



Article Modification of Canola Oil Physicochemical Properties by Hexane and Ethanol with Regards of Its Application in Diesel Engine

Rafał Longwic ¹^(b), Przemysław Sander ^{1,*}^(b), Bronisław Jańczuk ²^(b), Anna Zdziennicka ²^(b) and Katarzyna Szymczyk ²^(b)

- ¹ Department of Vehicles, Faculty of Mechanical Engineering, Lublin University of Technology, Nadbystrzycka 36, 20-618 Lublin, Poland; r.longwic@pollub.pl
- ² Department of Interfacial Phenomena, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Skłodowska University in Lublin, Maria Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland; bronislaw.janczuk@poczta.umcs.lublin.pl (B.J.); aniaz@hektor.umcs.lublin.pl (A.Z.); katarzyna.szymczyk@poczta.umcs.lublin.pl (K.S.)
- * Correspondence: p.sander@pollub.pl; Tel.: +48-081-5384255

Abstract: A mixture of canola oil (Co), n-hexane (Hex), and ethyl alcohol (Et) was proposed as a new energy material for powering diesel engines. For this purpose, surface tension, density, and viscosity measurements, as well as engine tests, were performed for 88%Co10%Hex2%Et and 83%Co15%Hex2%Et mixtures at 20 °C. The adsorption and volumetric properties of these mixtures were compared to those of individual mixture components, as well as diesel fuel (Df) and oleic, linoleic, α -linolenic, palmitic, and stearic acids. It was revealed that the values of surface tension, viscosity, and density of Co were higher than those of the Co components. The addition of 10% Hex and 2% Et to Co caused a more than twofold decrease in its viscosity, while the addition of 15% Hex and 2% Et caused a more than fourfold reduction of Co viscosity. In addition, a mixture of Co with 2% Et and 10% Hex had a density similar to that of Df. In turn, theoretical calculations showed that the addition of n-hexane and ethanol to canola oil only slightly changed its heat of combustion. Engine tests were carried out at fixed engine rotational speeds, with a direct gearbox ratio (4th gear). The quick-changing parameters of the combustion process were registered using an AVL Indimicro system. In these tests it was found that the addition of Et to the mixture of Co and Hex did not significantly shorten the auto-ignition delay, but the kinetic phase during combustion disappeared, which had an impact on the combustion start angle.

Keywords: alternative fuel; canola oil; diesel engine; common rail; diesel fuel; n-hexane; ethyl alcohol; injection; combustion

1. Introduction

For almost a century and a half, the common means of transport has been a vehicle equipped with an internal combustion engine fueled by liquid fuels. The primary fuel in diesel vehicles is diesel oil. It should be noted that, along with the development of diesel engine power supply systems, direct fuel injection systems were produced, which are characterized by several injections of fuel for one engine cycle and the combustion of an air–fuel mixture; laminated (excess air) in the range of low loads and homogeneous in the range of full loads. Precise control of the fuel injection process is carried out in order to obtain the desired operating parameters, i.e., average usable pressure, rotational speed, and general efficiency, and to reduce the toxicity of exhaust gases and engine noise, which depends mainly on the proper production of a combustible mixture [1–3]. This mixture must be characterized by a certain homogeneity and the fragmentation of the fuel into drops of the smallest possible diameter [4–6].



Citation: Longwic, R.; Sander, P.; Jańczuk, B.; Zdziennicka, A.; Szymczyk, K. Modification of Canola Oil Physicochemical Properties by Hexane and Ethanol with Regards of Its Application in Diesel Engine. *Energies* 2021, *14*, 4469. https://doi. org/10.3390/en14154469

Academic Editor: Theodoros Zannis

Received: 15 June 2021 Accepted: 20 July 2021 Published: 23 July 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Along with the growing environmental awareness of society and the related tightening of exhaust emission standards, research work has been undertaken to improve power supply systems and the design of the internal combustion engine. A significant direction of research, aimed at meeting the stringent exhaust emission standards, is to improve the properties of fuels used in internal combustion engines. The physicochemical properties of fuels have a direct impact on the injection and combustion process, and an indirect impact on the ecological parameters of exhaust gases. With regard to diesel engines, the works have been carried out mainly in the scope of obtaining fuels not derived from the refining of crude oil; the so-called alternative fuels (biofuels) [7–13]. Currently, a particularly important issue is the reduction of carbon dioxide emissions in the atmosphere. In this regard, the use of biofuel produced from oilseeds, e.g., canola oil, has significant benefits. It can be assumed that the amount of CO_2 emitted during the combustion of plant fuels are similar to those absorbed by plants in the photosynthesis process during plant growth (closed CO_2 cycle) [14,15].

Canola oil (*Co*) used as a fuel has some properties that are more advantageous than diesel fuel, and in particular the large amount of oxygen bound in the fuel is beneficial. Canola oil mainly consists of unsaturated higher fatty acids. They account for over 90% of the oil content [16,17]. These acids are oleic, linoleic, and α -linolenic. Canola oil also contains about 6% saturated higher fatty acids, such as stearic and palmitic acids. About 1% of *Co* are other acids. The molecular structure of canola oil has about 10% oxygen and less carbon and hydrogen than mineral diesel fuel, therefore it has a lower calorific value [14,15]. It also has very good lubricating properties. Difficulties in the use of canola oil to power diesel engines include different physicochemical properties compared to diesel oil, such as the density, viscosity, surface tension, cloud point, and fractional composition. Canola oil also has a high cold filter blocking temperature of approximately -12 °C (CFPP, cold fuel plugging point) [18–20]. It should be remembered that density, viscosity, and surface tension mainly affect the course of the pressing and injection process and the ease of creating a fuel-air mixture, while the fractional composition, the vapor pressure of the fuel, and the calorific value affect the combustion process and the energy parameters obtained [16]. When using canola oil to power diesel engines, it should also be borne in mind that these engines are designed for fuel with physical and chemical properties appropriate for diesel fuel (Df). Therefore, one should strive to change the physicochemical parameters of vegetable fuels so that they are close to *Df* properties. This effect can be obtained, for example, by the addition to vegetable fuels of n-hexane (Hex) and ethanol (*Et*). Taking this into account a series of engine tests in static and dynamic conditions, during which the diesel engine was powered with mixtures of canola oil with the addition of n-hexane were made [21–23]. Despite the fact that the addition of n-hexane to canola oil decreased the surface tension, slightly changed the density, and significantly decreased the viscosity of the mixtures, the values for diesel fuel were not obtained [24,25]. An analysis of the subject literature showed that the addition of ethanol to the above-mentioned mixtures may bring the physicochemical properties of canola oil closer to diesel fuel. Taking this fact into account, surface tension, density, and viscosity measurements, as well as engine tests, were performed for the 88%Co10%Hex2%Et and 83%Co15%Hex2%Et mixtures at 20 °C. Next, the adsorption and volumetric properties of these mixtures were compared to those of individual mixture components, as well as diesel fuel (*Df*) and oleic, linoleic, α —linolenic, palmitic and stearic acids. In addition, selected parameters of the injection process and thermodynamic parameters of the combustion process taking place in a diesel engine were analyzed.

2. Materials and Methods

Diesel fuel (*Df*) complying with EN590 [25], commercial canola oil (*Co*) (Kujawski, ZT "Kruszwica" S.A., Kruszwica, Poland), n-hexane (*Hex*) (ReagentPlus \geq 99%) Sigma Aldrich, ethanol (*Et*) (96% purity) POCH (Poland), oleic acid (POCH), linoleic acid (99%) Acros Organics, and α -linolenic acid (99%) Acros Organics were used in the tests. On the basis

of canola oil, two mixtures with n-hexane and ethanol were prepared. The first mixture contained 88% canola oil (mass fraction (MF) = 0.9074) + 10% n-hexane (MF = 0.0747) + 2% ethanol (MF = 0.079) (88%Co + 10%Hex2%Et) and the second 83% canola oil (MF = 0.8682) + 15% n-hexane (MF = 0.1136) + 2% ethanol (MF = 0.0181) (15% (83%Co15%Hex2%Et).

The equilibrium surface tension (γ_{LV}) of the studied mixtures and other substances were measured using a Krüss K9 (Krüss Germany) tensiometer, according to the platinum ring detachment method (duNouy's method) at 20 °C. The details of measurements were described earlier [22].

The density of the studied mixtures and other substances was measured with a U-tube densitometer, DMA 5000 Anton Paar (Anton Paar GmbH), with the precision of the density measurements equal to ± 0.000005 g cm⁻³. The uncertainty was calculated to be equal to 0.01%.

The measurements of viscosity were made using glass capillary viscometers in the form of a U-tube (130 A Visco3, Huber Kältemaschinenbau AG, Germany). The time was measured for the same standard volume of fluid to flow through the capillary under gravity. The capillary constant was equal to 0.02981 mm^2/s^2 . The viscosity of the studied mixtures was determined based on a calibration curve, which was obtained from the time measured for the model liquids: formamide, oleic acid, and glycerol of known viscosity values.

Traction tests were carried out using a diesel engine with a modern common rail injection system in a homologated Fiat Qubo car equipped with a mechanical gearbox. The vehicle's low fuel pressure system (around 3 bar) was modified with an additional tank and fuel pump. The high-pressure fuel system was not modified. The engine technical data and a view of the test vehicle are presented in the literature [26] and Figure 1. The test vehicle was equipped with an Indimicro 602 measuring system from AVL, allowing the recording of fast changing parameters in real time. Measurements of the compression-ignition engine operation under conditions simulating vehicle motion in traction conditions were made by simulating driving on a DF4FS-HLS chassis dynamometer. Tests were carried out on the chassis dynamometer in direct gear (gear IV) at engine speeds between 2000 and 4500 rpm. The vehicle was loaded with a rolling resistance force simulated by the chassis dynamometer.



Figure 1. Test stand consisting of: 1. Fiat Qubo test car with 1.3 Multijet engine; 2. computer with installed AVL Indicom V2.7 software; 3. Indimicro 602 engine indicator system; 4. DF4FS-HLS chassis dynamometer; 5. additional fuel system tank; 6. KTS Bosch diagnostic module.

3. Results

3.1. Properties of Fuel Mixtures

It is known that some of the physicochemical properties of canola oil important for its use as a diesel fuel differ significantly from those of diesel fuel. Properties such as the viscosity, density, and surface tension of canola oil at 20 °C are higher than those of diesel fuel [17,22]. The biggest differences occur in viscosity, which for canola oil is many times higher than that of *Df*. It is interesting that the *Co* viscosity is more than two times higher than that of its components (Figure 2). This means that there is a significant antagonism in the viscosity of canola oil in relation to its components. This may be due to the reduction of the intermolecular distance between the molecules of canola oil components of *Co*. This causes a significant increase in the intermolecular interactions, which, as is known, increase to the 6th power, while decreasing the distance between molecules.



Figure 2. Values of the viscosity of the canola oil/n-hexane/ethanol mixtures (88%Co10%Hex2%Et and 83%Co15%Hex2%Et), diesel fuel (*Df*), canola oil (*Co*), n-hexane (*Hex*), ethanol (*Et*), as well as oleic, linoleic, α -linolenic, palmitic and stearic acids (palmitic and stearic acids—https://pubchem.ncbi.nlm.nih.gov/compound, accessed on 15 March 2021).

To lower the canola oil viscosity, density, or surface tension, substances should be added which, not only are much lower for these properties, but can change the Co structure. Some authors suggested that knowledge of the viscosity at 40 $^{\circ}$ C (or 100 $^{\circ}$ C) and density at 15 °C is more appropriate for the description of practical applications of organic substances as diesel fuels [27,28]. However, to establish the influence of the concentration of the additives to canola oil on its physicochemical properties, studies should be made at a constant temperature. A temperature equal to 20 °C is the most appropriate, because in the literature there are available data for many substances. Thus it is possible to compare the properties of a mixture to those of individual components. It happened that the above mentioned conditions were satisfied by an n-hexane and ethanol mixture. The viscosity of n-hexane is equal to 0.3 mPa s, and ethanol to 1.144 mPa s, at 20 °C (Figure 2). The addition of 10% n-hexane and 2% ethanol in volume to canola oil causes a more than two times decrease of its viscosity (Figure 2). However, the addition of 15% n-hexane and 2% of ethanol to canola oil decreases its viscosity more than four times (Figure 2). Thus, by the addition of *Hex* and *Et* to *Co* it is possible to decrease its viscosity to value similar to diesel fuel. This decrease is higher than results from the use of low viscosity additives. This means that the mixture of canola oil with n-hexane and ethanol is not ideal. It also suggests that there is a synergetic effect in the reduction of canola oil viscosity by the addition of

n-hexane and ethanol. This effect probably results from changes of *Co* structure, causing a decrease of intermolecular interactions.

The surface tension of a diesel fuel decides the size of the drops in the diesel engine, and is comparable to the surface tension of some components of diesel fuel. However, the surface tension of *Co*, similarly to its viscosity, is higher than that of its components (Figure 3). This means that there is an antagonism in the reduction of canola oil surface tension. According to Fowkes [29], the surface tension of substances having large molecules depends on the type of group in the interface region, such as $-CH_2$, -CH, =CO, -OH. In turn, van Oss and Constanzo [30] stated that the surface tension of substances whose molecules have hydrophobic and hydrophilic parts depends on the orientation of these groups toward the air phase. To such substances, the components of *Co* can be included. Thus, it is possible that the orientation of the molecules of the particular components of canola oil at the canola oil–air interface and their density are different than for a single component. Probably for this reason, the *Co* surface tension is higher than that of its components. This tension is also higher by about 5 mN/m than *Df* (Figure 3). Similarly to the viscosity, the surface tension of canola oil can be decreased by the addition of substances having a lower surface tension than *Co*. Such substances can change the density and composition of the interface region.



Figure 3. Values of the surface tension of the canola oil/n-hexane/ethanol mixtures (88%Co10%Hex2%Et and 83%Co15%Hex2%Et), diesel fuel (*Df*), canola oil (*Co*), n-hexane (*Hex*), ethanol (*Et*), as well as oleic, linoleic, α -linolenic, palmitic, and stearic acids (palmitic and stearic acids, https://pubchem.ncbi.nlm.nih.gov/compound, accessed on 15 March 2021).

As shown in Figures 2 and 3, the viscosity and surface tension of n-hexane and ethanol are considerably lower than canola oil. The decrease of the surface tension is higher than that for the ideal mixture, for which this tension is equal to 30.21 and 28.98 mN/m for 88%Co10%Hex2%Et and 83%Co15%Hex2%Et mixtures, respectively. This means that there is a synergetic effect in the reduction of the canola oil surface tension. Probably, in the presence of n-hexane and ethanol, the number of hydrophobic groups in the interface region is higher than in "pure" canola oil.

The density of canola oil is not significantly higher than that of diesel fuel (Figure 4) and its components are close to having higher density [31]. This confirms our suggestion that the structure of canola oil is different than that of its single components. The density of *Hex* and *Et* is considerably lower than *Co*, and their addition decreases the density of canola oil (Figure 4). Similarly, to viscosity and surface tension, there is synergism in density behavior under the influence of n-hexane and ethanol. With the addition of 2% *Et* and 10% *Hex* the density of *Co* is close to that of *Df* (Figure 4).



Figure 4. Values of the density of the canola oil/n-hexane/ethanol mixtures (88%Co10%Hex2%Et and 83%Co15%Hex2%Et), diesel fuel (*Df*), canola oil (*Co*), n-hexane (*Hex*), and ethanol (*Et*), as well as oleic, linoleic, α -linolenic, palmitic, and stearic acids (palmitic and stearic acids—https: //pubchem.ncbi.nlm.nih.gov/compound, accessed on 15 March 2021).

Apart from the viscosity, surface tension, and density, the amount of oxygen consumed for combustion, the heat of combustion, and the flash point are very important for the use of canola oil as a fuel for diesel engines. The following chemical reactions were used for calculating the amount of oxygen needed to burn canola oil if the reaction products are carbon dioxide and water [22]:

$$C_{17}H_{33}COOH + 25.5O_2 = 18CO_2 + 17H_2O$$
 (1)

$$C_{17}H_{29}COOH + 24.5O_2 = 18CO_2 + 15H_2O$$
 (2)

$$C_{17}H_{31}COOH + 25O_2 = 18CO_2 + 16H_2O$$
(3)

$$C_{17}H_{35}COOH + 26O_2 = 18CO_2 + 18H_2O$$
(4)

$$C_{15}H_{31}COOH + 23O_2 = 16CO_2 + 16H_2O$$
(5)

Taking into account the volume fraction of the particular components of canola oil, the amount of oxygen needed to burn 1 dm³ canola oil was calculated and is about 80. Next, the oxygen number needed to burn 1 dm³ of the *Hex*, *Et*, and *Co* mixtures were determined, taking into account their volume percentage. It appeared that the addition of *Et* and *Hex* to *Co* does not practically change the amount of oxygen needed to burn the canola oil (Figure 5). To calculate the amount of oxygen used to burn the n-hexane and ethanol, the following reactions were applied:

$$C_6H_{14} + 9.5O_2 = 6CO_2 + 7H_2O \tag{6}$$

and

$$C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O$$
(7)



Figure 5. The amount of oxygen mole needed to burn off 1 dm³ of the canola oil/n-hexane/ethanol mixtures (88%Co10%Hex2%Et and 83%Co15%Hex2%Et), diesel fuel (*Df*), canola oil (*Co*), n- hexane (*Hex*), and ethanol (*Et*).

The number of oxygen moles needed to burn 1 dm³ of canola oil and its mixture with n-hexane and ethanol was about 7–8 moles lower than that for diesel fuel (Figure 5), which was calculated based on the data of the model liquids, such as n-hexane, n-hexadecane, benzene, and naftalene. The number of oxygen moles needed to burn 1 dm³ of mixtures with canola oil should be reflected in the values of the heat of combustion. The heat of combustion of *Co* and its mixture with *Hex* and *Et* was calculated from the heat of combustion of canola oil components, as well as n-hexane and ethanol.

From Figure 6, it can be seen that the addition of n-hexane and ethanol to the canola oil only changed its heat of combustion to a small extent. It should be noted that, in all cases the values of heat of combustion were expressed in kJ/dm^3 , because this is more useful from a practical point of view. It appeared that the heat of canola oil and its mixtures with ethanol and n-hexane was about 10% lower than that of diesel fuel.



Figure 6. Values of heat of combustion of canola oil/n-hexane/ethanol mixtures (88%Co10%Hex2%Et and 83%Co15%Hex2%Et), diesel fuel (*Df*), canola oil (*Co*), n-hexane (*Hex*), and ethanol (*Et*).

3.2. Engine Test Results

Maximum torque (Nm) and maximum power (kW) were determined during engine tests (Figure 7). For diesel fuel, the maximum torque and power values were 179.6 Nm at

2235 rpm and 56.6 kW at 4391 rpm, respectively. For vegetable fuels, lower torque values were obtained, by about 11% (88%Co10%Hex2%Et) and 8% (83%Co15%Hex2%Et), and power by about 7% (88%Co10%Hex2%Et) and 14% (83%Co15%Hex2%Et). The biggest differences in relation to *Df* occurred for *Co* 155.6 Nm at 2191 rpm and 45.9 kW at 4024 rpm, respectively; the difference was approximately 14% for torque and 19% for power (Table 1). The effect of the amount of *Hex* addition to *Co* on the obtained values of torque and engine power, as well as acceleration, which may be related to the influence of the physicochemical properties of the fuels, was observed.



Figure 7. Power (**a**) and torque (**b**) values, depending on the rotational speed, engine with diesel supplied with the tested fuels, i.e., *Df*, *Co*, 88%Co10%Hex2%Et, 83%Co15%Hex2%Et.

Table 1. The maximum torque and maximum engine power obtained when performing a test on a chassis dynamometer.

Parameter	Df	83%Co15%Hex2%Et	88%Co10%Hex2%Et	Со
Power	56.6 kW	52.4 kW	53.0 kW	45.9 kW
	4391 rpm	3962 rpm	4056 rpm	4024 rpm
Torque	179.6 Nm	164.8 Nm	159.5 Nm	155.6 Nm
	2235 rpm	2264 rpm	2527 rpm	2191 rpm

The highest mean indicated pressures (IMEP) of vegetable fuels were obtained for the mixture of 83% Co15% Hex2% Et, the values of which were greater than for Df by approx. 8%, with the exception of at 3000 and 4500 rpm, where this relationship was inverse. Despite significant differences in the calorific value of the fuels, the maximum combustion pressure had a direct impact on the average indicated pressure of the vegetable fuels, where it was comparable with respect to Df, except for the speed of 4000 rpm, where the Pmax for Df was approx. 12% lower than Co (Figure 8). Indirectly, the mean indicated pressure was influenced by the amount of injected fuel, injection time (Figure 9), and boost pressure (Figure 10).



Figure 8. Maximum combustion pressure (Pmax), tested fuels: i.e., *Df*, *Co*, 88%Co10%Hex2%Et, 83%Co15%Hex2%Et. Sampling frequency in 1 °C A, (**a**) engine speed 2500 rpm (max Torque), (**b**) engine speed 4000 rpm (max. power).



Figure 9. Injected fuel values, depending on the rotational speed, engine with diesel supplied with the tested fuels, i.e., *Df*, *Co*, 88%Co10%Hex2%Et, 83%Co15%Hex2%Et.



Figure 10. Boost pressure values depending on the rotational speed, engine with diesel supplied with the tested fuels, i.e., *Df*, *Co*, 88%Co10%Hex2%Et, 83%Co15%Hex2%Et.

The most important parameter for the course of the combustion process in a compression ignition engine is the auto-ignition delay time, i.e., the time that elapses from the moment of feeding the fuel dose to the combustion chamber of the engine until the beginning of combustion (Figure 11). Figures 12–15 show the main parameters of the combustion process of an engine powered by the tested fuels. As mentioned above, the addition of *Hex* and *Et* to *Co* causes the viscosity of the obtained fuel to be close to that of *Df*. During the tests, it was observed that the injection start angle was comparable for all fuels (pilot and main injection), while the main injection time was greater than *Df*, which can also be observed (Figure 7) for the amount of fuel injected.



Figure 11. Parameters of combustion process of the diesel engine with direct fuel injection system: (INJ_SIGI1) indicates fuel injection, (Q1) heat release rate, (Pcyl1) combustion chamber pressure, SOC—start of combustion, SOI—start of injection, (l1) heat discharge,(Pcyl1_der) speed of combustion.



Figure 12. Self-ignition delay angle (ID) values depending on the rotational speed, engine with diesel supplied with the tested fuels, i.e., *Df*, *Co*, 88%Co10%Hex2%Et, 83%Co15%Hex2%Et.



Figure 13. Start of combustion (SOC) values depending on the rotational speed, engine with diesel supplied with the tested fuels, i.e., *Df*, *Co*, 88%Co10%Hex2%Et, 83%Co15%Hex2%Et.



Figure 14. Heat release rate, (Q1) under dynamic engine operating conditions (**a**) engine speed 2500 rpm (max Torque); (**b**) engine speed 4000 rpm (max. Power), tested fuels: i.e., *Df*, *Co*, 88%Co10%Hex2%Et, 83%Co15%Hex2%Et.



Figure 15. Heat discharge (I1) under dynamic engine operating conditions, (**a**) engine speed 2500 rpm (max Torque max. power), (**b**) engine speed 4000 rpm (max. power), tested fuels: i.e., *Df*, *Co*, 88%Co10%Hex2%Et, 83%Co15%Hex2%Et.

The self-ignition delay time mainly depends on the physicochemical properties of the fuel, i.e., the cetane number of the fuel (the fuel's ability to self-ignite), viscosity, density, and surface tension (impact on the quality of atomization and dispersion of the fuel dose, air turbulence in the cylinder, mixing of fuel particles with air, subjecting the fuel to physical (evaporation) and chemical changes (partial oxidation of fuel)) [6]. The tested fuels (canola oil and its mixtures with n-hexane and ethanol) showed a tendency to increase the auto-ignition delay angle in the entire range of average engine speeds (with the exception of 83%Co15%Hex2%Et at 2000 and 4500 rpm) compared to diesel fuel.

The course of the combustion start angle of *Co* and its mixtures with *Hex* and *Et* in comparison to Df is shown in Figure 13. The angle of the onset of combustion had a direct impact on the observed delay of auto-ignition. The observed course of heat development (Figure 14) and the amount of spent fuel (Figure 15) indicate that there is a distinct kinetic combustion phase for diesel fuel; initiating ignition sufficiently before the upper piston turning point (TDC). Therefore, the main dose of fuel resulted in the creation of the maximum combustion pressure in the vicinity of the TDC. For Co and its mixtures with Hex and Et, the kinetic phase of combustion has smaller maxima in the heat release rate than Df (Figure 14). Such a course of combustion causes an increase in the auto-ignition delay time, and the angle of the maximum combustion pressure in the indicator diagram is shifted to the right in relation to Df, behind TDC, affecting the energy values of the engine's operation. For the speed of 4500 rpm, the pilot injection was decaying and the injection time parameters were comparable for all fuels. The influence on the method of heat release and the occurrence of the kinetic phase for *Df* could be associated with fuel evaporation, where 95% of Df evaporates at the temperature of 350 °C, while canola oil only decomposes above 250 $^{\circ}$ C and evaporates minimally. In gasoline engines, the addition of ethanol has a positive effect on reducing the fuel's ability to self-ignite. However, it seems that a small addition of ethanol to canola oil and n-hexane did not significantly affect the auto-ignition delay angle of the tested fuels. Greater auto-ignition retardation may result in a possible increase in the amount of toxic components in the vehicle exhaust.

4. Conclusions

The addition of n-hexane and ethanol significantly reduces the viscosity of canola oil. There is a synergetic effect in the reduction of this property. The addition of n-hexane and ethanol also reduced the density and surface tension of canola oil, but to a lower degree than the viscosity. In this case, a synergetic effect is also present.

The addition of n-hexane and ethanol does not practically change the amount of oxygen needed to burn 1 dm³ of the liquid. The same conclusion was reached in the case of the heat of combustion of canola oil and its mixtures with n-hexane and ethanol.

With the increase in the share of n-hexane in the mixture with canola oil, the engine torque and power approached the values obtained when fueling the engine with diesel oil.

The addition of ethanol to the mixture of canola oil and n-hexane did not affect the ignition delay angle in relation to *Df*, which indirectly affects the combustion pressure course.

Feeding the diesel engine with canola oil and mixtures with n-hexane and ethanol resulted in smaller maxima in the kinetic phase of combustion in the heat release rate than Df, which affected the angle of the start of combustion (occurred later relative to Df) and the self-ignition delay. This may have an effect on toxic exhaust emissions. In order to improve the ability of the tested mixtures to self-ignite, a component with a high cetane number should be added.

Author Contributions: B.J., R.L., P.S., A.Z., K.S.—signed the experiments, analyzed the experimental data, made figures, participated in the preparation of the manuscript, and wrote part of the manuscript B.J., R.L., P.S., A.Z., K.S.—conceived the concept of the studies, wrote the main part of the manuscript, supervised the studies, participated in the manuscript preparation, signed the experiments, analyzed the experimental data, and made figures. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available from the authors.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Wang, J.; Sun, H.; Dai, C.; Li, S. GPIO-based rail pressure control for diesel high pressure common rail injection system. *J. Eng.* 2019, 2019, 8293–8298. [CrossRef]
- Schöppe, D.; Atzler, F.; Kastner, O.; Kapphan, F. High Performance Diesel Direct Driven Piezo Common Rail Injection System. In Proceedings of the 23rd Aachen Colloquium: Automobile and Engine Technology, Aachen, Germany, 7–8 October 2014.
- 3. Chen, W.; Pan, J.; Fan, B.; Liu, Y.; Peter, O. Effect of injection strategy on fuel-air mixing and combustion process in a direct injection diesel rotary engine (DI-DRE). *Energy Convers. Manag.* **2017**, *154*, 68–80. [CrossRef]
- 4. Zimont, V.L. Theory of turbulent combustion of a homogeneous fuel mixture at high reynolds numbers. *Combust. Explos. Shock. Waves* **1979**, *15*, 305–311. [CrossRef]
- Longwic, R.; Sander, P.; Nieoczym, A.; Lotko, W.; Krzysiak, Z.; Samociuk, W.; Baąkowsk, H. Effect of some properties of hydrocarbon fuels on self-ignition delay. *Przem. Chem.* 2017, 96, 1123–1127. [CrossRef]
- Hasan, M.M.; Rahman, M.; Kadirgama, K. A review on homogeneous charge compression ignition engine performance using biodiesel-diesel blend as a fuel. Int. J. Automot. Mech. Eng. 2015, 11, 2199–2211. [CrossRef]
- Babu, A.K.; Devaradjane, G. Vegetable oils as fuel for diesel engines: An overview. In Proceedings of the ASME International Mechanical Engineering Congress and Exposition, Proceedings; American Society of Mechanical Engineers (ASME): New York, NY, USA; 2002; Volume 3, pp. 313–318. [CrossRef]
- Lotko, W.; Longwic, R.; Swat, M. The Effect of Rape Oil Diesel Oil Mixture Composition on Particulate Matter Emission Level in Diesel Engine. SAE Tech. Pap. Ser. 2001. [CrossRef]
- Rakopoulos, C.D.; Rakopoulos, D.C.; Kosmadakis, G.M.; Papagiannakis, R.G. Experimental comparative assessment of butanol or ethanol diesel-fuel extenders impact on combustion features, cyclic irregularity, and regulated emissions balance in heavy-duty diesel engine. *Energy* 2019, 174, 1145–1157. [CrossRef]

- Górski, K.; Sander, P.; Longwic, R. The assessment of ecological parameters of diesel engine supplied with mixtures of canola oil with n-hexane. In Proceedings of the IOP Conference Series: Materials Science and Engineering; IOP Publishing: Bristol, UK, 2018; Volume 421, p. 042025.
- 11. Vrabie, V.; Scarpete, D.; Zbarcea, O. Vegetable Oils as Alternative Fuel for New Generation of Diesel Engines: A Review. *Trans Motauto World* **2016**, *1*, 18–22.
- 12. Martins, J.; Brito, F.P. Alternative Fuels for Internal Combustion Engines. Energies 2020, 13, 4086. [CrossRef]
- 13. Bergthorson, J.M.; Thomson, M.J. A review of the combustion and emissions properties of advanced transportation biofuels and their impact on existing and future engines. *Renew. Sustain. Energy Rev.* **2015**, *42*, 1393–1417. [CrossRef]
- 14. Agarwal, D.; Agarwal, A. Performance and emissions characteristics of Jatropha oil (preheated and blends) in a direct injection compression ignition engine. *Appl. Therm. Eng.* 2007, 27, 2314–2323. [CrossRef]
- 15. Souza, S.P.; Pacca, S.; de Ávila, M.T.; Borges, J.L.B. Greenhouse gas emissions and energy balance of palm oil biofuel. *Renew. Energy* **2010**, *35*, 2552–2561. [CrossRef]
- 16. Ge, J.C.; Yoon, S.K.; Kim, M.S.; Choi, N.J. Application of Canola Oil Biodiesel/Diesel Blends in a Common Rail Diesel Engine. *Appl. Sci.* 2016, 7, 34. [CrossRef]
- 17. Liu, H.; Przybylski, R.; Dawson, K.; Eskin, N.A.M.; Biliaderis, C.G. Comparison of the composition and properties of canola and sunflower oil sediments with canola seed hull lipids. *J. Am. Oil Chem. Soc.* **1996**, *73*, 493–498. [CrossRef]
- McGrath, J.; Hickner, M.; Hofer, R. Introduction. In *Polymer Science: A Comprehensive Reference*; Elsevier: Amsterdam, The Netherlands, 2012; Volume 10, pp. 1–3.
- 19. Shahid, E.M.; Jamal, Y. A review of biodiesel as vehicular fuel. Renew. Sustain. Energy Rev. 2008, 12, 2484–2494. [CrossRef]
- 20. Von Wielligh, A.; Burger, N.; Wilcocks, T. Diesel engine failures due to combustion disturbances, caused by fuel with insufficient lubricity. *Ind. Lubr. Tribol.* 2003, *55*, 65–75. [CrossRef]
- 21. Longwic, R.; Sander, P. The course of combustion process under real conditions of work of a traction diesel engine supplied by mixtures of canola oil containing n-hexane. In Proceedings of the IOP Conference Series: Materials Science and Engineering; IOP Publishing: Bristol, UK, 2018; Volume 421, p. 042050.
- 22. Longwic, R.; Sander, P.; Zdziennicka, A.; Szymczyk, K.; Jańczuk, B. Combustion Process of Canola Oil and n-Hexane Mixtures in Dynamic Diesel Engine Operating Conditions. *Appl. Sci.* **2019**, *10*, 80. [CrossRef]
- 23. Longwic, R.; Sander, P.; Lotko, W.; Gorski, K.; Janczuk, B.; Zdziennicka, A.; Szymczyk, K. Self-ignition of rapeseed and n-hexane mixtures in diesel engine. *Przem. Chem.* 2020, *99*, 206–210. [CrossRef]
- 24. Zdziennicka, A.; Szymczyk, K.; Jańczuk, B.; Longwic, R.; Sander, P. Surface, Volumetric, and Wetting Properties of Oleic, Linoleic, and Linolenic Acids with Regards to Application of Canola Oil in Diesel Engines. *Appl. Sci.* **2019**, *9*, 3445. [CrossRef]
- Zdziennicka, A.; Szymczyk, K.; Jańczuk, B.; Longwic, R.; Sander, P. Adhesion of canola and diesel oils to some parts of diesel engine in the light of surface tension components and parameters of these substrates. *Int. J. Adhes. Adhes.* 2015, 60, 23–30. [CrossRef]
- Longwic, R.; Sander, P. The characteristics of the combustion process occurring under real operating conditions of traction. In Proceedings of the IOP Conference Series: Materials Science and Engineering; IOP Publishing: Bristol, UK, 2016; Volume 148, p. 012071.
- 27. Trost, D.; Polcar, A.; Boldor, D.; Nde, D.; Wolak, A.; Kumbár, V. Temperature Dependence of Density and Viscosity of Biobutanol-Gasoline Blends. *Appl. Sci.* 2021, *11*, 3172. [CrossRef]
- 28. Kumbár, V.; Polcar, A.; Votava, J. Fyzikální a mechanické vlastnosti směsí bioetanolu a benzinu. Listy Cukrov. Řepař 2015, 131, 3.
- 29. Fowkes, F.M. Attractive forces at interfaces. Ind. Eng. Chem. 1964, 56, 40–52. [CrossRef]
- Van Oss, C.; Costanzo, P. Adhesion of anionic surfactants to polymer surfaces and low-energy materials. J. Adhes. Sci. Technol. 1992, 6, 477–487. [CrossRef]
- 31. Gros, A.T.; Feuge, R.O. Surface and interfacial tensions, viscosities, and other physical properties of some n-aliphatic acids and their methyl and ethyl esters. *J. Am. Oil Chem. Soc.* **1952**, *29*, 313–317. [CrossRef]