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Physicochemical Properties of Diethyl Ether—Sunflower Oil Blends and Their Impact on Diesel Engine Emissions

Krzysztof Górski [1,*], Ruslans Smigins [2], Jonas Matijošius [3,4], Alfredas Rimkus [3,4] and Rafał Longwic [5]

1 Faculty of Mechanical Engineering, Kazimierz Pulaski University of Technology and Humanities in Radom, ul. Chrobrego 45, 26-200 Radom, Poland
2 Faculty of Engineering, Latvia University of Life Sciences and Technologies, J. Cakstes Blvd. 5, LV3001 Jelgava, Latvia; ruslans.smigins@llu.lv
3 Department of Automobile Engineering, Faculty of Transport Engineering, Vilnius Gediminas Technical University, J. Basanavičiaus Str. 28, LT-03224 Vilnius, Lithuania; jonas.matijosius@vilniustech.lt (J.M.); alfredas.rimkus@vilniustech.lt (A.R.)
4 Department of Automobile Transport Engineering, Technical Faculty, Vilnius College of Technologies and Design, Olandu Str. 16, LT-01100 Vilnius, Lithuania
5 Faculty of Mechanical Engineering, Lublin University of Technology, ul. Nadbystrzycka 38D, 20-618 Lublin, Poland; r.longwic@pollub.pl
* Correspondence: krzysztof.gorski@uthrad.pl; Tel.: +48-48-361-76-58

Abstract: In this paper, an analysis of the physico-chemical properties of diethyl ether/sunflower oil blends, as well as changes in emissions in work with AD3.152 diesel engine, were realized. The following properties of tested blends have been examined in detail: density (ρ) at 15 °C; kinematic viscosity (v) at 40 °C; cold filter plugging point (CFPP); lower heating value (LHV); flash point (FP); and surface tension (σ). In this research, different blends of diethyl ether (DEE) with sunflower oil (SO) in ratios of 10:90, 20:80 and 30:70% by volume were chosen. It was confirmed that DEE impacts significantly on reducing of SO viscosity. Furthermore, the density, as well as the surface tension of tested blends, have been reduced significantly when DEE was blended with SO. In this way, DEE impacts on better atomization of the SO injected into the combustion chamber. It was confirmed that DEE addition improves the low-temperature properties of SO significantly, which indicates the possibility of also using such blends in the winter season. On the other hand, the flammable DEE additive significantly lowers the flash point of the tested blends, which requires compliance with the transport safety rules applicable to gasoline. An engine tests carried out in condition of its partial load i.e., for 80 and 120 Nm, showed that combustion process of DEE/SO blends is more and more similar to the combustion of diesel fuel when adequately higher content of DEE is blended with SO. In particular, it was confirmed that the highest smoke concentration was observed for the engine operated with SO. However, 30% addition of DEE to SO brings this smokiness significantly closer to the value typical for the engine operated with diesel fuel. Additionally, concentration of unburned hydrocarbons (THC) and nitrogen oxides (NOx) are comparable for diesel fuel and DEE/SO blends.

Keywords: sunflower oil; diethyl ether; diesel fuel; renewable fuels; fuel properties

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1. Introduction

Based on the global pace of energy and transport, interest in alternative fuels and vehicles is growing year by year [1]. Despite the rapid growth of number of electric cars, there still exists wide range of alternative fuels for conventional diesel engines, which are still underestimated in certain transport sectors or industries [2]. These might be biofuels obtained from plant oils, like biodiesel, renewable diesel and biooil [3]. Biodiesel and renewable diesel could be considered as upgraded option of plant oils, with the aim to reduce disadvantages affecting their direct use in engines [4].

Straight vegetable oil (SVO), which was first used as a fuel directly in diesel engines in 1900, is still used in some limited applications [5]. Although originally vegetable oil was considered as emergency fuel in periods when availability of conventional fuel was limited [6], it demonstrated energy self-sufficiency in the agricultural sector, as well as outlined some ecological perspectives [7]. In overall, application of vegetable oil in transport mainly depends on excess in vegetable oil production in exact country, as well as oil prices in the global market [8].

At the moment, sunflower oil is one of the most important oilseed crops in the world, cultivated in developed and developing countries, with higher market demand than the production can provide [9]. Sunflower seed is the second most important oilseed crop in the EU-27 after rapeseed, reaching 10.8 million tons harvested in 2020, but it could be seriously reduced in 2022 due to the conflict in Ukraine, which is the world's largest exporter of sunflower oil. Last year's increase in harvest in sunflower cultivation could be observed based on the favorable sowing conditions and land redesignations [10]. Another situation could be observed with the output of vegetable oil in global scale, where sunflower oil occupies 4th place, with almost 10% of world output following after palm, soybean and rapeseed oils [11]. In any case, oilseeds grown in EU27, as well as worldwide, are pressed to produce vegetable oils, as well as joint products of pressing. Based on an increase in imports of low-price feedstocks as palm oil, as well as an increase of sunflower oil prices, it is not the most popular oil used for the production of biofuel, like biodiesel, and composes only 3% in EU [11]. At the same time, sunflower oil is considered as the most GHG emission-saving oil [12]. Additionally, oil can be used also as a pure fuel in the engine if it is adopted, or in the blends with another fuel stimulating reduction of viscosity, which is the main barrier for vegetable oil usage in diesel engines. As the application of sunflower oil in engines in pure form is not so popular, the number of researches are very limited, but still exist. Studies have been carried out on a wide variety of vehicles, not always indicating an unambiguous result for engine performance and emissions.

Tests with sunflower oil were widely carried out in the 1980s in the United States, as evidenced by the large number of published studies [13–17]. Mostly they were concentrated on fuel injection performance, short-term engine performance, nozzle deposits buildup and low temperature capability. After tests, mostly power loss, as well as injector coking, piston ring sticking and gumming, were reported by Deere and Company, International Harvest Company and Caterpillar Tractor Co [14]. Tahir et al. [15] tested sunflower oil as a replacement for diesel fuel in agricultural tractors, where it was found that engine performance using sunflower oil was similar to that of diesel fuel, but with a slight decrease in fuel economy. At the same time, engine testing with sunflower oil and diesel blend in 50/50% vol. was unsuccessful, where carbon buildup on the injectors and piston rings caused engine operating difficulties [16]. The same was confirmed also by German et al. [17] with the tractors fueled with 50% vol. sunflower oil addition to diesel than for those fueled with a 25% sunflower addition to diesel. Since then, improvements have affected both engines and the technical properties of sunflower oil. The focus is now more on the combustion process and ecological parameters.

For example, Rakopoulos [18] did not find a rapid difference for sunflower oil in comparison to other oils used in the tests (cottonseed, corn and olive). In overall, in an experimental study with the direct injection engine of Mercedes-Benz mini-bus, smoke reduction was observed, but at the same time NOx, CO and HC emissions slightly increased for all vegetable oils in comparison to neat diesel fuel.

Arapatsakos [19] has worked with diesel-sunflower fuel blends with diesel addition (10, 20, 30, 40 and 50% diesel fuel content volumetrically) on a four-stroke Ruggerini type RD-80 diesel engine, where an increase of CO and decrease of HC emissions was observed. At the same time, a reduction of NO emissions was observed for diesel-sunflower blends, while the engine was working in low turns.

Balafoutis [20] observed that operation with direct injection agricultural tractor engine using sunflower oil and three blends with diesel fuel (20, 40, and 70% oil content volumetrically) have not shown any problems during the short-term experiments, but oil content increase in the tested fuel enhanced torque, brake-specific fuel consumption and NOx. This was resolved by earlier injection timing. In another study comparing different vegetable oils [21], it was found that sunflower oil produces the lowest power output, torque and CO_2 emissions among rapeseed oil and cottonseed oil.

Over time, not only pure sunflower oil has been tested, but also its different variations. For example, Hemanandh [22] has realized tests on the stationary, vertical, 4-stroke DI diesel engine achieved reduction of all emission components (CO, HC, NOx) using hydrotreated refined sunflower oil. Results were confirmed on full load conditions in comparison to conventional diesel. Pavani [23] has tested refined waste sunflower oil in different blends (B15, B20 and B25) on a four stroke diesel engine, where increased engine performance and reduced emissions were found compared to neat diesel fuel, especially for the 20% blend.

Edible straight vegetable oil (SVO), like sunflower oil, forming part of first generation biofuels, is mainly considered for biodiesel production due to its main problem of application: lower energy content, poor cold flow properties, higher viscosity, compatibility, etc. [24]. Despite those application problems, the usage of SVO is possible after fuel or engine modification. In this case, reduction of fuel viscosity is the main problem for vegetable oils.

While there exist different techniques for the reduction of viscosity of vegetable oils, the most popular is the thermal option, which includes preheating of the fuel in such way increasing temperature and reducing viscosity. This method is based on preheating vegetable oil by heater before reaching the fuel injectors. Such vegetable oil becomes similar to conventional diesel fuel in case of technical characteristics. Ozsezen [25] has observed that preheated crude sunflower oil (at 75 °C) presents satisfactory results in terms of four-cylinder, naturally aspirated, indirect injection diesel engine performance and combustion characteristics—decrease of HC, CO, CO_2, smoke opacity and brake power—while brake thermal efficiency and brake specific fuel consumption has increased. At the same time, there is research [26] that has observed that the preheating method is effective and practicable without engine modification only for short-term usage of SVO.

Mostly SVO is used for production of biodiesel in a pure form, or even previously used in a food chain. However, the addition of a small amount of sunflower oil biodiesel to diesel significantly improves the lubrication properties [27], making sunflower biodiesel as an appropriate non-toxic additive used for the improvement of the lubrication properties of fossil diesel fuel. Other oil modification options are also available. It could blend with a low viscosity and volatile fuel, which allows to avoid from engine fuel system modifications and reduce the value of density for all blends. Similar suggestion was claimed in the literature review [28], with a focus on the use of different vegetable oils in diesel engines recognizing SVO as an appropriate substitute for diesel fuel in agriculture sector, but at the same time recommending to continue research on the development of additives, which can improve spray characteristics and combustion.

The most popular additives there could be conventional diesel fuel, but its usage will not ensure the appropriate reduction of main exhaust components. In that case, more valuable option could be ethanol-based fuels, which have more positive impact on emissions due to a higher oxygen content, but at the same time contains a number of undesirable properties like low flash point and cetane number, high water solubility and corrosivity, and especially low diesel solubility [29]. These properties can be adjusted by conversion ethanol to diethyl ether-additive, which has a higher diesel miscibility, energy content and cetane number in comparison to ethanol [30]. Numerous researches have shown that such addition could improve fuel combustion process in such a way, lowering harmful emissions from diesel engines. DEE have been added to: diesel [31], biodiesel [32], biodiesel-diesel blends [33] and different plant oils [34], and also in blends with diesel and kerosene [35–37], as well as in combination with water emulsion [38] and methanol/n-octanol [39].

Despite the relatively extensive experience with DEE's addition to different vegetable oils like rapeseed [40], linseed [24], cashew nut shell oil [41] and cottonseed oil in combination with diesel fuel, there are no extended studies which contained more detailed research on DEE addition directly to pure sunflower oil (SO). In this respect, the work [37] stands out. The kinematic viscosity of DEE/SO mixtures was tested as well, as other physicochemical properties of diesel/DEE/SO triple blends have been evaluated.

Taking this into account, the main objective of this study was to extend and verify the existing knowledge on physicochemical properties of DEE/SO blends and their effect on emissions of selected harmful components from diesel engine. This is achieved by choosing low concentrations (10, 20 and 30% vol.) of DEE mixtures with sunflower oil, which would not affect the performance of the engine, but at the same time allow to find out changes in the most common exhaust components. To clearly compare the results of the research, the experiments were performed at different loads and at different speeds. Therefore, in order to draw appropriate conclusions about the changes in the most common exhaust gas components, the physio-chemical properties of the above-mentioned mixtures were analyzed, and their connection with the changes in the exhaust gas components was sought. The novelty of this study is confirmed by the fact that the use of such mixtures of those two components in internal combustion engines has not been previously studied, in particular by analyzing the effect of their physio-chemical properties on the engine emissions of the tractor.

2. Selected Physicochemical Properties of Sunflower Oil

Starting the analysis of the properties of vegetable oils, significant attention must be paid to their structure. Sunflower oil contains the highest amounts of poly-unsaturated fatty acids (68% be weight) besides safflower and linseed oils, as well as the highest amount of linolenic acid [42]. As the nature of fatty acids largely determines their ability to burn correctly in the diesel engine [28], then analysis of fatty acid composition allows better to prescribe and predict the physical and chemical properties of an oil [43]. It should be noted that main characterizers of fatty acid are carbon chain length and the number of carbon-carbon double bonds [44]. In the case of sunflower oil, it is possible observe that average number of double bonds is 1.57 and the chain length is 17.92 [42]. Based on different researches [24,42], this allows us to predict cetane number, effect on ignition delay, lower heating value and cold filter plugging point (CFPP), as well as other properties.

Vegetable oil, like any fuel, needs to fit the most relevant physical properties for its usage in unmodified diesel engines [45], especially density and viscosity. As vegetable oils contains large molecule sizes of triglycerides [46], it could result in higher viscosity and density compared to diesel fuel. Lower viscosity ensures appropriate atomization, which is very important in case of modern diesel engines, but especially in direct injection (DI) diesel engines based on the high degree of atomization required for this engine type [47]. As fuel injection systems of modern diesel engines are very sensitive to viscosity changes, then more attention should be focused on choosing the right option for lowering viscosity. Fuel injection system of current diesel engines accepts the use of fuels with viscosity values from 1.9 to 5.0 mm^2/s at 40 °C (1.9 to 4.1 mm^2/s at 40 °C based from standard ASTM D975, 2.0 to 4.5 mm^2/s at 40 °C from standard EN 590:2004, 3.5 to 5.0 at 40 °C from EN 14214:2009), while some sources [48] recommend 1.6–7.0 mm^2/s values for operating at 40 °C. Following values of viscosity is important, as fuels with too low viscosity will not provide sufficient lubrication for the precision fit fuel injection pumps, resulting in leakage and increased wear, while higher viscosity means reduction of spray angle [49], higher Sauter Mean Diameter (SMD) and lower spray speed than conventional diesel fuel [50]. From the technical point of view, viscosity of vegetable oils should reach value close to upper limit of mentioned standards to avoid high viscosity problems. Regulations concerning fuels from vegetable oils are limited by DIN V 51605 for rapeseed oil, as well as further attempts for standard development for other oils [50]. Kinematic viscosity of sunflower oil is 8–18 times greater than that of diesel, which is based on unsaturation, carbon chain lengths and a decrease in temperature [28]. Such increase will require more energy for fuel pump operation, and it is expected to decline power and torque output from the engine, as well as increase of NOx emissions [51]. As sunflower oil has higher levels of polyunsaturated fats, higher NOx emissions could be observed.

Density, which is usually defined as a measure of the mass per unit volume, does not depend on unsaturation or chain length [42], but only temperature. Density of SVO decreases linearly with increasing of the temperature. A linear relationship also exists between density and the inverse of the square root of the kinematic viscosity, which was found in research with six SVOs, including sunflower oil [45]. Although the density of sunflower oil is about 10% greater than that of diesel [28], attention to these relationships should be taken into account in provision of fuel combustion and analysis. Spray formation is also affected by surface tension, and it depends on the number of unsaturated bands and length of the fatty acid chains. As the length of the chains increases, so does the surface tension. In any case balanced value of viscosity, density and surface tension is required for proper droplet formation in the injection system [52] and creating atomization properties strongly connected with the quality of ignition leaving further impact on engine performance and emissions. Research [46] has showed that sunflower oil does not have a large difference in surface tension value between other popular SVOs, like rapeseed or soybean, during heating in different temperature from 10 to 140 °C. But even at this maximum temperature, the value of the surface tension coefficient is still higher than 33% compared to diesel [46]. Besides that, it could be concluded that sunflower oil requires to be preheated at temperatures no lower than 120 °C to match the surface tension value corresponding to automotive diesel fuel at 40 °C [46].

CFPP is another important parameter of operability of diesel engine connected with low temperature climate zones. In overall, this is a temperature at which fuel flow is restricted through fuel lines and filters due to a crystal formation. As with other parameters, CFPP is mainly dependent on the fatty acid profile—an increase of the total unsaturated fatty acid content decrease CFPP [53]. Low temperatures stimulates the fatty acids and form cloud (CP—cloud point), semi solid fractions (PP—pour point) and form crystals [54]. However, a reduction of the saturated fatty acids is possible using blending. Furthermore, the transesterification process allows us to improve the low-temperature properties of the vegetable fuel [54].

Lower heating value (LHV), which characterizes the energy content of the fuel, is another fuel-related property, which should be taken into account in SVO analysis. Literature does not contain enough data on analysis of LHV of different SVO, and the reasons for it change, but it is known that the value of LHV increases with chain length [55]. The actual value of LHV could be measured under laboratory conditions or approximately estimated using equations. Calculations showed that variation of two composition elements (hydrogen and oxygen) plays a significant role in the value of LHV—it increase alongside hydrogen content, and decreases with an oxygen content increase. Different models exist allowing the prediction of the value of LHV, but mainly for biodiesel fuels. For example, Pinzi et al. [56] developed a LHV prediction model for biodiesel using chain length and unsaturation degree, another study [55] calculated LHV of methyl esters using bond energy method. Literature shows that value of LHV for sunflower oil does not differ significantly from the LHV values of other common vegetable oils, and is 13–15% lower than diesel [57].

3. Materials and Methods

In this research, selected physicochemical properties of all tested fuels have been examined. Diesel fuel tested in this research had been produced by ORLEN Co. and purchased at a gas station. Refined, "fresh" sunflower oil made by "Kruszwica S.A." was acquired from the local market. Measurements of physicochemical properties of DEE/SO blends were carried out at the Kazimierz Pulaski University of Technology and Humanities in Radom. In particular, following fuels were tested: sunflower oil, diesel fuel and diethyl ether. Fundamental properties of all these base fuels are listed in Table 1.

Table 1. Selected physicochemical properties of tested fuels.

Property	Method	Fuel		
		SO	DEE	DF
Density at 15 °C, g/cm^3	ISO 12185:1996	0.919	0.710	0.832
Viscosity at 40 °C, mm^2/s	ASTM D7042	34.50	0.23	3.45
LHV, MJ/kg	ASTM D240-02:2007	37.2	33.8	43.9
Surface tension, mN/m	ISO 304:1985	46.0	16.8	32.1
CFPP, °C	EN 116:1997	28.0	- [a]	3.0
FP, °C	PN-EN 2719	310	−40	60
HFRR, µm	ASTM D6079-18	180	- [b]	370
Cetane number	-	37	125 [c]	51

[a,b] unmesurable [c] data reported in ref. [30].

Physicochemical properties of the DEE/SO blends were examined for following ratios: 10, 20 and 30% by volume of diethyl ether mixed with SO. For these mixtures, physicochemical properties have been tested: density, viscosity, lower heating value, surface tension, flash point and a low-temperature fuel property represented by the CFPP value. The density was measured using an IROX DIESEL analyzer equipped with an oscillation U-tube. This tube is electronically excited to oscillate at its characteristic frequency, depending on the density of the filled fuel sample. The viscosity of all tested fuels were measured using an SVM 3000 Stabinger Viscometer according to ASTM D7042. The lower heating value was measured in agreement with ASTM D240-02:2007 procedure. In this test method the bomb calorimeter KL-10 made by PRCYZJA-BIT Co. has been utilized. The surface tension was measured with the LAUDA TD-1C tensiometer in accordance with the requirements of ISO 304 standard. The ISL FPP 5Gs analyzer was used for the measurement of the cold filter plugging point. The flash point was determined with the Cleveland Open Cup method using a Herzog tester. The lubricity test was carried out in accordance with the recommendations of the EN ISO 12156-1:2006 standard. An automatic HFRR device from PCS Instruments was used for this purpose. All measurements have been repeated three times according to methods listed in Table 1, and then the average value obtained for these repetitions was used as a result, as shown in Figures. The results of individual measurements are included in the Supplementary Materials too.

After that, the engine emission research was carried out. This was done in the Faculty of Mechanical Engineering at the Kazimierz Pulaski University of Technology and Humanities in Radom. In these tests the AD3.152 diesel engine was utilized. The view of the test stand setup is shown in Figure 1.

The AD3.152 engine is well known, 3—cylinder construction equipped with a distributor type fuel injection pump and the direct injection fuel system. The engine generates a maximum torque of 145 Nm at 1200–1400 rpm without turbocharging. The engine/4/was coupled with dynamometer/5/operated under control of the device/6/. The fuel system includes a fuel tank/1/, a fuel flow meter/2/and the fuel pump controller/7/. Concentration of unburned hydrocarbons and nitrogen oxides in the exhaust gas and smoke opacity was measured by the analyzer/3/. The most important technical details of this engine are listed in Table 2.

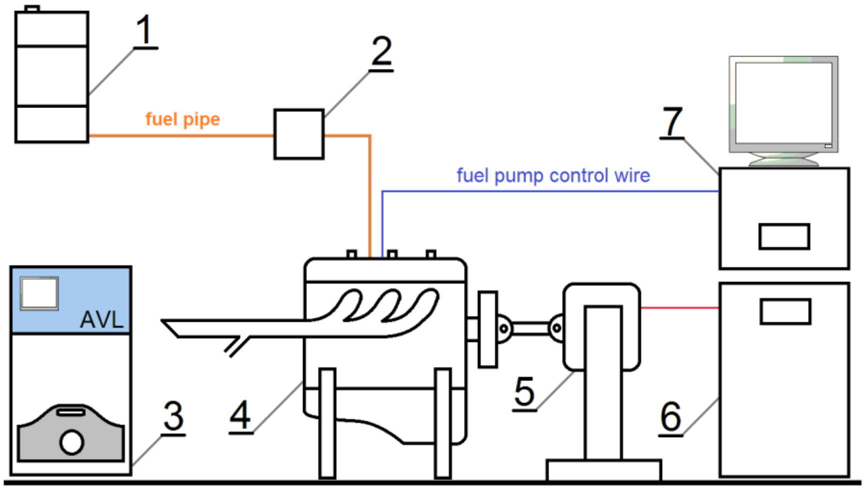

Figure 1. Test stand setup: 1—fuel tank, 2—fuel flow meter, 3—the AVL 4000 gas analyzer, 4—the AD3.152 diesel engine, 5—dynamometer, 6—dynamometer controller, 7—fuel pump controller.

Table 2. Technical data of the AD3.152 diesel engine.

Parameter	Value
Engine capacity	2502 cm^3
Cylinder number	3, in line
Top power	34.6 kW at 2150 rpm
Maximum torque	145 Nm at 1200–1400 rpm
Compression ratio	16.5
Fuel injection pressure	17 MPa
Crankshaft speed at idle run	750 rpm
Fuel injection system	Lucas—CAV type DPA
Start of injection	17° before TDC

Necessary engine tests were carried out in condition of its partial load i.e., for 80 and 120 Nm. For these loads the engine operated with the crankshaft rotational speed 1000, 1500 and 2000 rpm. In these conditions a concentration of THC, NOx and smoke emission has been measured using the AVL DiCom 4000 gas analyzer. The range and the accuracy of each measurement are given in Table 3.

Table 3. Technical specification of the AVL DiCom 4000 gas analyzer.

Parameter	Measurement Range	Accuracy
NO_X	0–5000 ppm vol.	1 ppm
HC	0–20,000 ppm vol.	1 ppm
CO	0–10% vol.	0.01% vol
Smoke opacity	0–100%	0.1%

Before the engine test begins, necessary setting has been validated i.e., beginning of fuel injection and injection pressure according to the producer requirements. After that, the engine was warmed up to the operational temperature.

4. Results

4.1. Physicochemical Properties of Tested Fuels

Density and viscosity are important fuel parameters affecting engine performance. In particular, the higher viscosity and density increase the fuel flow resistance, and the mechanical energy demand of the fuel pump increases. This leads to a reduction in the mechanical efficiency of the engine. Moreover, the atomization quality of the fuel deteriorates. In this case, larger fuel droplets are formed, which evaporate longer. This extends the delay period of physical preparation of the fuel for self-ignition. This is one of the reasons why the cetane number of vegetable oils is about 15 units lower than that of diesel fuel.

According to the EN 590 standard, the density of diesel fuels is required to be in the range of 0.820–0.845 g/cm^3. In case of biodiesel, the EN 14214 standard specifies a higher range of permissible fuel density, i.e., 0.860–900 g/cm^3. Taking this into account, it can be stated that SO does not meet the requirements of both mentioned standards regarding permissible density. However, as can be seen in Figure 2, the 10% or higher addition of DEE is sufficient for the density of the obtained blend to meet the requirements of EN 14214 standard. Figure 2 also confirms that the relationship of the density and composition of the DEE/SO blend is very well expressed by a linear regression.

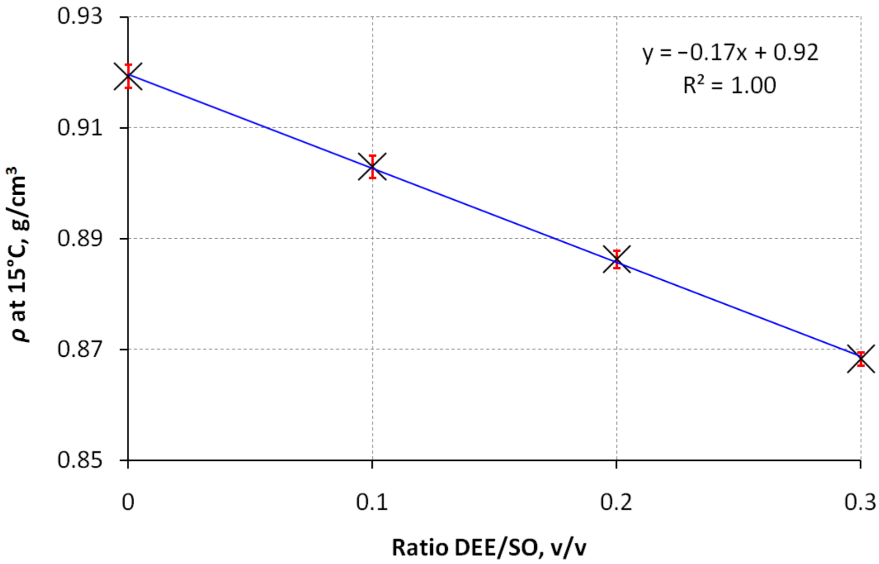

Figure 2. Impact of the DEE/SO ratio on the blend density (ρ) tested at 15 °C.

As mentioned above, the kinematic viscosity impacts on the engine performance and its emissions. Atomization of high viscosity fuels creates larger droplets affecting the quality of the combustion process. Particularly in winter conditions, it can make starting the engine significantly more difficult. For this reason, the kinematic viscosity must be kept within a narrow range of values, i.e., 2.0–4.5 mm^2/s or 3.5–5.0 mm^2/s, according to EN 590 and EN 14214 standards, respectively. The presented dependencies are obtained experimentally, so their dispersion is very difficult to estimate based on the laws of chemical kinematics. Since the resulting DEE/SO mixtures are not obtained to be constant but depend on the batch produced, it is complex, and requires separate statistical analysis to evaluate their changes based on theoretical results, where the available result is also error-prone, which is not the focus of this article. The authors focus on practical applicability, so the diffusion of results shown allows only current trends to be defined. Figure 3 clearly shows that the kinematic viscosity of SO is about ten times higher than recommended values set in both above mentioned EN standards. However, it can be seen that the addition of DEE significantly lowers the kinematic viscosity. Only 10% addition of DEE lowers the SO viscosity by about 50%. A further increase in the addition of DEE to SO no longer causes such favorable reduction of the kinematic viscosity. It results from the exponential dependence of this kinematic viscosity with the DEE/SO ratio expressed in Figure 3. The observed direct relationship between density and kinematic viscosity results allows us to define smaller variations of the test points, and to ensure more stable values of the obtained results. This tendency is especially noticeable when examining points 0.1 and 0.2 of the study, which shows that the kinematic viscosity values of the fuel mixtures stabilized the flow characteristics of the fuel mixture.

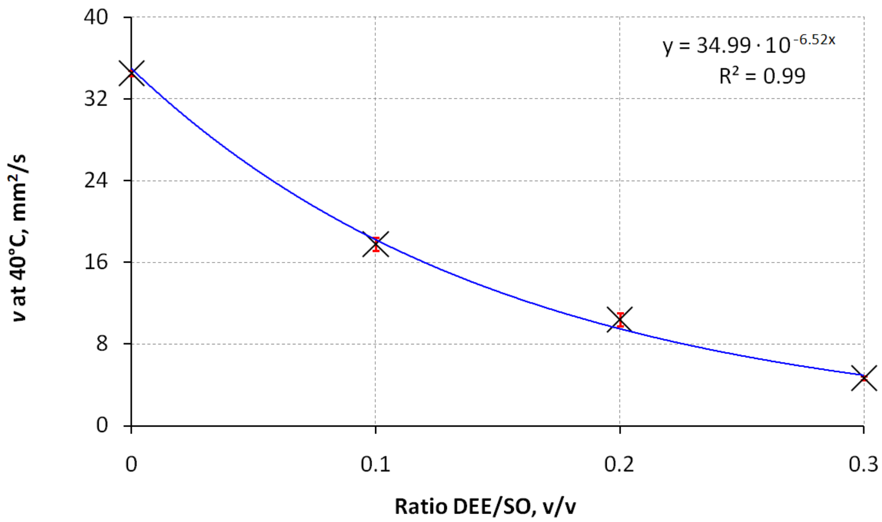

Figure 3. Impact of the DEE/SO ratio on the blend kinematic viscosity (v) tested at 40 °C.

The fuel atomization process is also dependent on the surface tension. Decreasing the value of this parameter facilitates the secondary breakup of the fuel droplets. This improves the fuel atomization, positively affecting the quality of combustion process. As shown in Figure 4, the surface tension is reduced even by 30% for the blend containing 30% of DEE. The tests showed that the changes in surface tension and the concentration of DEE/SO can be described by a linear relationship. As the individual components of the fuel mixture have different chemical and physical properties, the surface tension index characterizes this well. It is when examining it that variations in results are observed due to the inhomogeneity of the fuel mixture. Similar trends are observed when looking at the LHV indicator.

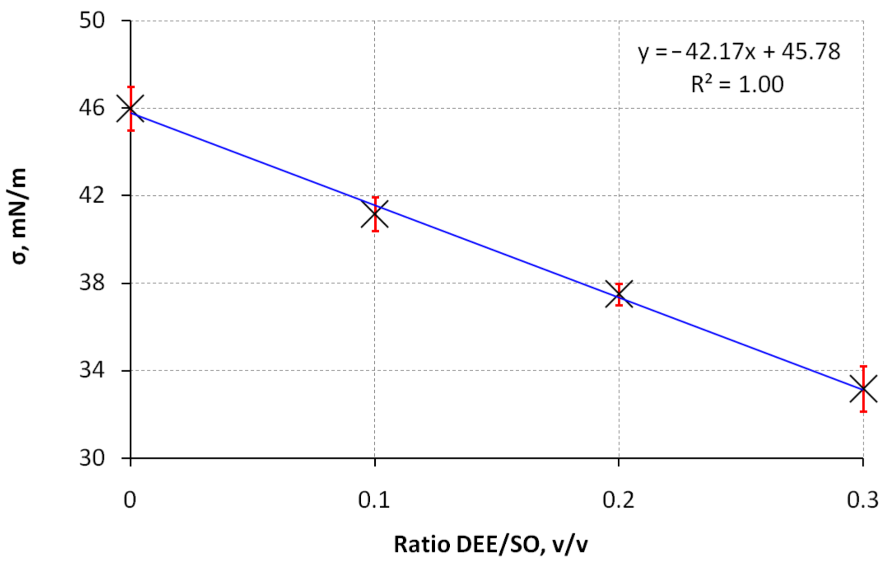

Figure 4. Surface tension (σ) of tested blends, SO and DF.

As mentioned in Table 1, the Lower Heating Value (LHV) of SO equals 37.2 MJ/kg. It is about 13% less than LHV of DF (43.9 MJ/kg). However, SO, like other plant oils, has a higher density than DF. For this reason, the LHV of SO expressed on a volume basis

(MJ/m^3) is comparable with DF. It details the LHV of DF expressed on volume basis is 36.5 MJ/m^3 i.e., about 6% more than for SO. Unfortunately, (Figure 5), addition of DEE to SO reduces LHV significantly. In particular, the LHV of SO containing 30% of DEE is reduced by 9%. This means that the engine operated with such a mixture will reach adequately lower top power and torque, or more fuel will need to be injected to maintain the same torque. As shown in Figure 5, the relationship of LHV with DEE/SO ratio is very well expressed by linear regression.

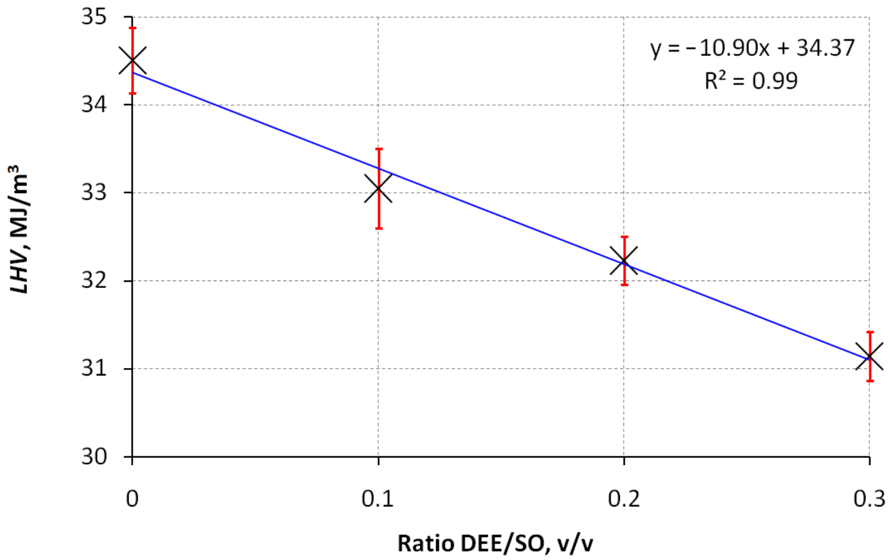

Figure 5. Lower heating value (LHV) of tested blends.

The high viscosity of vegetable fuels causes that their flow through the fuel system is difficult. It also increases the cold filter plugging point (CFPP). As shown in Figure 6, the CFPP of SO is around 30 °C. For this reason, vegetable oils cannot be used as winter fuels. However, the 30% addition of DEE significantly reduces the value of CFPP, making the mixtures obtained can also be used in winter season. Additionally in this case, the studied dependencies are very well described by linear regression. Examining the CFPP indicator, it is observed that with increasing share of the SO component, the variability of the results increases, which is explained by the fact that SO does not tend to keep the fuel mixture homogeneous in terms of its physical and chemical properties.

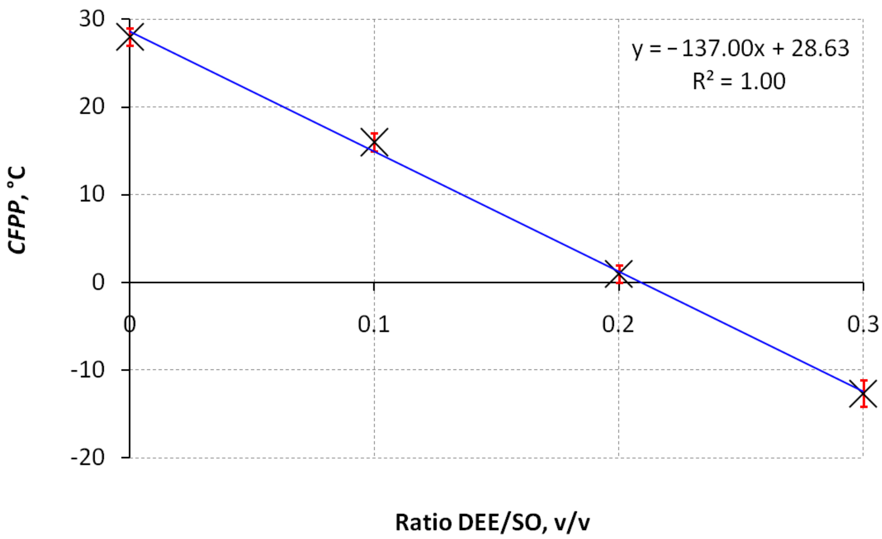

Figure 6. CFPP (°C) of tested blends, SO and DF.

The last parameter that has been assessed is temperature of flashpoint (FP). For most vegetable oils, the FP is very high. In the case of SO, it exceeds 300 °C (Figure 7). Such a high value of FP reduces the risk of fire and improves transport safety. It is worth recalling that according to the EN 590 standard, the minimum FP value is 55 °C. Unfortunately, the addition of DEE significantly lowers FP. Therefore, the safety rules for DEE/SO blends must be the same as for gasoline. The flash point is highly dependent on the amount of volatile fuel components, so the variability of the results at the measurement points was not significant.

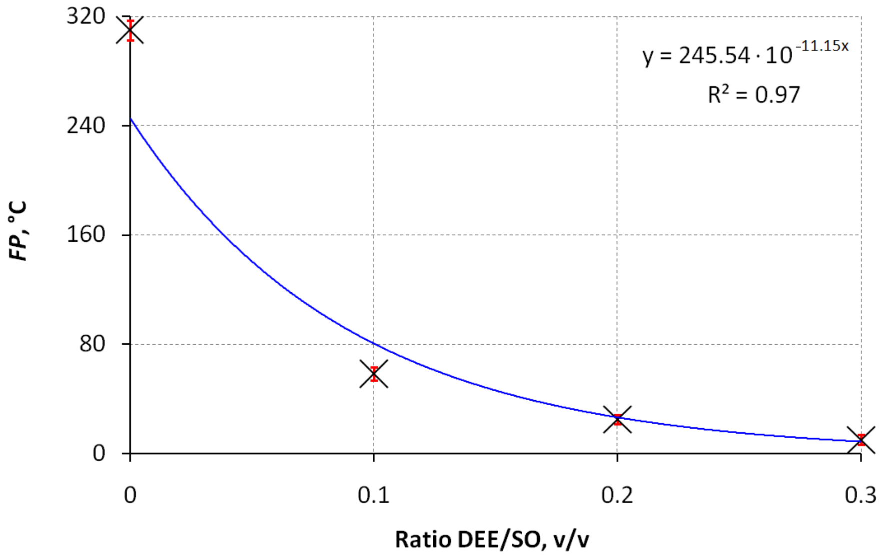

Figure 7. Flash point (FP) of tested blends, SO and DF.

4.2. Engine Emissions

Sunflower oil-based fuels have a large and complex hydrocarbon structure [58], the oxidation and further degradation of which directly affects the concentrations of harmful compounds in the engine exhaust [59]. In terms of smoke, this trend is clearly visible across the entire range of both revolutions and loads (Figures 8 and 9). Due to the different decomposition kinematics of the hydrocarbons that make up sunflower oil [60], a higher number of particulates is formed, as there is not enough oxygen present to fully oxidize these hydrocarbons [61,62]. This is clearly shown by the fact that the addition of DEE, which has a less complex hydrocarbon structure than SO, reduces the opacity depending on the proportion of DEE in the fuel mixture and approaches the opacity values in the diesel engine. Both the increase in speed and the load increase the amount of fuel supplied, which increases the opacity values.

The high viscosity of SO and the kinematics of fuel decomposition result [63] in the formation of relatively high amounts of unburned hydrocarbons in the cylinder, which further forms higher smoke values [64]. The following trends (Figures 10 and 11) are observed in the increase of DEE in fuel mixtures with SO: as the concentration of DEE increases, less THC is formed, but after estimating the measurement errors, these increasing trends are not so pronounced. Compared to diesel, all blends had slightly higher THC values, which can be explained by the fact that SO/DEE blends form a larger droplets after injection to the combustion chamber, which reduces the evaporation rate and at the same time increases the ignition delay [65]. This results in higher concentrations of incomplete combustion products such as THC in the exhaust gas. On the other hand, it is evident that DEE additive lowers THC, which is similar to engine fuelled with diesel fuel.

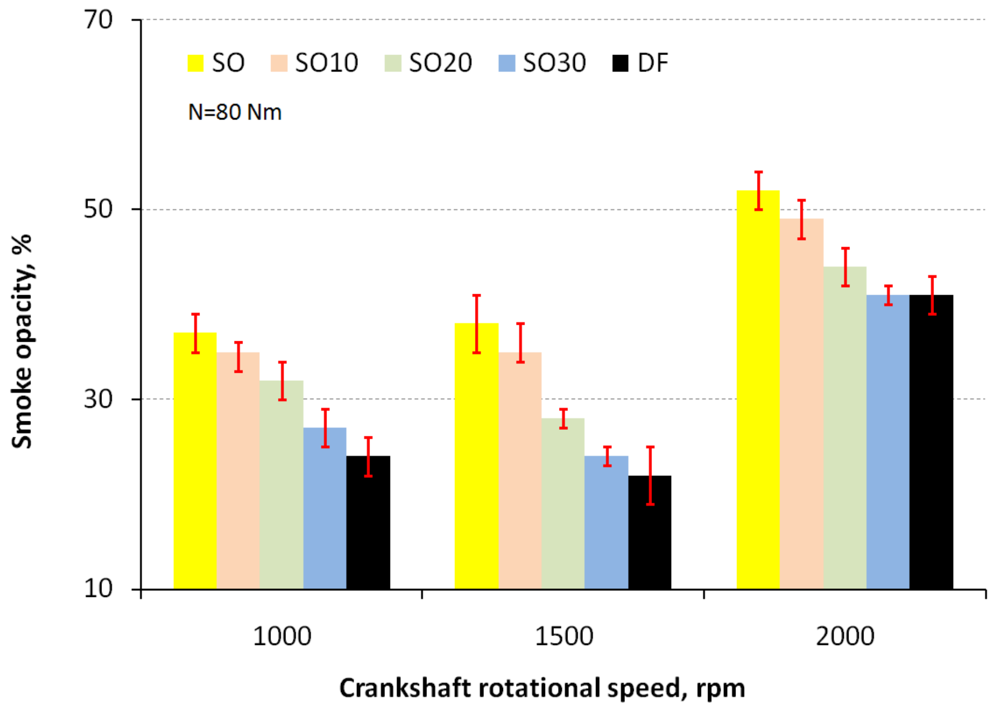

Figure 8. Smoke emission from the AD3 engine operated at 80 Nm.

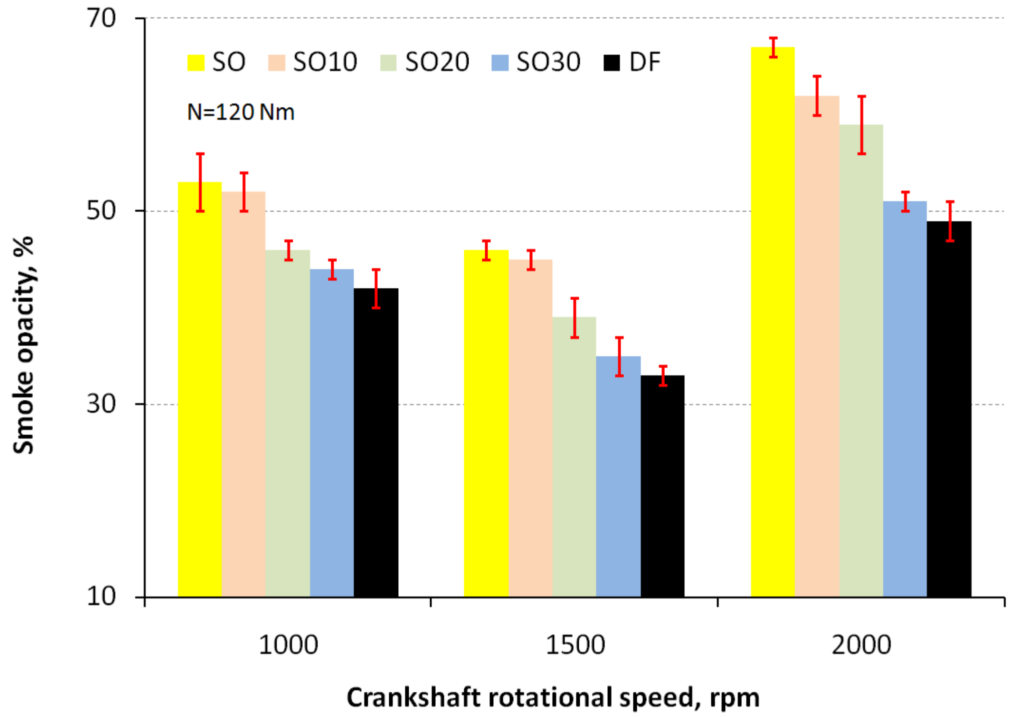

Figure 9. Smoke emission from the AD3 engine operated at 120 Nm.

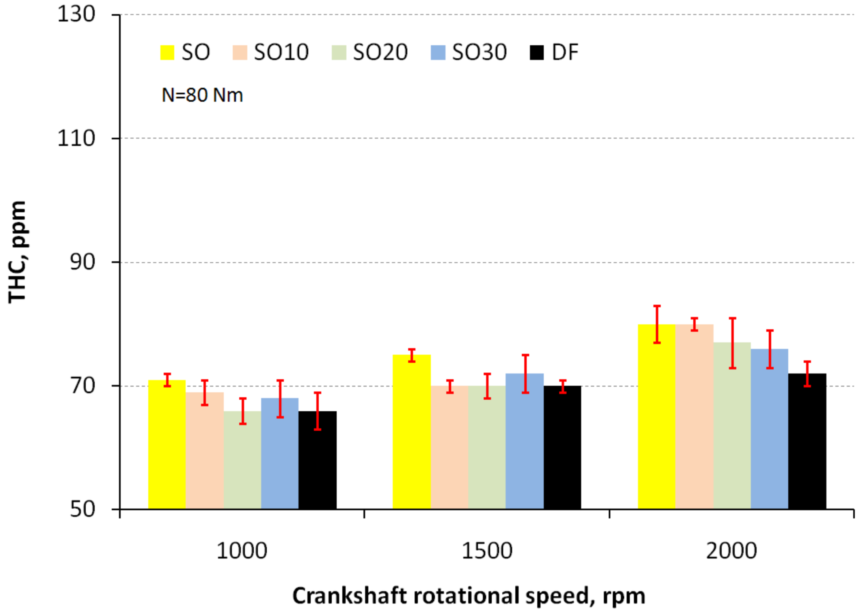

Figure 10. Concentration of THC from the AD3.152 engine operated at 80 Nm.

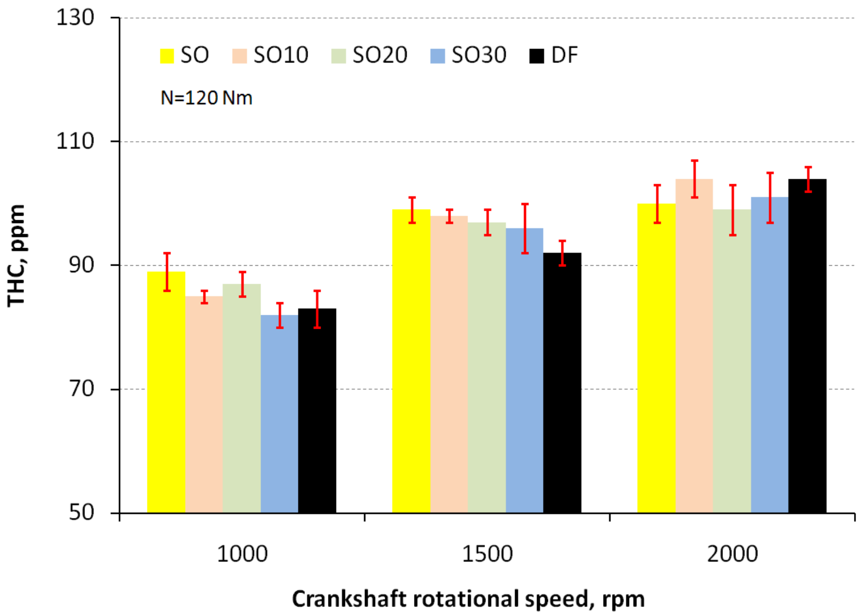

Figure 11. Concentration of THC from the AD3.152 engine operated at 120 Nm.

When using SO, a higher temperature of combustion and more complete combustion process is observed, which increases NOx emissions [66]. This is explained by the presence of oxygen in the oil molecules, which also influences these processes [66]. However, due to the physical-chemical properties of the fuel mixture, when the fuel droplet evaporates worse, the ignition delay increases, which directly affects the premixed combustion phase, which increases the temperature in the cylinder and the formation of thermal NOx [67,68]. Both Figures 12 and 13 confirms that DEE makes it possible to slightly reduce the NOx concentration in the exhaust gas. This can be explained by the DEE's higher latent heat of vaporization, which helps to lower the temperature in the cylinder.

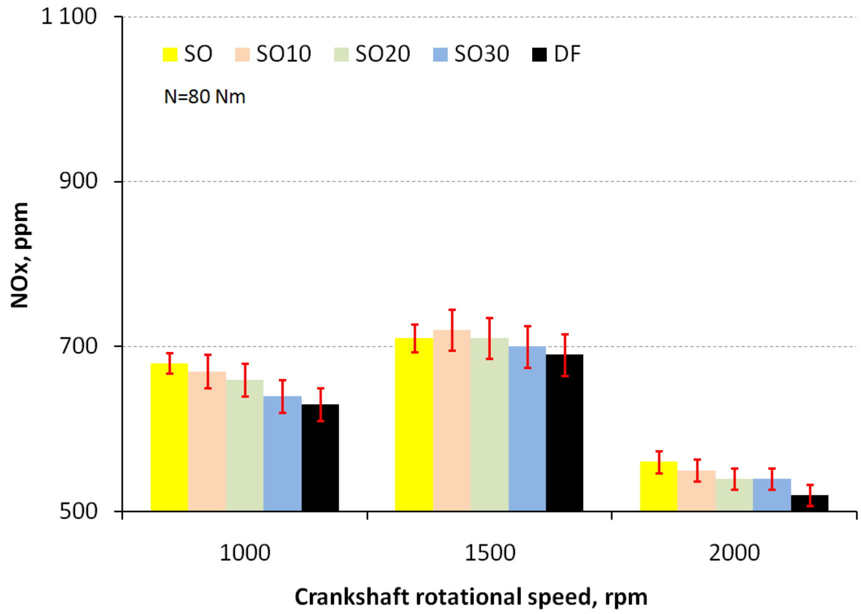

Figure 12. Concentration of NO_X from the AD3.152 engine operated at 80 Nm.

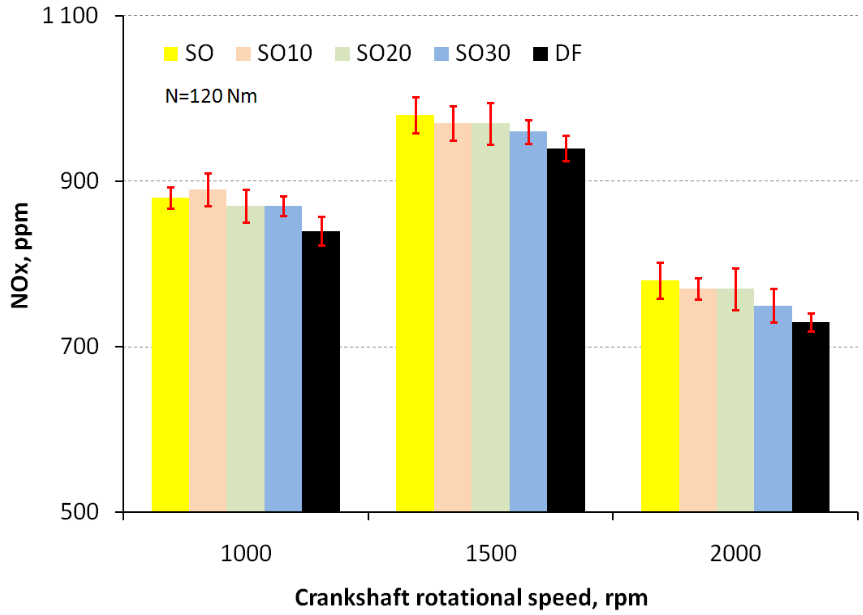

Figure 13. Concentration of NOx from the AD3.152 engine operated at 120 Nm.

5. Conclusions

In this paper, the impact of DEE on selected physicochemical properties of the blend with SO has been examined empirically. Smoke opacity, concentration of unburned hydrocarbons and nitrogen oxides in exhaust gas were also analyzed in relation to results obtained for the engine fueled with diesel fuel. Necessary tests were carried out for SO containing 10, 20 and 30% of DEE by volume.

The obtained results confirmed that the DEE additive improves the physicochemical properties of SO as a fuel for diesel engines. In particular, it has been noted that DEE improves the low temperature properties of the fuel blend. For this reason, DEE/SO blends can also be used in the winter season. The addition of DEE reduces the viscosity and density of SO to values comparable to those for diesel fuel. The surface tension of SO is also adequately lowered by the addition of DEE, which helps to improve the atomization of the fuel.

The physicochemical properties of SO affected the environmental performance of the engine over the full range of speeds and loads. SO is difficult to evaporate, which directly affects the combustion process, during which emissions of smoke, THC and NOx increased. The worst smoke opacity value was obtained for the engine fuelled with SO at torque of 80 Nm and a speed of 1500 rpm. In this case, the smoke opacity was even 70% greater than for the conventionally powered engine. However, the tests carried out have confirmed that the addition of DEE to SO allows to reduce this smokiness to the values comparable with the diesel fuel. In case of unburned hydrocarbons, the values obtained for the engine fuelled with SO were up to 10% worse than for the conventional powered engine operated with a torque of 80 Nm at 2000 rpm. For other conditions results were comparable or DEE addition to SO reduced THC concentration in the exhaust. Finally, the nitrogen oxides were examined. In this case, a minor reduction of NOx up to 8% was observed for the engine fuelled with DEE/SO blends. From our point of view, the combustion of any fuel in a conventional internal combustion engine will always result in the emission of nitrogen oxides. In this aspect, the use of DEE/SO blends does not constitute a significant technological breakthrough. Summarizing the obtained results, it can be concluded that the use of DEE as an additive to SO allows to obtain a fuel mixture with physicochemical properties comparable to diesel fuel. The obtained results also encourage the continuation of work on this type of fuel blends, which may constitute an unconventional source of energy for internal combustion engines. This may be of importance for countries struggling with a periodic shortage of diesel fuel on the markets.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/en15114133/s1, Table S1: Results of the density measurements; Table S2: Results of the viscosity measurements; Table S3: Results of the surface tension measurements; Table S4: Results of the lower heating value (LHV) measurements; Table S5: Results of the cold filter plugging point (CFPP) measurements; Table S6: Results of the flash point (FP) measurements.

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Abbreviations

ASTM	American Society for Testing and Materials
CFPP	Cold filter plugging point
CP	Cloud point
CO	Carbon monoxide
CO_2	Carbon dioxide
DEE	Diethyl ether
DF	Diesel fuel
DI	Direct injection
FP	Flash point
HC	Hydrocarbon
TDC	Top Dead Center
THC	Total hydrocarbons
HFRR	High Frequency Reciprocating Rig

LHV	Lower heating value
N	Torque
NO_X	Nitrogen oxides
PP	Pour point
SO	Sunflower oil
SO10	Blend containing 10% DEE by vol. and 90% SO
SO20	Blend containing 20% DEE by vol. and 80% SO
SO30	Blend containing 30% DEE by vol. and 70% SO
SVO	Straight vegetable oil
ρ	Density
ν	Kinematic viscosity
σ	Surface tension
v/v	Volumetric ratio

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