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# Perspective of safflower (*Carthamus tinctorius*) as a potential biodiesel feedstock in Turkey: characterization, engine performance and emissions analyses of butanol–biodiesel–diesel blends

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**ABSTRACT**

Safflower (*Carthamus tinctorius*) is widely farmed in Turkey. This study investigates the physicochemical properties of safflower biodiesel and its blends with Euro diesel and butanol. A polynomial curve-fitting method was used to predict kinematic viscosity and density of the ternary blends. Furthermore, characteristics such as DSC, FT-IR, UV-Vis and TGA were adopted to evaluate the influence of butanol addition on biodiesel–diesel blends. Engine performance parameters such as BP, torque and BSFC and emissions such as CO, HC, $NO_x$ and EGT were studied. Safflower methyl ester satisfied both EN 14214 and ASTM D 6751 standards regarding viscosity, flash point and density. However, iodine value was quite high. Oxidation stability fails to satisfy either standard. This is due to the high level of unsaturated fatty acids (91.05%). A reduction in BP, torque, HC and CO coupled with an increase in BSFC, $NO_x$ emissions and EGT was observed for all blends compared to Euro diesel. Overall, all blends appear to be good alternatives to biodiesel–diesel blends. This work supports that biodiesel can be blended with diesel and butanol as ternary blends (up to 20%) for use as a fuel in compression ignition (CI) engines. Therefore, combustion characteristics of blends shall be further investigated.

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Safflower methyl ester; DSC; FT-IR; TGA; engine and emissions performance

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## Nomenclature

| | |
|---|---|
| $A_i$ | Percentage of fatty acid |
| B | Biodiesel |
| BP | Brake power |
| BSFC | Brake specific fuel consumption |
| But | Butanol |
| CN | Cetane number |
| CSO | Crude safflower oil |
| CO | Carbon monoxide |
| D | Euro diesel |
| DSC | Differential scanning calorimetry |
| DU | Degree of unsaturation |
| EGT | Exhaust gas temperature |
| FAC | Fatty acid composition |
| FT-IR | Fourier transform infrared spectroscopy |
| HHV | Higher heating value |
| IV | Iodine value |
| LCSF | Long-chain saturated factor |
| Mi | Molecular weight of fatty acid |
| N | Number of double bonds of fatty acid |
| $NO_x$ | Nitrogen oxides |
| $\rho$ | Density |
| OS | Oxidation stability |
| SME | Safflower methyl ester |
| SN | Saponification number |
| TGA | Thermogravimetric analysis |
| UV-Vis | Ultraviolet–visible spectroscopy |

## Introduction

Exhaust emissions from internal combustion engines (IC) engines cause the release of harmful substances to the atmosphere such as hydrocarbons (HC), carbon dioxide ($CO_2$), nitrogen oxide ($NO_x$), carbon monoxide (CO), smoke, sulfur dioxide ($SO_2$), soot and particulate matter (PM). Due to increasing population growth and expected depletion of fossil fuels, scientists and researchers have begun moving toward the production and development of alternative fuels [1–3]. Biofuels (both gaseous and liquid fuels) can be used in the transport sector and they are mainly produced from biomass [4].

Oxygenated fuels play an important role in reducing CI diesel emissions, especially soot and PM emissions [5]. Biodiesel has 11% oxygen by weight, which leads to achieving complete combustion and reducing unburned emissions [6]. Biodiesel (methyl ester) is

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composed of long-chain fatty acids derived from edible and non-edible vegetable oils and animal fats [1]. Biodiesel has been widely accepted as a substitute for fossil diesel because it is renewable, non-explosive, non-flammable, non-toxic, biodegradable and ecologically friendly; it produces lower emissions, and has lower sulfur and aromatic contents; it has higher lubricity, higher flash point and excellent combustion efficiency; and it is a clean alternative that does not contribute to global warming [7 ]. Many countries have already subsidized biodiesel [8].

Universally, more than 350 oil crops have been classified as potential feedstocks for biodiesel generation. The high viscosity and low volatility of vegetable oils represent the main problem behind using them in CI engines. High viscosity induces some problems in the pumping and atomization system (fuel injector). Vegetable oils have a viscosity between 10 and 20 times greater compared with conventional diesel fuel. A transesterification process is the most common as well as commercial process for the production of the environmentally friendly fuel called biodiesel [7,9–11]. Through the conversion of vegetable matter into biodiesel, some properties of the product such as kinematic viscosity would be very close to those of conventional diesel fuel [2].

Biodiesel can be used alone or blended at different proportions with fossil diesel for use as alternative fuel in diesel engines. B20 has been already utilized with no/few modifications in CI engines [7]. The blending potential of biodiesel with fossil diesel has been much discussed in previous publications [12–14]. Moreover, the feasibility of blending ethanol with both diesel and biodiesel in CI engine has been also much investigated [15–18]. For instance, Aydogan [19] investigated the performance, emission and combustion characteristics of bioethanol (E)–safflower biodiesel (B)–diesel fuel (D) blends in a diesel engine. Three blends, E20B20D60, E30B20D50 and E50B20D30, were prepared for use, in addition to diesel fuel. The tests were performed at full load conditions and variable engine speeds. A decrease in brake power, torque, HC, CO and smoke density was reported with the use of bioethanol–biodiesel–diesel blends. However, $NO_x$ and brake specific fuel consumption (BSFC) increased.

Blending of biodiesel–diesel with other alternative fuels such as butanol remains a wide-open area of research. Butanol is becoming a popular fuel due to its renewable nature [5]. Butanol has a higher calorific value than ethanol, higher cetane number, and lower heat of vaporization [18]. Butanol is also more miscible in hydrocarbon than ethanol is. Butanol has a similar density and kinematic viscosity to diesel. The oxygen content in butanol is 21.6%. Therefore, the use of butanol in diesel engines improves combustion, and reduces particulate, CO and $NO_x$ emissions [20,21].

Work on safflower (*Carthamus tinctorius*) biodiesel production, properties and its blends with diesel has been extensively reported [3,22–25]. However, this paper aims to further study the prospective of ternary blends of biodiesel–diesel–butanol blends. For this purpose, measurement of properties such as DSC, FT-IR, UV-Vis and TGA was conducted for all blends.

Measurements of physical and chemical properties of the blends were made followed by predicting the kinematic viscosities and densities of the blends using a polynomial curve fitting method. Finally, engine and emissions performance parameters such as BP, torque, BSFC, CO, HC, $NO_x$ and EGT were studied to evaluate the overall performance of the blends. It is believed that such study opens new concepts in the biodiesel research area in terms of blending biodiesel–diesel blends with butanol.

## Overview of safflower (*Carthamus tinctorius*)

Safflower (*Carthamus tinctorius* L.) is a drought-resistant tree and falls within the family Compositae [26,27]. It is widely farmed in India, the USA, China, Spain, Ethiopia, Turkey and Mexico. The seed has an average oil content of 26–43% according to Flemmer et al. [28], which is similar to the values found by Akınerdem and Öztürk [29], who reported 30–45% oil content. Its oil is rich in linoleic acid with 70–87% [30]. Some herbalists suggest that the origin of safflower is the basin of the Euphrates River in Anatolia. However, it is generally believed that safflower had its origin in Eurasia, including Turkey and the neighboring countries [29]. It is called aspir or yalancı safran in Turkey [22].

## Materials and methods

### *Materials and equipment*

Crude safflower oil was purchased from a local farmer in Bünyan, Turkey. All chemicals used in this experimental work, such as butanol ($C_4H_9OH$), methanol ($CH_3OH$), sodium hydroxide (NaOH), sodium sulfate ($Na_2SO_4$), potassium hydroxide (KOH), phenolphthalein ($C_{20}H_{14}O_4$), as well as filter paper were purchased from a local supplier in Kayseri, Turkey. Euro diesel was purchased from a local fuel station in Kayseri, Turkey.

**Table 1.** Equipment list.

| Property measured | Model | Manufacturer | Origin |
|---|---|---|---|
| Kinematic viscosity | TV2000-AKV | PM Tamson Instrument | Bleiswijk, Netherlands |
| Flash point | NPM 450 | Normalab | Valliquerville, France |
| Cloud point | NTE 450 | Normalab | Valliquerville, France |
| Pour point | NTE 450 | Normalab | Valliquerville, France |
| Cold filter plugging point | NTL 450 | Normalab | Valliquerville, France |
| Density | DS7800 | A. Krüss Optronic GmbH | Hamburg, Germany |

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Table 1 shows a list of the equipment used in the current study to measure the physical and chemical properties of crude oil, methyl ester and blends.

The saponification number of SME was predicted by the following empirical equation [31]:

$$SN = SUM\left(\frac{560 * A_i}{MW_i}\right) \quad (1)$$

where $A_i$ is the percentage and $MW_i$ is the molecular mass of each component.

Iodine value (IV), cetane number (CN) and oxidation stability (OS) of SME were predicted by the following empirical equations [32]:

$$IV = 1.0617(DU) - 10.805 \quad (2)$$

$$CN = -0.1268(DU) + 67.926 \quad (3)$$

$$OS = -0.0518(DU) + 11.121 \quad (4)$$

where DU is the degree of unsaturation (section 3.3).

The higher heating value (HHV) of SME was predicted by the following empirical equation [33]:

$$HHV = [74.468 - (0.0382 \times \rho)] \quad (5)$$

where $\rho$ is density (kg/m$^3$).

## Biodiesel production and purification

The transesterification process converts lipids to biodiesel (fatty acid alkyl ester) and glycerol. In this study, 1 L of safflower oil was reacted with 25% (v/v oil) methanol (6:1 molar ratio) and 1% (m/m oil) KOH. The reaction was maintained at 60°C for 1 hr and 400 rpm stirring speed. The methyl ester was then removed from the glycerol using a separation funnel.

The methyl ester was washed with distilled water several times to remove the entrained impurities and glycerol, and then introduced into a rotary evaporator to remove the excess water and methanol. Afterward, it was further dried using sodium sulfate ($Na_2SO_4$). Finally, the product was filtered using qualitative filter paper (Fioroni Filters). The yield of methyl ester conversion in this study was reported to be 99% from safflower oil, and the color of the final SME product was light yellow.

## The gas chromatography (GC) method of safflower methyl ester (SME)

The FAC profile of SME was determined using a gas chromatograph (Shimadzu, Japan) equipped with a flame ionization detector and an RT2560 capillary column. The test was conducted using an optimized in-house GC method [34]. The carrier gas was helium, with a column flow rate of 1.03 mL per minute at a 50:1 split ratio. A 1-$\mu$L sample of SME was injected into the gas chromatograph. Table 2 shows a summary of the GC operating conditions.

**Table 2.** The GC operating conditions.

| Property | Specifications | Unit |
|---|---|---|
| Carrier gas | Helium | |
| Linear velocity | 19.10 | cm/sec |
| Flow rate | 1.03 (column flow) | mL/min |
| Detector temperature | 260 | °C |
| Column head pressure | 264.4 (flow control made) | kPa |
| Column dimensions | RT2560 | 100.0m × 0.25$\mu$m × 0.3 mm inner diameter |
| Injector column oven Temperature ramp | 240<br>140°C (hold for 2 min)<br>4°C/min to 165°C<br>2°C/min to 192°C<br>4°C/min to 240°C (hold for 5 min) | °C |

DU was calculated from the percentages of monounsaturated and polyunsaturated fatty acids (wt%; Table 8) by the following equation [32]:

$$\begin{aligned} DU = {} & (\text{monosaturated } C_n : 1,\ \text{wt\%}) \\ & + 2(\text{polyunsaturated } C_n : 2,\ \text{wt\%}) \\ & + 3(\text{polyunsaturated } C_n : 3,\ \text{wt\%}) \end{aligned} \quad (6)$$

LCSF was calculated from the percentages of the saturated fatty acids (wt%; Table 8) and their corresponding melting points (MP*n*) by the following equation [32]:

$$LCSF = \sum \frac{(MP_n \times C_{n\ wt\%})}{100} \quad (7)$$

## Biodiesel–diesel, butanol–diesel and biodiesel–butanol–diesel blending

Blending of SME with butanol and Euro diesel was carried out to examine the influence on some physical and chemical properties such as density, kinematic viscosity, pour point, cloud point, flash point and cold filter plugging point. In this work, five different blends including safflower methyl ester, butanol and Euro diesel were prepared: B20D80, B5But15D80, B10But10D80, B15But5D80 and But20D80. All blends were kept in a reagent bottle with a screw cap, at room temperature.

In this paper, a polynomial curve-fitting method was used to predict the kinematic viscosities and densities of biodiesel–butanol–diesel blends. Mathematically, a polynomial of order $k$ in $X$ is expressed in the following form [35]:

$$y = C_0 + C_1X + C_2X^2 + \ldots + C_k \quad (8)$$

## Differential scanning calorimetry (DSC) method of SME

DSC is an effective thermal analytical method to assess the cold flow properties of any fuel. In this study, SME

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**Table 3.** Summary of differential scanning calorimetry method by TA Q-2000 DSC.

| Instrument | TA Q-2000 DSC |
|---|---|
| Sample amount | 3 ± 0.5 mg |
| Gas | Nitrogen |
| Flow rate | 50 mL/min |
| Temperature range | −80 to +20°C |
| Ramp rate | 10°C/min |

(B100), butanol (But100), crude safflower oil (CSO), Euro diesel (D100) and their blends were analyzed with a DSC Q-2000 (TA) under a flow of nitrogen. The DSC curves were obtained in a calorimeter (model DSC Q20 with RCS90) coupled with a cooling system, both from TA Instruments. A portion of each sample (3 ± 0.5 mg) was loaded in an aluminum pan, and heat flow was measured differentially by comparison to the heat flow of an empty reference pan as a reference. The rate of heating/cooling was 10°C/min between −80 and +20°C under an inert nitrogen atmosphere ($N_2$) with a flow rate of 50 mL $min^{-1}$ (Table 3). Each DSC test takes about 17 min to complete a single sample. All results were evaluated with the help of TA Orchestrator Version V7.2.2.1.

DSC analyses were done to determine the crystallization onset temperature of each sample, which can be plotted against heat flow. This analysis is useful for monitoring the full range of crystallization which is used to characterize the cold flow properties of biodiesel samples, which are mixtures of long chain fatty acid esters. The evaluation of the crystallization phenomenon using DSC analysis provides relevant data about the properties of biodiesel samples which have different carbon chain lengths and degrees of saturation. Crystallization of esters depends on the length of fatty acid chains and interactions between the molecules. The crystallization of saturated and unsaturated methyl esters is different due to the structural configuration of the oil molecules with respect to the size of the chains and position of the double bonds. Crystallization temperature decreases with increased branching of the carbon chain of esters. Also, unsaturation has a significant effect on crystallization temperature. The spatial arrangement of molecules can disturb the packing capacity; thus unsaturation produces low crystallization temperatures by preventing molecular packing [36].

### *Fourier transform infrared spectroscopy (FTIR) method of SME*

FTIR analysis is the most widely used technology for measuring biodiesel content. FTIR is a rapid, cheap, reliable, precise and nondestructive method for biodiesel analysis. All these qualities make FT-IR a favorable method over GC, High-performance liquid chromatography (HPLC), and Nuclear mahnetic resonance (NMR) analyses [37–39]. In this study, SME (B100), butanol (But100), Euro diesel (D100), crude safflower oil (CSO) and their blends were characterized by FT-IR, using a Perkin Elmer device in the range 4000–650 $cm^{-1}$and processed with a computer software program spectrum. The resolution was 4 $cm^{-1}$ and 4 scans.

**Table 4.** Summary of TGA method by Shimadzu DTG 60H.

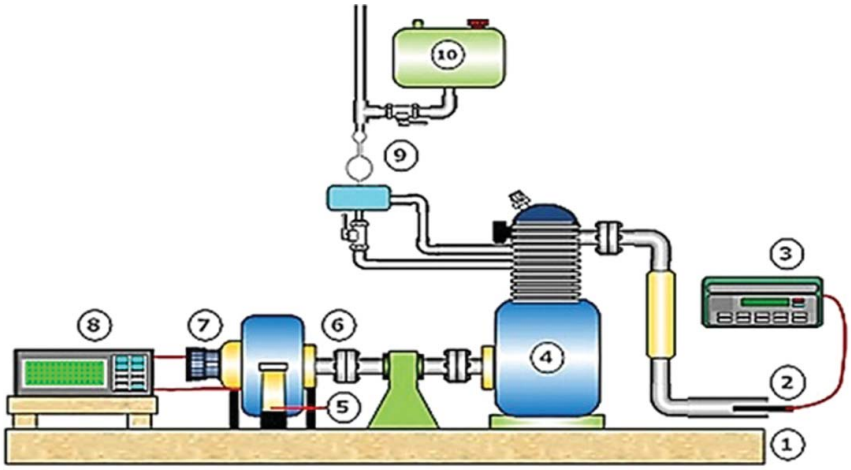
| Instrument | Shimadzu DTG 60H |
|---|---|
| Gas | Dry air |
| Flow rate | 100 mL/min |
| Temperature range | 25 to 700°C |
| Heating rate | 10°C/min |

### *Thermogravimetric analysis (TGA) method of SME*

Thermogravimetric analysis is used to determine the thermal properties of esters as a function of temperature. Thermal stability is defined as the fuel's resistance to degradation at elevated temperatures higher than atmospheric conditions. In this study, the thermogravimetric (TG) thermograms of SME (B100), butanol (But100), crude safflower oil (CSO), Euro diesel (D100) and their blends were quantified. These properties were expressed as weight change as a function of increasing temperature. TG curves show the weight loss at different temperatures and the first derivative of the weight loss in relation to the temperature curves. The analysis was performed in a TG analyzer (model Shimadzu DTG 60H) at a heating rate of 10°C/min from room temperature up to 700°C so that the sample weight remains constant until the end of the analysis, and all chemical reactions have completed. Dry air was used as a reactive gas at a flow rate of 100 mL/min for oxidative stability (Table 4). All the samples were measured in milligrams in a platinum crucible. TGA curves as well as their derivative curves (DrTGA) were used to obtain the onset temperature of the esters. Onset temperature was used to indicate the resistance of esters to thermal and oxidative degradation, and was determined by extrapolating the horizontal baseline of the TGA curve. TGA curves were used to evaluate the onset temperature of SME (B100), butanol (But100), crude safflower oil (CSO), Euro diesel (D100) and their blends [40].

### *Ultraviolet and visible spectroscopy (UV-Vis) method of SME*

UV-Vis spectra provide information about the electronic properties of molecules. All organic compounds absorb light in the visible and ultraviolet region. It is possible to see various aromatic compounds in diesel fuel [41]. In this study, blends of B5But15D80, B10But10D80, B15But5D80, B20D80 and B100 were prepared and tested. Biodiesel (B100) was diluted with butanol (But100) to bring a measurable absorbance interval in the spectrophotometer, since biodiesel samples absorb light in the high UV range. To obtain the spectra, quartz cuvettes were filled with blends. The UV absorption spectra of the biodiesel blends with




1) engine chassis, 2) exhaust gas analyzing probe, 3) exhaust gas analyzer, 4) single cylinder diesel engine, 5) load cell, 6) dynamometer, 7) tachometer, 8) control unit, 9) fuel burette, 10) fuel container

**Figure 1.** Schematic diagram of the test engine and exhaust analyzer. 1. engine chassis; 2. exhaust gas analyzing probe; 3. exhaust gas analyzer; 4. single-cylinder diesel engine; 5. load cell; 6. dynamometer; 7. tachometer; 8. control unit; 9. fuel burette; 10. fuel container.

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Euro diesel (D100) and butanol (But100) were obtained using an Agilent Technologies Cary 60 UV-Vis Spectrophotometer in a wavelength range of 500–200 nm at 1-nm intervals of different blends of SME, and were scanned using standard 1 cm quartz cuvettes at room temperature.

### *Engine and emissions tests*

A single-cylinder, four-stroke, naturally aspirated and direct injection (Antor 4 LD 820) diesel engine was utilized to monitor the engine performance and exhaust emissions parameters in this study. To adjust the load, a water brake dynamometer was coupled with the engine. An electronic control and measurement device was used to display performance data. The accuracies of the speed, fuel measurement and brake power were ± 5 rpm%, ± 0.5045% and ± 0.5055, respectively. Figure 1 shows the engine test rig and exhaust analyzer. Detailed specifications of the engine are listed in Table 5. The experimental investigation was carried out using Euro diesel, D80B20, But20D80, B5But15D80, B10But10D80 and B15But5D80. The engine was first run with Euro diesel for 15 min at 1500 rpm to warm the engine up before each blend was tested. Similarly, the engine was operated with Euro diesel before it was shut down to restore the engine to its original conditions. To carry out engine performance and emission tests, the engine was initially run at 3000 rpm without load. Then engine load was increased to full load using a water brake dynamometer; therefore, engine speed was decreased to 2500, 2000, 1500 and 1000 rpm. A portable emissions analyzer (model testo 350) was used to measure CO, HC, $NO_x$ and exhaust gas temperature. Details of the emissions analyzer are given in Table 6. Each test was repeated 3 times, and the results were averaged.

**Table 5.** Detailed technical specifications of the tested engine.

| | |
|---|---|
| Engine model | Antor 4 LD 820 |
| Engine type | Single cylinder, Four stroke |
| Fuel type | Diesel |
| Bore | 102 mm |
| Stroke | 100 mm |
| Swept volume | 817 $cm^3$ |
| Compression ratio | 17:1 |
| Cooling type | Air cooled |
| Maximum engine speed | 3000 rpm (limited by manufacturer) |
| Maximum power | 12.7 kW at 3000 rpm |
| Maximum torque | 50 N.m at 1600 rpm |
| Injection pressure | 20 MPa |
| Specific fuel consumption | 255 g/kW.h at 2800 rpm |
| Engine position | Vertical |

**Table 6.** Detailed technical specifications of the exhaust gas analyzer (testo 350).

| Measurement | Measurement range | Accuracy |
|---|---|---|
| CO | 0–10 000 ppm | ± 10% |
| HC | 100–40 000 ppm | ± 5% |
| $NO_x$ | 0–500 ppm | ± 5% |
| Exhaust gas temperature (EGT) | −200 to +1370°C | ± 1°C |

## Results and discussion

### *Properties of crude safflower oil (CSO)*

Table 7 shows the physicochemical properties of CSO found in this study in comparison with some published results [3,22,23]. The results for acid value (0.505 mg KOH/g oil) indicated that it is possible to use a one-step transesterification process to process safflower oil into biodiesel.

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**Table 7.** Physicochemical properties of CSO.

| Property | CSO | CSO[1] | CSO[2] | CSO[3] |
|---|---|---|---|---|
| Kinematic viscosity at 40°C ($mm^2/s$) | 29.79 | 28.3 | 28 | 29.64 ± 0.01 |
| Acid value (mg KOH/g oil) | 0.505 | – | – | 0.97 ± 0.06 |
| Density at 20°C ($g/cm^3$) | 0.921 | – | – | – |
| Density at 15°C ($g/cm^3$) | 0.925 | 0.91 | 0.95 | 0.93 ± 0 |
| Cloud point (°C) | −14 | −2 | −2 | – |
| Pour point (°C) | −22 | −14 | – | – |

[1] [22].
[2] [23].
[3] [3].
CSO = crude safflower oil.

### Fatty acid composition, Degree of unsaturation (DU) and Long-chain saturated factor (LCSF )of safflower methyl ester (SME)

Table 8 shows the fatty acid composition of SME in comparison with the results obtained by [24]. It can be seen that SME is primarily composed of 72.357% polyunsaturated fatty acid (linoleic acid; similar to the findings of [24,30]) followed by 18.6% monounsaturated fatty acids (oleic acid), while saturated fatty acids represent only 8.9%. The DU of SME (163.404) is comparable to that of [24] (167.38). The LCSF of SME in the current study (5.822) is comparable to that in [24] (5.428). DU has a direct correlation with some parameters such as iodine number, cetane number and oxidation stability, while LCSF is correlated with cold filter plugging point (CFPP) [32 ].

### Properties of safflower methyl ester (SME)

The main problem linked with the usage of vegetable oils as a substitute for diesel fuel in a diesel engine is caused by its extremely high kinematic viscosity. Table 9 shows the properties of SME in comparison with some published results [3,22,23,29,42]. Compared to the results for CSO, the kinematic viscosity of SME at 40°C is drastically reduced (87%). Density at 15°C has also been reduced, by about 4%. It can be seen that SME satisfies both EN 14 214 and ASTM D6751 standards regarding the kinematic viscosity (4.0167 $mm^2/s$), flash point (176°C) and density (0.8865 $g/cm^3$). The cetane number (47.21) only satisfies ASTM D6751 standards. However, the iodine value of SME was found to be quite high (162.68 g iodine/100 g). The same trend was observed in the saponification value of SME (200.78). The oxidation stability of SME (2.66 h) also fails to satisfy the limit of both EN 14 214 and ASTM D 6751 standards. This is due to the high level of unsaturated fatty acid (91.05%) in SME.

### Properties of safflower methyl ester (SME) and its blends with butanol and diesel

Table 10 shows the results of properties of SME and its complementary blends with butanol and Euro diesel.

**Table 8.** Fatty acid compositions, DU and LCSF of safflower methyl ester (SME).

| Fatty acid | Molecular weight | Structure | Systematic name | Formula | SME | SME[1] |
|---|---|---|---|---|---|---|
| Myristic | 228 | 14:00 | Tetradecanoic | $C_{14}H_{28}O_2$ | 0 | 0.07 |
| Palmitic | 256 | 16:00 | Hexadecanoic | $C_{16}H_{32}O_2$ | 6.335 | 6.19 |
| Palmitoleic | 254 | 16:01 | 9-hexadecenoic | $C_{16}H_{30}O_2$ | 0 | 0.09 |
| Stearic | 284 | 18:00 | Octadecanoic | $C_{18}H_{36}O2$ | 2.246 | 1.92 |
| Oleic | 282 | 18:01 | Cis-9-Octadecenoic | $C_{18}H_{34}O_2$ | 18.69 | 15.33 |
| Linoleic | 280 | 18:02 | Cis-9-cis-12 Octadecadienoic | $C_{18}H_{32}O_2$ | 72.357 | 75.83 |
| Linolenic | 278 | 18:03 | Cis-9-cis-12 | $C_{18}H_{30}O_2$ | 0 | 0.1 |
| Arachidic | 312 | 20:00 | Eicosanoic | $C_{20}H_{40}O_2$ | 0.372 | 0.22 |
| Heneicosanoic | 326.5 | 21:00 | Heneicosylic | $C_{21}H_{42}O_2$ | 0 | 0 |
| Saturated | | | | | 8.953 | 8.4 |
| Monounsaturated | | | | | 18.69 | 15.42 |
| Polyunsaturated | | | | | 72.357 | 75.93 |
| Total | | | | | 100 | 100 |
| DU | | | | | 163.404 | 167.38 |
| LCSF | | | | | 5.822 | 5.428 |

[1] [24].
SME = safflower methyl ester; DU = degree of unsaturation; LCSF = long-chain saturated factor.

**Table 9.** Physicochemical properties of SME.

| Property | ASTM D6751 | EN 14 214 | SME | SME[1] | SME[2] | SME[3] | SME[4] | SME[5] |
|---|---|---|---|---|---|---|---|---|
| Kinematic viscosity at 40°C ($mm^2/s$) | 1.9-6.0 | 3.5-5.0 | 4.0167 | 3.9 | 5.8 | 4.29 | 5.97 | 4.23 |
| Cloud point (°C) | Report | Report | −2 | −5 | −5 | −2 | 7.5 | −7 |
| Pour point (°C) | Report | Report | −7 | −24 | – | −8 | −8 | −13 ± 0.47 |
| Cold filter plugging point (°C) | Report | Report | −12 | – | – | −6 | −10 | – |
| Flash point (°C) | 93 min | 120 min | 176 | 187 | 148 | 176 | 133 | – |
| Density at 15°C ($g/cm^3$) | 0.88 | 0.86-0.90 | 0.8865 | 0.87 | 0.8885 | 0.874 | 0.896 | 0.88 |
| Iodine value (g iodine/100 g) | – | ≤ 120 | 162.68 | 91.18 | – | – | 117.9 | 145 ± 3.4 |
| Cetane number | 47 min | 51 min | 47.21 | 53.14 | 56 | 52 | – | – |
| Saponification number | – | – | 200.78 | – | – | – | – | – |
| HHV (MJ/kg) | – | – | 40.604 | 40.26 | – | – | 38.38 | – |
| Oxidation stability (h) | 3 h min | 6 h min | 2.66 | – | – | – | – | 0.57 ± 0.02 |

[1] [22].
[2] [23].
[3] [42].
[4] [29].
[5] [3].

**Table 10.** Properties of SME–butanol–diesel blends.

| Property | Diesel | N-butanol | SME | B20D80 | But20D80 | B5But15D80 | B10But10D80 | B15But5D80 |
|---|---|---|---|---|---|---|---|---|
| Kinematic viscosity at 40°C ($mm^2/s$) | 2.3255 | 2.2192 | 4.0167 | 2.99 | 2.211 | 2.2192 | 2.5415 | 2.6598 |
| Cloud point (°C) | −7 | ←60 | −2 | −3 | −2 | −2 | −2 | −3 |
| Pour point (°C) | −26 | >−35 | −7 | −26 | −39 | −39 | −36 | −33 |
| Cold filter plugging point (°C) | −25 | >−35 | −12 | −29 | −30 | −31 | −29 | −28 |
| Flash point (°C) | 65 | 37 | 176 | 69 | 41 | 51 | 51 | 51 |
| Density at 15°C ($g/cm^3$) | 0.8405 | 0.814 | 0.8865 | 0.8447 | 0.8282 | 0.8312 | 0.835 | 0.8387 |

Remarkable improvements in kinematic viscosity, cloud point, pour point, cold filter plugging point and density were obtained after blending, while flash points decreased but were still kept to an acceptable level. These results support that SME with Euro diesel and butanol as ternary blends (Up to 20%) can be used as a substitute in CI diesel engines. Butanol has a higher calorific value, higher cetane number and lower heat of vaporization than ethanol. Butanol is also more miscible in hydrocarbon than ethanol is. The use of butanol in diesel engines improves combustion, and reduces particulate, carbon monoxide and nitrogen oxide emissions [20,21].

Using Equation (8) and based on the input data in Table 10, the following correlations have been established to predict the density (at 15°C) and kinematic viscosity (at 40°C) for all biodiesel–butanol–diesel blends in the blend ratio range of 0–20%, as follows:

$$\begin{aligned}&\text{Density}(\text{SME}-\text{Diesel}-\text{Butanol}) = 0.1686x^2 + 0.0473x \\ &\quad +0.8283 \\ &0\% \leq x \geq 20\% \ (x \equiv \%\text{SME}) \\ &\left(R^2 = 0.9977\right)\end{aligned} \tag{9}$$

$$\begin{aligned}&\text{Kinematic viscosity}(\text{SME}-\text{Diesel}-\text{Butanol}) \\ &\quad = 27.54x^2 - 1.4614x + 2.2074 \\ &0\% \leq x \geq 20\% \ (x \equiv \%\text{SME}) \\ &\left(R^2 = 0.9761\right)\end{aligned} \tag{10}$$

## Analysis of fuel characteristics

### Kinematic viscosity

Kinematic viscosity is an important characteristic which indicates of the capability of a substance to flow. An increase in viscosity affects the fluidity of the fuel and therefore affects the operation of the fuel injection equipment and spray atomization [7]. The result for SME in the current study (4.0167 $mm^2/s$) was found to be very similar to that found in [22] (3.9 $mm^2/s$), and lower than that of [42] (4.29 $mm^2/s$) and [3] (4.23 $mm^2/s$). However, it was found to be much less than in [29] and [23], who reported kinematic viscosities of 5.97 $mm^2/s$ and 5.8 $mm^2/s$, respectively.

B20D80, But20D80, B5But15D80, B10But10D80 and B15But5D80 blends have further reduced the kinematic viscosity to 2.99, 2.211, 2.2192, 2.5415 and 2.6598 $mm^2/s$ respectively. It can be seen that blending biodiesel with Euro diesel and butanol, which have kinematic viscosities of 2.3255 and 2.2192 $mm^2/s$, respectively, has achieved kinematic viscosity results comparable to those of Euro diesel.

### Density

Density is an important property mainly in airless combustion systems because it influences the efficiency of atomization of the fuel [22]. The density of biodiesel is typically higher than that of diesel. According to the EN 14 214 biodiesel standard, biodiesel should have a density between 0.86 and 0.90 $g/cm^3$. The result for SME in the current study (0.8865 $g/cm^3$) was lower than that found by [23] (0.8885 $g/cm^3$) and [29] (0.896 $g/cm^3$), and higher than that of [22] (0.87 $g/cm^3$), [42] (0.874 $g/cm^3$) and [3] (0.88 $g/cm^3$).

B20D80, But20D80, B5But15D80, B10But10D80 and B15But5D80 blends have further reduced the density to 0.8447, 0.8282, 0.8312, 0.835 and 0.8387 $g/cm^3$ respectively. It can be seen that the density of SME decreased when blended with either Euro diesel or butanol, which have densities of 0.8405 and 0.814 $g/cm^3$, respectively.

### Flash point (FP)

The flash point of a fuel is the temperature at which it will ignite when exposed to a flame or spark. The flash point of biodiesel is higher than that of conventional diesel, which is safe for transport purposes [7,22 ]. The result for SME in the current study (176°C) was lower than that found by [22] (187°C), higher than that of [23] (148°C) and [29] (121°C), and the same as that of [42] (176°C).

The blends of SME with Euro diesel, or with butanol and Euro diesel, have flash points of 51 and 69°C, respectively. It can be seen that the flash point of SME decreased when blended with Euro diesel and butanol, which have flash points of 65 and 37°C, respectively.

### Iodine value (IV)

Iodine value is a measurement of total unsaturation of fatty acids measured in g iodine/100 g of biodiesel sample. Biodiesel, which has a high IV, is readily oxidized in the presence of air. Biodiesel with a high iodine amount has a high number of double bonds [43]. According to EN 14 214 standards the IV should not exceed 120 g iodine/100 g. The results show that SME has an IV of 162.68 g iodine/100 g. This shows that the IV is unacceptable according to the EN 14 214 standard. This is due to the high presence of linoleic

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acid (C18:02) in SME, leading to a high degree of unsaturation (Table 8). The DU in SME was 163.404. It was reported that any methyl esters with DU of $\leq$ 123.2 satisfy the EN 14 214 standard [32]. The result for SME in the current study was much higher than that found by [22] (91.18 g iodine/100 g), [29] (117.9 g iodine/100 g) or [3] (145 $\pm$ 3.4 g iodine/100 g).

### Cloud point (CP) and pour point (PP)

The CP is the temperature at which solid crystals start to form a cloudy suspension, potentially blocking fuel filters [44]. Biodiesel, in general, has a CP higher than that of conventional diesel fuel. However, the CP of biodiesel is influenced by the type of feedstock and its fatty acid composition (level of saturation). CP is determined according to ASTM D2500. The CP of SME is $-2^{\circ}$C, compared to $-7^{\circ}$C for Euro diesel.

The PP is the temperature at which the amount of wax formed out of the solution is sufficient to gel the fuel, and thus the fuel can no longer be pumped [7,22]. It is determined according to ASTM D 97. Biodiesel in general has a higher PP than Euro diesel. The PP of SME is $-7^{\circ}$C, compared to $-26^{\circ}$C for Euro diesel. SME has a higher CP and PP compared to Euro diesel. Therefore, blending SME with Euro diesel and butanol can result in a remarkable improvement in both properties.

### Cetane number (CN)

Cetane number is considered an important fuel property in assessing the quality of biodiesel. It is the indication of ignition characteristics or the ability of fuel to auto-ignite quickly after being injected. Better ignition quality of fuel is always associated with higher CN [7]. A fuel with a high CN starts to burn shortly after it is injected into the cylinder; therefore, it has a short ignition delay period. Conversely, a fuel with a low CN resists auto-ignition and has a longer ignition delay period [45]. CN affects a number of engine performance parameters including combustion, stability, drivability, white smoke, noise, and emissions of CO and HC [46]. Practically, biodiesel has a higher CN than conventional diesel fuel, which results in a higher combustion efficiency [22]. The CN of SME is 47.21, a result that is only acceptable according to ASTM D6751. This value is due to the high presence of linoleic acid (C18:02) in SME (Table 8). The DU in SME was 163.404. It was reported that any methyl esters with DU of $\leq$ 133.5 satisfy the EN 14 214 standard [32]. The result for SME in the current study was lower than that found in [22] (53.14), [23] (56) and [42] (52).

### Oxidation stability

Biodiesel is susceptible to oxidation, which can induce ester polymerization and form insoluble gums that can clog fuel filters [32]. The oxidation stability of SME is 2.77 h. This low oxidation stability is due to the high presence of polyunsaturated fatty acids in SME (Table 8). Therefore, this result is not acceptable according to both ASTM D6751 and EN 14 214 standards. The DU in SME was 163.404. It was reported that any methyl esters with DU of $\leq$ 98.9 satisfy the EN 14 214 standard for oxidation stability [32]. However, the result of oxidation stability of the current study was much better than that found by [3] (0.57 $\pm$ 0.02 h).

**Table 11.** Crystallization onset temperatures (°C) of SME (B100), butanol (But100), crude safflower oil (CSO), Euro diesel (D100) and their blends under $N_2$ atmosphere.

| Sample | Crystallization onset temperature (°C) |
|---|---|
| D100 | −11.49 |
| But100 | −15.13 |
| Crude oil | −15.03 |
| Blends | |
| B100 | −7.42 |
| B20D80 | −5.57 |
| BUT20D80 | −5.57 |
| B5BUT15D80 | −10.88 |
| B10BUT10D80 | −5.51 |
| B15BUT5D80 | −5.67 |

### DSC

The crystallization onset temperatures of SME (B100), butanol (BUT100), crude safflower oil (CSO), Euro diesel (D100) and their blends under $N_2$ atmosphere are presented in Table 11. The crystallization onset temperatures for SME (B100) and CSO are $-7.42^{\circ}$C and $-15.03^{\circ}$C, respectively. Biodiesel crystallizes faster than diesel and butanol; hence, the crystallization onset temperatures for But100 and D100 are $-15.13^{\circ}$C and $-11.49^{\circ}$C, respectively. The crystallization onset temperatures of SME blends of B20D80, But20D80, B5But15D80, B10But10D80, B15But5D80 are −5.57, −5.57, −10.88, −5.51 and $-5.67^{\circ}$C. respectively. The addition of diesel and butanol to biodiesel decreases the crystallization onset temperature of biodiesel [47]. The crystallization temperature of SME ($-7.42^{\circ}$C) is in a good agreement with that of macauba ethyl ester ($-9.9^{\circ}$C) [40], higher than that of coriander methyl ester ($-19^{\circ}$C) [48] and castor methyl ester ($-26^{\circ}$C) [49], and lower than that of jatropha methyl ester ($-1^{\circ}$C) [50].

### FT-IR

The infrared spectra of SME (B100), butanol (But100), crude safflower oil (CSO), diesel (D100) and their blends are shown in Figure 2 and Table 12. The main spectral region, which permits chemical definition between 1500 and 700 $cm^{-1}$, is known as the 'fingerprint' region. Broad peaks at 3550–3200 $cm^{-1}$ and 3331 $cm^{-1}$ indicate O-H stretching in alcohol and phenol compounds and O-H stretching in butanol (But100), respectively [51]. In FT-IR, there are units that use an integration of the side (1750–1760 $cm^{-1}$) of the ester carbonyl group stretching, showing strong bands at nearly $\sim$ 1744 $cm^{-1}$, to monitor the progress of the

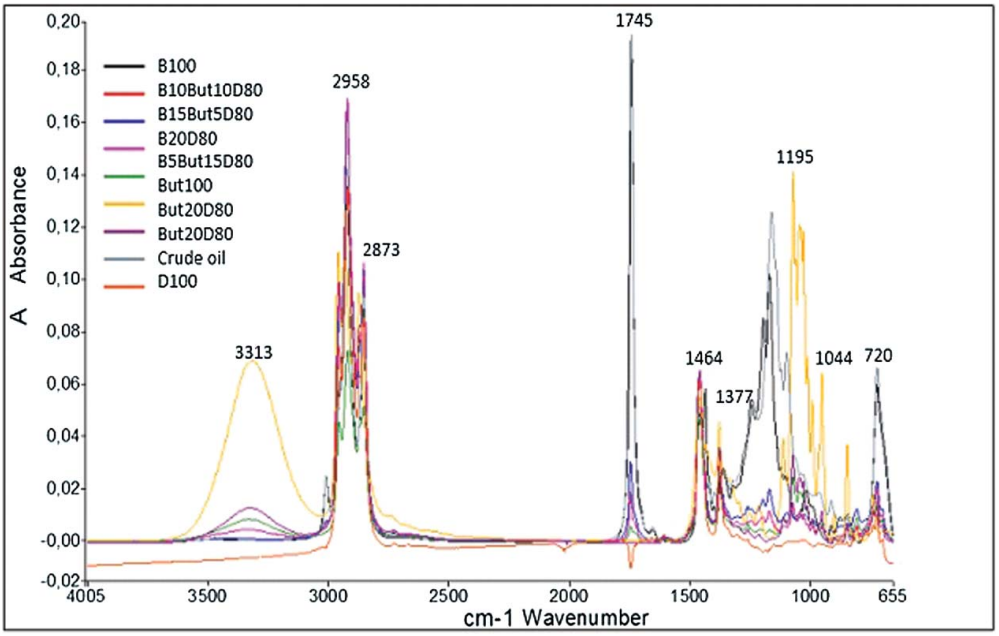



**Figure 2.** Infrared spectra and wavenumbers of safflower, (B100), butanol (But100), diesel (D100), crude safflower oil (CSO) and their blends.

**Table 12.** Absorbance bands interval of SME (B100), butanol (But100), crude safflower oil (CSO), diesel (D100) and their blends.

| Absorption bands ($cm^{-1}$) | Safflower blend | Functional group | Absorption intensity |
|---|---|---|---|
| 3320–3300 | But100 | O-H Stretching vibration | Strong |
| 3000–2900 | D100<br>But100<br>Crude oil<br>B100<br>Blends | C-H Stretching vibration | Strong |
| 2900–2850 | D100<br>But100<br>Crude oil<br>B100<br>Blends | $CH_2$ asymmetric and symmetric vibration | Strong |
| 1750–1700 | B5But15D80<br>B15But5D80<br>B10But10D80<br>Crude oil | C = O Stretching vibration (Ester) | Strong |
| 1500–1400 | D100<br>But100<br>Crude oil<br>B100<br>Blends | $CH_2$ Scissoring vibration | Middling |
| 1400–1300 | But100 | O-H Bending in plane vibration | Middling |
| 1300–1200 | D100<br>But100<br>Crude oil<br>B100<br>Blends | $CH_2$ and $CH_3$ deformation | Middling |
| 1200–1000 | D100<br>But100<br>Crude oil<br>B100<br>Blends | C-O-C symmetric stretching vibration | Middling |
| 1000–900 | But100<br>Crude oil<br>B100 | C-O-C anti-symmetric stretching vibration | Weak |
| 900–700 | D100<br>But100<br>Crude oil<br>B100<br>Blends | $CH_2$ rocking vibration | Weak |

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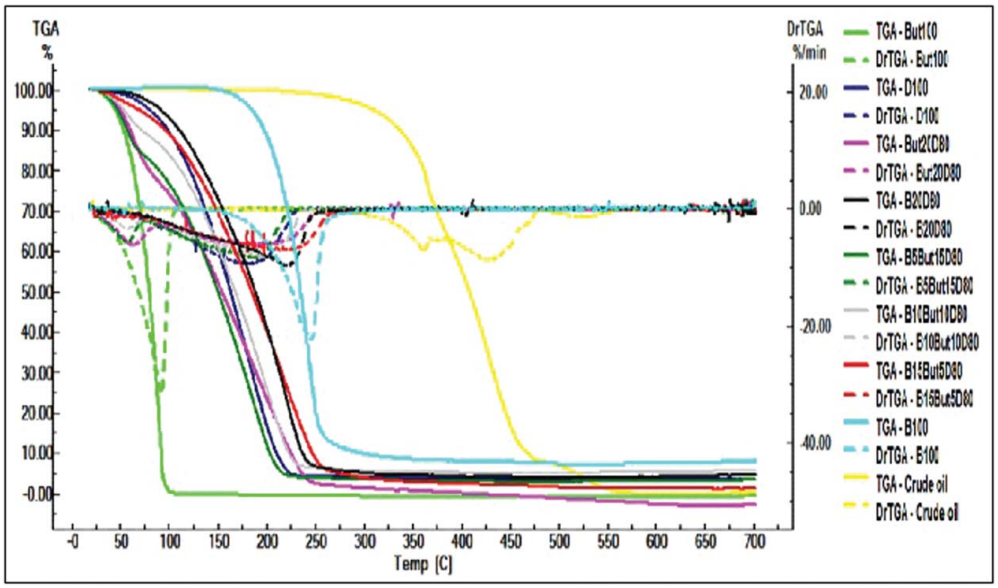



**Figure 3.** TGA and DrTGA curves of SME (B100), butanol (But100), crude safflower oil (CSO), Euro diesel (D100) and their blends for oxidative stability.

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reaction [52,53]. Esters have two characteristically strong absorption bands, arising from carbonyl (C = O) around 1750–1730 $cm^{-1}$ and 1465–1377 $cm^{-1}$, corresponding to methyl bending and rocking, respectively. A wavenumber of 1454 $cm^{-1}$ corresponds to the C-H rocking. The stretching of O-$CH_3$, represented by absorbance at 1196 $cm^{-1}$, is typical of biodiesel [53,54]. C-O antisymmetric and asymmetric axial stretching occurs around 1300–1100 $cm^{-1}$ and 1150–1000 $cm^{-1}$, respectively. The stretching vibrations and the bending vibrations of $(CH)_n$ (n = 1,2,3) appear at 3000–2900 $cm^{-1}$ and 1475–722$cm^{-1}$, respectively [55].

## TGA

As shown in Figure 3, TGA/DrTGA curves show that oxidative degradation occurred in a single continuous step in the temperature range 130–320°C for SME and its blends. In this temperature range, mass loss occurs at levels of 89.9–99.3% for biodiesel samples and their blends. In addition, mass loss temperatures of 384°C for CSO, 75.3°C for butanol (But100) and 117.7°C for diesel (D100) were reported. At these temperatures, mass loss occurs at levels of 99.3, 99.0 and 96.0% for CSO, But100 and D100, respectively. The oxidation onset temperatures are shown in Table 13.

## UV-Vis

Figure 4 shows a typical family of absorbance curves for diluted SME in the range of 800–200 nm. When the spectra are plotted for SME, the change in suction density can be ignored. The absorbance for SME and its blends with Euro diesel and butanol have shown very similar absorbances with little significant differences. Therefore, it was concluded that the absorbance in this band is not affected by the type of biodiesel, as blended biodiesel does not have chemical components that contribute to significant absorption in this range.

**Table 13.** TGA onset temperatures and mass loss of SME (B100), butanol (But100), crude safflower oil (CSO), Euro diesel (D100) and their blends for oxidative stability.

| Sample | Heating rate (°C/min) | Onset temperature for thermal degradation (°C) | Mass loss under dry air (%) |
|---|---|---|---|
| B5But15D80 | 10 | 145.3 | 96.1 |
| B10But10D80 | 10 | 155.9 | 93.5 |
| B15But5D80 | 10 | 143.1 | 93.6 |
| B20D80 | 10 | 139.7 | 97.2 |
| B100 | 10 | 230.7 | 86.2 |
| But20D80 | 10 | 131.4 | 94.2 |
| But100 | 10 | 75.3 | 99.3 |
| Crude oil | 10 | 385.1 | 91.8 |
| D100 | 10 | 117.7 | 96.0 |

Analysis of absorbance curves for SME and its blends showed that a single wavelength in the UV range could be used to determine the blend level for a single diesel fuel [56]. The absorbance decreased linearly with increasing concentration of blends (Figure 4). When percentage of biodiesel was plotted against

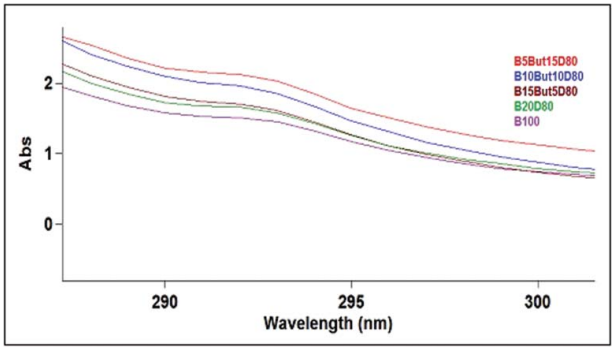



**Figure 4.** UV absorbance spectra of SME and its blends in butanol (But100).

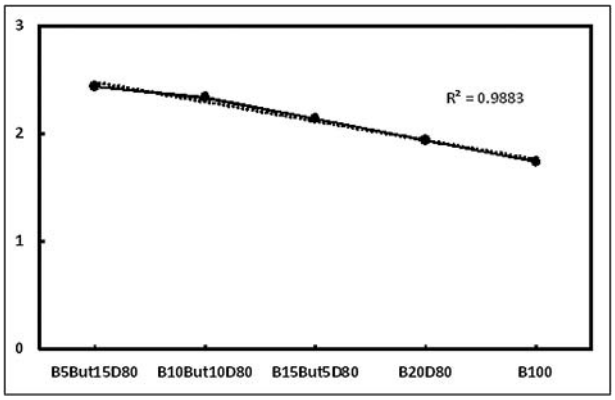



**Figure 5.** Absorbance of diluted SME blends at 290 nm wavelength.

absorbance for any given wavelength between 290 and 300 nm, a linear relation was observed for SME blends. This was attributed to the decreasing concentration of aromatic compounds in the fuel. The difference in absorbance for B5But15D80 and B100 was highest in the vicinity of 290 nm for SME. Linear lines fitted for absorbance versus concentration of biodiesel for all blends at 290 nm (Figure 5) showed a high coefficient of determination. Values of R2 were determined as 0.9908 and 0.9883 for HME and SME, respectively. Values of absorbance and $R^2$ are shown in Table 14 for SME at 290 nm wavelength.

**Table 14.** Absorbance of SME blends at 290 nm wavelength.

| Blend | $R^2 = 0.9883$ |
|---|---|
| B5But15D80 | 2.435 |
| B10But10D80 | 2.331 |
| B15But5D80 | 2.139 |
| B20D80 | 1.936 |
| B100 | 1.737 |

## Engine performance analysis

The engine performance parameters brake torque, brake power (BP) and brake specific fuel consumption (BSFC) of six fuel samples (Euro diesel, D80B20, But20D80, B5But15D80, B10But10D80 and B15But5D80) were studied in this work. The following sections discuss the findings for these parameters.

### Brake power (BP)

Figure 6 illustrates the variation of BPat full load with respect to the tested fuels at various engine speeds. For all tested fuels, maximum BP was obtained at 2500 rpm. The maximum BP of 11.22 kW was recorded for Euro diesel at 2500 rpm. The average BP for Euro diesel is 8.29 kW, compared to 7.37–7.83 kW for blends. Relative to Euro diesel, the average reductions in BP for all blends are in the range of 5.53–11.15%.

Biodiesel addition decreases BP output. Butanol addition further reduced BP compared to biodiesel–diesel blends. This reduction is due to the difference in heating values of the fuels [19,57], and the higher viscosities and higher oxygen content of both biodiesel and butanol. Furthermore, it has been reported that uneven combustion characteristics of blended fuels decreased engine BP[58–61]. The high density and kinematic viscosity of biodiesel caused poor spray characteristics in the injector, leading to lower BP [61].

### Brake torque

Figure 7 illustrates the variation of brake torque at full load with respect to the tested fuels at various engine speeds. The brake torque increases gradually up to a maximum value at 2000 rpm, and then falls at 2500 rpm. This is due to the mechanical friction loss as well as the lower volumetric efficiency of the engine due to increasing speed [58,59].

The maximum brake torque of 47.87 N.m was recorded for Euro diesel at 2000 rpm. The average brake torque for Euro diesel is 44.39 N.m, compared to 40.15-42.5 N.m for safflower blends. Relative to Euro diesel, the average reductions in brake torque for all blends are in the range of 4.25–9.56%.

Biodiesel addition decreases brake torque. Butanol addition further reduced brake torque compared to biodiesel–diesel blends. This reduction is attributed to the higher kinematic viscosities and lower energy

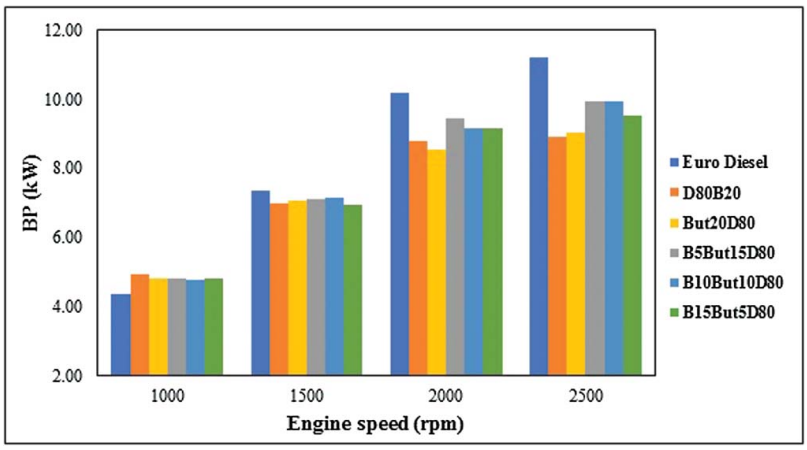



**Figure 6.** Brake power (BP) versus engine speed at full load.

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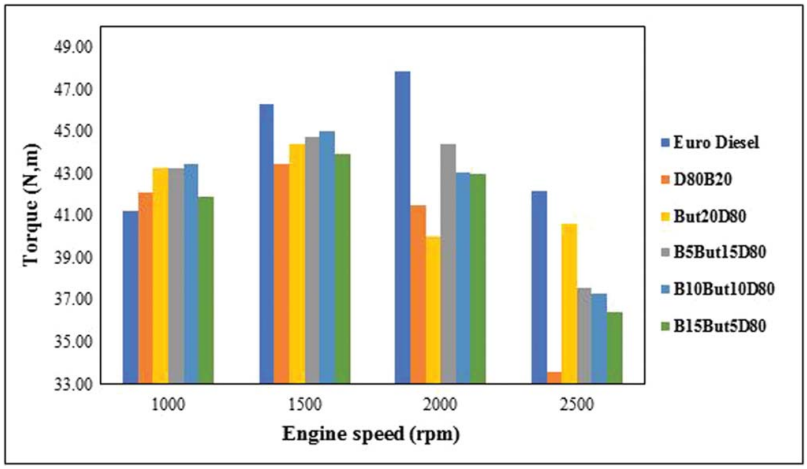



**Figure 7.** Brake torque versus engine speed at full load.

contents of both biodiesel and butanol [58,60,61]. The high density and kinematic viscosity of biodiesel caused poor spray characteristics in the injector, leading to lower brake torque [61].

### *Brake specific fuel consumption (BSFC)*

Figure 8 illustrates the variation of BSFC at full load with respect to the tested fuels at various engine speeds. The minimum BSFC of 254.16 g/kWh was recorded for Euro diesel at 2000 rpm. The average BSFC for Euro diesel is 285.22 g/kWh compared to 284.20-301.38 g/kWh for all safflower blends. Relative to Euro diesel, the average increase in BSFC for all blends is in the range of 2.33–5.67%.

Diesel has higher HHV and requires a lower mass than biodiesel and butanol to extract the same engine output [62]. Biodiesel addition increases BSFC. Butanol addition further increased BSFC compared to biodiesel–diesel blends. This increase is due to the higher density and kinematic viscosity and lower calorific value of biodiesel and butanol, leading to more fuel being delivered into the combustion chamber to produce the same amount of power [57–61].

### *Emissions performance analyses*

The emissions performance parameters of CO, HC, $NO_x$ emissions and exhaust gas temperature of six fuel samples (Euro diesel, D80B20, But20D80, B5But15D80, B10But10D80 and B15But5D80) were studied in this work. The following sections discuss the results of these parameters.

### *CO emissions*

Carbon monoxide (CO) emission is a byproduct of incomplete combustion of any carbon-containing fuels due to either insufficient oxygen or low gas temperature [57]. Therefore, it is an intermediate combustion product if it is not completely converted to $CO_2$ to indicate complete combustion [63]. CO emissions in exhaust gases represent the lost chemical energy that is not fully used in the engine [19]. Figure 9 shows the

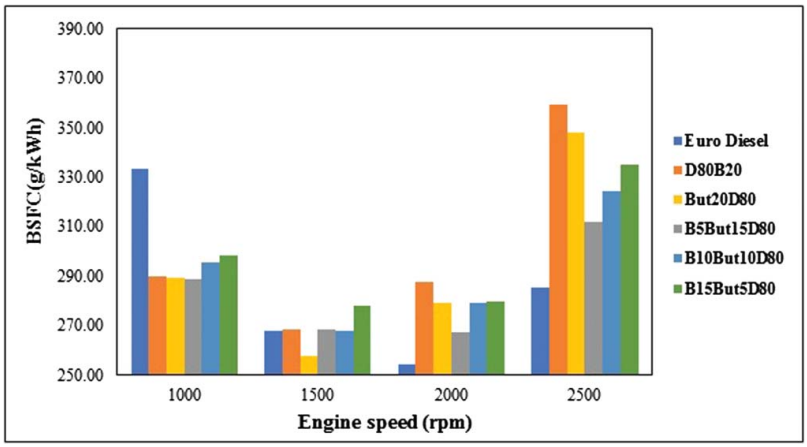



**Figure 8.** Brake specific fuel consumption (BSFC) versus engine speed at full load.

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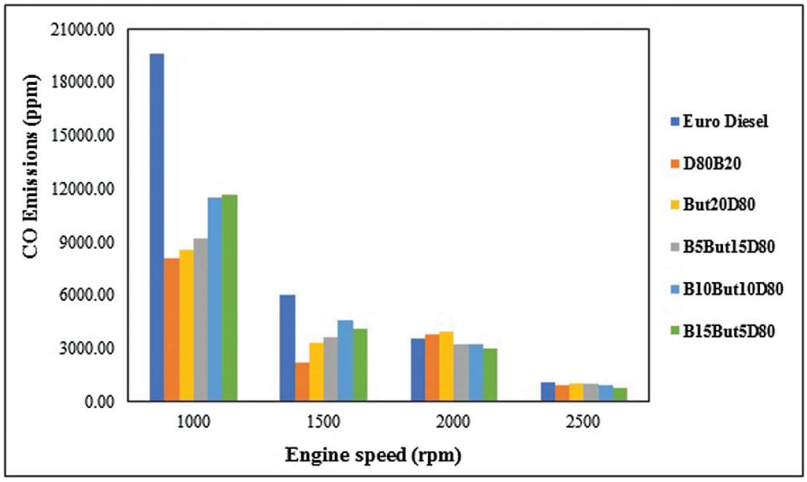



**Figure 9.** CO emissions versus engine speed at full load.

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results of CO emissions at full load with respect to the tested fuels at various engine speeds. The minimum CO emissions for all blends occurred at 2500 rpm. It can be observed that CO emissions decreased with increasing speed. The average CO emission for Euro diesel is 7581.5 ppm, compared to 3776–5074.25 ppm for safflower blends with Euro diesel and butanol. Relative to Euro diesel, the average decrease in CO emissions for all blends is in the range of 33.07–50.19%.

This decrease is due to the fact that both biodiesel and butanol have higher oxygen content (12% for biodiesel, whereas alcohol contains up to 34%). This allows more carbon molecules to burn and thus produces more complete combustion [57,59,60].

Moreover, the lowest CO emissions were recorded for biodiesel–diesel blends. As the butanol concentration in the biodiesel blends increases, CO emissions slightly increase as compared to biodiesel. These findings are in good agreement with the literature, which states that butanol–diesel and butanol–biodiesel–diesel blends reduce CO emissions compared to diesel [57,60,62,64–66].

### *HC emissions*

HC emissions are formed as a direct result of incomplete combustion [19,62,63]. HC emissions are caused by local flame extinction at cylinder walls, and are increasingly important for the 'lean outer flame zone' where combustion temperatures are lower [61]. Some operating variables such as speed, air–fuel ratio, temperature of mixture, load and mode of operation affect the production of HC emissions [63]. Combustion chamber deposit and misfire are also causes of excessive HC [67]. Figure 10 shows that the average HC emissions of safflower blends and its blends with Euro diesel and butanol are lower than those of Euro diesel. The minimum HC emissions for all blends occurred at 2500 rpm. Minimum HC emissions were recorded for D80B20 (1557.88 ppm) at 2500 rpm.

At all speeds, the average HC emission for Euro Diesel is 3666.5 ppm, compared to 1557.88–2358.38 ppm for safflower blends and its blends with Euro diesel and butanol. Relative to Euro diesel, the average decrease in HC emissions is in the range of 35.68–57.51% for all blends.

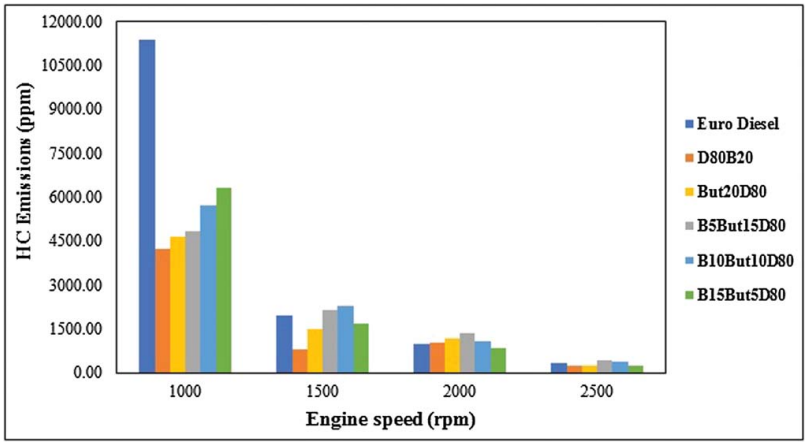



**Figure 10.** HC emissions versus engine speed at full load.

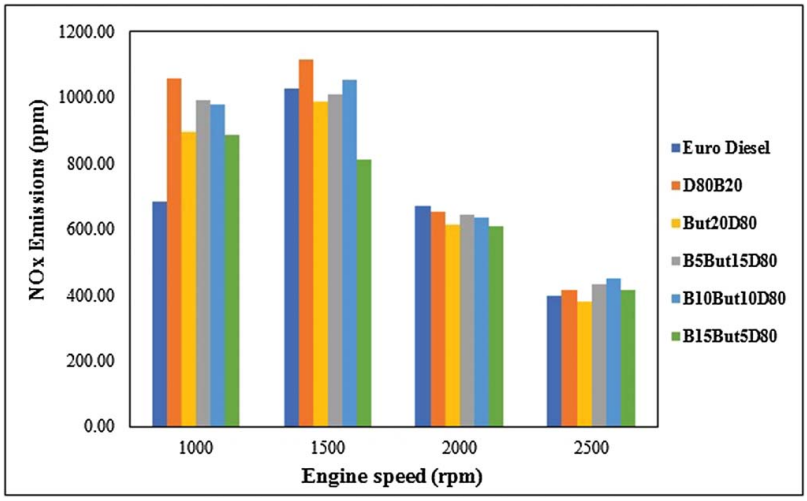



**Figure 11.** $NO_x$ emissions versus engine speed at full load.

Biodiesel produces the lowest HC emissions. As butanol is added to biodiesel, HC emissions slightly increase. However, this level is still lower than the HC emissions produced by pure Euro diesel. This is because biodiesel and butanol have higher oxygen content, which enhances complete combustion [19,57,59–63].

Moreover, these findings are in good agreement with the literature, which states that a decrease in HC emissions occurs when substituting diesel fuel with biodiesel and butanol [60, 62, 64–66].

### *$NO_x$ emissions*

Nitric oxide (NO) and nitrogen dioxide ($NO_2$) are usually grouped together as $NO_x$ emissions. NO is the predominant product [63]. $NO_x$ emission is the most important problem in CI diesel engines [19]. $NO_x$ formation is affected by adiabatic flame temperature and pressure during combustion [59–61]. During combustion, the high adiabatic flame temperature in the cylinder walls, besides the availability of oxygen, causes the nitrogen and oxygen in the air to combine and form $NO_x$ [19]. Figure 11 shows the variation of $NO_x$ emissions of all blends. For all blends, the minimum $NO_x$ emissions occurred at 2500 rpm. $NO_x$ emissions decreased with increasing speed. The average $NO_x$ emission for Euro Diesel was found to be 695.25 ppm, compared to 680–809.13 ppm for safflower blends and its blends with Euro diesel and butanol. Relative to Euro diesel, the average increase in $NO_x$ emissions for all blends is in the range of 3.24–16.38%. This is because biodiesel addition causes an increase in $NO_x$ emissions due to the high CN of biodiesel which leads to a shorter ignition delay [31,61]. However, $NO_x$ emissions slightly decreased with the addition of butanol to biodiesel–diesel blends. This is because butanol, as an alcohol, increases the overall oxygen content (21.59%) while decreasing the CN (17) of fuel blends. This creates a cooling effect and leads to longer ignition delay and a higher combustion temperature at the premixed stage of combustion. Lower combustion temperatures are produced due to the lower calorific value and CN of butanol [57,62,68].

### *Exhaust gas temperature (EGT)*

Figure 12 shows that the average EGT of both blends are higher than that of Euro Diesel. The maximum EGT occurred at 2500 rpm for all blends. Maximum EGT was recorded for D80B20 (619.9°C) at 2500 rpm. The average EGT for Euro Diesel is 460.7°C, compared to 461.18–492.54°C for all safflower blends. Relative to Euro diesel, the average increase in EGT for all blends is in the range of 0.1–6.91%.

Biodiesel addition causes an increase in EGT when blended with diesel. However, the addition of butanol causes lower EGT mainly because butanol has a low energy content (32.01 MJ/kg), low CN (17) and high latent heat of vaporization (592 kJ/kg) compared to diesel or biodiesel. Apart from that, the introduction of butanol into fuel blends increases the oxygen content while decreasing the overall energy content, both of which cause a cooling effect that lowers combustion and exhaust temperatures [61,62,68].

## Conclusions and recommendations

This study aimed to produce and characterize biodiesel obtained from safflower oil. Some important physical and chemical fuel characteristics of the crude oil, methyl ester, and blends with Euro diesel and butanol were compared and determined. Moreover, FT-IR, TGA, DSC and UV-Vis analyses were conducted. Finally, engine and emissions performance parameters such as BP, brake torque, BSFC, CO, HC, $NO_x$ and EGT were also studied. SME satisfied both EN 14 214 and ASTM D6751 standards regarding the kinematic viscosity, flash point and density. However, CN only satisfies the ASTM D6751 standard. Both iodine and saponification

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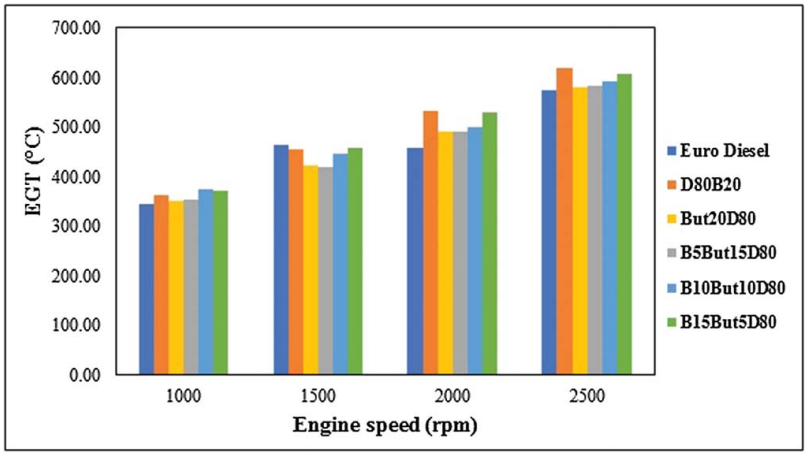



**Figure 12.** EGT versus engine speed at full load.

values were found to be extremely high. Oxidation stability also fails to satisfy the limits of both EN 14 214 and ASTM D 6751 standards. This is due to the high level of unsaturated fatty acid (91.05%) in SME.

The DSC analyses showed that SME crystallizes (−7.42°C) before diesel (−11.49°C) and butanol (−15.13°C), while oxidative degradation occurred in the temperature range 130–320°C for all blends. The results of engine performance analyses indicate that reductions in BP, HC and CO coupled with increases in BSFC, $NO_x$ and EGT were observed for all blends at full load compared to Euro diesel.

In general, this experimental work supports that blending safflower methyl ester with Euro diesel and butanol as ternary blends appears to produce good alternatives to biodiesel–diesel blends, which can be used as substitutes for fossil diesel in conventional CI diesel engines. It is expected that the role of butanol in CI engines will grow. This is especially true if butanol is produced on a mass scale as a biofuel. Moreover, combustion characteristics of all blends should be further studied.

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