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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.

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

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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.

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