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Influence on the oxidative potential of a heavy-duty engine particle emission due to selective catalytic reduction system and biodiesel blend

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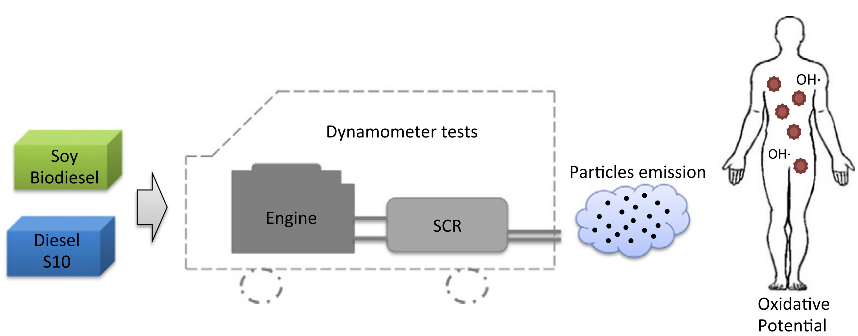
HIGHLIGHTS

- PM emission from biodiesel burning may be more harmful to human health than diesel.
- Euro V (SCR) engine fuelled with B5 and B20 tested in a bench dynamometer
- Electron Spin Resonance (ESR) to access the oxidative potential of PM emission
- Add biodiesel in the fuel blend increases OP while SCR system reduces it.
- Free radicals generation due biodiesel can cause deleterious effects in health.

GRAPHICAL ABSTRACT



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ABSTRACT

Although the particulate matter (PM) emissions from biodiesel fuelled engines are acknowledged to be lower than those of fossil diesel, there is a concern on the impact of PM produced by biodiesel to human health. As the oxidative potential of PM has been suggested as trigger for adverse health effects, it was measured using the Electron Spin Resonance (OP^{ESR}) technique. Additionally, Energy Dispersive X-ray Fluorescence Spectroscopy (EDXRF) was employed to determine elemental concentration, and Raman Spectroscopy was used to describe the amorphous carbon character of the soot collected on exhaust PM from biodiesel blends fuelled test-bed engine, with and without Selective Catalytic Reduction (SCR). OP^{ESR} results showed higher oxidative potential per kWh of PM produced from a blend of 20% soybean biodiesel and 80% ULSD (B20) engine compared with a blend of 5% soybean biodiesel and 95% ULSD (B5), whereas the SCR was able to reduce oxidative potential for each fuel. EDXRF data indicates a correlation of 0.99 between concentration of copper and oxidative potential. Raman Spectroscopy centered on the expected carbon peaks between 1100 cm^{-1} and 1600 cm^{-1} indicate lower molecular disorder for the B20 particulate matter, an indicative of a more graphitic carbon structure. The analytical

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techniques used in this study highlight the link between biodiesel engine exhaust and increased oxidative potential relative to biodiesel addition on fossil diesel combustion. The EDXRF analysis confirmed the prominent role of metals on free radical production. As a whole, these results suggest that 20% of biodiesel blends run without SCR may pose an increased health risk due to an increase in OH radical generation.

1. Introduction

Particulate matter (PM) from anthropogenic sources is of particular concern to human health and has been associated with adverse health effects (Wjst et al., 1993; Kim et al., 2004; Gauderman et al., 2005; Tonne et al., 2007; Ryan et al., 2007). Such effects are linked to particles size, composition, concentration and sources (Davidson et al., 2005; Smekens et al., 2005; Viana et al., 2008; Lee and Hieu, 2011). One particularly notable source of harmful particulate emissions is diesel engines. The PM output from these engines have been linked to cardiopulmonary mortality and morbidity including cancer (Tarkiainen et al., 2003; Nemmar et al., 2007; Peretz et al., 2008; Rivero et al., 2005; Benbrahim-Tallaa et al., 2012). Despite the increase in the health risk being relatively small, the incidence of exposure is high, thus demonstrating its significant importance as the population is exposed (Lim et al., 2012). Accordingly, technologies to reduce emissions associated with diesel vehicles have been implemented (Gill et al., 2012; Borillo et al., 2015). Examples include diesel particulate filters (DPFs), aftertreatment exhaust emission systems (e.g. selective catalyst reduction - SCR). In addition, in light of renewal energy sources, biodiesel is promoted as a sustainable source (Cheng et al., 2008; Hu et al., 2009; Chin et al., 2012).

In short, biodiesel is an ester-based fuel obtained from different vegetable oils, and in some countries, has become accepted as a partial or total substitute for fossil fuels. Introduction of Diesel engines operating with biodiesel is widespread in Brazil, where the majority of this study is based. It is imperative that biofuel emissions are of a higher quality that those of traditional diesel engines for biodiesel to be a suitable alternative. Literature indicates the reduction of PM mass concentration due to use of biodiesel compared to fossil diesel (Lapuerta et al., 2008; Bünger et al., 2012; Guo et al., 2014). Similarly, SCR aftertreatment engines have been shown to reduce the quantity of PM produced and gases (Tadano et al., 2014). However, it has been suggested that despite the reduced mass concentrations of PM, cytotoxicity and pro-inflammatory marker increase with use of biodiesel relative to fossil diesel release (Kooter et al., 2011; Swanson et al., 2011; Gerlofs-Nijland et al., 2013). The effect of engine exhaust particles on oxidative potential is of particular interest for this study because of its well documented association with acute and chronic health effects (Halliwell and Gutteridge, 1999; Valko et al., 2007; Patel et al., 2011). The specific cause of excess free radical production is yet to be proved conclusively (Betha et al., 2012). One possible explanation is the increased quantity of organic matter output from biodiesel fuelled engines, oxidizing once access is gained to the body (Yanamala et al., 2013). The contribution of organic content is again estimated by Jung et al. (2006) who report increased hydroxyl radical (OH•) production as a result of flame soot, compared to carbon black. However these concepts differ from the conventional explanation the influence of metal species. The Fenton reaction describes the production of OH• by the reduction of hydrogen peroxide and simultaneous oxidation of transition metal ions (Shi et al., 2003). Although the example equation features oxidation of iron, this process is observed for other metals such as copper (Kadiiska and Mason, 2002), tin (Lilley et al., 2013), chromium (Lou et al., 2013), even aluminium, despite the fact it only exists in one oxidation state (Kumar and Gill, 2014).

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + OH\bullet$$

The primary objective of this study is to assess the probable oxidative stress caused by exposure to PM of diesel and biodiesel fuelled engines using SCR aftertreatment. This was achieved by using the electron spin resonance analysis in order to measure the free radicals generation due to PM emitted by different aftertreatment/fuel settings. Raman spectroscopy and Energy Dispersive X-ray fluorescence spectroscopy (EDXRF) experimentation were carried out to provide a more in-depth understanding of the free radical chemical nature in biodiesel and diesel.

2. Experimental section

2.1. PM collection

Collection of total PM took place at Institute of Technology for Development, Lactec, Curitiba, Brazil. The engine emissions testing facilities used an engine dynamometer and an engine equipped with a urea SCR aftertreatment system, in accordance with the Euro V standard.

Table 1 shows the characteristics of the tested engine. The tested engine has an individual four-valve cylinder head, cross-flow arrangement; common rail injection system with 1800 bars and engine brake "power brake." It is used in trucks, minibuses and buses. The engine has a power output of 187 HP (2200 rpm), a peak torque of 720 Nm and follows the European Union regulation no. 715/2007 requirements Euro V with urea-SCR system. The European Union (EU) adopted Euro V engine since 2009 and the Euro VI engine in 2013. In Brazil, due to technological delays, especially according to high sulfur concentration in diesel fuel, the Euro V engine was established in 1 January 2012, through the PROCONVE seventh campaign. Nowadays, around 140,000 trucks and 30,000 buses equipped with SCR systems are being used in Brazil (Anfavea, 2013).

This engine works in conjunction with an AVL SESAM i60 FT dynamometer, 440 kW power output at 6,000 rpm and 2,334 Nm of torque. This set up uses the European Steady Cycle (ESC) test set up in accordance with the European emission regulations directive 1999/96/EC. The ESC uses different engine and dynamometer settings, designed to simulate a variety of different speeds and load weights, to allow collection of PM. The fuels used in this study were a blend of ultra-low sulfur diesel (ULSD) (10 ppm sulfur content) and soybean biodiesel in the following proportions: 5% (B5) and 20% biodiesel (B20). The same biodiesel were used to produce the B5 and B20 blends. The rationale behind this choice is two pronged: Firstly, to show the effect of 5% versus 20% biodiesel additions on emission profiles and secondly, both are representative of current usage all over the world. Total PM for each of these fuels was collected both with and without the SCR treatment, thus a total of four different conditions were analyzed in this study.

Table 1
Characteristics of tested engine.

Specifications	
Configuration	Euro V 'Heavy Duty'/proconve P7
Valves/cylinder	4
Displacement	4.8 L
Bore × stroke	105 × 137 mm
Combustion system	Direct injection
Injection system	Common rail electronic
Aspiration	TGV intercooler
Power output	187 cV (139.7 kW) 2200 rpm
Peak torque	720 Nm (73 kgf m^{-1}) 1200–1600 rpm
Aftertreatment	SCR