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Outlook for Direct Use of Sunflower and Castor Oils as Biofuels in Compression Ignition Diesel Engines, Being Part of Diesel/Ethyl Acetate/Straight Vegetable Oil Triple Blends

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Abstract: Today, biofuels are indispensable in the implementation of fossil fuels replacement processes. This study evaluates ethyl acetate (EA) as a solvent of two straight vegetable oils (SVOs), castor oil (CO), and sunflower oil (SO), in order to obtain EA/SVO double blends that can be used directly as biofuels, or along with fossil diesel (D), in the current compression-ignition (C.I.) engines. The interest of EA as oxygenated additive lies not only in its low price and renewable character, but also in its very attractive properties such as low kinematic viscosity, reasonable energy density, high oxygen content, and rich cold flow properties. Relevant fuel properties of EA/SVO double and D/EA/SVO triple blends have been object of study including kinematic viscosity, pour point (PP), cloud point (CP), calorific value (CV), and cetane number (CN). The suitability of using these blends as fuels has been tested by running them on a diesel engine electric generator, analyzing their effect on engine power output, fuel consumption, and smoke emissions. Results obtained indicate that the D/EA/SO and D/EA/CO triple blends, composed by up to 24% and 36% EA, respectively, allow a fossil diesel substitution up to 60–80% providing power values very similar to conventional diesel. In addition, in exchange of a slight fuel consumption, a very notable lessening in the emission of pollutants as well as a better behavior at low temperatures, as compared to diesel, are achieved.

Keywords: ethyl acetate; castor oil; sunflower oil; straight vegetable oils; vegetable oil blends; biofuels; diesel engine; soot emissions; engine power output

1. Introduction

Nowadays, fossil fuels such as coal, oil, and natural gas represent approximately 80% of the world energy consumption. Furthermore, it is expected that the industrialization, together with the growing population will increase energy demand in the next years, with the consequent negative effects on global climate [1]. Thus, it is mandatory the use of renewable energy sources, such as solar, wind, and biofuels, to avoid damaging the environment [2]. In this scenario, the production of fuels from biomass has become as one of the best options to provide renewable liquid fuels for transportation. On one hand, until today, biodiesel has been the mostly employed biofuel as substitute of fossil diesel. Biodiesel is produced through transesterification of triglycerides from vegetable oils (palm, corn, soybean, sunflower, etc.) with methanol or ethanol, being a sustainable and environmentally friendly

alternative. Furthermore, it has excellent properties operating in the current diesel engines, not only by itself but also in blends with fossil diesel. The main drawback in the biodiesel production is the generation of glycerol as by-product in around 10 wt. % of the total biodiesel, which makes the biodiesel production on an industrial scale economically unfeasible. Hence, the competitive commercialization of biodiesel is still a challenge [3].

On the other hand, the use of SVOs as fuel was already initiated by Rudolph Diesel, when he made the first demonstration of his compression ignition engine at the 1900 Paris Exposition with peanut oil, and their usage continued until the 1920s, when diesel engine was adjusted for running with a fraction of fossil petroleum (currently known as No. 2 diesel fuel) [4]. Nowadays, SVOs are considered a very attractive alternative to fossil fuels because of their renewable nature and their high availability. Moreover, some vegetable oils exhibit physicochemical properties analogous to conventional diesel, excluding their high kinematic viscosity that lead to engine problems (poor fuel atomization and coke formation). That is the reason why the use of vegetable oils as drop-in biofuels requires previous treatments (i.e., transesterification reaction to obtain biodiesel) that reduce their viscosity values.

Recently, it has emerged a new methodology, to the direct usage of SVOs as biofuels in C.I. engines, consisting of blending vegetable oil with a lower viscosity solvent (LVS), instead of undergoing them chemical process. This approach has the advantage of avoiding the energetic and economic costs associated to the transesterification process for the biodiesel production. Thereby, the high viscosity of oils can be reduced to limits imposed by EN 590 standard to operate in the present diesel engines. In this respect, an intensive investigation about different LVSs used as fuels has been reported in literature, including different alcohols (methanol, ethanol, and n-butanol) [5–8] and light vegetable oils (eucalyptus, camphor, orange, and pine oils) [9–12]. Generally, these compounds have been designated as LVLC (low viscous low cetane), since they exhibit low viscosity and energy density values and sometimes, low cetane number, as compared to conventional diesel [13].

Following this strategy, the low viscosity of gasoline has been harnessed to use it as LVS, in mixtures with SVOs from several seeds (canola, sunflower, camelina, and carinata). In this way, SVO/gasoline blends, with a content of gasoline ranging between 10 and 30% in volume, have allowed a higher level of fossil fuel substitution than their counterparts blends using fossil diesel. Aside from adequate density and viscosity values for being successfully employed in a diesel engine, the thermal efficiency of these blends was close to conventional diesel, although the biofuel consumption was approximately 10% higher than that of diesel fossil [14]. Gasoline/SVO blending methodology has been more recently applied even with castor oil, which has a high viscosity value of 226.2 cSt. Furthermore, this is non-edible oil, avoiding ethical problems [15]. Thus, it has been reported that diesel/gasoline/castor oil triple blends generate similar perform to fossil diesel, allowing a substitution of fossil fuel up to 24%. For its part, the same triple blend using sunflower oil provided 36% of fossil fuel substitution. Other advantages obtained with these diesel/gasoline/SVO blends were a considerably reduction in smoke opacity as well as a significative improvement of flow properties at cold climates [15].

In addition to gasoline, diethyl ether (DEE) [16] and acetone (ACE) [17] have been employed as effective LVS of CO and SO, in triple blends with diesel. Both additives can be obtained from ethanol which, in turn, can be obtained from biomass, making the process more sustainable. Both of these oxygenated additives were able to lower soot emissions considerably, maintaining a good engine performance. In spite of favorable fuel properties of DEE and ACE [16,17], the low calorific power was revealed as the limiting factor to incorporate percentages of biofuel LVS/SVO higher than 40%. Several studies have also been published fueling a diesel engine with diesel/DEE/SVOs triple blends. Among the oils employed, it can be highlighted cashew nut shell oil [18], bael oil [19], as well as sunflower and castor oil [16].

Additionally, ethyl acetate has been evaluated as a potential oxygenated biofuel since can be readily produced from renewable feedstocks by several processes such as the direct esterification of ethanol with acetic acid [20], through dehydrogenative dimerization of bioethanol with liberation of molecular hydrogen [21], or by a biochemical process that includes acidogenic fermentation of

agricultural wastes materials [22]. EA is an environmentally friendly compound that exhibit very low kinematic viscosity, high miscibility with VOs and fossil diesel, high oxygen content, high auto-ignition temperature which makes fuel safer for handling and transportation, and good cold flow properties (very low PP and CP values) to improve winter engine performance. Hence, the application of EA as solvent of second-generation oils, i.e., castor oil or waste cooking oils, could be an inexpensive and valuable alternative to accomplish the replacement of fossil fuel, which is mandatory to realize now with the operating car fleet.

Prominently improvements have been reported in brake thermal efficiency (BTE) but with a slightly higher brake specific fuel consumption (BSFC) using ethyl acetate as fuel or additive for C.I. engines [23]. In addition, exhaust temperature as well as CO, HC, and NO_x emissions have been diminished with this fuel [22–24]. Similarly, the addition of 10% EA to diesel has showed similar brake specific fuel consumption respect to diesel, but with a notable reduction of soot emissions [25]. On the other hand, the addition of ethyl acetate to some bio-oils has provided important advantages to enhance the storage stability, thanks to its non-hygroscopic nature [26]. This compound has been also applied in blends with gasoline, leading to decrease in CO and HC emissions by around 50% due to high oxygen content of ethyl acetate [27]. Moreover, EA has been also used as a surfactant to emulsify a 50% diesel/50% ethanol mixture, resulting in an increase in BTE and a decrease in BSFC, smoke density, particulate matter, exhaust gas temperature, HCs and CO [28].

In this research, the possibility of replacing fossil diesel by renewable biofuels obtained by blending EA with SVOs, either sunflower or castor oil, has been evaluated. First, the optimum EA/SVO blends that meet with viscosity requirements according to European normative, were chosen to be subsequently mixed with diesel fossil. Then, the different EA/SVO double and D/EA/SVO triple blends have been tested in a C.I. engine. Several parameters were measured, i.e., power output, fuel consumption and soot emissions. Moreover, some of the most crucial fuel properties, e.g., calorific value, cetane number, cloud point, pour point, and kinematic viscosity were determined to ascertain the suitability of the mixtures as (bio)fuels. In addition, all these measurements were performed with fossil diesel for comparison purposes.

2. Materials and Methods

Table 1 shows the main physicochemical properties of diesel, sunflower oil, castor oil, and ethyl acetate.

Table 1. Physicochemical properties of fossil diesel, sunflower oil, castor oil, and ethyl acetate [22,23,27,29,30]. Kinematic viscosity values have been experimentally measured in the present work.

Property	Diesel	Sunflower Oil	Castor Oil	Ethyl Acetate
Density at 15 °C (kg/m ³)	830.0	920.0	962.0	906.0
Kinematic viscosity at 40 °C (cSt)	3.20	37.80	226.20	0.45
Oxygen content (wt. %)	0	10	15	36
Calorific value (MJ/L)	35.52	36.43	38.00	21.55
Flash point (°C)	66.0	220.0	228.0	−4.0
Auto-ignition temperature (°C)	250	316	448	460
Cetane number	51	37	40	10

2.1. Ethyl Acetate/Vegetable Oil Double Blends and Diesel/Ethyl Acetate/Vegetable Oil Triple Blends

Sunflower oil was supplied by a local market, castor oil was purchased from Panreac Company (Castellar Del Vallès, Spain), and ethyl acetate was acquired from Sigma-Aldrich Chemical Company (St. Louis, MO, USA, ≥99.8% purity). Fossil diesel, used as reference fuel, was purchased from local Repsol service station. The experimental methodology is shown in Figure 1. The EA/SO and EA/CO double blends, and D/EA/SO and D/EA/CO triple blends were prepared by manual mixing of the

different components at room temperature. The mixtures were designated as B20, B40, B60, B80, and B100, where 100% fossil diesel is indicated as B0 and EA/SVO blend is B100, Table 2.

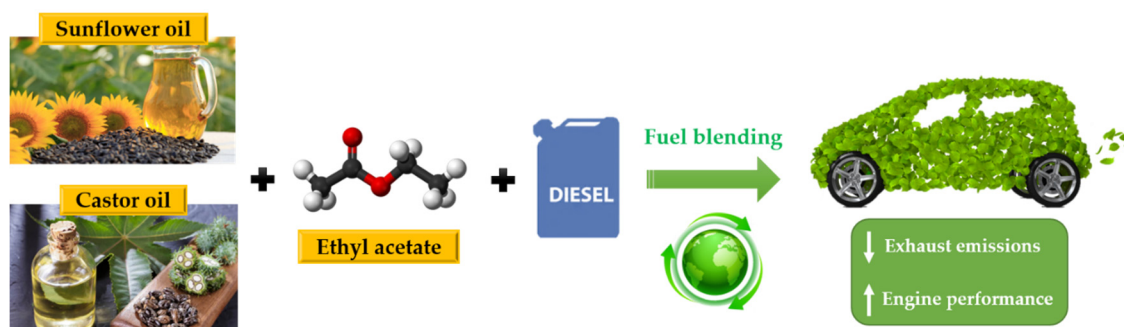


Figure 1. Scheme of experimental methodology.

Table 2. Diesel/ethyl acetate/sunflower oil blends containing 40% ethyl acetate, and diesel/ethyl acetate/castor oil blends containing 45% ethyl acetate.

Blend	Nomenclature	B0	B20	B40	B60	B80	B100
	% D	100	80	60	40	20	0
D/EA/SO	% EA	0	8	16	24	32	40
	% SO	0	12	24	36	48	60
D/EA/CO	% EA	0	9	18	27	36	45
	% CO	0	11	22	33	44	55

2.2. Characterization of the (Bio)fuel Blends

A fuel is defined by a series of properties that determine its performance in the engine, and consequently, its commercialization. Blends properties, including kinematic viscosity, pour point, cloud point, calorific value and cetane number, were determined through predictive equations or experimental methodology described below.

2.2.1. Kinematic Viscosity

The existence of maximum and minimum limits for the viscosity of a fuel is required for ensuring the engine works without any risk, and fuel injection system is unaffected [31]. The viscosity measures of mixtures were carried out in an Ostwald-Cannon-Fenske capillary viscometer (Proton Routine Viscometer 33,200, size 150) at 40 °C, according to the European standard EN ISO 3104 test method and following the methodology described in previous works [16,17].

2.2.2. Pour Point (PP) and Cloud Point (CP)

Cloud point and pour point are cold flow properties responsible for solidification of fuel at cold operating conditions. At low temperatures, fuel crystallization results in clog to fuel lines and filters, which causes problems to start engine as a consequence of the lack of fuel [32].

CP and PP measurements have been performed following the EN 23015/ASTM D-2500 and ISO 3016/ASTM D97 standards, respectively. The experiments are performed in accordance with the procedure described in previous investigations [16,17]. All results are presented as average values of duplicate determinations and error is calculated as standard deviation.

2.2.3. Calorific Value

Calorific value (CV) is a crucial fuel property since it is directly related to power output of the engine [30]. This parameter has been determined following the Kay Mixing rule (Equation (1)):

$$CV = \sum_i CV_i X_i \quad (1)$$

where CV_i is the calorific value of each component and X_i is the volumetric fraction of every component [33].

2.2.4. Cetane Number

Cetane number (CN) is one of key parameters to define the ignition quality of a fuel in a diesel engine. In general, CN of fuels must be above 51, as according norm EN 590, to facilitate autoignition and provide short ignition delay. However, CN values too high can cause the ignition delay is very short and combustion may start before the fuel and air are properly mixed, leading to an incomplete combustion [34]. Experimental determination of the CN of a fuel is a procedure tedious and expensive, and therefore estimation of cetane number of mixtures is carried out using the following simple equation:

$$CN = \sum_i CN_i X_i \quad (2)$$

where CN_i is the cetane number of each component and X_i is the volumetric fraction of every component [33].

2.3. Performance of a Diesel Engine-Electrogenerator Set Fuelled with EA/SVO and D/EA/SVO Blends

The performance and soot emissions of a diesel engine-electric generator set have been analyzed following the same experimental methodology previously reported [15–17]. Engine specifications are shown in Table 3. In addition, the operating conditions of the engine were not modified during the tests.

Table 3. Specifications of the Diesel Engine-Electrogenerator Set.

Model	AYERBE 4000 Diesel
Alternator	LINZ-SP 10MF 4.2 KVA
Engine	YANMAR LN-70 296 cc 6.7 HP
Speed	3000 rpm
Maximum power	5 KVA
Voltage	230 V
Consumption	1.3 L/H (75%)

The electrical power (P) in watts can be easily calculated using a voltmeter-ammeter by application of Equation (3):

$$P = V \cdot I \quad (3)$$

where V is the potential difference or voltage (in volts) and I is the electric current intensity or amperage (in amps).

The contamination degree (measured in Bosch number units) was determined from the opacity of the smoke generated in the combustion process, using a smoke density tester. In this research, the smoke density was measured by an opacimeter-type TESTO 338 density gauge (or Bosch smoke meter), Figure 2, according to standard method ASTM D-2156. The measurement range for smoke density is 0 to 2.5 with ± 0.03 accuracy, where the value 0 represents total clarity on the paper and 2.5 is the corresponding value to 100% cloudy.



Figure 2. Mechanical and environmental characterization of diesel engine-electrogenerator set [17].

The fuel consumption of diesel engine (in liters per hour) is calculated supplying to engine an identical fuel volume (0.5 L) of each proposed (bio)fuel and measuring the volume consumed after a specified time. These measurements were performed at three engine loads that are representative of low (1 kW), medium (3 kW), and high (5 kW) power demands of the engine. Tests were done in triplicate and the results are shown as average along with standard deviation, represented as error bars.

3. Results and Discussion

3.1. Fuel Properties of EA/SVO Double Blends, and D/EA/SVO Triple Blends

The kinematic viscosity results for ethyl acetate/sunflower oil (EA/SO) and ethyl acetate/castor oil (EA/CO) double blends are shown in Table 4. As can be noticed, a remarkable decrease in the viscosity values of SVOs was achieved by the use of ethyl acetate as solvent, as expected. In fact, only a 20% of EA reduce the viscosity of CO from 226.2 cSt to 26.26 cSt, while the same proportion of EA get to decrease the SO viscosity value from 37.80 to 11.52 cSt. Thus, increasing the volume of ethyl acetate in the blends we are able to fulfill the viscosity values for being employed as fuels in C.I. engines, as establish the European standard EN 590 ISO 3104. It is noticeable the stronger influence of EA on castor oil, in comparison with SO, to reduce the very higher viscosity value of this oil. Following the European normative (viscosities between 2.0 and 4.5 cSt), the blends with suitable viscosity values which were selected for the reformulation of diesel are obtained with a proportion 40/60 of EA/SO and 45/55 of EA/CO, Table 4.

Table 4. Viscosity values at 40 °C (cSt, centistokes) of ethyl acetate (EA)/sunflower oil (SO) and EA/castor oil (CO) double blends. Errors expressed as standard deviation have been calculated from average three measurement.

Property	Blend	Ethyl Acetate (% by Volume)					
		0	20	40	45	50	100
Kinematic viscosity (cSt)	EA/SO	37.80 ± 0.46	11.52 ± 0.30	4.42 ± 0.04	3.76 ± 0.06	3.16 ± 0.06	0.45 ± 0.01
	EA/CO	226.20 ± 0.55	26.26 ± 0.06	5.97 ± 0.07	4.47 ± 0.06	3.46 ± 0.12	0.45 ± 0.01

The best EA/SO and EA/CO double blends, containing 40% and 45% of ethyl acetate, respectively, were employed to prepare the D/EA/SVO triple mixtures by addition of different volumetric proportions to fossil diesel, which vary from 20% to 80% (B20 to B80). The kinematic viscosity results of triple mixtures are shown in Figure 3. As can be seen, the incorporation of the EA/SVO biofuels, from B0

to B100, promotes a slight increment in viscosity values of all blends, which was expected since they exhibit higher viscosities than fossil diesel. In general, the viscosities of the blends fulfill with European regulations EN 590, being in the range of 3.23–4.47 cSt.

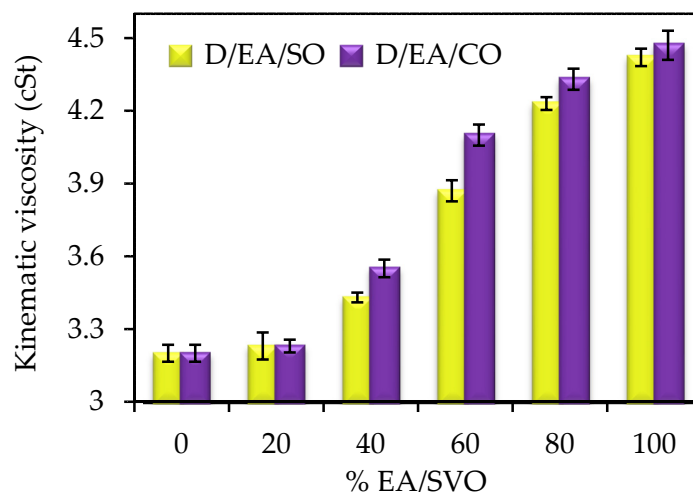


Figure 3. Kinematic viscosity values at 40 °C of diesel/ethyl acetate/sunflower oil (D/EA/SO) and diesel/ethyl acetate/castor oil (D/EA/CO) triple blends. The results are the average of three measurements and errors are represented as standard deviation through error bars.

Cloud point, pour point, calorific values, and cetane number of triple blends with SO are collected in Table 5, whereas those with CO are collected in Table 6. Flow properties of diesel at low temperatures are greatly improved by the presence of EA in the D/EA/SVO blends, independently on the vegetable oil employed. In fact, a small percentage of ethyl acetate (8% in B20 blends with SO) generates a significant decrease in the pour point (PP), from -16.0 to -19.9 °C, and in the cloud point (CP), from -6.0 to -12.0 °C. Likewise, the triple blend with 11% of castor oil and 9% of EA reaches a reduction in PP and CP of up to 5 °C and 7 °C, respectively. Based on these results, the blends which exhibit the best behavior at low temperature are composed by 40% of biofuel, i.e., 60/16/24 (D/EA/SO) and 60/18/22 (D/EA/CO), which has conducted to a reduction of up to 4.2–6.0 °C in PP and 7.6–9.8 °C in CP. Particularly, blends with castor oil as SVO allow to obtain a slight improvement of CP and PP than their counterparts with sunflower oil. This behavior is very similar to that found using others compounds such as diethyl ether [16] or acetone [17] as additives in triple mixtures with the SVOs.

Table 5. Cloud point, pour point, calorific value and cetane number of diesel/ethyl acetate/sunflower oil triple blends (EA = 40%). Errors have been calculated from average three measurement and expressed as standard deviation.

Diesel/Ethyl Acetate/Sunflower Oil Blend						
Nomenclature (% Renewable)	B0 100/0/0	B20 80/8/12	B40 60/16/24	B60 40/24/36	B80 20/32/48	B100 0/40/60
Cloud point (°C)	-6.0 ± 1.0	-12.0 ± 1.0	-13.6 ± 0.9	-12.5 ± 0.5	-12.2 ± 0.8	-10.6 ± 1.0
Pour point (°C)	-16.0 ± 1.2	-19.9 ± 0.8	-20.2 ± 1.1	-18.5 ± 0.7	-18.1 ± 1.0	-19.0 ± 0.8
Calorific value (MJ/L)	35.52	34.51	33.50	32.49	31.49	34.38
Cetane number	51.00	46.04	41.08	36.12	31.16	26.20

Table 6. Cloud point, pour point, calorific value and cetane number of diesel/ethyl acetate/castor oil triple blends (EA = 45%). Errors have been calculated from average three measurements and expressed as standard deviation.

Diesel/Ethyl Acetate/Castor Oil Blend						
Nomenclature (% Renewable)	B0 100/0/0	B20 80/9/11	B40 60/18/22	B60 40/27/33	B80 20/36/44	B100 0/45/55
Cloud point (°C)	-6.0 ± 1.0	-13.0 ± 1.0	-15.8 ± 0.7	-12.0 ± 0.6	-11.0 ± 1.0	-12.2 ± 1.0
Pour point (°C)	-16.0 ± 1.2	-21.0 ± 1.0	-22.0 ± 1.0	-19.4 ± 0.8	-18.5 ± 0.6	-20.0 ± 0.9
Calorific value (MJ/L)	35.52	34.54	33.55	32.57	31.58	30.60
Cetane number	51.00	46.10	41.20	36.30	31.40	26.50

Regarding the calorific values for triple blends (Tables 5 and 6), as the percentage of ethyl acetate in the blend increase, the calorific value decrease. This is logical since EA exhibits a lower calorific value than both, diesel, and SVOs. Therefore, the most favourable results are found in the B20 triple blends, which have the highest calorific values, 34.51 MJ/L for the blends with sunflower oil (2.84% lower than diesel), and 34.54 MJ/L for the blends with castor oil (2.76% lower than diesel), while the B80 triple blends with highest biofuel content (80%) show the lowest calorific values of 31.49 and 31.58 MJ/L, i.e., 11.35 and 11.09% lower than diesel, for SO and CO blends respectively. As can be observed, there is no appreciable differences between calorific values of blends containing either sunflower or castor oil, since both oils display a comparable calorific power (see Table 1). Overall, the calorific value of biofuels EA/SVO studied was around 14% lower than that of diesel (B0).

The results related to cetane number (Tables 5 and 6) of blends with SO and CO were very similar among them, showing a decrease in cetane number values as EA/SVO ratio increases. It can be seen that the cetane number of all blends is below 51, which is the minimum cetane number of diesel in European standard EN 14214. Therefore, the ignition delay of these fuels is expected to be longer respect to conventional diesel fuel.

3.2. Performance of a Diesel Engine Operating as Electric Generator

According to the characterization results, the mixtures proposed as (bio)fuels that comply with kinematic viscosity requirements established by European normative EN 590, were tested in a diesel engine. The engine loads employed for the tests were 0, 1000, 2000, 3000, 4000, and 5000 W. Figure 4 illustrates the impact of engine load on engine performance fueled with the different D/EA/SVO triple blends, containing SO (Figure 4a) and CO (Figure 4b). Furthermore, the performance of EA/SVO (B100) and fossil diesel were also included for comparison.

Generally, as the power supplied increases up to 4000 W, the power output also increases, whereas the highest engine load (5000 W) generated a drop in power output of engine. This behaviour is observed with D/EA/SO blends containing up to 60% of biofuel, and with D/EA/SO blends containing up to 80% of biofuel. On the contrary, blends B80 with SO and EA/SVO double blends display a different trend: firstly, the power generated increases from 0 to 3000 W; then, it falls down from 3000 to 4000 W; and finally, it remains stable when the highest load is applied to engine. It is noteworthy that, at the highest load conditions, i.e., 4000 and 5000 W, the blends D/EA/CO exhibit very similar or even higher power output values than diesel. Thus, fuels composed by up to 60% of biofuel, EA/SO (B20–B60), and up to 80% of biofuel EA/CO (B20–B80) revealed a very notable efficiency on engine. However, higher concentrations of EA/SVO led to a worst engine performance, in comparison with conventional diesel or analogous mixtures with lower biofuel content. Be that as it may, it is very interesting the fact that the EA/SVO double blends allow the running on engine without employing any fossil diesel content, which means a 100% of diesel substitution for renewable compounds. This achievement is even more remarkable for biofuel containing castor oil, since the decrease in the power output is between 7% and 30% in respect to diesel, which is lower than that obtained for biofuel with sunflower oil (50–74% lower than diesel). Usually, triple mixtures with castor oil exhibit better behavior as

(bio)fuels than those containing sunflower oil in any proportion investigated. In this sense, the usage of castor oil as part of these triple mixtures not only improves the power results as compared to sunflower oil, but also achieves better results with regard to fossil diesel, even with higher percentages of ethyl acetate up to 36% (B20–B80 blends). Taking into account that both SVOs exhibit very similar calorific values (Table 1), the better behavior of CO could be due to the higher cetane number of this oil, which improves the combustion quality. The progressive reduction in the engine performance observed with the blends B20 to B100 could be attributed to the low calorific value that ethyl acetate exhibit. Hence, a higher proportion of EA in the blend would promote the reduction in the energy content of blends (Table 1). This fact agreed with the results reported in previous investigations where triple blends containing ethanol [6], diethyl ether [16], or acetone [17] were employed as LVLCs. Nonetheless, the influence of other operating parameters on engine performance cannot be ruled out.

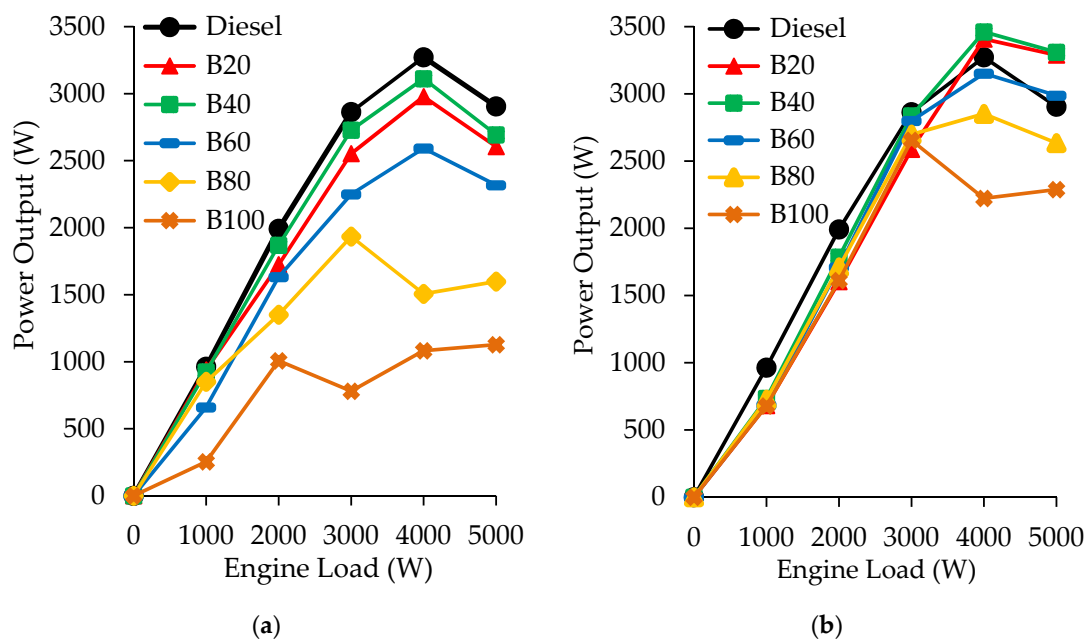


Figure 4. Power output (W) at different engine loads (1000–5000 W) for (a) diesel/ethyl acetate/sunflower oil; (b) diesel/ethyl acetate/castor oil blends. The error in measurements was always less than 3%.

3.3. Smoke Emissions: Opacity

Figure 5 shows the smoke emissions (expressed in Bosch number) of the different blends tested. As can be seen, the higher the amount of EA/SVO in the blend, the higher the reduction of soot emissions. As we previously reported, this behavior is explained by the increase of the oxygen content in the fuel. Oxygen acts reducing the formation of rich zones and promoting the oxidation of soot nuclei during fuel combustion. Although the oxygen content is the dominant factor on soot emissions, in turn a lower cetane number has also demonstrated to decrease soot particles emissions due to that a longer ignition delay provides more time for the premixing of fuel and air prior to the start of combustion, which increases the oxidation of soot particles [35].

Accordingly, the lowest opacity values are obtained with pure biofuels EA/SVO (B100), independently on the vegetable oil used, since they have the highest concentration of EA and the lowest CN. These B100 blends decrease soot emissions up to 85% when sunflower oil is employed and up to 96% for the blends containing castor oil as SVO. For B20–B80 D/EA/SO triple blends, the opacity is reduced from 16 to 80% of the total opacity value attained with fossil diesel, Figure 5a. For its part, the reduction is even higher when B20–B80 D/EA/CO triple blends are employed, up to 94% lower than opacity obtained with diesel for B80 blend, Figure 5b. The slightly better behavior obtained with CO blends can be attributed to the lower presence of unsaturation that ricinoleic acid of

CO exhibit, in comparison to that exhibit by linoleic acid of SO. As it is well-known, unsaturation in fuels contributes to the formation of soot precursor species [36]. The results are in agreement with previous studies where triple mixtures with other oxygenated compounds reported a similar behavior in term of emissions reduction [6,16,17].

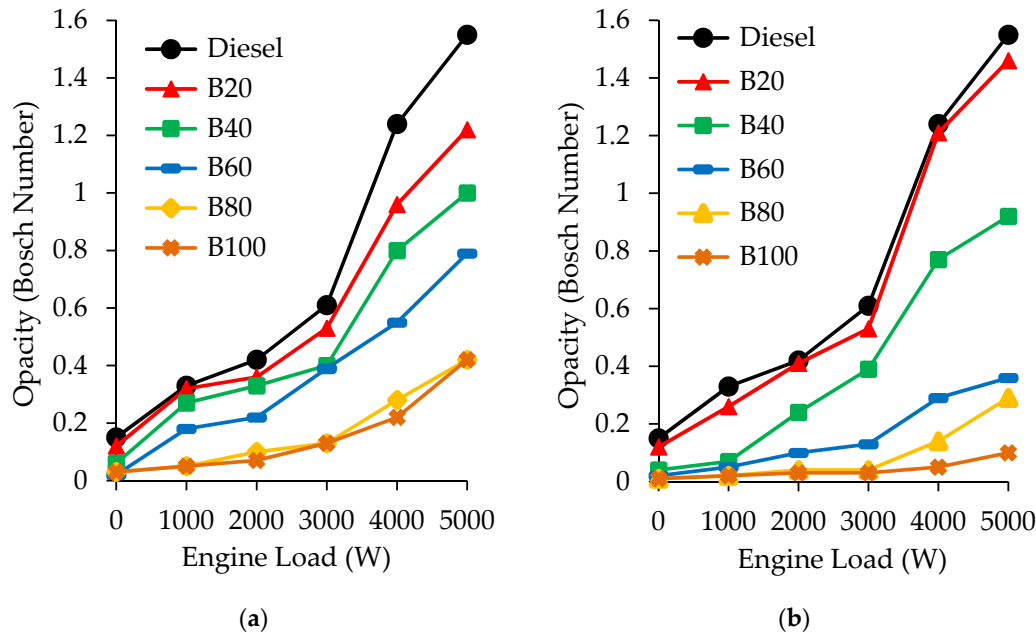


Figure 5. Smoke emissions (Bosch number) at different engine loads (1000–5000 kW) for (a) diesel/ethyl acetate/sunflower oil; (b) diesel/ethyl acetate/castor oil blends.

3.4. Fuel Consumption

The fuel consumption is also an important parameter to commercialize a new (bio)fuel. Figure 6 shows the influence of the different EA/SVO and D/EA/SVO blends with SO (Figure 6a) and CO (Figure 6b), on consumed volume (in liters per hour) by a diesel engine at low (1000 W), medium (3000 W), and high engine loads (5000 W). As biofuel ratio added to blends is rising, from B20 to B100, the volume consumed by the engine is greater. This fact is attributed to the fact that ethyl acetate has a lower calorific value than diesel (Table 1), which results in a reduction in the energy content of the mixtures, and therefore it is necessary to introduce more fuel on the engine to reach the required output power. As all the studied mixtures have lower calorific values than those of diesel, the engine consumes more fuel. The presence of sunflower oil leads to slightly higher fuel consumption compared to the analogous mixture that it contains CO, probably due to the lower cetane number of sunflower oil that increases the ignition delay, which deteriorates combustion process and leads to a higher fuel consumption. Particularly, blends B20–B80 with SO consume between 14 and 24% more than diesel, whereas the consumption of same blends with CO is about 4–21% more than diesel. On the other hand, as it is expected, the B100 blends display the highest percentage of consumption, 33% and 29% for EA/SO and EA/CO, respectively. For all the blends tested, the highest consumption as compared to diesel is usually produced at the highest engine load (5000 W).

To sum up, blends with ethyl acetate as LVS of sunflower and castor oils here evaluated has showed a greater efficiency on C.I. diesel engine than analogous mixtures tested in previous researches [16,17]. Triple blends containing DEE as renewable solvent achieved the best result with a proportion 60/18/22 D/DEE/CO, which led to a maximum of 40% of diesel replacement, and up to 77% of smoke emissions reduction [16]. Likewise, the same ratio in a blend containing ACE [17] gave rise to an equal percentage of fossil fuel substitution, but with emissions slightly lower (82%). In these cases, the engine does not work with higher amounts of DEE and ACE due to knocking problems attributed to the low energetic content of blends. Herein, the use of ethyl acetate allows to replace up to 100% of fossil diesel,

with up to 94% in soot reduction respect to diesel. This means that all blends proposed can run in a conventional diesel engine, although it should be taking into account that a loss in engine power is produced as the concentration of pure biofuel EA/SVO supplied to the engine is increased.

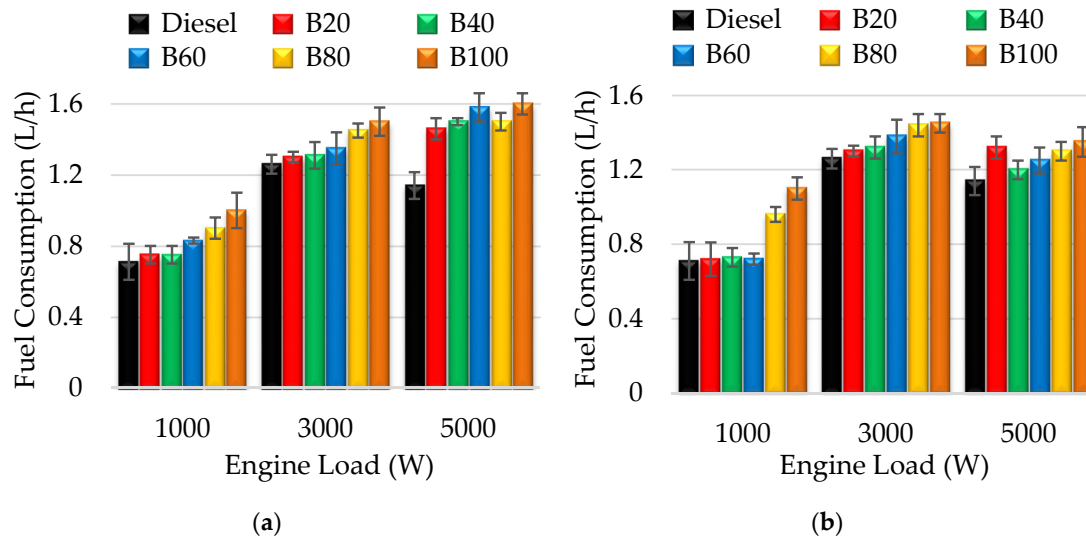


Figure 6. Fuel consumption values (L/h) at different engine loads (1, 3, and 5 kW) for (a) diesel/ethyl acetate/sunflower oil; (b) diesel/ethyl acetate/castor oil blends. The results are the average of three measurements and errors are represented as standard deviation through error bars.

4. Conclusions

In view of the current need for alternate fuels to supply the growing energy demand and also comply with new environmental requirements related to its renewable character, the objective of this research was to evaluate the potential of ethyl acetate as renewable biofuel in double blends with two different straight vegetable oils, castor or sunflower oil, and also, in triple blends along with fossil diesel. For that, the influence of these fuel blends on efficiency and emissions of a C.I. diesel engine was investigated. Considering the experimental results, the following points are concluded:

1. All investigated blends comply with requirements of kinematic viscosity (2.0–4.5 cSt) established by the European diesel standard EN 590, for usage in current diesel engines. However, calorific value and cetane number were reduced by the incorporation of ethyl acetate.
2. The addition of ethyl acetate led to remarkable improvements in flow properties of fuels at low temperatures in comparison to conventional diesel, which makes these fuels more suitable for engine running in colder climates.
3. Excellent results of power output were achieved with the B20–B60 D/EA/SO and with the B20–B80 D/EA/CO blends. The best performance was shown by fuels composed of castor oil, especially the B20 and B40 mixtures, exhibiting even better results than diesel at high engine load (4000 and 5000 W).
4. The consumption of engine fueled with the studied blends was greater than with conventional diesel due to low calorific value of ethyl acetate.
5. The high oxygen content of ethyl acetate was the key factor to enhance the combustion process and to achieve a very notable reduction of soot emissions. Higher proportion of EA/SVO in mixtures decrease the opacity generated by the engine. Hence, the mixtures B100 provided the better behaviour in term of achieving lower emissions.
6. This study also reveals that the EA/SVO double blends can be employed as direct biofuels without adding fossil diesel, making these fuels completely renewable.

7. The best results were achieved over the B40 blend with CO, which generated similar or even higher power output than diesel at the highest engine load values, with lower soot emissions and very similar fuel consumption. Moreover, this blend exhibited the best CP and PP values. With the B40 blend, a 60% of fossil diesel substitution was achieved. Furthermore, the production of ethyl acetate through renewable process like acidogenic fermentation from low-value biomass, constitutes a fundamental tool towards more sustainable production of alternative fuels for transportation sector.
8. Finally, the multi-component blending is a promising strategy to attain higher percentages of fossil fuel substitution, at the same time that exhaust emissions from the transportation sector are significantly diminished, keeping very good engine performance. This initial experimental study represents an advance in the search for new biofuels that can replace the fossil fuels used in the present fleet of vehicles.

Author Contributions: D.L. designed the study; L.A.-D. performed the experiments and wrote the paper; R.E. reviewed and edited the paper; R.E., D.L., and F.M.B. supervised the study and revised the manuscript; C.L., J.H.-C., J.C., A.P., and A.A.R. made intellectual contributions to this study. All authors have read and agreed to the published version of the manuscript.

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Nomenclature

ACE	Acetone
ASTM	American society for testing and materials
B0	100% diesel
B20	80% diesel + 20% EA/SVO blend
B40	60% diesel + 40% EA/SVO blend
B60	40% diesel + 60% EA/SVO blend
B80	20% diesel + 80% EA/SVO blend
B100	100% EA/SVO blend
BTE	Brake thermal efficiency
BSFC	Brake specific fuel consumption
CI	Compression ignition
CN	Cetane number
CO	Castor oil
CP	Cloud point
cSt	Centistokes
CV	Calorific value
D	Diesel
DEE	Diethyl ether
ISO	International Standards Organization
LVLC	Lower viscosity and lower calorific value
LVS	Low viscosity solvent
PP	Pour point
rpm	Round per minute (min^{-1})
SO	Sunflower oil
SVO	Straight vegetable oil
VO	Vegetable oil
W	Watts

Symbols

A	Amperage (amps)
C	Calibration constant (mm ² /s)/s
P	Electrical power (watts)
t	Flow time (s)
V	Voltage (volts)
ν	Viscosity (centistokes)

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