Diethyl Ether as an Oxygenated Additive for Fossil Diesel/Vegetable Oil Blends: Evaluation of Performance and Emission Quality of Triple Blends on a Diesel Engine

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Abstract: The aim of this work is to analyze the effect of using diethyl ether (DEE) as an oxygenated additive of straight vegetable oils (SVOs) in triple blends with fossil diesel, to be used in current compression ignition (C.I.) engines, in order to implement the current process of replacing fossil fuels with others of a renewable nature. The use of DEE is considered taking into account the favorable properties for blending with SVO and fossil diesel, such as its very low kinematic viscosity, high oxygen content, low autoignition temperature, broad flammability limits (it works as a cold start aid for engines), and very low values of cloud and pour point. Therefore, DEE can be used as a solvent of vegetable oils to reduce the viscosity of the blends and to improve cold flow properties. Besides, DEE is considered renewable, since it can be easily obtained from bioethanol, which is produced from biomass through a dehydration process. The vegetable oils evaluated in the mixtures with DEE were castor oil, which is inedible, and sunflower oil, used as a standard reference for waste cooking oil. In order to meet European petrodiesel standard EN 590, a study of the more relevant rheological properties of biofuels obtained from the DEE/vegetable oil double blends has been performed. The incorporation of fossil diesel to these double blends gives rise to diesel/DEE/vegetable oil triple blends, which exhibited suitable rheological properties to be able to operate in conventional diesel engines. These blends have been tested in a conventional diesel engine, operating as an electricity generator. The efficiency, consumption and smoke emissions in the engine have been measured. The results reveal that a substitution of fossil diesel up to 40% by volume can be achieved, independently of the SVO employed. Moreover, a significant reduction in the emission levels of pollutants and better cold flow properties has been also obtained with all blends tested.

Keywords: diethyl ether; castor oil; sunflower oil; straight vegetable oils (SVO); biofuel; diesel engine; electricity generator; smoke opacity; Bosch smoke number

1. Introduction

Nowadays, so many countries have established a climate and energy policy framework, advancing in decarbonization to arrive towards a new friendly climate economy [1]. In this respect, an unprecedented effort is being made to implement energy alternatives (photovoltaic, wind, hydrogen,
and nuclear energy) that allow the gradual replacement of natural gas, coal and fossil fuels in the field of electricity generation for reducing the high consumption of fossil fuels [2,3]. However, there is no such equivalent in transport, since vehicles using fuel cells or electric motors cannot compete yet with fossil fuel engines, especially in the field of heavy trucks [4], aviation [5], or the shipping sector. In this context, the incorporation of biofuels as fossil fuel substitutes is the strategy assumed to accomplish this necessary energetic progress since there is no need of modifying the compression-ignition (CI) diesel engines of the current car fleet [6,7]. Therefore, the use of biofuels leads to easy and gradual integration into the worldwide transportation logistics systems.

Among the existing biofuels, biodiesel has emerged as one of the best options. Biodiesel is obtained through homogeneous or heterogeneous alkaline transesterification of vegetable oil or animal fat with methanol, giving rise to a mixture of mono-alkyl esters of long-chain fatty acids (FAMEs) [8,9]. Over the past decade, biodiesel has been of interest by contributing to reduce energy dependence on fossil fuels and to minimize greenhouse-gas emissions from transportation [10].

Despite the fact the replacement of fossil diesel by biodiesel seems easy, this process is still considered economically unfeasible. The main reason is the high production cost associated, among other things, to the purification process needed because of the generation of glycerol as a by-product (10wt% of the total biodiesel produced). Considering the economic difficulties in the production of biodiesel, the search for different alternative biofuels is still mandatory.

In this regard, the transformation of vegetable oils into high-quality diesel fuels, avoiding the glycerol formation, has been deeply investigated [11]. These biodiesel-like biofuels, such as Gliperol [12], DMC-BioD [13,14] or Ecodiesel [15,16], avoid the generation of residues or by-products, integrating glycerol in the reaction products. Thus, these new biofuels can be obtained as soluble derivatives in transesterification processes, analogous to that for the production of FAME [17]. Besides, it has been reported as a high-quality diesel fuel known as “green diesel”, which can be obtained by several treatments, such as cracking, pyrolysis, hydrodeoxygenation, and hydrotreating of vegetable oils [18].

Very recently, the use of straight vegetable oils (SVO) has become an interesting option for the replacement of fossil diesel. On one hand, vegetable oils can be obtained easily from agricultural or industrial sources, avoiding energetic costs associated with the transesterification required to obtain biodiesel. On the other hand, all the relevant physicochemical properties of vegetable oils are analogous to conventional diesel, except for the viscosity, which is much higher in oils. The high viscosities cause poor fuel atomization by premature injector contamination. To solve this issue without the need for carrying out the transesterification reaction, researchers have focused their attention on the reduction of high-viscosity oils by blending them with low viscous biofuels. Thus, it is possible to obtain double blends that comply with the requirements stipulated in the current diesel engines (EN 590 standard). Several blends have been reported employing plant-based sources such as vegetable oils and organic compounds [19,20]. These compounds exhibit a relatively short carbon chain, low viscosity values and also low cetane number since they have been identified as LVLC (Low Viscosity Low Cetane) fuels [21].

Employing this strategy, low viscous vegetable oils, such as pine oil or camphor oil, have also been studied in several blends with different biodiesels [22,23], vegetable oils [19] or with fossil diesel [24–26], to improve performance in the CI engines. So far, the additives studied as LVLC are natural compounds (pine oil, eucalyptus oil, camphor oil or orange oil), obtained from crops, which may contribute to reducing the world’s dependence on oil imports, providing benefits to local agricultural industries. Similarly, compounds obtained by chemical synthesis from renewable products, mainly alcohols (methanol, ethanol, and butanol), are also applied as LVLC [27–29]. This strategy has even been applied with a non-renewable compound such as gasoline, capable of reducing the viscosity of vegetable oils in double and triple blends with fossil diesel [30,31]. Following this methodology, high levels of fossil fuel substitution have been obtained in a technically and economically feasible way.

Therefore, if a renewable compound like diethyl ether (DEE) is employed, instead of a non-renewable one such as gasoline, we can make the process greener. In fact, DEE can be easily obtained from ethanol, which can be obtained from biomass. Despite the fact that DEE is known as
a cold-start aid for engines, its potential as a transportation fuel in blends with vegetable oil and/or with fossil diesel has not been much investigated. This molecule has several favorable properties for blending with diesel fuel, including very low kinematic viscosity, low autoignition temperature, high oxygen content, broad flammability limits, high miscibility with vegetable oils and diesel fossil, and very low values of cloud point (CP) and pour point (PP) that improves cold flow properties [29]. Therefore, it is expected that by blending the DEE with SVO, a notable improvement of some of the fuel properties will be obtained, such as a reduction of the CP and PP and so on. However, the calorific power of this compound is relatively low, so this fact could limit the percentage of substitution of fossil fuel by the DEE/oil blend to operate in today’s internal combustion diesel engines, maintaining the appropriate parameters of EN 590 standard. In fact, we have recently reported that the low calorific power of ethanol and 2-propanol (27 and 33 MJ/kg, respectively) constitutes the greatest limitation for its use in double blends with oils [32]. This calorific power is very similar to that for DEE (34 MJ/kg) and, therefore, it is foreseeable it will show similar behavior.

Another aspect to take into consideration is the very low ignition quality of some diesel/DEE blends [27] that promote a high ignition delay, given the low heat of evaporation value that DEE exhibits [33]. This ignition delay can be overcome by the addition of vegetable oils to the blend. Therefore, a mutual benefit can be obtained by the use of DEE with vegetable oils in triple blends with diesel, i.e., DEE reduces the high viscosity of the oils, whereas the oils could compensate for the heat and evaporation of DEE. In fact, DEE has been reported as a low-emission renewable fuel and high-quality combustion improver in blends with diesel fossil [27,28], with biodiesel [27,29,34,35], with oils [27,29] or with diesel/oil [36–38]. Besides, better performance of compression-ignition engines operating with DEE/diesel/biodiesel triple blends has been achieved [39,40].

Waste cooking oil (sunflower oil) and castor oil have been selected as the vegetable oils for this work since they come from crops that are not destined to human or livestock food and they are easily available, not competing with oils for food uses. Sunflower oil has been selected as a standard reference to study the behavior of waste cooking oils because the use of any waste cooking oil from different sources, implies the difficulty of reproducing the results obtained. Castor oil is currently the only inedible vegetable oil available on an industrial scale.

The present study intends to advance the strategy of the substitution of fossil fuels by others of a renewable nature that can be used in current diesel engines in a viable way, not only from a technical point of view but also economically and even more importantly, applicable in the most immediate way. To do so, DEE has been employed as an oxygenated additive in blends with diesel and vegetable oil. In this respect, the optimum proportion of DEE/vegetable oil blend will be evaluated based on the most significant parameter, the kinematic viscosity, to meet with appropriate parameters of EN 590 standard that allow its use in internal combustion diesel engines. Additionally, flow cold properties (cloud and pour points) will be studied to ascertain the applicability of the fuel in cold climates. The diesel/DEE/oil triple blends obtained have been tested in a diesel engine. The most important parameters, such as fuel consumption and power generation have been studied to know the viability of the new fuel produced. The degree of pollution of all blends will be also evaluated from the generated smoke opacity values.

2. Materials and Methods

Some of the significant physicochemical characteristics of diesel, diethyl ether, and SVOs (sunflower oil and castor oil) have been collected in Table 1.
Table 1. Properties of diesel, sunflower oil, castor oil, and diethyl ether. All data collected in the Table were taken from the literature [36,41–43], except for the kinematic viscosity values which were experimentally measured in this work.

| Property                          | Diesel      | Sunflower Oil | Castor Oil | DEE        |
|----------------------------------|-------------|---------------|------------|------------|
| Density at 15 °C (kg/m³)         | 830         | 920           | 962        | 713        |
| Kinematic viscosity at 40 °C (cSt) | 3.20 ± 0.01 | 37.80 ± 0.05  | 226.20 ± 0.05 | 0.21 ± 0.01 |
| Calorific value (MJ/kg)          | 42.8        | 39.5          | 37.2       | 33.9       |
| Flash point (°C)                 | 66          | 220           | 228        | 16         |
| Auto-ignition temperature (°C)   | 250         | 316           | 448        | 160        |
| Cetane number                    | 50          | 37            | 40         | >124       |

1 Viscosity value errors were obtained from the average of 3 measurements.

2.1. Diethyl Ether/Vegetable Oil Double Blends, and Diesel/Diethyl Ether/Vegetable Oil Triple Blends

Sunflower oil was bought from a local market and castor oil (Panreac, Castellar Del Valles, Spain) was purchased from a local commercial representative. DEE (≥99.5% purity) was procured from Sigma-Aldrich Chemical Company. First of all, sunflower oil (food grade) and castor oil were mixed with DEE in different concentrations to find out the optimum DEE/SVO double blends. The best double blends, which comply with the established requirements by European petrodiesel standard EN 590 for being employed as biofuels, were selected to be mixed with conventional diesel fuel (Repsol service station) in different proportions, from 20% to 100% by volume, denoted as B20, B40, B60, B80, and B100. The percentage of biofuel (DEE/SVO blend) added to fossil diesel is expressed as B, where B0 corresponding to 100% of fossil diesel and B100 means 100% of renewable DEE/oil biofuel. The components of all blends were manually mixed at room temperature. Additionally, all components were completely miscible with petroleum diesel, allowing the blending of these in any proportion. The obtained diesel/DEE/SVO triple blends were investigated as biofuels in this work.

2.2. Characterization of the Biofuel Blends

Fuel reformulation can affect the physicochemical and safety properties of the fuel. Hence, knowledge of these properties is especially important. In this work, some of the most crucial properties to evaluate the suitability of biofuels have been determined either experimentally or using specific equations to predict them.

As aforementioned, kinematic viscosity and cold flow properties are the rheological properties more influenced by blends of vegetable oils with fossil diesel and other additives. In fact, these properties play a crucial role in the correct performance of conventional diesel engines [32]. Kinematic viscosity significantly affects the quality of fuel atomization and the combustion process. Low viscosity can cause leakage in the fuel system while high viscosity can lead to incomplete combustion because of premature injector contamination [44].

Cold flow properties, such as cloud point and pour point, are responsible for solidification of fuel, causing operability problems as solidified material clogs fuel lines and filters. The temperature at which the crystals become visible (diameter ≥ 0.5 mm) is defined as the cloud point (CP), whereas the pour point (PP) is defined as the temperature at which the liquid ceases to flow. The CP usually occurs at higher temperatures than the PP [45]. Crystallization of fuel takes place when fuel molecules condensate forming a gel at low temperatures. Crystallization occurs in two general steps: The first step is the nucleation and crystal growth and the second step is the organization of the molecules creating a stable nucleus in a crystalline network. The continuous growth of the crystalline network generates the interruption of fuel flow, causing fuel starvation and incomplete combustion, which leads to starting problems in the vehicle in cold weather [46].

The flash point (FP) is a crucial property for production, handling, transportation and storage of fuels. This parameter provides an indication of the fire hazard of fuel under ambient conditions. The flash point is defined as the lowest temperature at which a liquid produces enough vapors to ignite in the presence of a flame or spark. Generally, a lower flash point is related to higher vapor
pressure, so this property provides information on both flammability and volatility. The values of the flash point can be predicted from Kay’s mixing rule:

\[ T_{FP} = \sum_i y_i T_i \]  

where \( T \) is the temperature corresponding to the flash point of the blend (°C), \( y_i \) is the volume fraction of each component in the blend and \( T_i \) is the flash point of each component [47].

Another important property to define the efficiency of fuels is the calorific value (CV), also called the heat of combustion or calorific power, which is the quantity of heating energy released during complete combustion of a unit mass of the fuel, usually expressed in kilojoules per kilogram. The calorific value increases with increasing chain length and decreases with increasing unsaturation, and it is important for estimating the fuel consumption, the greater the calorific value the lower the fuel consumption. Calorific value is usually determined experimentally by a bomb calorimeter, but a theoretical value can be calculated, according to the volumetric concentration of each component in the blend, from the following equation:

\[ CV = \sum_i CV_i X_i \]  

where \( CV_i \) is the calorific value of each component and \( X_i \) is the percentage of each component in the blend [37].

2.2.1. Viscosity Measurements

The kinematic viscosity measurements were performed in an Ostwald-Cannon-Fenske capillary viscometer (Proton Routine Viscometer 33200, size 150) at 40 °C, by determining the flow time (\( t \)), expressed in seconds, required for a certain volume of liquid to pass under gravity between two marked points on the instrument, placed in an upright position. The kinematic viscosity (\( \nu \)) expressed in centistokes (cSt) is obtained from the equation \( \nu = C \cdot t \), where \( C \) is the calibration constant of the measurement system, supplied by the manufacturer (0.037150 (mm²/s)/s = cSt at 40 °C) [28,33]. The procedure for the determination of the kinematic viscosity meets with the specifications established by the European standard (EN 590 ISO 3104). All the viscosities values reported here are the media of three determinations.

2.2.2. Determination of Pour Point and Cloud Point

Cloud Point (EN 23015 and ASTM D-2500) and Pour Point (ASTM D-97) were determined according to specifications required by standard methods. Firstly, the double or triple blends, of different compositions, were introduced in a flat-bottomed glass tube. The tube was tightly closed with the help of a cork carrying a thermometer with a temperature measuring in the range of −36 to 120 °C. The tube was introduced in a digitally controlled temperature refrigerator for twenty-four hours; the tubes were brought out from time to time and checked until the oil did not show any movement when the tube was horizontally tilted for 5 s. After this time, the loss of transparency of the solutions is evaluated. The appearance of turbidity in the samples is indicative that the CP temperature has been reached. After a progressive decrease in temperature, the samples are kept under observation until they stop flowing (PP) [31,32]. All values are the media of duplicate determinations.

2.2.3. Mechanical and Environmental Characterization of a Diesel Engine Electric Generator Fuelled with Different Biofuel Double and Triple Blends

Following the experimental methodology previously described [32], the energy performance and pollutant emissions generated in a C.I. diesel engine, has been carried out, working at a rate of 3000 rpm coupled to an AYERBE AY4000MN electric generator with a power of 5 KVA 230 V, for the generation of electricity, operating under different degrees of demand for electrical power. This is
achieved by connecting heating plates of 1000 watts each (Figure 1a). The diesel engine operated at a constant rate of rotation of the crankshaft and torque so that the different values of electrical power obtained are an exact consequence of the mechanical power obtained after the combustion of the corresponding biofuel. Tests were carried out by providing to the engine double and triple blends of different biofuels. The electrical power generated can be easily determined from the product of the potential difference (or voltage) and the electric current intensity (or amperage), Equation 3, both obtained utilizing a voltmeter-ammeter, Figure 1b:

\[
\text{Electrical power generated (watts)} = \text{voltage (volts)} \times \text{amperage (amps)} \quad (3)
\]

The consumption of the diesel engine, fueled with the different biofuels studied, was calculated estimating the speed of consumption of the engine when it operates under a determined demand of electric power (1, 3 or 5 kW). Thus, the operation times are achieved by operating under the same fuel volume (0.5 L).

The contamination degree is evaluated from the opacity of the smoke generated in the combustion process, which is measured by smoke opacity meters. The smoke opacity meters are instruments capable of measuring the optical properties of diesel exhaust. These instruments have been designed to quantify the visible black smoke emission making use of physical phenomena like the extinction of a light beam by scattering and absorption. There are two groups of instruments: opacity meters, which evaluate smoke in the exhaust gas, and smoke number meters, which optically evaluate soot collected on paper filters. The density gauge is a handheld instrument for determining the filter smoke number (FSN), the Bosch number, and the soot concentration of diesel engines. This instrument is composed of an optical sensor (photodiode) and a differential pressure sensor. The photodiode calculates the paper blackening based on the reflected light intensity by a white LED. The more soot is deposited on the filter paper, the less light is reflected. The probe volume determined by the differential pressure sensor is used to calculate the probe volume under reference conditions with the input height and the temperature measured by the instrument. This probe volume and the measured paper blackening are then used to calculate the FSN (filter smoke number), soot concentration (mg/m³) or Bosch smoke number. Herein, the exhaust emissions were measured by a Bosch smoke meter or opacimeter-type smoke tester TESTO 338 density gauge, following the EU Directive 2004/108/EC, at the operating conditions previously reported [32], Figure 1c. The Bosch number is a standardized unit which is calculated from the level of soot on the paper (effective filter loading) [48]. The instrument evaluates smoke density on a scale from 0 to 2.5, where the value 0 represents total clarity on the paper and 2.5 is the value corresponding to 100% cloudy, as established by ASTM D 2156-94, Standard Test Method for Smoke Density in Flue Gases from Burning Distillate Fuels.

Figure 1. (a) Electrogenerator AYERBE AY4000MN, 5 KVA, 230 V connected to heating plates of 1000 watts of power each (b) voltmeter-ammeter devise; (c) TESTO 338 smoke density tester.
The data here compiled are the media of three repeated measures, attaining an experimental error lower than 9%. The results obtained with the biofuels evaluated were compared with the measurements obtained when conventional diesel was fueled.

3. Results and Discussion

3.1. Properties of DEE/Oil Double Blends, and Diesel/DEE/Oil Triple Blends

The high viscosity values that the vegetable oils exhibit, 10–20 times greater than fossil diesel fuel, prevents its use like biofuels in conventional diesel engines. Most of them have viscosity values in the range of 30–45 cSt, concretely, castor oil has a much higher value, 226.2 cSt, very superior to values required by European standard EN 590 ISO 3104. Therefore, to achieve adequate viscosity values, the proportion in which the oils must be mixed with DEE has been investigated.

The viscosity values of the DEE/SVOs double blends are shown in Figure 2. As expected, an increase in the DEE content in the blends contributes to decreasing the viscosity values. It is interesting to confirm how DEE can promote very strong action on castor oil, in comparison with sunflower oil, in terms of reducing the viscosity of their blends, since castor oil has initially a much higher viscosity than sunflower oil. As can be observed, only 20% of DEE reduces considerably the kinematic viscosity of both oils, from 226.2 to 17.1 cSt in the case of castor oil and from 37.8 to 13.7 cSt when DEE is added to sunflower oil. For both oils, the viscosity values required by UNE EN 14214 ISO 3104, in the range from 2.0 to 4.5 mm²/s, were achieved with an analogous DEE/vegetable oil ratio (45/55).

![Figure 2. Kinematic viscosity values at 40 °C of different blends of DEE/SVOs.](image)

According to the previous study of the kinematic viscosity in double blends, the optimum and most favorable blend ratio was found to be DEE/SVO 45/55 (% by volume), independently of the oil employed. Hence, different proportions of biofuel containing 45% of DEE were mixed with fossil diesel to obtain the diesel/DEE/oil triple blends. The kinematic viscosity, cloud point, pour point, flash point and calorific values of the investigated triple blends are collected in Tables 2 and 3. A higher amount of biofuel in the blend, from B0 to B100, generates higher viscosity values, as expected since the viscosity of the added biofuels is slightly higher than that of diesel (3.20 cSt). Kinematic viscosity values are in the range of 3.20–4.25 cSt, so these biofuels present suitable values for being employed in diesel engines, complying with the European regulations EN 590, which establishes that viscosity at 40 °C must be in the range of 2.0–4.5 cSt.
Table 2. Physicochemical properties (kinematic viscosity at 40 °C, cloud point, pour point, flash point, and calorific values) of diesel/DEE/sunflower oil triple blends, obtained by adding different proportions of fossil diesel to the DEE/sunflower oil double blend containing 45% diethyl ether. All values are calculated as the average of three measurements.

| Nomenclature | B0  | B20 | B40 | B60 | B80 | B100 |
|--------------|-----|-----|-----|-----|-----|------|
| (%) renewable| 100/0 | 80/9/11 | 60/18/22 | 40/27/33 | 20/36/44 | 0/45/55 |
| Kinematic Viscosity (cSt) | 3.20 ± 0.01 | 3.21 ± 0.01 | 3.26 ± 0.02 | 3.32 ± 0.02 | 3.52 ± 0.02 | 4.25 ± 0.03 |
| Cloud point (°C) | −6.0 ± 1 | −15.0 ± 1 | −15.3 ± 1 | −15.0 ± 1 | −10.6 ± 1 | −15.5 ± 1 |
| Pour point (°C) | −16.0 ± 1 | −21.6 ± 1 | −22.5 ± 1 | −21.9 ± 1 | −20.5 ± 1 | −21.0 ± 1 |
| Flash point (°C) | 66.0 | 78.4 | 90.9 | 103.3 | 115.8 | 128.2 |
| Calorific value (MJ/kg) | 42.8 | 41.6 | 40.5 | 39.4 | 38.1 | 36.9 |

* The flash point values and calorific values were calculated by using Equations 1 and 2, respectively.

Table 3. Physicochemical properties (kinematic viscosity at 40 °C, cloud point, pour point, flash point, and calorific values) of diesel/DEE/castor oil triple blends, obtained by adding different proportions of fossil diesel to the DEE/castor oil double blend containing 45% diethyl ether. All values are calculated as the average of three measurements.

| Nomenclature | B0  | B20 | B40 | B60 | B80 | B100 |
|--------------|-----|-----|-----|-----|-----|------|
| (%) renewable| 100/0 | 80/9/11 | 60/18/22 | 40/27/33 | 20/36/44 | 0/45/55 |
| Kinematic Viscosity (cSt) | 3.20 ± 0.01 | 3.21 ± 0.01 | 3.24 ± 0.01 | 3.32 ± 0.01 | 3.37 ± 0.02 | 3.48 ± 0.02 |
| Cloud point (°C) | −6.0 ± 1 | −16.0 ± 1 | −16.8 ± 1 | −15.2 ± 1 | −14.2 ± 1 | −16.3 ± 1 |
| Pour point (°C) | −16.0 ± 1 | −22.3 ± 1 | −22.8 ± 1 | −21.5 ± 1 | −20.1 ± 1 | −22.0 ± 1 |
| Flash point (°C) | 66.0 | 79.3 | 92.6 | 106.0 | 119.3 | 132.6 |
| Calorific value (MJ/kg) | 42.8 | 41.4 | 39.9 | 38.5 | 37.1 | 35.7 |

* The flash point values and calorific values were calculated by using Equations 1 and 2, respectively.

Regarding the cold flow properties, the DEE has an important effect in the cloud and pour point of the triple blends, independently of the vegetable oil employed. In fact, it is found that only 9% of DEE (B20 blend) is enough to reduce the PP value 6 °C (from −6 to −15 °C) and the CP value 10 °C (from −6 to −16 °C). The best CP and PP values were obtained adding 18% of DEE, with 22% of castor oil and 60% of diesel, resulting in a CP of −16.8 °C and a PP of −22.8 °C. That is, the DEE promotes a significant improvement, with regard to fossil diesel, on the cold flow properties in all the blends studied, maintaining the appropriate viscosity to be used as a biofuel in conventional diesel engines. Additionally, the use of DEE overcomes one of the major challenges when using biodiesel as an alternative to fossil diesel in current engines, which is its poor cold flow properties.

Tables 2 and 3 show the calorific values of triple blends containing sunflower and castor oil, respectively. The calorific values decreased as the percentage of diethyl ether in the blend increased. As can be observed, there is no notable difference in the respective values for blends with either sunflower or castor oil, since these oils have similar calorific power. The results show that the B20 triple blends exhibited the highest calorific value, 41.6 MJ/kg in the case of sunflower oil and 41.4 MJ/kg for castor oil. In addition, an inverse correlation between calorific value and kinematic viscosity can be observed, since the calorific value of the biofuels increases as the kinematic viscosity decreases.

The results of the flash point of the analyzed mixtures (Tables 2 and 3) show an increment of this value as the DEE/oil ratio is greater, with both sunflower and castor oil. As it can be seen, the incorporation of SVOs in mixtures allows the FPs values to improve, since these oils exhibit a higher FP than both diesel and DEE. The highest FP was presented by B100 blends containing castor oil (132.6 °C) and sunflower oil (128.2 °C). The FP values are situated in the range 78.4–128.2 °C for diesel/DEE/sunflower oil blends, and 79.3–132.6 °C for diesel/DEE/castor oil blends. These values can be compared with FP requirements specified by EN 590 standard, which establishes that the fuel must have a minimum FP of 55 °C. In this case, each of the blends has FPs above the required value, so they are compliant with the requirements. Additionally, these biofuels do not have too high a
flash point that they can self-ignite thereby causing no safety problems during handling, storage or transportation, and they are recommended for use in CI engines.

3.2. Mechanical Performance of the Diesel Engine

To determine the optimal proportion of DEE that guarantees an adequate engine performance, the biofuel blends characterized in Tables 2 and 3 have been tested in a compression ignition engine. In this study, it was also included for comparative purposes, conventional diesel fuel as a reference. Hence, Figure 3 shows the power generated at different power demanded for by the triple blends employing either sunflower oil (3a) or castor oil (3b). In all cases, the power generated increased as the power supplied to the engine also increased from 1 to 3 kW and then, a stabilization of the power generated occurred, slightly decreasing when the maximum value of power supplied (5 kW) was reached. This behavior was improved using castor oil, where the power generated increased as the power supplied was also increased up to 4 kW.

![Generated Power vs Demanded Power](image)

**Figure 3.** Power generated (in Watts) based on the power demanded (in Watts) by the triple blends diesel/DEE/sunflower oil (a) or diesel/DEE/castor oil (b).

It is noteworthy the excellent results obtained with the B20 and B40 blends, achieving similar (diesel/DEE/sunflower oil) or even higher values (diesel/DEE/castor oil) of power generated than that obtained with fossil diesel at the highest values of demanded power (4 and 5 kW). Independently on the oil employed, a general trend was observed for B20 and B40 blends, where the rise of the DEE content caused the higher power generated. It is important to note that, despite obtaining a very slight increase in the power generated from B20 to B40 blends, when the proportion of DEE in triple mixtures increases above 25%, i.e., B60, B80, and B100 blends, the diesel C.I. engine did not work correctly. This behavior could be associated with the low calorific power of the DEE, confirming the previous results obtained with diesel/ethanol/oil [32].

3.3. Smoke Opacity Emissions

Regarding the pollutants emission (Figure 4), the results obtained showed a significant reduction in smoke emissions in diesel engines, compared to those of conventional diesel, especially for B40 blends. This fact was even more evident with castor oil, achieving a reduction of 77% in the pollutant emission at the highest demand employed (5 kW). This important change is mainly due to the contribution of DEE to higher oxygen content in the blend, which improves the combustion and reduces the contamination. So, improved and complete combustion could be the reason for obtaining lower smoke...
opacity values when the oxygenated additive is added to the blends. Additionally, as can be seen in Figure 4b, a slight but noticeable decrease in smoke emissions is observed when mixtures containing castor oil are employed, compared with the mixtures using sunflower oil in the same proportion (Figure 4a). In previous studies, it has been shown that the presence of unsaturations influences soot formation [49]. So, this may be explained by the differences in the fatty acid composition for the two vegetable oils used, since the linoleic acid present in sunflower oil has a greater number of double bonds than the ricinoleic acid present in castor oil.

It should be noted that independently of the blend tested, from demanded powers of 1000 W onwards, all the blends performed better than fossil diesel in terms of achieving better combustion, which allows a reduction of emissions. The lowest smoke emissions are mainly obtained at medium and high demand (from 2000 W onward). Concretely, a reduction in smoke opacity values of about 66% is achieved with diesel/DEE/sunflower oil blends, whereas the same blends containing castor oil reduce emissions up to 77%.

### 3.4. Fuel Consumption

Additionally, a key parameter in the development of new fuel as an alternative to diesel, is its consumption. Figure 5 shows the consumed volume (in liters per hour) by the engine fueled with the different diesel/DEE/sunflower oil and diesel/DEE/castor oil blends, at different power demands (1, 3, and 5 kW).

As can be seen, at lower power demands (1 kW), the consumption of the blends is always higher than that obtained with the fossil diesel, independently of the oil employed. This is probably due to the initial engine start requires a greater amount of fuel. However, at the higher powers demanded (3 and 5 kW), there have been no noticeable differences in fuel consumption compared to conventional diesel fuel. It can also be seen that mixtures with castor oil (Figure 5b) have slightly higher consumption than sunflower equivalents (Figure 5a). For all fuels tested, the fuel consumption increased as the biofuel ratio (DEE/SVO) is increased in the blends (from B0 to B40). The explanation for this increment could be the reduction in engine power when the concentration of diethyl ether is higher because the energy content in blends is reduced as a consequence of its lower calorific value. In the case of the B40 blend with sunflower oil, fuel consumption was between 3–29% higher than that of diesel, while the biofuel containing castor oil in the same proportion consumed 8–29% more than the diesel case. A reduction of fuel volume up to 9% can be achieved by employing biofuels with 9% of DEE and 11% of vegetable.
oil, especially when sunflower oil is employed (B20 blend). It was definitive that the tested triple blends B20 and B40 show an excellent ability to eliminate smoke emissions, generate very similar and even higher power values than those with diesel, and a biofuel consumption analogous to diesel.

![Figure 5](image_url)  
**Figure 5.** Consumption values (L/h) as a function of the power demanded by the engine for the blends diesel/DEE/sunflower oil (a) and diesel/DEE/castor oil (b).

3.5. Comparison with Reported Studies in Literature

The diesel replacement and smoke emissions of the blend, with which the best results are obtained in the present work, have been compared with the results of some of the reported blends as biofuels in the literature, Table 4. It is important to take into account the different parameters in the engine as well as the different fuel loads that have been employed in each study. As can be seen in Table 4 and, to the best of our knowledge, literature about diesel engine fueled with diesel/DEE/oils blends is very recent and limited to a few studies belonging to M. Krishnamoorthi and A. Kumar [36–38,50]. Among these diesel/SVO/DEE triple blends, the greater percentage of substitution has been reached in [38,50] and, also, in the present study (40%). However, with regard to soot emission, a higher reduction of 77%, is achieved in this work, comparing to a reduction from 9.2% to 64.6% obtained with the other triple blends [37,38,50]. The blend containing biodiesel from vegetable oil instead of SVO shows lower diesel replacement and minor reduction of opacity, 22.5% and 8.1%, respectively [40]. In another study, the incorporation of a non–renewable fuel like kerosene only allows a fossil diesel replacement of 13% and the smoke opacities decreased by 6% [51]. There are two trends when double blends containing DEE are employed. On one hand, the blends containing diesel lead to a substitution of diesel up to 24% and to a considerable decrease in emissions [28]. On the other hand, if a renewable fuel like oil derived from waste plastic pyrolysis is used [52], the entire replacement of diesel is attained, at the same time, the pollutant emission is reduced by almost 20% in comparison with the diesel/DEE blend. It has been seen that the triple blends which do not use DEE as an oxygenated additive, for example, the diesel/gasoline/sunflower oil blend [31], allow higher incorporation of SVO than the rest of blends, and generate a similar performance in the diesel engine.

| Nomenclature | Blend Description | Diesel Replacement (%) | Smoke Opacity * | Reference |
|--------------|------------------|------------------------|-----------------|-----------|
| B40          | 60% Diesel/22% castor oil/18% DEE | 40 | ↓ 77% | Present study |
| B2           | 60% Diesel/30% aegle marmelos oil/10% DEE | 40 | ↓ 64.6% | [50] |
| B1           | 70% Diesel/20% aegle marmelos oil/10% DEE | 30 | ↓ 9.2% | [37] |
| B2           | 60% Diesel/30% bael oil/10% DEE | 40 | ↓ 64.5% | [38] |
### Table 4. Cont.

| Nomenclature | Blend | Diesel Replacement (%) | Smoke Opacity * | Reference |
|--------------|-------|------------------------|------------------|-----------|
| B20D15       | 68% Diesel/17% cashew Nut Shell Oil/15% DEE | 32 | ↑ 7.3% | [36] |
| B20DEE2.5    | 77.5% Diesel/20% Cottonseed oil biodiesel/2.5% DEE | 22.5 | ↓ 8.1% | [40] |
| DE15K15D     | 72.25% Diesel/15% kerosene/12.75% DEE | 13 | ↓ 6% | [51] |
| D+24DEE      | 76% Diesel/24% DEE | 24 | ↓ 31% | [28] |
| WD05         | 95% Waste plastic pyrolysis oil/5% DEE | 100 | ↓ 50% | [52] |
| B60          | 40% Diesel/24% gasoline/36% sunflower oil | 36 | ↓ 40% | [31] |

* Smoke opacity reduction with respect to conventional diesel.

### 4. Conclusions

The present study aims to make the process of replacing fossil diesel feasible, without making mechanical changes in the engines of the current car fleet. In this way, not only the pollution produced by petroleum is minimized, but also the dependence of the countries that produce the fuels is reduced. Given the relatively high economic cost of any additional chemical transformation of the vegetable oils, either in biodiesel or in other biofuels of appropriate viscosity values, a novel strategy employing green fuels derived from vegetable oils has been investigated. In this respect, to get high levels of fossil fuel substitution in a technically and economically feasible way, a renewable compound like DEE, which can be obtained from biomass, has been studied as an additive in triple blends with diesel and different SVOs on the engine performance and exhaust emissions. DEE has contributed to a reduction of viscosity values in SVOs through its very low viscosity, complying with European regulations to operate as biofuel in current diesel engines. Additionally, all blends comply with EN 590 specifications concerning the flash point.

According to the results obtained, the tests were carried out successfully up to 18% blending of DEE and 22% of SVO with diesel, this means that substitution of 40% of fossil diesel can be achieved by the use of diesel/DEE/SVO triple blends, using either sunflower or castor oil, performing similarly to diesel in terms of power. Furthermore, several advantages of using these blends were obtained. On one hand, DEE addition leads to an improvement in the combustion, since an important reduction of pollutant emissions occurred (up to 77% lower than fossil diesel), which is mainly due to the oxygen content of DEE. Likewise, an enhancement in the cold flow characteristics of the blend in respect to fossil diesel was also attained, which means the diesel engines can run at lower temperatures. On the other hand, the increment of the flash point in blends with respect to fossil diesel, makes these biofuels safer for handling, storage, and transportation. All the abovementioned shows the competitive value of diethyl ether as an oxygenated additive in comparison to other natural products studied of greater economic cost. Hence, the addition of this oxygenated additive up to 18% (by volume) is a promising way for using diesel/vegetable oil blends efficiently in diesel engines without any modifications in the engine. It can be concluded that this research proffers a practical and economically viable alternative to the chemical production of biofuels.

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Nomenclature

ASTM American society for testing and materials
B0 100% diesel
B20 80% diesel + 9% DEE + 11% oil
B40 60% diesel + 18% DEE + 22% oil
B60 40% diesel + 27% DEE + 33% oil
B80 20% diesel + 36% DEE + 44% oil
B100 45% DEE + 55% oil
CI Compression ignition
CN Cetane number
CP Cloud point
cSt Centistokes
CV Calorific Value
DEE Diethyl ether
FAME Fatty acids methyl esters
FP Flash point
FSN Filter smoke number
ISO International Standards Organization.
LVLC Low viscous and low cetane
PP Pour point
rpm Round per minute (min$^{-1}$)
SVO straight vegetable oils
T$_{FP}$ Flash point temperature
W Watts

Symbols

υ Viscosity (centistokes)
t Flow time (s)
C Calibration constant (mm$^2$/s)/s

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