

Regulated and Unregulated Emissions of a Euro 4 SUV Operated with Diesel and Soy-based Biodiesel Blends

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ABSTRACT

In this study, regulated, unregulated exhaust emissions and fuel consumption with ultra low sulphur diesel and soy-based biodiesel blends at proportions of 10 and 30% v/v have been investigated. A Euro 4 compliant SUV, equipped with a 2.2 litre common-rail diesel engine and an oxidation catalyst was tested on a chassis dynamometer with constant volume sampling (CVS) technique. Emission and fuel consumption measurements were performed over the New European Driving Cycle (NEDC) and the non-legislated Artemis driving cycles which simulate urban, rural, and highway driving conditions in Europe. The regulated pollutants were characterized by determined NO_x , PM, CO, and HC. CO_2 was also quantified in the exhaust. Overall, 16 PAHs, 4 nitro-PAHs, 6 oxy-PAHs, 13 carbonyl compounds and particulate alkanes ranged from C_{13} to C_{35} were determined in the exhaust. The experimental results showed that the addition of biodiesel decreased the emissions of PM, CO and HC and increased NO_x emissions during real-world driving. CO_2 emissions and fuel consumption followed similar patterns and increased. Carbonyl compounds were increased for all fuel/cycle combinations. PAH emissions were found to decrease with biodiesel, with some exemptions in certain compounds. An increase was observed on the straight-chain alkanes composition with biodiesel over all driving cycles.

INTRODUCTION

Vehicular traffic makes a major contribution to both gaseous and particulate emissions, and to toxic species such as carbonyl compounds and polycyclic aromatic hydrocarbons (PAHs) [1]. Diesel vehicles can be considered as an important source of these emissions, particularly in the case of nitrogen oxides (NO_x), and particulate matter (PM). These environmental concerns, along with the increasingly stringent emission regulations, have imposed the need to seek alternatives to partially replace automotive diesel fuel. Amongst them, Fatty Acid Methyl Esters (FAMEs), commonly known as biodiesel, is the most widely accepted and is being promoted by EU countries in order to reduce both the greenhouse effect and dependency on foreign oil.

Biodiesel is biodegradable, non-toxic, free of sulphur and aromatics biomass derived fuel with similar physicochemical properties with those of middle distillate diesel fuel [2]. From an air quality perspective, many studies have pointed out that biodiesel combustion can reduce the emissions of carbon monoxide (CO), unburned hydrocarbons (HC), PM, and the overall life cycle emissions of carbon dioxide (CO_2) [3-5]. However, while the aforementioned types of pollutants are reduced, NO_x emissions, mostly NO and NO_2 increase. In the literature, there are two diverse interpretations concerning NO_x emissions of biodiesel. Most studies [6-

8] reported higher NO_x production, whereas some studies [9-10] have shown lower NO_x emissions in respect to diesel fuel. It has been shown that a number of fuel properties (heating value, cetane number, degree of unsaturation, bulk modulus, etc), driving cycle and vehicle technology strongly influence NO_x formation [11-14].

Although biodiesel fuels have been widely investigated regarding the criteria pollutants, there is limited information on the unregulated vehicular emissions of PAHs, nitrated PAHs, oxygenated PAHs and carbonyl compounds (aldehydes and ketones). PAHs are a class of complex organic chemicals, which include carbon and hydrogen with fused ring structure containing at least 2 benzene rings. PAHs may originate from unburned fuel and lubricating oil or they can be formed during the combustion process from simpler organic compounds [15-16]. PAH compounds are identified as toxic, mutagenic and human carcinogens. 16 PAHs ranging in size from naphthalene (2-rings) to benzo[*g,h,i*]perylene (6-rings) have been identified as priority pollutants by the U.S. Environmental Protection Agency (US EPA) [17]. Nitro-PAHs, which have elicited the most concern due to their mutagenic potential, can be created by the reaction of PAHs with hydroxyl (OH) and nitrate (NO₃) radicals in the presence of NO_x or through nitration during combustion processes [18]. Oxygenated PAH (oxy-PAHs) compounds are mainly emitted from combustion processes. They may also originate from heterogeneous reactions between PAHs and ozone. In contrast to their parent PAHs, most of the oxy-PAHs found in diesel particulate phase are directly toxic and mutagenic [19-20]. Most authors have observed some decrease in the aromatic and polyaromatic emissions when using biodiesel [21-23]. These reductions occurred mainly due to the absence of PAH compounds in biodiesel fuels [24]. However, certain authors have shown insignificant differences in PAH emissions between biodiesel and diesel fuel or even some increases with biodiesel use [25-26].

The atmospheric carbonyls in urban areas are mainly emitted by vehicular exhaust. They are finally found in the atmosphere, where they play a critical role on the tropospheric chemistry. They are important precursors to free radicals (HO_x), ozone, and peroxyacylnitrates [27-28]. Light aldehydes, such as formaldehyde, acetaldehyde and acrolein are known to have mutagenic and/or carcinogenic activity. Literature data for carbonyl emissions are rather conflicting due to both differences in the biodiesel composition, origin and quality, and to different experimental conditions. However, most studies have shown that the use of either pure or blended biodiesel as fuel increases most carbonyl compounds. This increase is mainly attributed to the presence of oxygen atoms in the ester molecule [29-30].

This study differs from previous studies conducted by the same authors [22, 29], since the employed vehicles are of newer technology and the applied driving cycles are highly transient and widely acknowledged to be

simulating different operating conditions in Europe. The current study is a part of a complete as possible assessment conducted by this group of authors investigating the short-term effects of mid-level biodiesel blends in modern passenger vehicles on the regulated and unregulated exhaust emissions. This ongoing project offers experimental information regarding the use of low biodiesel blends in various vehicles over several driving conditions and their impact on criteria pollutants and on toxic emissions. These blends were chosen as being more realistic for utilization in the current European fleet.

This work offers an opportunity to characterize both the regulated and unregulated exhaust emissions from a commercially available special utility vehicle (SUV) operated over the European certification driving cycle (NEDC) and the real-traffic based Artemis driving cycles. The vehicle was fuelled with a typical automotive diesel fuel and soy methyl ester blends at proportion of 10 and 30% v/v. Emission and fuel consumption measurements were conducted on a chassis dynamometer, using constant volume sampling (CVS) according to the European regulated technique. One of the aims of this study was to determine the effect of biodiesel concentration and physical properties on the criteria emissions. A further objective was to identify the impact of biodiesel on the unregulated pollutants with a special emphasis on PAHs, nitro-PAHs, oxy-PAHs, carbonyls and particulate alkane species composition.

EXPERIMENTAL

TEST VEHICLE - A Euro 4 compliant Hyundai Santa-Fe 2.2 VGT equipped with a turbocharged direct injection common-rail diesel engine and an oxidation catalyst, was employed in this study. All emission tests were performed with the stock engine exhaust after-treatment system configuration. The technical specifications of the test vehicle are listed in Table 1.

Table 1: Technical specifications of the vehicle

Fuel injection system	Direct injection (DI)
Cylinders	4
Valves	16
Bore x Stroke (mm)	87 x 92
Displacement (cm ³)	2188
Compression ratio	17.3:1
Maximum power (kW)	155/4000 rpm
Maximum torque (Nm)	335/2500 rpm
Inertia class (kg)	1950

FUELS - Three fuels were employed in this study. Methyl ester derived from soybean oil was used as a blending feedstock to create 10 (B10) and 30% (B30) v/v blends with diesel fuel. The biodiesel was examined according to the automotive FAME Standard EN 15941, published by the European Standard Organization

(CEN) that establishes specifications for biodiesel use as a blendstock for conventional diesel fuel. Biodiesel properties are shown in Table 2. The reference diesel fuel and the biodiesel blends were examined as automotive fuels, according to the present fuel quality requirements for diesel vehicles (EN 590 – Directive 98/70/EC). The main physicochemical properties of diesel fuel and the biodiesel blends are given in Table 3.

It was found that the methyl ester and the diesel fuel fulfilled the specifications of EN 14214 and EN 590 respectively. The biodiesel blends were also found to

agree with the specifications, except for the density of B30 which was found above the specification limit. The oxidation stability of the biodiesel blends was determined using the modified Rancimat method (EN15751). It was found that the stability of the final blend was clearly influenced by the biodiesel content, with B30 producing an oxidation stability close to the minimum induction period of 20 h. It was assumed that these relatively high blends met the specification limit due to the presence of an antioxidant additive in the biodiesel. The diesel fuel had a relatively high cetane number and a low content of polyaromatics.

Table 2: Physicochemical properties of the soy-based methyl ester

Properties	Biodiesel	EN 14214 Limits	Test Methods
Kin. Viscosity (mm ² /s, 40 °C)	4.38	3.50-5.00	EN ISO 3104
Density (g/cm ³ , 15 °C)	0.8827	0.860-0.900	EN ISO 3675
Flash Point (°C)	>140	120 min	EN 22719
Sulfur Content (mg/kg)	4.7	10 max	EN ISO 20846
Cold Filter Plugging Point, CFPP (°C)	-9	+5 max	EN 116
Water Content (mg/kg)	330	500 max	EN ISO 12937
Cetane number	52	51 min	EN ISO 5165
Iodine Number	117	120 max	EN 14111
Acid Number (mgKOH/g)	0.33	0.5 max	EN 14104
Oxidation stability, 110 °C (Hours)	9.1	6 max	EN 14112
Monoglyceride content % (m/m)	0.46	0.80 max	EN 14105
Diglyceride content % (m/m)	0.13	0.20 max	EN 14105
Triglyceride content % (m/m)	0.18	0.20 max	EN 14105
Free glycerol % (m/m)	0.00	0.02 max	EN 14105, EN 14106
Total glycerol % (m/m)	0.41	0.25 max	EN 14105
Ester content % (m/m)	97.8	96.5 min	EN 14103
Linolenic acid methyl ester % (m/m)	4.5	12 max	EN 14103
Gross heating value (cal/g)	9726	-	IP 12

Table 3: Main quality parameters of the reference diesel fuel and the biodiesel blends

Property	Diesel	B10	B30	EN 590 Limits	Test Methods
Kin. Viscosity (mm ² /s, 40 °C)	3.39	3.44	3.62	2.00-4.50	EN ISO 3104
Density (g/cm ³ , 15 °C)	0.8325	0.8381	0.8499	0.820-0.845	EN ISO 3675
Flash Point (°C)	86	89	96	55 min	EN 22719
Sulfur Content (mg/kg)	8	5	4	10 max	EN ISO 20846
CFPP (°C)	0	-1	-2	-5 min	EN 116
Water Content (mg/kg)	120	131	149	200 max	EN ISO 12937
Oxidation stability, 110 °C (Hours)	-	40.08	21.36	20 max	EN 15751
Cetane number	56			51 min	EN ISO 5165
Cetane index	58.4	57	55.5	46 min	EN ISO 4264
Distillation					EN ISO 3405
IBP	197	210	210		
10	238	237	246		
50	279	286	305		
90	336	340	341		
FBP	373	362	351		
Polycyclic aromatic hydrocarbons % (m/m)	2.7	-	-	11 max	EN 12916
Gross heating value (cal/g)	11109	11032	10258	-	IP 12

DRIVING CYCLES AND MEASUREMENT PROTOCOL

- In order to investigate the impact of biodiesel on the emissions and fuel consumption over type approval and realistic driving conditions, the Artemis driving cycles were used in addition to the New European Driving Cycle (NEDC). The NEDC is the driving cycle used for passenger car certification in Europe. NEDC is consisted of two distinctive sub-cycles, the UDC (Urban Driving Cycle) simulating low speed driving followed by the Extra Urban Driving Cycle (EUDC) which simulates higher speed driving conditions. According to the European legislation, NEDC is a cold start cycle conducted after the vehicle has soaked for at least 8h at approximately 20°C. The Artemis cycles (all warm-start cycles) are distinguished into 3 cycles simulating different operating conditions in Europe, Artemis urban (URBAN) resembling urban driving conditions, a semi-urban cycle (ROAD) simulates the operation of the vehicle in a rural speed road and the motorway cycle (MOTORWAY) the operation in high speed freeway [31]. The speed profiles of the driving cycles are presented in Figure 1.

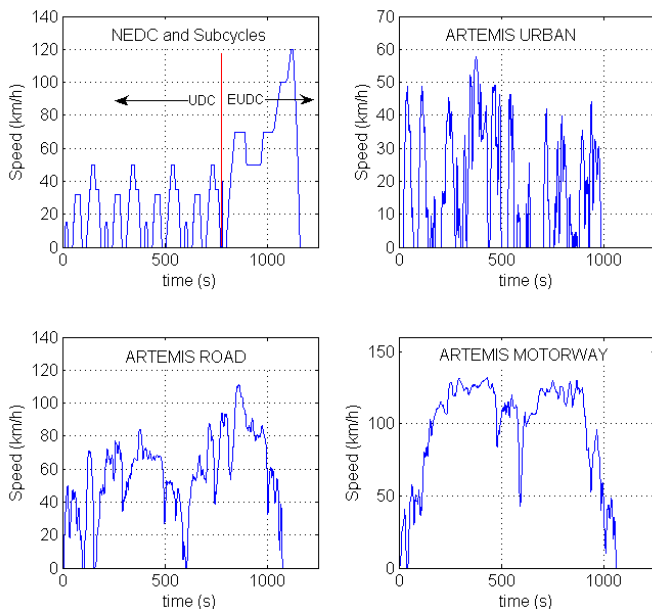


Figure 1: Speed profiles of the NEDC and the Artemis driving cycles

Prior to each measurement, the vehicle was driven for about 200 km before testing, whenever a fuel change was required. The measurement protocol started with the entire NEDC (cold-start) followed by a period of steady cruising speed of 90 km h⁻¹ for conditioning purposes. The three Artemis driving cycles were then conducted.

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.

CARBONYL COMPOUNDS ANALYSIS - For the determination of the carbonyl compounds (CBCs) in the exhaust gas, samples were collected in 3 L Tedlar bags (SKC-3L). In each configuration, sampling was carried out in duplicate and in two different Tedlar bags. Diluted exhaust was drawn through cartridges at a rate of 150 mL min⁻¹ using a small pump. These cartridges contained 2,4-dinitrophenylhydrazine (Chromafix-DNPH, Macherey-Nagel) supported on a silica substrate. A total volume of 3 L was pumped through the cartridge. The DNPH reacts in-situ with the carbonyl compounds in the gas phase to yield derivative compounds, which are more stable than their reactive counterparts. The carbonyl-DNPH derivatives were analyzed according to ISO 16000-3 using an Integral 4000 HPLC system (Perkin Elmer) with an ultraviolet-visible detector ($\lambda=360$ nm). For the separation of the CBCs a C₁₈ column (3 μ m in film thickness, 4.6 mm i.d., and 150 mm in length) was used (Waters, USA). A mixture of CH₃CN/H₂O was used as mobile phase with gradient elution from 50:50 to 75:25. The flow rate was maintained at 1.5 mL min⁻¹ and the injection volume was 20 μ L. The LODs of CBCs ranged from 0.067 to 2.89 ng. The recovery efficiency of CBCs varied from 65% to 105%. The mean relative standard deviation (RSD) in recovery efficiencies was below 15.0%.

ALKANE, PAH, NITRO-PAH AND OXY-PAH ANALYSIS

- Particulate-phase samples for PAH analysis were collected on a glass-fiber filter. After the sampling, the filters containing the particulate matter were extracted with dichloromethane in ultrasonic bath for 20 min. The extraction was repeated three times using 30 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, 1 g of 6% deactivated silica gel, 2 g of 5% deactivated alumina and 0.5 g of anhydrous sodium sulphate. The column was conditioned by passing 10 mL of n-hexane. After loading the sample in the cleanup column, the sample was collected and washed firstly with 4 mL of n-hexane (2 steps x 2 mL) and then with 10 mL of CH₂Cl₂/n-hexane 60/40. This fraction was collected and the volume was reduced to 1 mL under a gentle stream of nitrogen for the analysis. A gas chromatograph (GC) (Agilent 6890) with a mass

spectrometric (MS) detector (Agilent 5975B) was used for the PAHs (Electron Ionization, EI) and nitro-PAHs and oxy-PAHs analysis (Negative Chemical Ionization, NCI). The GC–MS was equipped with a capillary column (HP 5 MS, 30m×0.25µm×0.25mm, 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-PAHs and oxy-PAHs ions were determined by using the scan mode for pure PAH and nitro-PAHs standards (Supelco). Quantification of PAHs, nitro- and oxy-PAHs was performed by using the selected ion monitoring (SIM) mode. The recovery efficiencies of the studied PAHs ranged from 85.0% and 105.0%. For the studied nitro-PAHs the recovery efficiencies ranged from 75.0% and 93.0% and for the oxy-PAHs from 66.5% to 89.5%. The repeatability of the PAHs ranged from 2.7 to 5.4%. For the n-PAHs the repeatability ranged from 3.2 to 8.4% and for the oxy-PAHs from 8.7 to 11.1%.

RESULTS AND DISCUSSION

NO_x EMISSIONS – Figure 2 shows the NO_x emissions produced for the reference diesel fuel and the biodiesel blends over the type approval and the Artemis driving cycles. Over the cold-start NEDC, NO_x emissions were slightly reduced for both biodiesel blends in the order of -3 and -4%. However, it should be noted that the emission levels were above the Euro 4 emission limits. The opposite trend was observed over the three Artemis cycles. During rural driving conditions, B10 and B30 blends produced the highest NO_x increase (14 and 18% respectively).

The effect of oxygenated fuel blends on NO_x emissions is complex and inconclusive. Higher NO_x emissions with biodiesel can be related to effects due to premixed combustion, injection timing (bulk modulus effects), driving cycle, and fuel chemistry [11-12, 32]. However, none of the above should be considered to be uniquely responsible for the NO_x emissions profile of the biodiesel blends. It is possible for all of the above to be considered as contributing factors to NO_x emissions. Biodiesel NO_x emissions are generally higher than those of diesel fuel for steady-state and transient engine dynamometer (FTP) tests [33]. On the contrary, NO_x emissions may be lower than those of diesel fuel in the case of chassis dynamometer tests. This is attributed to the lower load on the chassis dynamometer, compared to the FTP transient and steady-state engine tests, which comes to an agreement with other studies demonstrating that biodiesel does not necessarily lead to higher NO_x

emissions at low load conditions. This could be the result of lower combustion temperature due to delayed injection [8, 34]. It is therefore possible that the observed reductions were mainly due to the smooth acceleration profile of NEDC, where the engine uses only a very small area of its operating range, rather on the effect of certain physicochemical properties of biodiesel.

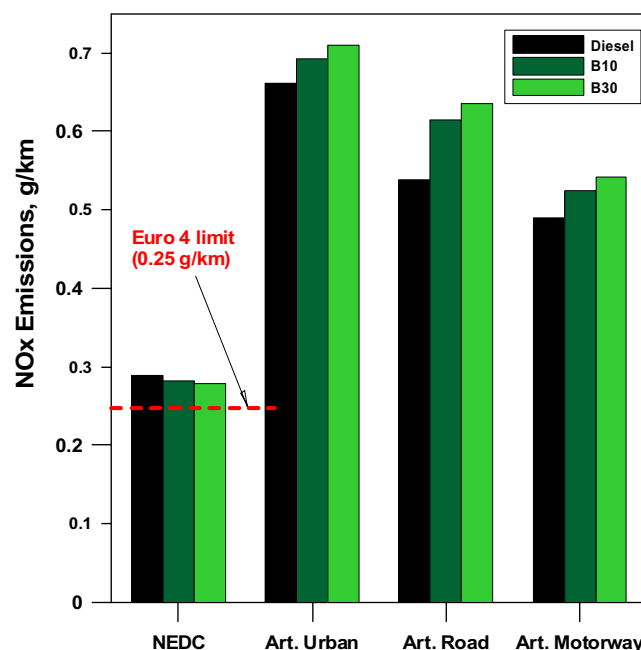


Figure 2: NO_x emission measurements

In contrast to NEDC, NO_x emission levels were found significantly higher during the Artemis driving cycles which are more aggressive and highly transient. During real-world driving conditions there is a constant trend for increasing biodiesel concentration to increase NO_x emissions. It is possible that the lower cetane number of biodiesel was a contributing factor for the NO_x increase. This was due to a longer ignition delay time, where the reactants in the combustion chamber are increasingly preheated, which in turn increases the adiabatic flame temperature and therefore causes higher NO_x emissions [11, 35]. Moreover, the relatively high iodine number (degree of unsaturation) and the excess oxygen content in the biodiesel molecule could also promote NO_x formation [36].

PM EMISSIONS – PM emission results for all fuel/cycle combinations are presented in Figure 3. The general picture shows that PM emissions reduced with the addition of biodiesel over all driving cycles, except for B30, during the cold-start NEDC. This result was expected and agrees with previous studies [37]. The increased PM emissions with the high concentration biodiesel blend mainly occurred during the urban part of the cycle, where the temperature was cold and the catalyst was below the light-off temperature in the starting phase. An additional reason is that the lower volatility of biodiesel makes the fuel atomization and

evaporation in the cold conditions of the start-up period especially difficult. The most beneficial reductions were observed during Artemis Road (-19% for B10 and -15% for B30) and Motorway (-10% for B10 and -14% for B30). These reductions may be explained by the almost nil sulphur content and the higher oxygen content of the fuel, which contributes to complete fuel oxidation even in locally rich zones [38].

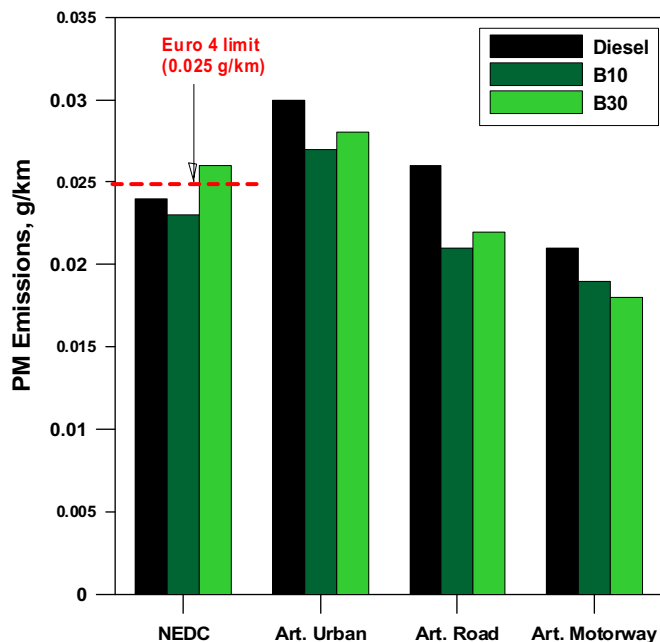


Figure 3: PM emissions during several driving conditions

CO AND HC EMISSIONS – CO exhaust emissions clearly decreased with the addition of biodiesel over the test cycles (Figure 4). Biodiesel contains about 10-11% oxygen on a mass base and has lower carbon content than conventional diesel which may have contributed in this decrease. Similar to CO, HC emissions were reduced with the addition of biodiesel (Figure 5), which can be attributed to the increase in oxygen content in the fuel blends and to the lower volatility of the biodiesel blends. In general, both emission levels decrease as the mean driving cycle power increases [39].

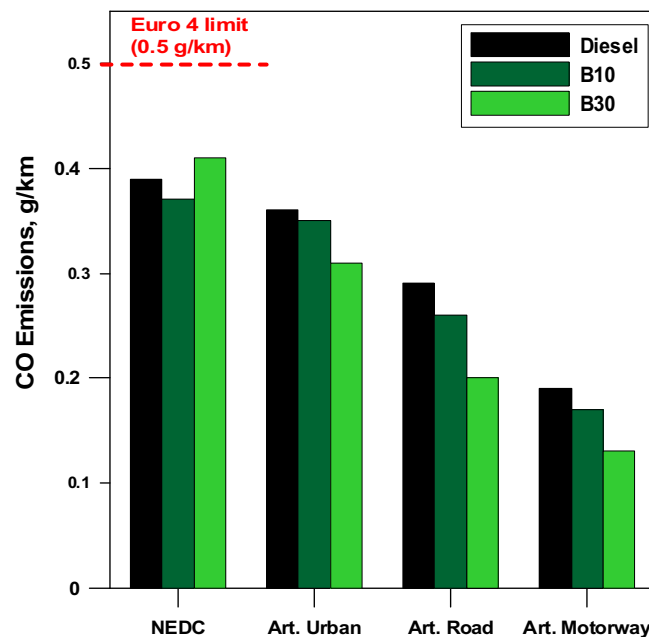


Figure 4: CO emission measurements

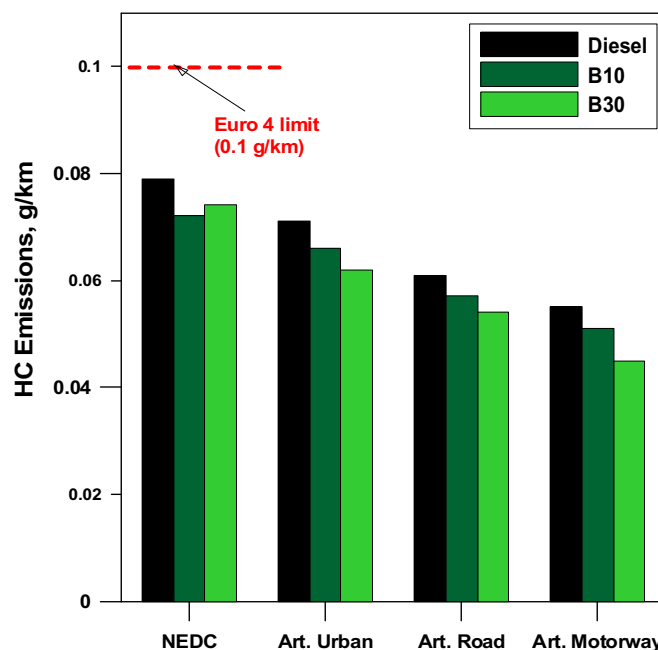


Figure 5: HC emission measurements

CO₂ AND FUEL CONSUMPTION – Measurement results for tailpipe CO₂ emissions and fuel consumption are presented in Figures 6 and 7 respectively. Regarding CO₂ emissions, some minor increases were observed with the use of biodiesel during all fuel/cycle combinations. Fuel consumption, expressed in L/100 km, followed similar patterns with CO₂ emissions and increased with biodiesel. It must be mentioned that the fuel consumption increases are in proportion to the difference in energy content of the various fuels. The heating values of B10 and B30 are approximately -1 and -8% lower than that of the baseline diesel. Since engine