ALDEHYDE EMISSIONS FROM A STATIONARY DIESEL ENGINE OPERATING WITH CASTOR OIL BIODIESEL – DIESEL OIL BLENDS

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ABSTRACT

The presence of aldehyde in the exhaust gas of a stationary, direct injection, compression ignition engine operating with castor oil biodiesel/diesel oil blends (B5, B10, B20 and B35) is analyzed. The diesel engine was operated with constant speed of 1800 rev/min and load of 37.5 kW. The gas sample was collected directly from the exhaust. Aldehydes were identified and quantified using gas chromatography (GC) with flame ionization detector analyzer (FID). Acetaldehyde presented higher exhaust concentration than formaldehyde for all fuel blends tested. In general, the exhaust aldehyde levels were very low and did not present significant differences between the fuel blends tested.

Keywords: Aldehydes, diesel engine, gas chromatography.

NOMENCLATURE

CC	Carboxylic compound
CH_2O	Formaldehyde
C_2H_4O	Acetaldehyde
DNPH	2,4-dinitrophenilhydrazine
EGR	Exhaust gas recirculation
ES	Electrospray
ESI	eletrospray ionization
FID	Flame Ionization Detector
FTIR	Fourier transformed infra-red spectroscopy
GC	Gas Chromatography
HC	Hydrocarbons
HCO	Aldehydes
HPLC	High Performance Liquid Chromatography
NO_X	Oxides of Nitrogen
MS	Mass spectrometry
PM	Particulate mass
UV	Ultraviolet photo-oxidation

INTRODUCTION

Aldehydes (HCO) are non-regulated pollutants, but cause harmful effects to humans. Aldehydes can participate of complex reactions in the atmosphere, generating other gaseous oxidants such as ozone, which causes respiratory problems. In Brazil, the legislation only limits the emissions of formaldehyde (CH_2O) and acetaldehyde (C_2H_4O) from vehicles equipped with spark ignition engines, as ethanol is largely used as fuel and it is known to be a potential aldehyde source. Although the legislation does not consider diesel engines, it is necessary to further investigate aldehyde emissions from diesel vehicles, especially after the introduction of biodiesel to diesel oil.

At present, Brazilian diesel fuel is constituted by a blend of 5% of biodiesel in diesel oil. The standard method to measure exhaust aldehydes is High Performance Liquid Chromatography (HPLC). In this work gas chromatography (GC) is used as an alternative method for aldehyde analysis to investigate its exhaust emission levels from a stationary diesel engine fuelled by castor oil biodiesel-diesel oil blends.

LITERATURE REVIEW

Methods of aldehyde analysis

Swarin et al. (1992) studied analytical methods based on the use of 2,4-dinitrophenilhydrazine (DNPH) as derivation reagent for collection and subsequent analysis of aldehydes and ketones by HPLC. The authors verified that formaldehyde does not produce a satisfactory reply to flame ionization detector (FID), but the remaining aldehydes, such as acetaldehyde and benzaldehyde, and ketones could be analyzed by GC if the concentration in the sample is big enough. Kataoka et al. (1998) demonstrated that aromatic and aliphatic, saturated and not saturated aldehydes can accurately be determined by GC with flame photometric detector. Christensen et al. (2001) measured formaldehyde and acetaldehyde using Fourier transformed infra-red spectroscopy (FTIR). An analytical method that uses high performance liquid chromatography and ultraviolet photo-oxidation with electrospray mass spectrometry (HPLC/UV/ES/MS) was developed as an analytical tool for carboxylic acid and aldehydes identification. Beyond the differentiation, eletrospray ionization with mass spectrometry (ESI/MS) could identify low concentration species, but, for longer retention times, the concentrations of some species are very low for the ultraviolet (UV) detector. Lewis et al. (2005) presented a new analytical method using liquid chromatography with ultraviolet eletrospray ionization mass spectrometry (LC-ESI-MS-UV), which was developed to analyze long chains of aldehydes and carboxylic acid. Zárante (2008) concluded that GC is an interesting alternative to the conventional HPLC method to determine aldehydes qualitatively and quantitatively in the exhaust of internal combustion engines

Roy (2008) introduced a new method of gas sampling for aldehyde analysis by HPLC, called bag sampling, which was used instead of the trapping gas sampling method. The superiority of the bag sampling method was claimed to be its transient gas checking capability. Guarieiro et al. (2008) compared the two most widely used carboxylic compounds (CC) collection methods: C18 cartridges coated with an acid solution of 2,4-dinitrophenylhydrazine (2,4-DNPH) and impinger bottles filled in 2,4-DNPH solution. The impinger system was able to collect CC more efficiently and with lower error than the C18 cartridge system. Furthermore, propionaldehyde was nearly not sampled by C18 system at all. A new method for aldehyde analysis in the exhaust of internal combustion engines is developed by. The method uses gas chromatography with flame ionization detector, with the gaseous sample collected directly of the exhaustion collector. Formaldehyde and acetaldehyde had been identified and quantified for a 1,4 liters spark ignition production engine, fed with hydrate ethanol. The formaldehyde and acetaldehyde retention times had been consistent for all tested conditions. The results demonstrate that gas chromatography method is.

Aldehyde emissions from diesel oil and biodiesel mixtures

Graboski et al. (2003) evidenced that more than 75% of exhaust aldehydes from a diesel fuelled engine was composed by formaldehyde and acetaldehyde. No significant difference was found between aldehyde emissions from biodiesel of different origins and diesel oil. Sluder et al. (2004) verified that aldehyde emissions from a diesel engine are initially reduced with the increase of exhaust gas recirculation (EGR) and they are increased for low oxides of nitrogen (NO_X) and low particulate matter (PM) combustion regime, especially formaldehyde and acetaldehyde, but also benzaldehyde, propionaldehyde and acrolein. High aldehyde emissions are consistent with low-temperature combustion regimes. Abrantes et al. (2005) verified that formaldehyde/acetaldehyde emissions ratio from light commercial diesel vehicles is constant around 74%/26%. Aldehyde emissions from diesel vehicles were significant lower when compared with spark ignition vehicles.

Corrêa and Arbilla (2007) observed that CC emissions from a heavy duty diesel engine showed different behavior when biodiesel-diesel oil mixtures were used instead of diesel oil. Benzaldehyde showed reduced emission, but all the remaining carbonyl compounds showed significant increase: 2.6% to 35.5% for formaldehyde; 1.4% to 15.8% for acetaldehyde; 2.1% to 22.0% for acroleine + acetone; 0.8% to 10.0% for propionaldehyde; and 3.3% to 26.0% for butyraldehyde. The dominant exhaust aldehyde components from engines fuelled by biodiesel-diesel oil blends are formaldehyde and acetaldehyde, accounting for over 75% of total aldehyde emissions (Peng et al., 2008). He et al. (2009) noticed that the use o soybean biodiesel multiplied by almost three times CC emissions in comparison with diesel oil, and contribute to increase total hydrocarbon (HC) emissions. Formaldehyde is the most abundant CC emitted from both, biodiesel and diesel oil, participating with 46.2% and 62.7% respectively, followed by acetaldehyde, acroleine and acetone. The experimental results by Yuan et al. (2009) indicated that formaldehyde is the main exhaust CC from a heavy duty diesel engine fuelled by palm biodiesel-diesel oil blends following a European transient cycle, contributing with 70.1%-76.2% of the total carbonyl concentration. Close numbers have been found by Lin et al. (2009). Of more than 150 organic species, the largest portion of exhaust emissions from a diesel engine is consisted of formaldehyde, acetaldehyde, and naphthalene and its derivatives, which are significantly reduced with the use of EGR system, crankcase emissions coalescer, and diesel particulate filter (Liu et al., 2009).

EXPERIMENTS

The general characteristics of the diesel engine and the power generator used in the experiments are shown in Tabs. 1 and 2. The generator electric load was supplied by a 50 kW bank of electric resistances. The resistances were grouped in seven modules, being two of 2.5 kW, one of 5 kW, and four of 10 kW, allowing for load increments 2.5 kW. The tests were performed with the diesel engine operating at 1800 rev/min crankshaft speed, with load of 37.5 kW. The engine was fuelled with diesel oil (B0) and fuel blends containing 5% (B5), 10% (B10), 20% (B20), and 35% (B35) of castor oil biodiesel in diesel oil.

Table 1. Diesel engine details.

PARAMETER	TYPE OR VALUE
Manufacturer	MWM
Model	D229-4
Serial Number	B1N426219
Construction Type	4 strokes, in line
Injection Time	Direct
Diâmeter x stroke	102 x 120 mm
Cylinder number	4
Piston displacement	0.980 liters
Total piston displacement	3.922 liters
Aspiration	Natural
Rotation	1800 rpm
Power	44 kW (60 hp)

Table 2. Power generator details

PARAMETER	TYPE OR VALUE
Manufacturer	GRAMACO
Model	G2R
Power	50 kVA
Regimen	S1 (continuous)
Phases number	3
Pole number	4
Speed	1800 rpm
Tension	220 V
Frequency	60 Hz
Current	132 A
Power factor	0.80

An Agilent 6850 GC model gas chromatograph was used for formaldehyde and acetaldehyde analysis. The sample was collected directly from the exhaust pipe and directed into the chromatograph. The chromatograph parameters for aldehyde determination were modified from base values obtained from the equipment manufacturer, to optimize the analysis. A capillary, non-polar, chromatograph column composed by stationary phase of poly-dimethyl siloxane (DB-1), with -60 to 350°C temperature range, was used in the analysis. The chromatograph oven temperature was adjusted in a preliminary analysis, in order to get a good separation of the components analyzed. The chromatograph response was stored in a microcomputer through a program, including date, peak retention times, peak areas and peak type, allowing for the calculation of the component concentration. The chromatograph was calibrated for aldehydes and hydrocarbon analysis through chromatograms supplied by the manufacturer at the same operating condition of the equipment. The carrier gas used was helium, hydrogen was used as fuel for the FID detector, and nitrogen was used as make up gas, all with 99.99% degree of purity. Tab. 3 describes the adjusted method in the present work.

Table 3. GC program adjustment for formaldehyde and acetaldehyde analysis.

PARAMETER	SPECIFICATION
Carrier gas	Helium
Carrier gas speed	36 cm/s @ 35°C
Oven temperature	35°C /40ºC isothermal
Injector division reason	1:100
Injector temperature	300°C
Detector	FID
Detector temperature	200°C
Composition gas	Nitrogênio
Gas composition flow	30 ml/min

RESULTS and DISCUSSION

In the Figs. 1 to 5 it is observed the chromatographic analysis of the exhaust gas from the diesel engine fuelled by diesel oil and mixtures of diesel oil /biodiesel (B5, B10, B20, B35) at 37.5 kW and 1800 rev/min At this operating condition exhaust aldehyde concentration was observed to be the highest for the engine studied. Formaldehyde was identified just as a trace for all fuel blends, as it was below the detection level of the equipment. Acetaldehyde was below the detection level for B5 and B20 blends, but it was adequately identified for diesel oil and B35 fuel blend. Both formaldehyde and acetaldehyde retention times were consistent with the values supplied by the equipment manufacturer. Methane peak in the exhaust gas analysis appeared late in comparison with the retention time obtained for methane in pure air, which was previously analyzed using a standard gas mixture.

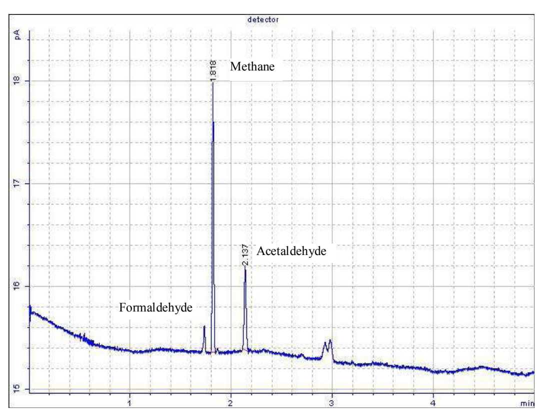

Figure 1. Chromatogram of exhaust aldehydes and methane. Fuel: diesel oil, load: 37.5 kW, speed: 1800 rev/min, column: poly-dimethyl-siloxane.

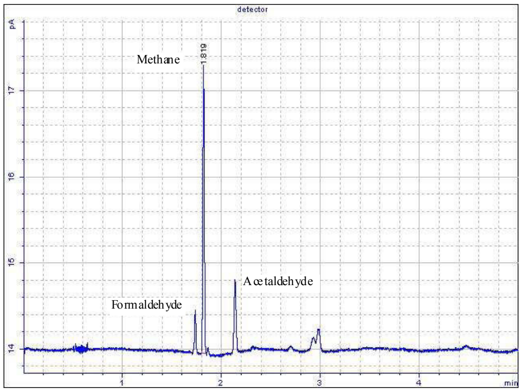

Figure 2. Chromatogram of exhaust aldehydes and methane. Fuel: B5, load: 37.5 kW, speed: 1800 rev/min, column: poly-dimethyl-siloxane.

Tab. 4 shows the acetaldehyde concentrations obtained from the chromatograms for the tests with diesel oil, B10 and B35 blends (Figs. 1, 3 and 5). The results are the average of three tests performed for each fuel at the operating condition described. There is not a significant difference between the acetaldehyde concentration produced by diesel oil in comparison with the biodiesel blends tested, although it is noticed a slight reduction of acetaldehyde concentration with biodiesel concentration in the blend. This trend is probably due to the higher viscosity of castor oil biodiesel in comparison with diesel oil (Valente et al., 2011), which increases the fuel amount injected (Valente et al., 2010) and, thus, decreases combustion temperature as a result of fuel evaporation. As mentioned by Sluder et al. (2004), lower combustion temperatures produces higher aldehyde concentrations. Overall, for all fuels, aldehyde concentration in diesel engine exhaust is very low, agreeing with the findings by Corrêa and Arbilla (2007), Peng et al. (2008), He et al. (2009), Yuan et al. (2009), and Lin et al. (2009).

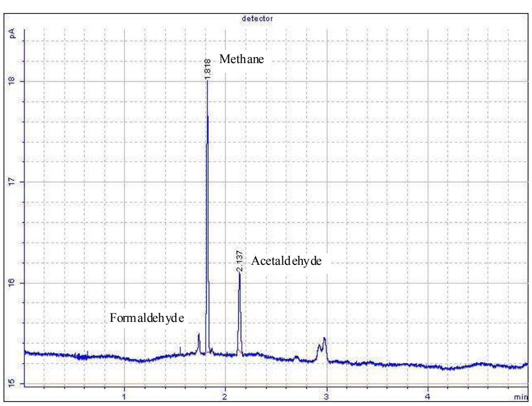

Figure 3. Chromatogram of exhaust aldehydes and methane. Fuel: B10, load: 37.5 kW, speed: 1800 rev/min, column: poly-dimethyl-siloxane.

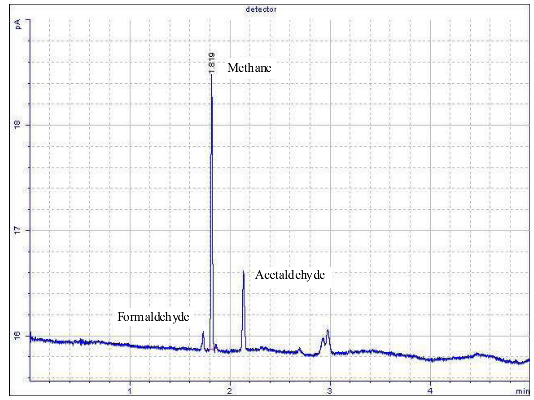

Figure 4. Chromatogram of exhaust aldehydes and methane. Fuel: B20, load: 37.5 kW, speed: 1800 rev/min, column: poly-dimethyl-siloxane.

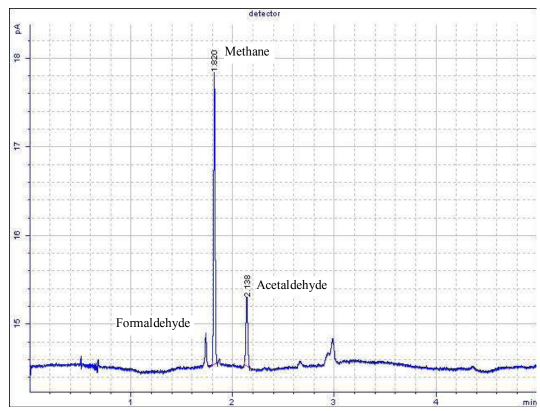

Figure 5. Chromatogram of exhaust aldehydes and methane. Fuel: B35, load: 37.5 kW, speed: 1800 rev/min, column: poly-dimethyl-siloxane.

Table 4. Exhaust acetaldehyde concentration evaluated from chromatograms for diesel oil, B10 and B35.

FUEL	CONCENTRATION (ppm)
Diesel oil	84.87
B10	84.46
B35	81.45

CONCLUSIONS

Gas chromatography has proved to be an useful tool for engine exhaust aldehyde measurement, but it requires high sample amounts to perform an adequate analysis. Detectable amounts of aldehydes were obtained just with high engine load. Overall, aldehyde concentration from a diesel engine fuelled by diesel oil or castor oil biodiesel/diesel oil blendes is very low. Acetaldehyde is the aldehyde with higher concentration present in diesel engine exhaust. Only traces of formaldehyde were detected for all fuels tested. No remarkable difference was found between the aldehyde levels produced by diesel oil and castor oil biodiesel/diesel oil blends.

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