EXPERIMENTAL EVALUATION OF BIODIESEL IMPACT ON VEHICLE REGULATED AND NON-REGULATED EXHAUST EMISSIONS OVER LEGISLATED AND REAL WORLD DRIVING CYCLES

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ABSTRACT

This paper attempts an experimental evaluation of various diesel/biodiesel blends as automotive fuels for passenger cars. Being at the forefront of the European biofuels policy, fatty acid methyl esters (biodiesel) are continuously increasing their share in the European automotive fuels market. In this study, five biodiesels produced from different oils were blended with diesel fuel, on a 10-90% v/v ratio each, and were applied on a Euro 3 common rail vehicle. Chassis dynamometer measurements were conducted including both regulated gaseous pollutants and non regulated pollutants such as carbonyl compounds, particle number and size distribution. In addition to the legislated procedure, the Artemis driving cycles were used in the experiments for quantifying the fuels' impact over realistic driving conditions. The results indicate that all diesel/biodiesel blends present good operating characteristics and have limited effects on gaseous emissions and vehicle performance. Important reductions up to 25% were observed on PM emissions for all test fuels, while particulate number and size distributions remained close to baseline levels. It is concluded that the biodiesel content in the fuel can be raised to 10% v/v in order to increase the CO_2 *savings without any significant impact on vehicle emissions.*

Keywords: *Biodiesel, exhaust emissions, non-regulated pollutants, Artemis*

1. INTRODUCTION

Driven by the Kyoto protocol commitment, the need to reduce their dependency on fossil fuel imports and the continuous rise of oil prices, EU member states are in search of new renewable, domestic energy sources. In this context, directive 2003/30/EC proposes that biofuels should replace by the end of 2010 the 5.75% of the total fuel energy content used in transport (EC, 2003). Additionally the EU has announced its intention to set new targets aimed at a 10% substitution by the year 2020. In spite of the current scepticism (EEA, 2008) regarding the viability of the European biofuels policy, it is expected that since diesel consumption in EU road transport has surpassed that of gasoline (IFP, 2005) and bioethanol

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production is still low, the biodiesel share in diesel fuel will increase beyond 5.75% in the years to come in order to fulfil the 2010 goal. Such a transition however should not affect vehicle operation nor result in pollutant emissions increase and urban air quality deterioration.

In this study blends of 10% v/v biodiesel (B10) derived from different raw materials, were applied on a common rail diesel engine passenger car. The main target was to investigate the environmental performance and the long term impact of B10 application on car operation. Secondly, the effect of the biodiesel origin on pollutant emissions was studied in order to identify if there are favourable raw materials or biodiesel quality characteristics.

2. METHODOLOGY

A Euro 3 compliant, Renault Laguna 1.9 dCi Common Rail passenger car, was used for the measurements. The car was fuelled with B10 diesel/biodiesel blends for approximately 18,000km. The biodiesels were derived from soybean oil (SME), used frying oil (UFOME), palm oil (PME), sunflower oil (SUME) and rapeseed oil (RME). A set of measurements was conducted according to the protocol presented below for each B10 blend and in addition two baseline measurements were performed at the beginning and at the end of the project with pure diesel fuel. The baseline diesel fuel met the present fuel quality requirements for diesel vehicles (EN 590-Directive 98/70/EC). This diesel fuel was already blended with a low biodiesel content which varied between 1.5 and 3% v/v. Since no straight diesel fuel is available in the Greek fuel market this biodiesel content fluctuation was difficult to tackle, but since the concentration was limited the impact is considered negligible. As a result the actual biodiesel concentration in the test fuels varied between 11.5 and 13%.

The biodiesel blends were tested as automotive fuels following the European standard methods. The main physicochemical parameters of the test fuels are shown in Table 1. The cetane number was found well above the specification limit (51 min) for both the reference diesel and the biofuels tested. The fuel properties of the biodiesel blends were all found to comply with EN 590. It was observed that the distillation characteristics of the blends presented noticeable variations when compared to the baseline diesel fuel.

It was important to examine the operation of the vehicle not only under type approval but also under realistic driving conditions. This approach offers a more complete picture of vehicle operation and can support a thorough analysis of the real environmental impact of the proposed 10% biofuel introduction. For these reasons the Artemis driving cycles were used in combination with the standard European type approval procedure. The protocol used included one cold New European Driving Cycle - NEDC, one hot Urban Driving Cycle -UDC (urban sub-cycle of NEDC) and flowingly the Artemis driving cycles (Andre, 2004). The Artemis cycles are comprise 3 different driving cycles that simulate different operating conditions, the Artemis urban cycle (URBAN) reproducing urban driving conditions, a semi-urban cycle (ROAD) simulating the operation of the vehicle in a medium speed road and the extra urban cycle (MOTORWAY) the operation in high speed freeway. After the driving cycles, full throttle acceleration tests with 4th gear were performed in order to measure the 60-100km/h time as a means of engine performance comparison. For each measurement 2 repetitions of the aforementioned protocol were conducted.

Table 1: Test fuel properties

Property	Diesel	SME10%	RME10%	PME10%	SUME10%	UFOME10%	Test Methods
Density (g/cm3, 15 °C)	0.834	0.836	0.835	0.837	0.836	0.837	EN ISO 3104
Viscosity (mm2/s, 40 °C)	3.61	3.75	3.73	3.72	3.74	3.8	EN ISO 3675
Flash Point (°C)	71	78	82	80	78	81	EN ISO 2719
Sulphur Content (mg/kg)	34	31	30	29	28	29	EN ISO 20846
Water Content (mg/kg)	36	70	78	76	82	76	EN ISO 12937
Cetane Number	55.5	52[1]	54.5[1]	56.5[1]	52[1]	59.5[1]	EN ISO 5165
CFPP (°C)	-12	-9	-9	-5	-9	-7	EN 116
Gross Heating Value (cal/g)	10935	10774	10750	10770	10760	10801	IP 12
Distillation							
IBP	188	175	179	176	178	180	EN ISO 3405
10	225	226	228	226	228	229	
50	285	289	290	288	291	290	
90	346	342	345	343	345	338	
FBP	363	361.2	361	360	360	359	

[1] These values refer to the cetane number of pure Biodiesel. The cetane number of the B10 blends presented limited variations (±1CN) compared to that of Diesel fuel.

Fuel consumption and regulated pollutant emissions were measured under the legislated sampling and analysis procedure. Particle emissions measurements were also extended to non legislated particle properties, such as number concentration and size distribution. Samples were taken from the constant volume sampler (CVS) with a Dekati Fine Particle Sampler (FPS- 4000) operating at a nominal dilution ratio of 12:1. Additionally, two calibrated ejector-type diluters were employed in order to bring the particle emissions levels within the measuring limits of the instruments. A Condensation Particle Counter (TSI's 3010 CPC) was employed to monitor the total particle number concentration. A Dekati's Electrical Low Pressure Impactor (ELPI) provided the aerodynamic size distribution in real time. The ELPI operated with wet (oil-soaked) sintered plates and a filter stage that extended the lower cutpoint to ~7 nm (Marjamaki et al., 2002). ELPI was sampling aerosol through a Thermodenuder, operating at 250°C, which removed volatile and semivolatile exhaust components. Over steady–state tests (50-90-120 km/h), a scanning mobility particle sizer (Model 3936 SMPS) was used instead of CPC, monitoring the number weighted size distribution.

For the determination of the carbonyl compounds (CBCs) in the exhaust gas, samples were collected in 3 l Tedlar bags (SKC-3l). Diluted exhaust was drawn through cartridges contained 2, 4-dinitrophenylhydazine (Chromafix-DNPH, Macherey-Nagel) supported on a silica substrate. The carbonyl-DNPH derivatives were analyzed according to ISO 16000-3 using an Integral 4000 HPLC system (Perkin Elmer).

3. RESULTS

Fuel consumption and regulated emissions results did not indicate major differences between the regular diesel fuel and the B10 blends. In most cases the variations observed lay within the repeatability limits for such experiments. In order to facilitate the presentation of results, normalised emissions and fuel consumption values are presented in Figure 1, subfigures a to f.

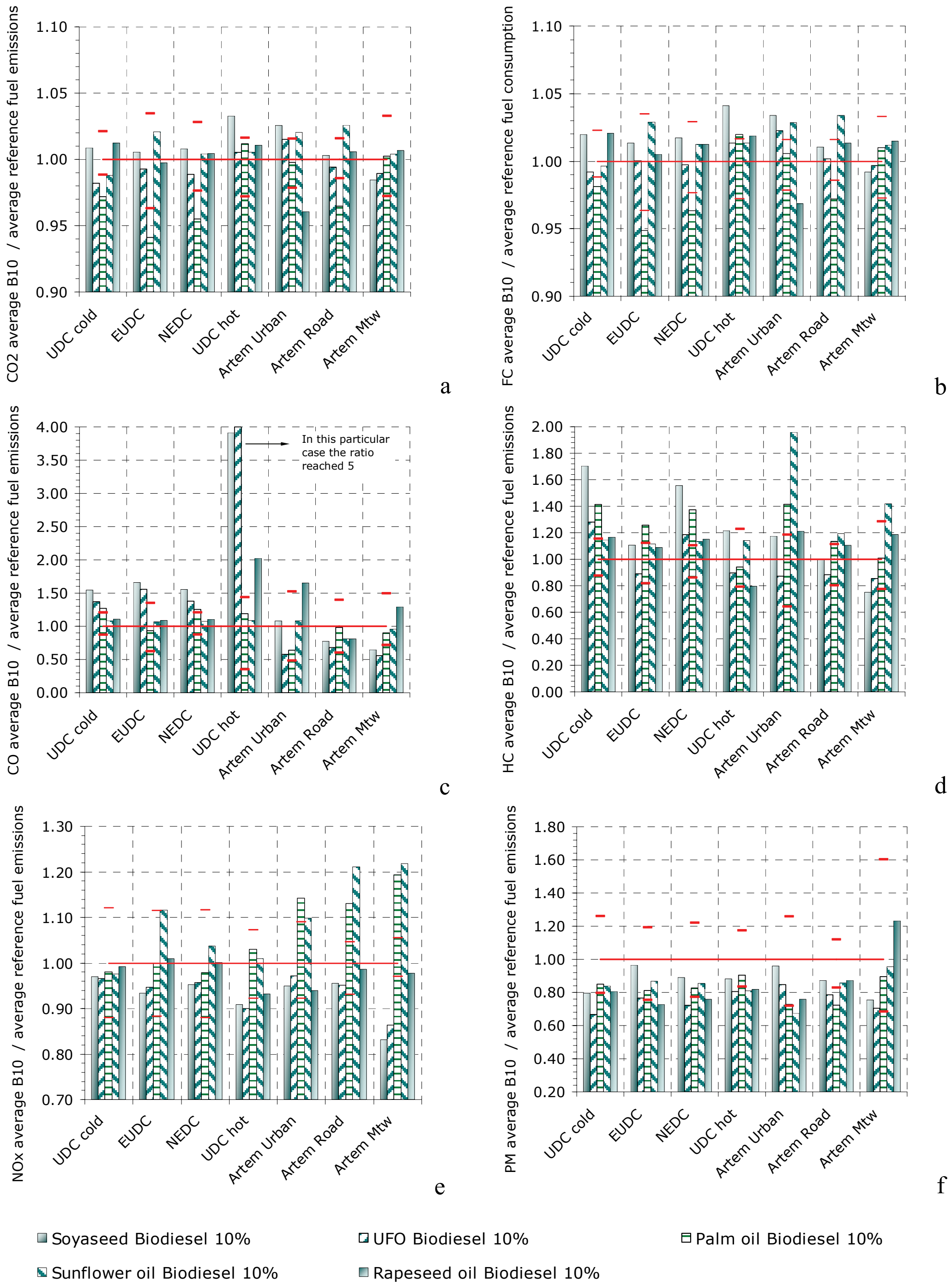
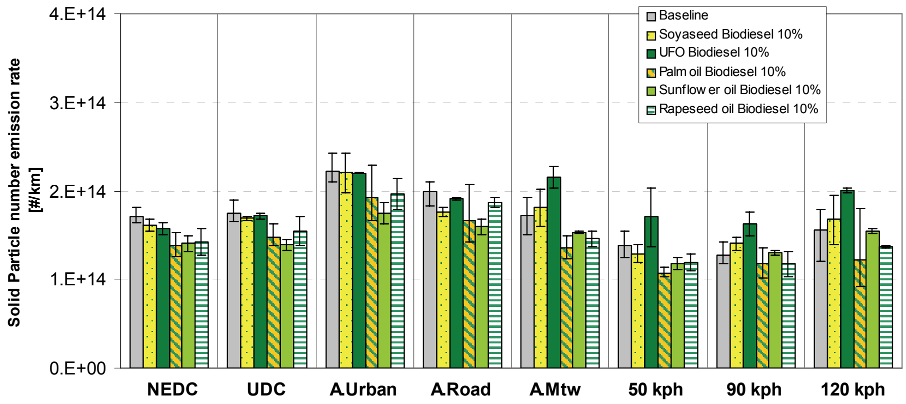


Figure 1: Normalised regulated pollutant emissions and fuel consumption (B10 average measured value / diesel average measured value). Dashes indicate the scatter of the baseline measurements

Each subfigure presents the B10 average emissions normalised to the baseline average for a particular pollutant over the various driving cycles and different blends. Dashes indicate the maximum and minimum **baseline** measurement value measured.

In accordance with the gravimetric results, the number emission rates have been expressed per kilometre driven. It should be noted that the ELPI data reduction requires the knowledge of the effective particle density. As this information is not available, a unit effective density was assumed (a common assumption in studies where an ELPI is employed). Moreover the ELPI results have been corrected for diffusion and space charge losses (Virtanen et al., 2001) as well as thermophoretic losses (Dekati, 2001) inside the thermodenuder. The results of the non regulated particle measurements are presented in Figures 2 and3.



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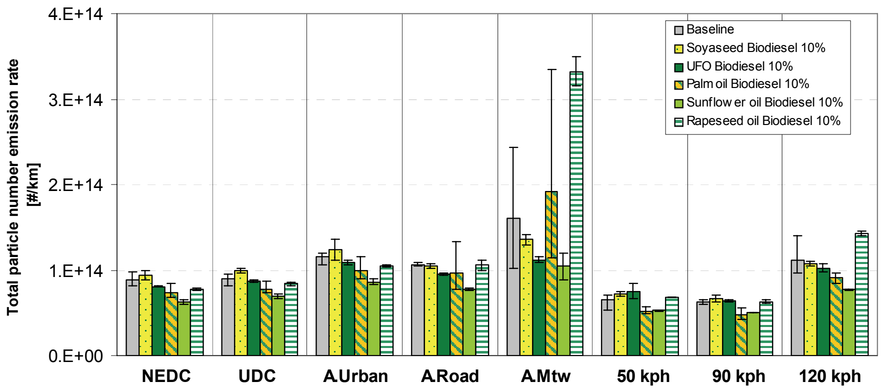

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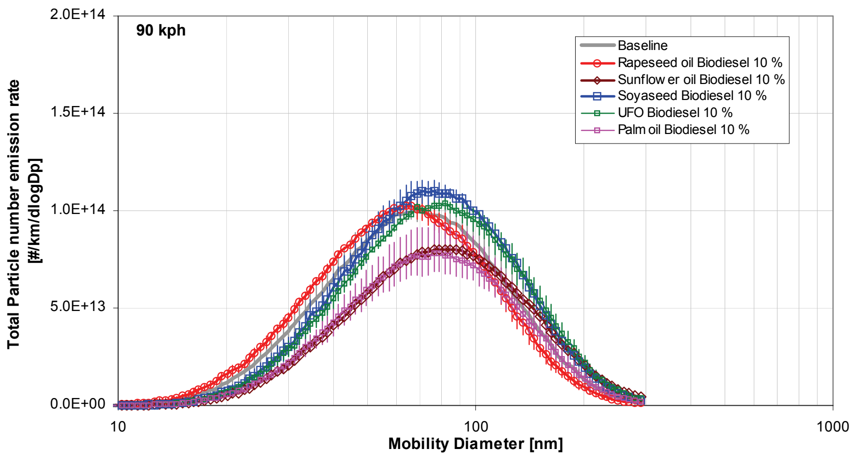
B

Figure 2: Solid (a) and total (b) particle number emission rate for the various fuels employed

Figure 2a shows the solid particle number population for each fuel-cycle combination. The use of biodiesel blends resulted systematically in lower solid particle number emissions. The actual decrease ranged between 4% (UFOME) and 18% (SUME) on average under all cycles. Only under motorway driving conditions, SME and UFOME blends resulted in increase of the solid particle population 5% and 25% respectively. Over the steady speed cruising tests the results were similar. SME and UFOME blends resulted in higher solid particle number population. The actual increase was moderate and ranged between 9 % and 26 % respectively for the two blends. The other employed blends led to lower solid particle number emissions. The decrease ranged between 5 % and 18 % on average.

Figure 2b shows the total particle number population for each fuel-cycle combination. SUME blend seems to cause a systematic decrease of the total particle number population. The decrease was in the order of 26% (CoV=20 %) on average for all cycles, including steady speed cruising tests. PME led to similar results. The use of it resulted in lower total particle emissions. The decrease was in the range of 16 % on average (CoV=30 %). In contrary, under motorway driving the use of palm oil biodiesel blend caused an almost 19% increase of total particle number population. No consistent effect could be identified from the use of the other blends. Nevertheless, the great increase of the total particle number population should be noted that RME blend causes under motorway driving conditions. In particular, the increase is in the order of 107% and 28% over Artemis Motorway cycle and 120 kph steady - state cruising respectively. This great increase points towards volatile particle production over the particular tests, and is consistent with the number weighted number distribution obtained under 120 kph steady state cruising shown in Figure 3 a.



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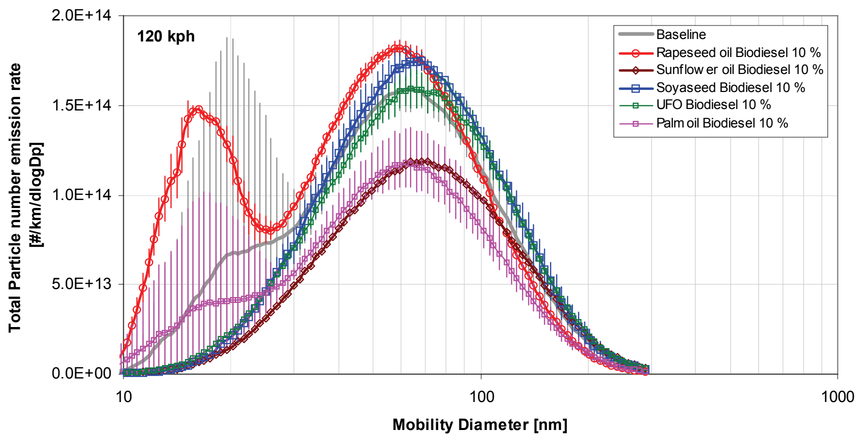

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Figure 3: Number weighted size distributions at 90 (a) and 120 (b) kph steady speed cruising

Figure 3a shows the number weighted size distributions at 90 kph. A nearly lognormal distribution was obtained from all blends. The geometric mean diameter for all blends agreed within ± 6 nm to those determined when diesel fuel was used. RME blend is the only fuel that shifts the peak of the distribution towards smaller diameters. The trends of the absolute levels are consistent with the results shown in Figure 2b.

Figure 3b shows the number weighted size distributions at 120 kph. The distribution obtained using RME explains the great increase of total particle number population compared to that of baseline fuel. A distinct nucleation mode is formed, with a peak at 18 nm, in the same order of magnitude as the accumulation mode. The dispersion of the results is quite small (based on the error bars size of the distribution), which shows repeatable formation of nanoparticles. The other blends resulted in a slight shift of the geometric mean diameter towards bigger diameters, around 65 nm. The baseline distribution has a peak at 54 nm.

Thirteen carbonyls (aldehydes and ketones) were identified and quantified in the exhaust, including formaldehyde, acetaldehyde, acroleine, acetone, propionaldehyde, crotonaldehyde, methacroleine, 2-butanol, butyraldehyde, benzaldehyde, valeraldehyde, p-tolualdehyde, and hexanaldehyde. The concentrations of those carbonyl compounds in the exhaust for the test fuels over NEDC and Artemis driving cycle are listed in Tables 2 and 3.

Finally the results of full throttle acceleration tests where in all cases within the ±3% limit from the baseline average time indicating no significant impact of B10 application on engine power output.

4. DISCUSSION

Starting from CO_2 emissions and fuel consumption (Figure 1, a, b) mild variations were observed with no systematic trend. It appears that PME10 leads to slightly reduced emissions, while SME10 and SUME10 to slightly increased ones. However, even for these blends, vehicle behaviour varied between driving cycles indicating that each fuel might have a different impact depending on the driving and engine operating conditions. Generally over Artemis cycles the CO_2 emissions differentiations were limited compared to the legislated cycles.

Regarding CO and HC (Figure 1c, d) a trend was observed towards higher emission values during the cold start cycle. This observation is important as in cold start the emissions rates of these pollutants are significantly higher compared to those of hot operation. The average values for these pollutants lay close to the highest values measured with baseline fuels and in some cases are quite higher. These phenomena are related to the oxidation catalyst operation and the overall engine management during cold start which is optimised for diesel fuel. For the rest of the cycles the emission levels fall within the baseline ranges.

With respect to NOx emissions (Figure 1e) some differences were observed between the various blends. Under all circumstances the variations were within the usual ranges for the particular vehicle. Concerning the various biodiesels, SME10, UFOME10 and RME10 appear to have a positive effect on NOx, while PME10 and SUME10 resulted in higher NOx emissions. There are several biodiesel characteristics affecting NOx formation. For the biofuels tested, the more saturated esters (low iodine number) have higher cetane numbers as reported in other studies as well (McCormick et al. 2001). Some authors have suggested that feedstocks containing unsaturated fatty acid chains produce significantly higher NOx emissions than more saturated materials (Knothe et al. 2006; Fernando et al. 2006). The experimental results showed that UFOME and RME had cetane numbers of 59.5 and 54.5 respectively, and produced lower NOx emissions than diesel. However PME which had the second higher cetane number produced higher NOx emissions compared to diesel fuel. Therefore it is assumed that the important factors affecting

Table 2: Carbonyl emissions over NEDC

Carbonyls mg/km	NEDC					
	Diesel	SME10	RME10	PME10	SUME10	UFOME10
Formaldehyde	0.070	0.025	n.a.	0.102	0.374	0.008
Acetaldehyde	0.053	0.002	n.a.	0.048	0.295	0.015
Acroleine/Acetone	0.066	-	n.a.	0.080	0.327	0.011
Propionaldehyde	0.0033	-	n.a.	-	-	-
Crotonaldehyde	-*	-	n.a.	-	-	-
Methacroleine	0.002	-	n.a.	-	0.019	0.004
2-Butanol	0.0037	-	n.a.	-	-	-
Butyraldehyde	0.001	-	n.a.	-	-	-
Benzaldehyde	0.0031	-	n.a.	-	-	0.009
Valeraldehyde	-	-	n.a.	-	-	-
p-Tolualdehyde	0.0004	-	n.a.	-	-	-
Hexanaldehyde	0.0052	-	n.a.	-	0.068	0.001

** Below the limit of detection, n.a.: not available*

Table 3: Carbonyl emissions over Artemis Urban driving cycle

Carbonyls mg/km	Artemis Urban Driving Cycle					
	Diesel	SME10	RME10	PME10	SUME10	UFOME10
Formaldehyde	0.021	0.308	n.a.	0.570	0.438	0.011
Acetaldehyde	0.103	0.089	n.a.	0.204	0.111	0.077
Acroleine/Acetone	0.092	0.087	n.a.	1.204	0.926	0.265
Propionaldehyde	0.0007	-	n.a.	0.158	0.092	0.009
Crotonaldehyde	-*	-	n.a.	0.203	0.103	-
Methacroleine	0.026	-	n.a.	0.133	0.084	0.015
2-Butanol	0.001	0.006	n.a.	0.135	0.074	-
Butyraldehyde	-	-	n.a.	0.178	0.091	0.005
Benzaldehyde	-	-	n.a.	-	-	-
Valeraldehyde	-	0.009	n.a.	-	-	-
p-Tolualdehyde	0.015	0.012	n.a.	0.142	0.081	-
Hexanaldehyde	0.002	-	n.a.	0.022	0.013	-

** Below the limit of detection, n.a.: not available*

NO_x emissions are engine operation and driving cycle profile rather than the properties of the biodiesel used in the blends (Martini et al 2007).

PM emissions (Figure 1e), presented important reductions with the addition of biodiesel. The measured PM emission values lay in all cases close to or below the lower values recorded with the regular diesel. This is an observation reported in other studies of diesel-biodiesel blends (Kousoulidou et al 2008) and is attributed to the presence of oxygen in the biofuel.

With respect to particle number emissions palm oil biodiesel is the fuel that was found to cause the greatest reduction of solid particle number emissions. The reduction is in the range of 17% on average over all tests, with a CoV equal to 29%. Sunflower oil biodiesel is the fuel that consistently decreases the total particle number population. The reduction is in the range of 26 % on average over all driving conditions with a CoV equal to 20%. RME is the only fuel that favours the formation of nanoparticles. As a result it leads to the highest total particle number emissions level compared to the baseline fuel. The behaviour of the various blends, concerning their effects on particle number emissions, is controversial. This is a result of the competitive nature of different parameters that affect the formation of the particles. For example, the oxygen content of biodiesel may contribute to improved fuel oxidation, thus resulting in lower formation of nanoparticles. In contrast, the increased viscosity of biodiesel fuels may lead in an injection advance, which is associated to an increased number of nanoparticles.

It was found that formaldehyde and acetaldehyde were the most abundant carbonyls. Concerning the driving profile, Artemis Urban produced higher carbonyl emissions compared to NEDC. The use of PME10, SUME10, and SME10 resulted in higher concentrations of carbonyl emissions with respect to diesel fuel and UFOME10. It is believed that biodiesel could increase emissions of these oxygenated compounds as a consequence of the oxygen content in the molecule (Peng et al. 2008). In fact, carbonyl emissions were increased with the addition of biodiesel under the present test conditions. The increased formaldehyde in the exhaust mainly comes from the incomplete combustion of saturated aliphatic hydrocarbons. PME10 being the fuel containing the most saturated acids resulted in higher formaldehyde emissions. However, this trend was not kept constant since SUME10 and SME10, which are mainly unsaturated methyl esters compared to PME10 and UFOME10, produced the second and third highest formaldehyde emissions respectively. Taking into account that the reference diesel fuel contained an amount of biodiesel, some of the differences observed were insignificant. Nonetheless, no conclusive trend has been found regarding the emissions of carbonyl compounds and more investigations are required to clearly establish the reasons of biodiesel impact on these contaminants.

5. CONCLUSIONS

Based on the analysis presented, it is concluded that B10 effect on vehicle operation, fuel consumption and pollutant emissions is limited. Minor increases were observed for CO and HC emissions during cold start that are caused by the performance of the oxidation catalyst and engine management which are optimised for diesel fuel operation. NOx fluctuate around the baseline value while PM emissions are reduced about 20% under most conditions. The use of biofuels also appears to suppress the solid and total particle number in most cases. Carbonyl emissions gave discordant results. Although that the addition of biodiesel produced higher carbonyl emissions in most cases, no conclusive trend has been found regarding the impact of biodiesel source material on these compounds. Overall, a potential rise of biodiesel content in automotive diesel is expected to have limited impacts on urban air quality.

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