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Impact of engine operating cycle, biodiesel blends and fuel impurities on soot production and soot characteristics

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ABSTRACT

The impact of engine operating cycle, Biodiesel blends and fuel impurities on soot production and soot properties are evaluated in the present work. To this end, soot were produced on engine test bench and then collected inside a Diesel Particulate Filter (DPF). Two engine cycles (a Natural Loading and an Accelerated Loading) were tested. A standard Euro VI fuel blended with 7% of Biodiesel (B7) and a pure Biofuel (B100 RME EN 14214) were used. This latter was additivated with potassium and phosphorus at a low ($B100^+$) or at a high ($B100^{++}$) concentration. Soot characterization through elemental analyses, nitrogen adsorption, Raman spectroscopy, TGA and TPO experiments show that the engine operating cycle impact the soot reactivity through modifications of their texture and structure. Test bench experiments also show that increasing Biodiesel blend from B7 to $B100^+$ divides by five the soot production. Moreover, soot obtained with $B100^+$ are more reactive because of higher oxygen and ash content. When the inorganic content of the fuel is increased, few effects on the soot production are observed but the soot reactivity is significantly increased. In fact, analyses highlight that impurities present in the fuel are retrieved inside the soot composition and then catalyze their oxidation. K has a beneficial effect on both passive and active regenerations. On the contrary, P inhibits the active regeneration but has a significant catalytic impact on the $C–NO_2–H_2O$ reaction. Finally, a numerical simulation allows to extract the kinetic constants of real B7- and $B100^+$-soot, whose values confirm the differences of the soot reactivity.

1. Introduction

Nowadays, improving air quality is attracting more and more attention. In fact, the increase in industrialization and transportation has a negative impact on the daily environment because of the emission from mobile sources of several pollutants like greenhouse gases and particles. To limit such emissions, standards are becoming more and more stringent. Euro VI, which currently regulates Diesel heavy-duty trucks exhaust gas emissions, limits, among others, the emissions of NO_x at 0.46 g/kWh and of particles in mass at 0.01 g/kWh but also in number at $6.0x10^{11}$ particles per kWh for a cold/warm WHTC (World Harmonized Transient Cycle) cycle [1]. To comply with these standards, vehicles are now equipped with a complex exhaust gas post-treatment line including an oxidation catalyst (DOC) for CO and hydrocarbons oxidation as well as NO oxidation, a Diesel particulate filter (DPF) and a catalyst for the selective catalyzer reduction of NO_x (SCR). These devices have further to prove their durability over 7 years or 700,000 km in the case of heavy duty trucks.

Another way to decrease pollutant emissions from Diesel engines is the use of Biodiesel. This fuel is obtained by transesterification of triglycerides contained in vegetable oils or animal fats and is characterized by its high oxygen content [2,3]. Besides complying with the European Directive 2009/28/CE promoting renewable energies [4], the use of Biodiesel as vehicle fuel has globally a positive impact on pollutant emissions, as it reduces the overall carbon footprint and soot production [2,3,5–7]. Salamanca et al. [6], indeed observed that B100 produces three times less soot than conventional Diesel. Shukla et al. [3] showed that a 20% Biodiesel fuel (B20) can be sufficient to decrease soot production by 50% in comparison to B0. Studying a DPF cross-section, Liati et al. [7] showed that, in contrast with B0 and B20 fuels, no soot cakes were formed inside DPF channels with B100 fuel. The low soot production of Biodiesel is generally attributed to its high oxygen content which allows a better combustion of the fuel but also of the soot produced [2,3,8–10].

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Biodiesel is also known to produce more reactive soot than conventional Diesel [9,11–13]. Thus the regeneration of DPF could be easier and quicker when Biodiesel is used [14]. Song et al. [11,12], studying B0 and B20 soot, showed that B20 soot are more reactive under air than B0 soot because of their more amorphous carbon structure. Lamharess et al. [13], studying B0 and B30 particles, and Yehliu et al. [15], using B15 and B100 soot, also concluded that soot reactivity is linked to their structure. According to Yehliu et al. [15], soot oxidation reactivity is not dominated by the abundance of surface oxygen content but rather by the disorder of the carbonaceous nanostructure and accessible carbon atoms on the edge sites which are the most active sites. On the contrary, Löpez-Suarez et al. [9] attributed the highest reactivity of B100 soot to their highest oxygen and ash contents. In fact, inorganic elements, and in particular alkali metals, present in the ash can act as catalysts toward carbon oxidation [16–19].

Biodiesel is distinguishable from conventional Diesel fuel by its inorganic content. These impurities, mainly alkali metals, are coming from catalysts used for the transesterification. Although the presence of these elements inside the Biofuel are regulated by European standards [20], when Biodiesel is used on long driving distance, the exhaust gas line can be perturbed by high amounts of inorganic elements. Captive fleets of buses and trucks currently operate exclusively on Biodiesel (B100). In this case, based on an average consumption of 35 L/100 km for a truck exclusively running with Biodiesel, the exhaust gas post-treatment system will be subjected to about 1 kg of alkali metals and 1 kg of phosphorus after 700,000 km. These very high quantities generate a high challenge in achieving the durability, requested by the regulation of post-treatment systems (and in particular of the DPF), even for lower levels of alkali and phosphorus. In this context, some authors studied the impact of Biodiesel impurities on DPF properties in accelerated aging by fuel-doping [21,22]. Brookshear et al. [21] tried to simulate a 700,000 km driving by doping the fuel by Na and S (5000 ppm Na + 5000 ppm S) with dioctylsulfosuccinate. After test bench operating, they observed some ash clogging of DPF channels and the penetration of Na inside the wall. Williams et al. [22] doped B20 fuel with either Ca, Na or K (with respectively calcium napthenate, dioxtyl sulfonate sodium salt or potassium dodecylbenzene) to represent a 240,000 km driving exposition. They observed no evidence of supplementary cracking or corrosion due to Ca, Na or K. These studies focused on the impact of inorganic elements on DPF operating but not on soot properties. In another study [23], A. Williams et al. investigated which Biodiesel properties impact the soot reactivity. They tested different Biofuels, one of them being a B20 fuel doped with sodium oleate at 7 ppm. After soot production on a test bench, the soot reactivity was tested by TGA under an air flow. These authors concluded that neither lower aromatic levels nor the presence of alkali metals are determinant contributors to faster DPF regeneration when using Biodiesel. On the contrary, the presence and form of fuel oxygen were proved to be determinant contributors. Using 20% Biodiesel blended into ultra-low sulfur Diesel (B20) doped with 14 ppm Na, Lance et al. [24] intended to simulate a 700,000 km aging. They concluded that B20-Na resulted in 50% more ash into the DPF. However, the Na did not diffuse into the cordierite DPF nor degrade its mechanical properties.

So far, no paper discussing the impact of given elements present in the fuel on soot characteristics and reactivity under passive regeneration conditions seems to be published. The purpose of the present work is to evaluate the impact of Biodiesel blends, and especially Biodiesel impurities, on soot properties. Three fuels are thus tested: commercial 7% and 100% Biodiesel and the 100% Biodiesel doped with K and P to simulate an accelerating aging of soot. The impact of the engine operating cycle is also investigated testing two different cycles: a representative real driving cycle and an accelerated load one. After test bench production, soot were collected inside the DPF and then characterized by elemental analyses (FAAS, ICP and CHONS), nitrogen physisorption, thermogravimetric analyses (TGA) and temperature programmed oxidation (TPO). Finally, a model of carbon oxidation is proposed to extract the kinetic constants associated to the reaction. This work is part of a bigger project named AppiBio which intends to determine the impact of Biodiesel impurities on the whole exhaust gas line post-treatment system [19].

2. Experimental conditions

2.1. Fuel doping

Two types of fuel: 7% Biodiesel (standard Euro VI fuel) and 100% Biodiesel (B100 RME EN 14214 from TOTAL) were used to study the impact of the Biodiesel blends on soot production and their characteristics. One aim of this work is also to study the impact of Biodiesel impurities. But fuel analyses proved that the initial B100 used in this study is very clean (Table 1).

On a short time soot production, these inorganic traces did not allow to appreciate their impact on soot properties. It was thus decided to enrich the fuel in inorganic elements by an external doping to simulate an accelerated aging. The challenge was to find precursors which are soluble in Biodiesel, which do not react between them and finally which are free from sulfur and chlorine. Taking into account these restrictions, it was only possible to dope simultaneously the fuel by phosphorus and potassium, using triethylphosphate ($(Et)_3PO_4$) and a KOH solution in methanol (1 M KOH). Two concentrations were chosen: a low one corresponding to 0.06 times lower than the high limit of the standard for K and equal to the high limit of the standard for P and a high concentration equals to, respectively, 6 and 18 times the high limit of the standard for K and P. Elemental analyses were performed after the fuel doping to control the obtained concentrations. Results are given in Table 1. It was also verified that the density and viscosity of the doped fuels are good.

2.2. Soot production

The production of real Diesel soot was carried out at Renault Trucks on an engine bench equipped with 8 L Euro VI engine. Soot were collected from the DPF by air blowing with a protocol allowing the recovery of two thirds of the total soot mass.

Two types of operating engine cycles were tested: a Natural Loading cycle and an Accelerated Loading cycle. The first one is a low loading cycle operating at low temperatures which is representative of very severe cold real driving cycles. To keep real conditions, a DOC was placed upstream the DPF. Because this cycle produced low amounts of soot, a smoking patch (increased soot engine out) was sometimes applied to ensure the collection of sufficiently large amounts of soot. The smoking patch consists in a specific engine calibration which artificially increases the engine out soot emissions. The smoke increase induced by this specific calibration consists in increasing the EGR (exhaust gas recirculation) rate, decreasing the rail pressure, using no post injection and for the transient phases using less fuel limitation and no smoke limitation. The second cycle is an Accelerated Loading cycle which produced large amounts of soot. This Accelerated Loading cycle was used for fuels which are known to produce low amounts of soot (100% Biodiesel). To promote the soot production, no DOC was placed upstream the DPF for this cycle.

Thus, four soot samples were produced on the engine test bench with these two engine cycles and three different fuels. Their denominations and associated operating conditions are summa-