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Polycyclic Aromatic Hydrocarbons (PAHs) and nitrated analogs associated to particulate matter emission from a Euro V-SCR engine fuelled with diesel/biodiesel blends

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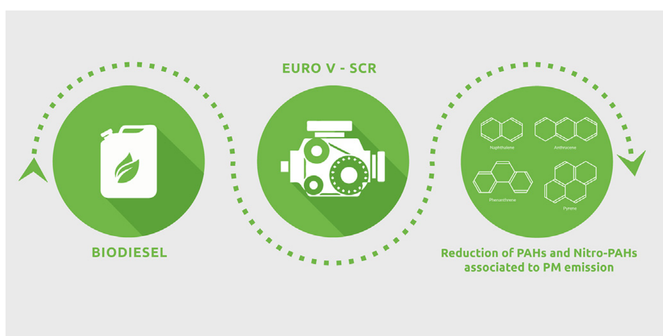
HIGHLIGHTS

- Unregulated carcinogenic emission from heavy-duty engine with SCR aftertreatment
- PM sampling using Biodiesel blends and 13 steady-state engine operation cycle
- The synergic effect of biodiesel/SCR reduces PAHs and Nitro-PAHs particle emission.
- The tested SCR system does not appear to promote PAHs nitration.
- Biodiesel addition may reduce the emission toxicity and the risk to human health.

GRAPHICAL ABSTRACT



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ABSTRACT

Among the new technologies developed for the heavy-duty fleet, the use of Selective Catalytic Reduction (SCR) aftertreatment system in standard Diesel engines associated with biodiesel/diesel mixtures is an alternative in use to control the legislated pollutants emission. Nevertheless, there is an absence of knowledge about the synergic behaviour of these devices and biodiesel blends regarding the emissions of unregulated substances as the Polycyclic Aromatic Hydrocarbons (PAHs) and Nitro-PAHs, both recognized for their carcinogenic and mutagenic effects on humans. Therefore, the goal of this study is the quantification of PAHs and Nitro-PAHs present to total particulate matter (PM) emitted from the Euro V engine fuelled with ultra-low sulphur diesel and soybean biodiesel in different percentages, B5 and B20. PM sampling was performed using a Euro V – SCR engine operating in European Stationary Cycle (ESC). The PAHs and Nitro-PAHs were extracted from PM using an Accelerated Solvent Extractor and quantified by GC–MS. The results indicated that the use of SCR and the largest fraction of biodiesel studied may suppress the emission of total PAHs. The Toxic Equivalent (TEQ) was lower when using 20% biodiesel, in comparison with 5% biodiesel on the SCR system, reaffirming the low toxicity emission using higher percentage biodiesel. The data also reveal that use of SCR, on its own, suppress the Nitro-PAHs compounds. In

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Nitro-PAHs
Toxic Equivalent (TEQ)

general, the use of larger fractions of biodiesel (B20) coupled with the SCR aftertreatment showed the lowest PAHs and Nitro-PAHs emissions, meaning lower toxicity and, consequently, a potential lower risk to human health. From the emission point of view, the results of this work also demonstrated the viability of the Biodiesel programs, in combination with the SCR systems, which does not require any engine adaptation and is an economical alternative for the countries (Brazil, China, Russia, India) that have not adopted Euro VI emission standards.

1. Introduction

Diesel engine exhaust emissions were classified as a carcinogen by the International Agency for Research on Cancer (IARC) in 2013, thereby increasing the prior challenges that policymakers in several countries face (Diaz-Sanchez et al., 1994; Lighty et al., 2000; Ravindra et al., 2008; Reşitoğlu et al., 2015; Zielinska et al., 2004). Polycyclic Aromatic Hydrocarbons (PAHs) and Nitro-PAHs (nitrated PAHs) are the most toxic compounds among the complex mixture of gases and particles that comprise Diesel engine exhaust aerosols (Hu et al., 2013; HHS USA, 2004; Slezakova et al., 2013; Wang et al., 2013; Yilmaz and Davis, 2016). Composed of two or more fused aromatic rings, these organic compounds have been tested for their carcinogenic activity by the IARC, with benzo[*a*]pyrene being classified as group 1 (carcinogenic to humans), by this agency. Dibenzo[*a,l*]pyrene is considered as probably carcinogenic to humans (group 2A) and dibenzo[*a,i*]pyrene and dibenzo[*a,h*]pyrene as possibly carcinogenic to humans (group 2B) (IARC, 2018; Zielinska et al., 2004). When these compounds are associated with diesel/biodiesel blends exhaust particle-phase emissions, which are characterized by high concentrations of fine particulate matter ($PM_{2.5}$) (Guan et al., 2017; He, 2016), there is an intensification of many acute and chronic cardiopulmonary diseases, including asthma, respiratory system inflammation and lung cancer (Martin et al., 2017; HHS USA, 2004; Ravindra et al., 2008).

Current emission regulations implemented in the United States of America (U.S.) and European Union (EU), US 2010 and Euro VI, respectively, adopt a limit for NO_x and PM emission that is ten times lower than the levels allowed in 2000. Countries where these emission limits are enforced and implemented (U.S., EU, Canada, Japan and South Korea) project a 26-fold reduction in PM emissions by 2045 (Posada et al., 2016). On the other hand, Brazil, Russia, India, China, Australia and Mexico whose gross domestic product heavily depends on heavy-duty vehicle transport, have yet to fully implement the equivalent emission standards, even though the increased risks are acknowledged. These regulations require extensive deployment of advanced engine tuning, the addition of two or more aftertreatment devices and the use of low sulphur diesel content, therefore potentially fleet renovations. Instead, these countries still enforce the Euro V and equivalent regulations where Selective Catalytic Reduction (SCR) or Exhaust Gas Recirculation (EGR) aftertreatment systems remain the main strategies to reduce NO_x and PM emission (Du and Miller, 2017).

As an additional strategy to reduce pollutants from Diesel vehicles, many countries like Canada, Australia, Brazil, China and Germany are promoting the development, production and use of alternative fuels (biofuels and natural gas) seeking a better balance to fuel economy and thereby improving green freight programs in the long term (Du and Miller, 2017). Biodiesel is already used in several countries and seems to be a promising alternative, as it can be used in diesel engines without major modifications. Despite the high cost of production when compared to diesel, biodiesel can qualitatively and quantitatively reduce regulated pollutant emissions (He et al., 2010; Ratcliff et al., 2010; Sadiktsis et al., 2014). Several researches successfully demonstrated a consistent reduction for hydrocarbons (HC), PM and carbon monoxide (CO) emissions while recognizing an increase in nitrogen dioxide (NO_x) when biodiesel is used (He, 2016; Ravindra et al., 2008; Sadiktsis et al., 2014). On the other hand, there is no agreement whether the biodiesel promote or not a reduction on PAHs and Nitro-PAHs emissions. Guarieiro et al. (2014) concluded that the biodiesel additions decrease PAHs emissions, which is in agreement with the conclusions made by He et al. (2010), Lim et al. (2014) and Yilmaz and Davis (2016). Westphal et al. (2013) tested PAHs emissions using a turbo-intercooled engine with 6 cylinders operating in the European Stationary Cycle (ESC) fuelled with hydrotreated vegetable oil and jatropha methyl ester. The authors also demonstrated a slight reduction in PAHs emission when low percentages of biodiesel were added and showed that toxicological effects depend on the biodiesel origin. Casal et al. (2014) tested a Euro III engine fuelled with standard diesel (B0), B5 (5% biodiesel) and B20 (20% biodiesel) and concluded that biodiesel mixed with diesel increases the production of PAHs and Alkyl PAHs in the engine exhaust emissions.

Changes in fuel alone are however not sufficient to meet the new or the old standards and use of aftertreatment systems is crucial. The SCR system is still the most widely used in many countries, due to its selectivity to reduce NO_x emissions (Tadano et al., 2014). The injection of urea and a catalyst ensures reductions of up to 90% in NO_x emissions, through a reduction reaction of NO_x and NH_3 resulting in nitrogen and water (Amanatidis et al., 2014; Bacher et al., 2015). Nevertheless, SCR technology is not without its challenges, such as the emission of NH_3, stoichiometric disproportion of urea consumption, cost, and deactivation of the catalyst by deposition (Cheruiyot et al., 2017). The best reported SCR efficiency is achieved at high engine loads and temperatures (approximately 400 °C) (Cheruiyot et al., 2017). However, the added urea increases the probability of unintended formation of Nitro-PAHs through PAHs nitration (Liu et al., 2015).

The combination of low sulphur fuels (ultra-low sulphur diesel-ULSD), new engine technologies, aftertreatment systems (SCR, EGR, DOC – Diesel oxidation catalyst, DPF – Diesel particulate filter) and the use of biofuels are the current strategy to achieve the regulatory reductions worldwide (Wang et al., 2009; Ratcliff et al., 2010; Carrara and Niessner, 2011; Hu et al., 2013; Sadiktsis et al., 2014; Reşitoğlu et al., 2015; He, 2016). However, there is insufficient knowledge and some disagreement in open literature with regards to the potential synergistic effect on unregulated emissions by vehicles equipped with SCR and the use of different biodiesel blends.

This paper describes the PAHs and Nitro-PAHs emission concentrations from a Diesel engine, which is in compliance with the standard emissions determined in PROCONVE P7/Euro V. Furthermore, the potential synergistic effect of the SCR after-treatment and the use of different soybean biodiesel blends (B5 and B20) on emissions have been investigated. Those pollutants are not regulated worldwide, even though they are proven to present several harmful effects on human health.

2. Material and methods

2.1. Sampling and engine parameters

The engine emission tests were performed at the Lactec Institute's Laboratory for Vehicular Emissions in partnership with the Federal University of Paraná, Curitiba, Brazil. The tested engine is currently used in trucks and buses around the world, and has an individual four-valve cylinder head, cross-flow arrangement, common rail injection and SCR