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Evaluation of Advanced Biofuels in Internal Combustion Engines: Diesel/Fusel Oil/Vegetable Oil Triple Blends

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Abstract: In this research work, the feasibility of using fusel oil, a by-product of the sugar–alcohol industry, as an LVLC solvent in blends with straight vegetable oils (SVOs) and diesel was investigated. Concretely, diesel/fusel oil/sunflower oil (D/FO/SO) and diesel/fusel oil/castor oil (D/FO/CO) triple blends were prepared and characterized by measuring the most important physicochemical properties, i.e., viscosity, density, cold flow properties, flash point and cetane number. An appreciable improvement in cold flow values has been achieved with triple blends, without compromising properties such as calorific value and cetane number. Likewise, the triple blends meet the viscosity and density requirements specified by the European quality standard EN 14214 and the American standard ASTM D6751. After characterization, the triple blends were used on a diesel engine, evaluating different parameters such as power output, opacity, exhaust emissions (CO and NO_x) and consumption at different engine loads. The results indicate that as the biofuel content in the blend increases, engine power decreases while fuel consumption rises. Nevertheless, the values obtained with D/FO/CO are better than those for D/FO/SO and are also very similar to those of fossil diesel. Regarding opacity values and NO_x emissions obtained with the utilization of the triple blends, they are lower than those produced by diesel. However, in the case of CO emissions, it depends on the type of oil used, with the samples prepared with castor oil exhibiting the best results.

Keywords: fusel oil; straight vegetable oil; castor oil; sunflower oil; biofuel; diesel engine

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1. Introduction

Presently, there is an intense search ongoing for carbon-neutral fuels that can be used in transport vehicles designed for fossil fuels. This is the only way to achieve a significant reduction in CO_2 emissions from personal cars, vans and trucks within the deadlines that different countries have set to achieve climate neutrality [1]. In this transition period, which is presumed to be quite long, straight vegetable oils (SVOs) have emerged as a promising renewable alternative to fossil diesel due to their ease of production and low cost. Thus, unlike new vehicles that use fuel cells or electric motors, biofuels do not rely on technological innovations [2]. In addition, it is absolutely urgent to combat the current emissions of polluting gases resulting from the burning of fossil fuels by the enormous vehicle fleet operating worldwide (over one billion vehicles) [3]. These emissions are the primary cause of atmospheric pollution, significantly contributing to global warming and causing damage to human health in urban areas [4].

Therefore, although the total electrification of transport is considered the best long-term solution for reducing vehicle emissions, there is no doubt that this process will take several decades, so in the short term, a combination of green propulsion technologies, i.e., the use of renewable fuels, e-fuels, hydrogen and electrical energy, will be the fastest way to advance in reducing CO_2 emissions from urban vehicle fleets and reach the goal of neutral emissions [5].

In this context, triglycerides, which constitute vegetable oils, are seen as one of the most promising alternatives for achieving a feasible energy transition. Derived from living plants, vegetable oils are renewable and readily available biofuels. However, their main drawback is that they exhibit kinematic viscosity values at least 10 times higher than fossil diesel. In some cases, such as with castor oil, the viscosity can be up to 50 times higher [6].

Hence, several strategies have been developed to transform the triglycerides of biological origin into new biofuels that meet the requirements set by the European standard EN 590:2022 and the American standard ASTM D6751. These biofuels are referred to by different names, i.e., green diesel [7], renewable diesel [8], bio-hydrogenated diesel (BHD) [9], hydrogenated vegetable oils (HVOs) [10], alternative fuels [11] or advanced biofuels [12], and obtained using diverse catalytic processes such as cracking or pyrolysis, hydrodeoxygenation or hydrotreating [13,14]. The main advantages of these processes over biodiesel production are that they can be carried out in facilities where conventional fuels are manufactured, and the problem of glycerol is avoided as well [15,16]. As for the main drawback, the production costs are still high.

Recently, a promising new research line consisting of the use of SVOs as renewable fuels in C.I. engines at lower manufacturing costs is being developed [17]. To this end, SVOs are blended with several organic solvents to reduce their high viscosity values. These solvents, preferably of a renewable nature, must exhibit relatively low viscosity values, which usually requires that they have a short hydrocarbon chain, which entails a relatively low energy density and low cetane number. In fact, these solvents are usually called low-viscosity, low-cetane (LVLC) solvents [18]. By using these double mixtures, all costs associated with the chemical transformation of the oil to reduce its viscosity can be eliminated, and no waste is generated. Accordingly, in recent years, several studies on the performance and emissions of compression ignition engines fueled with binary blends of vegetable oils and various solvents, such as gasoline, due to its lower viscosity [19], or hydrocarbons obtained from the pyrolysis of plastic wastes [20], have been performed. Nevertheless, most studies have focused on bio-alcohols (from methanol to octanol) as LVLC solvents [21–24] since the renewable nature of these alcohols enhances the renewability of the blends. Following this line of research, many other organic compounds of vegetable origin have also been investigated, such as Melaleuca Cajuputi oil [25], pine oil [26], eucalyptus oil (No. 2017) or camphor oil [27,28]. In general, these biofuels exhibit higher calorific values than alcohols but values similar to fossil diesel fuel, resulting in better performance for the mixtures. Therefore, alcohols have economic advantages over these organic compounds since they are the most suitable candidates to achieve the sustainable transport objectives because they can be obtained from biomass [29].

Given the superior economic viability of this methodology compared to other existing proposals, the techno-economic feasibility of various LVLC solvents of renewable origin is currently being intensively investigated. This includes mixtures of various solvents, such as the ABE blend (acetone/butanol/ethanol). The ABE blend can be produced from the fermentation of carbohydrates to obtain acetone, butanol, and ethanol in a ratio of 3:6:1 [30], which is an economically competitive industrial process that does not require further purification [31]. Another by-product of the sugar–alcohol industry in the bioethanol synthesis process is fusel alcohol (FA). This by-product is a complex mixture of higher-boiling-point alcohols, primarily composed of isopentyl alcohol (3-methyl-1-butanol) (~75%), with smaller amounts of 2-methyl-1-butanol, 2-methyl-1-propanol, and n-propanol, as well as trace levels of other alcohols, carboxylic acids, aldehydes and esters [32]. Because of the high global production of ethanol through fermentation processes, various mixtures of fusel alcohol are being produced in substantial quantities. These mixtures are currently being used in the production of biodiesel and bio-lubricants [33] and blended with gasoline [34] or fossil diesel [35,36]. Therefore, fusel alcohol is a promising LVLC solvent for forming suitable double blends with second-generation vegetable oils, castor oil and waste cooking oil, to produce biofuels.

It is crucial to evaluate oils that are not in competition with food supplies and are readily available in industrial quantities. Thus, castor oil is a non-edible vegetable oil currently used industrially in lubricants, paints and pharmaceuticals, with a production volume of about 220,000 tons/year, so it can be used as a biofuel immediately. On the other hand, to avoid the variability associated with using waste oils from different sources, commercial sunflower oil is used as a standard. In this respect, over 190 million metric tons of waste vegetable oils is generated annually worldwide [37], highlighting the importance of exploring this potential feedstock as a component of triple blends for fossil fuel replacement. Thus, the application of LVLC solvents in blends with castor oil, or waste cooking oils, could be a valuable and feasible methodology for the replacement of fossil diesel due to its relatively lower economic cost. In addition, several investigations have demonstrated that it is possible to replace a significant portion of fossil fuel in a C.I. diesel engine without compromising performance while achieving a notable reduction in emissions [31,38].

Therefore, this study evaluates the use of fusel alcohol as a low-viscosity, low-cetane (LVLC) solvent in triple blends with castor oil or sunflower oil for use as biofuels in C.I. diesel engines. This research focuses on optimizing the proportions of SVO/LVLC solvent/fossil diesel in triple blends to achieve blends with properties that meet engine requirements. These blends must achieve viscosity values within the 2.0–4.5 cSt range, as specified by the EN590:2022 standard, to be suitable for use in current diesel engines. Additionally, they should have calorific values that maximize efficiency, resulting in adequate engine power and reduced fuel consumption.

2. Materials and Methods

2.1. Fusel Oil (FO) as an LVLC Solvent in Double Blends (FO/SVOs) and Triple Blends (Diesel/FO/SVOs)

Sunflower oil (SO) was obtained from a local market; castor oil (CO), 3-methyl-1-butanol, ethanol, isobutanol and n-propanol (≥99.5% purity) were obtained from Panreac (Castellar Del Valles, Barcelona, Spain); and diesel oil was obtained from a local Repsol service station. The standard FO blend was prepared from commercial alcohols in the following proportions: 3-methyl-1-butanol (65%), ethanol (21%), isobutanol (10%) and n-propanol (4%). The main physicochemical properties of the compound used for the blends are shown in Table 1.

Table 1. Kinematic viscosity values and other physicochemical properties of different compounds used as biofuels obtained from the literature [31,39], excluding the kinematic viscosity values which were experimentally measured in this research.

Property	Diesel	Sunflower Oil	Castor Oil	Fusel Oil Blend
Density at 15 °C (kg/m^3)	830	920	962	800.3
Kinematic viscosity at 40 °C (cSt) [1]	3.20 ± 0.01	37.80 ± 0.05	226.20 ± 0.05	4.16 ± 0.01
Calorific value (MJ/kg)	42.8	39.5	37.2	28.3
Flash point (°C)	66	220	228	--
Auto-ignition temperature (°C)	250	316	448	465
Cetane number	51	37	40	42

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

Both SVOs were mixed in different proportions with FO to obtain the FO/SO and FO/CO double blends. FO was added to the SVO at the following volume percentages: 0%, 10%, 30%, 50%, 60%, 70%, 80% and 100%. The double blends that meet the requirements of the European diesel standard EN 590:2022 were selected to prepare the triple blends with fossil diesel in different proportions, expressed as volume percentages: B20, B40, B60, B80 and B100. The percentage of biofuel (FO/SO or FO/CO) added to fossil diesel is expressed as BX, where X is the volume percentage of biofuel added to the fossil diesel. For example, B40 corresponds to 40% biofuel and 60% fossil diesel.

2.2. Characterization of the Physical–Chemical Properties of the Biofuel Blends

The most important physicochemical properties that biofuels must have for use in diesel engines were analyzed, such as kinematic viscosity, density, pour point (PP), cloud point (CP), calorific value and cetane number, all of which were determined either experimentally or from the proper theoretical equations.

The kinematic viscosity of the blends was measured in accordance with the European standard (EN 590:2022) specifications. An Ostwald–Cannon–Fenske capillary viscometer (Proton Routine Viscometer 33200, size 150) was used, operating at 40 °C. The measurement involved the determination of the flow time (t), expressed in seconds, which is the time taken for a fixed volume of liquid to pass between two marked points on the instrument under the influence of gravity. The kinematic viscosity (ν), expressed in centistokes (cSt), was then calculated using Equation (1).

$$\nu = C \cdot t \tag{1}$$

Finally, the calibration constant (C) is 0.037150 (mm^2/s)/s (cSt at 40 °C), as described by the manufacturer for the measurement system. This methodology follows the procedures described in previous studies [31,38], which are in accordance with the ASTM standard D2270-79. The viscosity values reported in this study are the averages of three measurements, with a variation of less than 0.35%.

The cold flow properties were measured using standard methods for cloud point (EN 23015 and ASTM D-2500) and pour point (ASTM D-97). Fuels were added to flat-bottomed glass tubes fitted with a thermometer to measure temperatures from −36 to 120 °C. The tubes were refrigerated for 24 h and checked periodically until the oil showed no movement. Afterward, the appearance of turbidity in the solutions was evaluated, indicating whether the cloud point temperature had been reached. After gradually reducing the temperature, the samples were observed until they stopped flowing, indicating the pour point [31,38]. Each value represents the average of two measurements.

The calorific value, expressed in kJ/kg, was calculated theoretically from the volumetric concentration of each component in the mixture using the Kay mixing rule given in Equation (2):

$$\mathrm{CV} = \Sigma_{\mathrm{i}}\ CViXi \tag{2}$$

where CVi is the calorific value and Xi is the volumetric fraction of each component.

The cetane number of the mixtures was calculated using Equation (3):

$$\mathrm{CN} = \Sigma \mathrm{i}\ CNiXi \tag{3}$$

where CNi is the cetane number and Xi is the volumetric fraction of each component.

2.3. Performance and Exhaust Emissions of a Diesel Engine Electric Generator Fueled with FO/SVO Double Blends and Diesel/FO/SVO Triple Blends

The experimental setup, as detailed in previous research [31,38], involved the evaluation of the blends prepared in this investigation for energy performance and pollutant emissions using a compression ignition diesel engine (model: AYERBE AY-4000 D, Vitoria, Spain) designed for electricity generation. Table S1 shows the main specifications of this engine.

To evaluate the different biofuel blends, the engine was operated at a constant crankshaft rotation speed while varying the electrical power demands. Since the engine speed and torque were kept constant, the electrical power generated reflected the mechanical power produced by the combustion of each biofuel. The electrical power (P) in watts was calculated using Equation (4), as the product of voltage (V) in volts and current (I) in amperes, which were obtained using a voltmeter–ammeter:

$$P = V \cdot I \tag{4}$$

Fuel consumption was calculated by the volume consumed over time under different electrical demands: low (1 kW), medium (3 kW) and high (5 kW). The initial fuel volume for each measurement was 600 mL. In addition, fuel consumption over time for a given task is expressed as the brake-specific fuel consumption (BSFC), measured in g/h·kW, indicating the fuel used per hour per kW of power output. Each test was conducted in triplicate, with the results shown as the average of the three measurements. Standard deviations were calculated to assess experimental errors, which are displayed as error bars in the figures.

The following emissions from the diesel engine were measured: the opacity of the smoke generated during combustion and the quantities of carbon monoxide (CO) and nitrogen oxides (NO_x) as the sum of NO and NO_2. Opacity was measured using an opacimeter TESTO 338 smoke density meter, following the ASTM D-2156 standard method. The smoke emissions were calculated using the Bosch number, a standardized unit, based on the amount of soot on the filter paper. CO and NO_x exhaust gases were measured using a Testo 340 combustion product analyzer. All analyses were calibrated with zero gas prior to each measurement. The results are presented as the average of three measurements, with an experimental error below 6%. All analyses were performed in triplicate, and the precision of each parameter is shown in Table S2.

3. Results and Discussion

3.1. Physicochemical Properties of FO/SVO Double Blends and D/FO/SVO Triple Blends

The viscosity values of the double FO/SVO blends are shown in Table 2. As can be seen, by increasing the addition of fusel oil to any of the two SVOs studied, the viscosity values of SVOs drastically decrease, up to values close to that of conventional fossil diesel. Therefore, by mixing pure castor oil in an appropriate proportion with fusel oil, it is possible to reduce its high viscosity from 226.2 cSt to values that fulfill the requirements of the European standard EN 590:2022.

Table 2. Viscosity values at 40 °C (cSt) of FO/sunflower oil (SO) and FO/castor oil (CO) double blends with increasing volumes of standard fusel oil added. Values are the median of three measurements, with errors expressed as standard deviations.

Property	Blend	FO (% by Volume)							
		0	10	30	50	60	70	80	100
Kinematic viscosity (cSt)	FO/SO	37.80 ± 0.46	32.12 ± 0.26	17.74 ± 0.06	9.88 ± 0.10	7.00 ± 0.03	5.59 ± 0.06	5.09 ± 0.04	3.06 ± 0.01
	FO/CO	226.20 ± 0.55	211.10 ± 0.31	129.20 ± 0.09	26.93 ± 0.12	14.08 ± 0.05	10.91 ± 0.1	4.90 ± 0.09	3.06 ± 0.02

Thus, the proper viscosity values were achieved with 80/20 FO/SVO for sunflower oil and castor oil.

Likewise, Table 3 collects the physicochemical parameters of diesel/FO/SVO triple blends, i.e., kinematic viscosity, density, cloud point, pour point, calorific value and flash point. In addition, diesel was also characterized for comparison.

Table 3. Viscosity values, cloud point, pour point, calorific value and cetane number of diesel/FO/SVO triple blends. Errors are calculated from the average of three measurements.

Nomenclature (% Renewable)	D/FO/SVO	Density (kg/m^3)	Kinematic Viscosity (cSt)	Cloud Point (°C)	Pour Point (°C)	Calorific Value (MJ/kg) [1]	Cetane Number [1]
B0	100/0/0	820 ± 4	3.20 ± 0.04	−6.0 ± 0.4	−16.0 ± 0.8	35.10	51.00
B20SO	80/16/4	815 ± 3	3.52 ± 0.04	−7.8 ± 0.8	−16.5 ± 0.7	34.04	48.95
B20CO	80/16/4	818 ± 5	3.60 ± 0.04	−9.0 ± 0.8	−19.3 ± 0.6	34.02	49.12
B40SO	60/32/8	805 ± 5	4.06 ± 0.04	−8.3 ± 0.6	−19.7 ± 0.5	32.97	46.80
B40CO	60/32/8	815 ± 6	3.81 ± 0.04	−11.0 ± 0.4	−21.4 ± 0.6	32.95	47.24
B60SO	40/48/12	798 ± 4	4.20 ± 0.04	−9.0 ± 0.8	−20.0 ± 0.9	31.91	44.85
B60CO	40/48/12	810 ± 4	3.92 ± 0.09	−12.0 ± 0.8	−22.5 ± 0.4	31.87	45.36
B80SO	20/64/16	782 ± 5	4.42 ± 0.07	−10.8 ± 0.3	−20.3 ± 0.7	30.84	42.80

Table 3. *Cont.*

Nomenclature (% Renewable)	D/FO/SVO	Density (kg/m^3)	Kinematic Viscosity (cSt)	Cloud Point (°C)	Pour Point (°C)	Calorific Value (MJ/kg) [1]	Cetane Number [1]
B80CO	20/64/16	808 ± 7	4.70 ± 0.02	−13.0 ± 0.7	−23.0 ± 0.7	30.79	43.48
B100SO	0/80/20	742 ± 1	5.09 ± 0.04	−11.5 ± 0.7	−23.7 ± 0.5	26.95	36.55
B100CO	0/80/20	806 ± 6	4.90 ± 0.09	−14.0 ± 0.5	−24.0 ± 0.3	29.72	42.00

[1] The flash point values and cetane number were calculated by using Equations (2) and (3), respectively.

As expected, adding fossil diesel to the double blends (B100SO and B100CO) promotes a reduction in the viscosity since fossil diesel exhibits a lower viscosity value (3.20 cSt). In fact, the higher the amount of diesel in the blend, the lower the viscosity of the mixture, with both B20 blends having exhibited the lowest viscosity values of the triple blends. An analogous tendency was observed for the density values.

Considering the cold flow properties of the blends (pour point and cloud point), a notably improvement in both parameters with respect to diesel was observed by mixing B100 with diesel. Thus, in blends with sunflower oil, the CP varies from −6 °C (diesel) to −11.5 °C (B100SO). A similar behavior was observed for PP measurements, ranging from −16 °C (diesel) to −23.7 °C (B100SO). Regarding the results obtained with castor oil, the decrease observed in both parameters, CP and PP, was significant. The CP decreased from −6 °C (diesel) to −14 °C (B100CO), and the PP decreased from −16 °C (diesel) to −24 °C. These changes enhance the usefulness of these blends in cold climates. The calorific and cetane number values obtained for the triple blends decreased as the percentage of B100SO or B100CO increased in the mixture, which was expected taking into account the lower energetic density and cetane number of the pure FO/SVO double blends.

3.2. Mechanical Performance of Diesel/Fusel Oil/Straight Vegetable Oil Triple Blends

Figure 1 shows the performance of the engine fueled with all the (bio)fuels studied. In addition, fossil diesel and pure biofuels were also tested for comparison. As can be seen, for all the blends tested, the power output increased as the engine load increased from 0 to 4 kW, and it seemed to stabilize at this value, with values at 5 kW being similar to or slightly lower than those at 4 kW. Additionally, for the same engine load value, the power output values decreased as the percentage of FO/SVO biofuel mixed with diesel increased, with this reduction being more pronounced at higher engine loads (4 and 5 kW), especially for blends containing sunflower oil. For instance, at 5 kW, B100SO exhibited a power output value of 1.8 kW, which was 40% lower than that of fossil diesel (2.9 kW), whereas B100CO displayed a value of 2.25 kW, only 20% lower. This can primarily be attributed to the lower energy content of the studied blends compared to fossil diesel, as has previously been observed with other organic solvents [31]. The better performance of the D/FO/CO blends could be explained by their slightly higher cetane numbers compared to the D/FO/SO blends. In fact, blends that have similar cetane number values exhibit comparable power output values, while the blends B100SO and B100CO, which have a cetane number difference of one unit, show the greatest differences in power output.

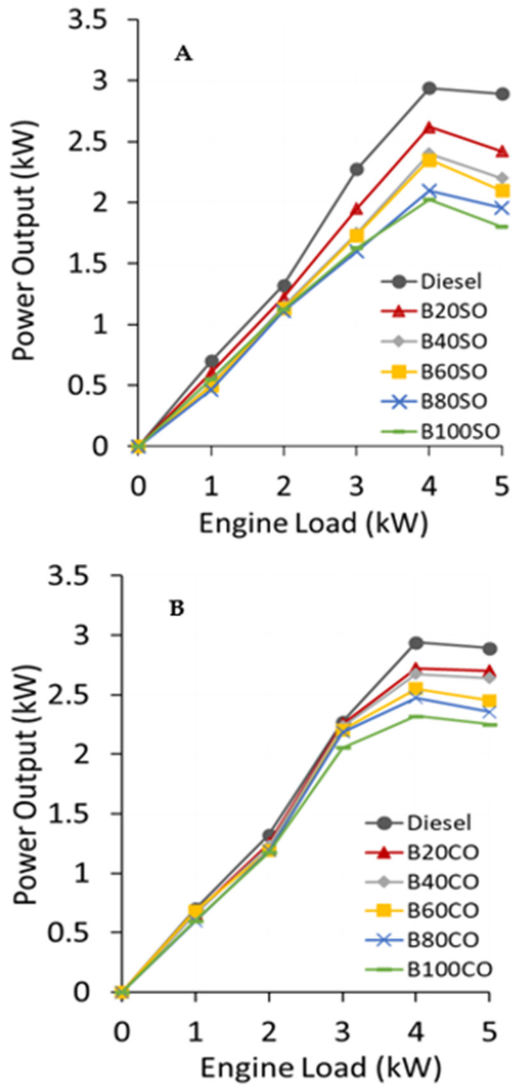
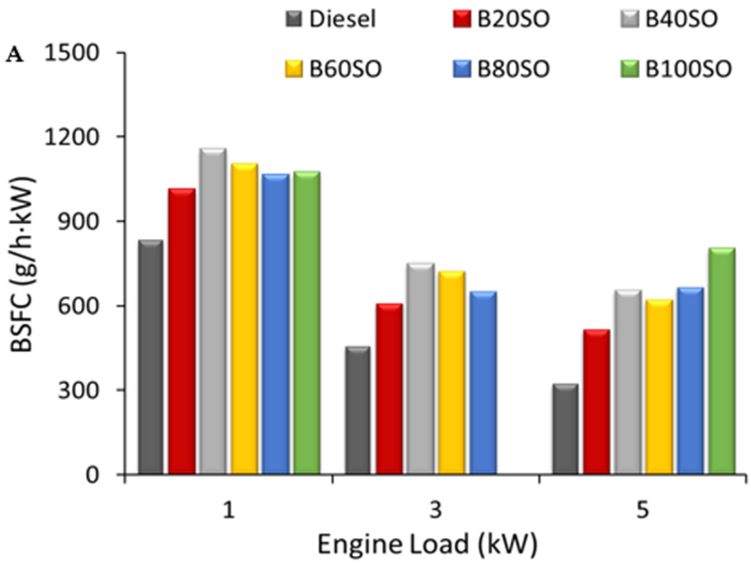


Figure 1. Power output (in kW) based on the different engine loads (in kW) when operating with triple blends: (**A**) D/FO/SO and (**B**) D/FO/CO.

3.3. Brake-Specific Fuel Consumption (BSFC)

BSFC is one of the most important parameters for evaluating the performance characteristics of a (bio)fuel, and lower BSFC indicates greater engine efficiency for a given power output. Figure 2 shows the BSFC values for different engine loads with the D/FO/SO (Figure 2A) and D/FO/CO (Figure 2B) triple blends. Likewise, the values obtained with diesel, FO/SO and FO/CO were also depicted for comparison. Independently of the vegetable oil employed and engine load, diesel always exhibited the lowest BSFC, indicating that diesel would be the most efficient fuel. In addition, for all the blends tested, the BSFC values decreased as the engine load increased from 1 kW to 3 kW and then stabilized. This reduction in BSFC with higher engine load may be linked to increased cylinder temperature, which improves the combustion process [31,40]. Furthermore, for the same power output, a higher diesel substitution in the triple blend leads to an increase in BSFC values, which makes sense considering that diesel is the most efficient fuel. However, this increase seems to stabilize starting from the B60 blend for both the sunflower oil blends and the castor oil blends. Comparing the values obtained with the SO and CO blends, it can be observed that the BSFC values for the blends with castor oil are slightly lower than those of the sunflower oil blends. This fact can be attributed to the higher energy density of the fuels containing castor oil, which would improve the engine's power output. Additionally, the lower cetane number of the sunflower oil blends extends the ignition delay, resulting in more fuel being burned during the premixed combustion phase [38]. These results are in agreement with those reported in the literature [31,41,42].



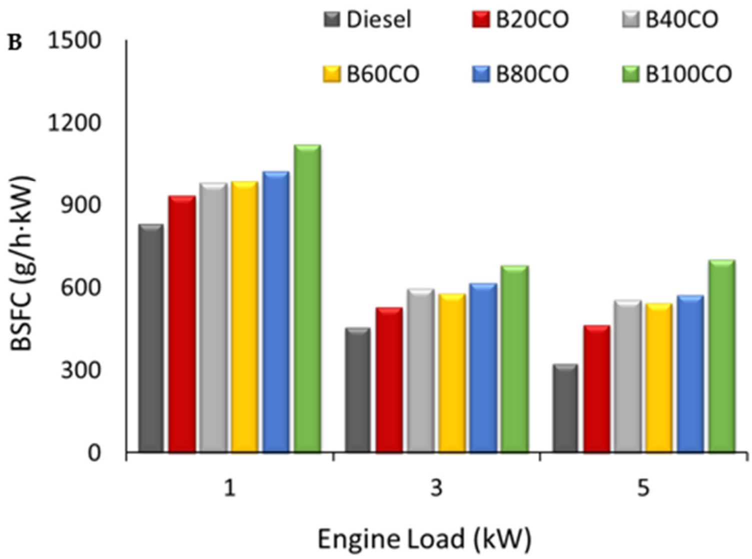


Figure 2. BSFC values of triple blends, (**A**) D/FO/SO and (**B**) D/FO/CO, at low, medium and high engine loads (1, 3 and 5 kW, respectively).

3.4. Exhaust Emissions from Diesel Engine

3.4.1. Opacity of Smoke Emissions

Figure 3 shows the opacity values as a function of engine load for the different (bio)fuel blends containing SO (Figure 3A) or CO (Figure 3B). The results indicate that, independently of the vegetable oil employed, all the triple blends significantly reduced smoke emissions compared to conventional diesel, except B20SO and B20CO, which displayed a similar behavior to diesel at an engine load of between 1 and 4 kW. This reduction becomes more pronounced as the volume of FO/SVO in the triple blend rises. In fact, the highest difference in opacity values was found for both B100 blends, decreasing by up to 60% in the case of B100SO and a remarkable 90% for B100CO at high energy demands (5 kW). As described in the literature [43], these results can be explained by the higher proportion of oxygen in the triple blends compared with diesel, which promotes the oxidation of carbon, leading to better combustion efficiency. When comparing the vegetable oils, the blends containing castor oil produced lower opacity values than those with sunflower oil. Castor oil has an additional hydroxyl group in its structure and, therefore, the oxygen content of D/FO/CO is higher than that of D/FO/SO. In addition, castor oil, which consists mainly of ricinoleic acid, has a lower level of unsaturation compared to the linoleic acid in sunflower oil, helping to prevent the formation of polycyclic aromatic hydrocarbons (PAHs) from the decomposition of these unsaturated compounds, which could be transform into soot particles [44].

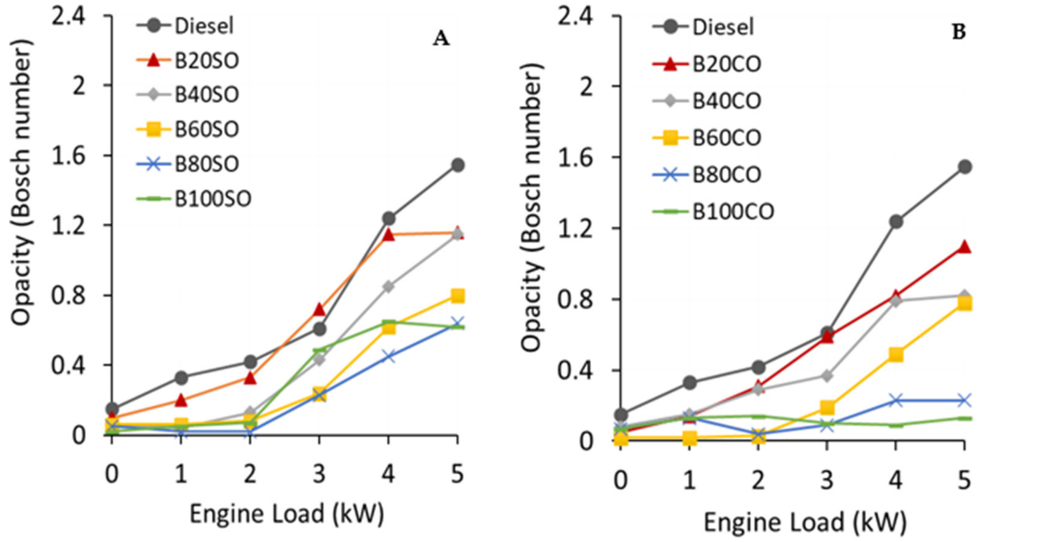


Figure 3. Opacity (Bosch number) produced (from 0 to 5 kW) by triple blends, (**A**) diesel/FO/SO and (**B**) diesel/FO/CO, at different engine loads.

3.4.2. Smoke Carbon Monoxide (CO) Emissions

With the D/FO/SO triple blends, two tendencies are observed depending on the engine load values, Figure 4. At low and medium engine loads (1, 2 and 3 kW), the triple blends exhibited similar or, in some cases, lower CO emissions compared to fossil diesel. However, blends with a higher proportion of FO/SO, such as B80SO and B100SO, displayed higher CO emissions at these engine loads. Conversely, at 4 and 5 kW, all the D/FO/SO triple blends showed lower CO emissions compared to fossil diesel. In contrast, the D/FO/CO triple blends consistently exhibited lower CO emissions than fossil diesel, regardless of the engine load. However, similar to the sunflower oil blends, those with a high proportion of FO/CO had the highest CO emissions among the triple blends.

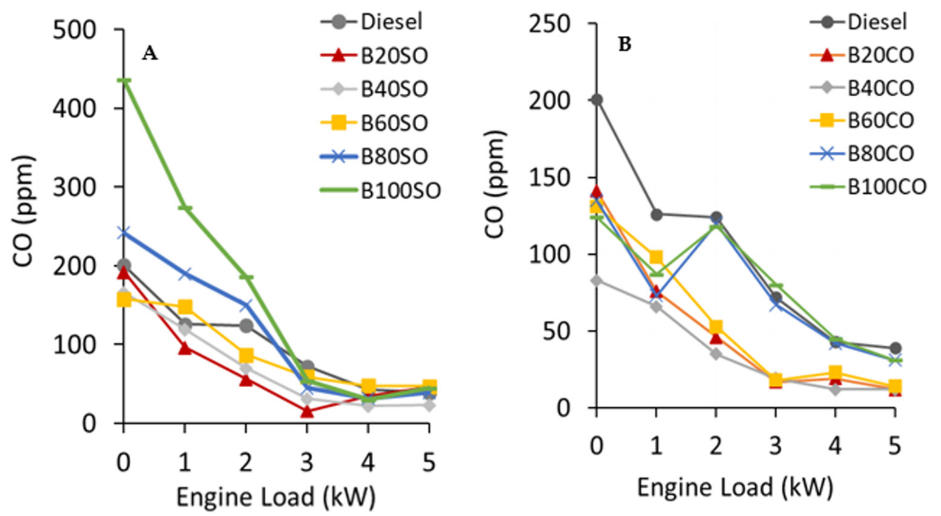


Figure 4. Carbon monoxide (CO) emissions (in ppm) generated at different engine loads: (**A**) D/FO/SO and (**B**) D/FO/CO.

Therefore, in both cases, the triple blends containing between 20 and 40% biofuel showed the best behavior in terms of CO emission reduction, which can be explained by the higher calorific value and cetane number of the B20 and B40 mixtures in comparison with the other blends.

In both cases, the B100 blends generated high levels of carbon monoxide (CO). Among the fuels studied, those containing the lowest proportion of biofuel (20%) showed the best results in terms of CO emission reduction. This is related to the higher calorific value and cetane number of the B20 mixtures compared to the rest. Furthermore, it is striking how the CO levels are even lower than those obtained with diesel when the B20CO mixture is used at all the power values studied.

3.4.3. Nitrogen Oxide (NO_x) Emissions

Figure 5 shows the NO_x emissions produced by the engine under different loads for all the studied blends. In general, the NO_x emissions increased as the engine load increased, which was expected since at high engine loads, a rise in the temperature and pressure inside the cylinder occurs, promoting the formation of NO_x, as has previously been reported [45]. Nevertheless, it must be highlighted that all the blends emitted less NO_x than fossil diesel, with this reduction becoming higher as the engine load increased. In addition, the substitution of diesel with either FO/SO or FO/CO promotes a decrease in NO_x emissions. Thus, the best results were obtained with B80SO, B100SO and B100CO, attaining up to an 85% reduction in NO_x emissions with this last blend. This fact is a consequence of the lower calorific value of the blends compared to diesel (Table 3), which decreases the formation of NO_x [36].

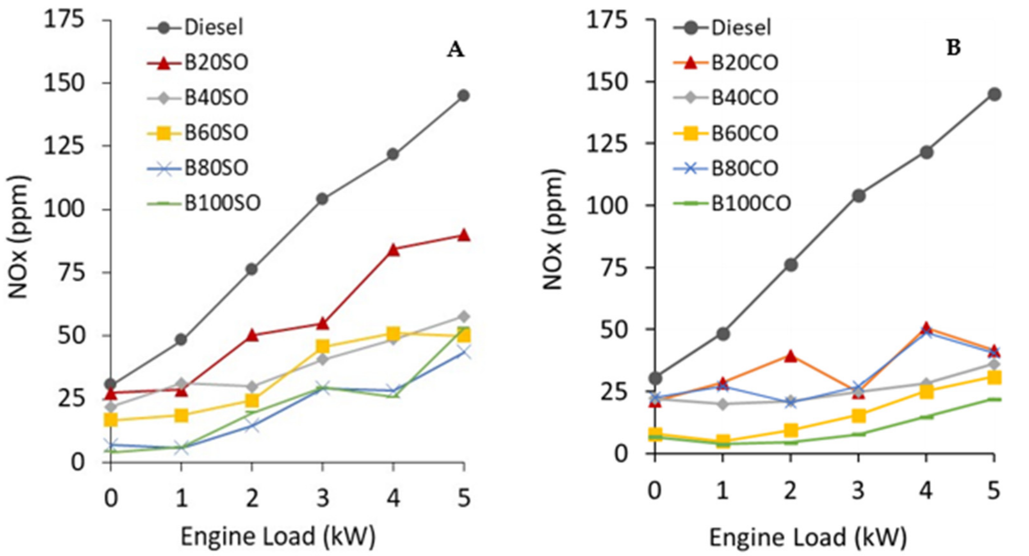


Figure 5. Nitrogen oxide (NO_x) emissions (in ppm) generated at different engine loads: (**A**) D/FO/SO and (**B**) D/FO/CO.

4. Conclusions

Fusel oil, a by-product of the sugar industry, was used as an LVLC solvent for two straight vegetable oils, sunflower oil and castor oil. An 80% v/v addition of fusel oil was necessary to reduce the viscosity of both oils to levels that meet the European and American biodiesel regulations. Then, diesel/fusel oil/vegetable oil (sunflower or castor oil) triple blends were prepared by adding different amounts of diesel to a previous selected fusel oil/vegetable oil double blend. These blends were characterized by measuring the most relevant physicochemical properties and tested in a diesel engine.

In general, triple blends significantly improve the cold flow properties of diesel. Regarding the mechanical performance of the engine, as the proportion of biofuel in the blends increases, the power output decreases, especially at high power levels (4–5 kW).

The most significant decrease was observed with the B100SO blend, which showed a 38% reduction in power with respect to diesel. Nevertheless, the blends with castor oil maintained power values close to those of diesel even at higher power levels. For instance, diesel produced 2.9 kW, while the B20CO and B40CO blends performed well at 2.7 kW and 2.62 kW, respectively. In terms of fuel consumption, substituting diesel with biofuel led to an increase in the brake-specific fuel consumption (BSFC). However, the blends with castor oil exhibited better performance compared to those with sunflower oil.

Regarding emissions, all the triple blends showed lower opacity values than diesel, with the B80CO and B100CO blends reducing diesel opacity by 92%. A similar trend was observed for NO_x emissions, with the greatest reduction (85%) seen in the B100CO blend. For CO emissions, the BXSO blends produced similar values to diesel, although the blends with high biofuel content emitted more carbon monoxide at low power levels than diesel. Conversely, the castor oil blends consistently outperformed diesel in terms of CO emissions, regardless of the biofuel content.

Overall, the castor oil blends demonstrated superior results compared to the sunflower oil blends in terms of both mechanical performance and emissions. Among these, the B40CO blend appears to offer the best compromise between engine performance (with a power and fuel consumption similar to diesel) and significantly improved emissions. Therefore, it can be concluded that up to 40% of diesel can be optimally substituted using fusel oil and castor oil.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/fuels5040036/s1. Table S1: Technical specifications of the diesel engine electric generator set; Table S2: Accuracy of the measurements for different parameters.

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