

An Experimental Study on the Impact of Biodiesel Origin and Type on the Exhaust Emissions from a Euro 4 Pick-up Truck

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ABSTRACT

This study investigates the impact of mid-high biodiesel blends on the criteria and PAH emissions from a modern pick-up diesel vehicle. The vehicle was a Euro 4 (category N1, subclass III) compliant common rail light duty goods pick-up truck fitted with a diesel oxidation catalyst. Emission and fuel consumption measurements were performed on a chassis dynamometer equipped with CVS, following the European regulations. All measurements were conducted over the certification New European Driving Cycle (NEDC) and the real traffic-based Artemis driving cycles. Aiming to evaluate the fuel impact on emissions, a soy-based biodiesel, a palm-based biodiesel, and an oxidized biodiesel obtained from used frying oils were blended with a typical automotive ultra low sulphur diesel at proportions of 30, 50 and 80 % by volume. The experimental results revealed that CO₂ emissions and fuel consumption exhibited an increase with biodiesel over all driving conditions. NO_x emissions were found to be above the Euro 4 limit and increased with biodiesel except the blends prepared with the palm-based methyl ester. In general, the emissions of PM, HC, and CO decreased with the addition of biodiesel; however, some increases were observed over the NEDC which may be attributed to the cold-start conditions during the first phase of the cycle, along with certain physicochemical characteristics of biodiesel. Regarding the unregulated emissions, the results showed that the application of biodiesel may negatively affected the toxicological characteristics of diesel particulate

matter due to potential increases of certain toxic compounds in its composition. Sharp increases in most PAH, nitro-PAH and oxy-PAH compounds were observed with the application of biodiesel. These increases were particularly noticeable with the use of the oxidized blends, a phenomenon that it is related with the type and quality of this fuel. The emissions were also affected by the operating conditions of the engine. It was found that most PAH compounds were decreased as the mean speed and load of the driving cycle increased.

INTRODUCTION

Vehicle emissions have long been recognized as one of the most important anthropogenic sources to both gaseous and particulate emissions, and of toxic species such as polycyclic aromatic hydrocarbons (PAHs). Diesel vehicles are a major source of these emissions, particularly in the case of nitrogen oxides (NO_x) and particulate matter (PM) (1). Consequently, concerted efforts have been made to reduce the impact of vehicular emission on ambient air quality, including the use of alternative fuel formulations. Fatty acid methyl esters (FAMES), collectively referred to as biodiesel, have received a growing interest since biodiesel offers several fuel advantages over petroleum diesel, including improved lubricity, a higher flash point, lower toxicity, biodegradability, and reduced contribution to the greenhouse effect (2-3).

Many studies have examined emissions from biodiesel and revealed that emissions of PM, unburned hydrocarbons (HC)

and carbon monoxide (CO) are reduced relative to petroleum diesel (4, 5, 6). However, the positive or negative effect on the aforementioned pollutants varied significantly among vehicles, engine technology and test cycles. Previous studies have shown that poor benefit in these emissions with biodiesel over the NEDC mainly due to the cold-start effect and the partially deactivation of the oxidation catalyst (7-8). Most studies reported an increase in NO_x emissions with the application of biodiesel. The cause of the increased NO_x emissions for biodiesel is still inconclusive; however, a number of fuel properties have been shown to affect emissions of NO_x, including different fuel chemistry (bulk modulus, degree of unsaturation, cetane number) and fuel spray characteristics (9, 10, 11).

The information given in literature about the effect of biodiesel on the emissions of PAH compounds is limited and often contradictory. PAHs are a class of complex organic molecules, which include carbon and hydrogen with a fused ring structure containing at least 2 benzene rings. PAHs are released during incomplete combustion of coal, petroleum products and wood. These compounds are widely distributed in the atmosphere and are one of the first pollutants to have been identified as suspected carcinogen (12, 13, 14). 16 PAHs ranging in size from naphthalene (2-rings) to benzo[*g,h,i*]perylene and indeno[1,2,3-*c,d*]pyrene (6-rings) have been identified as priority pollutants by the U.S. Environmental Protection Agency (US EPA). Research has shown that alternative fuels of biological origins can reduce PAH emissions, despite the fact that such fuels usually increase the level of soluble organic fraction (SOF). Most authors have observed some decrease in PAH emissions with pure and/or blended biodiesel, although a noticeable dependence on engine operation conditions is usually acknowledged (15, 16, 17). On the other hand, a number of authors did not observe significant differences in PAH emissions or even found some increase with biodiesel (18-19). All of the above, raise additional concerns regarding the actual impact of biodiesel fuels on PAH emissions and ultimately on air quality, since PAH compounds along with their nitrate (nitro-PAH) and oxygenated (oxy-PAH) derivatives are considered to be among the key compounds in PM toxicity.

Despite biodiesel's advantages and superior properties over diesel fuel, its chemical nature makes it more sensitive to oxidation than petroleum diesel during long-term storage (20). Oxidation stability, a parameter that describes the degradation tendency of biodiesel, is of great importance in the context of possible problems with engine parts. Several studies have shown the impact of biodiesel source material on the exhaust emissions; however, limited studies have been done to date to characterize the unregulated pollutant emissions of oxidized biodiesel fuels. This work attempts to provide insight on the impact of mid-high biodiesel blends of

different origin and quality on the regulated and PAH emissions under various driving conditions. The vehicle was tested over the New European Driving Cycle (NEDC) and the real traffic-based Artemis driving cycles on a chassis dynamometer with constant volume sampling (CVS) according to the European regulated technique. The effect of biodiesel source material and type on the criteria emissions, carbon dioxide and fuel consumption was measured and compared. The unregulated emissions were characterized by determining 12 PAH, 4 nitro-PAH and 6 oxy-PAH compounds associated with the particle phase.

EXPERIMENTAL PROCEDURE

TEST VEHICLE

A 2007 model year Mitsubishi L-200 (4D56 DI-D) equipped with a common-rail direct injection diesel engine and meeting Euro 4 emission standards was used in this study. PM emissions in this vehicle were controlled by a diesel oxidation catalyst (DOC). All emission tests were performed with the vehicle in its original configuration. The technical specifications of the vehicle are listed in [Table 1](#).

FUELS

A total number of ten fuels were employed in this study. An ultra low sulphur diesel meeting the current fuel quality requirements for diesel vehicles (EN 590:2008), was used as blendstock to create blends with three types of methyl esters. Soy-based (SME), palm-based (PME) and used frying oil methyl esters (UFOME) were blended with the reference diesel at proportions of 30, 50 and 80 % v/v. The neat biodiesels were examined according to the automotive FAME standard EN 14214 ([Table 2](#)). It should be mentioned, that UFOME was an oxidized fuel. The main quality properties of the diesel fuel and its blends with biodiesels are given in [Table 3](#) (see [Appendix](#)).

DRIVING CYCLES AND MEASUREMENT PROTOCOL

In order to investigate the impact of biodiesel on the exhaust emissions and fuel consumption, the certification NEDC and the non-legislated Artemis driving cycles were used. The Artemis cycles are distinguished into an urban (Urban), a rural (Road), and a motorway (Motorway) part, each representative of the corresponding driving condition. The speed profiles of the applied driving cycles are presented in [Figure 1](#).

The daily measurement protocol started with the NEDC, which is a cold-start driving cycle. This comprises two parts; an urban part (UDC) where the engine starts from room temperature (20-30 °C) and an extra-urban part (EUDC), which aims at testing the car at higher than urban speeds. The NEDC was then followed by the three Artemis cycles. This

Table 1. Technical specifications of the test vehicle

Fuel Injection System	Direct injection, Common-rail
Category	N3, >1760 kg
Cylinders/Valves	4/16
Bore/Stroke (mm)	95.1/95
Compression Ratio	17.5:1
Displacement (cm ³)	2477
Maximum Power (kW)	136/4000 rpm
Maximum Torque (Nm)	314/2000 rpm
Weight (kg)	1860

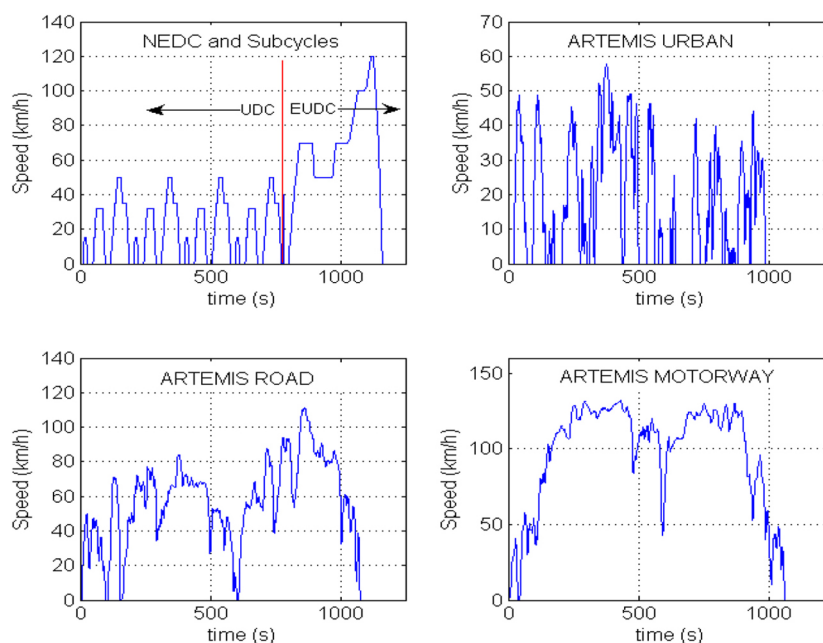


Figure 1. Speed profiles of the NEDC and the Artemis driving cycles

protocol was repeated twice per fuel blend, while two sets with the reference fuel were conducted at the beginning and end of the campaign. Prior to each measurement, the vehicle was conditioned for about 350-400 km of road driving before testing whenever a fuel change was required.

EXHAUST SAMPLING AND EMISSION ANALYZERS

The sampling and analysis of regulated pollutants were performed in accordance to the European regulation (Directive 70/220/EEC and amendments), following the Constant Volume Sampling (CVS) technique. The particulate

samples were collected on 47 mm Pallflex primary and back-up filters. Before and after sampling, the filters were conditioned at 25 °C and 50 % rel. humidity for about 24 h. Sample flow rate was kept below 50 l min⁻¹ and the temperature of the exhaust steam was well below 52°C. Horiba Models AIA-23 and AIA-23 <AS> were the gas analyzers based on non-dispersive infrared ray method (NDIR) for continuously monitoring the concentration of CO and CO₂ sample gases. Automotive NO_x emissions were determined by Horiba Model CLA-53 Series NO/NO_x analyzers by means of chemiluminescence. Horiba Model FIA-34-2 Series Total Hydrocarbons Analyzers were used for continuously measuring the concentrations of the THC

present in the exhaust, by means of a hydrogen flame ionization detection (FID) method.

PAH ANALYSIS

PAH samples were collected on a glass-fiber filter. Each collected sample was extracted with dichloromethane in ultrasonic bath for 20 min. The extraction was repeated three times using 80 mL of the solvent each time. The extract was then concentrated by rotary evaporation to nearly 2 mL for further cleanup. The cleanup column (inner diameter, 1 cm) was filled with glass wool, 3 g of 6% deactivated silica gel, 2 g of 5% deactivated alumina and 0.5 g of anhydrous sodium sulphate. After loading the sample in the cleanup column, the column was washed firstly with 20 mL of n-hexane and then with 25 mL of the 30% CH₂Cl₂ in cyclohexane. Both fractions were reduced to 1 mL under a gentle stream of nitrogen for the analysis. The fraction of CH₂Cl₂/cyclohexane was analyzed for PAHs and their products. A gas chromatograph (Agilent 6890) with a mass spectrometric (MS) detector (Agilent 5975B) was used for the PAHs (Electron Ionization, EI) and nitro-PAHs analysis (Negative Chemical Ionization, NCI). The GC-MS was equipped with a capillary column (HP 5 MS, 30 m × 0.25 μm × 0.25 mm, Agilent); an auto sampler (Agilent 7673A), with an injection volume of 1 μL, pulsed splitless injection. For PAHs analysis the injector temperature was set at 310 °C and the ion source temperature at 280 °C. Oven operating temperature ranged from 55 to 325 °C at 20 °C min⁻¹. For nitro-PAHs and oxy-PAHs analysis the injector temperature was set at 280 °C and the ion source temperature at 280 °C. Oven operating temperature ranged from 60 to 200 °C at 20 °C min⁻¹, and from 200 °C to 300 °C at 5 °C min⁻¹. The oven remained at this temperature for 10 min. The masses of primary and secondary PAH, nitro-PAH and oxy-PAH ions were determined by using the scan mode for pure standards of these compounds. Quantification was performed by using the selected ion monitoring (SIM) mode. The efficiencies of the studied PAHs ranged from 85.0% to 105.0%. For the studied nitro-PAHs the efficiencies ranged from 75.0% to 93.0% and for the oxy-PAHs from 66.5% to 89.5%. The repeatability of PAHs ranged from 2.7% to 5.4%. For the nitro-PAHs the repeatability ranged from 3.2% to 8.4% and for the oxy-PAHs from 8.7% to 11.1%. The combined uncertainty for the overall emission measurements was calculated to be: PAHs (4.1-8.3%), nitro-PAHs (4.7-12.4%) and oxy-PAHs (10.4%-14.7%).

RESULTS AND DISCUSSION

CO₂ EMISSIONS AND FUEL CONSUMPTION

Figure 2 (a-b) shows the experimental results obtained for the CO₂ (a) emissions and fuel consumption (b). Regarding CO₂,

some increases were observed with biodiesel over all driving conditions. Higher increases were found over the NEDC, which may be attributed to the cold-start UDC phase of the cycle. This phenomenon indicates a possible drop in engine efficiency when using high concentrations biodiesel blends under low speed-low load conditions. The application of biodiesel blends had limited effects on CO₂ emissions over the Artemis driving cycles. These increases ranged from 2% to 3%, which falls within the scatter of the baseline results.

Fuel consumption, expressed in L/100 km, presented similar patterns with CO₂ emissions. An increasing trend was observed with increasing concentration of biodiesel into diesel fuel, which was approximately proportional to the difference in energy content of the biodiesel blends. However, this wasn't the case with the oxidized UFOME sample, which exhibited the lower energy content probably due to the presence of oxidized products.

REGULATED EMISSIONS

NO_x Emissions

Figure 3 presents the NO_x emission measurements for all fuel/cycle combinations. Most biodiesel blends resulted in higher NO_x emissions than the reference diesel fuel over all driving conditions. It is worthy of note that the PME blends resulted in noticeable decreases over the NEDC, while marginal differences were observed over the Artemis cycles. A strong correlation was found with the degree of unsaturation and NO_x formation. Emissions of NO_x tend to increase with increasing of unsaturation (high iodine number) in the methyl ester hydrocarbon chain. Thus the highly unsaturated fatty acid profile in the soy-based biodiesel blends resulted in higher NO_x emissions than the saturated palm-based biodiesel blends and the reference diesel fuel. Therefore, the increase in NO_x emissions may result from the participation of the double bonds in the combustion chemistry (9, 21).

Emissions of NO_x were clearly influenced by the operating characteristics of the driving cycle. Higher emission levels were observed during the highly transient Artemis cycles when compared to those of NEDC. This observation support the hypothesis that the engine control is optimized to use regular automotive diesel and its calibration was based upon the operating points of the NEDC. Over the NEDC, the engine only uses a very small area of its operating range, and since NO_x positively influenced at low load conditions, this has an opposite effect during operation on the Artemis cycles.

PM Emissions

PM emission results are shown in Figure 4. Large reductions in PM were achieved with biodiesel blends over all driving cycles. These reductions may be explained by the increase in

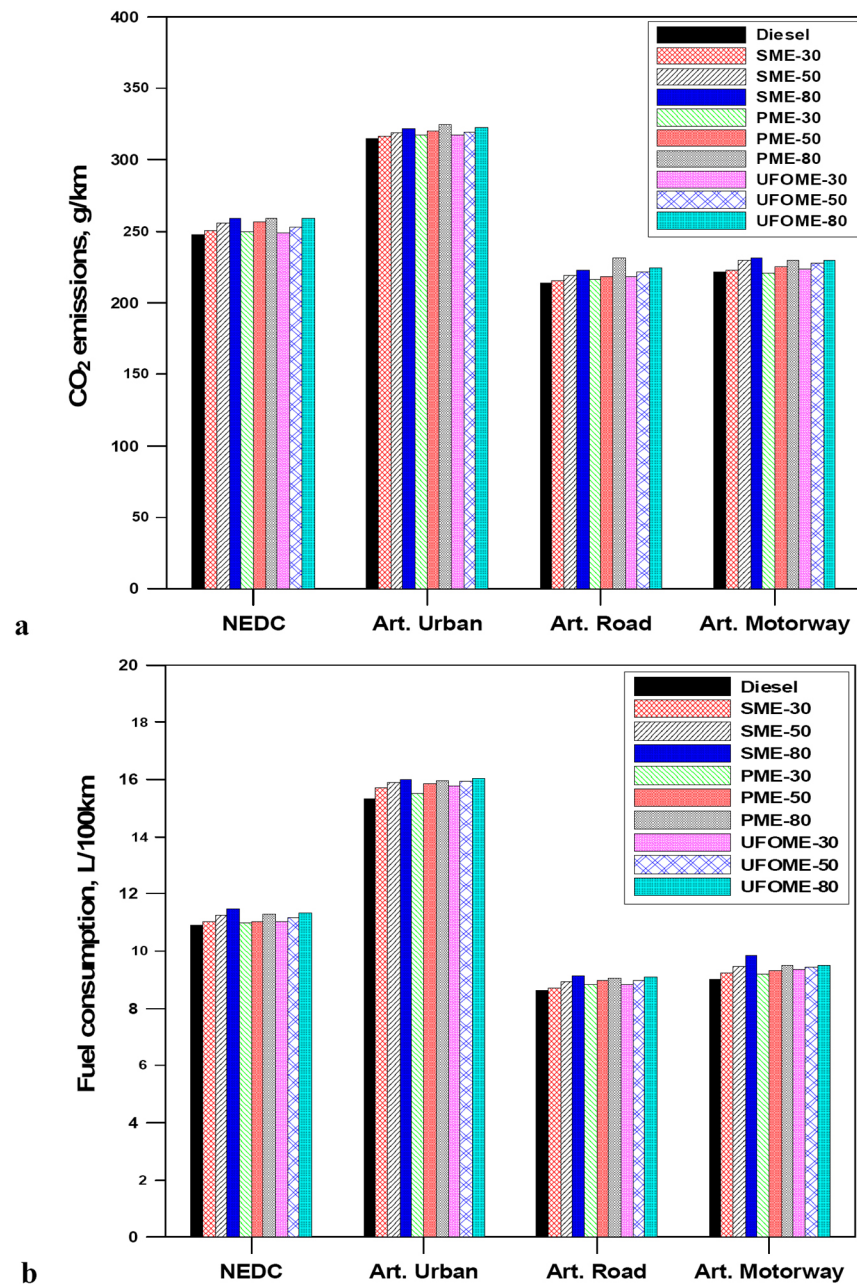


Figure 2 (a-b). CO₂ emissions and fuel consumption measurements over the NEDC and Artemis cycles.

oxygen content in the fuel which contributes to complete fuel oxidation even in locally rich zones and the lack of sulphur and aromatics since these compounds increase the soot nucleation rate (22). However, some increases were observed during the NEDC for the high concentration biodiesel blends, which still remained below the Euro 4 emission limits. The results obtained under the present test conditions indicate the PM emission benefits are questionable when using high concentration biodiesel blends over a cold-start driving cycle. These results suggest that the combined effect of the cold-start UDC phase and the lower volatility of biodiesel negatively influenced the formation of PM emissions during

the NEDC. This could be a consequence of the poorer combustion due to the non-optimal viscosity of the engine oil, and lower fuel vaporization at low-temperature, which was the case with the biodiesel blends and also due to the reduced efficiency of the catalytic converter, which was below the light-off temperature in the starting phase of the cycle (4, 7, 8). It should be mentioned that a weak trend was derived between fuel saturation and PM emission. It appeared that the more saturated the blend, the lowest the PM emissions, an observation also reported by Schönborn et al., 2009 (23).

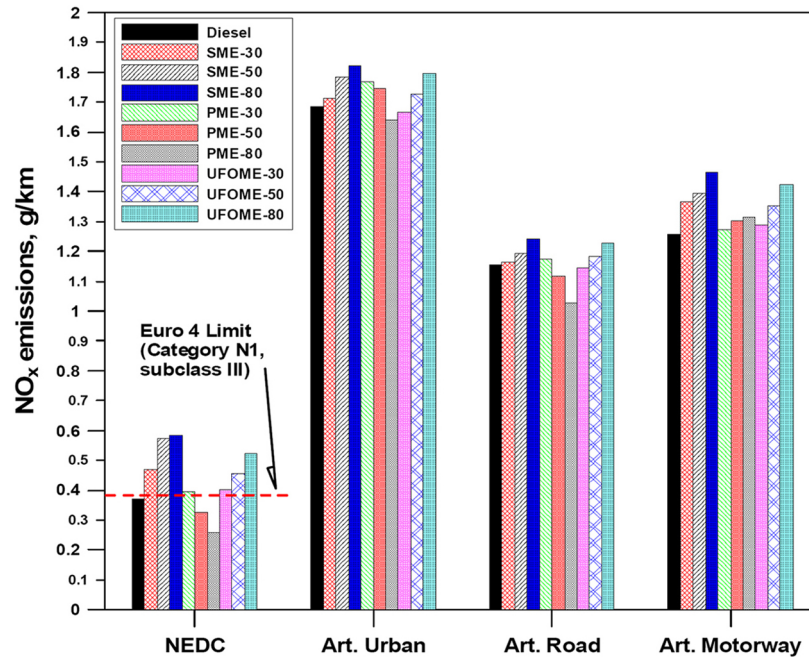


Figure 3. NO_x emission measurements for fuel/cycle combinations

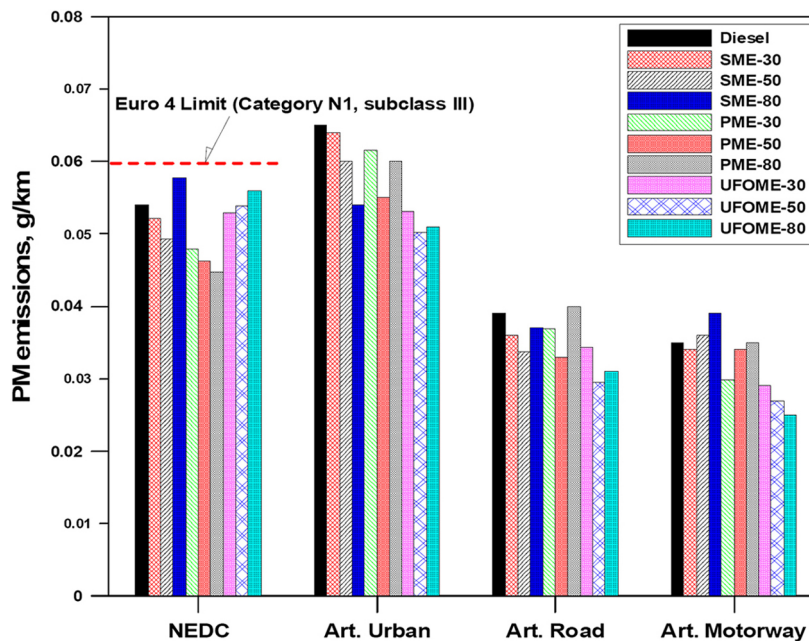


Figure 4. PM emissions for the reference diesel fuel and its blends with biodiesels

CO and HC emissions

The addition of biodiesel resulted in some important reductions in CO emissions almost over all driving conditions (Figure 5a). A trend towards higher emission levels was observed with biodiesel over the legislated NEDC, which can be attributed to the poor catalyst efficiency during the start-up period of the cycle. It should be stressed, that CO emission levels remained well below Euro 4 emission limits. Similar to

CO, HC emissions were also reduced with the addition of biodiesel (Figure 5b). However, a trend towards higher emission levels was observed with biodiesel over the legislated NEDC. This phenomenon may be due to the lower volatility of the biodiesel blends and the cold-start effect during the UDC operation. In general, both pollutants seem to be reduced as the mean driving cycle power increases.