

Article

Optimization of Biodiesel–Nanoparticle Blends for Enhanced Diesel Engine Performance and Emission Reduction

Yasmeen A. Mikky ¹, Ahmed A. Bhran ^{2,*} , Reham Y. El-Araby ³, Adel M. A. Mohamed ⁴ ,
Abdelrahman G. Gadallah ^{2,3} and Abeer M. Shoaib ¹

¹ Petroleum Refining and Petrochemical Engineering Department, Faculty of Petroleum and Mining Engineering, Suez University, Suez 43512, Egypt; yasmeen.mekky@pme.suezuni.edu.eg (Y.A.M.); a.shoaib@suezuni.edu.eg (A.M.S.)

² Chemical Engineering Department, College of Engineering, Imam Mohammad Ibn Saud Islamic University (IMSIU), Riyadh 11432, Saudi Arabia; agadallah@imamu.edu.sa

³ Chemical Engineering and Pilot Plant Department, Institute of Engineering Research and New and Renewable Energy, National Research Centre, Giza 12622, Egypt; rehamelaraby@hotmail.com

⁴ Department of Metallurgical and Materials Engineering, Faculty of Petroleum and Mining Engineering, Suez University, Suez 43512, Egypt; adel.mohammed@suezuni.edu.eg

* Correspondence: aabahran@imamu.edu.sa; Tel.: +966-58-077-2698

Abstract: Biodiesel is a promising alternative fuel that represents a sustainable and environmentally friendly energy source. Due to its complete carbon cycle, it reduces dependence on fossil fuels and lowers greenhouse gas emissions. However, the use of biodiesel in diesel engines is associated with several challenges, including an increase in nitrogen oxide and particulate emissions, incompatibility with cold climates, and lower calorific value. By using nanoparticles as fuel additives, there is a potential to improve the properties of biodiesel and address its shortcomings. In this work, the characteristics of biodiesel derived from waste cooking oil have been enhanced using nanoparticle additives, which result in the usage of a higher percentage of the biodiesel in diesel engines. Nanoparticles of cerium oxide, silicon dioxide, and aluminum oxide have been investigated in different concentrations as biodiesel additives. Two mathematical models are introduced in this work and solved by LINGO optimization software (version 18); the first one seeks to predict the characteristics of biodiesel with nanoparticles in any blend of diesel–biodiesel–nanoparticles, while the second model aims to maximize the biodiesel ratio in a biodiesel–diesel–nanoparticles blend. The application of the combined two models aids in the selection of the optimal nanomaterial that improves the properties of biodiesel and permits an increase in the biodiesel mixing ratio in the fuel. The results show that the best nanoparticle type is cerium oxide at a concentration of 100 ppm, and the optimal mixing ratio of biodiesel blended with CeO₂ nanoparticles is 24.892%. An unmodified diesel engine is operated and evaluated with the optimum blend (24.892% biodiesel + 75.108% petrol diesel + 100 ppm CeO₂ nanoparticles). It is found that significant improvements in engine performance and emissions compared with the conventional diesel are achieved. The reductions in brake-specific fuel consumption (BSFC), smoke opacity, and carbon monoxide emissions are 24%, 52%, and 30%, respectively.

Keywords: biodiesel; nanotechnology; nanoparticles; emissions; diesel engine performance



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1. Introduction

Biodiesel is a preferred alternative fuel to petrol diesel since it is renewable, non-toxic, environmentally friendly, and virtually sulfur-free. Moreover, compared with traditional fossil fuels, it has a higher cetane number, oxygen content, and carbon-to-hydrogen ratio (C/H). These characteristics lead to a reduction in particulate matter, carbon monoxide, and hydrocarbon emissions [1–3]. While biodiesel has several benefits over petrol diesel, some disadvantages are associated with its usage, such as increased nitrogen oxide (NO_x) emissions and decreased fuel efficiency in compression ignition (CI) engines. Additionally,

it causes piston ring sticking as well as other undesirable effects like poor atomization, higher density, and lower pour and cloud points.

Several attempts have been made to mix different alcohols and methyl esters with diesel to enhance performance and lower exhaust emissions [4,5]. However, the blended catalysts improved engine performance by quickening the combustion process, which consequently resulted in fuel instability [6]. The physical and chemical qualities of fuel regulate internal combustion engine fuel economy and emission characteristics. The primary raw materials used for producing biodiesel are vegetable oils such as castor oil, sunflower oil, soybean, hazelnut, rubber seed, jojoba, rapeseed, and palm oil, in addition to animal fats, microalgae oils, and waste cooking oil (WCO). The massive development of the human population is causing a significant increase in the amount of WCO created by homes and restaurants [7]. WCO is used to produce biodiesel in this study since it is two or three times less expensive than fresh vegetable oil, which results in a major decrease in the overall processing cost. Furthermore, there is no potential problem in this case because using WCO does not deplete food supplies, unlike using virgin edible oils [8].

The high surface area-to-volume ratio, thermal conductivity, and mass diffusivity of fuels have all been improved recently due to the application of nano-catalysts and nano-additives [9]. The integration of diesel fuel, nano-additives, and biodiesel has been demonstrated to enhance various properties such as the fire point, kinematic viscosity, and flash point [10].

A broad class of materials known as nanoparticles (NPs) includes particulate materials with at least one dimension of less than 100 nm. Depending on their size, shape, and chemical composition, NPs can be broadly classified into several categories. Metal, non-metal ceramic, semiconductor, and carbon nanoparticles are among the different types of nanoparticles. Iron, titanium, carbon, and aluminum oxide nanoparticles are among the most well-known types [11–13]. The catalytic activity of metal nanoparticles is enhanced by their large surface area and high energy level [14].

Alumina (Al_2O_3) nanoparticles were added to cashew nut shell-derived biodiesel (B100) to lower emissions of carbon monoxide (CO), hydrocarbons (HCs), and nitrogen oxides (NOx), as well as smoke opacity, by 8.8%, 10.1%, 12.4%, and 18.4%, respectively. Nevertheless, it also led to a 3.8% rise in brake-specific fuel consumption (BSFC) and a 1.1% drop in brake thermal efficiency (BTE) [15]. When 250 ppm and 500 ppm of Al_2O_3 nanoparticles were added to the diesel and biodiesel blend, a constant-speed direct-injection diesel engine produced an increase in BTE of 1.32%. Furthermore, with the addition of 250 ppm, the percentage of HC and CO dropped by 17.5% and 20%, respectively. On the other hand, NOx emissions increased by 5% while smoke opacity decreased by 27% [16].

Biodiesel containing cerium oxide (CeO_2) nanoparticles has shown good effects when used as a fuel for diesel engines; the variable valence conversion capability, significant oxygen storage, and advantageous thermal properties make them promising additives. Vairamuthua et al. [17] investigated how this combination affects the engines' performance, breakdown, combustibility, emissions, and combustion behavior. Their results showed that low levels of soot, smoke opacity, NOx, CO, and HCs are produced when these particles are added to biodiesel. They also aid in improving BTE, braking force, and BSFC. CeO_2 nanoparticles have been the subject of several studies regarding their potential applications as diesel fuel additives as well as oxygen donation catalysts for oxidizing CO and absorbing oxygen to reduce NOx [18–21]. They also improve air–fuel mixing, and their quick evaporation is credited with this improvement. Additionally, by improving the physical and chemical properties of the fuel and reducing exhaust emissions, fuel economy is also increased [22]. Anbarasu and Karthikeyan [16] investigated the impact of adding 200 ppm CeO_2 to the diesel and biodiesel blend in a direct-injection diesel engine operating at a constant speed. They found that the percentage of NOx and BTE increased by 3.8% and 2.1%, respectively, while the percentages of HCs, CO, and smoke opacity decreased by 6.8%, 11.9%, and 4.8%, respectively.

Adzmi et al. [23] studied the effect of adding silica (SiO_2) nanoparticles to a blend of palm biodiesel and diesel fuel on engine performance and emissions. Tests were carried out on a single-cylinder diesel engine under changing operating loads and constant engine speed. They reported a 43% increase in braking performance (BP), 25% reduction in CO emissions, and 4.48% reduction in NOx emissions under different circumstances when silica nano-additives are used.

Saravankumar et al. [24] added silica nano-additives at 50 ppm, 75 ppm, and 100 ppm to 20% maize oil methyl ester blended with diesel. Test results showed that the SiO_2 nano-additives reduced HC and smoke emissions by promoting full combustion and enhancing fuel oxidation and evaporation. However, they observed an increase in NOx emissions due to the higher oxygen content and combustion temperature. Özgür et al. [25] studied the effect of adding SiO_2 nano-additives at 25 ppm and 50 ppm to rapeseed methyl ester, finding reduced NOx and CO emissions with a slight improvement in engine performance.

All earlier research introduced experimental work for specified percentages of biodiesel and with specified doses of nanoparticles as additives to a biodiesel–diesel blend to enhance its specification and choose the best percentage of biodiesel in the blend; this does not guarantee that the selected biodiesel ratio is optimum.

The application of fuel additives, such as cerium oxide, alumina, and silica oxide, to improve combustion and lower engine emissions has been well studied in the past. Nevertheless, no research has optimized the diesel-to-biodiesel mixing ratio using nano-additives. Rather, previous studies concentrated on experimental work with blend properties improving the percentages of biodiesel and doses of nano-additives to find the best biodiesel ratio.

The main contributions of this study are as follows:

- Biodiesel is produced from waste cooking oil (WCO) and characterized.
- Two mathematical models are introduced:
 - The first model predicts biodiesel specifications when blended with nanoparticles based on the properties of diesel and the biodiesel–diesel–nanoparticle blend.
 - The second model determines the maximum allowable biodiesel mixing ratio according to standard fuel limits for diesel engines.
- The models are used to select the most suitable nanoparticles, as identified in previous work, to enable a higher percentage of biodiesel in blends.
- LINGO optimization software (version 18) is utilized to solve the introduced models.
- The study examines the effects of alumina, silica oxide, and cerium oxide nanoparticles at various concentrations in biodiesel derived from WCO, aiming to enhance combustion and identify the optimal nanoparticles that yield the best physicochemical properties (density, kinematic viscosity, flash point, and calorific value) for biodiesel.
- The optimal nanoparticles are then incorporated into the diesel and biodiesel mixture at the best mixing ratio to evaluate their impact on diesel engine performance and emissions.

This article consists of three main stages. The first stage considers the production of biodiesel from WCO, where the main materials and method to produce the biodiesel are discussed. The second stage focuses on obtaining the optimum nanoparticles that can be added to achieve the maximum mixing ratio between the biodiesel and conventional diesel blend (optimum blend). This stage is carried out by introducing two mathematical models using LINGO optimization software (version 18). The third stage is directed to studying the effect of adding nanoparticles on engine performance and emissions by making a comparative study between conventional diesel and the optimum blend.

2. Materials and Methods

Silicon dioxide, cerium oxide, and aluminum oxide nanoparticles were purchased from Merck Company, Cairo, Egypt. Software used in this study is Demo Lingo/Win64 (version 18).

2.1. Production of Biodiesel from Waste Cooking Oil (WCO)

Waste cooking oil (WCO) is collected from households and restaurants as a byproduct of food preparation. The first step in pre-treating the WCO is to filter it through a paper filtration system to remove contaminants like food particles and other suspended solids. Prior to the next step of transesterification, the WCO is heated to 120 °C in order to lower the moisture content to less than 0.5%. This is an important pre-treatment to ensure the oil meets the required specifications before further processing.

Methoxide is created from the reaction of methanol and the basic catalyst, KOH, when mixed. A sufficient volume of alcohol was added to equal three times the amount of triglyceride consumed; typically, an excess of 6:1 alcohol to triglyceride is taken to complete the reaction [26,27]. After adding the synthesized methoxide to the oil, the magnetic stirrer was used to agitate it aggressively.

The mixture was transferred to a separator funnel after being continuously stirred for an hour. The mixture should be left undisturbed for at least 7–8 h to ensure that all of the glycerol has settled out, even though the settling will start right away. About one-fifth of the initial oil content was represented by the volume of glycerol that was recovered. The primary goal at this stage was to simply remove the settled glycerol layer from the top biodiesel layer [28].

Glycerol is dark and opaque in contrast to the yellow biodiesel. Cleaning the unprocessed biodiesel is one of the most crucial stages. Water washing was carried out by spraying water droplets onto the fuel and then removing the water from the bottom [28,29]. The flowsheet in Figure 1 illustrates the steps of producing biodiesel from WCO.

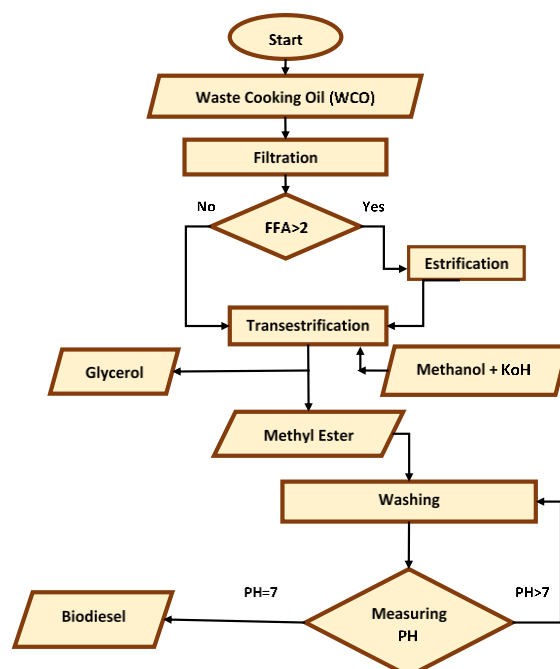


Figure 1. Flowsheet of biodiesel production from WCO.

In this study, a large quantity of biodiesel, weighing 50 Kg, was produced, necessitating the use of industrial-scale equipment in the National Research Center (Egypt). Figure 2 illustrates the various steps involved in the industrial-scale production of biodiesel from waste cooking oil (WCO).

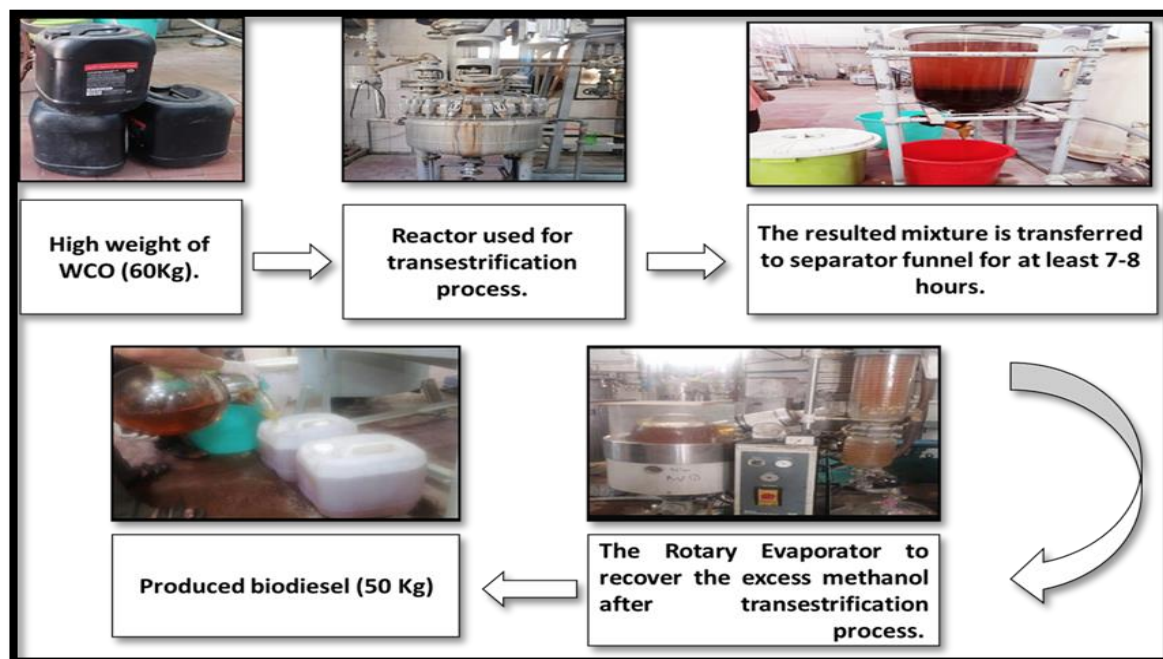


Figure 2. Industrial production of biodiesel from WCO.

2.2. Properties of Produced Biodiesel

The most important and crucial fuel characteristics that are involved in using biodiesels in diesel engines are cetane number, kinematic viscosity, pour point, flash point, and calorific value. Various standardization techniques, such as ASTM D6751 and EN14214 [30,31], specify the fuel qualities of biodiesels [32].

The biodiesel produced was characterized using several analytical methods, where density was determined using hydrometers at 15 °C as per ASTM D4052 [33], while kinematic viscosity was measured using Cannon-Fenske viscometer (Cannon Instrument Company, State College, PA, USA) at 40 °C according to ASTM D445 [34]. The flash point was measured using Pensky–Martens closed-cup apparatus (Tanaka Scientific Limited APM-7, Shanghai, China) following ASTM D93 [35]. Calorific value was determined using oxygen bomb calorimeter (Parr 6200 Calorimeter, Parr Instrument Company, Moline, IL, USA) following ASTM D240 [36]. All analyses were performed in triplicate, with results reported as mean values $\pm$ standard deviation. The characterized properties were compared against the ASTM biodiesel standards to assess the quality of the produced biodiesel.

2.3. Mathematical Modeling

In the following subsection, equations used in two proposed mathematical models are illustrated. The proposed models are solved by LINGO optimization software (version 18); LINGO is an all-inclusive tool for quickly, simply, and effectively building and solving linear, nonlinear (convex and no convex/global), quadratic restricted, second order cone, semidefinite, stochastic, and integer optimization models.

2.3.1. Predicting the Specifications of Biodiesel Blended with Nanoparticles Based on the Specifications of Diesel and Biodiesel–Diesel–Nanoparticle Blend

In most published works, the available data are petrol-diesel properties and mixing ratio, in addition to the characteristics of the final blend with nanoparticles and biodiesel. It is required to know the characteristics of biodiesel blended with nanoparticles before blending with petrol diesel. This helps in predicting the maximum allowable mixing ratio of biodiesel based on the standard range of fuel properties in diesel engines. This consequently leads to the right choice of nanoparticles that allow the maximization of biodiesel usage without violating the standard range of fuel properties.

Four properties are taken into consideration in this model: flash point (FP), kinematic viscosity (KV), density (D), and calorific value (CV). The values of these properties for petrol diesel and final blend (diesel–biodiesel–nanoparticles), in addition to the mixing ratio, are the model inputs. The blend mixing rules for each of these properties are put in the model, considering that some of these properties are additive properties (FP, D, CV), while viscosity is not an additive property. All additive properties can be calculated for the blend depending on the simple relation given in Equation (1),

$$P_b = \sum P_i \times X_i \quad (1)$$

where P_b is the property value of the blend, P_i is the property value for component i , and X_i is the volumetric fraction of component i .

The kinematic viscosity mixing rule is illustrated in Equation (2) [37],

$$\ln KV_b = \sum X_i \times \ln KV_i \quad (2)$$

where KV_b is the kinematic viscosity of the blend, KV_i is the kinematic viscosity for component i , and X_i is the volumetric fraction of component i .

In the present model, the blend is considered as two components; the first is biodiesel mixed with nanoparticles, and the second is petrol diesel.

2.3.2. Maximizing Mixing Ratio of Biodiesel for Biodiesel–Diesel Blend

It is necessary to find the maximum mixing ratio between biodiesel blended with nanoparticles and diesel. The maximum mixing ratio depends mainly on the following data:

- Properties of biodiesel blended with nanoparticles.
- Properties of petrol diesel.
- Standard range of fuel properties in diesel engines illustrated in Table 1.

Table 1. Standard range of fuel properties in diesel engines.

Property	Standard Lower and Upper Limits
Flash point (°C)	52–96
Kinematic viscosity @ 40°C (CSt)	3–8
Density (Kgm/m ³)	800–850
Calorific value (MJ/Kg)	40–50

The introduced model, which aims to obtain the maximum allowable mixing ratio of biodiesel (X_1), is updated from the model proposed by Shoaib and Bhran [38]. Equations (3)–(12) illustrate the model formulation.

$$\text{Maximize } X_1 \quad (3)$$

Subject to:

$$\sum X_i = 1 \quad (4)$$

$$D_b = \sum D_i \times X_i \quad (5)$$

$$FP_b = \sum FP_i \times X_i \quad (6)$$

$$CV_b = \sum CV_i \times X_i \quad (7)$$

$$\ln KV_b = \sum X_i \times \ln KV_i \quad (8)$$

Constraints for the lower and upper limits of the produced fuel are given in the following set of equations to guarantee the production of fuel suitable for diesel engines:

$$D_b^l \leq D_b \leq D_b^u \quad (9)$$

$$FP_b^l \leq FP_b \leq FP_b^u \quad (10)$$

$$CV_b^l \leq CV_b \leq CV_b^u \quad (11)$$

$$KV_b^l \leq KV_b \leq KV_b^u \quad (12)$$

where D_b , FP_b , CV_b , and KV_b are density, flash point, calorific value, and kinematic viscosity of the blend, respectively. D_i , FP_i , CV_i , and KV_i are density, flash point, calorific value, and kinematic viscosity for component i , respectively. D_b^l , FP_b^l , CV_b^l , and KV_b^l are the lower limits for density, flash point, calorific value, and kinematic viscosity of the blend, respectively. D_b^u , FP_b^u , CV_b^u , and KV_b^u are the upper limits for density, flash point, calorific value, and kinematic viscosity of the blend, respectively.

2.4. Enhancement of Produced Biodiesel Properties by Adding Nanoparticles

2.4.1. Selection of Types of Nanoparticles Added to Produced Biodiesel

There are many types of nanoparticles that can be added to biodiesel, and through previous studies, the different types of nanoparticles with their different concentrations have been identified, which are summarized in Table 2.

Table 2. Types of nanoparticles added to biodiesel.

Nanoparticles Type	Concentrations (ppm)	References
Silicon dioxide	25, 50, 75	[39]
	40, 80, 120	[40]
Zinc oxide	25, 50, 75	[41]
	40, 80, 120	[42]
Aluminum oxide	25, 50	[43]
	30, 60, 90	[44]
	25, 50, 75, 100	[45]
Cerium oxide	50	[46]
	50, 100	[47]

In this work, three types of nanoparticles—silica dioxide (SiO_2), alumina (Al_2O_3), and cerium oxide (CeO_2)—were purchased from Aldrich (Merck Company, Cairo, Egypt) and added to biodiesel at varying concentrations to evaluate their effects on fuel properties. Silica dioxide (SiO_2) nanoparticles (Merck Company), with an average particle size between 10 and 20 nm, were added at concentrations of 20 ppm, 40 ppm, and 60 ppm. Alumina (Al_2O_3) nanoparticles (Merck Company), averaging 50 nm, were tested at 25 ppm, 35 ppm, 50 ppm, and 60 ppm. Cerium oxide (CeO_2) nanoparticles, with a particle size of 25 nm, were added at concentrations of 75 ppm, 100 ppm, and 125 ppm. These varying concentrations were selected to optimize biodiesel performance based on the established literature practices for similar nanomaterials.

2.4.2. Preparation of Blend of NPs and Biodiesel with Different Concentrations

The necessary amount of the nanoparticle sample required for each dosage level was quantified using a precision electronic balance, and by utilizing an ultrasonic shaker with a continuous agitation duration of 30 min, a homogeneous suspension was created. The fuel blends with specifications of B100SiO220, B100SiO240, B100SiO260, B100Al2O325, B100Al2O335, B100Al2O350, B100Al2O360, B100CeO275, B100CeO2100, and B100CeO2125

were prepared for experiments. Figure 3 shows the ultrasonic device used to prepare nanoparticles and nanoparticle–biodiesel–diesel blends.



Figure 3. Preparation of nanofuels using the ultrasonicator.

2.4.3. Maximum Mixing Ratio Between Biodiesel and Diesel After Adding Different Types of NPs with Different Concentrations

A series of biodiesel fuel samples were prepared, incorporating three types of nanoparticles: silicon dioxide, alumina, and cerium oxide. Each nanoparticle type was added to separate biodiesel samples at varying concentrations. Following the preparation, these samples were subjected to comprehensive testing at Misr Petroleum Company, Giza Egypt. The analysis focused on four key properties of the modified biodiesel: density, kinematic viscosity, flash point, and calorific value. This systematic approach aimed to evaluate how different nanoparticles and their concentrations affect the essential characteristics of biodiesel fuel.

Table 3 presents the properties of each biodiesel–nanoparticle sample. To determine the optimal mixing ratio between diesel and nanoparticle-enhanced biodiesel, LINGO optimization software (version 18) was employed. The optimization process considered three key factors: the properties of conventional diesel fuel, the measured properties of each biodiesel–nanoparticle mixture, and the standard range of acceptable fuel properties for diesel engines (as outlined in Table 1). By analyzing these parameters, the software calculated the maximum allowable proportion of nanoparticle-enhanced biodiesel that could be blended with conventional diesel while still meeting the required fuel property standards for diesel engines.

Table 3. The properties of biodiesel–nanoparticle samples.

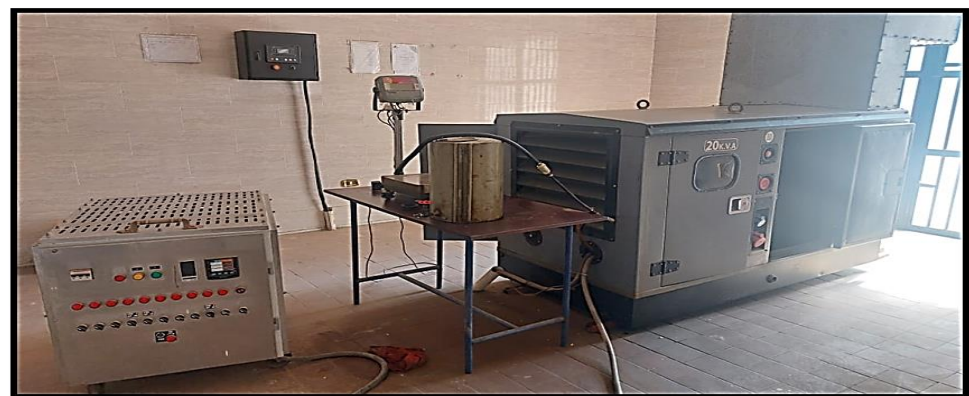
Code	Definition	Flash Point (°C)	Kinematic Viscosity (cSt)	Density (Kg/m ³)	Calorific Value (MJ/Kg)
1	Silica dioxide (20 ppm)	103	4.17	885.2	44.91
2	Silica dioxide (40 ppm)	95	4.22	885.3	44.91
3	Silica dioxide (60 ppm)	91	4.5	885.4	44.92
4	Alumina (60 ppm)	140	4.5	886.8	44.97
5	Alumina (25 ppm)	127	4.49	885.9	44.99
6	Alumina (35 ppm)	132	4.45	886.1	45
7	Alumina (50 ppm)	138	4.38	886.5	44.95
8	Cerium oxide (75 ppm)	100	4.5	887.4	44.97
9	Cerium oxide (100 ppm)	125	4.41	887.6	44.9
10	Cerium oxide (125 ppm)	140	4.51	887.9	45

2.5. Description of the Test Engine

A diesel generator set consisting of Perkins engine (model 404A-22G), Stafford dynamo (model G1-SOL2), and a load bank was used to conduct the performance and emission studies. Standard constant speed tests were also performed on the engine. An electronic scale with 5 g sensitivity was used for measuring fuel consumption rates. Diesel opacity meter (WAGER 6500) was also used for diesel engine opacity measurement. Specifications of the engine used for the performance study are given in Table 4. Figure 4 shows the diesel engine used for conducting the performance and emission studies.

Table 4. Engine specifications.

Type	Perkins Engine (Model 404A-22G)
Dynamometer	Stafford dynamo (model G1-SOL2)
Max rpm	1500 rpm
Cylinders and arrangement	In-line four cylinder
Displacement	2.216 L
Compression ratio	23.5:1
Firing order	1-3-4-2
Injection	Indirect

**Figure 4.** Diesel engine used for conducting the performance and emission studies.

3. Results and Discussion

One of the main objectives of this work is to obtain the biodiesel maximum mixing ratio and to study the effect of the investigated nanoparticles on the biodiesel's physical and chemical properties. These properties include the studied biodiesel's density, viscosity, flash point, and calorific value. Moreover, the optimum biodiesel–diesel–nanoparticles blend is obtained by applying LINGO software (version 18). LINGO provides a completely integrated package that includes a powerful language for expressing optimization models, a full-featured environment for building and editing problems, and a set of fast built-in solvers. This work also considers studying the effect of nanoparticles on diesel–biodiesel fuel performance and emissions.

3.1. Physicochemical Properties of Produced Biodiesel and Diesel Fuels

It should be noted that WCO can be used without any additional treatment if the acid value of the WCO is lower than 2 mg NaOH per 1 g of WCO. The experimental results show that the acid value for the collected WCO is 1.5 mg NaOH per 1 g, which is lower than the required acid value. Therefore, the WCO does not require extra treatment to reduce the free fatty acid (FFA) content. The physicochemical properties of the produced biodiesel and diesel fuels, measured by Misr Petroleum Company, are shown in Table 5.

Table 5. Physical and chemical properties of biodiesel and diesel fuels.

Properties	Diesel	Biodiesel	Test Method
Density (Kgm/m ³)	838.4	885.2	ASTM D4052 [33]
Kinematic viscosity at 40 °C (cSt)	3.39	4.55	ASTM D445 [34]
Flash point (°C)	79	123	ASTM D93 [35]
Calorific value (MJ/Kg)	45.6	22.59	Tables

3.2. Maximum Mixing Ratio Between Biodiesel and Diesel

The maximum mixing ratio between biodiesel and diesel was obtained before adding the nanoparticles using LINGO optimization software (version 18), which was used also to determine the physical and chemical properties of the blend such as viscosity, density, flash point, and calorific value. The obtained results showed that the maximum mixing ratio of the tested biodiesel–diesel blend is 24.37%. This means that, in the absence of nanoparticles, the optimum blend is composed of 24.37% biodiesel and 75.63% conventional diesel; this mixture is called B24.37. To validate the LINGO optimization software's results, a blend of diesel and biodiesel was prepared with a biodiesel mixing ratio of 24.37%, and the blend's physical and chemical properties were measured by Misr Petroleum Company. The achieved experimental results of these properties were compared with those obtained by the LINGO optimization software. Table 6 shows a comparison between the experimental results and those obtained from LINGO optimization software for the physical and chemical properties of the investigated diesel and biodiesel blend.

Table 6. Comparison between experimental and LINGO results for the blend properties.

Property	LINGO Software Results	Experimental Results	Error %
Flash point (°C)	89.72445	88	1.9
Kinematic viscosity at 40°C (cSt)	3.642101	3.55	2.5
Density (Kgm/m ³)	849.8	849.5	0.036
Calorific value (MJ/Kg)	40	42.7	6.3

As presented in Table 6, the error % between the obtained experimental and LINGO results for the physical and chemical properties of the mixture is small. Therefore, LINGO

software could be used to determine the optimal mixing ratio between diesel and biodiesel as well as to evaluate the blend's physical and chemical properties.

3.3. Selection of Nanoparticle Types

The maximum mixing ratio was obtained by using LINGO optimization software (version 18) for each investigated concentration of each type of nanoparticle. The obtained results are illustrated in Table 7. As shown in this table, the maximum mixing ratio between diesel and biodiesel when adding different concentrations of zinc oxide nanoparticles is small, and therefore, it can be excluded as an additive for increasing this mixing ratio. The selected nanoparticles are those that achieve a mixing ratio (%) close to or exceeding the biodiesel–diesel mixing ratio without nanoparticles, as determined by the mathematical model in Section 3.2 (24.3%). The nanoparticles, silica dioxide (SiO_2), alumina (Al_2O_3), and cerium oxide (CeO_2), were chosen based on their proven effectiveness in enhancing fuel properties in previous studies, including improvements in thermal stability, oxidation resistance, and combustion characteristics. These specific types were selected due to their stability at high temperatures, compatibility with biodiesel, and ability to improve fuel efficiency.

Table 7. Biodiesel maximum mixing ratio when adding nanoparticles at different concentrations.

Nanoparticles	Concentration (ppm)	Mixing Ratio (%)
Silica dioxide	25	22.73
	40	27
	50	27.78
	75	31.25
	80	31.86
Zinc oxide	40	6.52
	80	10.52
	120	20.05
Aluminum oxide	25	26.86
	50	21.25
Cerium oxide	50	25
	75	27.7
	100	29.85

Different concentrations were tested to determine their impact on optimizing the biodiesel properties following established practices in the literature for these materials. The selection of concentrations for each type of nanoparticles is dependent on the mixing ratio results presented in Table 7. As shown by the results in Table 7, the concentration of silicon dioxide nanoparticles that is close to the mixing ratio of the biodiesel–diesel blend (24.3%) is 25 ppm, and by increasing the concentration of silicon dioxide nanoparticles, the mixing ratio is increased. So, the selected concentrations for silicon dioxide nanoparticles were 20 ppm, 40 ppm, and 60 ppm. Similarly, for cerium oxide nanoparticles, the concentration that is close to the mixing ratio of the biodiesel–diesel blend (24.3%) is 50 ppm, and the maximum mixing ratio is increased with an increasing concentration of cerium oxide nanoparticles. It was thought to give an indication that the properties of biodiesel are affected by high concentrations of cerium oxide nanoparticles. This is why the selected concentrations of cerium oxide nanoparticles were 75 ppm, 100 ppm, and 150 ppm. For aluminum oxide nanoparticles, it was noticed that increasing the concentration of aluminum oxide nanoparticles led to a decrease in the maximum mixing ratio, and it was thought to give an indication that the properties of biodiesel are affected by low concentrations

of aluminum oxide nanoparticles. Thus, the selected concentrations of aluminum oxide nanoparticles were 25 ppm, 35 ppm, 50 ppm, and 60 ppm.

3.4. Effect of Adding Nanoparticles on Biodiesel Properties

The following subsections consider the nanoparticles' effects on the chemical and physical properties of the biodiesel. These properties include density, kinematic viscosity, flash point, and calorific value of the investigated biodiesel.

3.4.1. Effect of Nanoparticles on Biodiesel Density

Density is one of the most important biodiesel properties that can be affected by adding nanoparticles. Because nanoparticles are frequently denser than biodiesel, the addition of nanoparticles increases the biodiesel density. Changing the density can significantly affect the energy content and combustion characteristics of biodiesel [48,49]. Biodiesel may have a decreased calorific value due to its greater density, which could have an undesired impact on the biodiesel's effectiveness as a fuel. Thus, it is important to make the trade-off between improved combustion qualities brought about by nanoparticle additions and decreased calorific value, which may have an adverse effect on the overall fuel efficiency [50].

Figure 5 shows the effect of the tested nanoparticles on the biodiesel density. As a general trend for all investigated nanoparticles, the density of the mixture of biodiesel and nanoparticles is increased by increasing the concentration of nanoparticles. However, it is noted that the density of the mixture of biodiesel and cerium oxide nanoparticles is higher than the biodiesel mixed with silicon dioxide or aluminum oxide nanoparticles. It is also clear that the density of biodiesel with aluminum oxide nanoparticles is very close to the density of biodiesel mixed with cerium oxide, and it is still significantly higher than the density of biodiesel containing silicon dioxide nanoparticles. This can be attributed to the higher density of cerium oxide or aluminum oxide nanoparticles compared with the density of silicon dioxide nanoparticles.

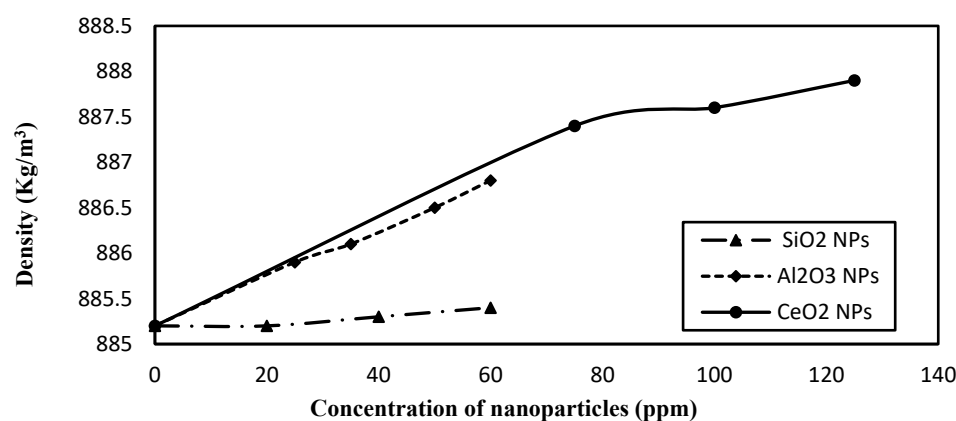


Figure 5. Effect of adding nanoparticles on the biodiesel density.

3.4.2. Effect of Nanoparticles on Biodiesel Kinematic Viscosity

The biodiesel's viscosity directly affects the biodiesel's flow characteristics and its suitability for use in traditional diesel fuel systems [51,52]. The viscosity of biodiesel determines its capacity to flow, atomize, and burn effectively in diesel engines. It is well known that biodiesel's viscosity is decreased by adding nanoparticles [53,54]. This viscosity decrease is caused by a number of factors, including the lubricating qualities of nanoparticles and their interaction with the long hydrocarbon chains of biodiesel [55]. Decreased viscosity of biodiesel has the ability to increase atomization during combustion, which improves the biodiesel's fuel efficiency and reduces its adverse effect on the environment [56,57]. Furthermore, reducing viscosity enhances the flow characteristics of biodiesel, facilitating easier handling, pumping, and injection into diesel engines. The main feedstock for biodiesel, along with the type and concentration of nanoparticles and the operating temperature, are

the key factors influencing the extent of viscosity reduction [58]. Consequently, to attain the necessary viscosity properties without losing other essential fuel features, blends of biodiesel enhanced with nanoparticles should be carefully developed and optimized [59].

Figure 6 shows the influence of nanoparticles' addition at different concentrations on the biodiesel's kinematic viscosity. Regarding Figure 6, as a general trend, the addition of any type of nanoparticles leads to a reduction in the biodiesel kinematic viscosity until a specific nanoparticle concentration is reached. The obtained optimum concentrations of silicon dioxide, aluminum oxide, and cerium oxide nanoparticles are 25 ppm, 50 ppm, and 100 ppm, respectively. At these optimum concentrations, the biodiesel reaches the lowest value of its viscosity. However, increasing the concentration of nanoparticles beyond the optimal levels can strengthen the fluid layer's resistance, ultimately resulting in an increase in the biodiesel viscosity. It is noticed that the addition of silicon dioxide has the highest influence in decreasing the biodiesel viscosity, while cerium oxide nanoparticles show the lowest influence in reducing the considered biodiesel viscosity.

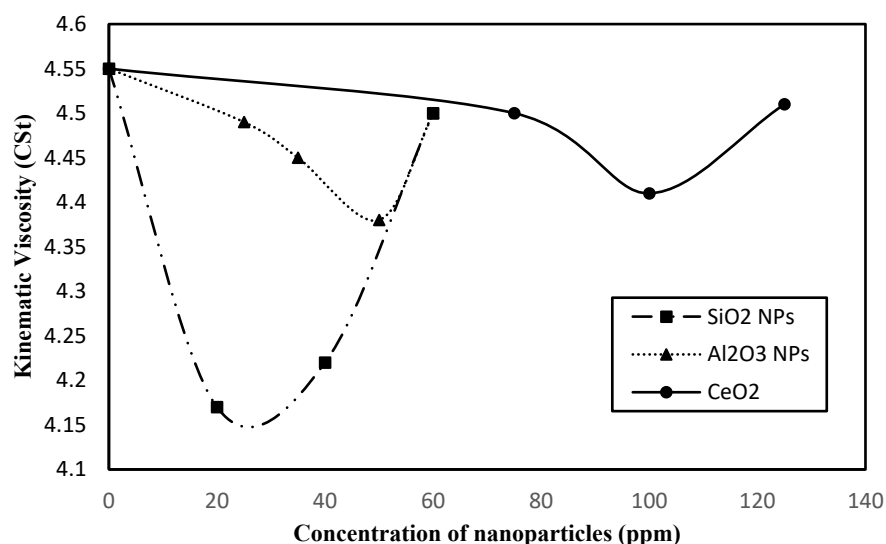


Figure 6. Effect of adding nanoparticles at different concentrations on biodiesel kinematic viscosity.

3.4.3. Effect of Nanoparticles on Biodiesel Flash Point

The flash point is an important property that affects the safety and combustion properties of fuels. Adding nanoparticles to biodiesel can affect its flash point [54,60]; it appears that adding nanoparticles to biodiesel raises its flash point [53,61]. This is because nanoparticles are solid materials that take longer to evaporate at typical fuel temperatures. The temperature at which the biodiesel and air mixture ignites might therefore be increased by nanoparticles [55,62]. Biodiesel with a higher flash point is safer to be handle, store, and transport [60,63]. Diesel engines may take longer to ignite if the fuel flash point is higher [64,65]. Delayed ignition can negatively affect engine performance and lead to the generation of pollutants. Therefore, balancing safety and combustion efficiency is crucial when developing biodiesel blends improved by adding nanoparticles [58,59].

Figure 7 depicts the effects of the investigated nanoparticles on the biodiesel flash point. The results indicate that incorporating aluminum oxide raises the flash point of biodiesel at all tested concentrations, with higher concentrations resulting in a further increase in the flash point. On the other hand, the silicon dioxide addition decreases the biodiesel flash point, and this reduction in flash point is increased with an increase in the silicon dioxide concentration. However, the biodiesel flash point is decreased by increasing the cerium oxide concentration up to 80 ppm. Above this concentration, the flash point is increased by increasing the cerium oxide concentration. These results show that the addition of aluminum oxide has the best and preferable influence on increasing the investigated biodiesel flash point.

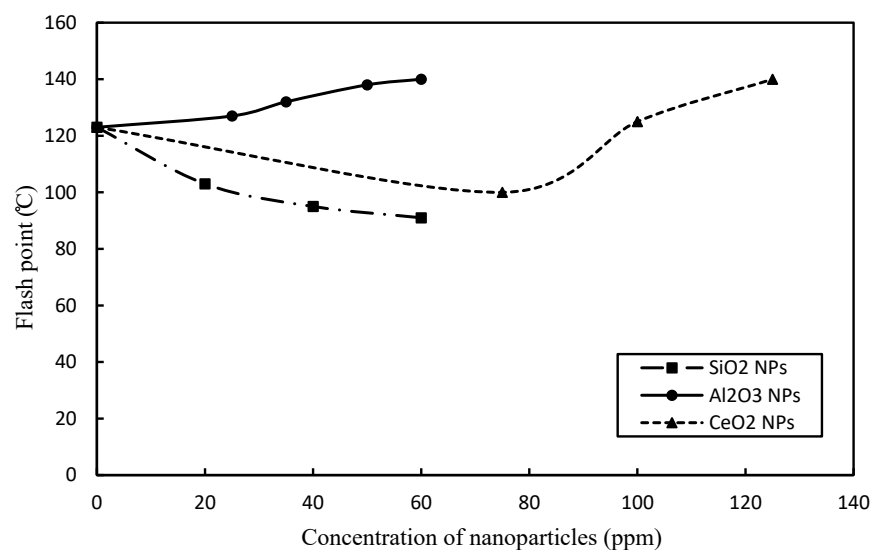


Figure 7. Effects of nanoparticle concentrations on the biodiesel flash point.

3.4.4. Effect of Nanoparticles on Biodiesel Calorific Value

Biodiesel's energy content can be altered with the addition of nanoparticles, which consequently affects the biodiesel's calorific value [54,60]; biodiesel's calorific value can be raised by adding nanoparticles. Adding nanoparticles improves the biodiesel's cetane number, and this consequently leads to an enhancement in the quality of the biodiesel's ignition and combustion [66]. It is important to choose nanoparticle types and concentrations carefully in order to modify these qualities as needed without losing other important fuel features [57,67–69].

The nanoparticles' influence on biodiesel calorific value is illustrated in Figure 8. It is noticed that silicon oxide and aluminum dioxide nanoparticles significantly enhance the calorific value of biodiesel, with the peak effect observed at a concentration of 25 ppm for both nanoparticle types. Beyond this concentration, their impact on the biodiesel calorific value becomes negligible. Additionally, increasing cerium oxide concentrations boosts the biodiesel calorific value up to 80 ppm, while concentrations above 80 ppm show no notable influence.

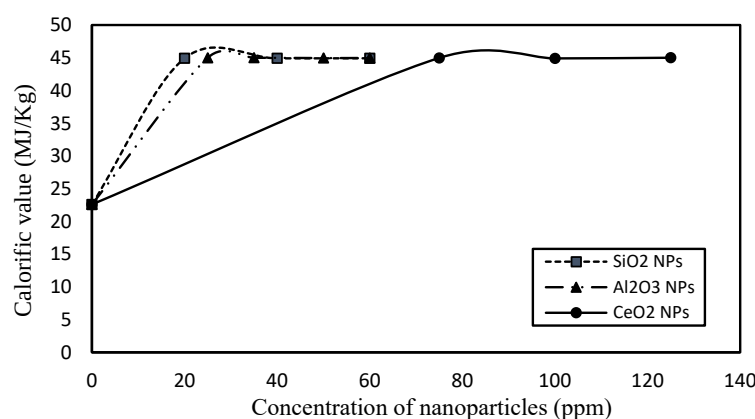


Figure 8. Effect of nanoparticles on the biodiesel calorific value.

3.5. The Optimum Mixture of Diesel and Biodiesel with Added Nanoparticles

The maximum mixing ratios between conventional diesel and the studied biodiesel–nanoparticle mixtures were determined by using LINGO optimization software (version 18), and the achieved results are shown in Table 8.

Table 8. Maximum mixing ratio between conventional diesel and biodiesel–nanoparticle mixtures.

Code	Definition	Flash Point (°C)	Kinematic Viscosity (cSt)	Density (Kg/m ³)	Calorific Value (MJ/Kg)	Max. Mixing Ratio
1	Silica dioxide (20 ppm)	103	4.17	885.2	44.91	24.79
2	Silica dioxide (40 ppm)	95	4.22	885.3	44.91	24.73
3	Silica dioxide (60 ppm)	91	4.50	885.4	44.92	24.68
4	Alumina (60 ppm)	140	4.50	886.8	44.97	14.28
5	Alumina (25 ppm)	127	4.49	885.9	44.99	3.40
6	Alumina (35 ppm)	132	4.45	886.1	45	4.34
7	Alumina (50 ppm)	138	4.38	886.5	44.95	24.37
8	Cerium oxide (75 ppm)	100	4.50	887.4	44.97	2.44
9	Cerium oxide (100 ppm)	125	4.41	887.6	44.9	24.89
10	Cerium oxide (125 ppm)	140	4.51	887.9	45	3.22
	Biodiesel	47	4.55	885.2	22.59	24.38
	Conventional diesel	79	3.39	838.4	45.61	

Regarding Table 8, the maximum mixing ratio between biodiesel and conventional diesel without adding any type of nanoparticles is 24.38%, which can be called biodiesel B24.38. After adding nanoparticles to biodiesel, the mixtures of biodiesel and diesel fuel that have a mixing ratio higher than B24.38 are mixtures that take the codes 1, 2, 3, or 9, which are designated for a mixture with 20 ppm SiO₂, 40 ppm SiO₂, 60 ppm SiO₂, or 100 ppm CeO₂, respectively. As presented in Figure 6, the optimum concentration of silicon dioxide is 25 ppm. Thus, the optimum code chosen from the 1, 2, and 3 codes is code 1, which is a mixture of biodiesel and diesel fuel after adding 20 ppm of SiO₂. Based on Table 9, the optimal mixing ratio of biodiesel to diesel is achieved with the addition of 20 ppm of SiO₂ or 100 ppm of CeO₂. To determine the best type of nanoparticle to be added (either 20 ppm of SiO₂ or 100 ppm of CeO₂), LINGO optimization software was utilized to analyze the properties of each mixture and compare them with those of the mixture containing only diesel and biodiesel, without any nanoparticles.

Table 9. Properties of biodiesel and conventional diesel mixtures after and before adding 20 ppm of silicon dioxide or 100 ppm of cerium oxide.

NP Type	NP Concentration (ppm)	Properties of Biodiesel–Diesel Blend			Error %
		Property	Before Adding NPs	After Adding NPs	
Silica Dioxide (SiO ₂)	20	Mixing ratio (%)	24.4	24.79	(+) 1.56
		Density (Kg/m ³)	849.81	850	0.0
		Kinematic viscosity at 40 °C (cst)	3.64	3.58	(−) 1.7
		Flash point (°C)	89.72	84.95	(−) 5.32
		Calorific value (MJ/Kg)	40	45.44	(+) 11.97
Cerium Oxide (CeO ₂)	100	Mixing ratio (%)	24.4	24.89	(+) 2
		Density (Kg/m ³)	849.81	850.65	0.0
		Kinematic viscosity at 40 °C (cst)	3.642	3.62	(−) 0.6
		Flash point (°C)	89.72	90.45	(+) 0.8
		Calorific value (MJ/Kg)	40	45.43	(+) 11.95

As illustrated in Table 9, adding 20 ppm of silicon dioxide nanoparticles results in an increase of 1.56% in the maximum mixing ratio and an increment of 11.97% in the calorific values of the conventional diesel–biodiesel blend. However, this addition leads

to a decrease in kinematic viscosity and flash point of 1.7% and 5.32%, respectively, with no change in density. Conversely, incorporating 100 ppm of cerium oxide into the diesel–biodiesel blend increases the maximum mixing ratio, flash point, and calorific value by 2%, 0.8%, and 11.95%, respectively. The kinematic viscosity decreases by 0.6%, while the mixture density remains unchanged.

It is observed that the addition of 20 ppm of silicon dioxide lowers the flash point of the diesel–biodiesel blend, which negatively impacts the combustion process and increases emissions. As a result, it is advisable to avoid this type of nanoparticle. In contrast, adding 100 ppm of cerium oxide nanoparticles enhances all properties of the diesel–biodiesel mixture. Therefore, 100 ppm of cerium oxide is deemed the best option for improving the diesel–biodiesel blend’s characteristics. It is concluded that the optimal blend consists of 25% biodiesel, 75% conventional diesel, and 100 ppm of cerium oxide nanoparticles.

3.6. Effect of Nanoparticles on Diesel–Biodiesel Fuel Performance and Emissions

The following subsections discuss the influence of nanoparticles on the investigated diesel–biodiesel fuel’s performance and emissions when used as a fuel for compression ignition (CI) engines. One of the most important fuel performance parameters is the brake-specific fuel consumption (BSFC), which is applied to evaluate the economy of an engine. The BSFC refers to the weight of fuel consumed per unit of power output by the engine per unit of time [70].

3.6.1. Brake-Specific Fuel Consumption (BSFC)

When compared with plain diesel, the BSFC of biodiesel blends is higher, and it was discovered that the BSFC is increased with an increase in the biodiesel mixing ratio. This is because biodiesel has a higher density and a lower calorific value when compared with diesel [71,72]. With the addition of cerium oxide nanoparticles to a biodiesel–diesel mixture, BSFC is decreased by 2.4% compared with that of pure diesel. The reason can be attributed to the existence of oxygen molecules along with the cerium oxide nanoparticles, which leads to a drop in viscosity that coincides with a higher calorific value of the studied diesel fuel. According to the research work of Basha and Anand [73], the catalytic effect during combustion inside the engine cylinder is increased because of the large surface area-to-volume ratio. This is, in turn, an indication of the improved fuel performance. Figure 9 shows the variation in specific fuel consumption with brake power for diesel and the investigated biodiesel when mixed with 100 ppm of cerium oxide nanoparticles. The obtained results illustrate that the BSFC of the optimum blend (25% biodiesel + 75% diesel + 100 ppm CeO₂) is lower than that of pure diesel fuel for all loads.

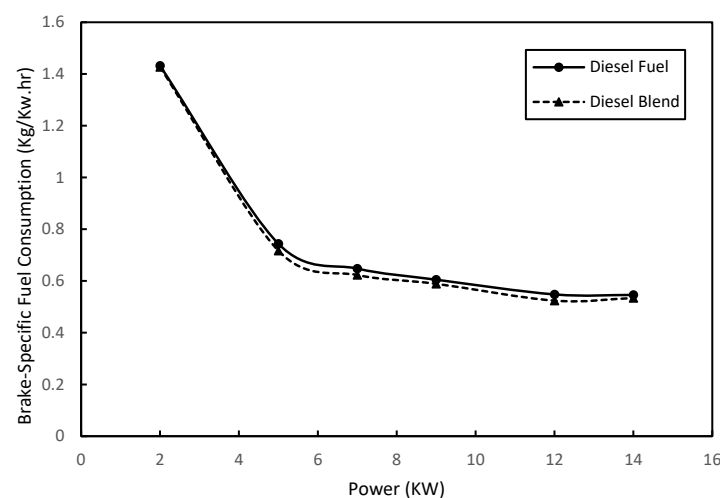


Figure 9. Brake-specific fuel consumption versus brake power relationship.

3.6.2. Emissions

Emissions such as carbon monoxide, carbon dioxide, and smoke opacity are measured twice at the optimum conditions for the diesel engine. The first, by using conventional diesel as a fuel in the diesel engine, and the second, by fueling the diesel engine with the optimum blend of biodiesel enhanced with cerium oxide nanoparticles (100 ppm) and diesel. Table 10 shows the variation in combustion emissions generated by a diesel engine fueled by the obtained optimum fuel mixture of biodiesel–diesel–CeO₂ compared with pure diesel. It is noticed that the smoke emission of this optimum fuel blend has decreased by 5.26% compared with that of neat diesel. This can be attributed to the higher oxygen concentration in the biodiesel fuel blends, which encourages full combustion and causes a decrease in smoke emissions. Due to the shorter ignition delay (ID) and enhanced igniting properties of the nanoparticles, similar trends were seen with the fuels that contained nanoparticles. According to Sadhik Basha and Anand [73]’s work, shorter ID results in less fuel accumulating in the combustion chamber, which results in complete combustion of the nanoparticle-blended biodiesel and lower smoke emissions when compared with neat diesel.

Table 10. Emissions of the achieved optimum blend compared with pure diesel.

Emissions	CO (vol. %)	CO ₂ (vol. %)	Smoke Opacity (%)
Pure Diesel	0.013	3.44	1.9
Optimum Blend	0.009	3.45	1.8
% Change	(−) 30.77	(+) 0.3	(−) 5.26

Resitoglu et al. [74] stated that too-large injector droplets or insufficient turbulence in the combustion chamber can lead to increased CO emissions. The uniform dispersion of nanoparticles present in the biodiesel–diesel fuel blend is the other reason for the secondary atomization occurrence in the combustion chamber [73]. Nanoparticles act as an oxidation catalyst, promoting complete combustion and increasing the activation of carbon combustion [75]. Fuels containing mixtures of nanoparticles burned more quickly due to their decreased ignition delay. A shorter ignition delay could result in more fuel–air mixing and homogenous burning. Consequently, the emissions of carbon monoxide from biodiesel containing nanoparticles were considerably decreased [43].

The optimal biodiesel–diesel–CeO₂ blend shows an increased oxygen content and calorific value compared with fossil diesel, leading to a 30.77% reduction in CO emissions. The higher oxygen concentration in biodiesel enhances the oxidation of fuel particles, which slightly increases CO₂ emissions as the biodiesel blending percentage rises [76]. When nanoparticles are added to the diesel–biodiesel blend, catalytic combustion is improved, resulting in a 30.77% decrease in CO emissions and a 0.3% increase in CO₂ emissions, as detailed in Table 10.

4. Conclusions

The main objective of the current study is to obtain the optimum conventional diesel and biodiesel (derived from WCO) blend enhanced by adding nanoparticles. The selected nanoparticles (silica dioxide (SiO₂), alumina (Al₂O₃), and cerium oxide (CeO₂)) were chosen for their demonstrated effectiveness in enhancing fuel properties in previous research, which highlighted improvements in thermal stability, oxidation resistance, and combustion characteristics. The best type of nanoparticles was selected after studying the effect of these nanoparticles on density, kinematic viscosity, flash point, and calorific values of the considered biodiesel. The experimental results showed that silicon dioxide has the highest effect in decreasing the biodiesel kinematic viscosity, while cerium oxide nanoparticles had the lowest influence. As a general trend, the density of the biodiesel was increased by increasing the concentration of the added nanoparticles. However, it was observed that the density of biodiesel with cerium oxide or aluminum oxide nanoparticles was higher than that of the biodiesel mixed with silicon dioxide. Adding aluminum oxide had the best

and preferable influence in increasing the investigated biodiesel's flash point. It was also observed that silicon oxide and aluminum dioxide nanoparticles had the highest effect in increasing the biodiesel's calorific value.

The maximum mixing ratio between conventional diesel and the studied biodiesel–nanoparticles mixtures was determined by using LINGO optimization software (version 18). The results indicated that cerium oxide nanoparticles are the best choice, with an optimum concentration of 100 ppm, which can be added to the diesel–biodiesel mixture to achieve the maximum diesel–biodiesel mixing ratio of 25% and to improve its properties. Therefore, the obtained optimum blend consists of 25% biodiesel, 75% conventional diesel, and 100 ppm of cerium oxide nanoparticles. The experimental results showed also that the BSFC of the achieved optimum blend is reduced by 2.4%, and CO and smoke opacity emissions of this blend are reduced by 30.77% and 5.26%, respectively, compared with pure diesel. However, CO₂ emissions of the optimum blend are increased by 0.3% compared with conventional diesel.

The developed fuel blends obtained from mixing WCO biodiesel with pure diesel and 100 ppm of CeO₂ nanoparticles can be considered as a promising alternative fuel to be used for diesel engines. Hence, the addition of CeO₂ nanoparticles to other types of biodiesels can lead to increasing the mixing ratio of biodiesel and improving the diesel–biodiesel fuel performance with an observed reduction in the combustion emissions from the diesel engine.

5. Limitations and Suggestions

This article reached an optimum mixing ratio between biodiesel enhanced with 100 ppm cerium oxide nanoparticles and petrol diesel of 25% (B25), but in many countries that have a very cold climate, this ratio will be not efficient, because biodiesel has a poor low-temperature flow property. In addition, using a high concentration of biodiesel may be ineffective, because biodiesel can attack plastic and rubber components such as seals and fuel lines. It is suggested that future research can also explore other areas, such as the following:

1. Examining how stable and long-lasting nanoparticle-enhanced biodiesel is under various storage and transportation scenarios.
2. Assessing how well biodiesel enriched with nanoparticles performs in various engine types and operating environments.
3. Researching the possible toxicity of nanoparticle-enhanced biodiesel to both aquatic and terrestrial species as well as its possible effects on the environment.
4. Examining the possibility of increasing the production of biodiesel improved by nanoparticles for use in commercial settings.
5. A filter that can remove unburned nano-additives from diesel vehicle exhaust is being developed.
6. By using optimization software in biodiesel systems, it is possible to quickly and easily determine the optimal concentration and size of nano-catalysts without having to perform costly and time-consuming practical experiments on numerous samples. Furthermore, until now, there has not been much research performed on the use of NPs as fuel additives.

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