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Experimental Investigation of Engine Performance for 2nd Generation Biodiesel Derived from $Mg_2Zr_5O_{12}$ Catalyst

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Abstract: In the present study, experimental analyses were conducted by using biodiesel derived from second-generation feedstock. In terms of cost and accessibility, second-generation feedstock has gained more attention due to its environmental approach. Waste-cooking-oil-derived methyl ester was produced through a transesterification reaction in the presence of a synthesized magnesium zirconate ($Mg_2Zr_5O_{12}$) heterogeneous catalyst. This trans-esterified waste cooking oil (WCO) was used as biodiesel and was blended with diesel in 10%, 20%, 30%, 40%, and 50% by volume ratio for further analysis. The fuel properties of pure and blended biodiesel were investigated in terms of flash point, density, kinematic viscosity, and lower heating value as per the American Society for Testing and Materials (ASTM) D-6751 standards. For each blended fuel, the engine performance and gaseous emissions trend with engine loads of 0, 3, 6, 9, and 12 kg were measured on a Kirloskar TV1 IC engine. The results indicated that the 40% blended biodiesel has the maximum brake thermal efficiency (BTE) of 19.13% and exhaust gas temperature (EGT) of 6.98% increment, also showing an increase with respect to engine load. On the other hand, brake-specific fuel consumption (BSFC) was highest for 40% blending as 36.48% increase, and that decreases with the increase in engine loads. Significant reductions in carbon monoxide (CO) and unburned hydrocarbon (HC) emissions were observed for 40% blended fuel and were 34.78% and 38.1% reduction, respectively. CO and HC emissions decreased with respect to the engine load. Meanwhile, reverse trends for carbon dioxide (CO_2) and nitrogen oxide (NO_x) have been observed as 14.57% and 27.85% increases for 100% biodiesel. CO_2 and NO_x increased with increase in engine load. The mass balance and environmental factor of crude and purified biodiesel were studied to show the environmental suitability of synthesized product. Overall, the results showed that the blended biodiesel can be used as a substitute and has an advantage over diesel fuel. The main contribution derived from this work is to improve engine performance and gaseous emission by using blended biodiesel derived from a recyclable heterogeneous catalyst and waste-cooking-oil feedstock.

Keywords: second-generation biodiesel; E-factor; emission; $Mg_2Zr_5O_{12}$; performance; sustainability

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1. Introduction

The universal fact is that we need to stop consuming fossil fuels instantly to control carbon emission and eventually climatic change in order to minimize global warming. As per BP's Energy Outlook, the global demand for energy will rise drastically up to thrice by the end of 2040, due to living standard progresses, especially in India, China, and across Asia.

Around 80% of the population lives in average energy intake countries, that is, around <100 GJ per person. To fulfil this demand, the world would need an extra 65% of energy by 2040, as compared to the present situation. We are facing the dual challenge of attaining less carbon with more energy and an easily available energy source so that, globally, carbon emission could drop by 45% through 2030 [1]. The increasing cost of fossil fuels and environmental concerns have gained imperative consideration to search for substitute fuel. Among various alternative fuels, biodiesel has gained more attention due to its eco-friendly behavior. While considering environmental pollution, many countries have ignored this issue liable for climate change such as transportation sector contributing significant amount of GHG emission, particularly in developed, also in developing, countries. As compared to conventional diesel, biodiesel offers a better solution to reduce greenhouse gases' emission by up to 50%. Biodiesel production can contribute to decrease any country's dependency on the imported oil reservoir because it can be produced domestically and can be utilized in a diesel engine with further modifications in the diesel engine or in fuel. In terms of fluctuation in price for conventional diesel, biodiesel will be reasonable and, above all, can be extremely vital for environmental and social welfare.

One of the initiatives has been taken by original equipment manufacturers, including Volkswagen, DaimlerChrysler, and Mercedes Benz in Germany, via supporting biodiesel usage with a prolonged warranty period. For example, DaimlerChrysler has plans to increase the engine's warranty coverage if the customer uses 20% blended biodiesel. This will encourage the adoption of biodiesel for automotive sectors. In certain European nations, for example, France and Germany, the government has set regulations for 5% to 10% biodiesel blended fuel norm for vehicles. On the other hand, the Asia-Pacific region produces large quantities of raw materials for biodiesel production; thus, the biodiesel market is at a growing phase as compared to the European and North American market, and this motivates the shifting of manufacturers toward Asia-Pacific, due to the reliable raw materials. Therefore, worldwide shifting toward developing regions for biodiesel production is a center of attraction [2]. According to data from the biodiesel 2020 world market outlook, global biofuel fiats prevailing in different countries' biodiesel level vary from 1 to 2%. The topmost biodiesel-producing countries are the USA, Brazil, Germany, Indonesia, and Argentina, whereas Europe is the leading biodiesel consumer, with 54% of the total world's demand, followed by North America at 17%, Latin America at 14%, and Asia at 12%, respectively [3].

Biodiesel has an enormous capability to replace conventional fossil fuels to fulfil energy demands. Even though biodiesel has several benefits, such as low carcinogenic aromatic carbon and less toxic contents, it also has some drawbacks, including a lower calorific value and higher viscosity, that are major obstacles for the complete replacement of diesel in engines. Several works have been reported to improve biodiesel efficiency so that it can fit a diesel engine. In most of the cases, the proportion of biodiesel to diesel differs from country to country. The properties and composition of biodiesel vary from diesel fuel and lead to differences in performance, emission, and combustion from the engine. From the literature, it has been understandable that biodiesel helps in reducing GHG emissions due to the nonappearance of aromatic compounds and sulfur; it is also renewable, nontoxic, and has high oxygen content that decreases emissions associated with poor combustion [4]. However, in some cases, the use of biodiesel shows drawbacks such as the extensive emission of oxygenated hydrocarbons, a higher specific fuel consumption, poor flow at low temperatures, and an expensive production [5]. The NO_x emission has shown increases for biodiesel due to excess oxygen content, as well as a greater adiabatic flame temperature [6], whereas few researchers have observed contradictory results for biodiesel that are major obstacles for direct application in diesel engines.

In the present study, we referred to some of the literature based on different feedstock for biodiesel emission and performance data. For instance, Teja et al. [7] reported B20 blends of three biodiesels derived from cashew nutshell (CHNOB (B20)), jackfruit seed (JACKSOB (B20)), and Jamun seed (JAMNSOB (B20)) oils. In the JAMNSOB (B20) blend, BTE and NO_x increased by 4.04% and 0.56% respectively. However, HC and CO decreased by 5.12% and 6.25%, respectively, compared with the jackfruit B20 blend. Nguyen et al. [8] studied fish-oil biodiesel in different ratios on a single-cylinder common rail diesel engine. They observed that BSFC and NO_x emissions increased with reducing HC and CO emissions for blended biodiesel. Sharma et al. [9] have reported coconut, castor, jatropha, palm, karanja, and waste-cooking-oil biodiesel to study combustion and emission characteristics in a CI engine. They concluded that highly saturated and poly-unsaturated fatty acid gave a better performance than mono-unsaturated biodiesels. Can et al. [10] observed combustion, performance, and emissions of biodiesel from WCO for a single-cylinder diesel engine by considering different engine loads. They concluded that the addition of biodiesel increased the BSFC and caused a reduction in the BTE. In addition to this, the CO, HC, and smoke emissions dropped, whereas the NO_x emission increased. Behcet et al. [11] analyzed fish-oil biodiesel (FOB), rapeseed-oil biodiesel (ROB), hazelnut-oil biodiesel (HOB), and waste-cooking-oil biodiesel (WCOB) for diesel engine performance and emission characteristics. They observed that the torque power and break power of all biodiesels improved from 13.11 to 20.12% and 9.3 to 20.58%, respectively, and the BSFC of all biodiesels improved by 2.36–9.92%, with respect to diesel. For the emissions, they reported that CO emissions were lowered up to 29.67%. In addition to this, the average exhaust gas temperature was higher, so that NO_x emissions were raised by 4.76–9.77% for all biodiesels. Amongst all biodiesels, better a performance and better emissions were observed for fish-oil biodiesel. Rahman et al. [12] observed a reduction in CO and HC emission, whereas they observed an increment in NO_x emissions for blending compared to pure diesel. As compared with palm biodiesel, the emissions of CO and HC were higher in Jatropha, and blends of 5%, 10%, and 20% were studied. Hassan et al. [13] experimentally studied the effect of Australian beauty leaf tree-derived biodiesel. They concluded that CO and NO_x emissions decreased with biodiesel concentration increment, whereas the reverse trend was obtained for CO_2 emissions. They observed that 10% Australian beauty leaf-tree-oil-derived biodiesel blend gave a better performance. Banapurmath et al. [14] studied honge-oil-derived methyl ester and its blends in a single-cylinder diesel engine. They reported that the BTE and EGT decrease with the incrementation of biodiesel content. However, the emissions of CO, HC, and smoke decreased and the NO_x emissions increased for 20% blended fuel.

Among various feedstocks, our focus was on the second generation of feedstocks, namely waste cooking oil (WCO), for the present work. WCO is left over from used edible oil and cannot be reused for further cooking purposes. WCO affects and disturbs marine life by polluting water resources, aquatic life, and human health, as well as the environment. To overcome these problems, it is essential to utilize this WCO for worthy reasons such as the making of soaps and lubricants, or as a feedstock for biodiesel. Due to rapid growth in the worldwide population, the consumption of and demands for edible oil are also rising. That ultimately caused WCO generation and disposal in water bodies or sewage, and, thereby, it is responsible for environmental pollution. As there are many resources available for this waste-oil production, it can be easily available and will be cheaper; thus, the biodiesel production from WCO is more economical and environmentally sustainable. Mandal et al. [15] reported biodiesel production from multiple fry soya bean oil for agricultural CI engine and observed that emission and engine performance were affected based on frying time. They also reported that the use of WCO is a potential replacement for diesel. Ali et al. [16] have reported that the biodiesel produced from WCO are more eco-friendly, as well as economical, for the long term. One should have an appropriate setup and continuous source of feedstock for the mass production of biodiesel. Li and Yu [17] reported that waste-cooking-oil biodiesel has better quality and higher yield as compared to other feedstock and promoted the collection of feedstock from households and restaurants, so that WCO can be obtained in bulk quantities for biodiesel production.

Even though there are numerous studies based on engine performance and gaseous emission for blended biodiesel, there is still a need for the performance improvement of fuel. To meet this gap, we used a heterogeneous catalyst for biodiesel production and analyzed various characteristics of diesel engine. Since heterogeneous catalysts are non-corrosive in nature, and due to their ease of separation from product and reusability, it is advantageous to use them over homogeneous catalysts. Our previous study was based on the synthesis, characterization, and application of magnesium zirconate ($Mg_2Zr_5O_{12}$) for biodiesel production and process optimization with response surface methodology (RSM) [18]. The present work is an extended study of our previous work; in this study, we produced a large-scale biodiesel from WCO feedstock by using a $Mg_2Zr_5O_{12}$ catalyst and performed a further investigation. The present study aimed to examine diesel engine performance and gaseous emissions at various engine loads of 0, 3, 6, 9, and 12 kg for 10%, 20% 30%, 40%, and 50% blended biodiesel, in addition to pure biodiesel. Performance and emission analyses have never been conducted by using $Mg_2Zr_5O_{12}$ heterogeneous catalyst-based biodiesel and its blending. The objective of the present study was to investigate the effect of blending and loading on engine performance, such as BTE, BSFC, and EGT, besides the emission of gases such as CO, CO_2, NO_x, and UHC to improve the overall performance through the combustion of fuel in a diesel engine. Furthermore, the present work studied the mass balance and environmental factors, in addition to a sustainability perspective, for biodiesel production.

Initially, we synthesized WCO-derived biodiesel by using optimized parameters of reaction temperature, molar ratio (methanol:oil), reaction time, and catalyst concentration from our previous study [18]. Then we purified and blended the biodiesel for further investigation of physicochemical properties, engine performance, and gaseous emission. We discussed in detail the influence of the engine load and blending ratio on engine performance for BTE, BSFC, and EGT. We also showed trends for gaseous emission of CO, CO_2, NO_x, and UHC, depending on engine loads and blended ratio. Moreover, we compared obtained data with the reported literature and summarized for engine performance and emission from waste-cooking-oil feedstock. Finally, the environmental factor was calculated for crude biodiesel and purified biodiesel, showing that the complete process is viable and sustainable.

2. Materials and Methods

2.1. Biodiesel Production

Magnesium zirconate ($Mg_2Zr_5O_{12}$) as a heterogeneous catalyst was synthesized and studied in detail for biodiesel production, recyclability, and successfully, as reported in our previous work [18], and summarized in Table 1.

Table 1. Summarized characterization of $Mg_2Zr_5O_{12}$ catalyst [18].

Analysis	Purpose	Result
Thermogravimetric analysis (TGA)	To study decomposition behavior of material	Calcination temperature 900 °C
X-ray diffraction (XRD)	To detect crystallinity of a catalyst	The XRD peaks corresponding to standard JCPDS data No: 80-0967 indicates rhombohedral $Mg_2Zr_5O_{12}$ phase
Attenuated total reflectance–Fourier-infrared spectra (ATR–FTIR)	To detect the presence functional group in catalyst	The intense absorption peaks at 835, 620, 530, and 490 cm^{-1} due to Zr-O, Zr-O-Zr, and Mg-O stretching frequency
Scanning electron microscopy (SEM)	To explore surface morphology of catalyst	Agglomeration and non-uniform particles
Energy dispersive X-ray spectroscopy (EDS)	To analyze elements in catalyst	Catalyst contains 10.5 wt.% Mg, 63.25 wt.% Zr, and 26.25 wt.% O content
Surface area	To measure the surface area of catalyst	Single point surface area of catalyst at P/Po 0.310432720 was 6.7842 m^2/g; Langmuir surface area was 10.1937 m^2/g and BET surface area was 6.7976 m^2/g
Basicity (Hammett indicator benzene carboxylic acid titration method)	To calculate basicity of catalyst	Total basicity of catalyst was 1.05 mmol/g
Optimization reaction for FAME conversion	To detect the optimum reaction parameters	Optimum operating reaction conditions was 18:1 methanol:oil molar ratio, 2.5 wt.% of catalyst and 150 min of reaction time
Reusability of catalyst	To calculate reusability of the catalyst	FAME conversions was 75.78% after 7th run

For the present work, we used the same optimized reaction condition for the WCO transesterification reaction. A maximum conversion of 98.09% FAME was obtained by using operating parameters of 18:1 M ratio (methanol: oil), 2.5 wt.% of catalyst, and 65 °C reaction temperature for 150 min. The obtained FAME was purified by washing with hot water twice, followed by heating in oven at 120 °C for 30 min to remove excessive moisture content for further study. The mass balance and E-factor for biodiesel were also studied. The schematic representation of the experimental approach for the present study is as shown in Figure 1.

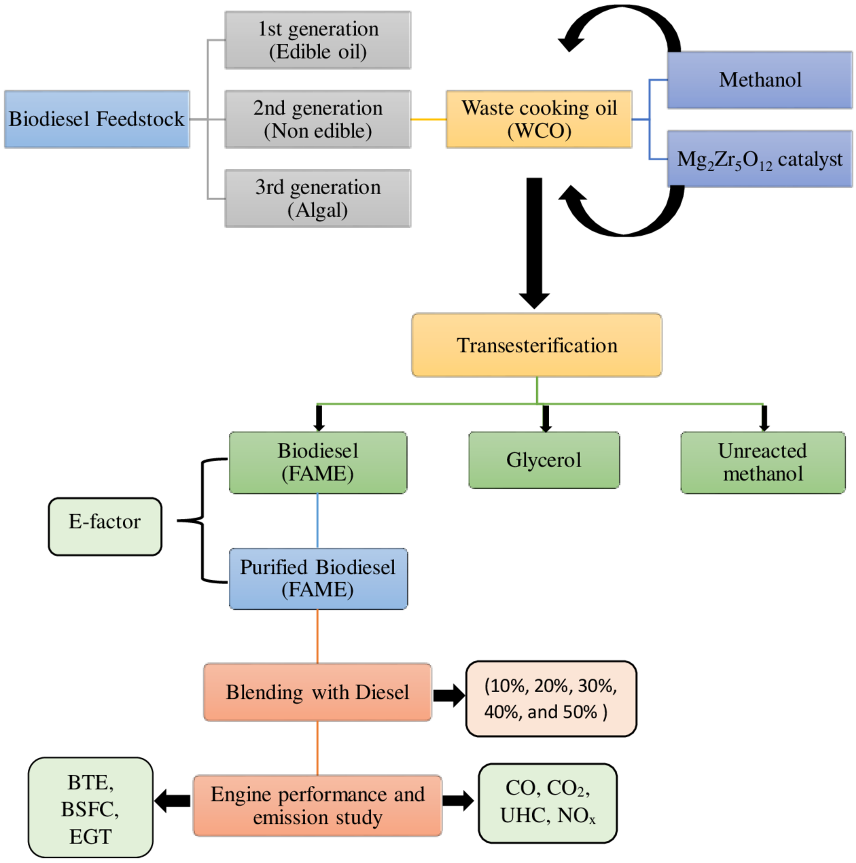

Figure 1. Flowchart of the experimental approach for the present study.

2.2. *Blending of Biodiesel and Fuel Properties*

To study the effect of biodiesel on engine performance and gaseous emission of diesel engine, WCO methyl ester was blended with the diesel fuel in ratios of 00%, 10%, 20%, 30%, 40%, and 50%. Blending was performed at 40 ± 5 °C in a water bath by mixing appropriate amounts of diesel at 300 rpm speed for 25 min. Physicochemical properties of these blended fuels, including flash point, density at room temperature, kinematic viscosity cSt at 40 °C, and lower heating value calculated and compared with neat diesel fuel as per ASTM D6751 standard, are shown in Table 2.

Kinematic viscosity of neat diesel fuel WB00% was observed to be 2.30 cSt at 40 °C and increased by increments in blending, and, for neat biodiesel WB100%, it was 4.02 cSt. Density and flash point also increased with blending and were highest for WB100% as 0.880 g/cm^3 and 142 °C, whereas, for WB00%, it was 0.840 g/cm^3 and 58 °C, respectively. Lower heating value decreased with blended ratio. For WB00%, it was observed to be 43.45 MJ/kg, and for WB100%, it was 38.81 MJ/kg. These changes in properties play a vital role for performance and emission of diesel engine, as shown and discussed in the following section.

Table 2. Physicochemical properties of petrol–diesel and blended biodiesel.

Properties	ASTM Test Method	WB00%	WB10%	WB20%	WB30%	WB40%	WB50%	WB100%
Flash point (°C)	D 93	58	65	70	77	85	91	142
Density (g/cm^3) at room temperature	D 1298	0.840	0.842	0.845	0.847	0.850	0.853	0.880
Kinematic viscosity (cSt at 40 °C)	D 445	2.30	2.44	2.69	2.86	3.08	3.19	4.02
Lower heating value (MJ/kg)	D 4809	43.45	42.87	42	41.54	40.87	40.31	38.81

(WB00%—diesel fuel; WB10%—biodiesel 10% + diesel 90%; WB20%—biodiesel 20% + diesel 80%; WB30%—biodiesel 30% + diesel 70%; WB40%—biodiesel 40% + diesel 60%; WB50%—biodiesel 50% + diesel 50%; WB100%—pure biodiesel).

2.3. Engine Performance and Exhaust Emission

The engine performance and emission characteristics of single cylinder diesel engine were analyzed by comparing diesel and waste-cooking-oil biodiesel (WB) blends. In the present work, a four stroke IC diesel engine made by Kirloskar TV1 with one cylinder was used for performance and emission study of diesel and blended biodiesel. The diesel engine specifications, dynamometer, and engine loads are shown in Supplementary Materials Table S1. The engine was operated at a power of 3.5 kW and a speed of 1500 rpm. Cylinder diameter and stroke length were 87.5 mm and 110 mm, respectively, at a CR ratio of 18:1. All measurements were performed at room temperature.

Consequential engine performance parameters, such as brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), and exhaust gas temperature (EGT) for diesel and its blends with WCO biodiesel were calculated. An exhaust gas analyzer Neptune Opax2000 was used to investigate emissions of pollutants such as CO, CO_2, UHC, and NO_x. Emissions were checked at a CR of 18 for diesel and WCO biodiesel blending (WB) of 10%, 20%, 30%, 40%, 50%, and 100% at different engine loadings of 0, 3, 6, 9, and 12 kg. For these measurements, 0 kg load indicates an ideal condition without any load to the engine, and, further, the higher values with increasing loads of 3, 6, 9, and 12 kg to engine, respectively. Fuel flow rate was constant for all measurements. The load values used to conduct the experiment were 0, 3, 6, 9, and 12 kg, corresponding to the torque values of 0, 5, 10, 15, and 20 Nm, respectively. Detailed specification of exhaust gas analyzer is shown in Supplementary Materials Table S2.

Experimental setup for engine performance and emission measurement, and the schematic diagram of experimental setup are represented as Figures 2 and 3.

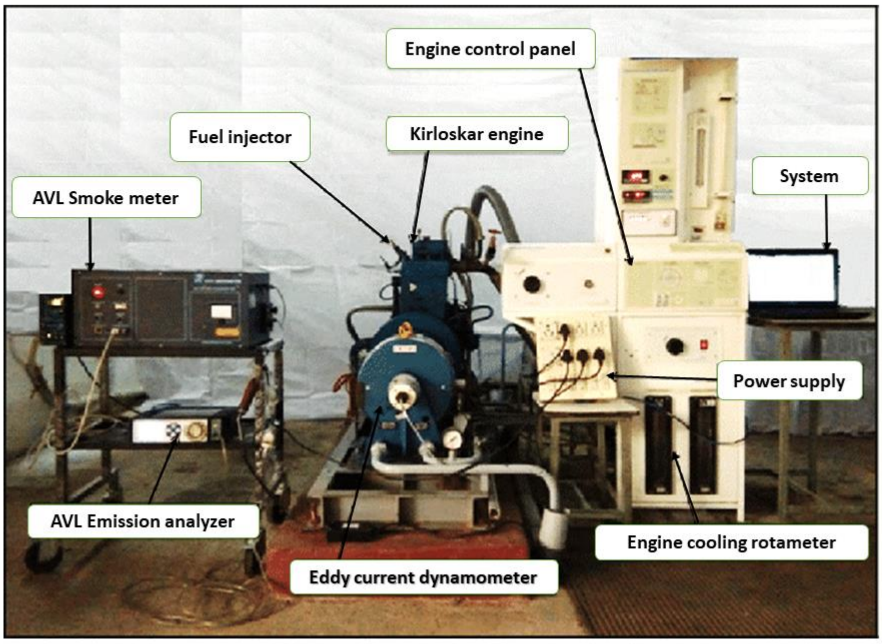

Figure 2. Experimental setup for engine performance and emission measurement.

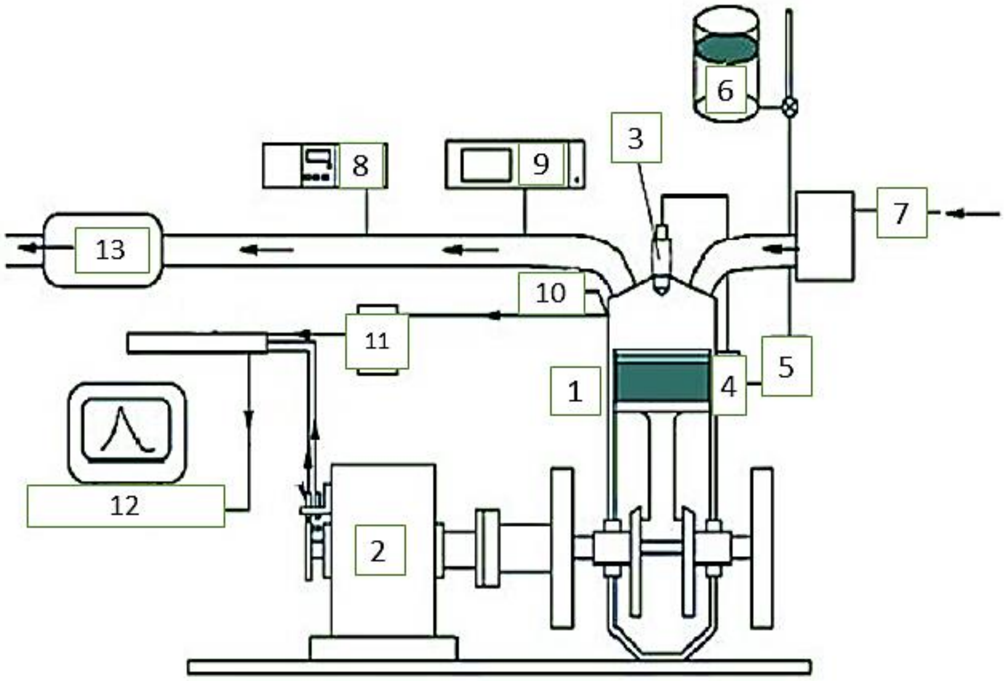

Figure 3. Schematic diagram of the experimental setup (Kirloskar TV1 engine, 1; eddy current dynamometer, 2; fuel injector, 3; fuel pump, 4; fuel filter, 5; fuel tank, 6; air filter, 7; AVL smoke meter, 8; AVL emission analyzer, 9; pressure transducer, 10; charge amplifier, 11; screen, 12; and exhaust silencer, 13).

2.4. Uncertainty Analysis

The percentage uncertainty and accuracy for BTE, BSFC, EGT, CO, CO_2, NO_x, and UHC were evaluated and are shown in Table 3.

Table 3. Uncertainty and accuracy of parameters.

Parameter	Uncertainty (%)	Accuracy
BTE	0.89	±0.2%
BSFC	0.9	±0.01 kg/kWh
EGT	1.0	±1 °C
CO	0.5	±0.06%
CO_2	0.45	±0.5%
NO_x	0.6	±3 ppm
UHC	0.5	±12 ppm

The overall uncertainty was calculated by using Equation (1) [19] as ±1.91%:

$$\text{Uncertainty }(\%) = \pm\sqrt{\begin{array}{c}(\text{uncertainty of BTE})^2 + (\text{uncertainty of BSFC})^2 + (\text{uncertainty of EGT})^2 \\ +(\text{uncertainty of CO})^2 + (\text{uncertainty of CO}_2)^2 + \\ (\text{uncertainty of HC})^2 + (\text{uncertainty of NO}_x)^2\end{array}} \quad (1)$$

3. Results and Discussion

3.1. Engine Performance

The fuels consumed in the engine were studied for engine performance, as well as their impact on the environment. Performance parameters such as brake thermal efficiency (BTE), brake-specific fuel consumption (BSFC), and exhaust gas temperature (EGT) obtained with 10%, 20%, 30%, 40%, 50%, and 100% blended biodiesel are found to be influenced through fuel blends besides 0, 3, 6, 9, and 12 kg of engine loading.

3.1.1. Effect on BTE

The brake thermal efficiency (BTE) of the engine is a direct relation of brake power and energy released per unit time from the engine. The BTE is one of most important parameters for engine performance estimation. An et al. [20] have reported the use of waste cooking biodiesel and its blending performed on four stroke, four cylinder, and a direct injection Euro IV diesel engines at various speeds and load conditions. They reported an improved BTE for the blended biodiesel compared diesel at full loading, whereas, at 25% of load condition, the result was reversed. This could be due to the low equivalence ratio of fuel and air for biodiesel at 25% load that was unable to turn its oxygenated nature. More kinematic viscosity of biodiesel was responsible for dominating atomization, and mixing with air led to poorer combustion, resulting in reduction of BTE.

The BTE of the engine fueled by pure diesel and biodiesel blending at different loads are shown in Figure 4. From Figure 4, it can be observed that efficiency increases with loading up to definite value for all blends and for diesel of 0%, 10%, 20%, 30%, 40%, 50%, and 100% blending. At 0 kg of loading, the BTE was 4.0316, 4.6517, 4.7368, 4.7744, 4.8776, 4.7416, and 4.9942%; for 3 kg of loading, the BTE was 5.2033, 5.7172, 6.6895, 6.4094, 6.9992, 6.6783, and 6.8874%; for 6 kg of loading, it was 6.0117, 6.4123, 6.6917, 6.7952, 7.1094, 6.8393, and 6.6093%; for 9 kg loading, it was 7.0581, 7.9119, 7.9930, 8.0016, 8.2881, 7.9712, and 7.8529%; and for 12 kg loading, the BTE was 8.2912, 8.599, 8.56, 8.7744, 9.1781, 8.7543, and 8.9999% for 0%, 10%, 20%, 30%, 40%, 50%, and 100% blended biodiesel, respectively.

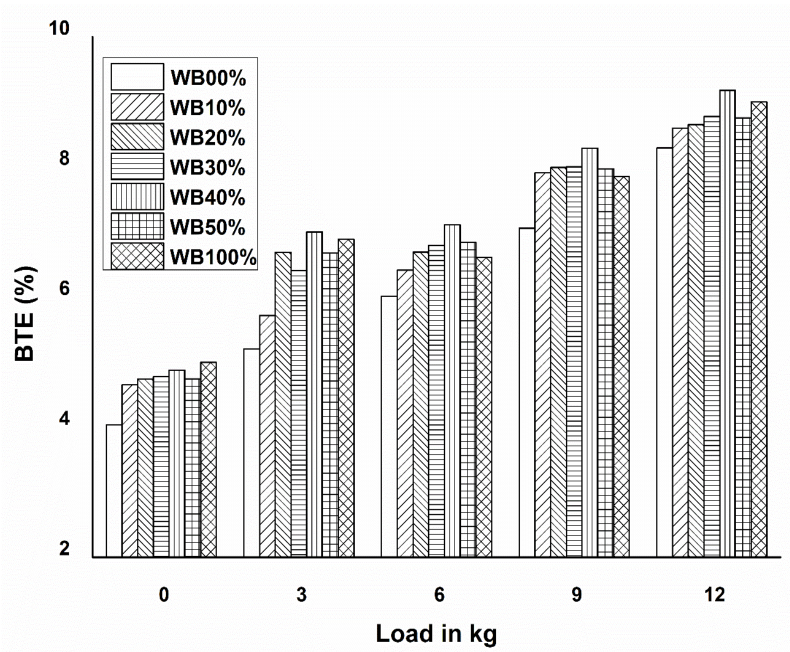

Figure 4. BTE variation against load in kg (WB00%—diesel fuel; WB10%—biodiesel 10% + diesel 90%; WB20%—biodiesel 20% + diesel 80%; WB30%—biodiesel 30% + diesel 70%; WB40%—biodiesel 40% + diesel 60%; WB50%—biodiesel 50% + diesel 50%; WB100%—pure biodiesel).

The average increments with load for the blends WB10%, WB20%, WB30%, WB40%, WB50%, and WB 100% were 8.98%, 13.61%, 13.59%, 19.13%, 14.34, and 15.52%, respectively. It can be seen that the BTE for biodiesel blend results in a higher thermal efficiency. With an increase of the engine load, the BTE also increases, and at maximum load of 12 kg, the BTE is at its highest. The rise in thermal efficiency with blending specifies complete combustion of biodiesel in comparison to diesel fuel. This may be because the viscosity effect is negligible at full load condition and, hence, thermal efficiency is higher. The maximum BTE is obtained at 12 kg of loading for WB40% blend. Figure 4 shows that the BTE was significantly improved with the engine load. The BTE is the ratio of power output vs. energy applied via fuel injection. Besides the heating value, the BTE is more appropriate for assessing the performance of various fuels. The BTE was improved and increased with engine load, since loss of power was comparatively low for higher loads. The results indicate that a significant improvement in thermal efficiency could be obtained at maximum engine load and with 40% blending.

3.1.2. Effect on BSFC

The brake-specific fuel consumption (BSFC) was used to measure the efficiency of fuel for an engine that produces rotational power output through the burning of fuel. The main parameter to investigate BSFC is the calorific value, and this value specifies engine efficiency. Utlua et al. [21] used waste frying-oil methyl ester in a four-cylinder, turbocharged, direct-injection diesel engine and observed that the BSFC was 14.34% higher in biodiesel than diesel fuel. They concluded that a higher density and lower heating value of WFO methyl ester were responsible for the increments in the BSFC rate. Zhu et al. [22] reported the BSFC for the blending of WCO biodiesel with ethanol and diesel on a four-cylinder, naturally aspirated, water-cooled, direct-injection diesel engine. They observed a BSFC increment by 13% for biodiesel due to the low calorific value in comparison to diesel. Anand et al. [23] studied WCO biodiesel blending and reported a 17% higher BSFC than mineral diesel. This was attributed to the combined effect of the lower calorific value and higher viscosity of biodiesel in single-cylinder and four-cylinder diesel engines. Aksoy [24] reported the effect of methyl ester of WFO and soybean oil on a four-stroke, single-cylinder, and air-cooled diesel engine and observed BSFC increments of 18.5% and 14.2% as compared to diesel, due to low calorific value of biodiesel.

In this study, Figure 5 shows that the BSFC of biodiesel was higher as compared to diesel at all loading conditions. The BSFC decreased with an increment in engine loads for 0%, 10%, 20%, 30%, 40%, 50%, and 100% blended biodiesel, respectively. At 0 kg of loading, the BSFC was 0.7112, 0.75, 0.7819, 0.79, 0.82, 0.83, and 0.84 kg/kWh; for 3 kg of loading, it was 0.5, 0.55, 0.59, 0.63, 0.6555, 0.62, and 0.65 kg/kWh; for 6 kg of loading, BSFC was 0.3754, 0.3902, 0.4257, 0.4535, 0.4972, 0.4876, and 0.5027 kg/kWh; for 9 kg loading, it was 0.2684, 0.3062, 0.3861, 0.4875, 0.4997, 0.4630, and 0.4987 kg/kWh; and for 12 kg of loading, the BSFC was 0.1146, 0.1349, 0.1618, 0.1852, 0.2155, 0.193, and 0.2062 kg/kWh. All data were for 0%, 10%, 20%, 30%, 40%, 50%, and 100% of blended biodiesel, respectively. The average increments for biodiesel and blending in comparison to diesel fuel were 8.23%, 19.09%, 29.27%, 36.48%, 31.73%, and 39.8% for 10%, 20%, 30%, 40%, 50%, and 100% WB, respectively.

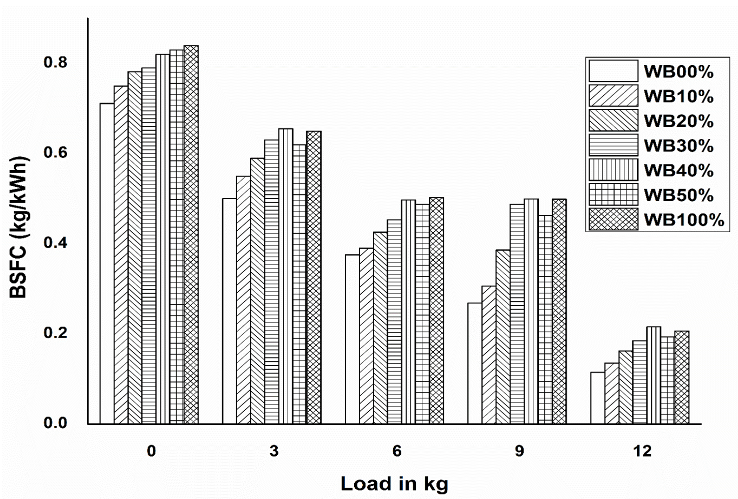

Figure 5. BSFC variation against load for biodiesel and the blends in kg (WB00%—diesel fuel; WB10%—biodiesel 10% + diesel 90%; WB20%—biodiesel 20% + diesel 80%; WB30%—biodiesel 30% + diesel 70%; WB40%—biodiesel 40% + diesel 60%; WB50%—biodiesel 50% + diesel 50%; WB100%—pure biodiesel).

It can be observed that BSFC decreases with the engine load for all blends. This is mostly due to the increase in the BTE with the engine load. The experimental results showed that, when the engine load increased from 0 to 3 and onward, it resulted in earlier combustion during compression stroke at full load, 12 kg, and this, in turn, led to a drop in engine power, as well as thermal efficiency. Figure 5 shows the BSFC at different loads. From Figure 5, we can observe that a BSFC of WB10% is close to pure diesel at maximum load. With a further increase in oxygen content for 20%, 30%, 40%, 50%, and 100%, the BSFC increases significantly, as shown in Figure 5. This is mainly due to the decrease in the lower heating value or lower calorific value of biodiesel as compared to diesel and, hence, more fuel required for the same power [25]. Another contribution is made by the high viscosity of biodiesel. When a diesel engine is operating at 0 kg of engine load, the fuel/air ratio is low, and, in that case, the oxygenated nature of the biodiesel blend is not helpful. A higher viscosity of biodiesel dominates the fuel atomization and effects on combustion.

3.1.3. Effect on EGT

The rate of heat released during combustion and its consumption to produce power were studied in terms of exhaust gas temperature (EGT). This depends on the combustion nature and heat loss related to the rate of fuel consumption. As the rate of fuel consumption increases, the quantity of heat released increases and results in more EGT [26]. In the case of biodiesel, fuel consumption is higher as compared to diesel, and the enhancement of combustion has been observed due to excess oxygen.

Lin et al. [27] studied various feedstocks from, for example, peanut, soybean, corn, rapeseed, sunflower, palm kernel, palm, and waste frying oil, on four-stroke, single-cylinder, water-cooled, and direct-injection diesel engines. They obtained a lower exhaust gas temperature for biodiesel than diesel fuel due to the lower energy content of biodiesel, which reduces the heat released during combustion. Utlua et al. [21] reported a reduction of 6.35% in the exhaust gas temperature.

Figure 6 clearly shows the EGT trend by using biodiesel blending at various load conditions at identical operating conditions. The EGT represents combustion temperatures of the inside cylinder for 0%, 10%, 20%, 30%, 40%, 50%, and 100% WB blending. At 0 kg of loading, the EGT was 160, 161, 165, 168, 171, 170, and 173 °C; for 3 kg of loading, it was 164, 164, 171, 173, 175, 173, and 176 °C; at 6 kg of loading, the EGT was 169, 172, 178, 179, 180, 181, and 183 °C; for 9 kg loading, it was 178, 180, 180, 182, 186, 185, and 189 °C; and for 12 kg loading, the EGT was 189, 190, 196, 199, 208, 209, and 211 °C for 0%, 10%, 20%, 30%, 40%, 50%, and 100% of biodiesel blending, respectively. The average increment of the EGT in biodiesel and its blending was 0.81%, 3.49%, 4.77%, 6.98%, 6.74%, and 8.37% for 10%, 20%, 30%, 40%, 50%, and 100% WB, respectively. It can be observed that the EGT increases with the engine load for all blends. The experimental results showed that, when the engine load increased from 0 to 3 and further, this resulted in better combustion, due to excessive oxygen content. Figure 6 shows that, at the maximum engine load of 12 kg, the EGT was highest. The highest EGT is reported for pure biodiesel at the maximum engine load. This increase is obvious and was due to the requirement of more fuel to generate extra power that needs to work at higher engine loadings. This can be attributed to the better combustion of biodiesel, owing to the excess oxygen content in the fuel that results in a high EGT [6].

3.1.4. Comparison of Engine Performance

From all of the abovementioned engine performance results, it can be observed that the BTE increased by around 20% for biodiesel as compared to diesel and increased with the engine load. The increase in the BSFC was up to 40% for biodiesel compared to diesel, but it decreased with the engine load. The EGT was higher for biodiesel and its blend compared to diesel, and ~8% of increment was observed for pure biodiesel, which increased with the engine load.

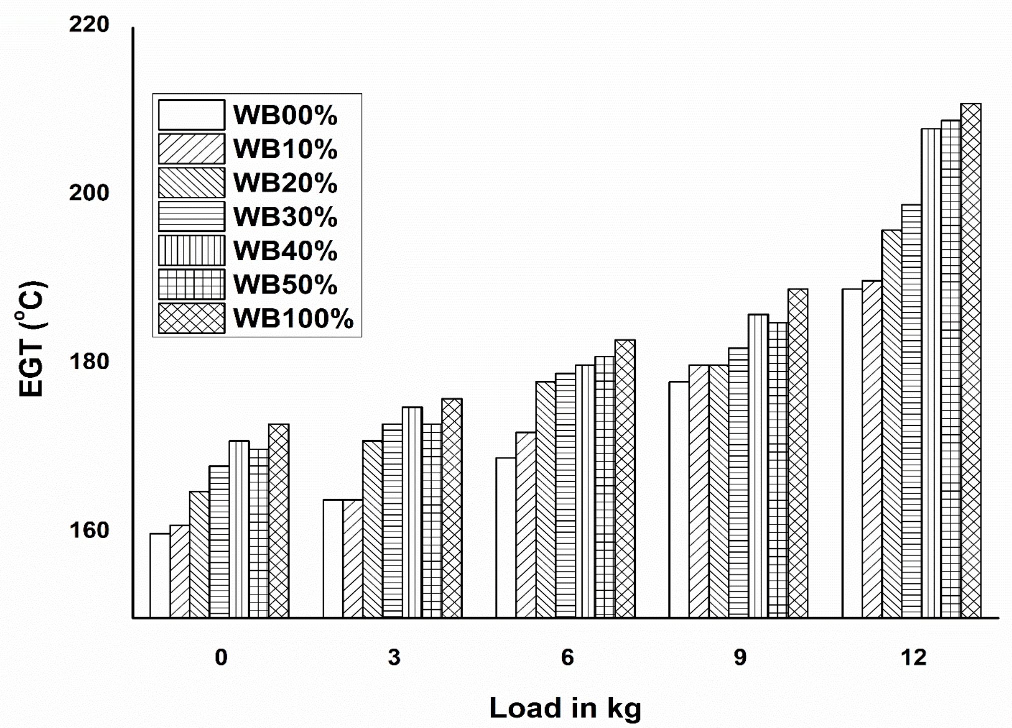

Figure 6. EGT variation against load for biodiesel and the blends in kg (WB00%—diesel fuel; WB10%—biodiesel 10% + diesel 90%; WB20%—biodiesel 20% + diesel 80%; WB30%—biodiesel 30% + diesel 70%; WB40%—biodiesel 40% + diesel 60%; WB50%—biodiesel 50% + diesel 50%; WB100%—pure biodiesel).

The engine performance at common operating conditions for WCO biodiesel at various blended ratios has been reported by many researchers, and some of the results are summarized and compared in Table 4 [20–24,27]. The increases and decreases in performance in terms of BTE, BSFC, and EGT are shown in Table 4 with respect to diesel.

Table 4. Comparison of engine performance with respect to diesel fuel based on previous work.

Sr. No.	Biodiesel and Blending	Catalyst	BTE	BSFC	EGT	References
1.	WCO (B10, B50, B100)	*	Increase	-	-	[20]
2.	WFO (B100)	NaOH	-	14.34% increase	6.35% decrease	[21]
3.	WCO (B100)	*	Increase	13% increase	-	[22]
4.	WCO (B10, B20, B40, B80, B100)	KOH	Decrease	17% increase for B100	-	[23]
5.	WFO (B100)	NaOH	-	Increase	Decrease	[24]
6.	WFO (B100)	CH_3NaO	-	18.5% increase	-	[27]
7.	WFO (WB10, WB20, WB30, WB40, WB50, WB100)	$Mg_2Zr_5O_{12}$	Increase of 8.98%, 13.61%, 13.59%, 19.13%, 14.34%, 15.52%	Increase of 8.23%, 19.09%, 29.27%, 36.48%, 31.73%, 39.08%	Increase of 0.81%, 3.49%, 4.77%, 6.98%, 6.74%, 8.37%	Present work

(* commercial biodiesel samples).

The BTE of an engine is influenced by several factors, including fuel properties, such as calorific value (lower heating value), density, and viscosity. The calorific values of biodiesel and blended biodiesel were less than those of diesel, while the density and viscosity were higher. The reduction in calorific value was responsible for the higher BSFC in biodiesel; moreover, with an increase in load, the BSFC decreases [28]. The higher and improved consumption of fuel due to excess oxygen in biodiesel results in a greater exhaust gas temperature [29].

3.2. Exhaust Emission

The exhaust emissions of CO, CO_2, NO_x, and UHC from the diesel engine with blended and pure biodiesel were observed to be affected by the blended ratio and engine load, as discussed below.

3.2.1. CO Emission

The incomplete combustion of carbon-containing constituents produces carbon monoxide (CO) through the burning of fuel within engine cylinder in the presence of oxygen. CO and CO_2 emissions are associated; if the emission of CO_2 is elevated, then the emission of CO drops and vice versa. It has been estimated that CO emissions decrease with increments in the percentage of biodiesel through blending, since biodiesel comprises 11% oxygen in its molecule.

Lin et al. [30] reported the reduction of CO emissions by 3.33 to 13.1% from blended waste-cooking-oil biodiesel used in a Cummins direct-injection diesel engine with a 250 bar constant injection pressure, 17.9:1 compression ratio, and 12.3° bTDC injection time. Shirneshan [31] obtained a reduction in CO emissions from a water-cooled, four-cylinder, heavy-duty diesel engine by adding waste frying oil biodiesel to petrol–diesel. Pugazhvadivu and Jeyachandran [32] studied CO emissions for waste frying oil on a Kirloskar single-cylinder diesel engine. They observed an increase in CO emissions that was attributed to higher the viscosity of WFO, and this was responsible for the poor combustion and air–fuel mixture formation suited for CO formation.

The variation of CO emissions for diesel and biodiesel blends on diesel engine is shown in Figure 7.

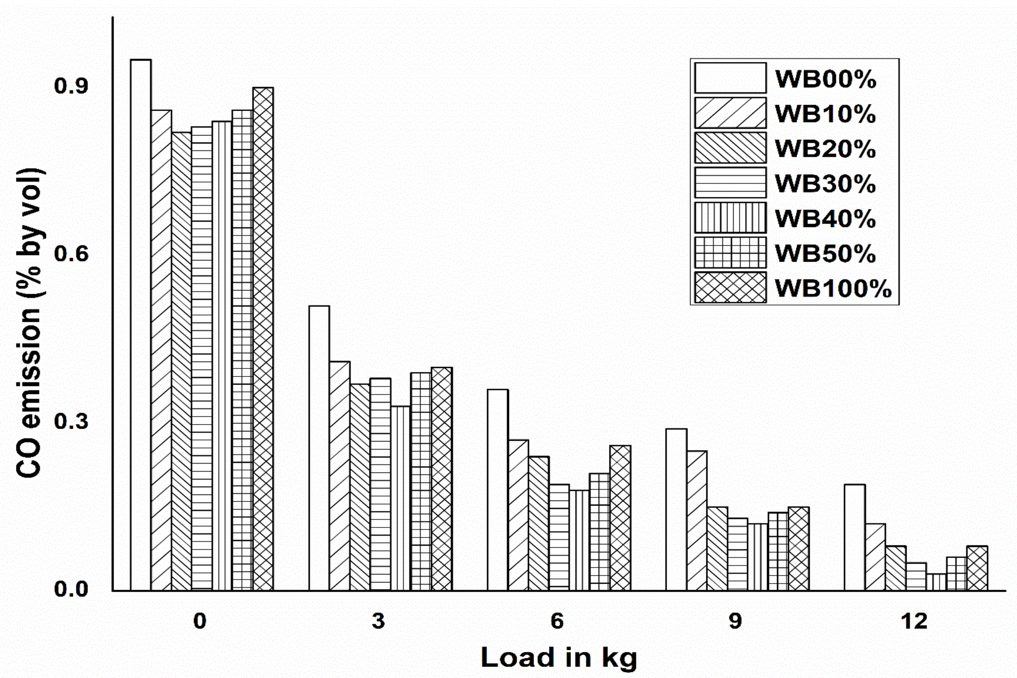

Figure 7. CO emissions' variation against load for biodiesel and the blends (kg).

Figure 7 shows the relation between CO emission and loads for different blends of biodiesel with diesel. It has been observed that emissions of CO decrease with the increments in load. At 0 kg of loading, the CO emission was 0.95, 0.86, 0.82, 0.83, 0.84, 0.86, and 0.9% by volume; for 3 kg of loading, the CO emission was 0.51, 0.41, 0.37, 0.38, 0.33, 0.39, and 0.4% by volume; for 6 kg of loading, it was 0.36, 0.27, 0.24, 0.19, 0.18, 0.21, and 0.26% by volume; for 9 kg loading, the emission was 0.29, 0.25, 0.15, 0.13, 0.12, 0.14, and 0.15% by volume; and for 12 kg loading, the emission was 0.19, 0.12, 0.08, 0.05, 0.03, 0.06, and 0.08% by volume. Data were recorded for 0%, 10%, 20%, 30%, 40%, 50% and 100%, of biodiesel blending for all conditions, respectively. The overall percentage decrements for blended fuels of 10%, 20%, 30%, 40%, 50%, and 100% WB were 16.96%, 27.83%, 31.3%, 34.78%, 27.83%, and 22.17%, respectively, as compared to diesel fuel. The maximum CO emission was for pure diesel fuel. It can be seen that, with an engine load from 0 to 3 kg and further, the load CO emission drops. With blending from 10% to 40%, this CO emission declines and is extremely low for the 40% blend at a 12 kg load. However, afterward, the CO emission shows a certain increment for 50% and 100% biodiesel. An increase in CO emission at a lower load is due to incomplete combustion of the fuel. Greater latent heat of evaporation causes deterioration in combustion, as well as rise in ignition delay responsible for increased CO emissions. Meanwhile, the decline in emission of CO with increment in blending at higher loads was due to the greater oxygen content in biodiesel, leading to the further oxidation of CO throughout the engine exhaust process. Higher-concentration blends (50% and 100%) show the rise in CO emission due to their higher viscosity that leads to less homogeneity in the mixture. From the graph, it can be observed that the CO emission was minimum for WB40% and was 34.78% less than diesel and, therefore, could be considered to be the optimum fuel blend at all loading conditions for this study.

3.2.2. CO_2 Emission

Complete combustion is responsible for the rapid increase in carbon dioxide (CO_2) emissions in the combustion chamber. The types of fuel, as well as the engine operating conditions, are responsible for complete combustion. Several researchers have reported carbon dioxide (CO_2) and carbon monoxide (CO) emissions and the relation between them. They have also reported that the increase in CO_2 emissions was due to improved combustion, consuming constituent oxygen present in the biodiesel. Yoon et al. [33] obtained greater CO_2 emissions for biodiesel. They elucidated that oxygen in biodiesel allows for the oxidation of CO into CO_2, and the life cycle of CO_2 was less with biodiesel than diesel, due to the absorption of CO_2 throughout harvesting for the photosynthesis process. Shirneshan [31] observed a reduction in CO_2 emissions for waste-frying-oil biodiesel compared to diesel. At higher blending, CO_2 emissions increased but were lower than those of diesel.

Figure 8 displays the CO_2 emissions with respect to different loading conditions and blending percentages. It can be observed that CO_2 emissions increase with blending and loading conditions. At 0 kg of loading, the CO_2 emissions were 1.3, 1.46, 1.5, 1.7, 1.58, 1.6, and 1.7% by volume; for 3 kg of loading, the emissions were 2.6, 2.9, 3.2, 3.3, 3.2, 3.3, and 3.4% by volume; for 6 kg of loading, the CO_2 emissions were 4.2, 4.6, 4.7, 4.5, 4.48, 4.7, and 4.9% by volume; for 9 kg loading, the emissions were 5.7, 6.1, 6.2, 6.4, 6.2, 6.3, and 6.3% by volume; and for 12 kg loading, the CO_2 emissions were 6.8, 6.9, 7.3, 7.1, 7.14, 7.4, and 7.3% by volume for 0%, 10%, 20%, 30%, 40%, 50%, and 100% of biodiesel blending, respectively, for all conditions. The overall differences in increments for blended fuels of 10%, 20%, 30%, 40%, 50%, and 100% WB were 6.6%, 11.17%, 11.65%, 11.58%, 13.11%, and 14.57%, respectively, in comparison to diesel fuel. CO2 emissions increase with the engine load from 0 to 12 kg. The CO_2 emissions were at their maximum at 12 kg of engine load for all fuels, including diesel fuel. At a 0 kg engine load, the CO2 emissions are comparable for 10% and 20% of biodiesel with respect to diesel fuel. The CO2 emissions are comparable for 10% and pure diesel fuel at a 12 kg engine load. However, for other blends, this CO2 emission is more as compared to diesel fuel. This percentage increase was due to the excess oxygen in biodiesel which leads to better combustion by converting CO into CO_2, and, hence, CO_2 emission increased.

CO_2 emissions become insignificant for the atmosphere, as plants consume it via photosynthesis [33]. Theoretical studies also validate the rise in CO_2 emissions from diesel engines with the blending of biodiesel to diesel, as the oxygen content in biodiesel improves combustion.

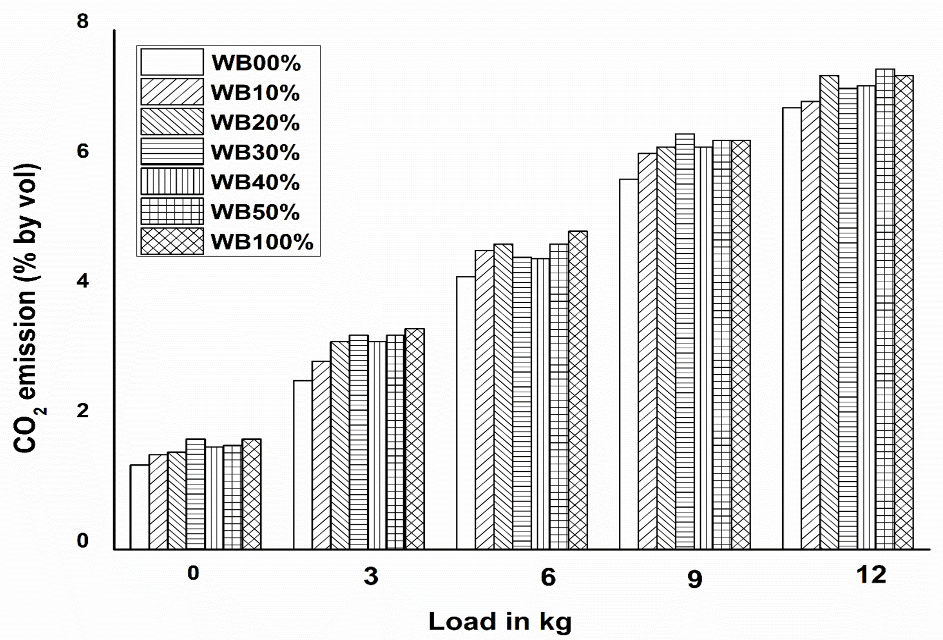

Figure 8. CO_2 emissions' variation against load for biodiesel and the blends (kg).

3.2.3. NO_x Emission

Nitric oxide (NO) and nitrogen dioxide (NO_2) are the main oxides of nitrogen formed during oxidation of nitrogen in air through combustion. NO_x emission is influenced by oxygen content, combustion temperature, and residence time of gases inside the high-temperature zone in the engine cylinder. Different studies have been reported for NO_x emissions in diesel engines by using biodiesel blends. Shirneshan [31] observed an increment of 11.66% in NO_x emission by using blended waste-frying-oil biodiesel than diesel for all conditions. Pugazhvadivu et al. [32] obtained a decrease in NO_x emissions for both normal and preheated WFO as a fuel compared to diesel.

The diesel-filled engine emits lower NO_x due to a low combustion temperature. Figure 9 shows the increase in NO_x emission with blending and loading over the complete range of engine operation. This is because nitrogen from the atmosphere mixes with oxygen inside the combustion chamber and produces NO_x. All data were recorded for 0%, 10%, 20%, 30%, 40%, 50%, and 100% of blended biodiesel, respectively. At 0 kg of loading, NO_x emissions were 24, 35, 39, 41, 42, 48, and 60 ppm; at 3 kg of loading, the emissions were 121, 137, 142, 140, 139, 146, 150 ppm; for 6 kg of loading, the NO_x emissions were 142, 162, 165, 168, 167, 177, and 186 ppm; for 9 kg loading, the emissions were 174, 189, 192, 195, 192, 197, and 208 ppm; and for 12 kg loading, the emissions were 189, 204, 210, 215, 213, 219, and 229 ppm. All data were recorded for 0%, 10%, 20%, 30%, 40%, 50%, and 100% of biodiesel blending, respectively. With loading, the NO_x emissions increased, perhaps due to additional rate of heat release, as well as oxygen concentration in blending, which has a dominant effect. Overall, the increment in NO_x emissions was observed for all blends of 10%, 20%, 30%, 40%, 50%, and 100% WB as 11.84%, 15.08%, 16.77%, 15.85%, 21.08%, and 27.85%, respectively, as compared to diesel fuel. NO_x emissions are very sensitive to the engine load. Figure 9 shows the variation of NO_x emissions with the engine load for pure diesel and biodiesel blends.

NO_x emission is comparatively higher for all biodiesel blends. For all engine loads, the NO_x emissions are highest for pure biodiesel and increase with the blend. With the engine load, the NO_x emissions are increased and highest for 12 kg of loading. From these data, it is ascertained that the oxygen content of biodiesel contributes to high NO_x emissions as compared to diesel. As the load of the engine increased, the ratio of supplied fuel to air also increased, and this resulted in an increase of average gas temperature in the diesel engine combustion chamber. Therefore, the NO_x emission increased.

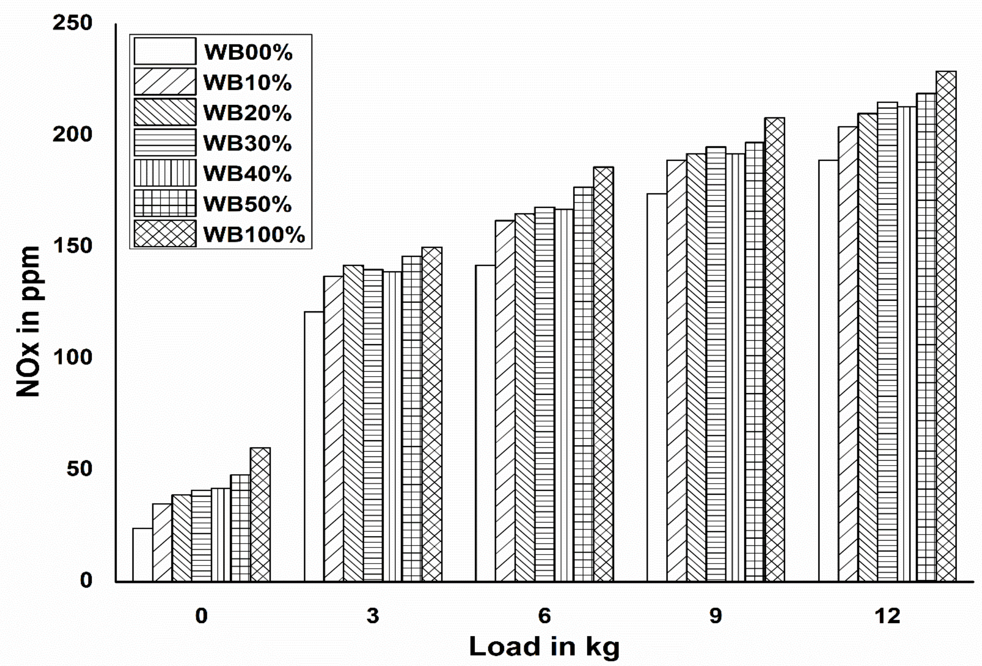

Figure 9. NO_x emissions' variation against load for biodiesel and the blends (kg).

3.2.4. HC Emission

Composition and combustion properties of fuel are responsible for unburned hydrocarbon (UHC or HC) emissions. By improving combustion, fuel will burn completely with low HC emissions, and vice versa. The presence of more oxygen in biodiesel promotes better combustion that results in reduced amount of HC emission than diesel [34].

Lin et al. [30] reported HC reduction for biodiesel as compared to diesel. They used different blends of waste-cooking-oil biodiesel and diesel, which showed a decrease of 10.5–36.0% in HC emissions. The low volatility of biodiesel could be one of the contributors for this HC emission difference between biodiesel and diesel.

Figure 10 showed the variation of UHC emission vs. load in kg for diesel, biodiesel, and their blends. A sharp drop in UHC emissions was observed for biodiesel as compared to diesel fuel. At 0 kg of loading, the UHC emissions were 66, 63, 58, 51, 46, 42, and 41 ppm; for 3 kg of loading, the UHC emissions were 54, 50 45, 40, 39, 40, and 38 ppm; for 6 kg of loading, they were was 43, 42, 38, 31, 26, 30, and 28 ppm; for 9 kg loading, UHC emissions were 31, 28, 25, 19, 16, 18, and 17 ppm; and for 12 kg of loading, the emissions were 27, 25, 22, 15, 12, 13, and 12 ppm for 0%, 10%, 20%, 30%, 40%, 50%, and 100% of biodiesel blends, respectively. The overall reduction in HC emission for 10%, 20%, 30%, 40%, 50%, and 100% WB was 5.88%, 14.93%, 29.41%, 38.1%, 35.29%, and 38.69%, respectively, as compared with diesel.

The HC emissions decrease with the increase in engine load. The HC emissions are highest at 0 kg of loading and lowest at 12 kg of engine load. For all engine loads, diesel fuel shows greater HC emissions than biodiesel. The lowest HC emissions are for the 40% biodiesel blend at 12 kg of engine load. Figure 10 also shows that the engine load has a vital influence on the behavior of HC emissions.

During combustion, oxygen from air intake, in addition to excess oxygen from biodiesel, improves oxidation. Hence, the engine emits low HC for neat biodiesel, due to the enhanced oxygenation process. The HC emissions were reduced for all engine loads, and biodiesel emits low HC compared to diesel fuel, even at high operating parameters. This was due to higher temperatures inside the cylinder, as they assist in better combustion. The HC emissions followed the same trend as that of CO.

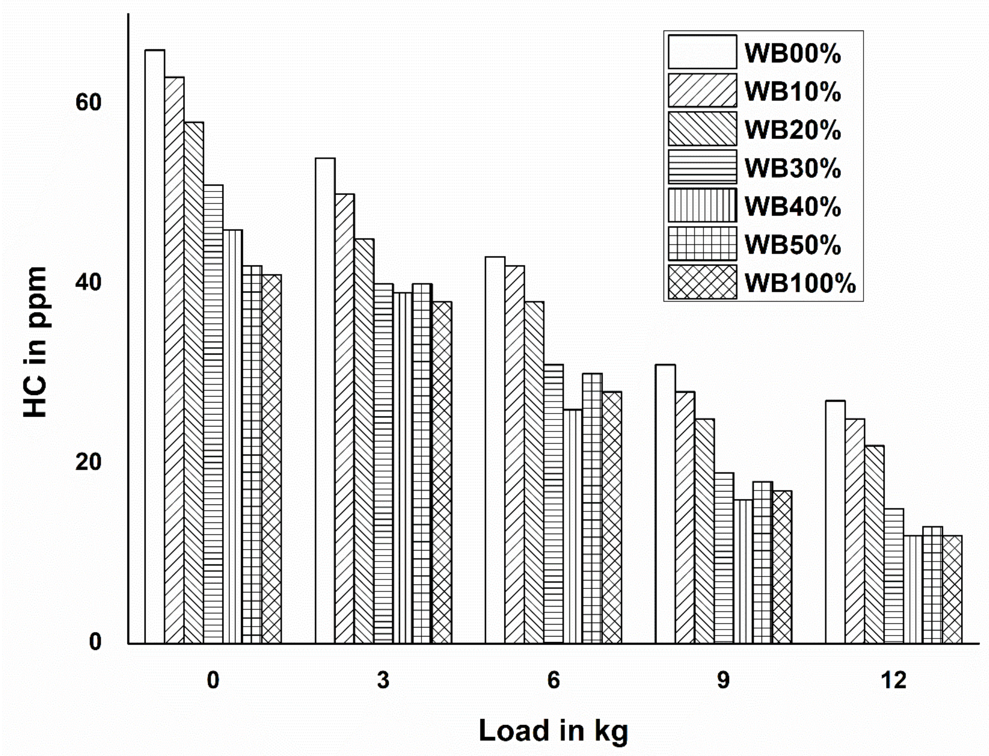

Figure 10. HC emissions' variation against load for biodiesel and the blends (kg).

3.2.5. Comparison of Exhaust Gas Emission

From all of these emission data, we can perceive that the fundamental presence of oxygen in biodiesel plays a vital role for pollutant emission. This additional oxygen improves the combustion when blended biodiesel is used as fuel instead of neat diesel. As a result, the CO and HC emissions were considerably reduced, but the temperature during combustion increased. This enhanced combustion of biodiesel blends with diesel increased the amount of CO_2 emission, whereas the combustion temperature increase caused elevations for NO_x emissions compared to neat diesel fuel. The emissions of gases reported by researchers by using WFO/WCO biodiesel and their blends with diesel are summarized and compared in Table 5 [21,24,26,30–32,35–40]. The increment and decrement (%) of pollutants are mentioned with respect to diesel at optimum operating conditions and compared with the present work. It has been concluded that the engine condition, biodiesel production methodology, purity of fuel, and avoidance of certain errors during experimentation play a major role in the improvement of biodiesel properties. The adverse effects on diesel engines by using biodiesel can be abolished by pretreatment of fuel, such as adding methanol and ethanol as a supplementation, in addition to pretreatment of fuel. Permissible emission limits for vehicles as per EU emission standards have been reported for vehicles. As per Euro VI norm [41], for heavy-duty vehicles, the CO emission limit is 1.5 g/kWh, the NO_x emission limit is 0.4 g/kWh, and the HC limit is 0.13 g/kWh. Several other references are also reported.

3.3. Mass Balance and E-Factor

We calculated and studied mass balance for both the product FAME and the by-product glycerol obtained after transesterification reaction and excluded the data for utilized water. For the transesterification reaction, in the present work, we used an 18:1 molar ratio of methanol:oil. By considering this ratio, 660.89 gm of methanol and 25 gm of $Mg_2Zr_5O_{12}$ catalyst were utilized per 1000 gm of waste cooking oil. Figure 11 shows the transesterification reaction of WCO biodiesel.

Table 5. Comparison of engine emission with respect to diesel fuel based on previous work.

Sr. No.	Biodiesel and Blending	Catalyst (Reusability Times)	CO	CO_2	NO_x	HC	Reference
1.	WFO (B0, B100)	NaOH (0)	17% decrement	-	1.5% decrement	-	[21]
2.	WFO (B100)	NaOH (0)	-	-	5.58–25.97% increment	22.47–33.15% decrement	[24]
3.	WCO (B5, B10, B20, B30)	*	6.75%, 7.33%, 8.32%, 13.1% decrement	-	-	10.5%, 19.9%, 27.7%, 36.0% decrement	[30]
4.	WFO (B20, B40, B60, B80, B100)	*	decrement	decrement	increment	decrement	[31]
5.	WFO (B100)	-	Significant increment	-	44% decrement	-	[32]
6.	WCO (B0, B30, B70, B100)	KOH (0)	-		Slight difference	Sharp reduction	[35]
7.	WCO (B0, B100)	NaOH (0)	17–19% decrement	-	3–5% decrement	-	[36]
8.	WCO (B0, B20, B40, B80)	KOH (0)	57% decrement	-	14.7% increment	40.3% decrement	[37]
9.	WCO (B0, B100)	*	4–16% decrement		10–23% increment	45–67% decrement	[38]
10.	WCO (B0, B5, B10, B20, B30, B50, B70, B100)	KOH (0)	25% decrement	-	6% increment	20% decrement	[39]
11.	WCO (D60B40N00 D60B40N30, D60B40N50, and D60B40N70)	TiO2 nano-catalyst and NaOH (NA)	Decrement	increment	increment	decrement	[40]
12.	WFO (WB10, WB20, WB30, WB40, WB50, WB100)	$Mg_2Zr_5O_{12}$ (7)	Decrement 16.96%, 27.83%, 31.3%, 34.78%, 27.83%, 22.17%	Increment 6.6%, 11.71%, 11.65%, 11.58%, 13.11%, 14.57%	Increment 11.84%, 15.08%, 16.77%, 15.85%, 21.08%, 27.85%	Decrement 5.88%, 14.93%, 29.41%, 38.1%, 35.29%, 38.69%	Present work

(* Commercial biodiesel samples).

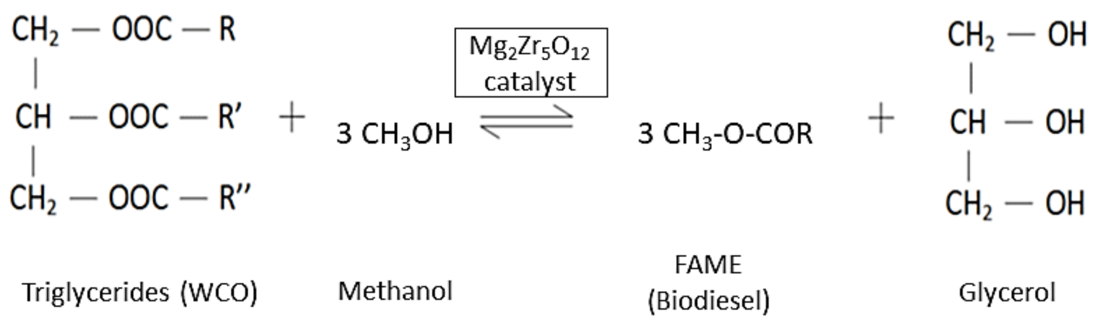

Figure 11. Transesterification reaction of WCO biodiesel.

After the transesterification reaction, we measured 800.35 gm of crude biodiesel, 150.09 gm of crude glycerol by-product, and approximately 40.45 gm of unreacted methanol. The recovered $Mg_2Zr_5O_{12}$ catalyst was 24 gm. This crude biodiesel product was purified via further treatment, as discussed earlier in this study, and consumed for further application. After the purification of biodiesel, we measured 780.12 gm of pure biodiesel. It is possible to recover and recycle by-product glycerol through an acidification reaction [42] and unreacted methanol by removing excess water through a dehydration method such as distillation. Complete amounts of reactant and products are shown in Table 6.

Table 6. Mass calculation for biodiesel production process.

Reactant	Waste cooking oil	1000 gm
	Methanol	660.89 gm
	$Mg_2Zr_5O_{12}$ catalyst	25 gm
Products	Crude biodiesel	800.35 gm
	Crude glycerol	150.09 gm
	Unreacted methanol	40.45 gm
	$Mg_2Zr_5O_{12}$ catalyst	24 gm
Purified product	Biodiesel	780.12 gm

The E-factor, that is, the environmental factor, is a metric based on mass and derived by the Sheldon formula [43], as shown in Equation (2).

$$\mathbf{E-factor = Total\ waste\ in\ kg \div Product\ in\ kg} \quad (2)$$

This equation excludes the amount of water from total waste since water addition will significantly increase E-factor. This E-factor represents the environmental suitability of a particular product, and its ideal value is zero. An increase in the E-factor value means more waste generation and adverse influence on the ecosystem. For the present work, we considered WCO as raw material, methanol and magnesium zirconate as reagents, and biodiesel and glycerol as the product and by-product, respectively. We calculated the E-factor for biodiesel at the optimized reaction condition of 18:1 M ratio methanol:WCO, 2.5 wt.% magnesium zirconate and 65 °C reaction temperature for 150 min. To calculate the E-factor of biodiesel at this optimized condition, we assumed that glycerol and unreacted methanol were the waste.

$$\mathbf{E-factor(Crude\ biodiesel) = Total\ waste(Glycerol + unreacted\ methanol) \div Product\ (Crude\ biodiesel)} \quad (3)$$

$$\mathbf{E-factor(Purifiedbiodiesel) = Totalwaste(Glycerol + unreactedmethanol + washing) \div Product(Purifiedbiodiesel)} \quad (4)$$

From our calculations, we obtained an E-factor of 0.24 for crude biodiesel from Equation (3), and, after purification, it was 0.27 from Equation (4). These E-factor values suggest that WCO-derived biodiesel with this reaction condition is sustainable and viable in terms of the E-factors that were close to the ideal value of zero, meaning that less waste has been generated throughout the process.

3.4. Sustainability Perspective for Biodiesel Production

Biodiesel is produced from second-generation feedstock 'waste cooking oil', as presented in this work. This eliminates the food vs. land conflict because there is no requirement of first-generation or edible sources of feedstock or any special land for cultivation [44]. In a way, this waste oil was recycled and utilized for the production of clean renewable biodiesel. This plan will provide benefits for native economies due to the use of locally available materials, and it ultimately reduces dependency on supply from other external resources. The replacement of conventional diesel fuel by biodiesel has a positive impact on environment. Fossil-fuel combustion causes a substantial increase in GHG emissions and eventually contributes to global warming [45]. One of the major advantages for biodiesel is the excess of oxygen content that helps to reduce the emission of harmful gases via improving combustion in diesel engines. Based on different parameters, such as the engine design, biodiesel quality, and state of engine, the emission of gases showed variation for different outcomes. Due to the environmental advantages of biodiesel over conventional fossil fuel, worldwide, more focus has been placed on sustainable biodiesel production at the commercial scale. In the complete process of transesterification reaction biodiesel product and glycerol by-product, both products are applicable in different sectors. A lower amount of waste has been generated from this whole process, and its straightforward contribution is the sustainable production of biodiesel as an alternative for diesel fuel.

4. Conclusions

In the present study, WCO biodiesel was synthesized by using the $Mg_2Zr_5O_{12}$ heterogeneous catalyst via transesterification reaction. Furthermore, this WCO biodiesel was blended with diesel at various ratios: 10%, 20%, 30%, 40%, and 50%. The blended biodiesel, pure biodiesel, and pure diesel were investigated for physicochemical properties. Compared to diesel fuel, as the concentration of biodiesel in blending increases, the kinematic viscosity, density, and flash point rise and are maximum for 100% biodiesel. The lower heating value showed decrement with blending and was minimum for pure biodiesel.

These properties had a prominent influence, resulting in cleaner emissions shown through the performance and emission study of diesel engines.

BTE, BSFC, and EGT were increased for biodiesel in comparison to diesel fuel. BTE was highest for WB40% and increased for all loading conditions. BSFC rose with blending and was maximum for pure biodiesel and decreased with loading condition. EGT also rose with blending and was highest for biodiesel by increment with respect to the loading condition. The average increment for BTE with loading for blending WB10%, WB20%, WB30%, WB40%, WB50%, and WB 100% was 8.98%, 13.61%, 13.59%, 19.13%, 14.34, and 15.52%, respectively; hence, the optimum fuel blend obtained was for WB40% for BTE. The average increments for biodiesel and blending in comparison to diesel fuel were 8.23%, 19.09%, 29.27%, 36.48%, 31.73%, and 39.8% for 10%, 20%, 30%, 40%, 50%, and 100% WB, respectively, for BSFC. The average increments of EGT in biodiesel and their blending were 0.81%, 3.49%, 4.77%, 6.98%, 6.74%, and 8.37% for 10%, 20%, 30%, 40%, 50%, and 100% WB, respectively.

Biodiesel produces lower CO and HC emissions, whereas it produces greater CO_2 and NO_x emissions in comparison to the diesel fuel. As compared to diesel, WB40% gives lower CO and HC emissions at all loading conditions. The biodiesel blend emitted lower CO_2 and NO_x as compared to pure biodiesel. The CO_2 and NO_x emissions increased with the increment in loading condition. The percentage CO decrement for blended fuels of 10%, 20%, 30%, 40%, 50%, and 100% WB was 16.96%, 27.83%, 31.3%, 34.78%, 27.83%, and 22.17%, respectively, as compared to diesel fuel. The difference in CO_2 increments for blended fuels of 10%, 20%, 30%, 40%, 50%, and 100% WB were 6.6%, 11.17%, 11.65%, 11.58%, 13.11%, and 14.57%, respectively, in comparison to diesel fuel. The increments in NO_x emission observed for all blends of 10%, 20%, 30%, 40%, 50%, and 100% WB were 11.84%, 15.08%, 16.77%, 15.85%, 21.08%, and 27.85%, respectively, as compared to diesel fuel. The reduction in HC emission for 10%, 20%, 30%, 40%, 50%, and 100% WB was 5.88%, 14.93%, 29.41%, 38.1%, 35.29%, and 38.69%, respectively, as compared with diesel.

Thus, through our calculations, we obtained an E-factor of 0.24 for crude biodiesel, and, after purification, it was 0.27 by using the Sheldon formula. These E-factor values suggest that WCO-derived biodiesel with this reaction condition is sustainable and viable. When considering WCO feedstock, reusable $Mg_2Zr_5O_{12}$ catalyst, glycerol by-product, and E-factor values for crude biodiesel and purified biodiesel, this complete process is technologically safe and applicable for various purposes.

The main benefit from this work is to make available alternate sources of fossil fuels to fulfil the increasing demand of energy. Biodiesel is the most capable alternative fuel for fossil fuel. Despite its enormous benefits, it still has some drawbacks, including feedstock, recycling of catalyst, poor low-temperature property, more NO_x emission, etc. It is important to improve these properties for real applications in large scale. Therefore, more in-depth studies for biodiesel application in diesel engines are indispensable. Research for alternative feedstock is also one of the crucial factors, and, among other second-generation-generation fuels, feedstock is most promising and has potential to solve problems based on feedstock supply. By using heterogeneous catalysts with recyclable potential, problems based on catalyst reuse could be easily solved. However, limitations related to low temperature and NO_x emission can be improved via additives or alternative routes.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/en15114044/s1, Table S1. Technical specifications of diesel engine, dynamometer, and engine loads. Table S2. Technical specifications of exhaust gas analyser.

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Abbreviations

WCO	waste cooking oil
GJ	gigajoule
kW	kilowatt
MJ/kg	mega joules per kilogram
Rpm	revolutions per minute
bTDC	before top dead center
FAME	Fatty acid methyl ester
$Mg_2Zr_5O_{12}$	magnesium zirconate
BTE	brake thermal efficiency
BSFC	brake specific fuel consumption
EGT	exhaust gas temperature
CO	carbon monoxide
CO_2	carbon dioxide
NO_x	nitrogen oxide
UHC	unburned hydrocarbon
IC engine	internal combustion engine
GHG	greenhouse gases
WB	waste-cooking-oil biodiesel blend
ppm	parts per million
WB00%	diesel fuel
WB10%	biodiesel 10%+diesel 90%
WB20%	biodiesel 20%+diesel 80%
WB30%	biodiesel 30%+diesel 70%
WB40%	biodiesel 40%+diesel 60%
WB50%	biodiesel 50%+diesel 50%
WB100%	biodiesel

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