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Effectiveness of Selective Catalytic Reduction (SCR) systems on reducing gaseous emissions from an engine using Diesel and Biodiesel Blends

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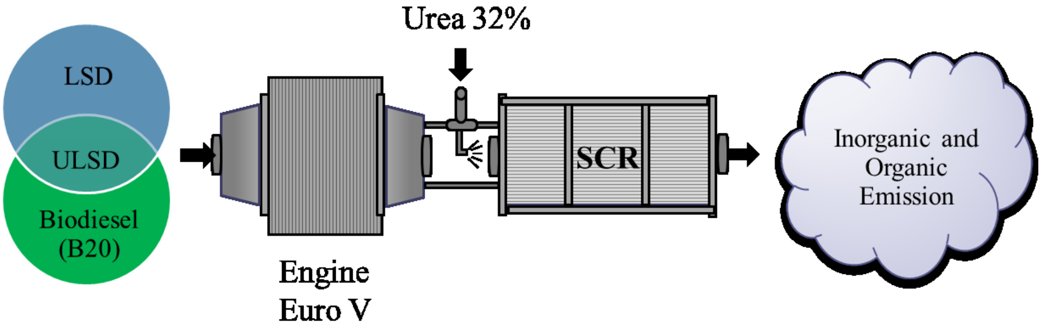
ABSTRACT

There is an urgent and pressing need to further understand petroleum-based emission control systems. To date, a limited number of emission studies have reported on the effects on automotive emissions when vehicles equipped with Selective Catalytic Reduction (SCR) systems run on a mixture of regular petroleum-based and biodiesel. The aim of this investigation was to quantify organic and inorganic gas emissions from a four-cylinder diesel engine equipped with urea-SCR system. Using a bench dynamometer, the emissions from the following mixtures were evaluated using an FTIR spectrometer: low sulphur diesel (LSD), ultra-low sulphur diesel (ULSD) and a blend of 20 % soybean biodiesel and 80% ULSD (B20). Our results confirmed that the use of the SCR system yields statistically significant ($p<0.05$) lower NO_x emissions in comparison to all the studied fuels. The LSD and ULSD fuels also significantly reduced emissions of compounds with high photochemical ozone creation potential, such as formaldehyde. However, the SCR system produced significantly ($p<0.05$) higher emissions of N_2O comparing the used fuels. In the case of LSD, the NH_3 emissions were elevated and in the case of ULSD and B20 fuels, the non-methane hydrocarbon (NMHC) and total hydrocarbon (HCD) emissions were significantly higher.

Keywords: Selective Catalytic Reduction (SCR); biodiesel; hydrocarbons; diesel; emissions; gaseous pollutants.



1. Introduction

There is an urgent and pressing need for in-depth understanding of petroleum-based emission control systems. Global pressure to meet emission standards lead to the development and use of new engine technologies and as of late also for the use of new fuels and fuel blends, such as ultra-low sulphur diesel and biodiesel blends.

Emissions depend on a variety of factors, such as engine technology, maintenance and emission control technology,[1] as well as the type and quality of the employed fuel. Besides the greenhouse gas pollutants with global warming potential, it is widely known that engine exhaust systems produce also organic gases that have an impact on photochemical ozone and other secondary pollutants' formation. Among such different gases emitted by petroleum-based systems, nitrogen oxides (NO_x) are one of the major threats to the environment and therefore its emission in diesel engines has been widely investigated.[2-5] NO_x suppression strategies consist of combustion controls, such as Selective Catalytic Reduction (SCR) systems, using a urea solution as reducing agent, a well-established technique of stationary diesel engines.[6-8] Biodiesel seems to be a promising alternative, as it can be used in diesel engines without major modifications,[9] reducing qualitative and quantitatively several pollutant emissions.[10-14] The use of biofuels and fuel blends, in combination with exhaust aftertreatment systems as a means of mitigating emissions, are promising and therefore the topic of this investigation.

New standard guidelines are being established worldwide concerning heavy-duty diesel engine emissions, aiming mostly at the simultaneous reduction of particles and NO_x (Euro V and Euro VI regulations in Europe and 40 Code of Federal Regulations 86.007-11).[15] In Brazil, the ruling legislation is equivalent to the Euro V emission standards and it was established on January 1st, 2012, as a result of the seventh stage of the Program to Control Vehicular Air Pollution (PROCONVE, in Portuguese). In order to achieve the Brazilian air quality guidelines, the sulphur content of diesel fuels was reduced and new aftertreatment systems have been implemented, with the urea-SCR (Selective Catalytic Reduction) system being mostly utilized.[4,5,16]

To date, a limited number of emission studies have reported on the effects of biodiesel additions to regular petroleum-based diesel on emissions from vehicles equipped with Selective Catalytic Reduction (SCR) systems.

In order to fill the gap, the aim of this investigation was to quantify organic and inorganic gas emissions (gas- and particle-phase) from a four-cylinder diesel engine equipped with an urea-SCR system using Diesel or Biodiesel blends.

2. Materials and methods

In this study, we used an engine dynamometer following the European Steady Cycle (ESC) testing cycle, in agreement with the Directive 1999/96/EC of the European Parliament and the Directive of the December 13th, 1999 Council,[17] which establishes engine and dynamometer settings, and also NO_x and other pollutants emission limits. The dynamometer used in this study has a power output of 440 kW at 6000 rpm and a torque of 2334 Nm. The engine employed is in accordance with the Euro V standards, using an urea-SCR after-treatment system. Table 1 specifies the engine details.

Table 1. Engine specifications, BR- model 2012.

Specifications	
Emission	Euro V "Heavy Duty"/Proconve P7
Configuration	4 cylinders, inline
Displacement	4,8 liters
Bore x Stroke	105 x 137 mm
Combustion System	Direct injection
Injection System	Common Rail Electronic
Aspiration	TGV Intercooler
Power Output	187hp (139,7kW) 2,200rpm
Peak Torque	720Nm (73kgf.m) 1,200 ~ 1,600rpm
Weight (dry)	426 kg
Aftertreatment	SCR
Dimensions (H x L x W)	900 x 975 x 826 mm

The emission data were sampled in the laboratory of vehicular emissions of the Federal University of Parana –Curitiba/Brazil, employing an engine dynamometer driving cycle using LSD (Low Sulphur Diesel - 50 ppm sulphur content), ULSD (Ultra Low Sulphur Diesel - 10 ppm sulphur content) and B20 (soybean biodiesel blended (20%) with ULSD). The main difference between LSD and ULSD is their sulphur content, which may affect SO_2 and particulate emissions. However, the cetane number also differs and is considered a key fuel property comprising NMHC and CO emissions.[9,18]

Table 2 shows the quality parameters of the reference diesel fuels and the biodiesel blend used in this research. The Standard Test Methods established by ASTM were followed. The main properties having an influence on exhaust emissions are sulphur content and cetane number, as will be discussed in the results section.

Table 2. Fuel Properties of LSD and ULSD diesel and B20 biodiesel.

Property	LSD	ULSD	B20
Sulphur, mg/kg	24	4	6
Cetane number	49.2	53.8	51
Glow point (°C)	58.5	44.5	70.5
Viscosity at 40°C (mm^2/s)	2.6	3.0	3.15
Specific mass at 20°C (kg/m^3)	835.2	830.5	848.1

The gas emission data were obtained by a SESAM i60 FT, a Fourier Transform InfraRed (FTIR) multi-component measurement system from AVL. Table 3 presents some important technical characteristics of the FTIR analysis. The FTIR was calibrated to detect specific hydrocarbons (HC), nitrogen compounds (NO, NO_2, N_2O and NH_3) and other pollutants. It also calculates NO_x, total (HCD) and non-methane hydrocarbons (NMHC) concentrations. The HCD is the sum of all hydrocarbons that FTIR can analyse using a method for diesel fuel (HCD = CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_6, nC_8 and AHC-aromatic hydrocarbons). The HCD expresses the total hydrocarbons (HC) for diesel emission analysis. The NMHC comprises the HCD concentration, except for the methane fraction.

Table 3. FTIR settings.

FTIR Spectrometer Data	
Sampling Rate	1 scan per second (1 Hz)
Data Rate	All measured gas components at 1 Hz
Spectral Resolution	0.5 cm^{-1}
Measurement Cell	Gas cell heated to 191 °C (375.8 °F)
Response Time	t_{10} to t_{90} within 1 s
Sample Flow Rate	10 l/min per stream
Detector Cooling	Liquid nitrogen, 50 ml/h
Zero/Purge Gas	Nitrogen / Synthetic Air, 0.6 – 1.5 l/min
Compressed Air	5 – 6 bar and max. 100 l/min per FTIR stream

3. Results and discussions

3.1 Nitrogen Compounds

Analysis of Variance (ANOVA), normal probability plot of residuals and Bartlett's test of homogeneity of variances were applied to the studied compounds. The statistical analysis were performed using R software.[19] A preliminary analysis showed that the residuals have a normal distribution and a parametric behaviour. The Bartlett's test presented, for almost all samples, p-values less than the significance level of 0.05, confirming the homogeneity of sample variances. In conclusion, the analysis of variance results are valid, except for C_2H_2 and C_2H_6.

According to the analysis of variance results the means differ due to fuel and after-treatment system choice. To analyse the interactions between fuel and after-treatment system, we applied the Tukey significant difference test. Differences between mean values at a level of $p < 0.05$ (95% confidence level) were considered statistically significant.[20]

Our results, presented in Table 4, have shown that, for all studied fuels the use of the SCR system presented statistically significant different means of nitrogen oxides (NO_x), nitrogen monoxide (NO) and nitrogen dioxide (NO_2) emissions, compared to results when the SCR system was not used. Quantitatively, the use of the SCR system decreased NO_x, NO and NO_2 concentrations.

According to Chin et al.[1], some biodiesel blends may reduce emissions of regulated pollutants, such as PM, CO, NMHC and CO_2. However, it usually increases fuel consumption and NO_x emissions.

Only NO_2 emission means showed statistically significant differences between LSD and ULSD fuels when the engine was not equipped with the SCR system. However this trend was not observed between the ULSD and the B20 fuels. In contrast, the use of different fuels statistically affected NO_x, NO and NO_2 emission means when the engine was equipped with the SCR system, where the highest emissions were observed for the ULSD and B20 fuels.

According to Chin et al.[1] and Agarwal and Das[21], a NO_x emission increase due to biodiesel blend fuels use, is a result of some fuel properties, such as viscosity, and also is a result of the advance in injection timing, temperature rise and abundance of oxygen available in the combustion chamber.[1,21] Viscosity interfere in the fuel nebulization generating different sizes of droplets in the combustion chamber. The burning efficiency is higher with small droplets, due to a lower viscosity, leading a lower NO_x emission.

Despite the fact that the WHO[22] has reported that sulphur content of fuels can increase NO_x emissions, as it reduces catalyst efficiency, our results showed similar concentrations to all tested fuels (scenarios without SCR system), although higher concentrations using ULSD in comparison to LSD with the use of SCR system were observed.

Table 4. Average and standard deviation of exhaust emissions for nitrogen compounds (g/kWh) using SCR system on and off.

	Low Sulfur Diesel		Ultra Low Sulfur Diesel		Biodiesel B20	
Pollutant	SCR off (±SD)	SCR on (±SD)	SCR off (±SD)	SCR on (±SD)	SCR off (±SD)	SCR on (±SD)
NO_x	7.55 ± 0.04	0.52 ± 0.02	7.66 ± 0.07	2.4 ± 0.8	7.6 ± 0.2	1.6 ± 0.4
NO	4.89 ± 0.02	0.34 ± 0.01	4.84 ± 0.03	1.5 ± 0.5	4.8 ± 0.1	0.98 ± 0.24
NO_2	0.06 ± 0.01	< M.D.C.	0.26 ± 0.04	0.15 ± 0.04	0.31 ± 0.07	0.06 ± 0.01
NH_3	0.004 ± 0.002	0.07 ± 0.02	0.002 ± 0.001	0.007 ± 0.003	0.0008 ± 0.0007	0.006 ± 0.001
N_2O	0.0133 ± 0.0001	0.0434 ± 0.0003	0.0127 ± 0.0005	0.044 ± 0.004	0.013 ± 0.001	0.061 ± 0.008

NO_x - Nitrogen Oxides, NO- Nitrogen Monoxide, NO_2- Nitrogen Dioxide, NH_3- Ammonia, N_2O-Nitrous Oxide.

* MDC (Minimal Detectable Concentration) is the detection limit of each gas component, determined as two times the standard deviation σ of zero gas measurement over 60 seconds.
Inferior to MDC: NO_2 – Nitrogen dioxide (MDC = 0,011 g/kWh).

While designed to reduce NO_x emissions, the SCR system may increase other pollutants' emissions. As demonstrated in our study, the SCR system satisfies its purpose of reducing NO_x emissions. However, it brings forth new problems, such as higher emissions of N_2O, NH_3 and some hydrocarbons.

Table 4 shows an increase in ammonia emissions due to SCR system use. The only increase considered statistically significant ($p<0.05$) was for LSD.

On the other hand, while the engine was equipped with the SCR system, there is a statistically significant difference between NH_3 emission means from LSD to B20 and from LSD to ULSD. The NH_3 emission means for ULSD and B20 could not be considered significantly different at a 95% confidence level.

Koebel et al.[6] reported that the SCR system uses continuous urea injections (ammonia content) to neutralize NO_x emissions, which may lead to an excess of urea, called ammonia slip. It is therefore not unreasonable to assume that the ammonia slip may be responsible for the higher NH_3 emissions observed.

When the injected urea solution fails to be completely decomposed below 200°C, it can produce ammonium nitrate (NH_4NO_3), cyanuric acid ($(HNCO)_3$), and other compounds as sub-products.[8] As a consequence, ammonia and ammonium salts have a relevant impact on the ecosystem, accounting for the modification of the atmosphere global radioactive balance, the reduction of atmospheric visibility, the acidification and eutrophication of the environment.[23]

As has been reported by European Environment Agency[24], road transport contributes only 2% of total ammonia (NH_3) emissions, though it is a significant source from a local perspective in urban areas. Many studies[25-29] reported that an increase in NH_3 emission has occurred due to introduction of vehicles equipped with catalytic converters and adoption of urea-SCR system.

The main source of anthropogenic N_2O is agriculture,[30] but some concern has arisen due to new diesel exhaust after-treatment systems being responsible for N_2O production, for example, the chemical reactions in urea-SCR system.[31]

In our experiment, the use of the SCR system increased N_2O concentrations for all studied fuels. With 95% confidence level, these increases can be considered statistically significant, with the highest increase observed for the B20 biodiesel blend (about 361%) and the lowest for the ULSD (about 83%). These results can be explained by the undesirable processes that may occur in the SCR systems, including several competitive, non selective reactions with oxygen that can produce secondary emission.[31]

While the engine was equipped with the SCR system, a statistically significant increase of N_2O emission due to B20 biodiesel use was verified, in comparison with ULSD and LSD fuels ($p<0.05$).

3.2 Hydrocarbons

The FTIR equipment is also able to detect the non-methane hydrocarbons (NMHC) and hydrocarbons of diesel (HCD). The results are shown in Table 5.

Table 5. Average exhaust emissions for hydrocarbons compounds (g/kWh).

	Low Sulfur Diesel	Ultra Low Sulfur Diesel	Biodiesel B20

Pollutant	SCR off (±SD)	SCR on (±SD)	SCR off (±SD)	SCR on (±SD)	SCR off (±SD)	SCR on (±SD)
NMHC	0.1888 ± 0.0002	0.1857 ± 0.0004	0.135 ± 0.003	0.159 ± 0.003	0.136 ± 0.007	0.164 ± 0.006
HCD	0.1917 ± 0.0004	0.1878 ± 0.0004	0.137 ± 0.003	0.161 ± 0.003	0.137 ± 0.007	0.166 ± 0.006
C_3H_6	0.0233 ± 0.0009	0.0236 ± 0.0002	0.012 ± 0.002	0.006 ± 0.001	0.0138 ± 0.0004	0.013 ± 0.003
C_2H_2	0.0142 ± 0.0003	0.0120 ± 0.0003	0.0125 ± 0.0008	0.0122 ± 0.0004	0.0104 ± 0.0006	0.0124 ± 0.0008
C_2H_6	0.0653 ± 0.0006	0.0673 ± 0.0007	0.064 ± 0.002	0.089 ± 0.003	0.068 ± 0.004	0.087 ± 0.002
C_3H_8	0.030 ± 0.001	0.0169 ± 0.0007	0.0276± 0.002	0.0281 ± 0.0008	0.0168 ± 0.0007	0.025 ± 0.005
CH_4	0.0028± 0.0003	0.00213 ± 0.00003	0.0021 ± 0.0002	0.0023 ± 0.0001	0.00165 ± 0.00007	0.0022 ± 0.0004
HCHO	0.0285 ± 0.0007	0.0063 ± 0.0005	0.011 ± 0.002	0.0037 ± 0.0002	0.010 ± 0.004	0.006 ± 0.002
nC8	0.056 ± 0.001	0.0659 ± 0.0002	0.0204 ± 0.0005	0.024 ± 0.002	0.027 ± 0.002	0.027 ± 0.004

NMHC- Non-Methane Hydrocarbons, HCD- Hydrocarbons of Diesel, C_3H_6-Propylene, C_2H_2-Acetylene, C_2H_6- Ethane, C_3H_8-Propane, CH_4 - Methane, HCHO- Formaldehyde and nC8- N-Octane.

Inferior to MDC: C_2H_4- Ethene (MDC = 0,0173 g/kWh), C_4H_6- 1, 3 Butadiene (MDC = 0,0666 g/kWh) and AHC- Aromatic hydrocarbon (MDC = 0,0134 g/kWh).

The NMHC emission means were statistically different between LSD and ULSD for both situations, SCR-on and SCR-off, showing a reduction of 30% for SCR off and 15% for SCR on. The influence of the SCR system in NMHC emissions means was statistically significant only for ULSD and B20. The means increased by nearly 20% using ULSD and B20 ($p<0.05$). Diesel hydrocarbons emissions (HCD) showed a similar trend to that observed for NMHC emissions described previously.

Fuels with a smaller cetane number has a higher ignition delay time, which "along with the combustion of a partially premixed charge results in excessive emissions from incomplete combustion, specifically total hydrocarbons (THC) and CO".[18]

Regarding recent changes on fuel properties, such as lower sulphur content in diesel and the use of biodiesel blends, considering measures of each hydrocarbon to engine not equipped with SCR system, the use of ULSD showed statistically significant difference on means in comparison to LSD to all hydrocarbons, with exception of ethane and acetylene (analysis of variance invalid). However, the only hydrocarbons showing significant differences on means ($p<0.05$) from ULSD to B20 were propane and n-octane, with decrease of propane and increase of n-octane.

Statistical treatment of data indicates that formaldehyde emissions were significantly ($p<0.05$) lower (78%) with LSD and (59%) with ULSD due to SCR system use. It also indicates that n-octane emissions were significantly ($p<0.05$) higher (18%) with LSD due to SCR system use.

Besides the toxicity of some organic compounds like BTEX and HPA’s, well known as potential carcinogenic compounds, Atkinson[32] pointed out that a variety of hydrocarbons may lead to ozone production in low latitudes, through their reaction to OH radicals in the presence of NO_x and SO_2.

The ground-level ozone is a well-known atmospheric pollutant, which can cause several deleterious impacts on the environment and human health. In high concentrations, the tropospheric O_3 can interfere with photosynthesis and the growing of some plant species.[33,22] The latest European directive 2002/3/CE recommends that at least 30 NMHCs (saturated, unsaturated or aromatic) should be measured.[34] As far as ozone formation due to high NMHCs and SO_x emissions are concerned, the critical situation in our study was that of LSD, which presented elevated NMHC and SO_2 emissions.

In this context, it is widely known that organic compounds participated in the formation of secondary pollutants that may contribute to some of the undesirable environmental effects associated with photochemical smog episodes.

Essentially, each compound has a different contribution due to the amount emitted and some properties that affect the secondary pollutants production during photochemical reactions. Some of these compounds are said to be more reactive than others. Consequently, the most reactive organic compounds should be addressed towards a strategy to reduce ozone and PAN (Peroxyacetylnitrate) exposure levels.[35]

A ranking of most reactive organic compounds, based on ozone formation under specific atmospheric conditions has been developed, the so-called reactivity scale. Derwent et al.[35] created a reactivity scale for Northwestern Europe. They estimated the Photochemical Ozone Creation Potentials (POCPs) and Photochemical PAN Creation Potentials (PPCPs) for 120 organic compounds and their sensitivity to NO_x emissions taking ethylene (POCP = 100) and propylene (PPCP = 100), respectively, as the reference compound. Table 6 presents the values calculated by Derwent et al. (1998).[35]

Table 6. Photochemical Ozone Creation Potential POCP and Photochemical PAN Creation Potential

Organic Compounds	POCP	PPCP
Propylene	112.3	100
Formaldehyde	51.9	14.8
N-octane	45.3	42.9

Propane	17.6	13.7
Ethane	12.3	17.3
Acetylene	8.5	2.2
Methane	0.6	0.9

Source: Derwent et al.[35]

Relating the results of Table 6 with our study, n-octane POCP is only 13% lower than formaldehyde's one, while its PPCP is 65% higher than the formaldehyde one. With regards to ozone and PAN formation, LSD fuel presented the higher concentrations for the compounds with the higher POCP and PPCP values: propylene, formaldehyde and n-octane.

Considering only the LSD fuel, it was statistically verified ($p<0.05$) an increase in n-octane emission and a decrease in formaldehyde when the SCR system was used. These results indicate a beneficial effect in ozone photochemical creation, as the formaldehyde POCP is higher than n-octane one. In addition, as reported by WHO[22], formaldehyde was classified as a carcinogenic compound.

The SCR system combined with ULSD or B20 has increased alkanes emissions, however their POCP and PPCP are lower than those of formaldehyde, propylene and n-octane. Therefore, the ULSD and B20 fuels are, apparently, a better alternative than LSD, considering the hydrocarbons emissions and their photochemical potentials.

Recently Derwent et al.[36] developed a similar study applying the same models to create an activity scale for different emission sources of organic compounds. They indicated road transport-exhaust as the major contributor to POCP levels. Furthermore, Derwent et al.[37] made the same conclusion for secondary organic aerosol formation from organic compounds.

The POCP and PPCP analysis applied in our study is interesting since the combination of megacities, atmospheric conditions and significant emissions of ozone and PAN precursors can favour photochemical reactions in smog systems, creating serious pollution episodes.

Regarding the use of the SCR system scenarios, the results are of similar magnitude for all tested fuels. However, when the engine was not equipped with the SCR system, the LSD showed higher emissions, with differences over 60% in comparison to ULSD, with little difference between ULSD and B20.

Open literature describes decreases in aldehyde emissions from some biodiesel fuels, in comparison to diesel.[38-40] However, specifically with regard to formaldehyde, some researchers observed an increase or no alteration in its emission.[41-43,9] Tan et al.[44] showed an increase of formaldehyde emissions mainly for pure biodiesel fuel in comparison to diesel, and showed little difference between diesel and B20 blend.

Taken together, this study showed that the emissions of NO and NO_2 while the engine was equipped with the SCR system using the ESC cycle were lower and statistically significant ($p<0.05$). However, the use of the SCR system produced significantly increased concentrations of: N_2O for all studied fuels; NH_3 just for LSD; and non-methane hydrocarbons (NMHC) and hydrocarbons of diesel (HCD) for ULSD and B20. On the other hand, the use of SCR system significantly ($p<0.05$) supressed formaldehyde emissions for LSD and ULSD fuels, having a beneficial impact since it has a huge POCP and PPCP and is considered as a carcinogenic compound.

Soybean biodiesel blend used, in combination with the SCR system, can successfully reduce harmful pollutant emissions such as NO_x, however, increases the HCD production.

4. Acknowledgement

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