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Effects of the Degree of Unsaturation of Fatty Acid Esters on Engine Performance and Emission Characteristics

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Abstract: Biodiesel is considered an environmentally friendly alternative to petro-derived diesel. The cetane number indicates the degree of difficulty in the compression-ignition of liquid fuel-powered engines. The allylic position equivalent (APE), which represents the unsaturated degree of fatty acid esters, was one of the key parameters for the cetane number of biodiesel. Due to the significant attributes of APE for biodiesel properties, the impact of APE on engine performance and emission characteristics was investigated in this study. The engine characteristics could be improved by adjusting the biodiesel fuel structure accordingly. A four-stroke and four-cylinder diesel engine accompanied by an engine dynamometer and a gas analyzer were used to derive the optimum blending ratio of the two biodiesels from soybean oil and waste cooking oil. Three fuel samples composed of various proportions of those two biodiesels and ultra-low sulfur diesel (ULSD) were prepared. The amounts of saturated fatty acids and mono-unsaturated fatty acids of the biodiesel made from waste cooking oil were significantly higher than those of the soybean-oil biodiesel by 9.92 wt. % and 28.54 wt. %, respectively. This caused a higher APE of the soybean-oil biodiesel than that of the biodiesel from waste cooking oil. The APE II biodiesel appeared to have the highest APE value (80.68) among those fuel samples. When the engine speed was increased to 1600 rpm, in comparison with the ULSD sample, the APE II biodiesel sample was observed to have lower CO and O₂ emissions and engine thermal efficiency by 15.66%, 0.6%, and 9.3%, while having higher CO₂ and NO_x emissions, exhaust gas temperature, and brake-specific fuel consumption (BSFC) by 2.56%, 13.8%, 8.9 °C, and 16.67%, respectively. Hence, the engine performance and emission characteristics could be enhanced by adequately adjusting the degree of unsaturation of fatty acid esters represented by the APE of biodiesel.

Keywords: biodiesel; cetane number; allylic position equivalents; fuel structure; engine performance



Citation: Lin, C.-Y. Effects of the Degree of Unsaturation of Fatty Acid Esters on Engine Performance and Emission Characteristics. *Processes* **2022**, *10*, 2161. <https://doi.org/10.3390/pr10112161>

Academic Editor: Jiaqiang E

Received: 22 August 2022

Accepted: 19 October 2022

Published: 22 October 2022

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1. Introduction

The advantages of biodiesel include lower emissions of toxic gases and particulate matter, and superior lubricity and combustion efficiency. As such, biodiesel has been considered an environmentally friendly alternative to petro-derived diesel [1,2]. Biodiesel, with a higher allylic position equivalent (APE) value, represents a higher degree of unsaturation, lower cetane number, and longer ignition delay for the compression-ignition engine [3]. Considering the example of the oxidation reaction of oleic acid (C18:1), the oxygen molecules of the surrounding air would activate the hydrocarbon compounds at the double bond of C=C of APE of the fatty acid esters. The activated hydrocarbon enhances the combination reaction of oxygen with carbon, resulting in the formation of hydroperoxides [4]. Those hydroperoxides are rather unstable, particularly at the bonds between oxygen and oxygen atoms. The bond strengths at the APE are weaker than those of general C-H bonds [5], resulting in the production of free radicals from dissociating the former C-H bonds.

The effects of various volumetric blends of crude palm oil (CPO) with diesel fuel on the engine performance, emission, and combustion characteristics were experimentally

investigated using a common rail direct injection (CRDI). The addition of CPO to diesel fuel caused a decrease in the peak in-cylinder pressure and the maximum heat release rate (HRR_{max}) [6]. A diesel engine powered by ternary blended fuels of diesel-palm biodiesel-ethanol under low idling conditions was found to have significant effects on brake-specific fuel consumption and ignition delay [7]. The variables of proportions of diesel fuel mixed with ethanol and multiple injection strategies (MISs) were also found to influence the emissions and engine performance [8]. Various fatty acids generally bear different carbon-chain lengths and numbers of double bonds. The fuel structure and chemical composition of biodiesel primarily account for its burning characteristics [9]. In particular, the carbon-chain lengths and saturation degree of fatty acid esters influence the fuel properties of biodiesel such as the cetane number and heating value [10,11]. The allylic position equivalents (APE) are the organic compounds close to alkene molecular groups of the biofuel structure [12]. The unsaturated chemical compounds of APE would significantly alter the fuel properties, particularly the oxidative stability and kinematic viscosity, of the biofuel [13]. The chemical bond strengths of the APE compounds are weaker than those of general hydrocarbon bonds by 10–15% [14]. Consequently, the chemical bonds with a weaker APE are susceptible to being attacked by oxidants, heat, or pressure, leading to the formation of free radicals from dissociating APE bonds. The deterioration of fuel properties and rancidity of fatty acid esters might thereafter occur [15].

The allylic position equivalent (APE) is one of the major indicators of the saturation degree of fatty acid esters. Fatty acid esters with a greater degree of unsaturation tend to have a longer ignition delay in a compression-ignition engine together with higher brake fuel consumption and superior cold flow behavior [16]. For example, the cetane numbers of stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:3) are 86.9, 59.3, 38.2, and 23.0, respectively. This implies that an ester composed of more double bonds has a higher APE value and is thus inferior regarding its auto-ignition characteristics. Inferior oxidative stability would also occur for fatty acid esters with a higher APE value [17]. The APE value of an ester is calculated by the following formula [18]:

$$\text{APE} = 2 \times (\text{weight percentage of oleic acid C18:1} + \text{weight percentage of linoleic acid C18:2} + \text{weight percentage of linolenic C18:3}). \quad (1)$$

The weight percentages of fatty acid esters are determined by a GC-MS (Gas chromatography–Mass spectrometry) analyzer. An ester consisting of more unsaturated fatty acids indicates a higher APE value and inferior thermal, storage, and oxidative stabilities [19,20]. Biodiesel is composed of various fatty acid esters with different weight percentages and corresponding APE values. The combined APE value of biodiesel can thus be calculated by summing up the multiplication of the APE value of each ester and its corresponding weight percentage based on the following formula:

$$\text{APE (allylic position equivalents)} = ap_1 \cdot AC_1 + ap_2 \cdot AC_2 + ap_3 \cdot AC_3 + \cdots + ap_i \cdot AC_i \quad (2)$$

where ap_i is the value of a certain type of allylic position equivalent and AC_i is the weight percentage of the corresponding allylic position equivalent. Similar models to estimate other combined fuel properties of biodiesel composed of various esters such as the cold filter plugging point, kinematic viscosity, flash point, and density were proposed in the literature as well [21].

Although APE is used to indicate the degree of unsaturation of fatty acid esters and significantly affects the fuel properties of biodiesel, the effects of relevant parameters of the fuel structure on the fuel characteristics of biodiesel have not been well investigated [22]. The APE parameter has been found to affect both the oxidative stability and cold flow property of biofuels [23,24]. However, there is no study to investigate the influences of unsaturation factors indicated by the APE of biofuel esters on engine performance and the emission characteristics of diesel engines [25]. Hence, three fuel sample mixtures of two various biodiesels and ultra-low sulfur diesel (ULSD) with different APE values were considered to analyze their influences on the compression-ignition characteristics using a four-stroke diesel engine and an eddy-current dynamometer. The engine performance including brake-specific fuel consumption (BSFC) and engine thermal efficiency (η) and engine emissions, such as carbon monoxide (CO) and nitrogen oxides (NO_x), were measured and analyzed in this experimental study.

2. Experimental Details

2.1. Preparation of Biodiesel for Engine Test

Waste cooking oil and soybean oil were used to produce biodiesel to prepare mixed biodiesel samples with various allylic position equivalents (APE). A mechanical homogenizer was used to stir the feedstock oil of either waste cooking oil or soybean oil with methanol and the strong alkaline catalyst sodium hydroxide (NaOH) at 60 °C to produce a transesterification reaction. The molar ratio of the feedstock oil and methanol was set at 1:6 and the added NaOH was weighed to be 1 wt. % of the feedstock oil. The stirring speed of the mechanical homogenizer was kept constant at 6000 rpm for 50 min to complete the transesterification reaction. Glacial acetic acid of the corresponding amount of the alkaline catalyst NaOH was mixed with the crude biodiesel product mixture and stirred for 5 min to neutralize its pH value.

The crude product was then separated into biodiesel at the upper layer and glycerol at the bottom by motionless settlement or centrifugal force by virtue of the obvious density difference between the two compounds. The separated crude biodiesel was then heated to 70 °C to vaporize volatile substances such as methanol. Deionized water of 10 vol. % of the crude biodiesel was used to water-wash the biodiesel and then settled down for 20 min to remove the liquid water at the bottom of the tank three times. The biodiesel was finally distilled to expel residual methanol, water, and other impurities by heating it to 110 °C for 15 min.

2.2. Analysis of Fatty Acid Compositions and Allylic Position Equivalents (APE)

A gas chromatograph (GC) analyzer (Model GC-14A, Shimadzu Inc., Kyoto, Japan) together with a Flame Ionization Detector (FID) and a chromatograph data management system (Avantech Inc., Taipei, Taiwan) was utilized to analyze the weight percentages of the fatty acid esters of biodiesel made from waste cooking oil and soybean oil, respectively. The size of the fused silica capillary column (Model Zebron ZB-5HT Inferon Column, Phenomenex Inc., Torrance, CA, USA) used in the GC analyzer was 30 m in length, 0.32 mm in diameter inside, and 0.25 µm in film thickness. Nitrogen gas was used as the carrier gas at a flow rate of 20–100 mL/min. The types of methyl esters in the biodiesel samples were chromatographically resolved based on the retention times and elution order. The oven temperatures for the GC were adjusted to an initial 50 °C for 5 min, followed by a heating increase to 250 °C at a rate of 5 °C/min, and finally, kept constant at 250 °C for 15 min.

The allylic position equivalent (APE) is located at the neighboring C=C of the molecular group of olefin compounds. The APE of the fatty acid esters was determined by the number of allylic positions equivalent to each fatty acid ester and their corresponding weight proportions, which is expressed in Equation (2). The increase in APE implies a greater degree of unsaturation of fatty acid esters and an elongated ignition delay in the compression-ignition engine. An adiabatic oxygen calorimeter (6772 model, Parr Inc., Moline, IL, USA) was used to measure the heating value of the biodiesels released from their complete combustion. The carbon residue in a unit of wt. % was determined by the weight percentage of carbon residue left after complete burning to the weight of the fuel sample before burning. The iodine value was measured by titrating 0.01 N sodium thiosulfate into the mixture of the fuel sample and chemical reagents until the appearance of a light yellow color. The standard ASTM D1298-99e2 test method was used to determine the specific gravity at 15 °C using a specific gravity meter. A capillary viscometer (50123/IIc model, Schott Geräte Inc., Mainz, Germany) was used to measure the kinematic viscosity of the fuel sample.

2.3. Engine Test Preparation

A naturally aspirated, direct-injection, four-stroke, four-cylinder diesel engine (Model UM4BD1, Isuzu Inc., Kanagawa, Japan) was aligned with an eddy-current dynamometer (Model FE-150S, Borghi & Saveri Inc., Pieve Di Cento, Italy). The engine torque can be varied from 0 to 176.4 N·m. The experimental engine data were acquired by an automatic engine acquisition and analysis system. The engine torque in this study was set at a constant of 98 N·m but had varied engine speeds from 600 to 1600 rpm. A gas analyzer (Model Chemist 606, Seitron Inc., Mussolente, Italy) was incorporated with a K-type thermocouple to measure the gaseous emissions including CO, CO₂, NO_x, and SO_x, and the exhaust gas temperature from the diesel engine fueled by the three fuel samples with various APE. The gas analyzer began to collect emission data after the diesel engine ran continuously for at least 30 min.

Brake-specific fuel consumption (BSFC) is defined as the amount of fuel consumed per power output from the engine. BSFC represents the conversion efficiency from the thermal energy of fuel

combustion to the engine power output. Thus, a lower BSFC indicates superior combustion efficiency and is favorable for engine operation. BSFC is calculated based on the following Equation (3):

$$\text{BSFC (g/kWh)} = \frac{\dot{m}_f \text{ (g/hr)}}{P_b \text{ (kW)}} \quad (3)$$

where

$$P_b \text{ (kW)} = 2\pi N \text{ (rev/s)} \cdot T_b \text{ (N}\cdot\text{m)} \times 10^{-3}. \quad (4)$$

is the braking power of the engine, N is the engine speed, T_b is the braking torque of the engine, and $\dot{m}_f$ is the fuel consumption rate of the engine.

Engine thermal efficiency η_f is the ratio of braking power output and the thermal energy released from the fuel combustion per engine cycle. The dimensionless engine thermal efficiency can be used to represent the conversion efficiency from heat release through fuel burning to the engine power output, which can be calculated based on Equation (5) below:

$$\eta_f = \frac{P_b}{\dot{m}_f Q_{HV}} = \frac{3600 \text{ (kW)}}{bsfc \text{ (g/kW} \cdot \text{hr)} \times Q_{HV} \left(\frac{\text{MJ}}{\text{kg}} \right)} \quad (5)$$

where Q_{HV} is the higher heating value of the engine fuel. The denominator of the above Equation (5) is the amount of heat supplied from fuel burning per engine cycle.

Biodiesel made from waste cooking oil and soybean oil was mixed with ultra-low sulfur diesel (ULSD) to obtain fuel samples with various compositions of fatty acid esters and APE values. Sample fuel 1 (termed APE I biodiesel) was composed of 30 wt. % biodiesel from waste cooking oil, 20 wt. % biodiesel from soybean oil, and 50 wt. % ULSD. Sample fuel 2 (termed APE II biodiesel) was mixed with 10 wt. % biodiesel from waste cooking oil, 40 wt. % biodiesel from soybean oil, and 50 wt. % ULSD. Sample Fuel 3 (termed ULSD) consisted of 100 wt. % ULSD. The combined allylic position equivalents (APE) of sample fuels 1 to 3 were calculated to be 74.04, 80.68, and 0, respectively. The compositions of those three fuel samples are shown in Table 1. The sample fuel of APE II biodiesel composed of 20 wt. % more soybean-oil biodiesel than APE I biodiesel sample appeared to have a larger combined APE value by 6.64.

Table 1. Compositions of three fuel samples in this study.

Fuel Sample	Compositions (wt. %)			APE
	Waste Cooking-Oil Biodiesel	Soybean-Oil Biodiesel	ULSD	
APE I biodiesel	30	20	50	74.04
APE II biodiesel	10	40	50	80.68
ULSD	0	0	100	0

3. Results and Discussion

3.1. Lipid Structure of the Biodiesels

The biodiesels made from waste cooking oil and soybean oil were analyzed by a gas chromatograph (GC) analyzer with a Flame Ionization Detector (FID) for their weight percentages of fatty acid esters. The results indicate that the fatty acid esters of the biodiesel made from waste cooking oil were primarily composed of carbon-chain lengths ranging between C16 and C20, while the biodiesel from soybean oil ranged between C18 and C20, as shown in Table 2. The amounts of saturated fatty acids and mono-unsaturated fatty acids in the biodiesel produced from waste cooking oil were significantly more than those of the biodiesel from soybean oil by 9.92 wt. % and 28.54 wt. %, respectively. This implies that the former biodiesel displayed superior oxidative stability and a higher cetane number than the latter. The weight percentage of polyunsaturated fatty acids with two or more double bonds in the lipid structure achieved as high as 59.1 wt. % in the latter biodiesel from soybean oil, in comparison with only 14.5 wt. % in the waste cooking-oil biodiesel. The biodiesel from soybean oil is thus considered to have relatively more desirable low-temperature fluidity and a lower cold filter plugging point (CFPP). The APEs of the biodiesels from waste cooking oil and soybean oil, which were calculated using Equation (2) based on the weight percentages of the distributions of

fatty acid esters in Table 2, are 134.8 and 168.0, respectively. This illustrates that the latter biodiesel with a larger APE by 33.2 bears a lower degree of lipid saturation and thus inferior oxidative and thermal stability after being attacked by the surrounding oxygen and thermal energy compared to the former biodiesel. The APEs of the three fuel samples for powering the diesel engine were adjusted by mixing different proportions of the two biodiesels and ultra-low sulfur diesel (ULSD). The iodine value, which indicates the extent of unsaturated fatty acid esters, of the soybean-oil biodiesel was shown to have a larger value than the waste cooking-oil biodiesel in Table 2. The specific gravity and carbon residue of the weight percentage of unburnt carbon after the complete combustion process of the biodiesel from waste cooking oil were larger than those of the soybean-oil biodiesel due to the larger amount of more viscous saturated fatty acid esters of the former biodiesel, which achieved 5.515 mm²/s. In addition, the cetane index of the waste cooking-oil biodiesel was shown to be lower (45.288).

Table 2. The weight percentages (wt. %) of the fatty acid esters for the biodiesel from waste cooking oil and soybean oil.

Fatty Acid Esters	Biodiesel from Waste Cooking Oil	Biodiesel from Soybean Oil
C16:0	20.2	11.3
C18:0	4.8	3.6
C18:1	52.9	24.9
C18:1-OH	0	0
C18:2	13.7	53
C18:3	0.8	6.1
C20:0	0.12	0.3
C20:1	0.84	0.3
Saturated fatty acids	25.12	15.20
Mono-unsaturated fatty acids	53.74	25.2
Poly-unsaturated fatty acids	14.5	59.1
APE	134.8	168.0
Heating value (MJ/kg)	43.24	43.17
Carbon residue (wt. %)	0.18	0.10
Specific gravity	0.890	0.885
Kinematic viscosity (mm ² /s)	5.515	4.125
Iodine value (mg KOH)	95.37	116.09
Cetane index	45.288	49.566

3.2. Effects of APE on Engine Performance

3.2.1. Brake-Specific Fuel Consumption

Brake-specific fuel consumption (BSFC) is the amount of fuel consumed in unit g/hr per engine power output in kW. Fuel with a lower bsfc to attain the same engine power output implies higher fuel economy and thus is more favorable. The BSFC values increased slightly with the increase in the engine speed due to a larger consumption of fuel required to provide more power output under a faster engine speed. The ultra-low sulfur diesel (ULSD) was found to have the lowest BSFC among the three sample fuels. This is primarily because the ULSD possesses the highest heating value of 46.20 MJ/kg in comparison with that of 43.17 MJ/kg for soybean-oil biodiesel and 43.24 MJ/kg for waste cooking-oil biodiesel. Hence, a lower fuel consumption rate is required for the ULSD. In addition, there is no APE in the ULSD. This implies that the ULSD is more chemically stable in the hydrocarbon structure and is, therefore, more prone to burning completely [26], which results in higher heat release from the burning process. Consequently, a lower fuel consumption rate and lower BSFC occurred for the ULSD compared to the other fuel samples composed of biodiesels from various feedstocks [27].

This study also found that an increase in biodiesel's APE required a larger amount of fuel consumption to attain the same engine power output. A biodiesel mixture with a larger APE value implies a greater degree of unsaturation of the fatty acid esters and, thus, less heat was released from burning that fuel sample. Hence, the fuel sample of APE II (with APE 80.68) was observed to have the highest BSFC while the ULSD fuel sample had the lowest BSFC among the three fuel samples (Figure 1). At an engine speed of 1600 rpm, the BSFC of APE II biodiesel reached 255.847 g/kWh, which was significantly higher than that of the ULSD fuel sample (219.29 g/kWh) by 16.67%.

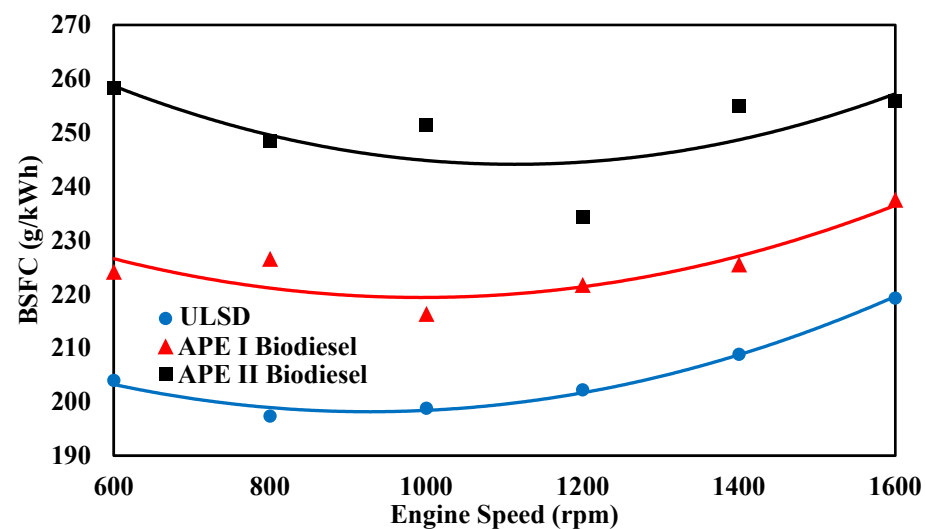


Figure 1. Effects of engine speed and APE on BSFC.

3.2.2. Engine Thermal Efficiency

An engine's thermal efficiency η_f is defined as the conversion ratio of braking power output from chemical energy released from fuel-burning processes as shown in Equation (5). A higher engine thermal efficiency indicates either superior engine performance of converting chemical energy to produce more engine braking power or a higher combustion efficiency of fuel burning in the engine cylinder. Therefore, the engine thermal efficiency is the inverse of the multiplication of BSFC and the heating value. Higher engine thermal efficiency is thus preferable for a diesel engine or fuel sample.

The engine thermal efficiency η_f decreased with an increase in engine speed, as illustrated in Figure 2. This is due to the larger fuel consumption rate required at higher engine speeds, resulting in a higher BSFC in Figure 1. Hence, the corresponding lower engine thermal efficiency was obtained at a faster engine speed in Figure 2. Fuel sample 3, which is the total ULSD, was observed to have the highest, while fuel sample APE II (with APE 80.68) had the lowest engine thermal efficiency among the three fuel samples in Figure 2. This is primarily ascribed to the fact that ULSD possesses the highest heating value, 46.2 MJ/kg, in comparison to the heating values of the biodiesel made from waste cooking oil, 43.24 MJ/kg, and the biodiesel from soybean oil, 43.17 MJ/kg. The fuel sample with a higher heating value required a lower fuel consumption rate to have the same engine power output, and thus, a lower BSFC and higher engine thermal efficiency η_f in Figure 2. In contrast, the biodiesel with a larger APE value indicated a lower saturation degree in the chemical structure of fatty acid esters, lower combustion efficiency [28], and, hence, less heat released from the burning processes. The combined APE value of the fuel sample APE II biodiesel reached 80.68, which was the highest one among the three fuel samples. As a result, higher fuel consumption is required for the fuel sample containing the esters with a higher combined APE value [29] to receive the same engine power output among the three fuel samples. The APE II fuel sample was thus found to have lower combustion efficiency and lower engine thermal efficiency represented in Figure 2. At the engine speed of 1600 rpm, the APE II biodiesel, which had the highest APE value of 80.68, was observed to have the lowest engine thermal efficiency (0.290), while the ULSD fuel sample appeared to have the highest one (0.317). The latter fuel sample had higher engine thermal efficiency than the latter by 9.3%.

3.2.3. Exhaust Gas Temperature

The exhaust gas temperature of the diesel engine fueled by the three fuel samples under different engine speeds is shown in Figure 3. The engine torque was set constant at 98 N·m. A K-type thermocouple incorporated with a gas analyzer was used to measure the temperature of exhaust gas. The increase in engine speed required more fuel consumption to attain greater engine power output. Higher heat was thus released from more fuel burning. Hence, higher exhaust gas temperature increased with the increase in engine speed for the three fuel samples in this study.

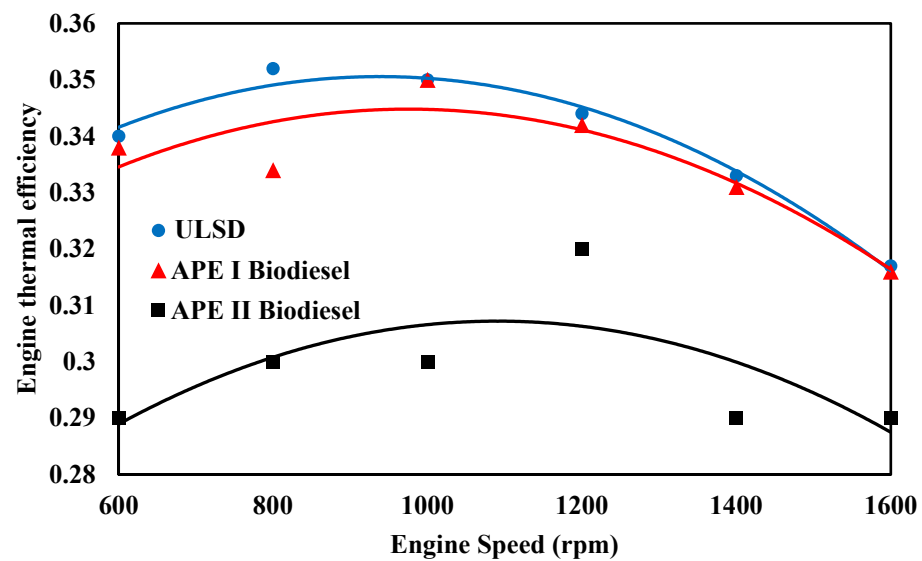


Figure 2. Effects of engine speed and APE on engine thermal efficiency.

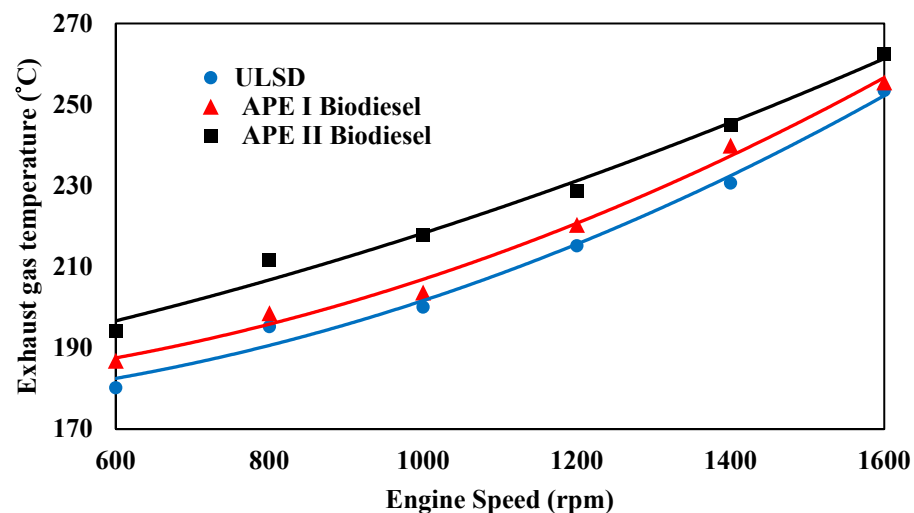


Figure 3. Effects of engine speed and APE on exhaust gas temperature.

The increase in the combined APE value of the fuel sample with a lower degree of saturation of the fatty acid esters caused an increase in the exhaust gas temperature. More oxygen and carbon atoms of the unsaturated fatty acids are prone to be broken up to produce an accelerated chemical reaction. Hence, a higher exhaust gas temperature was produced from the fuel sample composed of the biodiesel mixture with the highest combined APE value. In addition, the weight percentage of the biodiesel from soybean oil increased from 20 wt. % for the APE I fuel sample to 40 wt. % for the APE II biodiesel. The biodiesel from soybean oil is composed of less saturated fatty acid methyl esters, which is 15.2 wt. % in comparison with 25.12 wt. % of the biodiesel from waste cooking oil. Fatty acid esters of a higher degree of unsaturation tend to decompose their ester structure [30] to produce a higher exhaust gas temperature. The period of ignition delay of biodiesel tends to decrease with the increase in the unsaturation extent, resulting in a shorter premixed combustion stage than that of high saturated fatty acid [31]. As a result, the APE II fuel sample consisting of more unsaturated esters was observed to have the highest exhaust gas temperature among the three fuel samples in Figure 3. At an engine speed of 1600 rpm, the exhaust gas temperature from burning the APE II biodiesel sample with the highest unsaturated extent of fatty acid esters achieved the highest temperature of 262.4 °C in comparison to 253.5 °C from burning neat ULSD. The APE II biodiesel sample appeared to have a higher exhaust gas temperature than the latter fuel sample by 3.5%.

Compression-ignition diesel engines are generally operated under fuel-lean combustion conditions. Hence, their HC emission is frequently too low to be considered. In addition, the burning of biodiesel, which contains approximately 10 wt. % oxygen, to improve combustion efficiency would

emit nearly no black smoke from diesel engines. The combustion characteristics accompanied by various emissions from burning those three fuel samples in the diesel engine are discussed in the following sub-sections.

3.2.4. Carbon Dioxide Emission

The emissions of carbon dioxide (CO_2) from the diesel engine powered by the three fuel samples were measured by a gas analyzer. The engine speeds varied from 600 to 1600 rpm, but the engine torque remained constant. As the engine speed increased, a larger fuel consumption rate was required to raise the engine power output. The amount of CO_2 emission is determined by the weight percentage of elemental carbon and the equivalence ratio of the hydrocarbon fuel [32]. Biodiesel possesses a lower heating value primarily due to its lower elemental carbon content than petro-diesel. Hence, biodiesel has a larger equivalence ratio in comparison with ultra-low sulfur diesel (ULSD). This resulted in the lowest CO_2 emission from the burning process of ULSD among the three fuel samples (Figure 4). In contrast, the fuel sample APE II, which was composed of more unsaturated fatty acids and had a lower heating value [33], was observed to have the largest equivalence ratio. The largest amount of injected fuel was required to reach the same engine power output for the fuel sample APE II. Consequently, burning the APE II fuel sample in the diesel engine emitted the highest CO_2 emission, as illustrated in Figure 4. The increase in the APE value in the fuel mixture caused an increase in CO_2 emissions. The CO_2 concentration reached as high as 4.0% at an engine speed of 1600 rpm from burning the APE II biodiesel sample, which was higher than the lowest CO_2 emission from burning the fuel sample ULSD by 2.56%.

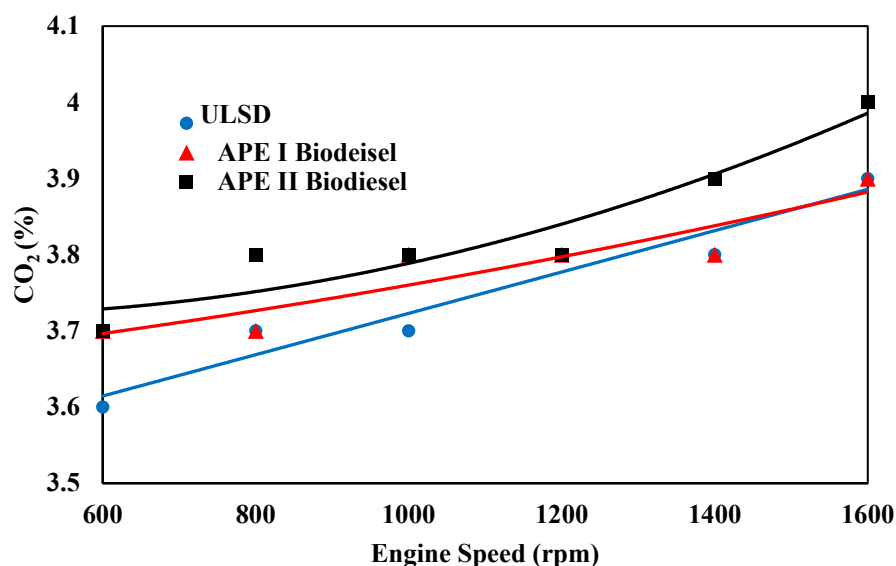


Figure 4. Effects of engine speed and APE on CO_2 emission.

3.2.5. Oxygen Emission

The diesel engine fueled with ULSD was shown to have the highest oxygen emission among the three fuel samples (Figure 5). This is ascribed to the highest engine thermal efficiency of the ULSD-powered engine (Figure 2). Hence, ULSD consumed less excess air to provide the same power output as the other two fuel samples and had the highest O_2 concentration in the exhaust gas. In addition, the use of ULSD as the engine fuel that required the lowest equivalence ratio among the three fuel samples indicates the least amount of fuel was injected into the combustion chamber of the diesel engine to react with the inlet air [34]. Therefore, the most unburnt oxygen remained in the exhaust gas from the engine fueled with ULSD (Figure 5). In contrast, the APE II sample fuel, which displays the lowest engine thermal efficiency (Figure 2) [35] and the highest equivalence ratio, reacted with the least amount of inlet air remaining in the engine chamber, leading to the lowest O_2 emission (Figure 5). The increase in engine speed rendered lower O_2 emissions due to a larger amount of air burned with the sample fuel to attain higher engine power at faster engine speeds. The amount of unburnt oxygen left in the exhaust gas is therefore decreased, as shown in Figure 5. The O_2 emission decreased to the lowest 15.6% from burning the APE II biodiesel sample, which possessed the highest

saturated extent of fatty acid esters among the three fuel samples and was lower than the highest O₂ emission (15.7%) from burning ULSD by 0.6% when the engine speed ran at 1600 rpm.

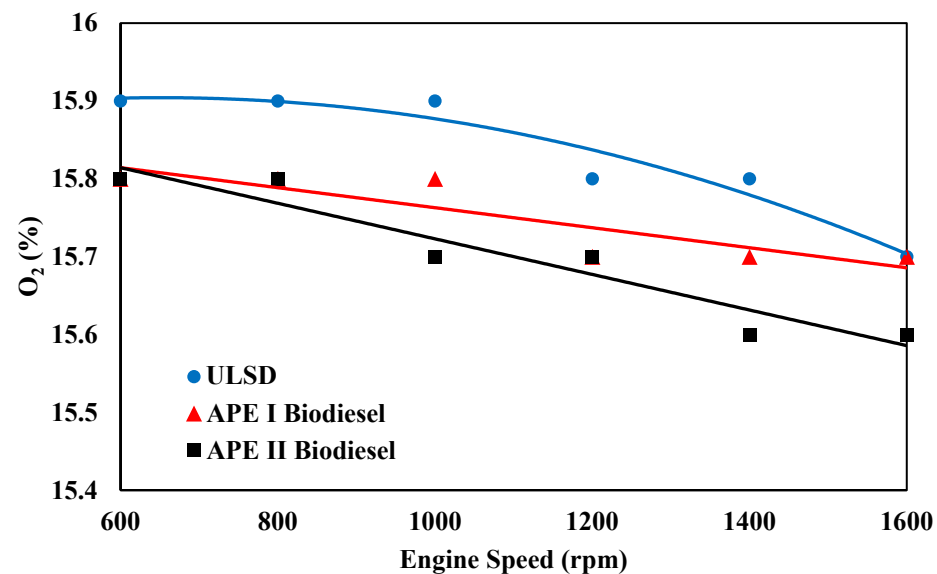


Figure 5. Effects of engine speed and APE on O₂ emission.

3.2.6. Carbon Monoxide Emission

The carbon monoxide (CO) emissions from the diesel engine powered with a fuel mixture of various APE values are shown in Figure 6. The increase in engine speed is found to increase CO emissions due to not having enough time to convert CO gas to produce CO₂ at higher engine speeds [36]. An increase in engine speed caused more power output and a higher in-cylinder gas temperature, resulting in a relatively higher conversion rate of CO. Hence, the increase in CO with engine speed was slower. The burning of ULSD fuel emitted the highest CO concentration in the exhaust gas of the engine in comparison with that of biodiesel. A similar finding was observed by Alam et al. [37]. This is primarily due to the highest elemental carbon content in ULSD compared to the three fuel samples in this study. In contrast, the APE II fuel sample, which displayed the highest number of double bonds and the lowest saturation degree, had the lowest CO emission. The burning of the ULSD fuel sample emitted the highest CO concentration (517 ppm) when the engine speed ran at 1600 rpm and was significantly higher than that of burning the APE II biodiesel sample (447 ppm) by 15.66%.

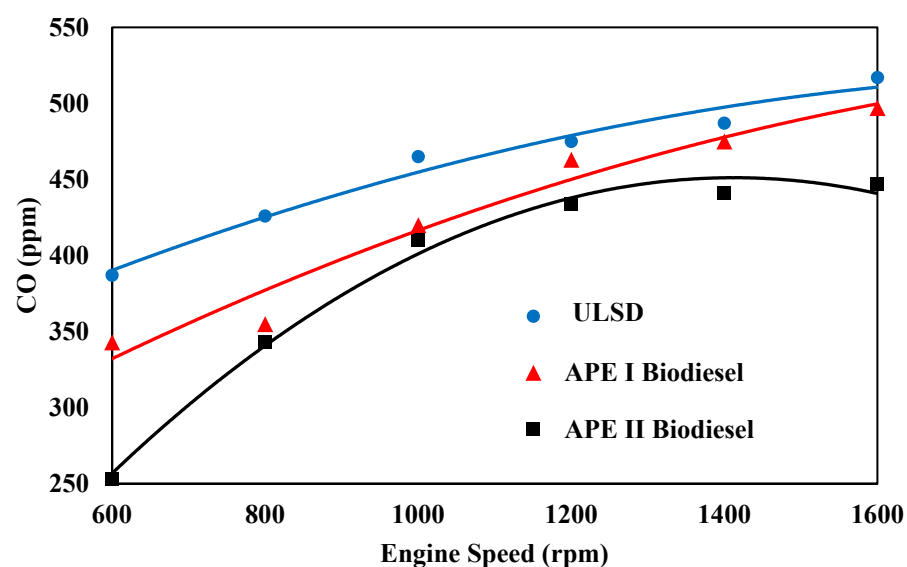


Figure 6. Effects of engine speed and APE on CO emission.

3.2.7. Nitrous Oxides Emission

The nitrogen oxides emitted from diesel engines consist of NO, N₂O, and NO₂, etc. Nitrogen oxide (NO), which is the primary compound of NO_x, is produced mainly through the oxidation of nitrogen contained in air or fuel under higher burning gas temperatures during its residence time in the engine cylinder based on the extended thermal NO Zeldovich mechanism [38]. The approximate 10 wt. % oxygen content in biodiesel plays a role in enhancing NO formation [39]. Hence, the fuel samples of APE I and II appeared to emit a higher amount of NO_x in exhaust gas than the ULSD fuel. In addition, the increase in engine speed rendered lower NO_x emissions ascribed to the shorter residence time of high-temperature gas in the engine cylinder under greater engine speeds. Moreover, the increase in APE values in the fuel samples from 74.04 of APE I to 80.68 of APE II caused higher NO_x emissions [40]. This is because a higher APE value of fatty acid esters indicates a larger degree of unsaturation and a greater unstable fuel structure. Therefore, APE II fuel is more susceptible than APE I fuel to react to the oxygen content in the surrounding air at high gas temperatures to produce NO_x emissions. Therefore, the APE II fuel was observed to have the highest NO_x emissions and the ULSD fuel the lowest (Figure 7). The NO_x concentration reached 206 ppm from burning the APE II biodiesel sample at the engine speed of 1600 rpm, which was higher than the lowest NO_x concentration of 181 ppm from burning the ULSD sample by 13.8%.

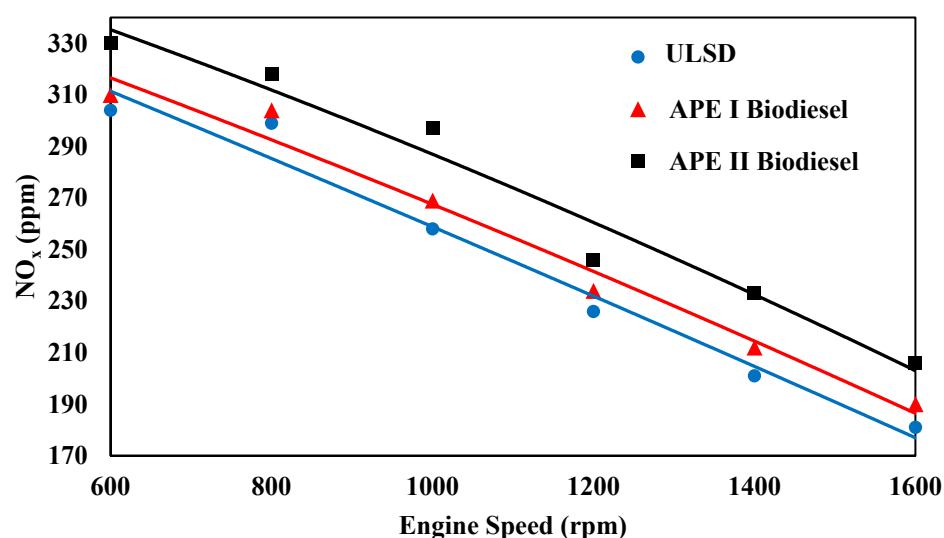


Figure 7. Effects of engine speed and APE on NO_x emission.

4. Conclusions

The effects of the allylic position equivalent (APE), which is a major indicator of the unsaturation degree of fatty acid esters on the engine performance and emission characteristics of diesel engines, were experimentally investigated in this study. Two different biodiesels made from waste cooking oil and soybean oil and ultra-low sulfur diesel (ULSD) were mixed in various weight percentages to form fuel samples with respective APE values. The significant results of this study are briefly summarized in the following points.

Fatty acid esters with a higher allylic position equivalent (APE) were observed to have a higher degree of unsaturation and tended to display properties of inferior storage and thermal stability with a superior low-temperature fluidity. The double bonds located at molecular groups of neighboring olefin C=C segments are prone to be activated to form unstable peroxides. Hence, the double bond strength is significantly weaker than that of general hydrocarbon bonds. The biodiesel made from waste cooking oil appeared to have significantly higher saturated fatty acids and mono-unsaturated fatty acids than those of the soybean-oil biodiesel by 9.92 wt. % and 28.54 wt. %, respectively. The APE values of the biodiesels made from waste cooking oil and soybean oil were 134.8 and 168.0, respectively. The APE II biodiesel sample, which was composed of 20 wt. % more soybean-oil biodiesel, had a higher combined APE value (80.68) than the APE I biodiesel sample (74.04).

In comparison with ULSD, the two biodiesels from waste cooking oil and soybean oil were observed to have higher exhaust gas temperatures and brake-specific fuel consumption (BSFC), higher CO₂ and NO_x emissions, lower O₂ and CO emissions, and lower engine thermal efficiency. This implies that a larger fuel consumption rate and inferior burning efficiency occurred for those biodiesels.

The increase in the allylic position equivalent (APE) value of biodiesel, which represents the rise of both the unsaturation degree and the number of double bonds of the esters, resulted in an increase in brake-specific fuel consumption (BSFC), the exhaust gas temperature, and CO₂ emissions, and a decrease in engine thermal efficiency and emissions of O₂ and CO. The higher unsaturation degree of fatty acid esters rendered more incomplete combustion and lower thermal engine efficiency. Larger fuel consumption requirements and higher BSFC and exhaust gas temperatures were also found for fatty acid esters with larger APE values.

When the engine ran at a higher speed of 1600 rpm, in comparison to those of the ULSD fuel sample, the APE II biodiesel sample appeared to have higher BSFC, exhaust gas temperature, CO₂ emission, and NO_x emission by 16.67%, 8.9 °C, 2.56%, and 13.8% and lower engine thermal efficiency, O₂ emission, and CO emission by 9.3%, 0.6%, and 15.66%, respectively.

Funding: This research was funded by the Ministry of Science and Technology, Taiwan, under grant numbers MOST 107-2221-E-019-056-MY2 and MOST 109-2221-E-019-024.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are contained within this article.

Acknowledgments: The author gratefully acknowledges the assistance of Xi-Tai Gao when acquiring the experimental data. The financial support from the Ministry of Science and Technology of Taiwan, ROC, under contract Nos. MOST 107-2221-E-019-056-MY2 and MOST 109-2221-E-019-024, is acknowledged.

Conflicts of Interest: The author declares no conflict of interest.

References

- Sharma, A.K.; Sharma, P.K.; Chintala, V.; Khatri, N.; Patel, A. Environment-friendly biodiesel/diesel blends for improving the exhaust emission and engine performance to reduce the pollutants emitted from transportation fleets. *Int. J. Environ. Res. Public Health* **2020**, *17*, 3896. [\[CrossRef\]](#) [\[PubMed\]](#)
- Lin, C.Y.; Ma, L. Influences of water content in feedstock oil on burning characteristics of fatty acid methyl esters. *Processes* **2020**, *8*, 1130. [\[CrossRef\]](#)
- El-Dalatony, M.M.; Sharma, P.; Hussein, E.E.; Elnaggar, A.Y.; Salama, E.S. Pig-and vegetable-cooked waste oils as feedstock for biodiesel, biogas, and biopolymer production. *Biomass Convers. Biorefin.* **2022**, 1–11. [\[CrossRef\]](#)
- Zhang, R.; Ran, T.; Cao, Y.; Zhang, Q.; Dong, F.; Yang, G.; Zhou, Y. Surface hydrogen atoms promote oxygen activation for solar light-driven NO oxidization over monolithic α -Ni(OH)₂/Ni foam. *Environ. Sci. Technol.* **2020**, *54*, 16221–16230. [\[CrossRef\]](#) [\[PubMed\]](#)
- Montes de Oca Zapiain, D.; Guziewski, M.; Coleman, S.P.; Dingreville, R. Characterizing the tensile strength of metastable grain boundaries in silicon carbide using machine learning. *J. Phys. Chem. C* **2020**, *124*, 24809–24821. [\[CrossRef\]](#)
- Ge, J.C.; Yoon, S.K.; Song, J.H. Combustion and emission characteristics of a diesel engine fueled with crude palm oil blends at various idling speeds. *Appl. Sci.* **2022**, *12*, 6294. [\[CrossRef\]](#)
- Ge, J.C.; Wu, G.; Yoo, B.O.; Choi, N.J. Effect of injection timing on combustion, emission and particle morphology of an old diesel engine fueled with ternary blends at low idling operations. *Energy* **2022**, *253*, 124150. [\[CrossRef\]](#)
- Ge, J.C.; Wu, G.; Choi, N.J. Comparative study of pilot–main injection timings and diesel/ethanol binary blends on combustion, emission and microstructure of particles emitted from diesel engines. *Fuel* **2022**, *313*, 122658. [\[CrossRef\]](#)
- Serin, H.; Yıldızhan, Ş. Hydrogen addition to tea seed oil biodiesel: Performance and emission characteristics. *Int. J. Hydrogen Energy* **2018**, *43*, 18020–18027. [\[CrossRef\]](#)
- Folayan, A.J.; Anawe, P.A.L.; Aladejare, A.E.; Ayeni, A.O. Experimental investigation of the effect of fatty acids configuration, chain length, branching and degree of unsaturation on biodiesel fuel properties obtained from lauric oils, high-oleic and high-linoleic vegetable oil biomass. *Energy Rep.* **2019**, *5*, 793–806. [\[CrossRef\]](#)
- Lin, C.Y.; Wu, S.H. Comparison of lipid and biodiesel properties of *Chaetoceros muelleri* cultured in deep sea water and surface sea water. *J. Renew. Sustain. Energy* **2017**, *9*, 013104. [\[CrossRef\]](#)
- Sharma, P.; Usman, M.; Salama, E.S.; Redina, M.; Thakur, N.; Li, X. Evaluation of various waste cooking oils for biodiesel production: A comprehensive analysis of feedstock. *Waste Manag.* **2021**, *136*, 219–229. [\[CrossRef\]](#) [\[PubMed\]](#)
- Pullen, J.; Saeed, K. Experimental study of the factors affecting the oxidation stability of biodiesel FAME fuels. *Fuel Process. Technol.* **2014**, *125*, 223–235. [\[CrossRef\]](#)
- Sternberg, J.; Sequerth, O.; Pilla, S. Green chemistry design in polymers derived from lignin: Review and perspective. *Prog. Polym. Sci.* **2021**, *113*, 101344. [\[CrossRef\]](#)

15. Lin, C.Y.; Wu, X.E. Determination of cetane number from fatty acid compositions and structures of biodiesel. *Processes* **2022**, *10*, 1502. [\[CrossRef\]](#)
16. Mujtaba, M.A.; Cho, H.M.; Masjuki, H.H.; Kalam, M.A.; Ong, H.C.; Gul, M.; Yusoff, M.N.A.M. Critical review on sesame seed oil and its methyl ester on cold flow and oxidation stability. *Energy Rep.* **2020**, *6*, 40–54. [\[CrossRef\]](#)
17. Sbihi, H.M.; Nehdi, I.A.; Mokbli, S.; Romdhani-Younes, M.; Al-Resayes, S.I. Study of oxidative stability and cold flow properties of Citrillus colocynthis oil and Camelus dromedaries fat biodiesel blends. *Ind. Crops Prod.* **2018**, *122*, 133–141. [\[CrossRef\]](#)
18. Rocha, J.G.; dos Santos, M.D.; Madeira, F.B.; Rocha, S.F.; Bauerfeldt, G.F.; da Silva, W.L.; Tubino, M. Influence of fatty acid methyl ester composition, acid value, and water content on metallic copper corrosion caused by biodiesel. *J. Braz. Chem. Soc.* **2019**, *30*, 1751–1761. [\[CrossRef\]](#)
19. Kumar, S.; Singhal, M.K.; Sharma, M.P. Predictability of biodiesel fuel properties from the fatty acid composition of the feedstock oils. *Arab. J. Sci. Eng.* **2022**, *47*, 5671–5691. [\[CrossRef\]](#)
20. Bukkarapu, K.R.; Krishnasamy, A. A critical review on available models to predict engine fuel properties of biodiesel. *Renew. Sustain. Energy Rev.* **2021**, *155*, 111925. [\[CrossRef\]](#)
21. Krishnasamy, A.; Bukkarapu, K.R. A comprehensive review of biodiesel property prediction models for combustion modeling studies. *Fuel* **2021**, *302*, 121085. [\[CrossRef\]](#)
22. Liang, Z.; Yu, Z.; Liu, H.; Chen, L.; Huang, X. Combustion and emission characteristics of a compression ignition engine burning a wide range of conventional hydrocarbon and alternative fuels. *Energy* **2022**, *250*, 123717. [\[CrossRef\]](#)
23. Sia, C.B.; Kansedo, J.; Tan, Y.H.; Lee, K.T. Evaluation on biodiesel cold flow properties, oxidative stability and enhancement strategies: A review. *Biocatal. Agric. Biotechnol.* **2020**, *24*, 101514. [\[CrossRef\]](#)
24. Razzaq, L.; Farooq, M.; Mujtaba, M.A.; Sher, F.; Farhan, M.; Hassan, M.T.; Imran, M. Modeling viscosity and density of ethanol-diesel-biodiesel ternary blends for sustainable environment. *Sustainability* **2020**, *12*, 5186. [\[CrossRef\]](#)
25. Abdulvahitoglu, A. Predicted fuel characteristics of prunus avium seed oil as a candidate for biodiesel production. *Int. J. Automot. Eng. Technol.* **2019**, *8*, 165–171. [\[CrossRef\]](#)
26. Das, A.K.; Shill, D.C.; Chatterjee, S. Potential of coconut oil as a dielectric liquid in distribution transformers. *IEEE Electr. Insul. Mag.* **2020**, *36*, 36–46. [\[CrossRef\]](#)
27. Aydın, S. Detailed evaluation of combustion, performance and emissions of ethyl proxitol and methyl proxitol-safflower biodiesel blends in a power generator diesel engine. *Fuel* **2020**, *270*, 117492. [\[CrossRef\]](#)
28. Shepel, O.; Matijošius, J.; Rimkus, A.; Duda, K.; Mikulski, M. Research of parameters of a compression ignition engine using various fuel mixtures of hydrotreated vegetable oil (Hvo) and fatty acid esters (fae). *Energies* **2021**, *14*, 3077. [\[CrossRef\]](#)
29. Yaşar, F. Comparison of fuel properties of biodiesel fuels produced from different oils to determine the most suitable feedstock type. *Fuel* **2020**, *264*, 116817. [\[CrossRef\]](#)
30. Chelladorai, P.; Varuvel, E.G.; Martin, L.J.; Nagalingam, B. The potential impact of unsaturation degree of the biodiesels obtained from beverage and food processing biomass streams on the performance, combustion and emission characteristics in a single-cylinder CI engine. *Environ. Sci. Pollut. Res.* **2019**, *26*, 5008–5019. [\[CrossRef\]](#)
31. Li, H.; Yang, W.; Zhou, D.; Yu, W. Numerical study of the effects of biodiesel unsaturation on combustion and emission characteristics in diesel engine. *Appl. Therm. Eng.* **2018**, *137*, 310–318. [\[CrossRef\]](#)
32. Nourbakhsh, H.; Shahrouzi, J.R.; Zamaniyan, A.; Ebrahimi, H.; Nasr, M.R.J. A thermodynamic analysis of biogas partial oxidation to synthesis gas with emphasis on soot formation. *Int. J. Hydrogen Energy* **2018**, *43*, 15703–15719. [\[CrossRef\]](#)
33. Zhang, Z.; Jiaqiang, E.; Deng, Y.; Pham, M.; Zuo, W.; Peng, Q.; Yin, Z. Effects of fatty acid methyl esters proportion on combustion and emission characteristics of a biodiesel fueled marine diesel engine. *Energy Convers. Manag.* **2018**, *159*, 244–253. [\[CrossRef\]](#)
34. Zheng, J.; Wang, J.; Zhao, Z.; Wang, D.; Huang, Z. Effect of equivalence ratio on combustion and emissions of a dual-fuel natural gas engine ignited with diesel. *Appl. Therm. Eng.* **2019**, *146*, 738–751. [\[CrossRef\]](#)
35. Niyas, M.M.; Shaija, A. Effect of repeated heating of coconut, sunflower, and palm oils on their fatty acid profiles, biodiesel properties and performance, combustion, and emission, characteristics of a diesel engine fueled with their biodiesel blends. *Fuel* **2022**, *328*, 125242. [\[CrossRef\]](#)
36. Prasad, B.N.; Pandey, J.K.; Kumar, G.N. Impact of changing compression ratio on engine characteristics of an SI engine fueled with equi-volume blend of methanol and gasoline. *Energy* **2020**, *191*, 116605. [\[CrossRef\]](#)
37. Alam, S.S.; Churkunti, P.R.; Depcik, C. Comparison of waste plastic fuel, waste cooking oil biodiesel, and ultra-low sulfur diesel using a Well-to-Exhaust framework. *Int. J. Environ. Sci. Technol.* **2022**, *19*, 5857–5876. [\[CrossRef\]](#)
38. Wang, Y.; Wang, Y.; Zhang, X.; Zhou, G.; Yan, B.; Bastiaans, R.J. Experimental and Numerical Study of the Laminar Burning Velocity and Pollutant Emissions of the Mixture Gas of Methane and Carbon Dioxide. *Int. J. Environ. Res. Public Health* **2022**, *19*, 2078. [\[CrossRef\]](#)
39. Lin, C.Y.; Ma, L. Effects of water removal from palm oil reactant by electrolysis on the fuel properties of biodiesel. *Processes* **2022**, *10*, 115. [\[CrossRef\]](#)
40. Mirhashemi, F.S.; Sadrnia, H. NO_x emissions of compression ignition engines fueled with various biodiesel blends: A review. *J. Energy Inst.* **2020**, *93*, 129–151. [\[CrossRef\]](#)