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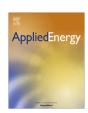
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# Impact of biodiesel fuel on engine emissions and Aftertreatment System operation \*

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#### HIGHLIGHTS

- The effect of biofuel on a Diesel Exhaust Aftertreatment System is studied.
- Biofuel is produced from Waste Cooking Oil.
- A model of a DOC and a DPF gives better insight to experimental data.
- Different reactivity and PM/NOx ratio gives lower backpressure to the DPF when biofuel is used.

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#### ABSTRACT

The effect of biofuel use on the operation of Diesel Exhaust Aftertreatment System is investigated both numerically and experimentally, by focusing on the contribution of three main factors: raw PM-NOx emissions trade-off, NO-NO<sub>2</sub> conversion efficiency of the Diesel Oxidation Catalyst (DOC) and PM reactivity toward oxidation.

The possibility of limited interventions on assessed engine technologies is key toward the deployment of the potential related to fuel based greenhouse reduction policies, for both road and non-road markets. To verify its impact on the Aftertreatment System, a Diesel engine for non-road applications has been tested with Waste Cooking Oil (WCO) biodiesel blended with commercial fossil fuel at 6% and 30% v/v. Six engine operating modes have been selected as the most representative of the reference standard cycle (NRTC) for non-road Diesel engines and have been run to evaluate the biodiesel impact on engine emissions. Experimental results indicate a significant reduction of soot emissions, in line with literature trends, especially at high loads, as fuel oxygen enhances oxidation in the fuel rich regions of the combustion chamber. On the other side, only a slight increase in NOx emissions has been observed, along with a similar trend of the equivalence ratio due to both the lower heating value and stoichiometric air/fuel ratio of biodiesel in comparison with fossil fueling.

The study has been also focused on the analysis of  $PM/NO_2$  ratio, in presence of the Diesel Oxidation Catalyst, when biodiesel is used. Engine tests have in fact demonstrated that, although the  $NO_2/NOx$  ratio on raw exhaust is almost unaffected, a slight reduction of the  $NO_2/NOx$  light-off temperature of the DOC is observed.

This gives, along with a greater PM reactivity oxidation, more favorable conditions for the Diesel Particulate Filter passive regeneration process, with the final aim of a higher engine conversion efficiency.

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#### 1. Introduction

European and worldwide regulations have been promoting the use of biodiesel to limit the greenhouse emissions. To fully address this potential, and besides the impact on engine performance, the use of biodiesel must be studied with a global focus on both the impact on engine raw emissions and the Aftertreatment System (AS) behavior.

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#### Nomenclature

Acronyms and abbreviations NOx Nitrogen Oxides

AS Aftertreatment System NRTC Non Road Transient Cycle
DOC Diesel Oxidation Catalyst PM Particulate matter

DPF Diesel Particulate Filter TGA Thermo Gravimetric Analysis

EGR Exhaust Gas Recirculation WCO Waste Cooking Oil

Since the '90s, several papers have presented results on how engine emissions are varied by using biofuels, through extended testing activities done with several engine technologies, displacements and power outputs, as well as operating conditions and calibrations [1–7]. A general reduction of PM, CO and HC emissions has been observed when using biodiesel, mainly due to the fuel oxygen content [6,8,9]; less evident effects have been observed in terms of NOx emissions. In the last case, although general trends may be outlined from literature available results [7], some studies found opposite results [10,11]. Indeed NOx emissions may be very sensitive to biodiesel properties [5,9,12–15] whose in turn strongly depend on the specific feedstock [16-20] and, secondarily, on the alcohol used for the transesterification process [9]. McCormick et al. [5] found correlations among NOx, fuel density and cetane number, as they, in turn, depend on the number of double bonds and the chain length of the fuel molecule. Also Bakeas [12] and Agudelo [15] confirmed that the degree of unsaturation gives a general increase in NOx emissions. Several studies by Knothe [18,19] proved that cetane number, heat of combustion, melting point, and viscosity increase with the chain length and decrease with the degree of unsaturation.

Therefore, the biodiesel properties affect the combustion process, although the injection technology has a key role as well. Several tests by Tat [16] reported of an advance of the injection timing with biodiesel due to its higher bulk modulus of compressibility. In their first studies, Boehman et al. [21,22] showed that this advance in fuel injection timing resulted in an earlier ignition timing, despite the fuel cetane number, and thus an advance in premixed combustion with higher bulk cylinder temperature during the combustion process. The same author [23] tested a common rail system with fixed injection timings and observed greater rail pressure and duration (proportional to injected fuel mass), to compensate for the biodiesel lower heat of combustion. Thus, if the increased NOx emissions still persist with similar injection timings, other factors have to be taken into account such as local temperature and equivalence ratio distributions within the combustion chamber [24,25]. They in turn can be affected in the flame zone by both the lower soot radiative heat transfer capabilities and the spray characteristics when biodiesel is used. Fleck [26] and Yoon [27] analyzed spray evolution observing larger droplet and longer tip penetrations with biodiesel, due to the poor atomization process for the higher surface tension. Moreover, a greater injection pressure determines increased droplet velocities, decreased sizing and thus better overall mixing processes between fuel and air, with shorter ignition delays and higher in-cylinder temperature, leading eventually to increased NOx emissions.

At the same time, Yoon [27] and Boehman [24] demonstrated that EGR is less effective for NOx emission reduction when biofuel is used, since its higher oxygen content allows for a more stable combustion process, especially at high EGR rate (greater than 30%). Another outcome related to the different oxygen content is an increase of soot emissions with high EGR rates. The latter observation was confirmed by Tsolakis [28], although an opposite result

about EGR effect on NOx emissions was found at high loads with an EGR rate of 20%.

Therefore, as previously described, although the effect of biodiesel fueling on engine emissions has been deeply investigated, very few studies on biodiesel have been focused on the Aftertreatment System (AS) behavior. Only in the last decade the attention has been given to the analysis of the DPF behavior during loading, passive regeneration and active regeneration processes with biodiesel fueling [29–32].

Most of the prior studies evaluated the Break Even Temperature (BET), which is defined as the temperature corresponding to the equilibrium between particulate deposition and oxidation processes. Szybist et al. [30] observed during low temperature regeneration (DPF inlet temperature below 360 °C) a 30 °C reduction of the BET with B100 if compared to ULSD and measured, at the same temperature, a greater NO<sub>2</sub> production by the DPF. Williams et al. [32] found a reduction of the BET of 45 °C with B20 and justified their result with a different soot reactivity as produced with diesel fuel and biodiesel. However, as stated in their paper, the effect of the different PM/NO<sub>2</sub> ratio on the BET was not very much explored. Similar conclusions on BET were commented in other studies [33,34], although in some cases controversial results were found [35,36] with low content biodiesel blends.

The cited studies of Szybist and Williams focused also on the DPF behavior with high temperature operation (DPF inlet temperature above 400 °C), observing that PM oxidizes more quickly when biodiesel blends are used. However, both Prati [33] and Lapuerta [34] observed an opposite behavior during an active regeneration process, since they measured a lower regeneration rate with biodiesel. Prati [33] explained this contradictory result with a deactivation of fuel post-injections as managed by the ECU, after an initial period with normal operation. Lapuerta [34] instead considered, with biodiesel, the effects of both a low accumulated mass of soot and a low DPF temperature due to the lower heating value of the fuel. So, both of them suggested the need for an optimization of the ECU strategy for DPF active regeneration when biodiesel is used.

In prior studies the different reactivity of soot, as emitted from different fuels, has been mentioned as a potential major reason for the different DPF behavior. This topic has been explored since years, being mainly done by looking at morphology and chemical factors. Several techniques have been used such as Raman, TGA, EELS, XPS, NEXAFS and HRTEM. First studies were mainly based on a comparison among carbon black and soot emitted by different combustion processes (i.e. spark, ethylene flames, Diesel engines) or from different fossil fuels. In few cases, the specific aim was the optimization of the DPF regeneration process. Only in the last decade the investigation regarded biofuel emitted soot (e.g. biodiesel and Fischer-Tropsch fuel), thus focusing only on specific features to better explain the different soot reactivities. The main considered factors are: ash content (i.e. presence of metallic particles) [37], carbon functionality (i.e. presence of C/O functional groups) [38] and surface area [39,40] related to SOF, primary particle diameter [34,37,41], fringe length and tortuosity [34].

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