Determination of Quality Properties of Low-Grade Biodiesel and Its Heating Oil Blends

Kleopatra Poyadji [1], Marinos Stylianou [1], Agapios Agapiou [1,*], Christos Kallis [2] and Nikolaos Kokkinos [3]

[1] Department of Chemistry, University of Cyprus, P.O. Box 20537, Nicosia 1678, Cyprus; poyiadji.kleopatra@ucy.ac.cy (K.P.); stylianou.a.marinos@ucy.ac.cy (M.S.)
[2] Nortest Cyprus, 98 Arch. Makariou III, Latsia, Nicosia 2224, Cyprus; nortest@nortest.com.cy
[3] Department of Petroleum & Mechanical Engineering, Faculty of Engineering, Eastern Macedonia and Thrace Institute of Technology, St. Loucas, 65404 Kavala, Greece; nck@teiemt.gr
* Correspondence: agapiou.agapios@ucy.ac.cy; Tel.: +357-22-895432

Abstract: This research work examined how biodiesel produced from frying oils affects the physicochemical properties of its mixtures with conventional heating oil. Through the characterization of biodiesel blends and heating oil, the purpose is to produce an improved heating oil that will meet the specifications of the existing legislation for heating oil, while positively contributing to reducing the production of pollutants. The percentage of biodiesel added to a conventional diesel fuel contributes to the reduction of the pollutants produced during combustion. The examined biodiesel is considered the residual product, which was produced at a factory in Cyprus, and was deemed unsuitable for export, because it does not meet the legal requirements. Using specific volumes of these mixtures, twelve parameters were determined in order to investigate the effect of the mixtures: kinematic viscosity, sulfur content, micro carbon residue (MCR), distillation curves, density, cloud point (CP), fatty acid methyl esters (FAMEs) content, heat of combustion, iodine value (IV), cetane index (CI) after distillation, oxidation stability, and cold filter plugging point (CFPP). A number of fuel properties including the kinematic viscosity, MCR, distillation temperature—up to 80% distillate—and density showed an increase as the percentage of FAMEs raised from 2.5 to 50%, while others showed a mixed behavior (e.g., IV, CP, CI, CFPP), and the rest an inverse trend (e.g., sulfur content, heat of combustion and oxidation stability). An efficient potential utilization of a residual domestic product is proposed, while the pollutants that accumulate on the urban atmospheres during the winter months, due to increased heating needs of homes and other public or private buildings, will be significantly reduced.

Keywords: biodiesel blends; biofuel properties; frying oil; heating oil

1. Introduction

Use of fossil fuels produces several negative effects on public health, climate change, and the environment. In order to sustain the worldwide economic growth and reduce the negative impacts on the environment, green energy solutions are promoted worldwide. Biodiesel highlights as such a strong alternative solution to diesel, as its wide usage confirmed its potentiality to reduce the serious environmental concerns, as well as oil dependency. Current biodiesel research is mainly focused on the production of third-generation feedstocks (e.g., engineered crops), after years of experimentation and tests on the second (e.g., non-edible food crops and vegetable oil, waste oils and fats) and first (e.g., food crops and edible vegetable oils) generation feedstocks [1]. The negative publicity of the early stages based on "food versus fuel" dilemma belongs to history, as today biodiesel has gained

worldwide acceptance, as a clean, biodegradable and biocompatible green product, which is in harmony with the political and environmental awareness and in line with future strategies on renewable fossil fuels. However, the high cost of biodiesel production remains the main disadvantage to its wide spread use.

Lately, the use of waste cooking (frying) oils has gained much attention as an alternative green, abundant, and sustainable feedstock for the production of biodiesel, due to its lower production cost in relation to other feedstocks and the elimination of the negative harmful environmental effects of throwing household and industrial waste oils into drains. Towards this, a number of review studies exist in the literature; these are focused on the production techniques and the relevant processes [2–4], as well as on the available analytical methods (e.g., gas chromatography (GC), thin-layer chromatography (TLC), high-performance liquid chromatography (HPLC), gel permeation chromatography (GPC), and thermogravimetric analysis (TGA)) for measuring the biodiesel quality and the fuel properties [5]. Yaakob et al. [6] highlighted a number of important parameters for the production of biodiesel reviewing the applied methods, the different types of reactors, the types and amounts of alcohol, as well as the catalysts. A number of other researchers worked towards studying the optimum parameters for biodiesel production from frying oils. In such a study, Felizardo et al. [7] examined the conditions of time, catalysts, and methanol/oil molar ratio for optimum biodiesel production in a laboratory scale. Similarly, Uzun et al. [8] investigated the best reaction conditions (i.e., catalyst concentration, reaction time, methanol/oil molar ratio, reaction temperature, catalyst type (hydroxides, methoxides and ethoxides), and purification type (washing with hot water, purification with silica gel and dowex) on the biodiesel yields and measured the fuel properties using the respective ASTM International and EN (European Norms) biodiesel standards. In the same context, Predojevic [9] applied a two-step alkali transesterification process and tested three purification methods (silica gel, 5% phosphoric acid and hot distilled water) to examine the best yields for the produced biodiesel; the two first methods were finally recommended. Furthermore, optimization of biodiesel production from waste cooking oil was investigated using waste eggshell as a base catalyst [10], and by utilization of lipase as a biocatalyst [11].

A step ahead, is the employ of artificial neural networks (ANN) for predicting the engine performance and the gas emissions, after using blends of waste frying palm oil biodiesel [12].

Nowadays, another green energy trend is that of circular economy, especially on industrial and homemade levels which implies, among others, the minimization and re-usage of waste. Towards this, biodiesel is now produced from spent coffee grounds (SCG), a popular food waste previously ending up unprocessed in landfills [13,14].

Biodiesel is a methyl ester product (a mixture of FAMEs: fatty acid methyl esters) derived from the transesterification of vegetable oils with methanol. The transesterification includes the splitting of vegetable oil molecules (triglycerides) in three chains of fatty acids and one glycerol molecule, separately. These alkyl chains are called biodiesel. Many raw materials are used in the production of biodiesels (e.g., vegetable oils, animal fats, and algae oil); the most known in Europe are rapeseed oil (rape methyl ester, RME) [15] and in USA soybean oil (soybean oil methyl esters, SME), whereas many other oils that can be converted to biodiesel exist, such as sunflower, palm oil, canola oil biodiesel (COB), etc. [16,17]. Initially, diesel engine was designed to run on vegetable oil, but because of weakness in the operation, a modification of vegetable oils was performed by transesterification, so that vegetable oils become compatible with existing diesel engines [18–20]. The data about the biodiesel production cost vary depending on the feedstock used and the production process. Biodiesel can be used in engines, either pure (B100, when the manufacturer accepts such usage), or as a blend with diesel. However, biodiesel has lower energy content than diesel and, as a result, the performance and fuel consumption can be influenced. Moreover, it shows the highest NO_x emission levels, lowers the oxidation stability of diesel [21] and potentially favors bacteria growth. Furthermore, unsaturated fatty acids react with oxygen to form peroxides; this leads to degradation yielding by-products that can cause sludge and varnish in the fuel system [22]. Also, FAMEs can cause corrosion of the fuel injector, block the low-pressure fuel system, increase dilution and

polymerization of the oil sump, clogging the pump due to high fuel viscosity at low temperature, increase injection pressure, elastomeric gaskets failures and blockage of the fuel injection [20,23,24].

Nevertheless, biodiesel usage shows a growing trend worldwide [25]. Biodiesel is highly biodegradable [26], presents low toxicity, better lubricity and can replace diesel fuel; it is an established alternative fuel for diesel engines. The use of biodiesel as fuel results in the reduction of major exhaust pollutants (SO_x, CO, Particulate Matter-PM, Volatile Organic Compounds-VOCs). Therefore, the negative environmental and health effects of diesel use are reduced [23,24,27]. In the study of Ozsezen and Canakci [12], where different blends of biodiesel (waste frying palm oil) were tested, a reduction in CO, unburned hydrocarbons and smoke opacity was observed, whereas NO_x and CO_2 emissions showed the opposite behavior, especially in high engine speeds. NO_x emissions remain a major problem when using biodiesel. Therefore, Agarwal et al. [28], suggested the use of exhaust gas recirculation (EGR) with biodiesel in order to reduce NO_x emissions. This is achieved as flame temperature is lower along with oxygen concentration in the combustion chamber; thus, less NO_x are produced.

Similarities between diesel fuel and heating oil (middle distillates) enable the blending of heating oil with biodiesel. Such a product already exists on the market of Germany (heating oil blended with 10% biodiesel for domestic heating) [29]. Towards this, storage stability of home heating oil was improved using 10–20% soybean-derived fuel (Soygold), along with the combustion properties [30].

The aim of the present work was to examine the potential re-usage of a biodiesel product that could not fulfil the export specifications legislation and therefore remained out of the market. As biodiesel is typically blended with diesel at different concentration levels, its addition to heating oil at various volumes (2.5%, 5%, 7%, 10%, 20%, and 50% *v/v*) was examined. Towards this, three main parameters were initially measured (cetane index (CI) after distillation, oxidation stability, and cold filter plugging point (CFPP)) and discussed [31]. In the same way, nine key points parameters were additionally measured (kinematic viscosity, sulfur content, micro carbon residue (MCR), distillation curves, density, cloud point (CP), FAMEs content, heat of combustion, iodine value (IV)), next to the three latter values, in order to provide a more comprehensive knowledge for the produced mixture.

2. Materials and Methods

2.1. Blend Preparation

In the current work, four different heating oils (HO) and biodiesel (B100) were used. Table 1 reveals the properties of biodiesel. HO were blended with biodiesel at percentages 10%, 20%, and 50% in biodiesel at ambient temperature. In Sample 1, the heating oil was mixed with biodiesel in a ratio of 2.5%, 7%, 10%, 20%, and 50% *v/v* biodiesel. Since the results in the ratios 2.5% and 7% were quite close, the rest of the samples (Samples 2, 3 and 4), were mixed at higher ratios, as shown in Table 2.

Table 1. Properties of biodiesel (B100) as provided by the manufacturing factory.

Parameter	Result	Units	EN 14214 Value
Visual Characteristics			
Appearance	clear liquid		
Colour	yellow		
Physical-Chemical Characteristics			
Density at 15 °C	881	kg/m^3	860–900
Water content	325	mg/kg	500 max
Oxidation Stability (110 °C)	7.1	h	6.0 min
Acid value	0.27	mg KOH/g	0.50 max
Potassium	1.0	mg/kg	5.0 max as (K & Na)
Iodine value	81.2	g I$_2$/100 g	120 max
Total glycerol	0.11	% mass	0.25 max
Linolenic acid methyl ester	2.02	% mass	12 max
Total Contamination	3	mg/kg	24 max
Phosphorous	1.8	mg/kg	10 max

Table 2. Preparation of mixtures by volume ratio of biodiesel with heating oil.

Samples	Volume Ratio (%)				
S1	2.50%	7%	10%	20%	50%
Biodiesel (g)	2.2	6.17	8.82	17.64	44.1
HO1 (g)	81.98	78.19	75.67	67.26	42.04
S2			10%	20%	50%
Biodiesel (g)			8.82	17.64	44.09
HO2 (g)			75.77	67.35	42.09
S3			10%	20%	50%
Biodiesel (g)			8.82	17.64	44.09
HO3 (g)			76.68	68.16	42.6
S4			10%	20%	50%
Biodiesel (g)			8.82	17.64	44.09
HO4 (g)			74.56	66.27	41.42

HO1: heating oil with destination outside Europe, HO2: heating oil with destination within Europe, HO3: heating oil for Cyprus trade and HO4: rural Cyprus oil.

2.2. Materials

A residual product (biodiesel B100), which cannot be placed on the market due to its lack of adequate properties, was purchased from a local factory in Cyprus. Such properties are the high iodine value content (Table 1) and oxidation stability, which were out of EN 14214 limit values (see Sections 3.9 and 3.11). Also, four HO (HO1: heating oil with destination outside Europe, HO2: heating oil with destination within Europe, HO3: heating oil for Cyprus trade and HO4: rural Cyprus oil) were mixed with B100. The reagents used in the synthesis, purification, and glassware cleaning procedures were hexane (≥96.0%, Merck, Nicosia, Cyprus), acetone (≥99.5%, Merck), propane (≥99.5%, Merck), distilled water (Water Purification System, Elga Purelab Option Q7, High Wycombe, UK) and heptane (≥99.0%, Merck).

2.3. Methods

2.3.1. Kinematic Viscosity

The kinematic viscosity was determined according to ASTM D7042-04 standard. It was analyzed by injecting a sample into the digital automatic viscometer analyzer (SVM 3000 Stabinger Viscometer, Anton Paar, St Albans, UK) and analyzed at 40 °C.

2.3.2. Sulfur Content

Sulfur was measured by X-ray fluorescence (XRF) according to ASTM D4294-10 (Ed Xrf, Oxford Instruments, Abingdon, UK) and ASTM D5453-09 (ultraviolet (UV)-fluorescence, Pac Antek Multitek, Belfast, Ireland) for lower sulfur range (1.0–8000 mg/kg).

2.3.3. Micro Carbon Residue (MCR)

Micro Carbon Residue (MCR) from oil samples continued with ashing of the residue was carried out according to ASTM D4530-06 (ASTM D1160 can be alternatively used). The sample was heated to 500 °C under inert atmosphere (N_2), kept at 500 °C for 15 min, and cooled.

2.3.4. Distillation Curves

Distillation curves were obtained according to the ASTM D86-12 standard test method in a distillation device (Automated Distillation Analyzer, Pac Optidist Herzog, Belfast, Ireland) using 100 mL oil sample.

2.3.5. Density

Determination of oils density was performed according to ASTM D4052-96 at test temperatures between 15 and 35 °C (Density Meter Dma 4500 M with Heated Sample Changer, X-Sample 452, Anton Paar, St Albans, UK).

2.3.6. Cloud Point (CP)

Cloud point (CP) and pour point were measured according to test method ASTM D2500-11, using the cloud and pour point apparatus (Cloud & Pour Point Tester, Normalab, Athens, Greece). The sample was cooled in a glass tube under prescribed conditions and inspected at intervals of 1 °C, until a cloud or haze appeared. This temperature was recorded as CP.

2.3.7. FAMEs Content

The % of FAMEs was measured according to EN 14078 test method with a Fourier transform infrared spectroscopy (FTIR) fuel analyzer (Miniscan IRXpert Professional, Grabner Instruments, Athens, Greece).

2.3.8. Heat of Combustion

Heat of combustion was measured according to ASTM D240-14 6200 with an Isoperibol Calorimeter (Parr Instrument Company, Athens, Greece).

2.3.9. Iodine Value (IV)

Iodine Value was determined through potentiometric titration (848 Oil Titrino Plus, Metrohm, Nicosia, Cyprus) according to ISO 3961 and ISO 661 test methods (for animal and vegetable fats and oils).

2.3.10. Measurement of Cetane Index (CI)

ASTM standard D86-12 was used to measure cetane index of diesel fuel and its mixtures with biodiesel. The cetane index was obtained in an automated manner by calculation after distillation of the examined fuel from the distillation measurement instrument (Automated Distillation Analyzer). It was calculated using the density measurements and boiling point curves of distillation according to ASTM standard D86-12.

2.3.11. Measurement of Oxidation Stability

The methods described in standards EN 14112 for biodiesel and EN 15751 for diesel and biodiesel blends were used to measure the oxidation stability of biodiesel, heating oils and their mixtures. The results were obtained at the constant temperature of 110.9 °C and at an air flow of 10 L/h by the measuring instrument (893 Professional Biodiesel Rancimat, Metrohm).

2.3.12. Measurement of Cold Filter Plugging Point (CFPP)

The method described by ASTM standard D6371-05 was used to measure the cold filter plugging point (CFPP) of the heating oil and its mixtures with biodiesel fuels. The cold filter plugging point was obtained in an automated way by the CFPP measurement instrument (Normalab).

3. Results and Discussion

3.1. Kinematic Viscosity

The viscosity of a fluid is a measure of the difficulty with which a liquid flows. Practically it indicates the high concentration of heavy components. Along with density, it is an important parameter for fuel atomization and distribution [7,9]. The longer the hydrocarbon chains in a fraction,

as well as the more branched the carbon chain, the more viscous the fraction will be. The EN 14214 standard specifies that a kinematic viscosity of 3.5–5 mm²/s is set for biodiesel to be used in diesel engines [7]. Kinematic viscosity measurements of the four oil samples presented in Table 3 showed an increase as the percentage of FAMEs increases. Also, comparatively for all oil samples, it appears that Sample 1 has a slightly higher kinematic viscosity than Samples 2, 3 and 4, which are at the same level.

3.2. Sulfur Content

As sulfur is strongly chemically combined with the hydrocarbon compounds (e.g., mercaptans (R-SH), sulphides (R-S-R), disulphides (R-S-S-R) and thiophenes), breaking of the respective chemical bonds is necessary for its removal. During fuel burning, mixtures of SO_x (mainly SO_2 and <5% SO_3) are emitted in the atmosphere causing serious health (i.e., respiratory irritants) and environmental problems (i.e., acid rain); therefore, the amount of sulfur in the fuel is monitored and regulated. The measurements of oil sulfur content presented a reduction in sulfur content as the percentage of FAMEs increases. Furthermore, for all oil samples, it was observed that Sample 1 shows a higher sulfur percentage compared to Samples 2, 3 and 4 (Samples 2 and 3 are about the same), while Sample 4 has the lowest sulfur content of all oil samples. Only Sample 1 is over the limit specifications (max 0.1% *w/w*) (Figure 1).
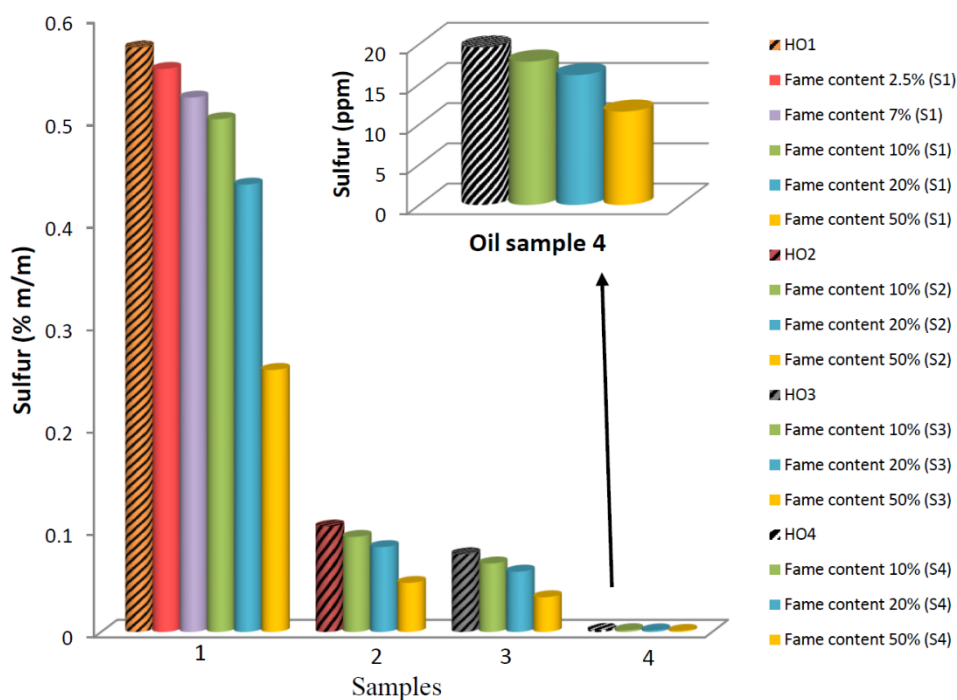

Figure 1. Sulfur content of oil samples. HO1: heating oil with destination outside Europe, HO2: heating oil with destination within Europe, HO3: heating oil for Cyprus trade and HO4: rural Cyprus oil.

Table 3. Kinematic viscosity and cetane index of oil samples.

Blends / Properties	Biodiesel (B100)	Heating Oil	FAMEs Content 2.5%	FAMEs Content 7%	FAMEs Content 10%	FAMEs Content 20%	FAMEs Content 50%
Kin. visc. (mm²/s)							
Sample 1	4.380	3.087	3.108	3.155	3.188	3.305	3.732
Sample 2	4.380	2.910	n.m. *	n.m.	3.052	3.135	3.545
Sample 3	4.380	2.897	n.m.	n.m.	3.019	3.165	3.563
Sample 4	4.380	2.890	n.m.	n.m.	2.995	3.108	3.513
Cetane index							
Sample 1	n.m.	52.6	52.5	52.8	52.7	53.0	52.6
Sample 2	n.m.	51.8	n.m.	n.m.	51.8	51.6	50.9
Sample 3	n.m.	47.6	n.m.	n.m.	48.2	48.5	49.1
Sample 4	n.m.	57.1	n.m.	n.m.	57.5	57.5	55.4

Europeans specifications for diesel (heating oil): min 46.0; max: --, Cyprus and Greek specifications: min 40.0; max: --. * n.m. = not measured.

3.3. Micro Carbon Residue (MCR)

Ash in liquid fuels causes fouling deposits in the combustion equipment; it creates an erosive effect on the burner tips and gives rise to high temperature corrosion and fouling. MCR measurements in the four oil samples (Figure 2), revealed an increase in MCR as the percentage of FAMEs increases. All samples were within specifications (max 0.3% *w/w* in line with EN ISO 10370).
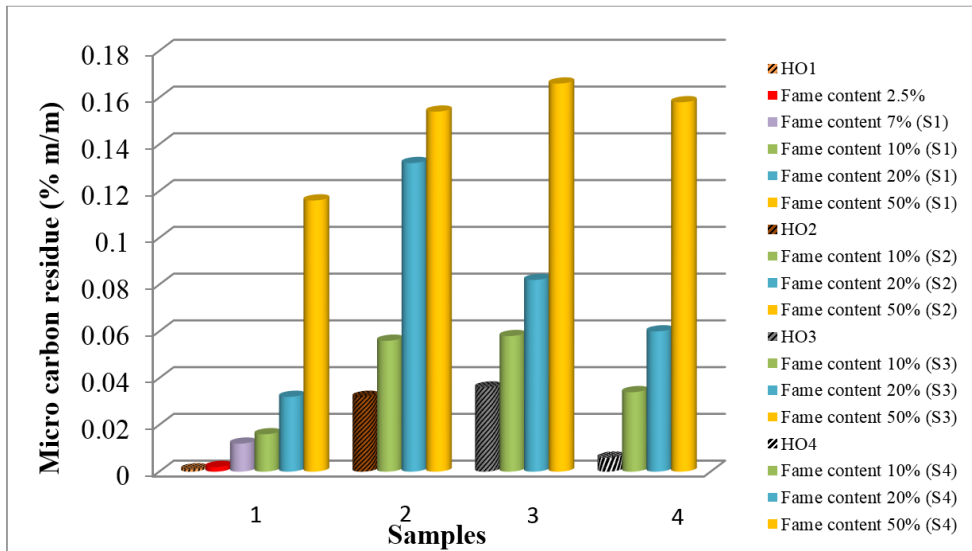

Figure 2. Micro carbon residue (MCR) of oil samples.

3.4. Distillation Curves

Distillation curves indicate the boiling range of the examined fuel. Distillation characteristics affect the density (fuel composition dependent), as well as the viscosity and CI. Therefore, distillation curve is an important factor for the control of fuel quality. During the distillation process, it is observed that as the percentage of FAMEs increases in oil samples (Figure 3), the distillation temperature is increased up to 80% distillate; after 85% distillate, the temperature tends to be equal. As reported by Smith et al. [32] the linearization of the curve implies that the mixture is becoming less complex in terms of the total number of components.
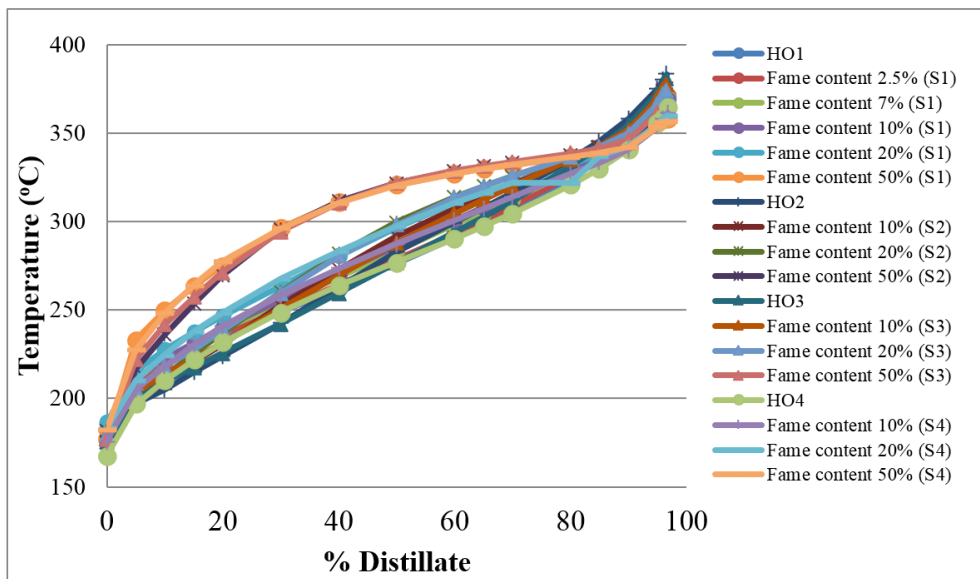

Figure 3. Distillation curves of oil samples.

3.5. Density

Density measurement is useful for determining fuel quantity and quality. It is an important property mostly for airless combustion systems, as it affects the efficiency of atomization of the fuel [7]. According to Predojević [9], biodiesel density is related to methyl esters content, and up to a point, to methanol quantity; thus, it is correlated to the vegetable oil type. When determining the density for each of the oil samples (Table 4), a gradual increase in density was observed following the percentage of FAMEs. It can be seen that all samples are within the limit values set by the standard for biodiesel (density between 860 and 900 kg/m^3). Also, compared to all oil samples, it appears that Samples 1 and 2 are in the same range, whereas Sample 3 presents the highest density value, and Sample 4 the smallest one. NguyenThi et al. [33] measured density over extended pressure and temperature ranges of waste cooking oil biodiesel and its blends (5% and 10% by volume) mixed with diesel. Their results showed higher density values at 20 °C and at high pressures (120–140 MPa), which was attributed to the high viscosity values of the biodiesel.

Table 4. Density of oil samples.

Density	Units: kg/m^3			
	Sample 1 (Biod. 1 *)	Sample 2 (Biod. 2)	Sample 3 (Biod. 2)	Sample 4 (Biod. 2)
Biodiesel	882.0	881.9	881.9	881.9
Diesel (Heating oil)	840.8	841.9	852.0	828.4
FAMEs content 2.5%	841.8	---	---	---
FAMEs content 7%	843.6	---	---	---
FAMEs content 10%	844.8	846.4	854.9	833.6
FAMEs content 20%	848.7	849.7	857.9	838.7
FAMEs content 50%	860.9	861.6	866.8	854.6

* Biodiesel 1 and 2 are the same product, but of different production date.

3.6. Cloud Point (CP)

CP measurement shows the temperature where crystals first appear; thus, the fuel filters and injectors of the engine clogged. When determining the CP (Figure 4), it is observed that for oil Samples 1 and 4, as the percentage of FAMEs increases, there is an increase in the cloud point. Also, for oil Sample 2, as the FAMEs rate is increased, there is a decrease in the cloud point, while for Sample 3, there is no particular change in temperature. Cold flow behaviour is usually affected by CP, pour point (PP), and CFPP. Cold flow properties are depended on fatty ester chain length, while oxidation stability on polyunsaturated fatty esters [34]. In a study by Chhetri et al. [35], it is reported that cloud point of ethyl ester produced from waste cooking oil was found to be −1 °C. Furthermore, cloud points of ethyl esters of linseed oil, canola, sunflower, and rapeseed oil were approximately 2 °C lower than those of the corresponding methyl esters, which indicates that the ethyl esters perform slightly better in cold temperatures than the corresponding methyl esters. Furthermore, Sadrolhosseini et al. [36] reported that CP depends on the concentration of saturated fatty acids such as $C_{16:0}$, $C_{18:0}$, and $C_{18:1}$ in the product and, through the production of biodiesel, if the new esters are derived from saturated fatty acids such as $C_{16:0}$ and $C_{18:0}$, the biodiesel will have high cloud point, because they act as a precursor for crystallization.
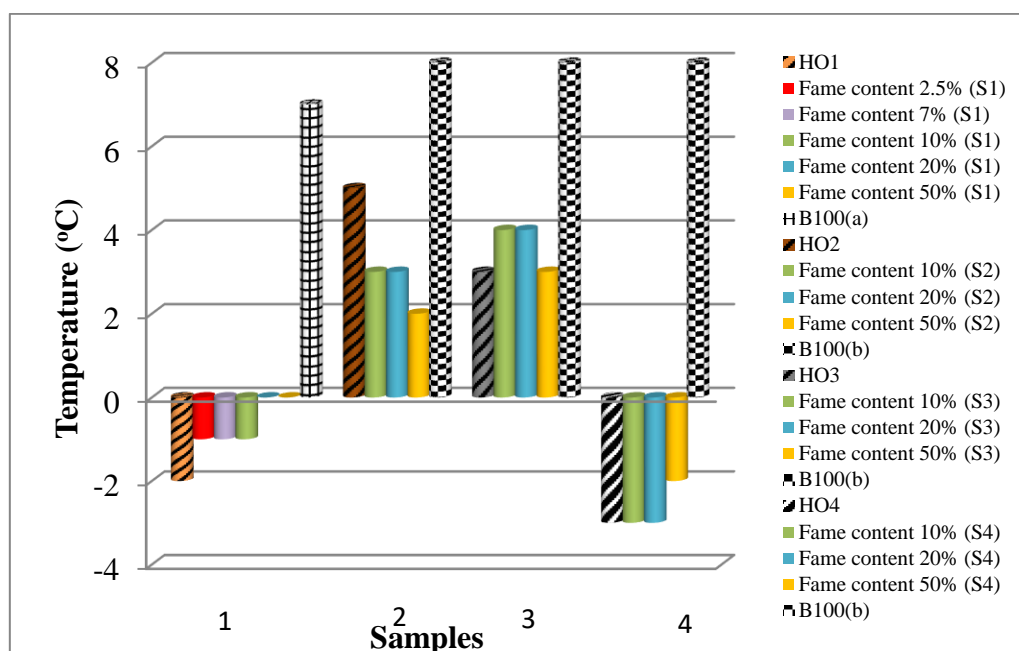
Figure 4. Cloud point (CP) of oil samples.

3.7. FAMEs Determination

The FAMEs content of the four examined samples was also confirmed by FTIR analysis in order to settle their characterization. Table 5 shows the percentage of FAMEs present in the examined samples. FAMEs addition reduces overall CO_2 emissions and results in performance benefits.

Table 5. Fatty acid methyl esters (FAMEs) content.

FAMEs Content	Unit: % *v/v*			
	Sample 1	Sample 2	Sample 3	Sample 4
Heating oil	0.11	0.17	0.23	0.33
FAMEs content 2.5%	2.7	---	---	---
FAMEs content 7%	7.2	---	---	---
FAMEs content 10%	11.1	11.9	11.1	10.7
FAMEs content 20%	19.8	>19.8	20.7	19.8
FAMEs content 50%	51.0	51.0	52.0	52.8

3.8. Heat of Combustion

The heat of combustion indicates the amount of energy released in the combustion of a certain fuel. The results from the heat of combustion tests in the oil samples revealed that FAMEs content is inversely proportional to the ratio of heat of combustion (Table 6). Moreover, in comparison to the fourth oil sample, no significant difference is observed, since each rate of FAMEs of each sample does not differ much from the other samples.

Table 6. Heat of combustion of oil samples.

Heat of Combustion	Units: MJ/kg			
	Sample 1	Sample 2	Sample 3	Sample 4
Biodiesel	---	40.683	40.683	40.683
Diesel	45.446	45.511	45.209	45.897
Fame content 10%	44.973	44.625	44.514	45.109
Fame content 20%	44.427	44.149	43.993	44.645
Fame content 50%	42.490	42.438	42.298	42.707

3.9. Iodine Value (IV)

The IV expresses the unsaturation degree of the fatty acid alkyl esters. In this context, this parameter is correlated with fuel oxidation and reveals the type of aging products and deposits that are gathered in the injectors of the diesel engines [9]. According to IV results, for oil Sample 1, there is a gradual increase in the IV as the percentage of FAMEs increases. For Samples 2 and 3, there is an increase of up to 20% and at 50% there is a decrease in the IV. Finally, for oil Sample 4, there is a fluctuation in the IV as the percentage of FAMEs increases. According to EN 14214 (2003), methyl esters used as diesel fuel must have an iodine value below 120 g I_2 per 100 g of sample [7]. As can be seen in Figure 5, all samples are above this limit because of the very high value of IV of the B100 used in the blend. The high iodine value is one of the main problems associated with vegetable oils being used as fuel in diesel engines [37].

In the literature, researchers are investigating new process conditions for the production of biodiesel from waste cooking oil in order to achieve better quality with lower IV. Hossain et al. [38] produced biodiesel from hydrolysed waste cooking oil using a S-ZrO_2/SBA-15 Super Acid Catalyst under subcritical conditions achieving an IV of 107.13 (g I_2/100 g).
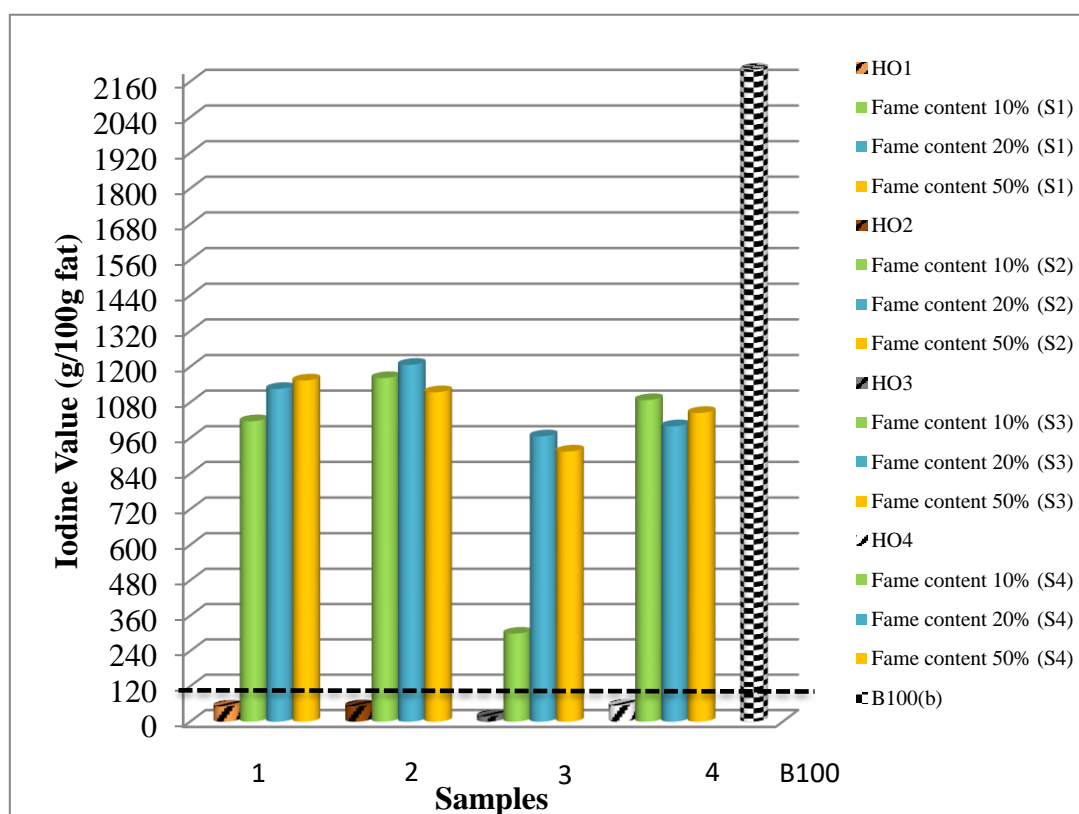

Figure 5. Iodine value (IV) of oil samples.

3.10. Cetane Number (Index)

The cetane number is a significant index of the quality of diesel fuel and related with the saponification number and the iodine value. The calculated cetane number (CCN) is a prediction method of cetane number (CN) with simpler tests, such as the density and distillation curve, providing useful results for the fuel ignition quality [39]. The CN affects the length of time from the start of fuel injection to the start of combustion in a diesel engine. The higher the CN, the shorter the period of ignition delay. The CN affects the ease of starting, combustion noise, and exhaust emissions of diesel engines [40,41].

Table 3 presents no noticeable behavior for heating oil Sample 1, as all measurements were approximately equal. For heating oil Sample 2, a reduction in cetane index was observed as percentage of FAMEs was increased. Cetane index in heating oil Sample 3 increased as percentage of

FAMEs was also increased. For Sample 4, there was a small increase in the cetane index. The cetane index of the fuels blends showed only marginal differences from the cetane index of the base fuel; it can be concluded that the addition of biodiesel to diesel fuels has an insignificant effect on the cetane index of the base fuels. Chhetri et al. [35] measured cetane index of waste cooking oil to be equal to 61 and also reports the cetane number of methyl esters of rapeseed oil, soybean oil, palm oil, lard, and beef tallow to be 58, 53, 65, 65, and 75 respectively. These increased values are linked to higher amounts of saturated fatty acids. Increased saturated fatty acids content positively enhanced the cetane number of biodiesel and its oxidative stability but cold filter plugging point will occur at a higher temperature.

3.11. Oxidation Stability

The oxidation stability is a measurement of fuel resistance to degradation by oxidation. The importance of oxidative stability of biodiesel was reviewed by Kumar et al. [42]. A series of properties seems to affect this parameter (e.g., fatty acid structure, external conditions, and storage materials), which impacts fuel properties, lubricity, performance, and emissions. The oxidation of diesel fuel can lead to the formation of gums and sediments, causing blockage of filters and engine deposits. It can also lead to darkening of the fuel color, although this is not a significant problem [23]. Determination of the oxidation stability is applied to biodiesel, for use as pure fuel or as a blending component for diesel fuel [43], based on oil containing minimum 2% by volume of the biodiesel.

As shown in Table 7, oxidation stability of heating oil samples decreased as the percentage of FAMEs was increased. Compared to all heating oil samples, it seems that Sample 2 is the most stable to oxidation, while Sample 4 is the least stable. The above observation can be interpreted on the basis of the specific composition of the individual samples and the fact that the heating oil of Sample 4 is a Cypriot rural oil with very low oxidation stability, while Sample 2 constitutes heating oil with high oxidation stability intended for inside Europe. Finally, it was noted that oxidation stability for Sample 1 was increased over time and is within the specification limits (>25 h).

Table 7. Experimental results for the oxidation stability of the tested samples.

Oxidation Stability	Units: h			
	Sample 1/after 4 Months *	Sample 2/after 4 Months *	Sample 3/after 4 Months *	Sample 4/after 4 Months *
Biodiesel [1]	0.07/n.m. [2]	0.03/14.45	0.03/14.45	0.03/14.45
Heating oil	125.67/140.90	141.90/210.34	110.87/190.54	50.97/60.75
FAMEs content 2.5%	>90/n.m.	n.m./n.m.	n.m./n.m.	n.m./n.m.
FAMEs content 7%	>90/n.m.	n.m./n.m.	n.m./n.m.	n.m./n.m.
FAMEs content 10%	110.43/134.55	112.81/226.79	75.02/181.02	17.33/25.78
FAMEs content 20%	88.30/111.64	112.41/135.65	46.99/64.85	11.16/16.70
FAMEs content 50%	39.81/37.47	11.14/10.31	0.03/0.03	0.03/0.03

* Sample 1 t = 0/Sample 1 t = 4 months. [1] European specifications for biodiesel: min 6.0 h; heating oil: min 20 h. [2] n.m. = not measured.

3.12. Cold Filter Plugging Point (CFPP)

CFPP is the lowest temperature at which fuel can pass through a standard test filter under standard conditions. The value of cold filter plugging point (°C) records the first temperature at which the sample fails to reach the 20 mL mark in less than 60 s or fails to flow back into the test vessel. Improving additives reduce the cold filter plugging point by changing the size and shape of the wax crystals formed at cold temperatures. The method is applicable to distillate fuels, including those that contain improved flow or other additive, intended for use in diesel and domestic heating installations [44]. The specifications are set in the EN 14214 or corresponding ASTM standards, and depending on the biodiesel class (and CFPP) it can be used under different climate conditions. The CFPP of the samples prepared in this study are shown in Table 8.

Table 8. Experimental results for cold filter plugging point of heating oil samples.

CFPP [1,2]	Units: °C			
	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**
Heating oil	−4	−10	0	−5
FAMEs content 10%	−3	−12	−1	−4
FAMEs content 20%	−3	−12	0	−7
FAMEs content 50%	−10	−10	−6	−11

[1] Category A (summer season): European/Cyprus/Greek specifications: max: +5 °C, from 1/4 to 30/9 each year. [2] Category B (winter season): European/Cyprus/Greek specifications: max: −5 °C, from 1/10 to 31/3 each year.

According to Table 8, test Sample 2 seems to belong to winter biodiesels based on the specification limits (5 °C max for summer, winter −5 °C), whereas Samples 1, 3 and 4 appear to be summer biodiesels. Blends with FAME content 50% showed an improvement of CFPP (winter); this is caused by the low CFPP of the B100 sample. Chhetri et al. [35] reported a relationship between saturated fatty acid chain content and the cold flow properties of biodiesel showing that as the content of the saturated fatty acids increases, the CFPP of biodiesel occurs at higher temperature.

4. Conclusions

The present paper assesses the possibility of using a biodiesel residual product that was characterized as unsuitable for export purposes (basic properties out of the specifications), as a feedstock to heating oil in order to improve its specifications. Twelve key parameters of the produced mixture were measured following EN and ASTM standards. Blends of biodiesel and heating oils were prepared at different ratios (2.5%, 7%, 10%, 20%, and 50% FAMEs). FAMEs addition from 2.5 to 50% resulted in raised values for a number of fuel properties (e.g., kinematic viscosity, MCR, distillation temperature up to 80% distillate, and density), and decreased values for sulfur content, heat of combustion and oxidation stability. Fuel parameters of IV, CP, CN, CFPP showed a mixed trend. Subsequently, some properties were improved such as oxidation stability, CFPP, cetane index (for Sample 2), sulfur content, while some others were not; albeit, were within specifications (e.g., viscosity and MCR). Nevertheless, further studies on fuel blending are necessary to estimate the potential limitations and advantages of the product mixture, before the wide use of biodiesel and heating oil as a fuel source to replace fossil diesel. Finally, further research and statistical analysis on the domestic residual biodiesel production ought to be performed, prior to a potential new industrial plant taking advantage of the current byproduct and using it as feedstock.

References

1. Riayatsyah, T.M.I.; Ong, H.C.; Chong, W.T.; Aditya, L.; Hermansyah, H.; Mahlia, T.M.I. Life cycle cost and sensitivity analysis of reutealis trisperma as non-edible feedstock for future biodiesel production. *Energies* **2017**, *10*, 877, doi:10.3390/en10070877.
2. Veljković, V.B.; Biberdžić, M.O.; Banković-Ilić, I.B.; Djalović, I.G.; Tasić, M.B.; Nježić, Z.B.; Stamenković, O.S. Biodiesel production from corn oil: A review. *Renew. Sustain. Energy Rev.* **2018**, *91*, 531–548, doi:10.1016/j.rser.2018.04.024.
3. Doğan, T.H. The testing of the effects of cooking conditions on the quality of biodiesel produced from waste cooking oils. *Renew. Energy* **2016**, *94*, 466–473, doi:10.1016/j.renene.2016.03.088.

4. Da Silva César, A.; Werderits, D.E.; de Oliveira Saraiva, G.L.; da Silva Guabiroba, R.C. The potential of waste cooking oil as supply for the Brazilian biodiesel chain. *Renew. Sustain. Energy Rev.* **2017**, *72*, 246–253, doi:10.1016/j.rser.2016.11.240.

5. Enweremadu, C.C.; Mbarawa, M.M. Technical aspects of production and analysis of biodiesel from used cooking oil—A review. *Renew. Sustain. Energy Rev.* **2009**, *13*, 2205–2224, doi:10.1016/j.rser.2009.06.007.

6. Yaakob, Z.; Mohammad, M.; Alherbawi, M.; Alam, Z.; Sopian, K. Overview of the production of biodiesel from Waste cooking oil. *Renew. Sustain. Energy Rev.* **2013**, *18*, 184–193, doi:10.1016/j.rser.2012.10.016.

7. Felizardo, P.; Neiva Correia, M.J.; Raposo, I.; Mendes, J.F.; Berkemeier, R.; Bordado, J.M. Production of biodiesel from waste frying oils. *Waste Manag.* **2006**, *26*, 487–494, doi:10.1016/j.wasman.2005.02.025.

8. Uzun, B.B.; Kiliç, M.; Özbay, N.; Pütün, A.E.; Pütün, E. Biodiesel production from waste frying oils: Optimization of reaction parameters and determination of fuel properties. *Energy* **2012**, *44*, 347–351, doi:10.1016/j.energy.2012.06.024.

9. Predojević, Z.J. The production of biodiesel from waste frying oils: A comparison of different purification steps. *Fuel* **2008**, *87*, 3522–3528, doi:10.1016/j.fuel.2008.07.003.

10. Peng, Y.-P.; Amesho, K.; Chen, C.-E.; Jhang, S.-R.; Chou, F.-C.; Lin, Y.-C. Optimization of Biodiesel Production from Waste Cooking Oil Using Waste Eggshell as a Base Catalyst under a Microwave Heating System. *Catalysts* **2018**, *8*, 81, doi:10.3390/catal8020081.

11. Yu, C.Y.; Huang, L.Y.; Kuan, I.C.; Lee, S.L. Optimized production of biodiesel from waste cooking oil by lipase immobilized on magnetic nanoparticles. *Int. J. Mol. Sci.* **2013**, *14*, 24074–24086, doi:10.3390/ijms141224074.

12. Canakci, M.; Ozsezen, A.N.; Arcaklioglu, E.; Erdil, A. Prediction of performance and exhaust emissions of a diesel engine fueled with biodiesel produced from waste frying palm oil. *Expert Syst. Appl.* **2009**, *36*, 9268–9280, doi:10.1016/j.eswa.2008.12.005.

13. Stylianou, M.; Agapiou, A.; Omirou, M.; Vyrides, I.; Ioannides, I.M.; Maratheftis, G.; Fasoula, D. Converting environmental risks to benefits by using spent coffee grounds (SCG) as a valuable resource. *Environ. Sci. Pollut. Res.* **2018**, 1–15, doi:10.1007/s11356-018-2359-6.

14. Caetano, N.S.; Silva, V.F.M.; Melo, A.C.; Mata, T.M. Potential of spent coffee grounds for biodiesel production and other applications. *Chem. Eng. Trans.* **2013**, *35*, 1063–1068, doi:10.3303/CET1335177.

15. Van Duren, I.; Voinov, A.; Arodudu, O.; Firrisa, M.T. Where to produce rapeseed biodiesel and why? Mapping European rapeseed energy efficiency. *Renew. Energy* **2015**, *74*, 49–59, doi:10.1016/j.renene.2014.07.016.

16. Ge, J.; Yoon, S.; Choi, N. Using Canola Oil Biodiesel as an Alternative Fuel in Diesel Engines: A Review. *Appl. Sci.* **2017**, *7*, 881, doi:10.3390/app7090881.

17. Vertès, A.A.; Qureshi, N.; Blaschek, H.P.; Yukawa, H. *Biomass to Biofuels: Strategies for Global Industries*; John Wiley & Sons: Hoboken, NJ, USA, 2010.

18. Ghannam, M.T.; Selim, M.Y.E.; Aldajah, S.; Saleh, H.E.; Hussien, A.M.M. Effect of blending on physiochemical properties of jojoba–diesel fuels. *Biofuels* **2016**, *7*, 173–180, doi:10.1080/17597269.2015.1123982.

19. Cheung, C.S.; Man, X.J.; Fong, K.W.; Tsang, O.K. Effect of Waste Cooking Oil Biodiesel on the Emissions of a Diesel Engine. *Phys. Procedia* **2015**, *66*, 93–96, doi:10.1016/j.egypro.2015.02.050.

20. Vieira da Silva, M.A.; Lagnier Gil Ferreira, B.; da Costa Marques, L.G.; Lamare Soares Murta, A.; Vasconcelos de Freitas, M.A. Comparative study of NOx emissions of biodiesel-diesel blends from soybean, palm and waste frying oils using methyl and ethyl transesterification routes. *Fuel* **2017**, *194*, 144–156, doi:10.1016/j.fuel.2016.12.084.

21. Kokkinos, N.; Lazaridou, A.; Stamatis, N.; Orfanidis, S.; Mitropoulos, A.C.; Christoforidis, A.; Nikolaou, N. Biodiesel Production from Selected Microalgae Strains and Determination of its Properties and Combustion Specific Characteristics. *J. Eng. Sci. Technol. Rev.* **2015**, *8*, 1–6.

22. Pullen, J.; Saeed, K. An overview of biodiesel oxidation stability. *Renew. Sustain. Energy Rev.* **2012**, *16*, 5924–5950, doi:10.1016/j.rser.2012.06.024.

23. Xue, J.; Grift, T.E.; Hansen, A.C. Effect of biodiesel on engine performances and emissions. *Renew. Sustain. Energy Rev.* **2011**, *15*, 1098–1116, doi:10.1016/j.rser.2010.11.016.

24. Karavalakis, G.; Tzirakis, E.; Stournas, S.; Zannikos, F.; Karonis, D.; Tzirakis, E.; Stournas, S.; Zannikos, F.; Karonis, D. Biodiesel Emissions from a Diesel Vehicle Operated on a Non-legislative Driving Cycle. *Energy Sources Part A* **2010**, *32*, 376–383, doi:10.1080/15567030802611871.

25. Papadopoulos, C.E.; Lazaridou, A.; Koutsoumba, A.; Kokkinos, N.; Christoforidis, A.; Nikolaou, N. Optimization of cotton seed biodiesel quality (critical properties) through modification of its FAME composition by highly selective homogeneous hydrogenation. *Bioresour. Technol.* **2010**, *101*, 1812–1819, doi:10.1016/j.biortech.2009.10.016.

26. Kokkinos, N.; Lazaridou, A.; Tzovenis, I.; Stamatis, N.; Orfanidis, S.; Mitropoulos, A.; Nikolaou, N.; Christoforidis, A. Properties and characterization of biodiesel from selected microalgae strains. In Proceedings of the International Conference and Exhibition on Energy, Science & Technology (EST), Karlsruhe, Germany, 20–22 May 2015.

27. Chiatti, G.; Chiavola, O.; Palmieri, F. Impact of waste cooking oil in biodiesel blends on particle size distributions from a city-car engine. *J. Energy Inst. J.* **2018**, *91*, 262–269, doi:10.1016/j.joei.2016.11.009.

28. Agarwal, D.; Sinha, S.; Agarwal, A.K. Experimental investigation of control of NOxemissions in biodiesel-fueled compression ignition engine. *Renew. Energy* **2006**, *31*, 2356–2369, doi:10.1016/j.renene.2005.12.003.

29. Eskiner, M.; Bär, F.; Rossner, M.; Munack, A.; Krahl, J. Determining the aging degree of domestic heating oil blended with biodiesel by means of dielectric spectroscopy. *Fuel* **2015**, *143*, 327–333, doi:10.1016/j.fuel.2014.10.080.

30. Mushrush, G.; Beal, E.J.; Spencer, G.; Wynne, J.H.; Lloyd, C.L.; Hughes, J.M.; Walls, C.L.; Hardy, D.R. An environmentally benign soybean derived fuel as a blending stock or replacement for home heating oil. *J. Environ. Sci. Health Part A* **2001**, *36*, 613–622, doi:10.1081/ESE-100103749.

31. Poyiadji, K.; Stylıanou, M.; Kokkinos, C.N.; Agapiou, A. Determination of biodiesel properties from residual feedstock. In Proceedings of the 15th International Conference on Environmental Science and Technology (CEST 2017), Rhodes, Greece, 31 August–2 September 2017; pp. 3–6.

32. Smith, B.L.; Ott, L.S.; Bruno, T.J. Composition-explicit distillation curves of commercial biodiesel fuels: Comparison of petroleum-derived fuel with B20 and B100. *Ind. Eng. Chem. Res.* **2008**, *47*, 5832–5840, doi:10.1021/ie800367b.

33. NguyenThi, T.; Bazile, J.-P.; Bessières, D. Density Measurements of Waste Cooking Oil Biodiesel and Diesel Blends Over Extended Pressure and Temperature Ranges. *Energies* **2018**, *11*, 1212, doi:10.3390/en11051212.

34. Monirul, I.M.; Masjuki, H.H.; Kalam, M.A.; Zulkifli, N.W.M.; Rashedul, H.K.; Rashed, M.M.; Imdadul, H.K.; Mosarof, M.H. A comprehensive review on biodiesel cold flow properties and oxidation stability along with their improvement processes. *RSC Adv.* **2015**, *5*, 86631–86655, doi:10.1039/C5RA09555G.

35. Chhetri, A.B.; Watts, K.C.; Islam, M.R. Waste Cooking Oil as an Alternate Feedstock for Biodiesel Production. *Energies* **2008**, *1*, 3–18, doi:10.3390/en1010003.

36. Sadrolhosseini, A.R.; Moksin, M.M.; Nang, H.L.L.; Norozi, M.; Yunus, M.M.W.; Zakaria, A. Physical properties of normal grade biodiesel and winter grade biodiesel. *Int. J. Mol. Sci.* **2011**, *12*, 2100–2111, doi:10.3390/ijms12042100.

37. Yoon, S.K.; Kim, M.S.; Kim, H.J.; Choi, N.J. Effects of canola oil biodiesel fuel blends on combustion, performance, and emissions reduction in a common rail diesel engine. *Energies* **2014**, *7*, 8132–8149, doi:10.3390/en7128132.

38. Hossain, M.N.; Bhuyan, M.S.U.S.; Alam, A.H.M.A.; Seo, Y.C. Biodiesel from Hydrolyzed Waste Cooking Oil Using a S-ZrO$_2$/SBA-15 Super Acid Catalyst under Sub-Critical Conditions. *Energies* **2018**, *11*, 299, doi:10.3390/en11020299.

39. Aburudyna, A.; Karonis, D.; Zannikos, F.; Lois, E. Impact of Biodiesel Addition on Distillation Characteristics and Cetane Index of Diesel Fuels. *J. Energy Eng.* **2015**, *141*, 1–9, doi:10.1061/(ASCE)EY.1943-7897.0000244.

40. Bezaire, N.; Wadumesthrige, K.; Simon Ng, K.Y.; Salley, S.O. Limitations of the use of cetane index for alternative compression ignition engine fuels. *Fuel* **2010**, *89*, 3807–3813, doi:10.1016/j.fuel.2010.07.013.

41. Candeia, R.A.; Silva, M.C.D.; Filho, J.R.C.; Brasilino, M.G.A.; Bicudo, T.C.; Santos, I.M.G.; Souza, A.G. Influence of soybean biodiesel content on basic properties of biodiesel–diesel blends. *Fuel* **2009**, *88*, 738–743, doi:10.1016/j.fuel.2008.10.015.

42. Kumar, N. Oxidative stability of biodiesel: Causes, effects and prevention. *Fuel* **2017**, *190*, 328–350, doi:10.1016/j.fuel.2016.11.001.

43. Park, J.-Y.; Kim, D.-K.; Lee, J.-P.; Park, S.-C.; Kim, Y.-J.; Lee, J.-S. Blending effects of biodiesels on oxidation stability and low temperature flow properties. *Bioresour. Technol.* **2008**, *99*, 1196–1203.

44. Yuan, M.H.; Chen, Y.H.; Chen, J.H.; Luo, Y.M. Dependence of cold filter plugging point on saturated fatty acid profile of biodiesel blends derived from different feedstocks. *Fuel* **2017**, *195*, 59–68, doi:10.1016/j.fuel.2017.01.054.