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1 Effectiveness of Selective Catalytic Reduction (SCR) systems on

2 reducing gaseous emissions from an engine using Diesel and Biodiesel

3 Blends

4

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32 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.
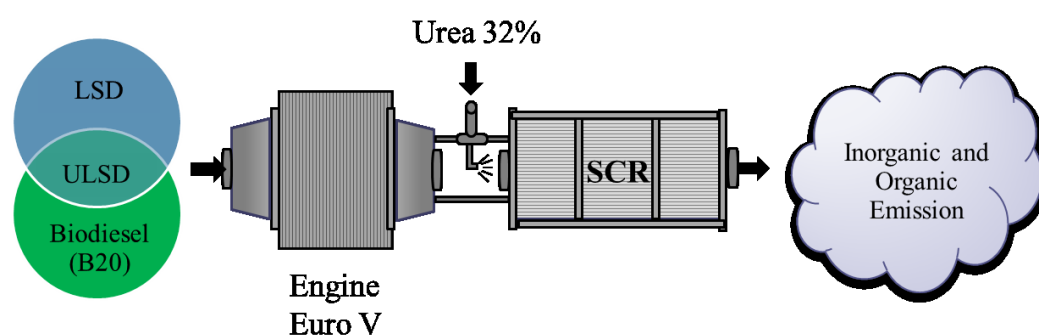
1.   Introduction

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

61 development and use of new engine technologies and as of late also for the use of new

62 fuels and fuel blends, such as ultra-low sulphur diesel and biodiesel blends.

63   Emissions depend on a variety of factors, such as engine technology,

64 maintenance and emission control technology,[1] as well as the type and quality of the

65 employed fuel. Besides the greenhouse gas pollutants with global warming potential, it

66 is widely known that engine exhaust systems produce also organic gases that have an

67 impact on photochemical ozone and other secondary pollutants' formation. Among

68 such different gases emitted by petroleum-based systems, nitrogen oxides (NO_x) are

69 one of the major threats to the environment and therefore its emission in diesel engines

70 has been widely investigated.[2-5] NO_x suppression strategies consist of combustion

71 controls, such as Selective Catalytic Reduction (SCR) systems, using a urea solution as

72 reducing agent, a well-established technique of stationary diesel engines.[6-8] Biodiesel

73 seems to be a promising alternative, as it can be used in diesel engines without major

74 modifications,[9] reducing qualitative and quantitatively several pollutant emissions.[10-14]

75 The use of biofuels and fuel blends, in combination with exhaust aftertreatment systems

76 as a means of mitigating emissions, are promising and therefore the topic of this

77 investigation.

78   New standard guidelines are being established worldwide concerning heavy-

79 duty diesel engine emissions, aiming mostly at the simultaneous reduction of particles

80 and NO_x (Euro V and Euro VI regulations in Europe and 40 Code of Federal

81 Regulations 86.007-11).[15] In Brazil, the ruling legislation is equivalent to the Euro V

82 emission standards and it was established on January 1st, 2012, as a result of the seventh

83 stage of the Program to Control Vehicular Air Pollution (PROCONVE, in Portuguese).

84 In order to achieve the Brazilian air quality guidelines, the sulphur content of diesel

85 fuels was reduced and new aftertreatment systems have been implemented, with the

86 urea-SCR (Selective Catalytic Reduction) system being mostly utilized.[4,5,16]

87   To date, a limited number of emission studies have reported on the effects of

88 biodiesel additions to regular petroleum-based diesel on emissions from vehicles

89 equipped with Selective Catalytic Reduction (SCR) systems.

90   In order to fill the gap, the aim of this investigation was to quantify organic and

91 inorganic gas emissions (gas- and particle-phase) from a four-cylinder diesel engine

92 equipped with an urea-SCR system using Diesel or Biodiesel blends.

93

94   ## 2.   Materials and methods

95

96   In this study, we used an engine dynamometer following the European Steady

97 Cycle (ESC) testing cycle, in agreement with the Directive 1999/96/EC of the European

98 Parliament and the Directive of the December 13th, 1999 Council,[17] which establishes

99 engine and dynamometer settings, and also NO_x and other pollutants emission limits.

100 The dynamometer used in this study has a power output of 440 kW at 6000 rpm and a

101 torque of 2334 Nm. The engine employed is in accordance with the Euro V standards,

102 using an urea-SCR after-treatment system. Table 1 specifies the engine details.

103

104   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

105

106   The emission data were sampled in the laboratory of vehicular emissions of the

107 Federal University of Parana –Curitiba/Brazil, employing an engine dynamometer

108 driving cycle using LSD (Low Sulphur Diesel - 50 ppm sulphur content), ULSD (Ultra

109 Low Sulphur Diesel - 10 ppm sulphur content) and B20 (soybean biodiesel blended

110 (20%) with ULSD). The main difference between LSD and ULSD is their sulphur

111 content, which may affect SO_2 and particulate emissions. However, the cetane number

112 also differs and is considered a key fuel property comprising NMHC and CO

113 emissions.[9,18]

114   Table 2 shows the quality parameters of the reference diesel fuels and the biodiesel

115   blend used in this research. The Standard Test Methods established by ASTM were

116   followed. The main properties having an influence on exhaust emissions are sulphur

117   content and cetane number, as will be discussed in the results section.

118

119   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

120

121   The gas emission data were obtained by a SESAM i60 FT, a Fourier Transform

122   InfraRed (FTIR) multi-component measurement system from AVL. Table 3 presents

123   some important technical characteristics of the FTIR analysis. The FTIR was calibrated

124   to detect specific hydrocarbons (HC), nitrogen compounds (NO, NO_2, N_2O and NH_3)

125   and other pollutants. It also calculates NO_x, total (HCD) and non-methane

126   hydrocarbons (NMHC) concentrations. The HCD is the sum of all hydrocarbons that

127   FTIR can analyse using a method for diesel fuel (HCD = CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6,

128   C_3H_8, C_4H_6, nC_8 and AHC-aromatic hydrocarbons). The HCD expresses the total

129   hydrocarbons (HC) for diesel emission analysis. The NMHC comprises the HCD

130   concentration, except for the methane fraction.

131

132   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

133

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

168 generating different sizes of droplets in the combustion chamber. The burning
169 efficiency is higher with small droplets, due to a lower viscosity, leading a lower NO_x
170 emission.

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

176

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

Pollutant	Low Sulfur Diesel		Ultra Low Sulfur Diesel		Biodiesel B20	
	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

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

181 * MDC (Minimal Detectable Concentration) is the detection limit of each gas component, determined as
182 two times the standard deviation σ of zero gas measurement over 60 seconds.
183 Inferior to MDC: NO_2 – Nitrogen dioxide (MDC = 0,011 g/kWh).
184
185

186 While designed to reduce NO_x emissions, the SCR system may increase other
187 pollutants' emissions. As demonstrated in our study, the SCR system satisfies its
188 purpose of reducing NO_x emissions. However, it brings forth new problems, such as
189 higher emissions of N_2O, NH_3 and some hydrocarbons.
190 Table 4 shows an increase in ammonia emissions due to SCR system use. The only
191 increase considered statistically significant ($p < 0.05$) was for LSD.

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

196 Koebel et al.[6] reported that the SCR system uses continuous urea injections
197 (ammonia content) to neutralize NO_x emissions, which may lead to an excess of urea,

198 called ammonia slip. It is therefore not unreasonable to assume that the ammonia slip

199 may be responsible for the higher NH_3 emissions observed.

200 When the injected urea solution fails to be completely decomposed below 200°C,

201 it can produce ammonium nitrate (NH_4NO_3), cyanuric acid (($HNCO)_3$), and other

202 compounds as sub-products.[8] As a consequence, ammonia and ammonium salts have a

203 relevant impact on the ecosystem, accounting for the modification of the atmosphere

204 global radioactive balance, the reduction of atmospheric visibility, the acidification and

205 eutrophication of the environment.[23]

206 As has been reported by European Environment Agency[24], road transport contributes

207 only 2% of total ammonia (NH_3) emissions, though it is a significant source from a

208 local perspective in urban areas. Many studies[25-29] reported that an increase in NH_3

209 emission has occurred due to introduction of vehicles equipped with catalytic

210 converters and adoption of urea-SCR system.

211 The main source of anthropogenic N_2O is agriculture,[30] but some concern has

212 arisen due to new diesel exhaust after-treatment systems being responsible for N_2O

213 production, for example, the chemical reactions in urea-SCR system.[31]

214 In our experiment, the use of the SCR system increased N_2O concentrations for all

215 studied fuels. With 95% confidence level, these increases can be considered statistically

216 significant, with the highest increase observed for the B20 biodiesel blend (about

217 361%) and the lowest for the ULSD (about 83%). These results can be explained by

218 the undesirable processes that may occur in the SCR systems, including several

219 competitive, non selective reactions with oxygen that can produce secondary

220 emission.[31]

221 While the engine was equipped with the SCR system, a statistically significant

222 increase of N_2O emission due to B20 biodiesel use was verified, in comparison with

223 ULSD and LSD fuels ($p < 0.05$).

224 3.2 Hydrocarbons

225

226 The FTIR equipment is also able to detect the non-methane hydrocarbons (NMHC)

227 and hydrocarbons of diesel (HCD). The results are shown in Table 5.

228

229 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

230 NMHC- Non-Methane Hydrocarbons, HCD- Hydrocarbons of Diesel, C_3H_6-Propylene, C_2H_2-
231 Acetylene, C_2H_6- Ethane, C_3H_8-Propane, CH_4 - Methane, HCHO- Formaldehyde and nC8- N-Octane.
232
233 Inferior to MDC: C_2H_4- Ethene (MDC = 0,0173 g/kWh), C_4H_6- 1, 3 Butadiene (MDC = 0,0666 g/kWh)
234 and AHC- Aromatic hydrocarbon (MDC = 0,0134 g/kWh).
235

236   The NMHC emission means were statistically different between LSD and ULSD
237 for both situations, SCR-on and SCR-off, showing a reduction of 30% for SCR off and
238 15% for SCR on. The influence of the SCR system in NMHC emissions means was
239 statistically significant only for ULSD and B20. The means increased by nearly 20%
240 using ULSD and B20 ($p < 0.05$). Diesel hydrocarbons emissions (HCD) showed a
241 similar trend to that observed for NMHC emissions described previously.

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

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

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

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

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

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

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

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

283 Table 6. Photochemical Ozone Creation Potential POCP and Photochemical PAN
284 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

285   Source: Derwent et al.[35]

286

287   Relating the results of Table 6 with our study, n-octane POCP is only 13% lower

288 than formaldehyde's one, while its PPCP is 65% higher than the formaldehyde one.

289 With regards to ozone and PAN formation, LSD fuel presented the higher

290 concentrations for the compounds with the higher POCP and PPCP values: propylene,

291 formaldehyde and n-octane.

292   Considering only the LSD fuel, it was statistically verified ($p < 0.05$) an increase in

293 n-octane emission and a decrease in formaldehyde when the SCR system was used.

294 These results indicate a beneficial effect in ozone photochemical creation, as the

295 formaldehyde POCP is higher than n-octane one. In addition, as reported by WHO[22],

296 formaldehyde was classified as a carcinogenic compound.

297   The SCR system combined with ULSD or B20 has increased alkanes emissions,

298 however their POCP and PPCP are lower than those of formaldehyde, propylene and

299 n-octane. Therefore, the ULSD and B20 fuels are, apparently, a better alternative than

300 LSD, considering the hydrocarbons emissions and their photochemical potentials.

301   Recently Derwent et al.[36] developed a similar study applying the same models to

302 create an activity scale for different emission sources of organic compounds. They

303 indicated road transport-exhaust as the major contributor to POCP levels. Furthermore,

304 Derwent et al.[37] made the same conclusion for secondary organic aerosol formation

305 from organic compounds.

306   The POCP and PPCP analysis applied in our study is interesting since the

307 combination of megacities, atmospheric conditions and significant emissions of ozone

308 and PAN precursors can favour photochemical reactions in smog systems, creating

309 serious pollution episodes.

310   Regarding the use of the SCR system scenarios, the results are of similar magnitude

311 for all tested fuels. However, when the engine was not equipped with the SCR system,

312 the LSD showed higher emissions, with differences over 60% in comparison to ULSD,

313 with little difference between ULSD and B20.

314   Open literature describes decreases in aldehyde emissions from some biodiesel

315   fuels, in comparison to diesel.[38-40] However, specifically with regard to formaldehyde,

316   some researchers observed an increase or no alteration in its emission.[41-43,9] Tan et al.[44]

317   showed an increase of formaldehyde emissions mainly for pure biodiesel fuel in

318   comparison to diesel, and showed little difference between diesel and B20 blend.

319   Taken together, this study showed that the emissions of NO and NO_2 while the

320   engine was equipped with the SCR system using the ESC cycle were lower and

321   statistically significant ($p<0.05$). However, the use of the SCR system produced

322   significantly increased concentrations of: N_2O for all studied fuels; NH_3 just for LSD;

323   and non-methane hydrocarbons (NMHC) and hydrocarbons of diesel (HCD) for ULSD

324   and B20. On the other hand, the use of SCR system significantly ($p<0.05$) supressed

325   formaldehyde emissions for LSD and ULSD fuels, having a beneficial impact since it

326   has a huge POCP and PPCP and is considered as a carcinogenic compound.

327   Soybean biodiesel blend used, in combination with the SCR system, can

328   successfully reduce harmful pollutant emissions such as NO_x, however, increases the

329   HCD production.

330

331

4. Acknowledgement

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336

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338

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