

Engine Performance of High-Acid Oil-Biodiesel through Supercritical Transesterification

Cherng-Yuan Lin* and Yi-Wei Lin

Cite This: *ACS Omega* 2024, 9, 3445–3453

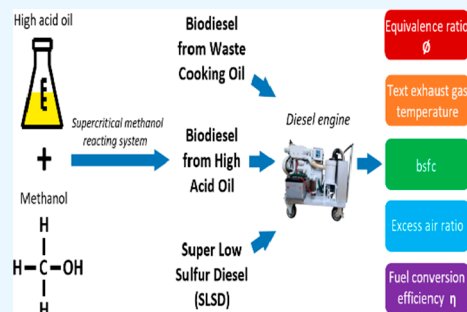
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: Relatively cheaper high-acid oil was used to make biodiesel through supercritical methanol transesterification, where high FFA contents in feedstock might conversely enhance the reaction extent. A direct-injection diesel engine and a dynamometer were used to analyze the engine characteristics of the high-acid oil-biodiesel. The experimental results show that the biodiesel made in this study had adequate fuel properties. This present biodiesel from high-acid oil was found to bear a lower heating value and equivalence ratio, with higher exhaust gas temperature, brake-specific fuel consumption (bsfc), and excess air ratio, than super-low sulfur diesel (SLSD). The biodiesel appeared to have larger-sized carbon residue left after the burning process in comparison with that of SLSD. The higher engine speed resulted in higher exhaust gas temperature and equivalence ratio, while lower bsfc, excess air ratio, was observed for the biodiesel. Supercritical methanol transesterification has been successfully proven to convert those low-cost feedstocks to renewable biodiesel products which own competitive engine performance in this study.



1. INTRODUCTION

Biodiesel which is sometimes called fatty acid methyl esters (FAME) is generally produced from a transesterification reaction. Biodiesel owns dominant advantages including superior combustion efficiency due to its about 10 wt % more oxygen compounds, lower pollutant emissions, excellent biodegradability, superior lubricity, etc.¹ in comparison with those of super-low sulfur diesel (SLSD). Biodiesel is a promising alternative fuel to petro-diesel. Feedstock cost is the major factor in determining the biodiesel price and its competitiveness in fuel markets. Vegetable oil, animal fats, or microalgae lipids whose primary constituents are triglycerides have been generally used as feedstocks to produce biodiesel.² However, the costs of those feedstocks are frequently too high to hinder their wide use and hinder their competence in the fuel market. Yaşar³ compared the fuel properties of biodiesel made from 10 different feedstock vegetable oils. He found that biodiesel from algae and olives appeared to have the highest ester contents and cetane number.

Vadivelu et al.⁴ investigated the engine performance of the blend of biodiesel made from degraded cashew nut shell liquid (CNSL) with diesel fuel, ethanol, and hydrogen. They found that the increase in hydrogen concentration in such a biodiesel blend caused an increase in brake thermal efficiency (BTE) and a decrease in brake-specific fuel consumption. The brake heat of such a biodiesel blend was reduced by 26.8 compared to the diesel fuel. The effects of *Simarouba glauca* biodiesel and exhaust gas recirculation (EGR) on the engine emission

and performance of a compression-ignition diesel engine were studied by Bedar et al.⁵ The 20% biodiesel blended with 80% diesel fuel (briefly termed B20) together with 15% EGR was found to have superior engine performance under all experimental conditions.

Strong alkaline-catalyst transesterification which is generally applied to produce biodiesel in the industry appears to have a rather low tolerance extent for the amounts of free fatty acids (FFAs) and water in the raw oil.⁶ However, low-cost feedstock such as waste cooking oil generally contains relatively high FFAs and water and might thus hinder the progress of transesterification and facilitate saponification formation, resulting in the reduction in yield of fatty acid methyl esters (FAME). The water content and free fatty acids for successful biodiesel manufacture are suggested to be under 0.06 and 0.5 wt %, respectively.⁷ Instead, soybean soapstock is the residual left after the oil squeeze process from the alkaline neutralization of the degummed soybean oil.⁸ It is produced at a rate of approximately 6 wt % of the degummed soybean oil and thus is considered the most abundant and cheapest byproduct of the soybean oil production process.⁹

Received: September 13, 2023

Revised: December 14, 2023

Accepted: December 14, 2023

Published: January 11, 2024



Soybean soapstock is primarily composed of free fatty acids, unsaponifiable compounds, hydrolyzed phosphatide, neutral oil, etc.¹⁰ Soybean soapstock after being mixed and stirred with strong sulfuric acids and high-temperature water steam carried out an acidification reaction to form the high-acid oil.¹¹ The free fatty acids in the byproduct high-acid oil might reach as high as 59.3 wt % and thus is not applicable to proceed through a strong alkaline-catalyst transesterification reaction for biodiesel manufacture.¹² The cost of the feedstock generally determines 75% of the manufacturing cost of biodiesel. Although degraded feedstocks are significantly cheaper than fresh vegetable oils, they may require more treatment processes to reduce their impurities, water, and free fatty acids. In consequence, the manufacturing cost of biodiesel from high-acid oil produced from soybean soapstock could be reduced by as much as 25% in comparison with those of general vegetable oils or animal lipids. Water in vegetable oil could hydrolyze methyl esters to curtail their yield rate from the feedstock. The mixing of water, free fatty acids, and strong alkaline catalyst during the transesterification process would result in the reduction of the formation of methyl esters.¹³ Other efficient transesterification methods than an acid- or alkaline-catalyst reaction to produce biodiesel from high-acid oil have attracted much research interest. When the pressure and temperature of a fluid exceed its corresponding critical pressure and temperature, it is termed a supercritical fluid. Hence, a supercritical fluid is prone to extracting a solute from a solvent mixture and enhancing the reaction rate as well. A noncatalytic supercritical methanol transesterification (scMeOH) was used to manufacture fatty acid methyl esters from candlenut oil.¹⁴ The parameters of the reacting pressure, reaction time, reacting temperature, and methanol-to-oil (M/O) molar ratio were varied to investigate their effects on the reaction process. They found that the optimum reaction pressure, reaction temperature, molar ratio of methanol to high-acid oil, and reaction time were 115 bar, 558 K, 30, and 22 min to obtain the maximum FAME yield of 96.35%. Hence, scMeOH was one of the effective methods for biodiesel production. Microwave and ultrasonic irradiation are also promising production methods for biodiesel. The liquid-phase plasma discharge method is considered an emerging technology that might achieve a 99.5% yield of FAME and the shortest reaction time (in seconds).¹⁵ Singh et al.¹⁶ considered that supercritical transesterification owned a fast and high conversion rate and was an environmentally friendly biodiesel production method in comparison with other traditional catalyst transesterification. The advantages of supercritical methanol transesterification for biodiesel production over other methods also include no pretreatment required, wide application of a variety of feedstocks and short reaction time.¹⁷ They also found that alcohol type, residence time, and cosolvents play significant roles in determining the yield rate and quality of the FAME produced. Qadeer et al.¹⁸ proposed that energy saving might achieve 71.6% by using supercritical methanol transesterification when compared with other biodiesel production methods. Sitepu et al.¹⁹ found that the formation rate of fatty acid methyl esters still can exceed 98% even when the water content in the vegetable oil was more than 50 wt % when a supercritical methanol transesterification reaction was applied. Soybean soapstock has a relatively lower economic value and frequently is discarded directly. Lin and Lin²⁰ investigated the fuel quality of soybean biodiesel from high-acid oil. Although the reaction process and fuel

characteristics of the biodiesel made from supercritical methanol transesterification have been investigated previously, the engine operation and performance of the biodiesel through supercritical transesterification have not been considered yet.^{21,22} The applicability of soybean soapstock to make high-acid oil for the production of biodiesel requires to be completely assessed. Soybean soapstock after proceeding with the acidification reaction is converted to high-acid oil which primarily consists of monoacylglycerol (MAG), diacylglycerol (DAG), and triacylglycerol (TAG).²³ The supercritical methanol transesterification is thus considered to make FAME. High free fatty acids and water contents generally exist in high-acid oil. The high-acid oil-biodiesel was fueled in a four-stroke and naturally aspirated diesel engine to analyze its engine performance and systematically evaluate the adequacy and competency of the biodiesel in this experimental study. Major engine performance characteristics such as equivalence ratio, fuel conversion efficiency, and brake-specific fuel consumption (bsfc) were analyzed to obtain reliable engine operating data.²⁴ The engine performance of high acid oil-biodiesel produced through supercritical methanol transesterification has not been carried out before.²⁵ The biodiesel from high acid oil derived from an extraction of soybean oil was first compared with commercial biodiesel made from traditional waste cooking oil through industrial strong alkaline catalyst-transesterification and with a super low sulfur diesel of fossil fuel. The application of the supercritical methanol transesterification method for biodiesel production is first objectively assessed based on the above comparison results of various engine performance properties.

2. EXPERIMENTAL DETAILS

2.1. Production of Biodiesel from High-Acid Oil. A reacting system for supercritical methanol with vegetable oil (Jeouou Rong Industrial Corp. in Kaohsiung City, Taiwan) was used to undergo transesterification of the high-acid oil. The soybean soapstock was used to produce high-acid oil by an acidification reaction.²⁶ The reacting system was allowed to tolerate a high pressure of 27.6 MPa and a high temperature of 723.15 K.²⁷ The allowable temperature and pressure of the reacting system far exceed the critical temperature and pressure of methanol, which are 513.2 K and 7.95 MPa, respectively. The available volumetric capacity of the reacting vessel reaches 5 L.

This study set the molar ratio of methanol to the high-acid oil (briefly denoted as the M/O molar ratio afterward) from soybean soapstock between 12 and 50. A lower M/O molar ratio than 12 might hinder the transesterification process, leading to longer reaction time, higher reaction temperature, and lower conversion rate from triglyceride to form fatty acid methyl esters (FAME).^{28,29} The fuel characteristics of FAME from the supercritical reaction under various molar ratios of M/O were analyzed to adjust the experimental conditions. The high-acid oil was added to the reacting vessel of the reacting system to mix with methanol at preset molar ratios ranging from 12 to 50. Neither strong alkaline nor acidic catalyst was used to facilitate transesterification in the supercritical transesterification system.³⁰ The mixture was then heated to reach 623 K, which was higher than the corresponding critical point of methanol at 512 K. The supercritical transesterification lasted 30 min under the temperature of 623 K to complete biodiesel production. The crude biodiesel was then split into the biodiesel product at the top and glycerol at

the lower layer of the reacting vessel by a centrifugal machine due to their obvious density difference.³¹ The unreacted mixture, water, and other compounds were heated away from the crude biodiesel using a rotary vacuum evaporator (R-2000 V1 model, Panchum Scientific Corp., Kaohsiung City, Taiwan).

The commercial biodiesel produced from used cooking oil through traditional strong alkaline-catalyst transesterification under atmospheric pressure was supplied by Codetech Technology Co., Ltd. (Taipei City, Taiwan). Super-low sulfur diesel (SLSD) was provided by CPC Corp., Taiwan. The engine characteristics among the present biodiesel from high-acid oil, commercial biodiesel, and SLSD were analyzed and compared afterward. The heating values of the various fuel samples were measured by an oxygen bomb calorimeter (1261 model, Parr Instrument Ltd., Moline, IL, U.S.A.). The weight compositions of the fatty acids of the biodiesel made from high-acid oil biodiesel through the supercritical-methanol transesterification were analyzed by a gas chromatograph (GC) accompanied by a Chromatography Data Management system.

2.2. Analysis of Diesel Engine Performance. The engine performance of the biodiesel manufactured through supercritical methanol transesterification from high-acid oil at varied molar ratios between 12 and 50 was analyzed using a four-stroke diesel engine. The marine diesel engine (UMBD1 model, Isuzu Ltd., Yokohama-shi, Kanagawa, Japan) is a direct compression-ignition, naturally aspirated, in-line four-cylinder, and water-cooling type. The displacement volume, minimum idle speed, and compression ratio of the diesel engine are 3856 cc, 500 rpm, and 17, respectively. The direct injection pressure of the liquid fuel to the combustion chamber is 150 bar, and the injection timing is 13°BTDC (before the top dead center). The injection pressure and injection timing remained unvaried when different test fuels were used in this study. An eddy-current dynamometer was aligned with the transmission shaft of the diesel engine to regulate the engine output torque. The maximum engine output power is 277.3 N·m, and the brake horsepower is 120 kW.

An engine dynamometer control system was used to regulate the engine speed, torque, and throttle opening. The control system was also used to install various test modes, such as modes of constant engine speed or constant engine torque. A safety alarm was set up to alert for low lubricating pressure or insufficient cooling water. The engine characteristics such as fuel-air equivalence ratio Φ , fuel conversion efficiency η , fuel consumption rate, bsfc, etc. were analyzed. The mean value of each result was obtained by repeating each experiment 3 to 5 times. The uncertainties and accuracies of the experimental data were calculated based on the evaluation methods described by Sonthalia and Kumar.³² Chauvenet's criterion was first used to determine if some data points can be rejected. When the ratio of maximum deviation to standard deviation is lower than some assigned value corresponding to the number of readings,³³ of the data points are considered outliers that do not fit with expectations and can be eliminated from other gross experimental data. The uncertainties of the exhaust gas temperature, brake-specific fuel consumption (bsfc), fuel conversion efficiency, excess air ratio, equivalence ratio, peroxide, kinematic viscosity, carbon residue, and heating value were 3.73%, 4.56%, 4.09%, 5.38%, 3.41%, 2.32%, 3.26%, 5.24%, and 4.18%, respectively.

3. RESULTS AND DISCUSSION

3.1. Elemental Compositions. The comparisons of the elemental compositions among the present biodiesel from high-acid oil, the commercial biodiesel produced under atmospheric pressure, and the super-low sulfur diesel (SLSD) are revealed in Table 1. About 10 wt % less of the

Table 1. Comparison of Elemental Compositions of the Biodiesel with Other Biodiesel and Super-Low Sulfur Diesel (SLSD)

Elements (wt %)	SLSD	Biodiesel from waste cooking oil	Present biodiesel
C	87.22 ± 1.57	77.12 ± 1.39	77.71 ± 1.40
H	14.06 ± 0.32	12.69 ± 0.29	12.41 ± 0.28
N	0.05 ± 0.002	0.08 ± 0.003	0.08 ± 0.003

elemental carbons of the present biodiesel made from the M/O equal to 42 and the commercial biodiesel than that of the super-low sulfur diesel (SLSD) were shown. Singh et al.³⁴ proposed that the physicochemical properties of biodiesel are influenced by the elemental compositions of its FAME compounds. Afif and Biradar³⁵ found that less carbon content of the Cannabis sativa seed-oil biodiesel than fossil diesel caused a reduction of HC, CO, and CO₂ emissions. It followed that the biodiesels had lower heating values than SLSD³⁶ due to their lower elemental carbon. In contrast, the biodiesel had about 10 wt % more elemental oxygen so that its burning efficiency was enhanced in comparison with that of the SLSD. Ulusoy³⁷ observed that the combustion efficiency, the amounts of soot, and particulate matter (PM) emissions from burning the used cooking oil-biodiesel were lower than the diesel primarily due to the biodiesel's relatively higher oxygen content. He also considered that the unsaturation degree of biodiesel was significantly affected by the elemental oxygen of the biodiesel. The biodiesel made in this supercritical methanol study appeared to have the least elemental hydrogen in Table 1. Wang et al.³⁸ considered the effects of atomic H/C ratio, copyrolysis reactor design, feedstock mixtures, the mass ratio of feedstock to the catalyst, etc. on the heating value, proximate, and elemental compositions, and product yields. They proposed that the atomic H/C ratio played a pivotal role in assuring the heating value of biofuels. In addition, the increase of the H/C ratio from 1.25 to 1.47 can improve the heating value. The biodiesels made through the supercritical methanol transesterification from high-acid oil under various M/O conditions were fueled in a diesel engine to analyze their engine performance.

After comparing the physicochemical properties of the biodiesels made from various M/O, the biodiesel from the

M/O molar ratio equal to 42 was found to have the most adequate fuel properties. The biodiesel made from the M/O molar ratio was primarily composed of 38.91 wt % oleic acid (C18:1), 25.38 wt % linoleic acid (C18:2), and 22.21 wt % palmitic acid (C16:0). The unsaturated fatty acids accounted for 67.12 wt %. The fuel properties of the biodiesel from high-acid oil and super-low sulfur diesel (SLSD) were compared in Table 2. The biodiesel was observed to leave a carbon residue of larger diameters after its burning than that of SLSD due to its larger gum and impurity contents. A lower peroxide value (PV) indicates a lesser extent of lipid oxidation, which is essential to refrain lipids from oxidation and quality deterioration in turn. Peroxide value can thus be used to

Table 2. Comparison of Fuel Properties of the High-Acid Oil Biodiesel and Super-Low Sulfur Diesel (SLSD)

Fuel properties	SLSD	Present biodiesel
Peroxide value (meq/kg)	N.A. ^a	13.45 ± 0.31
Kinematic viscosity (mm ² /s)	3.66 ± 0.12	5.2 ± 0.17
Carbon residue (wt.%)	1.11 ± 0.06	0.25 ± 0.02
Heating value (MJ/kg)	45.34 ± 1.87	39.55 ± 1.65

^aNot available.

monitor the lipid quality during its storage period. Lipid and other biomaterials are prone to autoxidation which is initiated with free-radical chain reaction.³⁹ The biodiesel was found to have a larger kinematic viscosity than SLSD due to its more viscous compounds of fatty acids. However, the carbon residue of the high-acid oil biodiesel is lower than that of SLSD due to its lower elemental carbon and larger oxygen content. Moreover, this also caused the present biodiesel to have the lowest heating value (39.55 MJ/kg) among those three fuels in Table 1. The biodiesels were further compared with super-low sulfur diesel (SLSD) and commercial biodiesel for their engine characteristics. The engine test was carried out under a preset engine torque and varied engine speeds. The experimental outcomes of the engine analysis are discussed below.

3.2. Exhaust Gas Temperature. The exhaust gas temperatures from the diesel engine powered with the sample fuels were compared in Figure 1. The increase in the engine

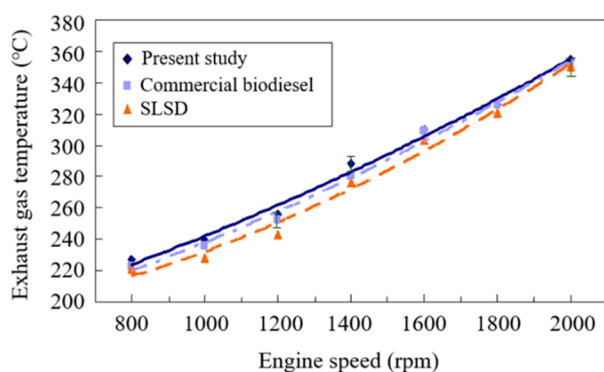


Figure 1. Comparison of the exhaust gas temperature of the biodiesels from present high-acid oil and waste cooking oil and super-low sulfur diesel.

speed resulted in a nearly linear increase in the exhaust gas temperature. This was because the amount of atomized fuel, equivalence ratio value, and engine output power were raised with an increase in the engine speed. The higher engine speed also reduced the heat loss time to the engine surroundings, resulting in a higher burning gas temperature inside the engine cylinder. In consequence, the exhaust gas temperature increased accordingly. The higher exhaust gas temperature fueled with biodiesels than super-low sulfur diesel (SLSD) was also observed in Figure 1. Cihan⁴⁰ also found that the use of biodiesel containing high oxygen compounds as engine fuel would enhance the combustion rate, shorten the ignition delay, and facilitate the fuel pyrolysis, leading to the increase of exhaust gas temperature. The biodiesel produced from the present supercritical methanol transesterification was found to achieve a peak exhaust gas temperature in comparison with those of commercial biodiesel and SLSD. In contrast, SLSD had the lowest exhaust gas temperature. The results conformed

well to those of Elkelay et al.⁴¹ This is ascribed to the about 10 wt % oxygen in biodiesel would enhance the reaction rate of the fuel, resulting in higher burning efficiency and higher exhaust gas temperature in turn. Chuah et al.⁴² and Zhang et al.⁴³ also observed that a larger blending percentage of biodiesel in diesel fuel caused higher brake-specific fuel consumption (bsfc) and exhaust gas temperature while lowering brake engine power and engine torque.

The exhaust gas temperature and brake-specific fuel consumption (bsfc) could be increased if the waste oil methyl ester was added with C3 or C4 alcohol such as propanol or n-butanol.⁴⁴ Abed et al.⁴⁵ compared the diesel engine emissions from a diesel engine fueled with waste cooking oil, Jatropha, algae, and palm oil. They considered that various emission results among those biodiesels from various feedstocks might be ascribed to different chemical structures of fatty acids and varied fuel properties such as the density, kinematic viscosity, cetane number, and heating value.

3.3. Brake-Specific Fuel Consumption (bsfc). Brake-specific fuel consumption (bsfc) is expressed as the rate of fuel consumption required (\dot{m}_f) per engine power output (P_b). Bsfc is formulated below:

$$\text{Bsfc (g/kW}\cdot\text{h)} = \frac{\dot{m}_f \text{ (g/h)}}{P_b \text{ (kW)}} \quad (1)$$

where P_b is the brake engine power and \dot{m}_f is the mass rate of fuel consumption in g/h. A higher bsfc indicates that a larger mass rate of liquid fuel is required to produce the same engine power output and hence is not favorable for engine operation. Heating value, specific gravity, and viscosity are the primary factors⁴⁶ to determine the bsfc value of a fuel. Biodiesel has about 10% less heating value than that of SLSD. Hence, those two biodiesels were shown to have higher bsfc than the SLSD in Figure 2. Rajak et al.⁴⁷ found that the SMB20 biodiesel

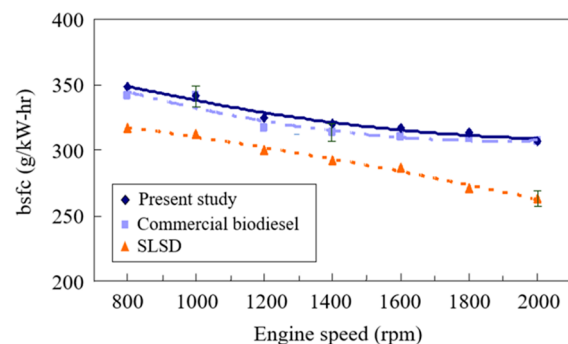


Figure 2. Comparison of the brake-specific fuel consumption (bsfc) of the biodiesels from present high-acid oil and waste cooking oil and super-low sulfur diesel.

which is composed of 20% spirulina microalgae biodiesel and 80% diesel fuel appeared to have lower engine torque, mechanical efficiency, and NO_x emission by 5.7%, 5.5%, and 4.96%, respectively than the neat diesel fuel due to the lower heating value of the former fuel. Razzaq et al.⁴⁸ observed the increase of biodiesel blend percentage with high-speed diesel (HSD) from B10 (i.e., 10% biodiesel blended with 90% diesel) to B50 would raise the bsfc significantly by 141%. The biodiesel produced through supercritical methanol transesterification from high-acid oil was found to obtain the highest while the SLSD reached the lowest bsfc because of

their various heating values among those three fuels. Fuel such as the present biodiesel, which bears with lower heating value, required a higher mass rate of fuel consumption to achieve the identical power release, and hence larger bsfc values appeared. The relatively higher viscosity of the biodiesels than SLSD fuel could cause clogging of fuel nozzles and poorer atomization,⁴⁹ leading to a slight increase of bsfc.

The higher engine speed rendered the reduction of bsfc for the three test fuels. The increase in the engine speed caused the increase in the engine brake power due to the rise in engine efficiency.⁵⁰ The variation of the mass fuel consumption rate with the engine speed was lower than the corresponding increase of the engine power. In consequence, the bsfc was found to be reduced with the engine speed in Figure 2. Gowrishankar and Krishnasamy⁵¹ also observed that the increase of engine speed or load led to an obvious decrease of bsfc due to the enhancement of brake engine efficiency. Gülüm⁵² observed that either the increase of compression ratio or decrease of the biodiesel blending ratio in diesel fuel resulted in higher brake effective power and lower bsfc.

3.4. Fuel Conversion Efficiency. The ratio of the engine brake power per heat supply rate from fuel burning for each engine cycle is defined as the fuel conversion efficiency η_f .⁵³ The fuel conversion efficiency can be expressed as follows:

$$\eta_f = \frac{P_b}{\dot{m}_f Q_{HV}} = \frac{3600 \text{ (kW)}}{\text{bsfc (g/kW}\cdot\text{h)} \times Q_{HV} \left(\frac{\text{MJ}}{\text{kg}} \right)} \quad (2)$$

in which P_b is the brake power output, \dot{m}_f is fuel mass consumption rate, and Q_{HV} is the high or low heating value. The higher engine speed caused the rise of the engine operating efficiency⁵⁴ and thus increased the fuel conversion efficiency. The decrease in bsfc was found to cause the corresponding increase in the fuel conversion rate with the increases in engine speed after comparing Figure 2 with Figure 3. Sabapathy et al.⁵⁵ studied the effects of fuel additives of 5%

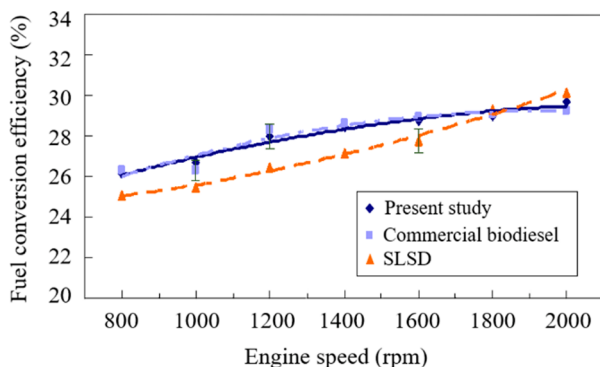


Figure 3. Comparison of the fuel conversion efficiency of the biodiesels from present high-acid oil and waste cooking oil and super-low sulfur diesel.

diethyl ether (DEE) and 2000 ppm butylated hydroxytoluene (BHT) in the palm kernel oil (PKO) biodiesel on combustion processes and engine performance. They found that the biodiesel added with the additive mixture would promote fuel spray and atomization, leading to enhancing brake thermal efficiency by 4.6% and reducing NO_x and black smoke emissions by 19.4% and 11.5%, respectively.

The biodiesels were observed to have higher fuel conversion efficiencies than the SLSD⁵⁶ mainly because of their higher

oxygen contents for enhancing the burning efficiency, resulting in higher fuel conversion efficiency. The result conformed well with Temizer et al.⁵⁷ which indicated the higher fuel conversion efficiencies accompanied by the higher biodiesel blend percentage in diesel fuel ascribed to the combustion enhancement of biodiesel. The commercial biodiesel through strong alkaline-catalyst transesterification was shown to have a relatively higher fuel conversion efficiency than the present biodiesel primarily owing to the somewhat lower heating value of the latter biodiesel. In addition, the turbulence extent of the burning gas increased at higher engine speeds to facilitate more mixing degrees⁵⁸ between the injected liquid fuel particles and reacting air and thus increased the burning efficiency. Hence, the fuel conversion efficiency of those test fuels approached together at larger engine speeds than 1800 rpm, as observed in Figure 3. The blend of diesel or biodiesel fuel with some adequate additives might enhance combustion characteristics. Zhao et al.⁵⁹ considered that polyoxymethylene dimethyl ethers (PODEn) are promising diesel additives to improve combustion and emissions of diesel engines. They found that diesel blended with PODEn might effectively improve the fuel conversion efficiency by 3.29%.

3.5. Excess Air Ratio. The excess air ratio of the exhaust gas was analyzed by a gas analyzer. The excess air ratio is defined below:⁶⁰

$$\text{Excess air (\%)} = \frac{100(m_a - m_{as})}{m_{as}} = \frac{100(n_{O_2} - n_{O_2(s)})}{n_{O_2(s)}} \quad (3)$$

where m_a , m_{as} , n_{O_2} , and $n_{O_2(s)}$ denote the actual air mass, stoichiometric air mass, actual molar number of oxygens, and stoichiometric molar number of oxygens, respectively. The excess air ratio was observed to increase with the rise of the engine speed when the speed was varied from 800 to 1000 rpm. This is probably ascribed to that the rate of inlet air mass flow increased slightly with the engine speed while the bsfc remained nearly unchanged in Figure 2, leading to the larger excess air ratio at higher engine speed. Malatak et al.⁶¹ found that the value of excess air ratio influenced the exhaust gas temperature and emissions of CO, NO_x, and PM (particulate matter), etc. The increase in excess air ratio was also observed to be accompanied by the decrease in in-cylinder pressure and the heat release rate.⁶²

The excess air ratio was thereafter decreased with the increase of the engine speed after the speed was increased from 1000 rpm. This is because the diesel engine was ignited by the diffusional mixture of inlet air and injected liquid fuel at high temperature and pressure in the combustion chamber. The combustion occurred after sufficiently mutual diffusion between the compressed air and injected diesel.⁶³ Hence, a low fuel consumption rate was sufficient at lower engine speeds, leading to a higher excess air ratio. In contrast, higher engine speed caused a larger consumption rate of diesel fuel and a higher amount of reacting air.⁶⁴ The excess air ratio was thus decreased in the exhaust gas. The biodiesel contained about 10 wt.% oxygen. Hence, lower air consumption was required for the biodiesels in comparison with SLSD.⁶⁵ The biodiesel made from waste cooking oil by traditional strong alkaline catalysts under atmospheric pressure contained more elemental oxygen than the biodiesel produced in this study. In consequence, the former biodiesel produced a larger excess air ratio than the present biodiesel in Figure 4. Attia et al.⁶⁶ also

proposed that the higher biodiesel proportion in the diesel fuel mixture led to a higher excess air ratio in the exhaust gas.

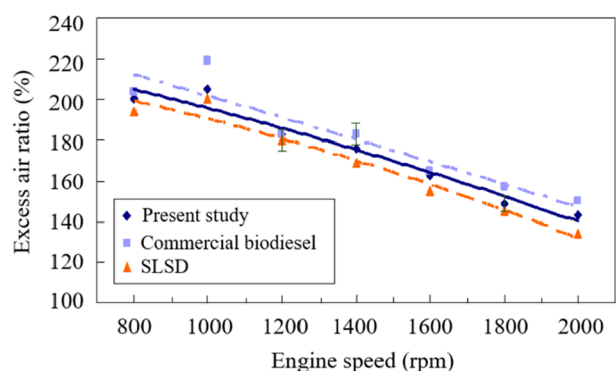


Figure 4. Comparison of the excess air ratio of the biodiesels from present high-acid oil and waste cooking oil and super-low sulfur diesel.

3.6. Fuel–Air Equivalence Ratio. The equivalence ratio (Φ) is expressed below:⁶⁷

$$\Phi = (m_F/m_A)_{\text{actual}} / (m_F/m_A)_{\text{stoichiometric}} \quad (4)$$

in which m_F/m_A denotes the mass fuel (F) to mass air (A) ratio, and the subscripts actual and stoichiometric represent actual and stoichiometric mass ratios. $\Phi < 1$ and $\Phi > 1$ indicate fuel-lean and fuel-rich burning conditions, respectively.

The excess air ratio can be related to the equivalence ratio based on the following equation:

$$\Phi = 1 / (\text{excess air ratio} + 1) \quad (5)$$

This implies that the excess air ratio is inversely proportional to the equivalence ratio in eq 5.⁶⁸ The excess air ratio or equivalence ratio value would influence the burning efficiency, flame temperature, and combustion products of a fuel sample.⁶⁹ The equivalence ratio was observed to increase when the engine speed was increased under a constant engine torque in Figure 5. This is ascribed to that the diesel engine is

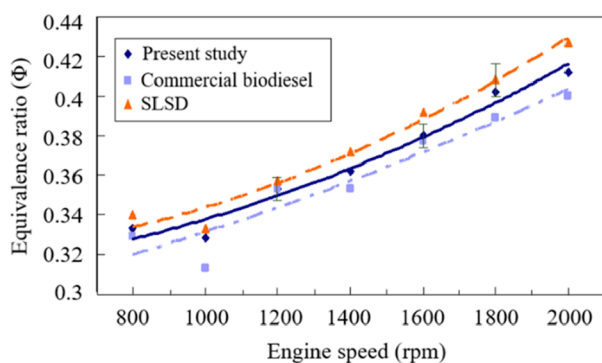


Figure 5. Comparison of the equivalence ratio of the biodiesels from present high-acid oil and waste cooking oil and super-low sulfur diesel.

operated frequently under a fuel-lean state⁷⁰ in which an equivalence ratio is less than 1. The rise in engine speed needed more injected fuel mass into the engine cylinder to sustain the engine operation, resulting in the rise of the equivalence ratio when the engine speeds were increased for those three test fuels in Figure 5.

Biodiesel is an oxygen-rich fuel, which contains about 10 wt. % oxygen. The required air consumption during the engine operation was thus reduced in comparison with SLSD,⁷¹ leading to a higher excess air ratio and lower equivalence ratio for the biodiesels. Moreover, the biodiesel made through supercritical methanol transesterification from high-acid oil had a heating value lower than that of the commercial biodiesel made through atmospheric pressure transesterification. It followed that a greater amount of the former biodiesel was needed to achieve the identical engine power output. Hence, the biodiesel made from the present study appeared to have a larger equivalence ratio than that of the commercial biodiesel in Figure 5. Gad et al.⁷² observed that the higher biodiesel blending percentage in diesel fuel mixture resulted in a larger fuel-air equivalence ratio because the biodiesel had lower heating value and larger fuel consumption in comparison with SLSD.

4. CONCLUSIONS

The biodiesel was produced from the high-acid oil of soybean soapstock with inferior fuel quality through supercritical transesterification. The biodiesel from the degraded raw oil, commercial biodiesel, and super-low sulfur diesel (SLSD) were used to perform the engine characteristics. The major findings obtained from this study are summarized below.

1. The biodiesel made from the inferior feedstock oil through the supercritical reaction at methanol to high-acid oil molar ratio (denoted as M/O) equal to 42 was found to have the optimum fuel properties. The biodiesel had a lower heating value than SLSD due to the lower elemental hydrogen and carbon of the former fuel.
2. The increase of the engine speed caused the increase of the exhaust gas temperature, and equivalence ratio while decrease of the brake-specific fuel consumption (bsfc) and excess air ratio (%).
3. The biodiesel made from degraded high-acid oil through the present supercritical transesterification appeared to have a higher bsfc.
4. The biodiesel was observed to have higher exhaust gas temperature, excess air ratio, and lower equivalence ratio, than SLSD.

■ AUTHOR INFORMATION

Corresponding Author

Cherng-Yuan Lin – Department of Marine Engineering, National Taiwan Ocean University, Keelung 20224, Taiwan; orcid.org/0000-0002-4076-6655; Email: Lin7108@ntou.edu.tw

Author

Yi-Wei Lin – Department of Marine Engineering, National Taiwan Ocean University, Keelung 20224, Taiwan

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.3c06997>

Author Contributions

Conceptualization, C.Y.L.; methodology, C.Y.L.; analysis, Y.W.L.; investigation, C.Y.L. and Y.W.L.; data curation, Y.W.L.; writing—original draft preparation, C.Y.L. and Y.W.L.; writing—review and editing, C.Y.L. administration, C.Y.L.

Funding

This research was funded by the National Science and Technology Council, Taiwan under the contract number NSTC 109-2221-E-019-024.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the National Science and Technology Council, Taiwan, under contract No. NSTC 107-2221-E-019-056-MY2.

NOMENCLATURE

Bsfc	Brake-specific fuel consumption
BTE	Brake thermal efficiency
CO	Carbon monoxide
FAME	Fatty acid methyl esters
FFA	Free fatty acids
HSD	High-speed diesel
M/O	Methanol to high-acid oil molar ratio
m_a	Actual air mass
m_{as}	Stoichiometric air mass
\dot{m}_f	Fuel mass consumption rate
m_F/m_A	Mass fuel (F) to mass air (A) ratio
P_b	Brake power output
PM	Particulate matter
PV	Peroxide value
NOx	Nitrogen oxides
n_{O_2}	Actual molar number of oxygens
$n_{O_2(s)}$	Stoichiometric molar number of oxygens
QHV	High or low heating value
SLSD	Super-low sulfur diesel
η_f	Fuel conversion efficiency

REFERENCES

- Lin, C.-Y.; Lu, C. Development perspectives of promising lignocellulose feedstocks for production of advanced generation biofuels: A review. *Renewable and Sustainable Energy Reviews* **2021**, *136*, 110445.
- Long, F.; Liu, W.; Jiang, X.; Zhai, Q.; Cao, X.; Jiang, J.; Xu, J. State-of-the-art technologies for biofuel production from triglycerides: A review. *Renewable and Sustainable Energy Reviews* **2021**, *148*, 111269.
- Yaşar, F. Comparison of fuel properties of biodiesel fuels produced from different oils to determine the most suitable feedstock type. *Fuel* **2020**, *264*, 116817.
- Vadivelu, T.; Ramanujam, L.; Ravi, R.; Vijayalakshmi, S. K.; Ezhilchandran, M. An Exploratory Study of Direct Injection (DI) Diesel Engine Performance Using CNSL-Ethanol Biodiesel Blends with Hydrogen. *Energies* **2023**, *16* (1), 415.
- Parashuram, B.; Chitragar, P. R.; Shivaprasad, K. V.; Kumar, G. N. Performance and Emission Analysis of a Single Cylinder CI Engine using Simarouba glauca Biodiesel. In *Fluid Mechanics and Fluid Power—Contemporary Research*; Saha, A. K., Das, D., Srivastava, R., Panigrahi, P. K., Muralidhar, K., Eds.; Springer India: New Delhi, 2017; pp 1519–1527.
- Kim, J. Y.; Jung, J.-M.; Jung, S.; Park, Y.-K.; Tsang, Y. F.; Lin, K.-Y. A.; Choi, Y.-E.; Kwon, E. E. Biodiesel from microalgae: Recent progress and key challenges. *Prog. Energy Combust. Sci.* **2022**, *93*, 101020.
- Al-Saadi, L. S.; Eze, V. C.; Harvey, A. P. A techno-economic analysis based upon a parametric study of alkali-catalysed biodiesel production from feedstocks with high free fatty acid and water contents. *Biofuels* **2022**, *13* (4), 401–413.
- Casali, B.; Brenna, E.; Parmeggiani, F.; Tessaro, D.; Tentori, F. Enzymatic Methods for the Manipulation and Valorization of Soapstock from Vegetable Oil Refining Processes. *Sustainable Chemistry* **2021**, *2* (1), 74–91.
- Gasparetto, H.; de Castilhos, F.; Paula Gonçalves Salau, N. Recent advances in green soybean oil extraction: A review. *J. Mol. Liq.* **2022**, *361*, 119684.
- Thangaraju, S.; Pulivarthi, M. K.; Natarajan, V. Waste from Oil-Seed Industry: A Sustainable Approach. In *Sustainable Food Waste Management: Concepts and Innovations*; Thakur, M., Modi, V. K., Khedkar, R., Singh, K., Eds.; Springer Singapore, 2020; pp 177–190.
- Wang, Y.; Zhang, S.; Wu, Q.; Duan, D.; Liu, Y.; Ruan, R.; Fu, G.; Dai, L.; Jiang, L.; Yu, Z.; et al. Microwave-assisted pyrolysis of vegetable oil soapstock: Comparative study of rapeseed, sunflower, corn, soybean, rice, and peanut oil soapstock. *International Journal of Agricultural and Biological Engineering* **2019**, *12*, 202–208.
- Lin, C.-Y.; Ma, L. Fluid Characteristics of Biodiesel Produced from Palm Oil with Various Initial Water Contents. *Processes* **2021**, *9* (2), 309.
- Riaz, I.; Shafiq, I.; Jamil, F.; Al-Muhtaseb, A. a. H.; Akhter, P.; Shafiq, S.; Park, Y.-K.; Hussain, M. A review on catalysts of biodiesel (methyl esters) production. *Catalysis Reviews* **2022**, No. 2108197.
- Shaah, M. A.; Hossain, M. S.; Allafi, F.; Ab Kadir, M. O.; Ahmad, M. I. Biodiesel production from candlenut oil using a non-catalytic supercritical methanol transesterification process: optimization, kinetics, and thermodynamic studies. *RSC Adv.* **2022**, *12* (16), 9845–9861.
- Bashir, M. A.; Wu, S.; Zhu, J.; Krosuri, A.; Khan, M. U.; Ndeddy Aka, R. J. Recent development of advanced processing technologies for biodiesel production: A critical review. *Fuel Process. Technol.* **2022**, *227*, 107120.
- Singh, C. S.; Kumar, N.; Gautam, R. Supercritical transesterification route for biodiesel production: Effect of parameters on yield and future perspectives. *Environmental Progress & Sustainable Energy* **2021**, *40* (6), No. e13685.
- Farobie, O.; Matsumura, Y. State of the art of biodiesel production under supercritical conditions. *Prog. Energy Combust. Sci.* **2017**, *63*, 173–203.
- Qadeer, M. U.; Ayoub, M.; Komiyama, M.; Khan Daulatzai, M. U.; Mukhtar, A.; Saqib, S.; Ullah, S.; Qyyum, M. A.; Asif, S.; Bokhari, A. Review of biodiesel synthesis technologies, current trends, yield influencing factors and economical analysis of supercritical process. *Journal of Cleaner Production* **2021**, *309*, 127388.
- Sitepu, E.; Heimann, K.; Raston, C.; Zhang, W. Critical evaluation of process parameters for direct biodiesel production from diverse feedstock. *Renewable and Sustainable Energy Reviews* **2020**, *123*, 109762.
- Lin, C.-Y.; Lin, Y.-W. Fuel Characteristics of Biodiesel Produced from a High-Acid Oil from Soybean Soapstock by Supercritical-Methanol Transesterification. *Energies* **2012**, *5* (7), 2370–2380.
- Muhammed Niyas, 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.
- Palani, Y.; Devarajan, C.; Manickam, D.; Thanikodi, S. Performance and emission characteristics of biodiesel-blend in diesel engine: A review. *Environmental Engineering Research* **2022**, *27* (1), 200338–200330.
- Chew, S. C.; Nyam, K. L. Kenaf (*Hibiscus cannabinus* L.) Seed Oil. In *Fruit Oils: Chemistry and Functionality*; Ramadan, M. F., Ed.; Springer International Publishing, 2019; pp 451–494.
- Tirkey, J. V.; Singh, D. K. Performance and emission optimization of CI engine fueled with coconut shell-based producer gas and diesel by using response surface methodology. *Biomass Conversion and Biorefinery* **2023**, *13* (11), 10243–10261.

- (25) Nayab, R.; Imran, M.; Ramzan, M.; Tariq, M.; Taj, M.; Akhtar, M.; Iqbal, H. Sustainable biodiesel production via catalytic and non-catalytic transesterification of feedstock materials - A review. *Fuel* **2022**, *328*, 125254.
- (26) Wubishet Degife, M. A.; et al. Extracted Biodiesel as Feed for Internal Combustion Engine. *Journal of Mechanical Design and Vibration* **2015**, DOI: 10.12691/jmdv-3-1-1.
- (27) Jeouo Rong Industrial Corp. *Manual of the Supercritical Methanol Reacting System*; Jeouo Rong Industrial Corp.: Kaohsiung City, Taiwan, 2020.
- (28) Hsiao, M.-C.; Liao, P.-H.; Lan, N. V.; Hou, S.-S. Enhancement of Biodiesel Production from High-Acid-Value Waste Cooking Oil via a Microwave Reactor Using a Homogeneous Alkaline Catalyst. *Energies* **2021**, *14* (2), 437.
- (29) García-Morales, R.; Verónico-Sánchez, F. J.; Zúñiga-Moreno, A.; González-Vargas, O. A.; Ramírez-Jiménez, E.; Elizalde-Solis, O. Fatty Acid Alkyl Ester Production by One-Step Supercritical Transesterification of Beef Tallow by Using Ethanol, Iso-Butanol, and 1-Butanol. *Processes* **2023**, *11* (3), 742.
- (30) Salaheldeen, M.; Mariod, A. A.; Aroua, M. K.; Rahman, S. M. A.; Soudagar, M. E. M.; Fattah, I. M. R. Current State and Perspectives on Transesterification of Triglycerides for Biodiesel Production. *Catalysts* **2021**, *11* (9), 1121.
- (31) Lin, C.-Y.; Lin, Y.-W.; Yang, H. Comparison of Engine Emission Characteristics of Biodiesel from High-Acid Oil and Used Cooking Oil through Supercritical Methanol and Alkaline-Catalyst Transesterifications. *Processes* **2023**, *11* (9), 2755.
- (32) Sonthalia, A.; Kumar, N. Comparison of fuel characteristics of hydrotreated waste cooking oil with its biodiesel and fossil diesel. *Environ. Sci. Pollut. Res. Int.* **2021**, *28* (10), 11824–11834.
- (33) Jiang, J.; Zhang, R.; Wu, Y.; Chang, C.; Jiang, Y. A fault diagnosis method for electric vehicle power lithium battery based on wavelet packet decomposition. *Journal of Energy Storage* **2022**, *56*, 105909.
- (34) Soni, S.; Kumari, D.; Singh, D.; Sharma, D.; Sharma, S. Chemical compositions, properties, and standards for different generation biodiesels: A review. *Fuel* **2019**, *253*, 60.
- (35) Afif, M. K.; Biradar, C. Production of Biodiesel from Cannabis sativa (Hemp) Seed oil and its Performance and Emission Characteristics on DI Engine Fueled with Biodiesel Blends. *International Research Journal of Engineering and Technology (IRJET)* **2019**, *06* (08), 246–253.
- (36) Kartal, F.; Özveren, U. A deep learning approach for prediction of syngas lower heating value from CFB gasifier in Aspen plus®. *Energy* **2020**, *209*, 118457.
- (37) Ulusoy, Y. Investigation of particulate matter by FTIR, TEM and elemental analyses in a diesel engine operating on diesel and waste cooking oil-biodiesel. *Environ. Sci. Pollut. Res. Int.* **2020**, *27* (1), 500–509.
- (38) Wang, Z.; Burra, K. G.; Lei, T.; Gupta, A. K. Co-pyrolysis of waste plastic and solid biomass for synergistic production of biofuels and chemicals-A review. *Prog. Energy Combust. Sci.* **2021**, *84*, 100899.
- (39) Zhang, N.; Li, Y.; Wen, S.; Sun, Y.; Chen, J.; Gao, Y.; Sagymbek, A.; Yu, X. Analytical methods for determining the peroxide value of edible oils: A mini-review. *Food Chem.* **2021**, *358*, 129834.
- (40) Cihan, Ö. Experimental and numerical investigation of the effect of fig seed oil methyl ester biodiesel blends on combustion characteristics and performance in a diesel engine. *Energy Reports* **2021**, *7*, 5846–5856.
- (41) Elkelawy, M.; Alm-Eldin Bastawissi, H.; Esmail, K. K.; Radwan, A. M.; Panchal, H.; Sadasivuni, K. K.; Ponnamma, D.; Walvekar, R. Experimental studies on the biodiesel production parameters optimization of sunflower and soybean oil mixture and DI engine combustion, performance, and emission analysis fueled with diesel/biodiesel blends. *Fuel* **2019**, *255*, 115791.
- (42) Chuah, L. F.; Bokhari, A.; Asif, S.; Klemeš, J.; Joe Dailin, D.; El Enshasy, H.; Halim, A.; Yusof, M. A review of performance and emission characteristic of engine diesel fuelled by biodiesel. *Chemical Engineering Transactions* **2022**, *94*, 1099–1104.
- (43) Zhang, Y.; Zhong, Y.; Wang, J.; Tan, D.; Zhang, Z.; Yang, D. Effects of Different Biodiesel-Diesel Blend Fuel on Combustion and Emission Characteristics of a Diesel Engine. *Processes* **2021**, *9* (11), 1984.
- (44) Ma, Q.; Zhang, Q.; Zheng, Z. An experimental assessment on low temperature combustion using diesel/biodiesel/C2, C5 alcohol blends in a diesel engine. *Fuel* **2021**, *288*, 119832.
- (45) Abed, K. A.; Gad, M. S.; El Morsi, A. K.; Sayed, M. M.; Elyazeed, S. A. Effect of biodiesel fuels on diesel engine emissions. *Egyptian Journal of Petroleum* **2019**, *28* (2), 183–188.
- (46) Maithomklang, S.; Sukjit, E.; Srisertpol, J.; Klinkaew, N.; Wathakit, K. Pyrolysis Oil Derived from Plastic Bottle Caps: Characterization of Combustion and Emissions in a Diesel Engine. *Energies* **2023**, *16* (5), 2492.
- (47) Rajak, U.; Nashine, P.; Dasore, A.; Balijepalli, R.; Kumar Chaurasiya, P.; Nath Verma, T. Numerical analysis of performance and emission behavior of CI engine fueled with microalgae biodiesel blend. *Materials Today: Proceedings* **2022**, *49*, 301–306.
- (48) Razzaq, L.; Imran, S.; Anwar, Z.; Farooq, M.; Abbas, M. M.; Mehmood Khan, H.; Asif, T.; Amjad, M.; Soudagar, M. E. M.; Shaukat, N.; et al. Maximising Yield and Engine Efficiency Using Optimised Waste Cooking Oil Biodiesel. *Energies* **2020**, *13* (22), 5941.
- (49) Gaur, A.; Dwivedi, G.; Baredar, P.; Jain, S. Influence of blending additives in biodiesel on physiochemical properties, engine performance, and emission characteristics. *Fuel* **2022**, *321*, 124072.
- (50) Mohammed, M. K.; Balla, H. H.; Al-Dulaimi, Z. M. H.; Kareem, Z. S.; Al-Zuhairy, M. S. Effect of ethanol-gasoline blends on SI engine performance and emissions. *Case Studies in Thermal Engineering* **2021**, *25*, 100891.
- (51) Gowrishankar, S.; Krishnasamy, A. Emulsification - A promising approach to improve performance and reduce exhaust emissions of a biodiesel fuelled light-duty diesel engine. *Energy* **2023**, *263*, 125782.
- (52) Gülüm, M. Effects of compression ratio, blending ratio and engine speed on fuel cost, performance and exhaust emissions of a diesel engine fueled with bio-derived alternative fuels. *Sustainable Energy Technologies and Assessments* **2022**, *53*, 102464.
- (53) Boretti, A. Advances in Diesel-LNG Internal Combustion Engines. *Applied Sciences* **2020**, *10* (4), 1296.
- (54) Simek, S. Effects of biodiesel obtained from Canola, sefflower oils and waste oils on the engine performance and exhaust emissions. *Fuel* **2020**, *265*, 117026.
- (55) Sabapathy, S. P.; Ammasi, A. M.; Khalife, E.; Kaveh, M.; Szymank, M.; Kuruvakkattu Reghu, G.; Sabapathy, P. Comprehensive Assessment from Optimum Biodiesel Yield to Combustion Characteristics of Light Duty Diesel Engine Fueled with Palm Kernel Oil Biodiesel and Fuel Additives. *Materials* **2021**, *14* (15), 4274.
- (56) Shekoffeh, M.; Gundoshmian, T. M.; Jahanbakshi, A.; Heidari-Maleni, A. Performance and emission characteristics of a diesel engine fueled with functionalized multi-wall carbon nanotubes (MWCNTs-OH) and diesel-biodiesel-bioethanol blends. *Energy Reports* **2020**, *6*, 1438–1447.
- (57) Temizer, İ.; Cihan, Ö.; Eskici, B. Numerical and experimental investigation of the effect of biodiesel/diesel fuel on combustion characteristics in CI engine. *Fuel* **2020**, *270*, 117523.
- (58) Silva, M.; Liu, X.; Hlaing, P.; Sanal, S.; Cenker, E.; Chang, J.; Johansson, B.; Im, H. G. Computational assessment of effects of throat diameter on combustion and turbulence characteristics in a pre-chamber engine. *Applied Thermal Engineering* **2022**, *212*, 118595.
- (59) Zhao, Y.; Xie, Y.; Wang, X.; Li, Z.; Niu, T.; Liu, S. Energy balance analysis, combustion characteristics, and particulate number concentration-NOx trade-off of a heavy-duty diesel engine fueled with various PODEn/diesel blends. *Energy Conversion and Management* **2020**, *225*, 113489.
- (60) Gong, C.; Zhang, Z.; Sun, J.; Chen, Y.; Liu, F. Computational study of nozzle spray-line distribution effects on stratified mixture formation, combustion and emissions of a high compression ratio DISI methanol engine under lean-burn condition. *Energy* **2020**, *205*, 118080.

(61) Malat'ák, J.; Gendek, A.; Aniszewska, M.; Velebil, J. Emissions from combustion of renewable solid biofuels from coniferous tree cones. *Fuel* **2020**, *276*, 118001.

(62) Aydoğan, B. Experimental Investigation of Tetrahydrofuran Combustion in Homogeneous Charge Compression Ignition (HCCI) Engine: Effects of Excess Air Coefficient, Engine Speed and Inlet Air Temperature. *Journal of the Energy Institute* **2020**, *93*, 1163.

(63) Velez Godino, J. A.; Torres Garcia, M.; Jimenez-Espadafor Aguilar, F. J. Experimental analysis of late direct injection combustion made in a compression-ignition engine fuelled with biodiesel/diesel blends. *Energy* **2022**, *239*, 121895.

(64) Hua, J.; Song, Y.; Zhou, L.; Liu, F.; Wei, H. Operation strategy optimization of lean combustion using turbulent jet ignition at different engine loads. *Applied Energy* **2021**, *302*, 117586.

(65) Lin, C.-Y. Blending Biodiesel in Fishing Boat Fuels for Improved Fuel Characteristics. *Frontiers in Energy Research* **2014**, DOI: 10.3389/fenrg.2014.00006.

(66) Attia, A.; Kulchitskiy, A. R.; Nour, M.; Elseesy, A.; Nada, S. A. The influence of castor biodiesel blending ratio on engine performance including the determined diesel particulate matters composition. *Energy* **2022**, *239*, 121951.

(67) 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. *Applied Thermal Engineering* **2019**, *146*, 738.

(68) Tan, J.; He, Y.; Zhu, R.; Zhu, Y.; Wang, Z. Experimental study on co-firing characteristics of ammonia with pulverized coal in a staged combustion drop tube furnace. *Proceedings of the Combustion Institute* **2023**, *39* (3), 3217–3225.

(69) Chen, Z.; Chen, H.; Wang, L.; Geng, L.; Zeng, K. Parametric study on effects of excess air/fuel ratio, spark timing, and methanol injection timing on combustion characteristics and performance of natural gas/methanol dual-fuel engine at low loads. *Energy Conversion and Management* **2020**, *210*, 112742.

(70) El Shenawy, E. A.; Elkelawy, M.; Bastawissi, H. A.-E.; Panchal, H.; Shams, M. M. Comparative study of the combustion, performance, and emission characteristics of a direct injection diesel engine with a partially premixed lean charge compression ignition diesel engines. *Fuel* **2019**, *249*, 277–285.

(71) Aldhaidhawi, M.; Chiriac, R.; Bădescu, V.; Descombes, G.; Podevin, P. Investigation on the mixture formation, combustion characteristics and performance of a Diesel engine fueled with Diesel, Biodiesel B20 and hydrogen addition. *Int. J. Hydrogen Energy* **2017**, *42* (26), 16793–16807.

(72) Gad, M.S.; El-Shafay, A.S.; Abu Hashish, H.M. Assessment of diesel engine performance, emissions and combustion characteristics burning biodiesel blends from jatropha seeds. *Process Safety and Environmental Protection* **2021**, *147*, 518–526.