NO_x despite the penalty in particulate matter (which is supposed to be completely removed in the DPF).

A related issue is the emitted NO_2, which increases when the exhaust gas flows through the diesel oxidation catalyst –DOC– and contributes to soot oxidation on the DPF. NO_x, and therefore NO_2, depend on the fuel tested. Published results prove that NO_2 oxidizes soot at temperatures as low as 150–300 °C [19,20], though at such temperature level soot oxidation is very slow. Results from Seong and Choi [21] obtained in a thermobalance showed a remarkable increase in the soot oxidation rate when using a NO_2 concentration of 1000 ppm in 8% O_2-containing atmosphere at 500 °C. Differently, in [22] atmospheres containing both NO_2 and oxygen showed higher reaction rates than those of only-NO_2 (500 ppm) or only-oxygen atmospheres. Muller et al. [23] found that 500 ppm NO_2 in 10% O_2 were enough to increase the reaction rate (compared to 10% O_2 only) in the temperature range 250–400 °C, approximately, but no substantial effect at higher temperatures.

In the present work, five conventional and alternative fuels projected in the near-future diesel pool were used to run a Euro 5 diesel engine at a low-load mode typical of the soot accumulation process in the DPF. Soot samples were collected and analyzed in a thermogravimetric balance to investigate the effect of the fuel on the soot oxidative reactivity. Timing and number of injections were also modified around the baseline calibration (to keep the original emission control strategy decided by the manufacturer for conventional diesel fuel) to investigate whether a slightly different combustion process imposes significant changes in soot reactivity. The presence of NO_2 during soot oxidation was considered, at a realistic concentration, to examine its effect on the soot oxidation.

2. Experimental

2.1. Instrumentation

Soot was generated in a 4-stroke, turbocharged-intercooled, Euro 5 Nissan diesel engine (model M1D). The engine features high pressure-cooled EGR (being its temperature externally controlled), oxidation catalyst (DOC) and diesel particle filter (DPF). The main specifications of the engine are given in Table 1. In addition, the engine bench was fitted with sensors for measuring and recording temperature and pressure in different locations (intake air, fuel, exhaust gases, lube oil). The INCA PC software and the ETAS ES 591.1 hardware were used for the communication with the electronic control unit (ECU) and for setting the injection parameters, as described later. More detail can be found in previous works [24,25].

The exhaust configuration was fitted with a by-pass line (see Fig. 1) to collect the soot in a cylindrical shell filled with stainless steel mesh, which acts as filtering medium. After every soot collection, the shell was disassembled and the mesh was softly shaken to separate the soot and to keep it for analysis. Compared to traditional collecting methods based on sucking a partial exhaust gas flowrate through a filter, this original system allows collecting a large mass of soot in a short time. The collection method has been used and validated in previous works [6,26].

A Thermogravimetric Analyzer –TGA– from TA Instruments, model Q500, was used to oxidize the soot collected. Weight and temperature uncertainties are 0.1% and 1 K, respectively. Weight and temperature were previously calibrated with standard weights and a Nickel specimen with a known Curie temperature. A soot sample of 3 mg, as recommended in [27], is located in a crucible inside a furnace, where the temperature is increased and the weight loss is continuously recorded. The sample was initially maintained at 400 °C for an hour under nitrogen atmosphere to remove water and volatile compounds. Then, the sample was cooled down to 100 °C and heated again up to 650 °C with a thermal ramp of 1 °C/min under oxidant atmosphere to complete the oxidation process [27]. Three oxidant atmospheres were used: synthetic air (21% v/v O_2 in N_2), 15% v/v O_2 in N_2 (to simulate the lower oxygen concentration in a diesel exhaust) and 200 ppm NO_2 + 15% v/v O_2 in N_2 (to examine the effect of NO_2 on soot oxidation pattern). 200 ppm is a typical concentration of NO_2 downstream DOC for the engine used in this study.

The oxidation pattern obtained from TGA is presented in the results section in terms of extent of conversion –α– and normalized oxidation rate –$d\alpha/dT$–, as it is common in solid-state reaction analysis [28]. According to Eq. (1), the extent of conversion is defined as a normalized mass which moves from zero to unity once all soot has been consumed. Therefore, the area under the trace in a $d\alpha/dT$ vs T diagram is the unity.

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \tag{1}$$

In Eq. (1), m_0 is the mass when the oxidation starts after the devolatilization process, m is the mass at any time and m_f is the final mass (which is usually distinct from zero because of metal traces and residues present in the soot sample). Additionally, two characteristic temperatures were obtained from the α and $d\alpha/dT$ traces as proposed in [27]: the starting oxidation temperature (SOT), defined as the temperature value when the α vs T trace reaches 0.05, and the temperature for the maximum mass loss rate ($MLRT_{max}$), defined as the temperature at the peak value of the $d\alpha/dT$ vs T trace. The oxidation temperature interval (the temperature difference between the end and the start of the oxidation process), as a means to quantify the oxidation duration, was also estimated. TGA tests were replicated to calculate the standard deviation, which is shown in the plots through error bars.

2.2. Fuels

Five pure diesel fuels were tested. One fossil EN-590 diesel fuel with no biodiesel content purchased from Repsol was used as a reference fuel for comparison. A gas-to-liquid –GTL– and a HVO fuel were selected for representing different production routes of

Table 1
Diesel engine specifications.

Fuel injection system	DI, common-rail
Number of cylinders	4
Valves	16
Bore (mm)	84
Stroke (mm)	90
Compression ratio	16:1
Displacement (cm³)	1994
Maximum power (kW)	111 (at 4000 rpm)
Maximum torque (Nm)	323 (at 2000 rpm)