Desert Palm Date Seeds as a Biodiesel Feedstock: Extraction, Characterization, and Engine Testing

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Abstract: The development of alternative fuels is increasingly important in order to maintain ongoing global economic and technological progress in the face of fossil fuel depletion and increasing environmental damage. Desert palm date seeds have clear potential as feedstock for biodiesel production given their high oil content and availability as food waste that requires no further cultivation. In this study we investigated the optimum production processes and conditions for date seed oil biodiesel, including characterizing the intermediate product and correcting its composition to meet international fuel standards. Four biodiesel blends were prepared (B5, B10, B15, and B20) and tested in a compression ignition engine at engine speeds from 1600 to 3600 rpm (200 rpm increments) and three engine loads (50%, 75%, and 100%). The highest oil yield and biodiesel conversion achieved were 10.74 wt.% and 92%, respectively. The biodiesel properties conformed well with the standards; the values for brake power, brake thermal efficiency, and brake specific fuel consumption were comparable with petrol diesel, though the latter was slightly superior. All blends produced lower levels of CO_2, CO, and HC but higher levels of NO_x emissions. These results demonstrate the fundamental suitability of date seeds as biodiesel feedstock, deserving of further research.

Keywords: biodiesel; date seeds; desert palm tree; transesterification; brake power; brake specific fuel consumption; engine emissions

1. Introduction

The rapidly increasing global consumption of liquid fossil fuels suggests that oil reserves may soon be depleted; oil supply shortages may occur by 2020–2030 [1]. This presents a dual challenge to humanity: To sustain global economic and technological development without compromising resources for future generations [2]. One specific solution to this challenge is to develop renewable fuels and feedstocks in sufficient amounts to partially or fully supply the needs of industry and transportation [3]. The use of such renewable fuels in combination with proper technology should help end the detrimental environmental consequences of fossil energy use. Renewable energy resources that command a significant share of the global energy market include solar, hydrogen, wind, geothermal, and energy derived from biomass (bioenergy), such as biodiesel. The latter has many advantages as a renewable fuel, including diversified potential feedstocks including an extended array of vegetable oils and animal fats, high cetane number, oxidative stability, biodegradability, lubricity characteristics, and compatibility with existing transportation infrastructure [4].

However, the production of first-generation biodiesel (produced from vegetable oils and animal fats) can also cause serious problems (such as deforestation, loss of biodiversity, excessive consumption of water resources, high production cost, and food shortages) that should be addressed before planning any larger-scale implementation in the transportation sector [5]. Most of these concerns can be addressed by considering second-generation biodiesel (produced from non-food feedstocks and waste streams) instead. Food waste is an inherent problem in the global food industry; more than 30% of food is sent to landfills or incinerators [6]. This waste stream represents a promising source of energy, especially for biodiesel production using materials such as spent coffee grounds [7,8] and used cooking oil [4].

Recently, desert palm date seeds have also been proposed as a potential parent feedstock for biodiesel production [9]. The date palm tree has been cultivated in the Middle East and North Africa for millennia, and is believed to be the oldest domesticated fruit tree [10]. Traditionally, it was the most precious fruit crop in harsh arid or desert environments where water scarcity and extreme temperatures are common, due to the range of resources it provides [11]. Nowadays, date palm trees are also grown in semiarid environments and other regions including southern Europe, Australia, and the Americas [12]. Globally, there are now more than 100 million date palm trees comprising more than 2000 cultivars [13]. The annual average yield of a palm tree is 500 kg of fresh dates; production starts at 5 years and lasts up to 60 years [14]. The global production and consumption of dates has increased rapidly, from 1.88 million t in 1965 to 3.43 million t in 1990 and 8.46 million t in 2016; production is dominated by Middle Eastern and African countries (Figure 1) [15]. The fruit ripens in different stages, up to 150 d after pollination (Figure 2) [16]. It is a pitted fruit that consists of a core seed surrounded by a fleshy pericarp (Figure 3). The seeds are very hard, range from 5 to 15 mm in length, and have an oblong shape and a ventral groove [10]. On average, they weigh 11–18% of the total fruit mass [17] and contain 4–13% oil [18,19]. Based on these numbers, an estimated 1.3 million t of date seed and 127,000 metric t of date seed oil (DSO) (and similar amount biodiesel) could be produced annually. This shows the potential for date-based biodiesel, given that the total annual production of biodiesel in the Middle East and Africa in 2015 was 38,700 t [20].
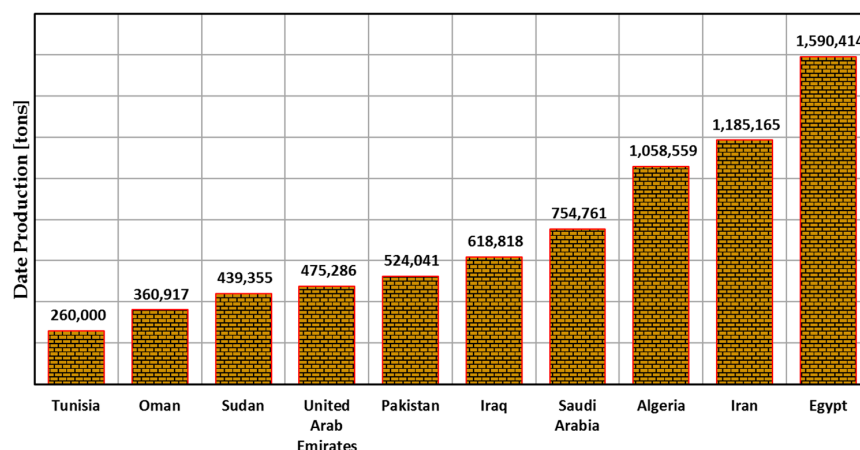

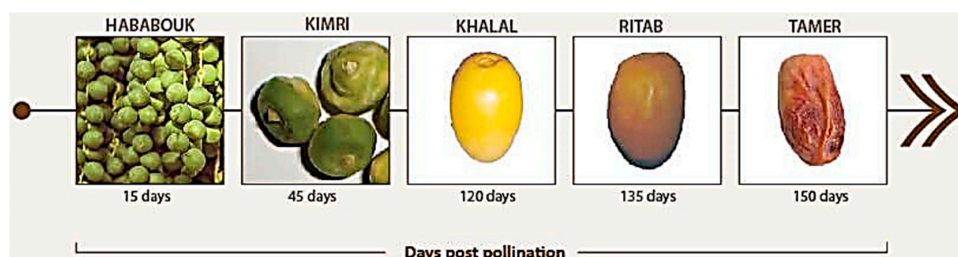**Figure 1.** Top 10 global date-producing countries [15].

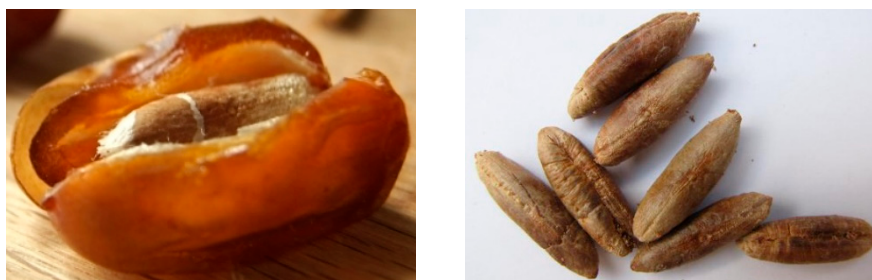**Figure 2.** Development of date fruit over time [16].

Figure 3. Date fruit and seed.

Date seeds are a byproduct of fruit production that are often discarded as waste [21]. Traditionally, they were used as fodder for domestic poultry and other animals [22,23], and have also been turned into caffeine-free coffee in the Arabian Peninsula [24,25] or pharmaceutical and cosmetic products [26]. A few recent studies have proposed using DSO as a potential feedstock for biodiesel production [9,27,28], but these only investigated the production processes and assessed the effects of various parameters on oil extraction and biodiesel yield. In addition, it remains unclear whether the final fatty acid methyl ester (FAME) product matches standard biodiesel specifications as few DSO biodiesel properties have been compared with such standards [9,27]. Table 1 summarizes previously reported parameter values and highest DSO yields under those conditions. Table 2 summarizes the parameters and reaction conditions for optimized biodiesel production as reported in the literature. In this study, we investigated production factors that could optimize DSO extraction and biodiesel production and tested four DSO biodiesel blends in a compression ignition (CI) diesel engine to evaluate engine performance and tailpipe emissions.

Table 1. Parameters for date seed oil (DSO) extraction using the Soxhlet method.

Combination Identifier	Solvent	Solvent: Ground Seed Ratio [wt/wt]	Temperature [°C]	Time [h]	Ground Particle Size [mm]	Highest Yield [wt.%]	Ref.
1	Hexane	16.37	80	12	2.36	11.7	[28]
2	Hexane	16.37	80	12	0.5		
3 *	Hexane	16.37	80	12	0.35		
1	Hexane	2	50	5	0.25–0.3	16.5	[27]
2	Hexane	3	60	6	0.25–0.3		
3 *	Hexane	4	70	7	0.25–0.3		
1 *	Petroleum ether	6.53	40–60	1.5	1–2	12.67	[21]
1 *	Hexane	5.24	40–50	8	1	10.36	[29]
1	Methanol	3.94	50	1	0.45	8.5	[30]
2	2-opropanol	3.925	50	2	1		
3	Chloroform	7.5	50	4	1.2		
4 *	Hexane	3.27	50	6	0.45		
5	Toluene	4.33	50	4	0.45		
1 *	Chloroform/methanol	11.43	160	0.5–4	4	9.3	[31]
2	Hexane	6.55	120	0.5–4	4		
3	Petroleum ether	6.53	100	0.5–4	4		
1 *	Hexane	16.37	55	4	0.6	4.5	[32]
2	Hexane	16.37	55	7	1.8		

* Condition of highest yield.

Table 2. Parameters and conditions for DSO transesterification determined by prior research.

Alcohol	Catalyst	Alcohol: Oil Molar Ratio	CMF % [wt./wt.]	Time [h]	Temp. [C]	Highest Yield [wt.%]	Ref.
Methanol	HCL	6	25 [a], 50 [a], 100 [a,*]	1.5	60	61	
	KOH	3	0.125, 0.25 *, 0.5	1.5	60	80.5	[9]
	Immobilized enzyme	5	3, 4 *, 5	10	40	80	

Table 2. *Cont.*

Alcohol	Catalyst	Alcohol: Oil Molar Ratio	CMF % [wt./wt.]	Time [h]	Temp. [C]	Highest Yield [wt.%]	Ref.
Methanol	NaOH	3, 4 *, 5	0.3 *, 0.5	0.5, 0.75, 1, 1.25 *	45, 55, 65, 75 *	91	[32]
Methanol	NaOH	5	10	6	40	30	[28]
Methanol	KOH	6	1	1	65		[27]
Methanol	Synthesized catalysts	12	5	1.5		93.5	[33]

[a] % by volume; * condition of highest yield.

2. Materials and Methods

2.1. Date Seed Collection and Characterization

We collected seeds (pits) from the Sharjah Dates facility in Sharjah, United Arab Emirates (UAE), which handles 25 date cultivars from the UAE and other countries in the region. High-quality seeds were hand-isolated and soaked in water for 12 h, then washed with tap water to remove any remaining date flesh. Seeds initially contain 3.1–7.1 wt.% moisture [18], which can increase up to 15–20 wt.% after such soaking and washing [27]. The seeds must be dried before oil extraction as the moisture can otherwise cause spoilage in the oil sample, and the dried seeds are far easier to grind. To accomplish this, the seeds were spread in the sun for 7 days followed by 12 h in an oven (SLN 180, POL-EKO) at 60 °C. Repeated weight measurements during the drying processes showed that an initial average 13.8 wt.% moisture content was evaporated, reaching a constant mass in each batch (±0.1 g). Date seeds are quite hard and thus difficult to grind, so a heavy-duty crusher was used to grind the seeds until they passed through a 0.6 mm mesh sieve. Scanning Electron Microscopy (VEGA3-SEM from TESCAN) was used to determine the elemental composition of the ground seeds (Table 3), which affects the properties of the DSO and thus the produced biodiesel (Section 2.3); we also examined the microstructure before and after oil extraction (Figure 4).

Table 3. Composition of ground date seed.

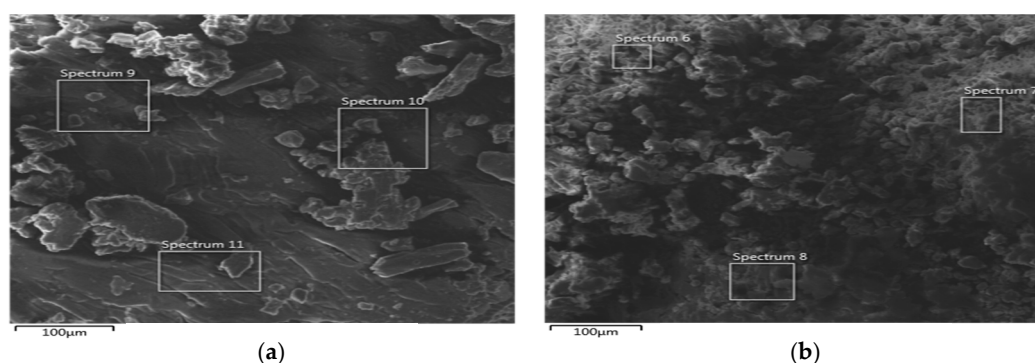| Component	Amount
Dry matter (dm), [%]	85.2 ∓ 0.15
Oil in dm, [%]	11.4 ∓ 0.1
Ash in dm, [%]	1.13 ∓ 0.02
Potassium, [mg/100 g dm]	242.6 ∓ 0.018
Phosphorus, [mg/100 g dm]	56.27 ∓ 0.76
Magnesium, [mg/100 g dm]	54.96 ∓ 0.31
Calcium, [mg/100 g dm]	50.26 ∓ 0.47
Sodium, [mg/100 g dm]	9.45 ∓ 0.18
Iron, [mg/100 g dm]	2.88 ∓ 0.31

Figure 4. SEM images of ground date seeds (**a**) before and (**b**) after oil extraction.

2.2. DSO Extraction

Several techniques can be used to extract DSO for biodiesel production, including the Soxhlet, supercritical fluid, ultrasonic, and microwave methods, all of which are influenced by various parameters. For example, many types of extraction solvent are available, including single solvents and binary solvents (combinations of two solvents); other parameters include the solvent to ground seed ratio, extraction time, and ground particle size. Table 1 summarizes previously reported parameter values and highest DSO yields under those conditions. We used the Soxhlet extraction method in this study because it represented the most practical option for our analytical scale, where parameters can be appropriately monitored and controlled.

We used a Model B-811 Extraction System (BUCHI) to extract the DSO; four extractors ran in parallel and concurrently to produce sufficient amounts for the subsequent transesterification process and engine tests. The entire process consists of three sequential stages: Extraction, rinsing, and drying. In the extraction stage, the sample was extracted by several cycles of solvent evaporation (by the heating element) and condensation (by the condenser). In the rinsing step, the remaining sample and extraction chamber interior were washed to remove the final traces of soluble matter. Here, the solvent was evaporated, condensed, and returned to the collection beakers repeatedly without any possibility of accumulating in the extraction chamber. The drying step compensated the need for a rotary evaporator. In this step, the solvent was evaporated, separated from the extract, and collected in the extraction chamber to repeat its function for the next batch.

Two solvents were tested: Hexane (S D Fine-Chem Limited, Mumbai, India) and petroleum ether (Fisher Chemical, Pittsburgh, PA, USA), with two solvent to ground seed ratios (wt./wt.) of 3 and 6, and at two temperatures, 40 and 60 °C. A 4 h extraction time was standard for all tests. Only one extraction unit was run for these tests since the purpose was to identify the optimum oil extraction conditions and parameters. The amounts required for biodiesel production were then extracted under the optimum conditions and parameters. Gum can occur in the final oil product, which causes difficulties in the subsequent transesterification process, so the oil went through a degumming process in which the gum was hydrated by a small amount of water (3 wt.%) added to the oil. The hydrated gum then precipitated and was removed with the water via a centrifuge.

At the same temperature, time, and solvent to seed ratios, hexane outperformed petroleum ether consistently in terms of oil yield. The highest oil extractions for hexane and petroleum ether were 10.74 and 8.19 wt.%, respectively, at conditions of 60 °C temperature, 4 h time, and a solvent:seed ratio of 6. This optimum set of parameters was applied repetitively in the next extraction batches.

2.3. DSO Characterization and Evaluation

Biodiesel can only be placed on the market if it satisfies strict standards (such as ASTM D6751 and ISO EN14214), and its specifications depend primarily on the characteristics of the DSO used to produce it. Thus, we characterized the DSO's properties (Table 4) and adjusted them systematically to meet the standards. Moisture is a minor but critical component of the oil as it reacts with the catalyst and forms soap and emulsions during transesterification. The measured moisture fraction (0.022% of oil weight) was less than the ASTM D6751 upper permitted limit (0.05 wt.%) [34]. Sulphur (S) content was 2.14 ppm (mg/kg), below the ASTM D6751 maximum accepted limit (15 ppm maximum). Sulphur is an undesirable element in fuel because it causes corrosion in metal engine parts and poisons catalytic converters, reducing their effectiveness. The unsaponifiable fraction defines the percentage of organic matter in the oil that cannot be turned into ester during the transesterification process; an acceptably low fraction (0.25 wt.%) was measured.

<p align="center">**Table 4.** Physiochemical properties of the DSO.</p>

Property	Unit	Value
Density @ 40 °C	kg/m^3	897.4
Viscosity @ 40 °C	mm^2/s	33.14
Higher heating value (HHV)	MJ/kg	32.63
Moisture	wt.%	0.022
Magnesium	ppm	2.82
Calcium	ppm	6.26
Sulphur	ppm	2.14
Phosphorous	ppm	14.16
Free fatty acids	%	0.42
Acid numbers (AcNo)	mgKOH/g	0.29
Saponification number (SaNo)	mgKOH/g	194.56
Unsaponifiable fraction	%	0.25

DSO and all other vegetable oils or animal fats are primarily made from triglycerides, which are composed of three long fatty acid (FA) chains attached to a smaller glycerin. The longer the FA chains, the better the candidate as a biodiesel feedstock. The transesterification reaction primarily takes place at the points where the FA chain meets the glycerin. If the glycerin does not connect with the FAs, they are referred to as free fatty acid (FFAs). The FAs themselves are composed of carbon chain ends with a carboxylic acid group, named as XX:Y (carbon atom number:double bond number). If the FAs are free of double bonds, they are said to be saturated fatty acids (SFAs). This context allows the proper description of other DSO properties.

The FFA content in DSO is a critical parameter because FFAs consume the catalyst and produce emulsions and soaps during transesterification, which result in difficulties with biodiesel separation, yield loss, extra cleaning steps, and extra cost [35]. The FFA content in the DSO produced for this study was 0.42 wt.%, below the upper permissible limit of 0.5 wt.%, allowing one-step transesterification. The acid number (AcNo) is another indication of the effect of FFA content and can be defined as the potassium hydroxide (KOH) amount (mg) that should be added to neutralize the acids in one gram of oil. One-step transesterification can be used if the AcNo is less than 2 mgKOH/g [36], which was true for this study (AcNo was 0.29 mgKOH/g). The saponification number (SaNo) is a measure of the total FAs (bound and free), defined as the quantity (g) of KOH required to entirely saponify 1 g of oil. This determines the carbon chain length and the mean molecular weight of all FAs. A SaNo value of 194.56 mgKOH/g was measured for the DSO, within the typical range for biodiesel feedstocks (185–210 mgKOH/g) [37].

ASTM D6751 specifies the maximum limit of combined magnesium (Mg) and calcium (Ca) as 5 ppm, and of phosphorous (P) as 10 ppm. However, the DSO values were 9.08 ppm and 14.16, respectively. Magnesium, calcium, and phosphorous are minor constituents but promote emulsification [38], cause damage to the after-treatment system [39], or form sediments, reducing the biodiesel yield during the transesterification reaction [40]. Therefore, we used a phosphoric acid treatment to reduce the levels of Mg, Ca, and P. The DSO was heated to 80 °C and mixed with 0.09 wt.% of 85%-phosphoric acid (H_3PO_4) (Sigma-Aldrich, St. Louis, MO, USA) in a blender at high speed for 2 min, then 0.047 wt.% of 0.5N-sodium hydroxide (NaOH) (Sigma-Aldrich, St. Louis, MO, USA) was added and blended. This mixture was then heated with stirring for half an hour and centrifuged for 10 min at 80 °C before removing the top oil layer. This pretreatment lowered the combined Mg and Ca to 3.27 ppm and the P to 7.88 ppm.

The FA profile governs biodiesel properties and the alkyl ester content. Specifically, the number of carbon double bonds in the FA decides the cetane number (CN), cold flow features, and oxidative stability of the biodiesel. 44.55 wt.% of the FAs in the DSO were SFAs (Table 5), potentially problematic as biodiesel made from SFAs tends to have a high melting point that increases the chance of cold weather gelling. On the other hand, biodiesel extracted from SFAs typically has higher CN [34],

produces lower nitrogen oxides (NO_x) emissions, and has better oxidative stability than that produced from unsaturated fatty acids (UFAs). Biodiesel with high oxidative stability is not susceptible to oxidation that forms sediments and varnish deposits [40]. In addition, such solidified oils will often capture significant amounts of moisture or impurities that should be freed before processing. The UFA (one or more double bonds in the FA chain) content of the DSO was 55.26 wt.%. High-UFA biodiesel is more appropriate for cold-weather use due to its lower gel point, but is more prone to oxidation and rancidification. Therefore, biodiesel produced from DSO with this high UFA content requires an oxidative stabilizer such as butylated hydroxytoluene (BHT) (3,5-di-tert-butyl-4-hydroxy-toluene) [41].

Table 5. Fatty acid (FA) profile of the DSO.

FA	Structure	Content (%)	Molecular Formula	Molar Mass (g/mole)
Linoleic acid	C18:2	9.95	$C_{18}H_{32}O_2$	280.45
Palmitic acid	C16:0	12.01	$C_{16}H_{32}O_2$	256.43
Oleic acid	C18:1	44.73	$C_{18}H_{34}O_2$	282.47
Arachidic acid	C20:0	0.21	$C_{20}H_{40}O_2$	312.54
linolenic acid	C18:3	0.11	$C_{18}H_{30}O_2$	278.44
Behenic acid	C22:0	0.46	$C_{22}H_{44}O_2$	340.59
Lignoceric acid	C24:0	0.24	$C_{24}H_{48}O_2$	368.65
Stearic acid	C18:0	4.54	$C_{18}H_{36}O_2$	284.48
Erucic acid	C22:1	0.38	$C_{22}H_{42}O_2$	338.58
Myristic acid	C14:0	10.14	$C_{14}H_{28}O_2$	228.38
Palmitoleic acid	C16:1	0.09	$C_{16}H_{30}O_2$	254.41
Lauric acid	C12:0	16.14	$C_{12}H_{24}O_2$	200.32
Caprylic acid	C8:0	0.34	$C_8H_{16}O_2$	144.21
Capric acid	C10:0	0.47	$C_{10}H_{20}O_2$	172.27

2.4. DSO Transesterification

Vegetable oils must be modified for suitable use as fuel. When first introduced, diesel engines benefitted from low operational costs as diesel fuel could be synthesized from distillates beyond the range required for gasoline as well as byproduct streams from gasoline refining. However, more rigorous modern standards have made diesel more expensive than gasoline and its availability has decreased [40]. Therefore, finding alternatives to diesel fuel became a necessity for industrial purposes. Vegetable oils were introduced as a fuel source during the late 1970s and early 1980s, as these were associated with well-established technologies that could be easily combined with diesel fuel infrastructure and their properties made them suitable for direct use in diesel engines, potentially over short and long periods [42,43]. Operation was acceptable for short periods, with comparable engine performance and reductions in emissions of carbon oxides and unburned hydrocarbons.

However, long-term operation resulted in excessive deposits and engine wear due to the oil's high viscosity. Many fuel treatments have been proposed to reduce this problem, such as blending (emulsifying) vegetable oil with lower-viscosity liquids such as water or alcohol [44]. Although this approach has benefits, it has never been considered a practical fuel formulation method due to concerns regarding low-viscosity liquid separation, especially at low temperatures along with performance deterioration and corrosion problems related to the presence of alcohol or water [40]. Using vegetable oils as fuel requires modifying their molecular structure through transesterification, in which the triglycerides (the source of the high viscosity) react with methanol (alcohol) in the presence of a catalyst, converting to alkyl esters to produce a fuel (biodiesel) having excellent compatibility with existing diesel engines [45].

Very few studies are available on DSO transesterification, but a variety of parameters and reaction conditions can be monitored and adjusted to optimize biodiesel production (Table 2). First, several short-chain alcohols can be used, including methanol and ethanol. Ethyl ester is more complicated to produce than methyl ester during transesterification [46]. The emulsions formed during the reaction

with methanol break down easily and quickly and accumulate in the lower glycerin layer, while ethanol emulsions are more stable, making biodiesel separation and purification more difficult [47]. Therefore, we chose to use methanol (CH_3OH) in this present study.

The molar ratio of alcohol to feedstock oil (AOMR) is a critical factor influencing yield capacity and production cost [48], with a stoichiometric ratio of 3:1. In practice, however, AOMR should be higher than this to bring the reaction toward completion by facilitating miscibility and improving the interaction between alcohol and triglycerides [49]. Previous research tested AOMR ranges between 6:1 and 30:1, showing that equilibrium and reaction completion could not be attained below 6:1 [50]. In addition, reduced biodiesel yield and difficulties in glycerol separation have been experienced with AOMR higher than 15:1 [51]. Therefore, a molar ratio of 9:1 has been suggested as optimum, which we used in this study [49,51].

The catalyst has a vital effect on the production rate. Both basic catalysts (such as potassium and sodium hydroxides) and acid catalysts (such as sulfuric acid) can be used. The former requires lower reaction temperatures (around 50 °C) and shorter reaction times (~1 h), whereas acid catalysts require 100 °C and ~4 h [52,53]. We used sodium hydroxide (NaOH) in this study. The catalyst mass fraction (CMF) depends on the FFA fraction in the feedstock: The higher the FFA content, the higher the basic CMF is required to neutralize the acidity and prevent alkaline deactivation [54]. However, adding superfluous catalyst promotes emulsification, forms gels, and raises the viscosity, resulting in incomplete separation of glycerin and reduced ester extraction [47]. This suggests that an optimum catalyst concentration exists; we used a catalyst mass fraction of 1%.

We conducted transesterification using a biodiesel production plant (model UPB/EV, Elettronica Veneta, Motta di Livenza, Italy; Figure 5). The plant's core consists of an 18 L elongated shape reactor (R1) made of steel and glass. The reactor is equipped with an electric heating system, motorized agitator, thermostat, sampling outlet, and air inlet valve for bubble washing. The tank (D1) has a motorized agitator for mixing the catalyst with alcohol before this mix is introduced to the reactor (R1) by gravity through an isolating valve. The glycerin is collected from the reactor after the reaction by the collection tank (D2). The condenser (E1) eliminates the vapors released from D1 and R1 during the processing stage and condenses the methanol during the recovery phase; this is eventually collected in the tank (D3).
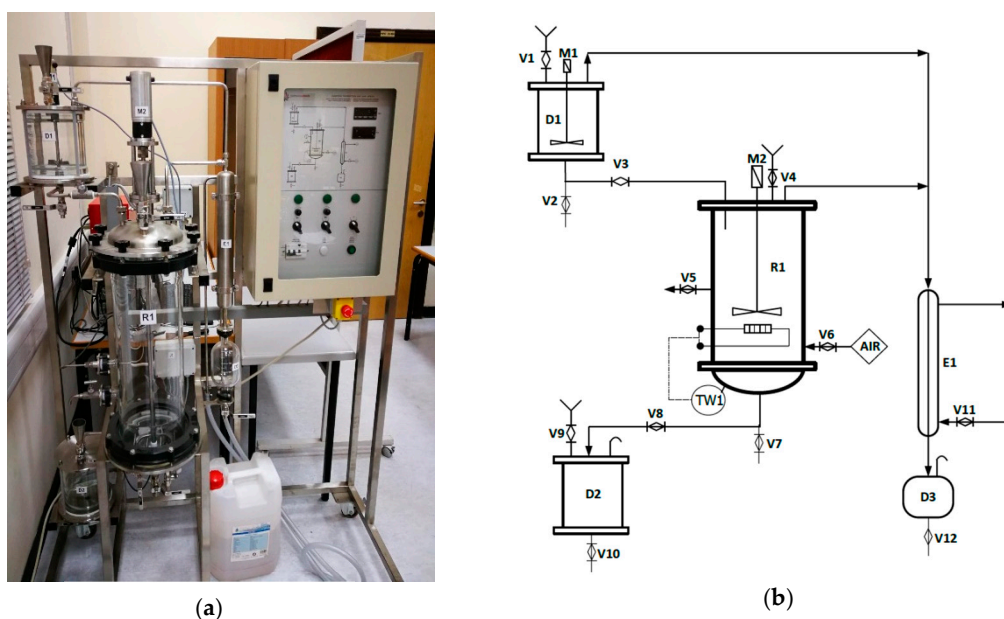

(**a**)　　　　　　　　　　　　　　　　　　　　　　　　　(**b**)

Figure 5. Biodiesel production plant: (**a**) Photograph and (**b**) schematic diagram with parts labelled for the tank (D), condenser (E), reactor (R), and valves (V) (see text for specific descriptions).

The DSO was introduced into the reactor R1, and the heating system was activated with the thermostat set at 55 °C (below the methanol boiling point, 64.7 °C). The methanol (in an AOMR of 9:1) and the NaOH catalyst (in a CMF of 1 wt.%) were added to tank D1 while the isolating valve was closed. The mixture inside tank D1 was then blended by the agitator until the catalyst was completely dissolved. The mixture was introduced to the oil in the reactor R1, taking this moment as the reaction starting time. The mixture was agitated vigorously and continuously for 1.5 h. Upon completion of the reaction, the glycerin was left to settle for 12 h, then separated from the methyl ester and collected in tank D2.

The raw biodiesel still contained contaminants such as traces of soap, NaOH, methanol, and free glycerides. Water purification (washing) is the safest, oldest, most common, and most flexible biodiesel purification technique. A distilled water amount of 50 vol.% was blended with the methyl ester in the reactor and stirred for 15 min. In addition, air at a proper pressure was introduced during this stage to create a flow of homogeneous air bubbles. The mixture was left to settle for 8 h and the water was parted from the ester. This washing process was repeated five times with 18 h settling time after the last wash. Eventually, the ester in the reactor was heated to 100 °C to free any traces of methanol or water. The unreacted methanol contained in the glycerin was released and recovered by heating the glycerin in the reactor at 100 °C. Then, methanol vapor was condensed and accumulated in tank D3.

2.5. Engine Test Rig

The DSO biodiesel we produced using the previously described processes was used to prepare four blends of biodiesel and petrol diesel: B5, B10, B15, and B20 (numbers refer to vol.% biodiesel content). These blends were then tested in a naturally aspirated single-cylinder CI diesel engine (Lombardini 15-LD-225) (Table 6). An automobile alternator fitted with a bridge rectifier circuit and resistive load bank was employed as a dynamometer that could load the engine. An extended range of engine speeds (1600–3600 rpm in 200 rpm increments) was considered at three engine loading conditions (100%, 75%, and 50%). The fuel flow rate was measured using a measuring burette (accuracy 0.5%) equipped in the fuel line connecting the fuel tank and the fuel pump. An ammeter and a voltmeter were also mounted in the test rig to measure the dissipated power. Moreover, the temperature of exhaust gases was measured by a thermocouple (accuracy of 2 °C). Four blends were developed from DSO biodiesel: B5, B10, B15, and B20 (with properties shown in Table 7), and evaluated technically using the following engine performance metrics: Brake power (BP), brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), and exhaust gas temperature (EGT). The environmental performance of the DSO biodiesel was assessed by measuring the tailpipe emissions of the engine for CO_2, CO, NO_x, and HC using an exhaust gas analyzer (EMS 5003) (Table 8).

Table 6. Test engine specifications.

Specifications	Unit	Description/Value
Engine model		Lombardini 15-LD-225
Bore	mm	69
Stroke	mm	60
Displacement volume	L	0.224
Compression ratio		21:1
Rated power @ 3600 rpm	kW	3.5
Rated torque @ 2400 rpm	N·m	10.4
Intake valve opening	Crank angle BTDC	6°
Intake valve closing	Crank angle ABDC	22°
Exhaust valve opening	Crank angle BBDC	58°
Exhaust valve closing	Crank angle ATDC	10°

Table 7. Properties of DSO biodiesel blends.

Blend	Lower Heating Value [MJ/kg]	Density [kg/m^3]	Viscosity [mm^2/s]	Cetane Number	C/H Mass Ratio	Oxygen Content [wt.%]
B5	43.6	839.1	2.7	51.6	6.2	0.6
B10	43.4	842.2	2.8	52.1	6.1	1.2
B15	43.2	845.3	2.9	52.7	6.1	1.8
B20	43	848.4	3.0	53.2	6.0	2.5

Table 8. Accuracy, resolution and range of the measurements of the exhaust gas analyzer (EMS 5003).

Exhaust Gas	Accuracy	Display Resolution	Range
CO_2 [%]	0.3	0.1	0–20
CO [%]	0.06	0.01	0–10
NO_x [ppm]	25	1	0–5000
HC [ppm]	4	1	0–2000

3. Results and Discussion

3.1. DSO Biodiesel Characterization and Evaluation

Diesel engine makers depend on fuel properties that optimize engine performance, efficiency, and durability while meeting emissions regulations. Thus, fuel standards have been developed to guarantee fuel compatibility for optimized engine operation, including the broadly accepted American ASTM D6751 and European Union EN 14214 standards. These regulate the properties determined by the FA profile along with factors related to production and storage [39] and are based on pure biodiesel (B100), ensuring the eligibility of blends with petrol diesel defined by ASTM D975 and EN 590 at any grade (1D, 2D, 1D low sulfur, or 2D low sulfur). Table 9 compares the DSO biodiesel properties with relevant American and European standards.

Table 9. Comparison of DSO biodiesel and different standards for biodiesel and petrol diesel.

Property	Units	Standard	DSO Biodiesel	ASTM D975 Diesel	ASTM D6751 Biodiesel
Sulfur	ppm ($\mu g/g^{-1}$)	ASTM D 5453	0.93	1D and 2D: S15 15 mg/kg S500 0.05% S5000 0.50%	15 ppm for S15 grade; 500 ppm for S500 grade
Fuel Filter Blocking Potential/Cold Soak Filterability Seconds	s	ASTM D 7501	-		200
Monoglyceride content	% weight	EN 14105	-		0.70% max
Calcium & Magnesium combined	mg/kg	EN 14538	3.27		5.0
Flash Point	°C	ASTM D 93	164	1D: 38 2D: 52	130 min
Water & sediment	% volume	ASTM D 2709	0.019	0.05% max	0.050% max
Kinematic viscosity	mm^2/s	ASTM D 445	4.38	1D: 1.3–2.4 2D: 1.9–4.1	1.9–6.0
Sulphated ash	% mass	ASTM D 874	< 0.02		0.020% max
Copper strip corrosion		ASTM D 130	1a	No. 3 max	No. 3 max
Cetane number		ASTM D 613	62	40 min	47 min
Cloud point	°C	ASTM D 2500	+9.4		Report
Carbon residue	% weight	ASTM D 4530	0.023	1D: 0.15% max 2D: 0.35% max	0.050% max

Table 9. *Cont.*

Property	Units	Standard	DSO Biodiesel	ASTM D975 Diesel	ASTM D6751 Biodiesel
Acid number	Mg KOH g^{-1}	ASTM D 664	0.29		0.5 max
Free glycerine	% weight	EN 14105	-		0.02% max
Total glycerine	% weight	EN 14105	-		0.25% max
Phosphorous content	% mass	ASTM D 4951	0.0002		0.001% max
Distillation 90% recovered	°C	ASTM D 1160	352.4	1D: 288 max 2D 282-338°C	360 max
				2D: 282–338	
Sodium & potassium combined	ppm (μg/g^{-1})	EN 14538	3.2		5 max
Oxidation stability	Hr @ 110 °C	EN 15751	7.4		6 min

3.1.1. Chemical Element Content

Sulphur, calcium, magnesium, phosphorus, sodium, and potassium are not contained in the biodiesel (ester) molecules but arise during the production process or are sourced from the feedstock. The presence of such elements poisons the emission control after-treatment system by plugging the particulate trap or the exhaust catalytic converter [39]. In addition, these elements cause higher harmful emissions. The amounts of S, Na, and K in the DSO biodiesel met the relevant standards (Table 9). After an application of phosphoric acid treatment to reduce the levels of Mg, Ca, and P, acceptable levels of these were also achieved.

3.1.2. Cetane Number

A CN of 62 was measured for the DSO biodiesel, well above the values for petrol diesel (43 in the US and 50 in the EU). We attribute this high value to the high fraction of saturated fats in the DSO feedstock (44.55 wt.%). The higher CN of DSO biodiesel enhances combustion because it means a shorter ignition delay. If ignition delay is too long, too much fuel is injected before ignition, resulting in very rapid burning, very high rates of pressure ascension, and possible occurrence of knocking [39].

3.1.3. Cloud Point

The cloud point (CP) is the temperature below which biowax (crystals) appear in the fuel and is thus a measure of fuel functionality in low-temperature weather conditions. The ASTM D6751 and EN 14214 standards do not specify a CP limit but require that a fuel's CP be reported so that clients can make informed decisions. The CP of the DSO was relatively high (9.4 °C), due to its production from saturated fats with high molecular weights. A higher CP means thicker fuel and potential clogging of fuel injectors and filters in cold weather. Of 35 biodiesels from various common feedstocks reviewed in this study, DSO biodiesel has the 6th highest CP [55].

Several treatments or modifications have been suggested to attenuate the effects of high CP in fuel. For stationary diesel engines in unheated locations, fuel lines and filters can be insulated, or fuel tanks and lines can be equipped with heaters. Another solution involves winterization, in which the methyl ester is crystallized by cooling, then the high-melting elements are filtered and separated [56]. However, this is not a preferred method because of the high fraction of biodiesel lost during the process (~25%). Using branched-chain alcohols (such as isopropyl and 2-butyl) instead of short-chain alcohols (such as methanol) is another option, as this can reduce CP by 7–14 °C [56]. However, branched-chain alcohols are more expensive and make it harder for the transesterification reaction to attain the equilibrium state, as compared with methanol. Blending high-CP biodiesel with low-CP biodiesel is another effective resolution [57]. Perhaps the most practical solution is to use cold flow improvers (additives) such as polymethacrylate and malan-styrene ester [58], which lower the CP by altering the shape and size of

the possible crystals. All tests in this study were conducted at temperatures above 25 °C, making this issue irrelevant for the test results.

3.1.4. Flash Point

Flash point (FP), the minimum temperature at which fuel releases adequate vapor to produce an ignitable mixture, is a safety criterion that guides the transportation and storage of fuel [59]. The FP of the DSO biodiesel was 164 °C, almost triple that of conventional diesel fuel (55–66 °C) and considerably higher than the standards (min. 130 °C in ASTM D6751 and min. 120 °C in EN 14214). Thus, the high FP of the DSO biodiesel is an attractive feature as the fuel can be considered intrinsically safe. The FP of the methyl ester depends on the vapor pressure of its constituents. Therefore, the presence of methanol residual (FP 10 °C) causes a dramatic drop in biodiesel FP, so the ASTM D6751 standard requires that the methanol content be less than 0.2 vol.%; this was met by the DSO biodiesel after purification.

3.1.5. Water and Sediment

The fuel injection systems in diesel engines are very sensitive to contaminants, so the filters in modern engines can capture foreign materials larger than 2 μm. However, under certain conditions, the fuel can undergo chemical changes downstream of the filters and form compounds such as sediments and varnish that block very fine orifices and coat moving parts, causing them to stick. In addition, water can be suspended as droplets or dissolved in the biodiesel, contributing to corrosion in fuel system components and promoting microbial development (sludge) that increases fuel acidity and plugs fuel filters [60]. The ASTM D6751 standard classifies water and sediment together with a maximum limit of 500 ppm (0.05 vol.%), well above the DSO biodiesel content of 190 ppm.

3.1.6. Viscosity

Fuel viscosity depends on the temperature and molecular structure of the fuel. Diesel engines employ positive displacement pumps with a plunger and barrel configuration to produce the required elevated injection pressure. With overly low fuel viscosity, a substantial fraction of engine power will be lost due to leakage passing the plunger during fuel compression. Overly high fuel viscosity means the pump cannot fill the pumping chamber and power will also drop, while spraying effectiveness is worsened (causing poor atomization) and the mechanical integrity of the pump is compromised [61]. Therefore, standards for both petrol diesel and biodiesel set narrow ranges for allowed viscosity. Biodiesel viscosity is an order of magnitude lower than the parent oil feedstock because methyl ester molecules are smaller and lighter than triglyceride molecules; the transesterification process reduces the viscosity. However, biodiesel viscosity is still higher than petrol diesel, especially at low temperatures. The kinematic viscosity of the DSO biodiesel was 4.38 mm^2/s, within the range set by the ASTM D 445 standard (1.9–6.0 mm^2/s) but greater than grade 2D diesel fuel (1.9–4.1 mm^2/s).

3.1.7. Sulfated Ash

The combustion of inorganic compounds contained in biodiesel (such as sodium, potassium, calcium, magnesium, phosphorous, or sulfur) generates ash that contributes to abrasive wear between the cylinder wall and the oscillating piston [60]. Sulfated ash is the most significant because it is more sensitive to sodium and potassium, which are likely the foremost producers of ash in biodiesel. The ASTM D 874 standard sets a maximum limit (0.02 wt.%) for sulfated ash, which was met by the DSO biodiesel.

3.1.8. Carbon Residue

Carbon residue (CR) quantifies the tendency of the biodiesel to form carbonaceous matter after combustion that accumulates inside the combustion chamber or clogs the injector tips. It is one of the most essential parameters for biodiesel quality because it is linked with several fuel characteristics

such as total glycerin, FFA, catalyst residue, soap, and contaminants [62]. Many procedures have been suggested for measuring CR against standards such as ASTM D5424. However, these procedures' results have limited correlation to actual engine deposits due to the complexity of emulating real conditions inside the combustion chamber. A CR of 0.023 wt.% was measured in the DSO biodiesel, well below the maximum limit set by ASTM D 4530.

3.1.9. Distillation

Petrol diesel is comprised of hundreds of various hydrocarbon compounds with different boiling points, whereas biodiesel fuel frequently consists of only 4–5 compounds with similar boiling points. A boiling (distillation) curve can be used to graphically represent the volume fraction boiled against progressive temperature increases, which reflects the bulk properties of the fuel [63]. Various engine parameters can be correlated to the distillation curve, such as the autoignition point and fuel vapor lock. We conducted a biodiesel distillation test under vacuum conditions to avoid the decomposition of biodiesel compounds due to their high boiling point. The ASTM D 1160 standard requires that a 90% volume fraction of the biodiesel boil below 360 °C, which was met by the DSO biodiesel (352.4 °C).

3.1.10. Acidity

The acidity of the biodiesel is an important consideration for storage and transportation, and can contribute to engine part corrosion and elevated deposits. Fuel acidity is identified by the acid number (AN), defined as the mass (mg) of the base KOH needed to neutralize 1 g of methyl ester [64]. AN is a direct measure of the FFA in the biodiesel, though the effect of strong mineral acids is higher than that of the weak carboxylic acids in FFAs. AN is also an indicator of water content or susceptibility to oxidation in the methyl ester. The AN of the DSO biodiesel was 0.29 mg KOH/g, well below the limit set by the ASTM D 664 standard (0.5 mg KOH/g).

3.1.11. Stability

Biodiesel stability refers to the fuel's ability to resist chemical reactions or changes under elevated temperatures (thermal stability) and under long-term storage conditions with temperatures near ambient (storage or oxidation stability). Biodiesel is more susceptible to oxidative degradation than petrol diesel due to the presence of unsaturated compounds (with double bonds) in its composition [39]. Specifically, linoleic acid (C18:2) (fraction in DSO: 9.95%) and linolenic acid (C18:3) (fraction in DSO: 0.11%) are the FAs with greatest susceptibility to oxidation. Even small fractions of unsaturated FA can contribute to serious oxidation. Biodiesel oxidation can be catalyzed by exposure to air at high temperatures, metal contaminants, and the presence of light, which can heighten oxidation by 30,000 times (causing what is called "photo-oxidation") [39]. Biodiesel oxidation forms hydroperoxides that polymerize under proper conditions, causing increases in acidity and viscosity. Nonetheless, oxidation of DSO biodiesel can be inhibited by tocopherols and tocotrienols, antioxidants that exist naturally in the date seed (51.5 mg of the total tocols has been detected per 100 g of date seed oil) [29]. Despite clear recognition of the biodiesel oxidation problem, so far, no widely accepted technique has been developed to quantify biodiesel stability. The Rancimat method widely adopted by the oil industry is currently used with biodiesel although engine makers have no experience with it. In this study, we used the EN 15751 standard (min. 6) because it represents the most up-to-date assessment of biodiesel stability; the DSO biodiesel met this standard (7.4).

3.2. Engine Performance

We averaged the values of the engine performance metrics for the four DSO biodiesel blends over all speeds and loads, then normalized the results against the benchmark petrol diesel (Figure 6). For BP, the DSO biodiesel became progressively inferior as the blend increased, due to its lower energy content (6.7% less) and higher viscosity, which adversely influences combustion [65]. A similar pattern occurred for BTE due to the decreased heating value and increased viscosity of higher blends, as

burning the same mass of fuel with lower heating value releases less energy while higher viscosity negatively affects fuel atomization, vaporization, and combustion. As for BSFC, the DSO biodiesel resulted in more fuel consumption as the fuel injectors injected the same volume of petrol diesel and biodiesel but a greater mass of biodiesel because of its higher density (7.4% greater) [66]. However, the biodiesel outperformed the petrol diesel in EGT due to the former's lower heating value and combustion temperature; lower EGT means less energy loss and less pollution emissions from the tailpipe [67].

	BP	BTE	BSFC	EGT
B5	-0.5	-1.2	1.6	-6.2
B10	-1.3	-2.5	3.3	-9.1
B15	-2.2	-4.2	5.5	-12.4
B20	-4.5	-7.7	9.8	-16.0
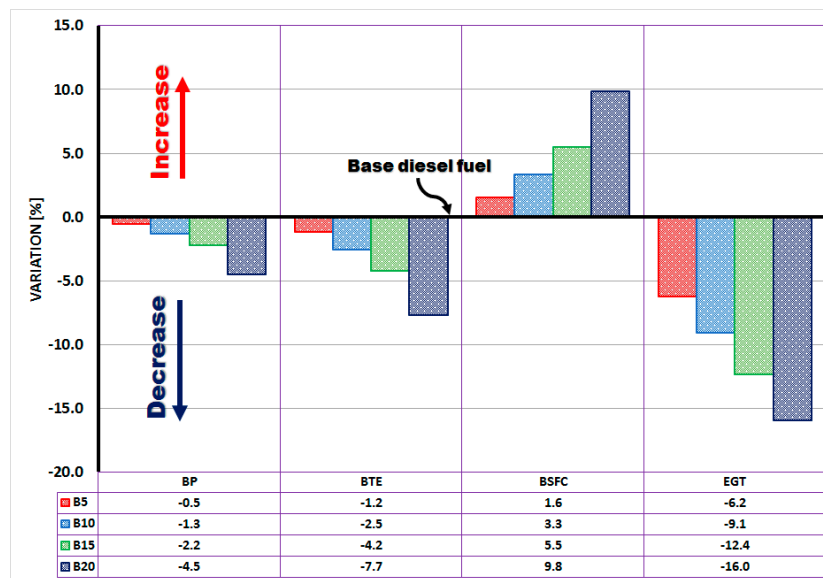
Figure 6. DSO biodiesel engine performance metrics averaged over all speeds and loads and normalized against baseline petrol diesel.

Figure 7 shows the trends of the performance metrics at 3000 rpm under the three considered loads. BP drops at partial load condition because fewer amounts of fuels are burned, and less energy is liberated. In addition, the engine's mechanical efficiency decreases due to the increase in the pumping losses when airflow is throttled. Likewise, BTE falls when the engine runs under partial load conditions because less amount of air is introduced into the cylinder, and consequently less amount of fuel is injected. Thus, less shaft work is produced by combustion. The BSFC increased significantly at half load because a significant fraction of engine power is wasted to overcome the pumping losses, and due to the increase in heat losses. From the other hand, running the engine under full load produces higher temperatures at the exhaust, because more mass of the fuel–air charge is trapped and combusted inside the combustion chamber, and thus more mass of product gases is exhausted at a higher temperature.
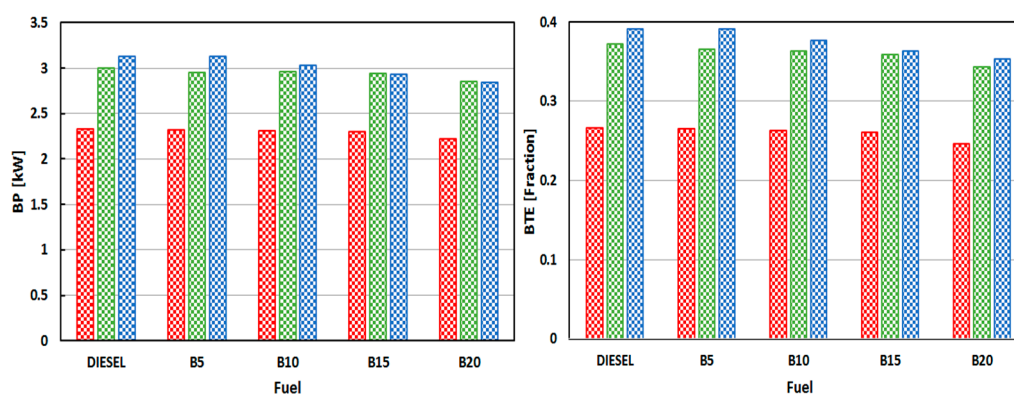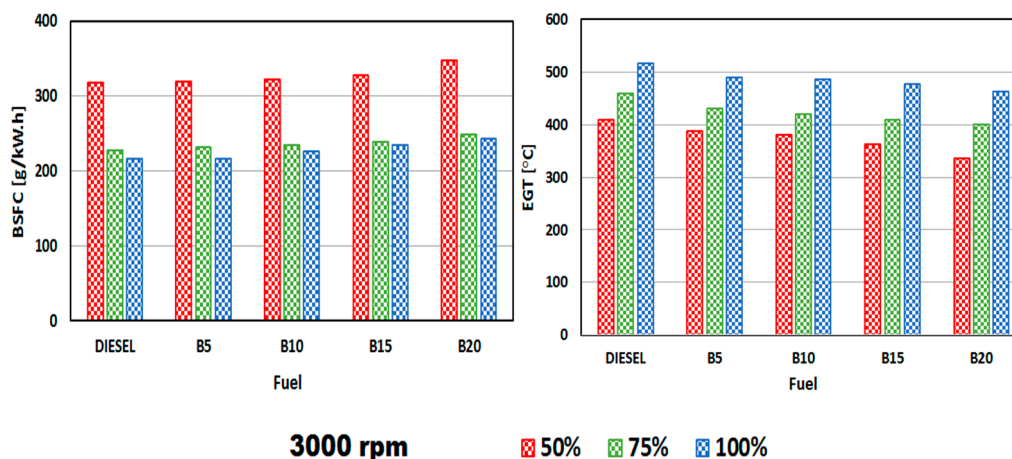

Figure 7. *Cont.*

Figure 7. DSO biodiesel engine performance metrics under three loads and 3000 rpm.

3.3. Engine Tailpipe Emissions

We averaged the values of the tailpipe emission metrics for the four DSO biodiesel blends over all speeds and loads, then normalized the results against the benchmark petrol diesel (Figure 8). The biodiesel blends emitted progressively less CO pollution with increasing blend %. This relates to the inherent oxygen in the biodiesel's chemical structure, which promotes complete combustion and reduces the chance for CO formation [68]. In addition, the relatively high CN of the DSO biodiesel (62) results in shorter ignition delay, less opportunity for the formation of fuel-rich spots inside the combustion chamber, and thus less opportunity for CO formation [68]. A similar pattern occurred for CO_2 emissions, again due to the biodiesel's oxygen content as well as its lower carbon/hydrogen ratio [69]. HC emissions also declined with increasing blend %, primarily due to DSO biodiesel's higher CN and thus shorter ignition delay and less chance for the air–fuel mixture to be diluted by more air before autoignition occurrence. Thus, it is improbable to have local mixtures that are lean to levels less than the flammability limits, causing misfires that release hydrocarbons outside the combustion chamber. In contrast, NO_x emissions increased slightly (<4%) with increasing blend %, possibly due to the oxygen content of the DSO biodiesel because this promotes complete combustion and higher temperatures in the combustion chamber, a main contributor to NO_x formation [70]. The higher CN of the blends is another contributing factor because this produces shorter ignition delays and thus advanced combustion that increases NO_x emissions [71].

Figure 9 describes the profiles of engine emission species under different loads at 3000 rpm. Under full load operation, greater amounts of CO_2 are emitted because more fuel is burned by the combustion. The CO emissions increased when engine load increased up to 75% loading condition because increasing the load initially results in a richer mix. However, at full or extremely high loading, the combustion temperature increases, leading to complete combustion and, eventually, a drop in CO emissions. Contrarily, the 75% is the loading condition at which lower amounts of HC emissions were produced compared with half and full load. Increasing the load extended the ignition delay time, giving more time for the mixing, and increasing the likelihood of lean mixtures that escape the cylinder without combustion. The emissions of NO_x reduced under low loading conditions due to the decrease in the temperature. Increasing the load raised the temperature in the combustion chamber, which is a main contributor to NO_x formation.

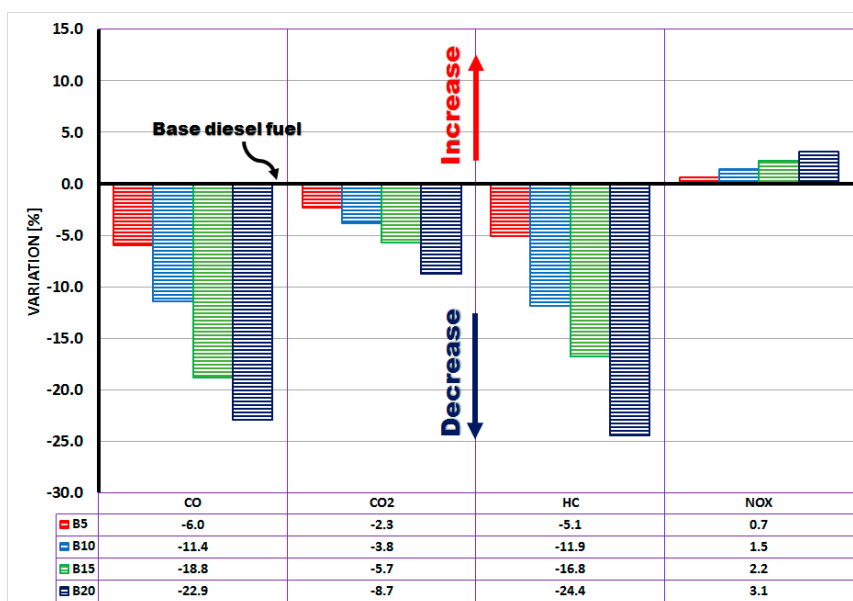|	CO	CO2	HC	NOX
B5	-6.0	-2.3	-5.1	0.7
B10	-11.4	-3.8	-11.9	1.5
B15	-18.8	-5.7	-16.8	2.2
B20	-22.9	-8.7	-24.4	3.1

Figure 8. DSO biodiesel engine tailpipe emission performance metrics averaged over all speeds and loads and normalized against baseline petrol diesel.
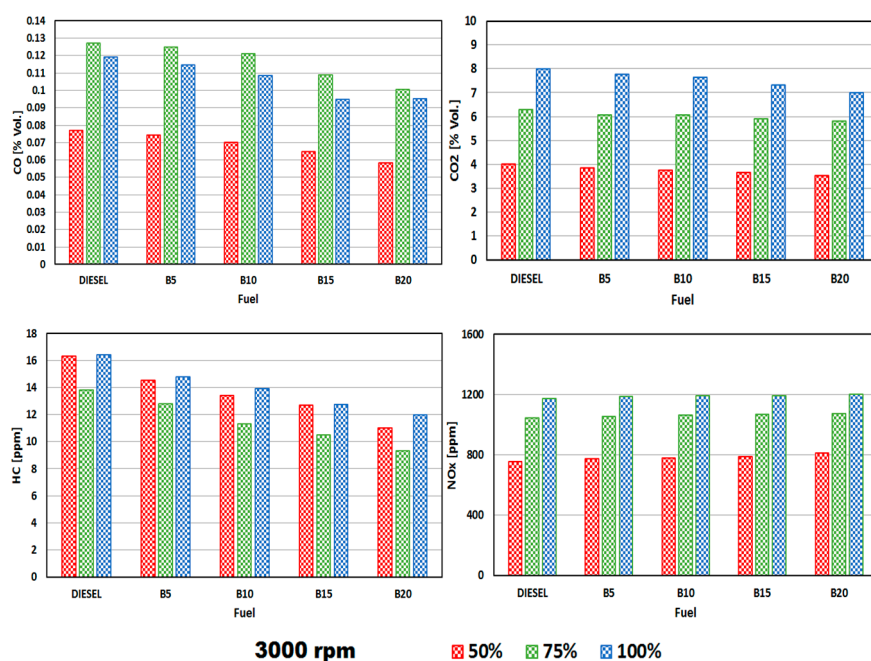

Figure 9. DSO biodiesel engine emission species under three loads and 3000 rpm.

4. Conclusions

This study introduces desert palm date seeds as a new parent feedstock for biodiesel production in order to diversify the biomass resources available for renewable and sustainable fuel production. We extracted DSO using the SE method after considering different solvents and extraction conditions in order to optimize the extraction process. The DSO was then converted to biodiesel by transesterification, under the optimum conditions defined in previous research. The resulting biodiesel was characterized and assessed based on widely used international standards (ASTM D6751 and EN 14214). We then prepared four blends of DSO biodiesel with petrol diesel and tested them in a CI engine to evaluate engine performance and tailpipe emissions. The following conclusions can be drawn:

(1)　At the same temperature, time, and solvent to seed ratios, hexane consistently outperformed petroleum ether in oil yields. The highest oil extraction (10.74 wt.%) was observed with hexane at 60 °C, 4 h extraction time, and a solvent:seed ratio of 6.

(2)　A DSO biodiesel yield of 92% was recorded at the following transesterification conditions: 55 °C, 9:1 AOMR, 1 wt.% CMf, and 90 min.

(3)　Phosphoric acid treatment of the DSO reduced levels of Mg, Ca, and P in the biodiesel to the ASTM D6751 allowable level.

(4)　The cloud point of the DSO was relatively high (9.4 °C), so the use of cold flow improvers would be necessary when this fuel is used in cold climates.

(5)　The BP, BTE, and BSFC values of the DSO biodiesel blends were comparable with the baseline diesel, though the latter was superior.

(6)　All biodiesel blends produced lower levels of CO_2, CO, and HC emissions.

(7)　All biodiesel blends produced higher levels of NO_x emissions.

References

1.　Kontorovich, A.E. Estimate of Global Oil Resource and the Forecast for Global Oil Production in the 21st Century. *Russ. Geol. Geophys.* **2009**, *50*, 237–242. [CrossRef]

2.　Labeckas, G.; Slavinskas, S.; Kanapkienė, I.; Labeckas, G.; Slavinskas, S.; Kanapkienė, I. Study of the effects of Biofuel-Oxygen of various origins on a CRDI diesel engine combustion and emissions. *Energies* **2019**, *12*, 1241. [CrossRef]

3.　Arunkumar, M.; Kannan, M.; Murali, G. Experimental Studies on Engine Performance and Emission Characteristics Using Castor Biodiesel as Fuel in CI Engine. *Renew. Energy* **2019**, *131*, 737–744. [CrossRef]

4.　Hirner, F.S.; Hwang, J.; Bae, C.; Patel, C.; Gupta, T.; Agarwal, A.K. Performance and emission evaluation of a small-bore biodiesel compression-ignition engine. *Energy* **2019**, *183*, 971–982. [CrossRef]

5.　Scheffran, J. The Global Demand for Biofuels: Technologies, Markets and Policies. In *Biomass to Biofuels: Strategies for Global Industries*; Vertes, A.A., Qureshi, N., Yukawa, H., Blaschek, H.P., Eds.; Wiley: West Sussex, UK, 2010; pp. 141–165.

6.　Luque, R.; Lin, C.S.K.; Wilson, K.; Clark, J.H. *Handbook of Biofuels Production: Processes and Technologies*, 2nd ed.; Woodhead Publishing: Duxford, UK, 2016.

7.　Kamil, M.; Ramadan, K.M.; Awad, O.I.; Ibrahim, T.K.; Inayat, A.; Ma, X. Environmental Impacts of Biodiesel Production from Waste Spent Coffee Grounds and Its Implementation in a Compression Ignition Engine. *Sci. Total Environ.* **2019**, *675*, 13–30. [CrossRef]

8.　Lee, M.; Yang, M.; Choi, S.; Shin, J.; Park, C.; Cho, S.-K.; Kim, Y.M.; Lee, M.; Yang, M.; Choi, S.; et al. Sequential Production of Lignin, Fatty Acid Methyl Esters and Biogas from Spent Coffee Grounds via an Integrated Physicochemical and Biological Process. *Energies* **2019**, *12*, 2360. [CrossRef]

9.　Azeem, M.W.; Hanif, M.A.; Al-Sabahi, J.N.; Khan, A.A.; Naz, S.; Ijaz, A. Production of Biodiesel from Low Priced, Renewable and Abundant Date Seed Oil. *Renew. Energy* **2016**, *86*, 124–132. [CrossRef]

10.　Akasha, I.A.M. Extraction and Characterisation of Protein Fraction from Date Palm (*Phoenix dactylifera* L.) Seeds. Ph.D. Thesis, Heriot-Watt University, Edinburgh, Scotland, 2004.

11. Johnson, D.V.; Al-Khayri, J.M.; Jain, S.M. Introduction: Date Production Status and Prospects in Africa and the Americas. In *Date Palm Genetic Resources and Utilization*; Al-Khayri, J.M., Jain, S.M., Johnson, D.V., Eds.; Springer: Dordrecht, The Netherlands, 2015; pp. 3–18.

12. Al-Yahyai, R.; Manickavasagan, A. An Overview of Date Palm Production. In *Dates Production, Processing, Food, and Medicinal Values*; Manickavasagan, A., Mohamed Essa, M., Eds.; CRC Press: Boca Raton, FL, USA, 2012; pp. 3–12.

13. Mrabet, A.; Ferchichi, A.; Chaira, N.; Mohamed, B.S.; Baaziz, Z.; Penny, T.M. Physico-Chemical Characteristics and Total Quality of Date Palm Varieties Grown in the Southern of Tunisia. *Pak. J. Biol. Sci.* **2008**, *11*, 1003–1008. [CrossRef]

14. Al-shahib, W.; Marshall, R.J. The Fruit of the Date Palm: Its Possible Use as the Best Food for the Future? *Int. J. Food Sci. Nutr.* **2003**, *54*, 247–259. [CrossRef]

15. Food and Agriculture Organization of the United Nations Organization, FAO. FAO Statistical Year Book, World Food and Agriculture. Available online: http://www.fao:faostat/en/#data/QC (accessed on 22 August 2018).

16. Atia, A.; Abdelkarim, D.; Younis, M.; Alhamdan, A. Effects of Gibberellic Acid (GA3) and Salicylic Acid (SA) Postharvest Treatments on the Quality of Fresh Barhi Dates at Different Ripening Levels in the Khalal Maturity Stage during Controlled Atmosphere Storage. *Int. J. Agric. Biol. Eng.* **2018**, *11*, 211–219. [CrossRef]

17. Afiq, A.; Rahman, A.; Man, C. Date Seed and Date Seed Oil. *Int. Food Res. J.* **2013**, *20*, 2035–2043.

18. Al-Farsi, M.; Alasalvar, C.; Al-Abid, M.; Al-Shoaily, K.; Al-Amry, M.; Al-Rawahy, F. Compositional and Functional Characteristics of Dates, Syrups, and Their by-Products. *Food Chem.* **2007**, *104*, 943–947. [CrossRef]

19. Besbes, S.; Drira, L.; Blecker, C.; Deroanne, C.; Attia, H. Adding value to hard date (*Phoenix dactylifera* L.): Compositional, functional and sensory characteristics of date jam. *Food Chem.* **2009**, *112*, 406–411. [CrossRef]

20. The British Petroleum Company, BP. BP Statistical Review of World Energy, June 2017. Available online: https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review-2017/bp-statistical-review-of-world-energy-2017-full-report.pdf (accessed on 23 August 2018).

21. Besbes, S.; Blecker, C.; Deroanne, C.; Drira, N.-E.; Attia, H. Date Seeds: Chemical Composition and Characteristic Profiles of the Lipid Fraction. *Food Chem.* **2004**, *84*, 577–584. [CrossRef]

22. Vandepopuliere, J.M.; Al-Yousef, Y.; Lyons, J.J. Dates and date pits as ingredients in broiler starting and Coturnix quail breeder diets. *Poult. Sci.* **1995**, *74*, 1134–1142. [CrossRef] [PubMed]

23. Al-Farsi, M.A.; Lee, C.Y. Usage of Date (*Phoenix dactylifera* L.) Seeds in Human Health and Animal Feed. *Nuts Seeds Health Dis. Prev.* **2011**. [CrossRef]

24. Rahman, M.S.; Kasapis, S.; Al-Kharusi, N.S.Z.; Al-Marhubi, I.M.; Khan, A.J. composition characterisation and thermal transition of date pits powders. *J. Food Eng.* **2007**, *80*, 1–10. [CrossRef]

25. Ali-Mohamed, A.Y.; Khamis, A.S.H. Mineral Ion Content of the Seeds of Six Cultivars of Bahraini Date Palm (*Phoenix dactylifera*). *J. Agric. Food Chem.* **2004**, *52*, 6522–6525. [CrossRef]

26. Devshony, S.; Eteshola, E.; Shani, A. Characteristics and Some Potential App.lications of Date Palm (*Phoenix dactylifera* L.) Seeds and Seed Oil. *J. Am. Oil Chem. Soc.* **1992**, *69*, 595–597. [CrossRef]

27. Jamil, F.; Al-Muhtaseb, A.H.; Al-Haj, L.; Al-Hinai, M.A.; Hellier, P.; Rashid, U. Optimization of oil extraction from waste "Date Pits" for biodiesel production. *Energy Convers. Manag.* **2016**, *117*, 264–272. [CrossRef]

28. Al-Zuhair, S.; Taher, H.; Al Dhaheri, S.; Wajeeh, S.; Nour, M.; El-Najjar, E. Biodiesel production from oils extracted from date pits. *Green Sustain. Chem.* **2017**, *7*, 48. [CrossRef]

29. Nehdi, I.; Omri, S.; Khalil, M.I.; Al-Resayes, S.I. Characteristics and chemical composition of date palm (*Phoenix canariensis*) seeds and seed oil. *Ind. Crops Prod.* **2010**, *32*, 360–365. [CrossRef]

30. Ali, M.A.; Al-Hattab, T.A.; Al-hydary, I.A.D. Extraction of date palm seed oil (*Phoenix dactylifera*) by soxhlet app.aratus. *Int. J. Adv. Eng. Technol.* **2015**, *8*, 261.

31. Yousuf, R.G.; Winterburn, J.B. Waste date seed oil extract as an alternative feedstock for poly (3–Hydroxybutyrate) Synthesis. *Biochem. Eng. J.* **2017**, *127*, 68–76. [CrossRef]

32. Akaagerger, S.M.; Giwa, S.O.; Ibrahim, M.; GIWA, A. Production of biodiesel from desert date seed oil. *Int. J. ChemTech Res.* **2016**, *9*, 453–463.

33. Farooq, M.; Ramli, A.; Naeem, A.; Mahmood, T.; Ahmad, S.; Humayun, M.; Islam, M.G.U. Biodiesel production from date seed oil (*Phoenix dactylifera* L.) via egg shell derived heterogeneous catalyst. *Chem. Eng. Res. Des.* **2018**, *132*, 644–651. [CrossRef]

34.　Knothe, G. *The Biodiesel Handbook*, 1st ed.; Knothe, G., Krahl, J., Gerpen, J.V., Eds.; AOCS Press: Champaign, IL, USA, 2005.

35.　Canakci, M.; Van Gerpen, J. Biodiesel Production from Oils and Fats with High Free Fatty Acids. *Trans. ASAE* **2001**, *44*, 1429–1436. [CrossRef]

36.　Gerpen, J.V. Biodiesel Processing and Production. *Fuel Process. Technol.* **2005**, *86*, 1097–1107. [CrossRef]

37.　Nitayaphat, W.; Jintakosol, T.; Engkaseth, K. Removal of methylene blue from aqueous solution by coffee residues. *Chiang Mai J. Sci.* **2015**, *42*, 407–416.

38.　American Society for Testing and Materials, ASTM. *ASTM Standard D6751, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels*; ASTM International: West Conshohocken, PA, USA, 2009.

39.　Hansen, A.C.; Kyritsis, D.C.; Lee, C.f.F. Characteristics of Biofuels and Renewable Fuel Standards. In *Biomass to Biofuels: Strategies for Global Industries*; Vertes, A.A., Qureshi, N., Blaschek, H.P., Yukawa, H., Eds.; Wiley: West Sussex, UK, 2010; pp. 1–26.

40.　Van Gerpen, J. Biodiesel from Vegetable Oils. In *Biomass to Biofuels: Strategies for Global Industries*; Vertes, A.A., Qureshi, N., Blaschek, H.P., Yukawa, H., Eds.; Wiley: West Sussex, UK, 2010; pp. 141–163.

41.　Lomonaco, D.; Maia, F.J.N.; Clemente, C.S.; Mota, J.P.F.; Costa, A.E.; Mazzetto, S.E. Thermal Studies of New Biodiesel Antioxidants Synthesized from a Natural Occurring Phenolic Lipid. *Fuel* **2012**, *97*, 552–559. [CrossRef]

42.　Suda, K.J. *Vegetable Oil or Diesel Fuel-A Flexible Option*; SAE Paper 840004; SAE International: Warrendale, PA, USA, 1984.

43.　Barsic, N.J.; Humke, A.L. *Performance and Emissions Characteristics of a Naturally Aspirated Diesel Engine with Vegetable Oil Fuels*; SAE Paper 810262; SAE International: Warrendale, PA, USA, 1981.

44.　Espinosa, E.A.M.; Rodríguez, R.P.; Sierens, R.; Verhelst, S. Emulsification of Waste Cooking Oils and Fatty Acid Distillates as Diesel Engine Fuels: An Attractive Alternative. *Int. J. Sustain. Energy Plan. Manag.* **2016**, *9*, 3–16. [CrossRef]

45.　Hawkins, C.S.; Fuls, J. Comparative Combustion Studies on Various Plants Oil Esters and the Long Term Effects of an Ethyl Ester on a Compression Ignition Engine. In Proceedings of the International Conference on Plant and Vegetable Oils as Fuels, Fargo, ND, USA, 23–26 September 1982; pp. 312–328.

46.　Zhou, W.; Konar, S.K.; Boocock, D.G.B. Ethyl Esters from the Single-Phase Base-Catalyzed Ethanolysis of Vegetable Oils. *J. Am. Oil Chem. Soc.* **2003**, *80*, 367–371. [CrossRef]

47.　Anastopoulos, G.; Zannikou, Y.; Stournas, S.; Kalligeros, S.; Anastopoulos, G.; Zannikou, Y.; Stournas, S.; Kalligeros, S. Transesterification of Vegetable Oils with Ethanol and Characterization of the Key Fuel Properties of Ethyl Esters. *Energies* **2009**, *2*, 362–376. [CrossRef]

48.　Ma, F.; Hanna, M.A. Biodiesel Production: A Review. *Bioresour. Technol.* **1999**, *70*, 1–15. [CrossRef]

49.　Lee, J.-S.; Saka, S. Biodiesel Production by Heterogeneous Catalysts and Supercritical Technologies. *Bioresour. Technol.* **2010**, *101*, 7191–7200. [CrossRef] [PubMed]

50.　Balat, M.; Balat, H. A Critical Review of Bio-Diesel as a Vehicular Fuel. *Energy Convers. Manag.* **2008**, *49*, 2727–2741. [CrossRef]

51.　Musa, I.A. The Effects of Alcohol to Oil Molar Ratios and the Type of Alcohol on Biodiesel Production Using Transesterification Process. *Egypt. J. Pet.* **2016**, *25*, 21–31. [CrossRef]

52.　Fukuda, H.; Kondo, A.; Noda, H. Biodiesel Fuel Production by Transesterification of Oils. *J. Biosci. Bioeng.* **2001**, *92*, 405–416. [CrossRef]

53.　Saka, S.; Kusdiana, D. Biodiesel Fuel from Rapeseed Oil as Prepared in Supercritical Methanol. *Fuel* **2001**, *80*, 225–231. [CrossRef]

54.　Freedman, B.; Butterfield, R.O.; Pryde, E.H. Transesterification Kinetics of Soybean Oil 1. *J. Am. Oil Chem. Soc.* **1986**, *63*, 1375–1380. [CrossRef]

55.　Sanford, S.; White, J.; Shah, P. *Feedstock and Biodiesel Characteristics Report*; Renewable Energy Group: Ames, IA, USA, 2009.

56.　Lee, I.; Johnson, L.A.; Hammond, E.G. Use of Branched-Chain Esters to Reduce the Crystallization Temperature of Biodiesel. *J. Am. Oil Chem. Soc.* **1995**, *72*, 1155–1160. [CrossRef]

57.　Moser, B.R. Influence of Blending Canola, Palm, Soybean, and Sunflower Oil Methyl Esters on Fuel Properties of Biodiesel. *Energy Fuels* **2008**, *22*, 4301–4306. [CrossRef]

58.　Bhale, P.V.; Deshpande, N.V.; Thombre, S.B. Improving the Low Temperature Properties of Biodiesel Fuel. *Renew. Energy* **2009**, *34*, 794–800. [CrossRef]

59. Fu, J. Flash Points Measurements and Prediction of Biofuels and Biofuel Blends with Aromatic Fluids. *Fuel* **2019**, *241*, 892–900. [CrossRef]

60. Bazooyar, B.; Ghorbani, A.; Shariati, A. Physical Properties of Methyl Esters Made from Alkali-Based Transesterification and Conventional Diesel Fuel. *Energy Sources Part A Recover. Util. Environ. Eff.* **2015**, *37*, 468–476. [CrossRef]

61. Ayetor, G.K.; Sunnu, A.; Parbey, J. Effect of Biodiesel Production Parameters on Viscosity and Yield of Methyl Esters: Jatropha Curcas, Elaeis Guineensis and Cocos Nucifera. *Alex. Eng. J.* **2015**, *54*, 1285–1290. [CrossRef]

62. Karmakar, R.; Kundu, K.; Rajor, A. Fuel Properties and Emission Characteristics of Biodiesel Produced from Unused Algae Grown in India. *Pet. Sci.* **2018**, *15*, 385–395. [CrossRef]

63. Al-Otoom, A.; Allawzi, M.; Ajlouni, A.; Abu-Alrub, F.; Kandah, M. The Use of Oil Shale Ash in the Production of Biodiesel from Waste Vegetable Oil. *J. Renew. Sustain. Energy* **2012**, *4*, 063123. [CrossRef]

64. Barbieri Gonzaga, F.; Pereira Sobral, S. A New Method for Determining the Acid Number of Biodiesel Based on Coulometric Titration. *Talanta* **2012**, *97*, 199–203. [CrossRef]

65. Aydin, H.; Bayindir, H. Performance and Emission Analysis of Cottonseed Oil Methyl Ester in a Diesel Engine. *Renew. Energy* **2010**, *35*, 588–592. [CrossRef]

66. Luján, J.M.; Bermúdez, V.; Tormos, B.; Pla, B. Comparative analysis of a di diesel engine fuelled with biodiesel blends during the European MVEG-A Cycle: Performance and Emissions (II). *Biomass Bioenergy* **2009**, *33*, 948–956. [CrossRef]

67. Özener, O.; Yüksek, L.; Ergenç, A.T.; Özkan, M. Effects of soybean biodiesel on a di diesel engine performance, emission and combustion characteristics. *Fuel* **2014**, *115*, 875–883. [CrossRef]

68. Lin, C.-Y.; Li, R.-J. Engine performance and emission characteristics of marine fish-oil biodiesel produced from the discarded parts of marine fish. *Fuel Process. Technol.* **2009**, *90*, 883–888. [CrossRef]

69. Chauhan, B.S.; Kumar, N.; Cho, H.M.; Lim, H.C. A study on the performance and emission of a diesel engine fueled with karanja biodiesel and its blends. *Energy* **2013**, *56*, 1–7. [CrossRef]

70. Xue, J.; Grift, T.E.; Hansen, A.C. Effect of biodiesel on engine performances and emissions. *Renew. Sustain. Energy Rev.* **2011**, *15*, 1098–1116. [CrossRef]

71. Meng, X.; Chen, G.; Wang, Y. Biodiesel production from waste cooking oil via alkali catalyst and its engine test. *Fuel Process. Technol.* **2008**, *89*, 851–857. [CrossRef]