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Impact of dual-fuel combustion with n-butanol or hydrous ethanol on the oxidation reactivity and nanostructure of diesel particulate matter

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HIGHLIGHTS

- Intake fumigation of alcohols increased soot oxidation reactivity, ASA and VOF.
- Hydrous ethanol was more reactive to oxygen than n-butanol soot.
- Soot oxidation reactivity, ASA and VOF were higher at low engine load.
- Soot nanostructure and PM morphology were not altered by alcohols fumigation.
- Engine load did not affect soot nanostructure nor PM morphology.

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ABSTRACT

This work evaluated the oxidation reactivity, nanostructure and morphological characteristics of the particulate matter (PM) produced by dual-fuel combustion with n-butanol or hydrous ethanol in an automotive diesel engine operating under two different engine loads (equivalence ratios) at the same engine speed (2410 min^{-1}). 10% and 15% of ultra-low sulfur diesel (ULSD) fuel on an energy basis were replaced by alcohol fumigation. Thermogravimetric analysis (TGA) showed that independently of engine load, the soot produced by alcohol fumigation was more reactive to oxidation and exhibited higher active surface area (ASA) than ULSD, following the order *hydrous ethanol > n-butanol > ULSD*. The same trend was obtained for the volatile organic fraction (VOF) of the particulate matter (PM). All PM samples exhibited higher soot reactivity, ASA and VOF at low load in comparison with high load. FTIR spectra showed significant differences on the content of OH group (3100–3600 cm^{-1} wavelength) and aliphatic groups (2850–2950 cm^{-1} wavelength) among all PM samples. Finally, it was found that soot nanostructure, determined with XRD and Raman spectroscopy, as well as PM morphological characteristics (primary particulate diameter and fractal dimension), determined through digital image analysis of TEM micrographs, were not modified significantly by alcohol fumigation neither by engine load. From this experimental setting and engine configuration, it can be concluded that independently of engine load, the intake fumigation of n-butanol or hydrous ethanol (ethanol to a greater extent) increases soot oxidation reactivity, ASA and VOF without affecting soot nanostructure, or PM morphology in comparison to ULSD fuel.

1. Introduction

The search for sustainable alternative fuels has been motivated mainly by oil depletion, high volatility of oil prices, restrictive environmental standards, global warming and public health issues. The so-called second generation biofuels produced from waste resources or non-edible crops have shown promising preliminary results as partial fossil fuel substitutes. Among them, hydrous ethanol and n-butanol are gaining attention since they can be used in diesel engines either in blends with diesel fuel or injected into the intake port (fumigation or dual-fuel). Alcohol fumigation has proven to reduce simultaneously NOx emissions and particulate matter in mass and number, although CO and THC emissions increase [1–5].

It has been reported that the composition and molecular structure of the fuel [6–9], as well as the engine operating conditions [10–13], play a major role in PM formation–growth–oxidation

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mechanisms, inducing changes on DPF regeneration times. Concerning fuel composition, it is known that the concentration and stereography of oxygen functional groups affect significantly diesel particulate oxidation reactivity and nanostructure [14–17]. At equivalent oxygen content, molecules having single oxygen atoms bonded to a carbon atom (such as alcohols) are more effective at reducing PM emissions than those having double bonds (such as alkyl esters) [14]. Williams et al. [18] suggested that the oxygen in 1-decanol was more available for incorporation into the soot as reactive surface oxygen than the oxygen of biodiesel by comparing an equivalent 2.2% oxygen content through a decanol–diesel fuel blend and a soy biodiesel–diesel fuel blend. Pepiot-Desjardins et al. [19] proposed a statistical approach based on group additivity theory to analyze the efficiency of a large number of oxygenated additives blended with hydrocarbon fuels. They found that the sooting tendency is strongly influenced by the base fuel and by the nature of the oxygenated groups. Some similarities can be identified between this work and that of Barrientos et al. from the same laboratory [20]. Both works reported that ethers and alcohols were more effective than esters in reducing soot formation for the same quantity of oxygen and that the carbonyl groups exhibited a high impact in suppressing soot. Both studies demonstrated that branched molecules have a higher tendency to produce soot.

With respect to engine operating conditions, some works have reported that engine load affects soot reactivity and nanostructure. At high loads, soot reactivity decreases because of more ordered graphene lattices due to the faster oxidation of particulates at high in-cylinder temperature [12,13,21,22]. In contrast, other researchers have reported that soot oxidation reactivity is not governed by engine load but by other parameters such as: engine speed [10], fuel and engine oil properties [23], EGR [24,25], or the relative amount of aliphatic C–H groups present in the diesel soot surface [7,26]. This contradiction could be attributed to differences in experimental setup and engine technology.

To the authorś knowledge, little literature has been published on the subject of the impact of alcohol fumigation on diesel particulate matter (DPM) characteristics. In a recent work, Gargiulo et al. [27] reported that independently of engine load, soot obtained with a dual-fuel ethanol/diesel system oxidizes faster than neat diesel soot. They also found that neither ethanol fumigation nor engine load affected significantly soot nanostructure and PM average size.

Considering (i) the worldwide availability of hydrous ethanol and the potential of n-butanol as a second generation biofuel; (ii) the emerging interest of alcohols as alternative fuels with fumigation technology [4,5,28,29]; (iii) the lack of information on their PM characteristics, and finally, (iv) the absence of literature comparing both alcohols; this work aims to analyze the impact of intake fumigation of hydrous ethanol and n-butanol on the oxidative reactivity, nanostructure and morphology of DPM produced by a turbocharged automotive diesel engine operated under two engine loads (at the same speed).

2. Methodology

2.1. Engine test rig

Experiments were carried out in a direct injection, 2.5 liter, in-line 4 cylinder, turbocharged automotive diesel engine, which was adapted with a homemade intake multipoint port injection system to substitute 10% or 15% of ULSD fuel on an energy basis by hydrous ethanol (*Et*) or n-Butanol (*Bu*). The experimental test rig and the electronic fumigation system configuration were described in detail in other work [5]. A substitution of 10% was selected because this concentration has been commonly adopted for several governments as mandatory, and it might be attractive for engine and injection systems manufacturers in order to keep their warranties, 15% was selected to analyze high alcohol substitution trends; higher substitutions were not possible due to hardware limitations.

2.2. Design of experiments and test fuels

The engine was started with neat ULSD fuel and maintained at the desired test load until reaching stationary conditions. A fixed speed of 2410 min^{-1} and two torques of 43 Nm (M4, $bmep$ = 0.216 MPa) and 95 Nm (M2, $bmep$ = 0.478 MPa) were selected. The M2 and M4 modes exhibited the highest specific NOx and PM emissions, respectively, among the most representative stationary operating modes obtained through vehicle dynamics from the FTP75 homologation cycle. At each operating point, the power output was de-rated to 90% and 85% by controlling engine speed and afterwards, the alcohol was injected until achieving the initial 100% brake power. The EGR valve was closed to avoid dispersion of the results. A 95% reliability level was reached through a repeatability study of the whole test cell. Particulate matter was collected without dilution with a stainless steel wool filter located 1.5 m downstream the exhaust manifold, where the gas temperature was below 200 °C in order to avoid further PM oxidative reactions. PM was recovered by scraping the steel wools. Similar results for soot oxidation reactivity were obtained when comparing the PM collection method used in this work with the conventional Teflon filter + vacuum pump method. A differential pressure sensor was installed before and after the filter to guarantee a maximum pressure drop of around 8 kPa during PM collection. Each fuel was tested for about 2 h in order to collect enough PM.

2.3. Analytical techniques

2.3.1. Thermogravimetric analysis (TGA)

The oxidative reactivity, thermal analysis and ASA of all PM samples were determined with a TA Instruments Q500 TGA analyzer following the procedures described in Table 1. The ASA was obtained through the amount of oxygen chemisorbed on the soot as described in detail in a previous work [7].

2.3.2. Infrared spectroscopy characterization (FTIR)

The FTIR method was adopted from a previous work [30]. For qualitative FTIR analysis a KBr pellet was prepared at 1 wt.% of soot. Each spectrum was the result of 300 scan accumulation, which provided the best signal/noise ratio. A Nicolet Magna 560 spectrometer was used with a MCT/A detector operated in a wavenumber range of 600–4000 cm^{-1}. Three measurements of each sample were taken to estimate the method repeatability. The uncertainty of the IR measurements was less than 5%.

2.3.3. X-ray diffraction spectroscopy (XRD)

XRD spectra were recorded in a Panalytical Xpert Pro MPD with a standby of 30 kV to 10 mA; the essay was run at 45 kV to 40 mA. A beam mask of 10 mm with a slit of 0.5 deg., with a copper radiation source of 1.54059 Å wavelengths was used. The start angle was 10° and the end angle was 80° with a step of 0.0263 and a time per step of 196.35 s [7]. The curve fitting for the determination of lattice parameters was carried out with four pseudovoigt functions over the non-smoothed spectra using a fixed background. The background was first fixed into the range of interest ($10° < 2\theta < 60°$) using a third order spline function. One pseudovoigt function was fitted for the first peak at $2\theta = {\sim}24°$, and the other three were fitted for the second peak at $2\theta = {\sim}43.4°$, 43.56° and ~50°, as shown in Fig. 1. A residual error (RMS) below 1.5% was selected for all soot samples to guarantee the reliability of