Full Length Article

Performance and emissions of a diesel engine using sunflower biodiesel with a renewable antioxidant additive from bio-oil

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Abstract

The aim of this study is to test the behaviour of sunflower biodiesel in a diesel engine after being treated with a natural antioxidant additive produced from bio-oil extraction (final dosage of bio-oil compounds in doped biodiesel of 1.9 wt%). The influence of this renewable additive in both the engine performance and the produced emissions was evaluated. Five more fuels were used for the sake of comparison: petroleum diesel, neat sunflower biodiesel without additives, commercial biodiesel, commercial B10 blend and another B10 blend prepared from petro-diesel and doped sunflower biodiesel. Brake power was found to be similar for the six fuels, while the brake specific fuel consumption and the brake thermal efficiency were higher for biodiesel fuels. Only slight differences (<1%) were observed between the doped biodiesel and the neat one, showing that the bio-oil based additive did not negatively affect the general performance of the engine. Regarding gas emissions (analysed according to the European Stationary Cycle), weighted average emissions of NO_x and CO_2 were higher for biodiesel fuels, while CO and opacity factor were lower in that case. Incorporating the bio-oil based additive reduced NO_x emissions and smoke opacity by 3.0% and 4.4% compared with neat biodiesel, respectively, whilst CO and HC emissions increased by 0.7 and 14.3% respectively, values still remaining below those of diesel.

Keywords: Sunflower biodiesel; Bio-oil antioxidant additive; Diesel engine; Emissions; Engine performance

1 Introduction

Increasing energy demand and the consciousness of environmental damages related to pollutant emissions from fossil-fuel burning have encouraged the investigation of alternative fuels to replace conventional petroleum fuels. Moreover, stringent emission legislation is a challenge for the automotive industry. By 2020, 10% of the transport fuel in the European Union should come from renewable sources (e.g. biofuels). In this context, biodiesel has received increasing attention as a renewable and cleaner substitute for petroleum diesel. Final properties of biodiesel are similar to those of diesel, hence, neat biodiesel or blended with petroleum diesel can be used in conventional CI engines without significant modifications [1].

Biodiesel consists of a mixture of fatty acids monoalkyl esters (FAME) obtained by transesterification of vegetable oils or animal fats [2] with a short chain alcohol, such as methanol or ethanol [3], and catalysed by acids or bases (usually NaOH or KOH) [4]. Compared to diesel derived from petroleum, biodiesel diminishes carbon monoxide and hydrocarbons emissions and reduces smoke formation [2,5,6]. In addition, biodiesel presents higher lubricity and biodegradability than diesel [5,6]. The absence of sulphur avoids the

formation of polluting compounds, such as SO_2, related to the acid rain phenomenon [7]. As biodiesel is obtained from plants which absorb CO_2 during their growth, it is considered that there is not a net increment of CO_2 concentration in the atmosphere due to biodiesel combustion. On the other hand, increases in the fuel consumption and NO_x emissions have been reported by most researchers [5,6].

The main disadvantages of neat biodiesel to be used in CI diesel engines are related to the low oxidation stability for long-term storage and poor cold flow properties (i.e. freezing point and flowability of the fuel at low temperatures). Both of them are highly dependent on the type of feedstock and their fatty acids composition. Saturated compounds are responsible for the poor cold flow properties of biodiesel, whereas unsaturated esters are mainly responsible for its oxidation [8]. Biodiesel can experience autoxidation in the presence of air and, therefore, the addition of antioxidants is usually required to fulfil the quality requirements for biodiesel commercialization defined in different standards, such as EN 14214 in Europe and ASTM 6751-3 from the American Standards for Testing Materials.

Many synthetic additives have been used by manufacturers to improve biodiesel characteristics, such as butylated hydroxyanisole (BHA) [9–11], butylated hydroxytoluene (BHT) [10–12], N,N'-diphenyl-1,4-phenylenediamine (DPPD) [13], N-phenyl-1,4-phenylenediamine (NPPD) [13] or *tert*-butyl hydroquinone (TBHQ) [10,11]. They are mainly phenolic and amine compounds that have been identified as free radical quenching agents, capable of preventing the oxidation process [14]. Natural phenolic compounds, such as tocopherols [11,12], have also been tested as antioxidant additives. The effect of the addition of antioxidant compounds on the performance and emissions of diesel engines has also been studied [9,13,15]. Most of the research has been especially focused on the NO_x emissions [16–18] since diesel engines are a significant source of this pollutant, precursor of acid rain and smog formation. Irrespective of the kind of biodiesel and the antioxidant additive, the same results were observed. The presence of antioxidants caused a reduction in NO_x emissions and smoke formation. In addition, CO and hydrocarbon concentrations in the exhaust gases rose. Power output generally increased whereas fuel consumption diminished with respect to the untreated biodiesel.

As commercial antioxidant additives are usually expensive and produced from non-renewable materials, there is a motivation to explore new alternative low-cost additives, obtained from biomass or residues. Ramalingam et al. [19] increased the oxidation stability of a B20 blend of *calophyllum* biodiesel by almost 200% just adding 1.5% of *P. pinnata* leaf extract to the biodiesel. Fernandes et al. [20] reported the use of *Moringa olefeira* oil for the production of biodiesel with a high oxidation stability (induction time of 19.3 h), while the leaves were utilized to prepare an antioxidant additive by extraction with 70% and 98% of ethanol. The 98% ethanolic extract showed a better performance than TBHQ at the same concentration when added to biodiesel derived from residual cooking oil and soybean oil.

Several authors have investigated the use of the liquid product coming from fast pyrolysis of lignocellulosic biomass to produce biodiesel antioxidants. The organic phase in this liquid, so-called bio-oil, is rich in phenolic compounds, whose antioxidant properties have been demonstrated [21,22]. For instance, García-Pérez et al. [8] added bio-oil to biodiesel and observed an increase in the oxidation induction temperature from 155 to 225 °C, attributed to the presence of antioxidant compounds in the bio-oil. In a previous work of our research group [23], an antioxidant additive was produced by two-stage liquid-liquid extraction of bio-oil coming from pinewood pyrolysis with different organic solvents and biodiesel itself. Sunflower oil biodiesel was treated with the obtained additives. The highest increase in the PetroOXY time with respect to neat biodiesel (from 6.5 min to 37.5 min with the additive) was found using isopropyl acetate as extraction agent. Storage stability of the biodiesel doped with the additive was studied and the antioxidant potential did not suffer any deterioration over five months of storage.

The aim of this study is to test sunflower biodiesel treated with an antioxidant additive produced from bio-oil (biomass pyrolysis) in a diesel engine in order to assess the influence of this renewable additive in the performance of the engine and the produced emissions. Engine performance was analysed at full load and varying speed conditions, while a European Stationary Cycle (ESC), consisting of 13 modes that combine different engine loads and speeds, was used to compare the effect of the operating conditions and the fuel properties on the exhaust emissions. The behaviour of the treated biodiesel was compared with the one of diesel, neat sunflower biodiesel, commercial biodiesel, a commercial B10 blend (10% biodiesel – 90% diesel) and a B10 blend prepared in our lab.

2 Materials and methods

2.1 Fuels

The base fuel in this work was biodiesel produced from sunflower oil (SB). This biodiesel was treated (DSB) with an antioxidant additive prepared from bio-oil coming from wood pyrolysis. Commercially available fuels, including diesel (D, Diesel Óptima, Cepsa) and biodiesel from waste vegetable oils (CB, BioArag, Spain), were selected with comparison purposes in the study of the performance and emissions of SB and DSB in further engine tests. Additionally, two B10 blends were also utilized. One of them was commercial (CB10, Cooperativa Nª Sª del Pilar, Novallas, Spain) and the second one was prepared by mixing D and DSB in the right proportions (SB10).

2.1.1 Biodiesel production

The biodiesel used in this study (SB) was produced in our laboratory by catalytic transesterification of refined sunflower oil (acidity < 0.5%) with an excess of methanol (molar ratio oil:methanol = 1:6) and KOH as alkaline catalyst (1 wt% of oil mass). The mixture was heated up to 60 °C for 3 h at atmospheric pressure and continuously stirred in a batch reactor under reflux. More details about the preparation method can be found elsewhere [23]. Several batches of biodiesel were prepared to get the amount needed for this work, around 25 L. After preparation, all the biodiesel batches were mixed and kept at −18 °C until its utilization.

2.1.2 Preparation of the antioxidant additive

The antioxidant additive was prepared from pine wood bio-oil, by a two-stage liquid-liquid extraction process using isopropyl acetate, which in a previous work has proved to be the most effective solvent, among several tested solvents, to extract compounds that improve oxidation stability, and biodiesel itself as sequential extraction agents. As biodiesel and bio-oil were not completely miscible, the insoluble fraction of bio-oil was removed by centrifugation after the extraction process. The final additive was mainly composed of biodiesel, with a concentration higher than

80%. More details about the preparation method can be found in the work by García et al. [23].

2.1.3 Characterization

Prior to the engine tests, the six fuels were characterized using several analytical methods that are listed in Table 1. Sample preparation procedure and parameters for the analysis method are described elsewhere [23]. Two or three replicates of each property analysis were conducted. Additionally, the content of monomeric phenols in DSB was also analysed by GC–MS-FID (Agilent 7890A GC/FID system combined with Agilent 5975C inert MSD). Phenolics were identified by mass spectroscopy and quantified by integration of the FID signal. Table 2 lists the most relevant method parameters for the GC–MS-FID analysis. The equipment was previously calibrated with prepared solutions of biodiesel and pure phenolic standards (p-cresol, guaiacol, creosol, 4-ethylguaiacol and eugenol, all of them supplied by Sigma Aldrich), using methanol as solvent.

Table 1 Analytical methods for the characterization of the fuels.

Property	Equipment	Standard
Density at 15 °C	Densimeter Densito, 30 PX Mettler Toledo	–
Kinematic viscosity at 40 °C	Viscosimeter Cannon-Fenske, model 150 T845	EN ISO 3104
HHV	Bomb calorimeter C2000 IKA	ISO 1928:2009
Oxidation stability	Fast oxidation instrument PetroOXY	ASTM D2274
CFPP	Automated analyser FPP 5GS model V22101	EN 16329
Water content	Coulometer Mettler Toledo C20 Compact KF	EN ISO 12937
Elemental analysis	Elemental analyser LECO CHN 628 and LECO 628S	–
FAME content	GC-FID Agilent 6890 GC System	EN 14103

**Table 2** Method parameters for GC–MS-FID analysis of monomeric phenols in DSB.

GC–MS-FID analysis of monomeric phenols	
Instrument	Agilent 7890A GC/FID system combined with Agilent 5975C inert MSD
Column	DB-17 ms (50%-phenyl)- methylpolysiloxane), 60 m x 250 µm x 0.25 µm
Injection volume	1 µL
Injector	Split/splitless inlet: 250 °C, splitless
Carrier gas	Helium (constant flow: 1 mL/min in column)
Oven program	100 °C (3 min); then to 181 °C at 3 °C/min; then to 203 °C at 2 °C/min, then to 230 °C (15 min) at 7 °C/min; then to 280 °C (15 min) at 10 °C/min; then to 320 °C (10 min) at 20 °C/min
Detector	**(i)** Front Detector FID (250 °C; H_2/air) **(ii)** MSD analyser (Trace Ion Detection; electron ionization)

2.2 Diesel engine test bench

The experiments were conducted in an Isuzu T4EC1 turbocharged diesel engine installed in a test bench and coupled to a Tecner E315 dynamometer, which allows the measurement of speed and load with an accuracy of ±5 rpm and ±0.5 Nm, respectively. Technical specifications of the engine are given in Table 3 and the schematic diagram of the test bench is shown in Fig. 1. The configuration of the engine was maintained as original, except for the cooling circuit that was modified to be coupled with the test bench cooling circuit. To avoid any thermal stress and preserve the mechanical system, the maximum absolute boost pressure was limited to 1.5 bar.

Table 3 Diesel engine specifications.

Engine type	Isuzu T4EC1 15DT turbocharged
Original fuel	Diesel
Number of cylinders	4 in line
Displaced volume	1487 cm³
Bore × Stroke	76 × 82 mm
Compression ratio	22:1
Valve timing	12-48-50-10
Fuel delivery system	Mechanical indirect fuel injection
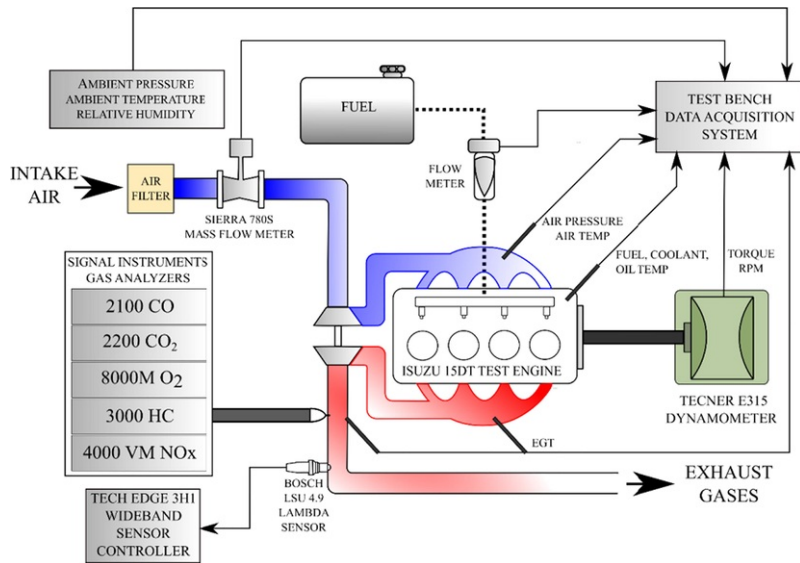
Fig. 1 Schematic diagram of the engine test bench.

Fuel consumption was measured with a volumetric liquid fuel flow meter. A flow meter (Sierra Instruments 780S) allowed the determination of the intake air mass. Ambient conditions, air temperature and pressure at the intake manifold were monitored. Exhaust, fuel, coolant and oil temperatures were also measured, together with the torque and engine speed. Two Advantech data acquisition cards (models PCL-813 and PCL-818) controlled by a specific software programmed in LabVIEW allowed the test bench data acquisition. The gaseous emissions were measured by two non-dispersive infrared CO and CO_2 analysers, one flame ionization detector (FID) for hydrocarbons (HC), one chemiluminescence-based NO_x analyser and one paramagnetic analyser for O_2, all of them manufactured by Signal Instruments. The values of opacity, expressed as mg of soot per m³, were provided by a Bosch smoke-meter for diesel engines (filter type, Model RFT 100 FD). More details about this installation can be found in [24].

2.2.1 Experimental procedure

Two different kinds of experiments were carried out in the engine test bench. First, the influence of the type of fuel and the presence of the antioxidant additive from bio-oil in the general performance of the diesel engine was investigated by running the engine from 1500 to 4000 rpm at full load with the six fuels. The evolution of the brake power (BP), brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE) was analysed.

The second test corresponded to the European Stationary Cycle (ESC) and allowed to evaluate and compare pollutant emissions characteristics with all the fuels tested (Directive 88/77, 1987). The ESC cycle consists of 13 phases, as shown in Fig. 2, combination of different speeds and loads that represent most of the possible working conditions of the engine. Gaseous emissions, including CO, hydrocarbons, NO_x and CO_2, and opacity factor were measured and averaged using a set of weighting factors over the 13 modes. In order to assure a proper reproducibility of the

data, data acquisition was performed according to the directive (exhaust gas flow rate precision better than 2.5%, engine speed held within 50 rpm of the set value) and gas analysers were calibrated prior each test run with an accuracy ranging from 10 to 50 ppm for CO, 0.1–0.2% for CO_2, 1–4 ppm for HC, and 1–4 ppm for NO_x, depending on the measured range for each pollutant.
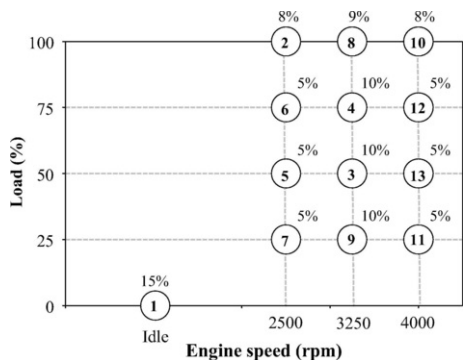

Fig. 2 Engine conditions in the ESC cycle and weighting factors (%).

3 Results and discussion

3.1 Fuel characterization

Characterization results of the tested fuels are listed in Table 4 (mean value and standard deviation). Density is an important property for fuels used in compression ignition engines. The variation of this property affects the power output and the combustion in cylinder [25]. As shown in Table 4, densities of the three types of biodiesel (CB, SB and DB) were very close to each other (880–886 kg/m³ at 15 °C), within the confidence interval. Non-significant differences were either found in the density values of diesel and B10 blends (839–840 kg/m³ at 15 °C). In general, biodiesel density has been found to be around 5% higher than that of diesel and B10 blends. In any case, all density values fulfil the standard requirements (820–845 kg/m³ for diesel according to EN 590 and 860–900 kg/m³ for biodiesel according to EN 14214). Similar values are reported by other authors using sunflower biodiesel. Thus, values of 882.2, 885, and 883.6 kg/m³ were obtained by Saydut el al. [26], Saba et al. [27] and Santos et al. [28], respectively.

Table 4 Physico-chemical properties of the tested fuels.

Fuel properties		D	CB	SB	DSB	CB10	SB10
Density at 15 °C	kg/m³	840 ± 2	880 ± 3	884 ± 4	886 ± 4	840 ± 5	839 ± 4
Viscosity at 40 °C	mm²/s	2.80 ± 0.01	4.58 ± 0.01	4.47 ± 0.05	4.30 ± 0.06	2.90 ± 0.01	2.79 ± 0.04
HHV	MJ/kg	45.62 ± 0.09	39.8 ± 0.1	39.83 ± 0.01	39.63 ± 0.03	45.09 ± 0.03	45.21 ± 0.02
Oxidation stability	min	94.2 ± 0.7	40.6 ± 0.1	13.8 ± 0.3	37.61 ± 0.01	43 ± 2	106.9 ± 0.7
CFPP	°C	−16.1 ± 1	0.4 ± 1	−5.1 ± 1	−2.9 ± 1	−15.6 ± 1	−16.1 ± 1
Water content	ppm	75 ± 27	189 ± 54	579 ± 4	587 ± 3	73 ± 19	115 ± 24
Carbon	%	86.6 ± 0.1	77.66 ± 0.03	78.04 ± 0.06	77.56 ± 0.07	86.11 ± 0.07	86.3 ± 0.2
Hydrogen	%	13.2 ± 0.1	12.25 ± 0.08	12.07 ± 0.04	12.05 ± 0.05	13.42 ± 0.00	13.4 ± 0.1
Nitrogen	ppm	1800 ± 400	2400 ± 100	1600 ± 200	1570 ± 80	1900 ± 200	1680 ± 50
Oxygen*	%	0.0	9.8	9.7	10.2	0.25	0.05
Sulphur	ppm	324 ± 16	269 ± 8	279 ± 24	257 ± 9	316 ± 3	281 ± 19
FAME content	wt%	—	93.4 ± 0.2	98.6 ± 0.2	96.7 ± 0.1	—	—

* Calculated by difference.

Other important concern when using biodiesel in a diesel engine is the detrimental effect caused by the high viscosity of the fuel. Kinematic viscosity values of biodiesel samples used in this work (CB, SB and DSB) were very close to each other (4.30–4.58 mm^2/s) and around 60% higher than that of D, CB10 and SB10 (2.79–2.90 mm^2/s). The addition of the bio-oil based additive to sunflower biodiesel did not suppose any negative impact in such property. Viscosity values of the six fuels remained all within the standard specifications (2–4.5 mm^2/s for diesel according to EN 590, and 3.5–5 mm^2/s for biodiesel according to EN 14214). In the bibliography, it is possible to find different viscosity values for biodiesel produced from sunflower within the range established by the standard. While Saydut et al. [26] and Santos et al.[28] reported values lower than those presented in this work (4.04 and 4.3 mm^2/s respectively), Saba et al. [27] obtained values of 4.7 mm^2/s. This difference in the values obtained may be due to the small differences in the composition of the raw material and to the amount and composition of the impurities present in the final product.

In general, calorific values of the three biodiesel samples (CB, SB and DSB) were found to be approximately 12–13% lower than those of diesel and B10 samples. While HHV of D, CB10 and SB10 were in the range of 45.1–45.6 MJ/kg, HHV of CB, SB and DSB hardly varied between 39.6 and 39.8 MJ/kg. The addition of the bio-oil based additive to biodiesel only led to a very slight reduction in the fuel calorific value (0.5% lower).

Oxidation stability is another important issue concerning biofuel properties. Unlike diesel, biodiesel is prone to oxidation because of the presence of unsaturated bonds in the fatty acid chain of the ester molecules. As can be seen in Table 4, a wide range of PetroOXY times was obtained for the six fuels, varying from 13.8 (SB) to 106.9 min (SB10). Oxidation stability of sunflower biodiesel (13.8 min) was proved to increase by 172% after adding the bio-oil based additive (37.6 min), thus allowing DSB to meet the EN 14214 oxidation stability requirement [29]. Oxidation stability of DSB was close to oxidation stability of CB (40.6 min). A similar PetroOXY value was also obtained for CB10 (43 min), whereas it was almost double for D (94.2 min). SB10 showed the best oxidation stability result (106.9 min).

Cold filter plugging point (CFPP) provides insight into fuel behaviour at cold temperatures. CFPP of diesel and B10 blends were around −16 °C. Biodiesel samples showed higher values, the commercial one leading to the worst result as a consequence of its chemical composition, coming from waste cooking oil. Moreover, CFPP of sunflower biodiesel worsened slightly (in 2 °C) with the incorporation of the additive, making both apt for the use in temperate climates, as standard EN 14214 sets a CFPP for moderate climates ranging from +5 °C to −20 °C.

Carbon content in fossil diesel was around 9 wt% higher than that in the biodiesels used, while the H content was only 1 wt% lower for the biodiesels. These differences are related to the content of atomic oxygen (calculated by difference). Biodiesel samples had about 10 wt% of oxygen, while oxygen in diesel and B10 blends is negligible. Regarding the presence of nitrogen and sulphur, the highest percentage of N was found in commercial biodiesel, while diesel showed the highest S content.

Fatty acid methyl ester (FAME) contents of the different biodiesels used are also shown in Table 4. The final FAME content of DSB was determined at 96.7 wt%. From the comparison o FAME content in SB and DSB, it can be inferred that DSB contained 1.9 wt% of bio-oil compounds.

Lastly, the concentration of monomeric phenols, which cause the improvement in the oxidation stability as discussed in the Introduction section, was determined in DSB by gas chromatography, and the results are summarized in Table 5. It is worth noting that concentrations of 4-propylguaiacol and 4-propenylguaiacol were calculated with the response factor of eugenol and concentrations of 3-methylphenol and 2,5-dimethylphenol were calculated with the response factor of p-cresol. Total content of 1240 ppm of monomeric phenols was detected in DSB, creosol being the most abundant phenolic compound identified by this technique.

Table 5 Concentration of monomeric phenols in DSB.

Compound	Retention time (min)	Concentration (ppm)
3-methylphenol	12.57	31
guaiacol *(2-methoxyphenol)*	13.83	285
2,5-dimethylphenol	15.18	63
creosol *(4-methylguaiacol)*	17.42	463
4-ethylguaiacol	20.60	123
4-proylguaiacol	23.86	27
eugenol *(4-(2-propenyl)-guaiacol)*	24.17	132
4-propenylguaiacol	26.71	61
(E)-4-propenylguaiacol	28.61	57
Vanillin	29.27	n.q.
acetoguaiacol	32.66	n.q.

Total	1242

n.q.: not quantified.

3.2 Full load tests

3.2.1 Brake power (BP)

Fig. 3 shows the variation of the brake power (BP), in kW, at full load condition under several engine speeds and using different fuels. As can be seen, BP increased until 3000 rpm where it reached a maximum regardless of the fuel used. After that, BP decreased, although a slight increase occurred again at 4000 rpm. Small differences were observed in the values of this parameter working with different fuels. Petroleum-derived diesel (D) produced the highest power at the lowest engine speeds (1500–2500 rpm), which was in agreement with the results found by other authors [30,31]. The differences observed between the different fuels were small and can be attributed to slight differences in density, kinematic viscosity and calorific values. The presence of the antioxidant additive from bio-oil (in DSB) reduced BP only about 1% with respect to neat sunflower biodiesel (SB), so it did not cause a significant negative effect on the brake power.
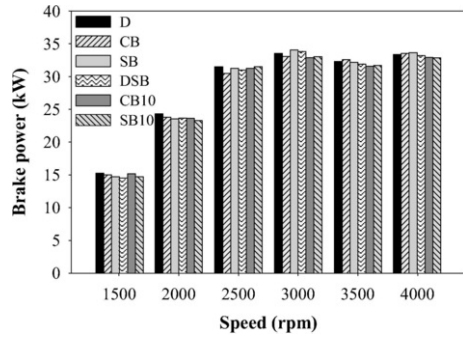

Fig. 3 Variation of brake power (BP) at different speeds working with different fuels.

3.2.2 Brake specific fuel consumption (BSFC)

The brake specific fuel consumption (BSFC), expressed in g/kWh, is defined as the ratio between the mass flow of fuel and the engine power. Fig. 4 shows the variation of this parameter working at engine velocities from 1500 to 4000 rpm and full load for different kinds of fuels. All fuels followed the same trend, with the lowest values at 1500–2500 rpm and a further increase up to 4000 rpm.
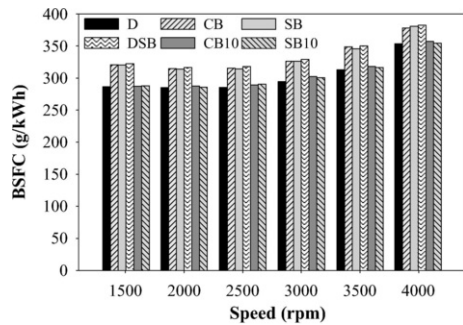

Fig. 4 Variation of brake specific fuel consumption (BSFC) at different speeds working with different fuels.

The lowest BSFC over the whole speed range corresponded to diesel (D). Fuel consumption with sunflower biodiesel (SB), as well as with the commercial biodiesel (CB), was about 10–12% higher than the diesel one. Moreno et al. [24] observed the same deviation in the BSFC of sunflower biodiesel with respect to diesel using the same test bench as in this work. They related the different BSFC values to the dissimilar behaviour of the fuel pump when utilizing both fuels, due to differences in density and viscosity, and the variations in the calorific values. The higher viscosity of the biodiesel (Table 4) could decrease internal pump leaks, while the larger density may increase the pump mass flow. Other authors [19,32] attributed the higher BSFC of biodiesel to the lower calorific value of this fuel. In order to produce the same power output of the engine, a higher mass flow injection is necessary in the combustion chamber to compensate the energy loss due to the lower calorific value. As expected, adding biodiesel to diesel (CB10 and SB10) enlarged the fuel consumption by 0.2–2.7%, depending on the operating conditions of the engine.

The calculated value of BSFC for DSB was about 1% higher than the one for SB, as a result of a slightly lower heating value in the presence of the phenolic antioxidant additive from bio-oil. The opposite trend has been observed by other authors using synthetic antioxidants composed of phenols, such as BHT and 2,2'-methylenebis (4-methyl-6-tert-butylphenol) (MBEBP) [33], and amines, such as DPPD [18], NPPD [13,31], EDA, and PPDA [12]. The reduction in specific fuel consumption was attributed to the friction reduction properties of such antioxidants in the fuel injection system. Varatharajan et al. [12] also observed that BSFC was slightly higher when ascorbic acid and tocopherol were added to jatropha biodiesel. The variation of biodiesel BSFC in the presence of antioxidant additives could be related to the composition and chemical structure of the additive.

3.2.3 Brake thermal efficiency (BTE)

The brake thermal efficiency (BTE) obtained with the fuels selected for this work, calculated as the ratio between the power output and the energy introduced through fuel injection, is depicted in Fig. 5. The six fuels followed the same trend during the engine test at full load. All the curves presented a maximum, detected at 1500–2000 rpm for diesel (D) and the B10 blends (CB10 and SB10). This maximum was shifted to 2000–2500 rpm for the three biodiesel fuels (CB, SB and DSB). From this point, increasing engine speed led to a decrease in BTE. According to Man et al. [34], higher engine speeds cause a rise in the specific fuel consumption and, consequently, a decrease in BTE.
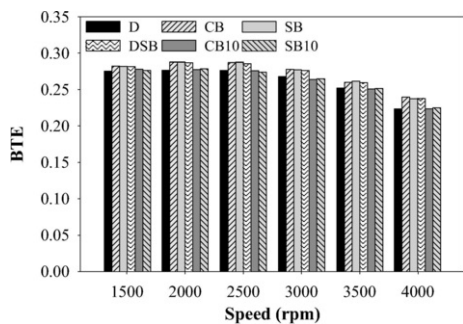

Fig. 5 Variation of brake thermal efficiency (BTE) at different speeds working with different fuels.

Diesel (D) presented the lowest BTE values at any engine speed, showing reductions between 2.3 and 7.3% in comparison with commercial biodiesel (CB) and sunflower biodiesel (SB), respectively. This seems to disagree with some results found in literature. Many research works have reported that BTE is lower in the case of biodiesel [35–37]. Nevertheless, Man et al. [34] found a higher BTE for biodiesel produced from waste cooking oil and attributed this result to a better combustion process because of the oxygen present in the biodiesel chemical structure, as well as to the lower friction loss in the injection system. Haşimoğlu et al. [38] investigated the performance of biodiesel prepared from sunflower oil in a 4-cylinder turbocharged DI diesel engine and their results were similar to the ones shown in this work (BTE 3% higher for biodiesel with respect to diesel).

Addition of 10% biodiesel to diesel in the B10 blends, CB10 and SB10, did not substantially affect the behaviour of the fuel, and provoked a negligible rise (0.1–0.9%) in BTE at 1500, 2000 and 4000 rpm compared to D. Lower BTE was found at the middle speeds, although the difference was also very small (0.1–1.2%).

BTE values for DSB, which contained the antioxidant additive from bio-oil, decreased by 0.1–0.8% with respect to the neat biodiesel, SB, suggesting that the presence of the additive did not significantly impact on the performance of the diesel engine. Different trends, including both decreases [39,40] and rises [13,33,37] in BTE, have been reported in literature when amine and phenolic antioxidants were used to improve the properties of biodiesel or diesel-biodiesel blends. BTE reductions in comparison with non-treated biodiesel were attributed to an incomplete and improper combustion resulting from the antioxidant addition.

3.3 Esc test cycle

The second set of experiments carried out in the diesel engine corresponded to the European Stationary Cycle (ESC), used to evaluate the effect of the fuel properties and engine operating conditions on gaseous emissions. Table 6 shows the weighted average results for NO_x, CO, CO_2, HC and opacity and for the six fuels tested.

Table 6 Weighted average emissions in ESC cycle test.

Fuel	NO_x	CO	HC	Opacity	CO_2
	g/kW·h	g/kW·h	g/kW·h	mg/m^3	g/kW·h
D	2.62	4.16	0.64	4.94	1187
CB	2.85	2.91	0.58	1.69	1214

SB	2.96	2.92	0.35	1.59	1207
DSB	2.87	2.94	0.40	1.52	1222
CB10	2.75	3.73	0.39	4.36	1129
SB10	2.81	3.97	0.43	3.58	1187

3.3.1 NO_x emissions

The term NO_x comprises the emission of nitric oxide (NO) and nitrogen dioxide (NO_2). The most common mechanisms of NO_x formation during diesel combustion are thermal (Zeldovich), prompt (Fenimore), N_2O pathway, fuel-bound nitrogen and NNH, being the first two the governing mechanisms in biodiesel combustion [41]. Some parameters like chemical properties of the fuel, adiabatic flame temperature (AFT), ignition delay time (IDT), injection timing, geometry of the combustion chamber (related to the velocity of flame propagation), equivalence ratio and pressure greatly affect NO_x emissions [10].

As shown in Table 6, average NO_x specific emissions for biodiesel fuels, CB and SB, were higher than those for diesel (D) on a percentage of 13.0 and 8.8%, respectively. In addition, NO_x emissions increased by 5.0 and 7.3% for CB10 and SB10 compared to D because of the presence of biodiesel in the blend. This agrees with the results found in literature [6,35,42]. The presence of oxygen in the biodiesel structure (9.8% in CB and 9.7% in SB, see Table 4) improves combustion and raises temperature in the combustion chamber. Also, even if it has not been measured in this work, is known that biodiesel has usually a higher cetane number (shorter IDT) than petroleum diesel. For example, Hoekman el al. reviewed several properties of diesel and biodiesel, finding values of cetane number for sunflower biodiesel of 51 ± 3.2, whereas it ranges between 40 and 45 for petroleum diesel [43]. Both effects would lead to NO_x formation increases.

NO_x formation was slightly reduced by 0.1 g/kW·h when SB was treated with the antioxidant additive obtained from bio-oil solvent extraction (DSB). Rashed et al. [31] suggested that the reaction between molecular nitrogen and hydrocarbon free radicals (CH, C_2, C and CH_2) plays a role on prompt NO_x emission during the combustion of biodiesel. Antioxidants can act as radical quenching agents and, therefore, diminish NO_x formation.

Fig. 6 illustrates NO_x formation in the diesel engine over the ESC cycle test working with different fuels. As can be seen, the amount of NO_x emitted depended on the operating mode. Increasing engine speed reduced NO_x formation, with the exception of modes 2, 8 and 10, where engine load reached 100%. According to Man et al. [34], increasing engine speed reduces the reaction time so that the residence time of the air-fuel mixture in the cylinder at high temperature lessens, leading to lower NO_x emissions. NO_x production was directly proportional to the engine load independently of the fuel used and the engine speed. An increase in the engine load led to more fuel injected. This caused a rise in the temperature and promoted NO_x formation [44].
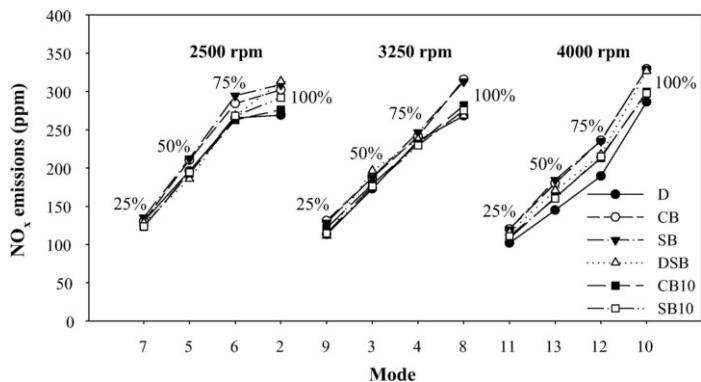

Fig. 6 NO_x emissions at different engine modes working with different fuels.

3.3.2 Carbon monoxide emissions

CO average specific emissions during the ESC test are included in Table 6. The highest value of CO specific emissions was observed when pure diesel was utilized. Biodiesel fuels (CB and SB) were the most advantageous in terms of CO emissions and showed significant decreases compared with diesel, up to 30%. CO formation is attributed to an incomplete combustion of the fuel. The reduction of CO emissions with biodiesel is mainly due to the oxygen content in the fuel structure (Table 4), that helps to get complete combustion of CO to CO_2 [9,45]. Blends of diesel with biodiesel (CB10 and SB10) reduced CO emissions by 10.3 and 4.6%, respectively, compared to fossil diesel.

Average CO specific emissions of DSB slightly increased by 0.6% in comparison to that of SB without additive and were 29.3% below diesel emissions. This result concurs with other works when different kinds of antioxidant additives were added to biodiesel [12,13,15]. During oxidation, the formation of several radicals takes place, peroxyl (HO_2) and hydrogen peroxide (H_2O_2) among them. They are further converted into hydroxyl radicals (OH), involved in the conversion of CO into CO_2, by

absorbing heat from the combustion chamber. Antioxidant additives reduce the concentration of peroxyl and hydrogen peroxide radicals and, as a consequence, the formation of OH radicals, affecting CO oxidation [9,18].

Variation of CO emissions, in ppm, during the 13-mode ESC cycle test using different fuels is shown in Fig. 7, grouped by the engine speed. A decrease in CO emissions was observed from the lower engine load (25%) to a minimum located at 50–75% engine load, depending on the fuel used and the engine speed. A further increase happened up to full load mode. At low engine loads (modes 7, 9 and 11), CO emissions were similar for the six fuels. When the engine load increased, CO emissions rose because of the higher fuel/air ratio under the operating conditions of modes 2, 8 and 10, at full load [34].
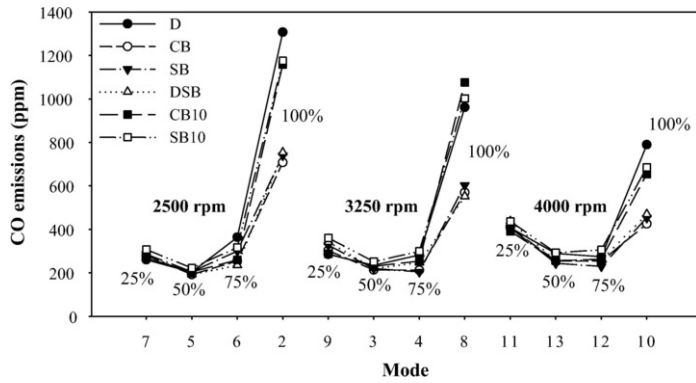

Fig. 7 CO emissions at different engine modes working with different fuels.

The variation of CO emissions as a function of the engine speed can also be observed in Fig. 7. When the engine load was 25% and 50%, the CO emissions increased with varying engine speed between 2500 and 4000 rpm, regardless the fuel utilized. At full load, the opposite trend was observed, with a clear decrease in CO emissions from 2500 rpm to 4000 rpm. When engine worked at 75% load, the observed pattern depended on the fuel used. Man et al. [34] attributed the increase in CO emissions with the increasing speed to a higher fuel to air ratio due to the reduction in volumetric efficiency and increase in fuel consumption.

3.3.3 CO₂ emissions

CO_2 specific emissions from both biodiesel fuels, the commercial one (CB) and the one prepared in the lab from sunflower oil (SB), were 2.3 and 1.7% higher, respectively, than diesel (D) emissions, as shown in Table 6, in line with the higher BSFC of biodiesel. Availability of oxygen in the biodiesel chemical structure and its lower carbon content improve combustion and enhance CO_2 formation [46]. On the other hand, commercial B10 blend (CB10) diminished CO_2 emissions by 4.9% with respect to diesel, while no variation in CO_2 emissions occurred when SB10 was used instead of diesel. When the antioxidant additive from bio-oil was added to the sunflower biodiesel, CO_2 emissions augmented 1.2% with respect to the neat biodiesel.

CO_2 emissions measured during the different phases of the ESC test are shown in Fig. 8. An increase in CO_2 emissions was observed with the variation of engine load at any engine speed due to a higher fuel consumption [40]. Several patterns were observed working at different engine loads. At the lowest load (25%), lowest CO_2 formation took place at 3250 rpm using any fuel. The highest emissions working at 50% load were observed at 2500 rpm and were very similar at 3250 and 4000 rpm. When working at 75% load, a decrease with engine speed was observed. Moreover, CO_2 emissions presented a maximum at 3250 rpm at full load.
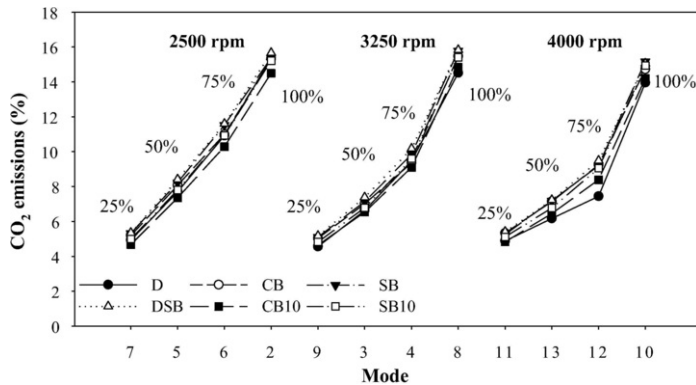
Fig. 8 CO_2 emissions at different engine modes working with different fuels.

3.3.4 HC emissions

The highest averaged specific emissions of unburnt hydrocarbons during the 13-mode ESC cycle corresponded to pure diesel (Table 6). SB emissions were determined the lowest, with a mean reduction of 45.3% compared to D, while commercial biodiesel (CB) lessened HC by only 10.5%. When diesel was partially substituted with biodiesel in CB10 and SB10, HC emissions were reduced by 39.3% and 32.5%, respectively. According to these results, the presence of biodiesel significantly decreased HC emissions. The higher amount of oxygen in biodiesel and its higher cetane number may create some advantageous conditions during air-fuel interactions, which result in the reduction of the ignition delay and enhance the oxidation of unburned HC with a significant emission decrease [9,19,43]. Moreover, the lower carbon content in biodiesel also enable complete combustion to a greater extent [46].

DSB led to a decrease in HC emissions of 37.4% with respect to diesel, although they were 14.4% higher than with SB. Most of the research works about the effect of amine and phenolic antioxidants on the emissions from diesel engines presented an increase in HC emissions when biodiesel was treated with such compounds. Reduction of peroxyl and hydrogen peroxide radicals, responsible for the conversion of CO into CO_2 and HC into H_2O and CO_2, in the presence of the antioxidant additives causes a significant increase in the amount of HC present in the exhaust gases [12,40].

Fig. 9 shows the variations of HC emissions during the 13 engine modes of ESC cycle. The amount of HC in the exhaust gases was higher during the modes 7, 9 and 11 (25% engine load at varying speeds) for CB, SB, DSB and CB10, while modes 2, 3 and 11 showed the highest emissions for D and modes 2, 9 and 11 for SB10. In general, HC emissions were inversely related to engine load working at 3250 and 4000 rpm and presented a minimum at 50% when engine speed was 2500 rpm. The influence of the engine speed on the HC emission did not show a clear pattern. Emissions increased with engine speed at the lower engine load (25%), while the opposite trend was observed at the highest load (100%). At middle engine loads, a maximum at 3250 rpm was found in most of the cases.
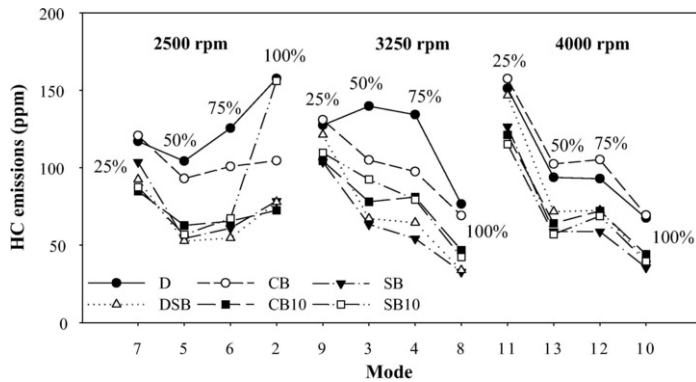

Fig. 9 HC emissions at different engine modes working with different fuels.

3.3.5 Opacity

Average opacity values, expressed as mg/m^3, that were obtained during the ESC test with the different fuels are summarized in Table 6. As referred in literature [6], biodiesel fuels, CB and SB, significantly diminished smoke opacity with respect to D by 65.8 and 67.8%, respectively. This reduction was attributed by Man et al. [34] to different factors, such as both the absence of aromatic content in biodiesel or its oxygen content that could enhance soot oxidation. B10 blends (CB10 and SB10) also showed lower smoke opacity than diesel (11.7% and 27.5%, respectively) due to the biodiesel content that contributed with some oxygen to the mixture. On the other hand, the addition of the bio-oil antioxidant in DSB reduced the opacity by 4.4% compared to SB, this value being 69.2% lower than with diesel. Ramalingan et al. [19] obtained the same results with the addition of an antioxidant additive obtained from *Pongamia pinnata* leaves to a B20 blend (Calophyllum oil). The addition of NPPD, DPPD and EHN to B20 blends (*Calophyllum inophyllum* biodiesel) also produced a decrease in smoke intensity [31]. Nevertheless, other authors observed an increase in the smoke production using antioxidant additives such as DPPD [47], BHA and BHT [17], but still below the diesel level. They attributed this rise to the reduction of oxygen availability and the increase in C—C bonds and aromatic content.

Smoke opacity measurements under the operation modes of the ESC test are shown in Fig. 10. Opacity increased with increasing engine load, likely due to the higher amount of fuel being consumed [34], this increase being much more remarkable when engine load varied from 75 to 100% (e.g. from 61 to 397 mg/m^3 for D at 2500 rpm). Maximum values were measured during modes 2, 8 and 10 that corresponded to 100% load at different speeds. At the lowest load (25%), variation in the engine speed did not affect the opacity, which reached very low values (3–10 mg/m^3). From 50% engine load to full load, opacity decreased with increasing engine speed.
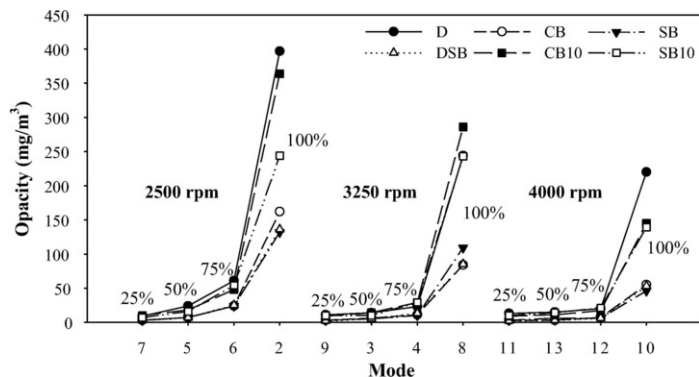
Fig. 10 Smoke opacity emissions at different engine modes working with different fuels.

4 Conclusions

In order to assess the utilization of a biodiesel antioxidant additive obtained from bio-oil (pyrolysis of biomass), the performance and emission characteristics of a diesel engine has been studied in this work. The behaviour of six different fuels has been compared. The obtained results suggest the following conclusions:

- The addition of a small amount (1.9 wt%) of bio-oil compounds to sunflower biodiesel enhanced its oxidation stability by 172%, giving a comparable value to commercial biodiesel. This was due to the presence of phenolic compounds, such as guaiacol, eugenol and others.

- Utilization of the antioxidant additive barely affected the behaviour of the three studied parameters (brake power, brake specific fuel consumption and brake thermal efficiency) with respect to neat biodiesel and very small differences (about 1%) were found. As expected, BP was higher when using diesel instead of biodiesel. On the contrary, BSFC and BTE were increased in the presence of biodiesel.

- When the diesel engine was fuelled with biodiesel (CB, SB) and with the B10 blends (CB and SB10), specific emissions of CO, hydrocarbons and smoke opacity from the engine significantly reduced when compared with that of diesel. NO_x emissions increased by 9–13% with biodiesel and 5–7.3% with B10 blends. Meanwhile, CO_2 augmented in average 2% with biodiesel and decreased with the commercial B10.

- The antioxidant additive combined with the sunflower biodiesel reduced NO_x emissions by 3.0% and smoke opacity by 4.4% compared with the neat biodiesel. CO and HC emissions of the engine increased with the additive addition (0.7 and 14.3%, respectively), but values were still lower than that of diesel.

As a general conclusion, it can be stated that significant differences in the performance and emissions of a diesel engine were not observed between neat sunflower biodiesel and the same biodiesel treated with the bio-oil additive, nor with the commercial biodiesel. Hence, bio-oil could be a suitable source of renewable and low-cost antioxidant additives for biodiesel as a replacement for synthetic and expensive compounds currently used.

Acknowledgements

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Highlights

- Biodiesel oxidation stability can be improved with a bio-oil derived additive.

- Performance and emissions of a diesel engine are not significantly modified by this additive.

- Biodiesel, with and without additive, improves most of the emissions measured.