

Synthesis of Fe–Ni–TiO₂/activated carbon nanoparticles and evaluation of catalytic activity in a palm oil/diesel fuel blended diesel engine and optimization with RSM

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Abstract. Although diesel engine emissions, which can pose serious risks to the environment and human health, can be reduced with biodiesel/diesel fuel blends, combining diesel fuel with an oxidation catalyst with a sizable oxygen storage capacity can more effectively reduce emissions from diesel engines. In this study, Fe–Ni–TiO₂/Activated Carbon (AC) catalyst was produced and used as an oxidation catalyst. Experimental studies were performed on a four-stroke diesel engine by adding at numerous concentrations (0–50–100 ppm) Fe–Ni–TiO₂/AC nanoparticles (NP) to the Palm Oil biodiesel (PO)-diesel fuel blend. Optimum conditions were determined by modelling the obtained data in response surface methodology (RSM). The Fe–Ni–TiO₂/AC catalyst outcomes in a considerable decrease in hydrocarbon (HC), nitrogen oxides (NO_x), carbon monoxide (CO), and smoke emissions. Optimization outcomes pointed out that the ideal diesel engine running requirements were determined to be 1750 W engine load, 100 ppm the NP amount, and 30% the PO ratio. Responses for these optimum conditions for Brake Specific Fuel Consumption (BSFC), Brake Thermal Efficiency (BTHE), CO, HC, NO_x, and smoke were determined as 999.06 g/kWh, 27.07%, 0.032%, 40.63 ppm, 818.18 ppm, and 4.26%, respectively. The R^2 values showed that the result obtained from the created model was in good agreement with the experimental results.

Keywords: Nanoparticles, Palm oil biodiesel, Catalyst, Emission, Response surface methodology.

Nomenclature

AC	Active Carbon
ANOVA	Analysis Of Variance
BSFC	Brake Specific Fuel Consumption
BTHE	Brake Thermal Efficiency
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
EGT	Exhaust Gas Temperature
F-value	Fisher's value
HC	Hydrocarbon
NO _x	Nitrogen Oxide
NP	Nanoparticle
P-value	Probability value
PM	Particulate Matter
PO	Palm Oil
R^2	Correlation coefficient
RSM	Response Surface Methodology

SEM	Scanning Electron Microscope
SO _x	Sulphur oxides
XRD	X-Ray Diffraction

1 Introduction

The need for alternative and renewable energy sources is growing every day as a result of the constant rise in energy demand brought on by the growing population and the diminishing fossil fuel reserves, which are the most common energy source [1, 2]. Among many alternative energy resources, biofuels are getting extraordinary attention thanks to their many advantages [3]. Various lipid feedstocks, including animal fats [4], vegetable oils [5, 6], waste cooking oils, and oily plants [7] are used to produce biodiesel. Methanol or ethanol reacts with oil or fats from plants or animals to produce biodiesel through transesterification. The side product of the transesterification is glycerol which can be reduced by using an appropriate catalyst [8].

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Biodiesel, produced after the transesterification process, is a non-toxic, environmentally friendly, and biodegradable alternative fuel that can be used instead of diesel. It can also be used in many diesel engines in any proportion blended with diesel fuel without the need for extra purification. Compared to diesel, biodiesel-oxygenated biofuels do not contain sulphur. They have a higher cetane number, therefore producing less toxic gases such as HC, CO, Sulphur Oxides (SO_x), and Particulate Matter (PM) emissions.

For biodiesel production, generally, palm, canola, sunflower, and soybean oils are used, but PO is one of the best-selling vegetable oils [9]. PO is not expensive and can produce biodiesel more cheaply than canola and soybean oils. Increasing the biodiesel rate in the diesel blends increases the thermal efficiency of diesel–biodiesel blends. Therefore, biodiesel combustion in diesel engines helps to reduce CO, HC, and NO_x emissions [10]. In addition, the new approach, adding NPs to biodiesel fuel, was introduced to reduce particulate matter, total HC, CO, and SO_x emissions. The NPs also provide high oxidation activity to soluble organic fractions and may have different reactions kinetic on the oxidation of different HC compounds. The catalyst activity depends on various variables, including fuel type, exhaust temperature, the fuel's sulphur amount, and catalyst size [11, 12]. The metal oxides of Cu, Fe, Ni, Ce, Pt, B, Al, and Co have been extensively employed as additives to promote the chemical oxidation of CO, HC, and SO_x in diesel and biodiesel fuel blends [13, 14]. The metal oxides are dispersed easily in the diesel fuel, shortening the ignition delay and extensively oxidizing the biodiesel blend. In addition, fuel additives are also required to stabilize the blend. [15]. Anbarasu *et al.* used aluminium oxide as an additive in the biodiesel–diesel blend and reduced CO, smoke, HC, and NO_x emissions by 1.8%, 3.3%, 3.9%, and 4.2%, respectively [16]. Another study in which cerium oxide was used as an additive investigated the effects on emissions. Findings proved that using cerium oxide as an additive decreased NO_x , CO, and smoke by 1.1%, 3.7%, and 4.2%, respectively [17]. D'Silva *et al.* studied the effect of titanium dioxide NPs addition on emissions and engine performances in the diesel engine. It is investigated that emission values decreased, and engine performances increased with titanium dioxide NPs. Moreover, the BTHE of the engine increased. Furthermore, it was observed that the CO emission decreased by 22%, and the HC emission decreased by 18%. Owing to its excellent catalytic property, including both oxidation and reduction reactions, titanium dioxide has been employed as a promising catalyst [18]. Sajith, V. *et al.* researched the influence of cerium oxide supplements in blends of biodiesel that could result in lower exhaust emissions and better engine performance. The authors exposed that HC and NO_x emissions decreased drastically with adding the cerium oxide NPs to the diesel engine [19]. Prabu analyzed the effects of aluminium and cerium NPs as additives in diesel blends on a compression ignition engine. The study demonstrated that the BTHE increased by 12%, and HC, NO_x , and CO decreased by 44%, 30%, and 60%, respectively [20]. Table 1 shows the changes in diesel engine performance and emission responses with different nanoparticles and biodiesel.

Although research into the accumulation of nanoparticles in diesel fuel is growing constantly, nanoparticles are expensive to make and purchase. This situation has revealed the need to determine the optimum conditions for both the monetary and labour force. Therefore, with few experiments using computer applications, precision optimization has become popular in recent years and RSM is one of the most suitable applications. RSM is a group of statistical and mathematical techniques used to improve procedures and product designs. RSM can be used when the response of interest is influenced by many variables [26]. RSM is used in many engineering applications as well as in internal combustion engines. RSM was applied to analyze the impacts of individual test variables (e.g., different engine loads, diesel–biodiesel fuel blend ratio, injection time, and NP concentration) and their interactions on the performance of diesel engines and exhaust gases [27–29]. Performance and emissions testing for diesel engines require extensive, expensive, and time-consuming testing. Therefore, RSM has recently received much attention to determine engine performance optimizations, combustion characteristics, and emissions using engine load, engine speed, and fuel blend input factors [30].

RSM was employed by Pandian *et al.* to examine how performance and emission quality were impacted by injection method restrictions. A four-stroke compression ignition engine powered by a Pongamia biodiesel–diesel blend was used by the authors. According to their findings, the optimum operating conditions for a test engine of 7.5 kW at 1500 rpm using diesel fuel combined with Pongamia biodiesel were 225 bar injection pressure, 21° before the top dead point injection timing, and 2.5 mm nozzle tip protrusion [31]. Krishnamoorthi *et al.* investigated the influence of injection timing and pressure in varying engine compression ratios. RSM was operated to optimize the experiments with injection pressure, compression ratio, and injection timing as the selected input variables. The ideal settings were an injection pressure of 250 bar, a compression ratio of 18, and an injection timing of 21° before the top dead point [32]. On a diesel engine operating on a combination of biodiesel, diesel, and tert-butyl hydroxyl quinone antioxidant fuel, Baranitharan *et al.* applied the RSM technique. The ideal results acquired by RSM were 0.33 kg/kWh, 22.01%, 0.67%, 224 ppm, 8.33%, and 351 ppm for BSFC, BTHE, CO, HC, carbon dioxide (CO_2), and NO_x , respectively. Indeed, the optimum value of the compression ratio at higher loads results in better enhancement during the performance characteristics of the diesel engine [33]. Simsek, S. and Uslu, S. used RSM to examine how different biodiesel/diesel fuel ratios made from canola, safflower, and leftover vegetable oil affected the performance of a four-stroke diesel engine. The researchers determined that the engine's ideal operating conditions were a 1484.85-Watt engine load, 215.56 bar of injection pressure, and a 25.79% biodiesel ratio. Moreover, the best responses were discovered as 20.54%, 199.88 $^\circ\text{C}$, 0.26%, 558.44 ppm, and 4.52% for BTHE, Exhaust Gas Temperature (EGT), smoke, NO_x , and CO_2 , respectively. In comparison, R^2 (correlation coefficient) were investigated as 99.81%, 99.36%, 98.84%, 98.31% and 99.00% for BTE, EGT, smoke,

Table 1. Variation of responses in studies using nanoparticles.

Blend	Performance	Emission	Ref.
Diesel/Ethanol/Nickel Zinc Iron Oxide ($\text{NiZnFe}_2\text{O}_4$)	Torque $\blacktriangle$ Power $\blacktriangle$ BSFC $\blacktriangledown$	HC $\blacktriangledown$ CO $\blacktriangledown$ CO ₂ $\blacktriangle$ NO _x $\blacktriangle$	[21]
Diesel/Pongamia biodiesel/Copper oxide	BTHE $\blacktriangle$ BSFC $\blacktriangledown$	HC $\blacktriangledown$ CO $\blacktriangledown$ $\blacktriangledown$ NO _x $\blacktriangledown$ Smoke $\blacktriangledown$	[22]
Diesel/corn oil methyl ester/ CeO_2	BTHE $\blacktriangle$ BSFC $\blacktriangledown$	HC $\blacktriangledown$ CO $\blacktriangledown$ NO _x $\blacktriangle$	[23]
Diesel/orange peel oil methyl ester/ CeO_2	BTHE $\blacktriangle$ BSFC $\blacktriangledown$ EGT $\blacktriangledown$	CO $\blacktriangledown$ NO _x $\blacktriangledown$ Smoke $\blacktriangledown$	[24]
Diesel/ <i>Ricinus communis</i> /Strontium-zinc oxide	BTHE $\blacktriangle$ BSFC $\blacktriangledown$	HC $\blacktriangledown$ CO $\blacktriangledown$ CO ₂ $\blacktriangledown$ Smoke $\blacktriangledown$ NO _x $\blacktriangle$	[25]

NO_x, and CO₂, respectively [34]. Optimum findings obtained from optimization studies using fuels containing nanoparticles are tabulated in Table 2.

The additive of nanomaterials to biodiesel/diesel fuel mixtures is emerging as a new strategy since it has been demonstrated by researchers and several studies that doing so can improve the fuel's combustion conditions and reduce harmful engine emissions. Researchers have focused on changing engine responses when different nanomaterials are added to diesel fuel or different biodiesel/diesel combinations. Before nanoparticle-based fuel can be sold commercially, more consideration must be given to its stability, cost-effectiveness, and ecological and environmental components. Studies of the influence of adding nanoparticles to biodiesel/diesel fuel mixtures on the responses of diesel engines are currently being investigated, however, not enough experiments have been done. No study on the usage of Fe–Ni–TiO₂/AC as nanoparticles could be located among these papers in the literature. The primary objectives and innovations of this research are to generate a resource for using Fe–Ni–TiO₂/AC/diesel/PO biodiesel mixtures in diesel engines. The study's second aim is to optimize both engine conditions and Fe–Ni–TiO₂/AC nanoparticles amount with RSM so that Fe–Ni–TiO₂/AC nanoparticle can be used efficiently in diesel engines. In this way, it aims to achieve improvements in engine responses and save money/time. Inspired by these purposes, this study assessed the performance of several amounts of Fe–Ni–TiO₂/AC catalyst in a single-cylinder diesel engine fed by different ratios of PO biodiesel–diesel mixtures and optimized with RSM.

2 Material and methods

2.1 Nanoparticle preparation

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\geq 99.95\%$), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 99.0\%$), TiCl_4 ($\geq 99.99\%$), and NH_4OH were provided from Sigma Aldrich. The activated carbon was obtained from Nanografi. All chemicals were applied without any further purification.

The preparation of nanoparticles is shown schematically in Figure 1. The desired amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added to 200 mL of distilled water and combined for an hour using a magnetic stirrer. An aqueous solution of 0.1 M NH_4OH was added to 0.5 M aqueous solution of TiCl_4 and stirred via a sonicator for 1 h. The Fe and Ni salt solution was included in the solution of TiCl_4 , and the combination was mixed and sonicated with a sonicator at 80 °C for 2 h. The mixture was then overnight dried at 105 °C in an oven. To create the Fe–Ni–TiO₂/AC catalyst, the sample was lastly calcined at 400 °C for 4 h in a vacuum tube furnace in an N₂ environment.

2.2 Characterization of the nanoparticles

The synthesised catalyst's structural characterization was depicted by the Rigaku X-Ray Diffraction (XRD) mechanism via Cu–K α ¹ radiation. The scanning level was 26/min in the range of $2\theta = 10\text{--}80^\circ$. Zeiss Sigma 300 Field Emission Scanning Electron Microscope (SEM) was employed for evaluating the SEM images of the catalyst, and EDX evaluated the elemental compositions.

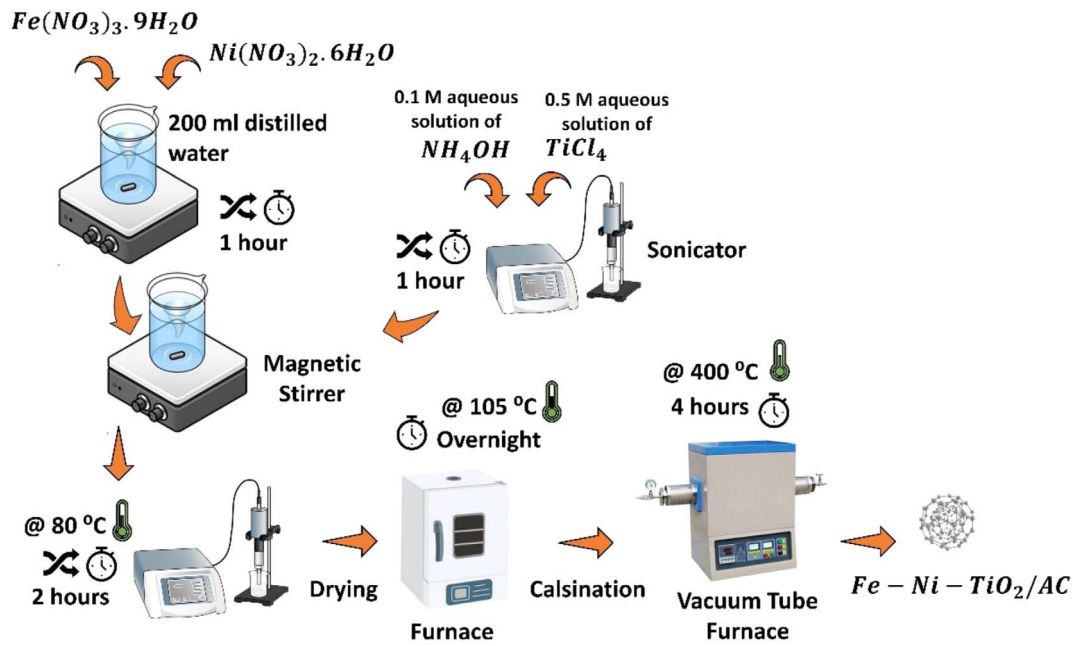
The SEM images of the produced catalyst are shown in Figure 2. It is seen from the images that the coating process of Fe, Ni particles, and TiO₂ NPs on the activated carbon was doped successfully. Some pores were also found on the surface of the activated carbon. The Fe, Ni, and TiO₂ NPs were immobilized on the activated carbon surface with high crystallinity.

The elemental composition of the Fe–Ni–TiO₂ doped activated carbon catalyst was illustrated in Figure 3. It is revealed from the EDX spectra that the elemental peaks of Ni, Ti, O, and C were attributed to the Fe, Ni, and TiO₂ doping on the activated carbon surface.

The synthesized catalyst's phase type and composition are determined by XRD analysis, as shown in Figure 4. The observed peaks at 27.7°, 36.32°, 38.06°, 48.4°, 54.5°, 63°, and 69.3° correspond to (1 1 0), (1 0 1), (1 1 1), (2 1 0), (2 1 1), (0 0 2) and (3 0 1) planes of rutile TiO₂. The sharp peak at 27.6° corresponds to the (0 0 2) plane of Activated Carbon (AC) and another peak appears at 25.52°, which may confirm graphitic carbon [40]. Moreover,

Table 2. Optimum results obtained with fuels containing nanoparticles.

Blend	Inputs	Optimum engine conditions	Ref.
Diesel/Waste cooking oil methyl ester/Alumina	• Engine speed • Nanoparticle concentration	• 1000 rpm engine speed • 160 ppm nanoparticle concentration	[35]
Diesel/Neem biodiesel/Nickel oxide	• Injection Timing • Nanoparticle concentration • Compression Ratio • Injection Pressure	• 26.998° before top dead centre • 227.86 bar injection pressure • 17.2585 compression ratio • 25.0003 ppm nanoparticle concentration	[36]
Diesel/Water hyacinth oil biodiesel/Hydrogen/Cerium oxide	• Engine load • Hydrogen blend • Nanoparticle concentration • Compression ratio • Injection Pressure	• 87.8788% engine load • 28.68% hydrogen blend • 80 ppm nanoparticle concentration • 19 compression ratio • 194.54 bar injection pressure	[37]
Diesel/Sesame oil/Graphene oxide	• Engine load • Nanoparticle concentration	• 1950 W engine load • 100 ppm graphene oxide	[38]
Diesel/Acacia concinna biodiesel/titanium dioxide	• Engine load • Nanoparticle concentration • Injection Timing	• 150 mg/L nanoparticle concentration • 22.5° before top dead centre • 82.37% engine load	[39]

**Fig. 1.** The preparation of nanoparticles.

the appearing peaks at 41.4, 55.24, and 62.9 corresponds to peaks of Fe_3O_4 , which indicates that the doping of Fe_3O_4 particles to activated carbon surface has been loaded successfully [41]. Two distinct crystallinity peaks emerge at 44.5° and 52.0°, as well as two known Ni diffraction peaks that appear at $2\theta = 44\text{--}76^\circ$. Because of the small quantity of NiO_2 phase in the particle's overall composition, these peaks are not visible (JCPDS No. 03-065-2865) [42].

2.3 Experimental study

In the tests carried out within the scope of this study, fuels obtained with a mixture of PO, diesel and Fe-Ni-TiO₂/AC NPs were used to examine engine performance and emissions. Table 3 displays the properties of the experiment fuels. Experimental fuels were obtained together with diesel fuel by using three different ratios (0–15–30%) of PO and

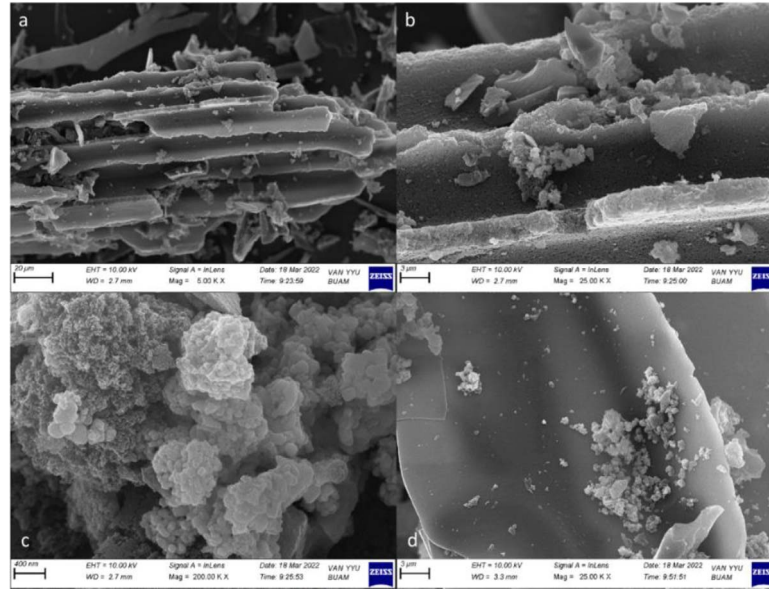


Fig. 2. The SEM images of the Fe-Ni-TiO₂/AC catalyst.

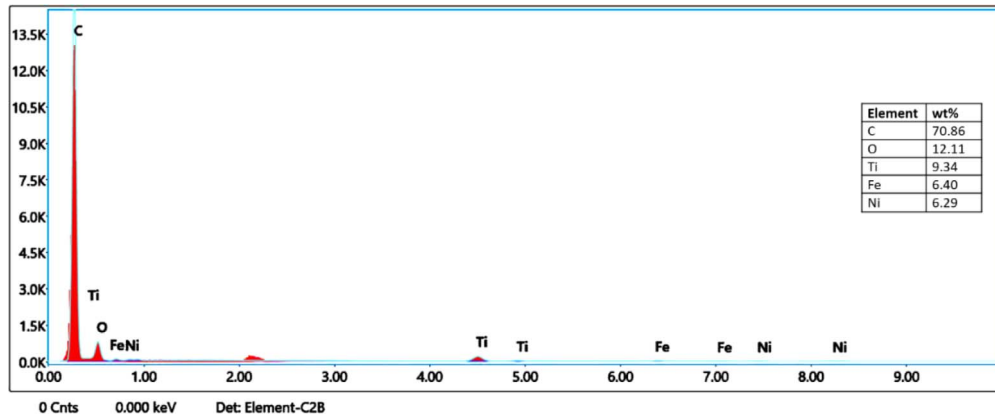


Fig. 3. The EDX result of the Fe-Ni-TiO₂/AC catalyst.

three different amounts (0–50–100 ppm) of Fe-Ni-TiO₂/AC NP. The combination was mixed for 2 h to ensure uniformity and complete dispersion of NPs and then used in engine experiments.

All the tests were organized in a single-cylinder diesel engine. The technical information of diesel engine is presented in Table 4. Before the testing fuel blends, the engine was run with only diesel fuel for 5 min to obtain cleaner test results. Engine tests were carried out at 1000–1500–2000 and 2500 W engine loads at a constant engine speed of 3000 rpm. Halogen bulbs with 500 and 750 W of power were used in engine loadings. The change in fuel consumption and the change in emissions were observed by increasing the engine load at 500 W intervals. Three different results were recorded for each response and the average was determined as the final result. The emission properties of the test fuels were examined using

an exhaust gas analyzer that was connected to the computer. Emissions were considered using the Bilsa MOD 2210 WINXP-K exhaust gas analyzer, whose measurement accuracy is given in Table 5.

There may be some mistakes and inaccuracies during the trials because there are so many variables, including the equipment's service, maintenance, and operational state, which affect the engine output factors and the surroundings. The measuring instruments operated in the tests were calibrated, and each test was run three times in order to lower the measurement error rate to the lowest possible percentage and maximize the precision of the observations. Based on the methodology developed by Kline and McClintock [43], the uncertainties of measured responses have been calculated and are displayed in Table 6. According to the chart below, the uncertainty percentage for this investigation was 3.3598%:

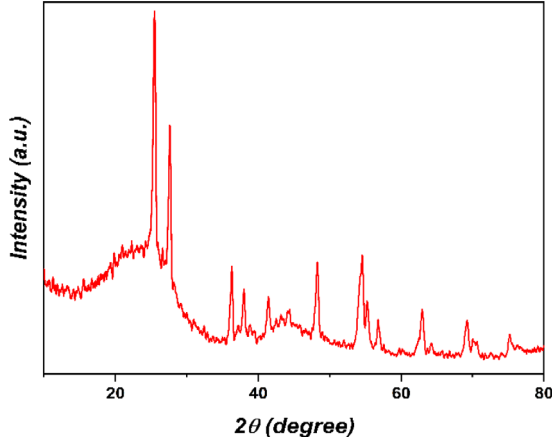


Fig. 4. The XRD results of the Fe-Ni-TiO₂/AC catalyst.

Table 3. Fuel properties [41].

Characteristic	Diesel	Palm oil biodiesel
Number of cetane	54	64
Lower calorific value (kJ/kg)	43 000	38 500
Kinematic viscosity (mm ² /s)	3.09	4.61
Density (kg/m ³)	839	880
Flash point (°C)	50	314

$$\begin{aligned}
 &= \sqrt{[(U_{\text{Load}})^2 + (U_{\text{BSFC}})^2 + (U_{\text{CO}})^2 + (U_{\text{HC}})^2 + (U_{\text{NO}_x})^2 + (U_{\text{Smoke}})^2]} \\
 &= \sqrt{[(1.33)^2 + (1.08)^2 + (1.21)^2 + (1.15)^2 + (1.56)^2 + (1.77)^2]} \\
 &= \pm 3.3598\%
 \end{aligned}$$

2.4 Response surface methodology

By analyzing the relationship between numerous independent and dependent variables, RSM is a collection of mathematical and statistical tools that can identify the ideal experimental circumstances [44]. The meaningful output of RSM's mathematical and statistical experiments is based on important factors. The method's primary goal is modelling and optimizing the outputs [29, 45].

The first-order polynomial that underlies the simplest model must be used for the responses to be well fitted to the equation in equation (1):

$$y = \beta_o + \sum_{i=1}^k \beta_i x_i + \varepsilon. \quad (1)$$

According to the equation presented in equation (2), the polynomial function must have quadratic terms in order to establish a good relationship between the output and the inputs and identify the critical point [46]:

$$y = \beta_o + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{1 \leq i < j \leq k} \beta_{ij} x_i x_j + \varepsilon, \quad (2)$$

Table 4. Technical information regarding the diesel engine.

Properties	Specification
Model	Katana KM 178FE
Max. engine speed	3000 rpm
Volume	296 cm ³
Compression ratio	18:0:1
Injection angle	31° crankshaft angle
Injection pressure	205 bar
Bore	78 mm
Stroke	62 mm

Table 5. Measurement properties of exhaust gas analyzer.

Emission	Measurement scale	Correctness
CO	0–10.0% vol.	0.001%
NO _x	0–5000	1 ppm
HC	0–10 000 ppm vol.	1 ppm
Smoke	0–100%	± 0.1%

Table 6. Uncertainties of measurements.

Measurement	Uncertainty
Load	±1.33
BSFC	±1.08
CO	±1.21
HC	±1.15
NO _x	±1.56
Smoke	±1.77

where β_o is the constant term, β_i is the coefficients of linear parameters, β_{ij} represents the coefficients of the interaction parameters, k is the number of variables, x_i and x_j represent the variables, and ε is the detected noise or errors in the reply [46]. The engine load, NP amount, and PO ratio were chosen as the input parameters, and the output parameters were BTHE (%), BSFC (g/kWh), CO (%), HC (ppm), NO_x (ppm), and smoke (%).

Analysis of Variance (ANOVA) was used to determine the statistical importance of the individual effects of each variable and their interaction with the emissions. The probability value (p -value) and Fisher's value (F -value) provide control of the significance of each independent variable according to the obtained data. An independent variable's significance is indicated by a smaller p -value and a higher F -value [47].

The main indicators showing the accuracy and quality of the created regression model are R^2 , adjusted R^2 and predicted R^2 values.

The R^2 and adjusted R^2 are calculated using equation (3) and equation (4). Predicted R^2 is calculated using equations (5)–(7) [48];

$$R^2 = 1 - \left[\frac{SS_{\text{residual}}}{SS_{\text{residual}} + SS_{\text{model}}} \right], \quad (3)$$

$$\text{Adjusted } R^2 = 1 - \frac{\left[\frac{SS_{\text{residual}}}{df_{\text{residual}}} \right]}{\left(\frac{SS_{\text{residual}} + SS_{\text{model}}}{df_{\text{residual}} + df_{\text{model}}} \right)}, \quad (4)$$

$$\text{Predicted } R^2 = 1 - \left[\frac{\text{PRESS}}{SS_{\text{residual}} + SS_{\text{model}}} \right], \quad (5)$$

$$\text{PRESS} = \sum_{i=1}^n (e - 1)^2, \quad (6)$$

$$e - 1 = \frac{e_i}{1 - h_{ii}}, \quad (7)$$

where the *Sum of Squares* (SS) is variations between the overall average and the quantity of diversity described by the source, the *model* shows how much diversity is defined in the model with the general model test for importance, and *residuals* identify the amount of diversity not specified in the answer.

3 Results and discussion

3.1 ANOVA results

ANOVA is one of the applications that show the contribution levels of the factors on the selected response and how effective they are. In this study, R^2 values, ANOVA tables showing the effects of load, PO ratio, and NP amount on selected responses, and regression equations are presented in Tables 7, 8, 9, 10, and 11, respectively. Since the 95% confidence level was chosen in the model setup, factors with a p -value bigger than 5% (0.05) are expected to not affect the response. It is seen in the tables that the resulting p -value of engine load for all responses is 0. In addition, the factor with the highest contribution rate on all other responses except HC emission is engine load. The most influential factor in HC emission is the amount of NP. Moreover, the amount of NP stands out as the second most influential factor for BTHE, CO, NO_x, and smoke responses. The PO ratio was generally found to be more ineffective on responses than other factors.

3.2 RSM results

Simultaneous effects of NP amounts, engine loads, and PO ratios on engine performance and emissions are shown by 3D plots in Figures 5–10 created by RSM. Pareto charts are also shown in Figures 5–10 to better evaluate each selected variable's individual and combined effects. Pareto charts are a more useful type of chart used to understand the degree of influence of selected variables. The vertical red line in the Pareto charts reveals whether the variables are effective or not. The bars to the right of the red line indicate that the variable is more effective, and the bars to the left indicate that the degree of effect is low [49].

Table 7. R^2 values of responses.

Responses	R^2	Adjusted R^2	Predicted R^2
BTHE	98.24%	96.65%	93.97%
BSFC	99.38%	98.82%	97.67%
HC	98.62%	97.38%	89.53%
CO	97.88%	95.98%	88.40%
NO _x	99.41%	98.87%	97.74%
Smoke	97.21%	94.70%	89.01%

3.2.1 Engine performance

BTHE results

BTHE represents the ability of the consumed fuel per unit of time to convert the chemical energy of the engine into actual work [50]. Figure 5 shows the pareto chart and simultaneous effects of NP amounts, engine loads, and PO ratios on BTHE. As shown in Figure 5a, the order of influence on BTHE is engine load, NP amount, and PO ratio. Table 8 reveals that this effect is caused by 58.68% engine load, 31.77% NP content and 4.59% PO ratio. The simultaneous effects of the variables show (Figs. 5b–5d) that BTHE increases with increasing engine loads and NP amounts. Due to the thermal conductivity of Fe–Ni–TiO₂/AC NPs, rapid chain reactions can occur that accelerate fuel combustion. Moreover, the superior oxygen storage ability of Fe–Ni–TiO₂/AC NPs promotes the complete combustion of fuel and improves BTHE. As it is a well-known fact that BTHE will increase with growing temperature and pressure, BTHE is expected to rise with increasing engine loads. In addition, since PO biodiesel is a fuel containing oxygen, it increases the rate of complete combustion and BTHE. The highest BTHE values were measured at 2500 W engine load, where raising the PO ratio from 0% to 30% resulted in a 2.61% rise in BTHE. At the same engine load, BTHE increased by 1.04% with the addition of 50 ppm NP to the fuel mixture containing 70% diesel/30% PO, while this growth increased to 2.46% with the addition of 100 ppm NP.

BSFC results

BSFC describes the amount of fuel consumed to reach an equivalent speed with the fuel blends during the experiments [50, 51]. Figure 6a presents the pareto chart of the BSFC. According to the pareto chart of the BSFC, the most effective parameters are load, PO percentage, and load * load with the contribution of 81.19%, 9.86%, and 6.04%, respectively (Tab. 8). The p -value of NP amount for BSFC (0.546) is higher than 0.05, which shows its effect on BSFC is insignificant. Figures 6b–6d demonstrate the simultaneous effects of NP amounts, engine loads, and PO ratios on BSFC. It is seen in Figure 6 that BSFC decreases with increasing engine loads and NP amounts and increases with growing PO ratios. Biodiesel, which has a lower calorific value than diesel, requires more fuel to produce the same amount of power as diesel [52]. Some studies have found close results that BSFC is increased

Table 8. ANOVA results of BTHE and BSFC.

	BTHE			BSFC		
	Contribution	<i>F</i> -value	<i>P</i> -value	Contribution	<i>F</i> -value	<i>P</i> -value
Model	98.24%	61.98	0.000	99.38%	177.46	0.000
Linear	95.03%	154.25	0.000	92.03%	421.51	0.000
L-Load (W)	58.68%	305.08	0.000	81.19%	1131.98	0.000
N-NP (ppm)	31.77%	22.17	0.001	0.99%	0.39	0.546
P-PO (%)	4.59%	21.71	0.001	9.86%	50.44	0.000
Square	3.01%	4.3	0.034	6.74%	27.98	0.000
L ²	0.55%	2.49	0.146	6.04%	82.72	0.000
N ²	2.46%	10.79	0.008	0.68%	0.77	0.399
P ²	0.00%	0.01	0.919	0.03%	0.29	0.602
Two-way interaction	0.19%	0.37	0.778	0.60%	3.23	0.069
L * N	0.05%	0.13	0.730	0.27%	0.98	0.346
L * P	0.00%	0.02	0.888	0.11%	1.72	0.219
N * P	0.14%	0.79	0.394	0.22%	3.6	0.087
Error	1.76%			0.62%		
Total	100.00%			100.00%		

Table 9. ANOVA results of CO and HC.

	CO			HC		
	Contribution	<i>F</i> -value	<i>P</i> -value	Contribution	<i>F</i> -value	<i>P</i> -value
Model	97.88%	51.39	0.000	98.62%	79.42	0.000
Linear	74.65%	115.37	0.000	96.44%	207.22	0.000
L-Load (W)	40.26%	208.12	0.000	1.92%	29.6	0.000
N-NP (ppm)	32.70%	33.58	0.000	89.39%	189.71	0.000
P-PO (%)	1.68%	9.1	0.013	5.13%	13.27	0.005
Square	5.47%	6.11	0.012	1.23%	2.14	0.159
L ²	3.67%	11.23	0.007	0.02%	0	1.000
N ²	0.20%	0.6	0.456	1.10%	5.42	0.042
P ²	1.60%	5.47	0.041	0.12%	1.03	0.334
Two-way interaction	17.76%	27.97	0.000	0.95%	2.29	0.140
L * N	17.23%	43.74	00.000	0.95%	4.7	0.055
L * P	0.44%	2.09	0.179	0.00%	0	0.993
N * P	0.09%	0.42	0.53	0.00%	0.01	0.937
Error	2.12%			1.38%		
Total	100.00%			100.00%		

based on palm oil use [53]. On the other hand, the addition of Fe–Ni–TiO₂/AC NPs to the fuel blend increases the heating value and results in lower BSFC.

3.2.2 Emission characteristics

HC and CO emissions

Both HC and CO emissions result from incomplete fuel combustion in the engine combustion chamber. During

the combustion of oxygen-poor fuels, the combustion reaction cannot be fully realized, so incomplete combustion occurs. As the carbon molecules remaining as a result of incomplete combustion cannot turn into CO₂, CO, which is an intermediate product of incomplete combustion, emerges [51, 52]. Similarly, HC emissions are caused by a lack of oxygen in the fuel or a poor air-fuel mixing ratio [54]. Figures 7 and 8 demonstrate the simultaneous effects of NP amounts, engine loads, and PO ratios on CO and HC. In addition, the effect degrees of the variables on CO

Table 10. ANOVA results of NO_x and smoke.

	NO _x			Smoke		
	Contribution	<i>F</i> -value	<i>P</i> -value	Contribution	<i>F</i> -value	<i>P</i> -value
Model	99.41%	186.21	0.000	97.21%	38.7	0.000
Linear	98.28%	474.72	0.000	84.21%	98.12	0.000
L-Load (W)	96.24%	1385.53	0.000	46.85%	153.56	0.000
N-NP (ppm)	1.44%	3.59	0.087	28.39%	38.96	0.000
P-PO (%)	0.60%	4.99	0.050	8.97%	2.88	0.121
Square	1.05%	4.85	0.025	6.34%	1.47	0.281
L ²	0.85%	11.9	0.006	0.77%	0.2	0.666
N ²	0.13%	1.47	0.253	3.76%	0	0.948
P ²	0.07%	1.11	0.318	1.81%	4.11	0.070
Two-way interaction	0.08%	0.46	0.718	6.66%	7.96	0.005
L * N	0.08%	1.02	0.336	2.31%	3.3	0.099
L * P	0.00%	0.01	0.910	0.22%	0.85	0.378
N * P	0.00%	0.05	0.832	4.13%	14.81	0.003
Error	0.59%			2.79%		
Total	100.00%			100.00%		

Table 11. Regression equations for each response.

Regression equations	
BTHE	15.80 + 0.00165 L - 0.0117 N + 0.1016 P + 0.000001 L * L + 0.000559 N * N + 0.00016 P * P - 0.000003 L * N - 0.000003 L * P - 0.000439 N * P
BSFC	1911.7 - 0.9215 L - 0.372 N + 3.52 P + 0.000183 L * L + 0.00523 N * N + 0.0280 P * P - 0.000281 L * N - 0.001036 L * P + 0.0327 N * P
HC	171.4 - 0.0197 L - 1.400 N - 0.117 P - 0.000000 L * L + 0.00336 N * N - 0.0128 P * P + 0.000149 L * N - 0.000002 L * P - 0.00034 N * P
CO	1.472 - 0.000835 L - 0.00764 N - 0.01389 P + 0.000000 L * L - 0.000008 N * N + 0.000211 P * P + 0.000003 L * N + 0.000002 L * P + 0.000020 N * P
NO _x	464.0 + 0.0697 L - 0.554 N + 0.02 P + 0.000054 L * L + 0.00563 N * N + 0.0427 P * P + 0.000224 L * N - 0.000072 L * P - 0.0029 N * P
Smoke	0.35 + 0.00639 L + 0.0151 N + 0.2362 P - 0.000000 L * L - 0.000014 N * N - 0.00368 P * P - 0.000018 L * N - 0.000025 L * P - 0.002321 N * P

and HC are given in Figures 7a, and Figure 8a, respectively. The CO pareto chart shows that the engine load is the most influential parameter on CO emission, followed by load * NP amount and NP amount. ANOVA results show that load has a 40.36% contribution to CO emission while NP amount was 32.70% and load * NP amount was 17.23%. Simultaneous effects of variables show increasing NP amounts, and engine loads promote a decrease in CO emission. When the pareto chart of HC (Fig. 8d) is examined, it is seen that the variable with the highest degree of effect is the amount of NP, followed by the engine load and PO percentage. According to ANOVA results, the NP amount provides the highest contribution with 89.39%. Like CO, HC emission also decreases with increasing engine loads and NP amount (Figs. 8b-8d). It is

thought that adding NPs to the fuel mixture reduces HC and CO emissions and improves the combustion quality of the fuel by lowering the combustion temperature due to the catalytic impact provided by the high energy surface area of Fe-Ni-TiO₂/AC NPs. Furthermore, secondary atomization of Fe-Ni-TiO₂/AC NPs can improve the oxidation rate and enhance fuel combustion. On the other hand, the use of PO also contributed to the reduction of both CO and HC emissions. Thiruselvam *et al.* [55] found a similar result.

NO_x emissions

NO_x emission, a significant pollutant with harmful effects on the environment and human health, is caused by the

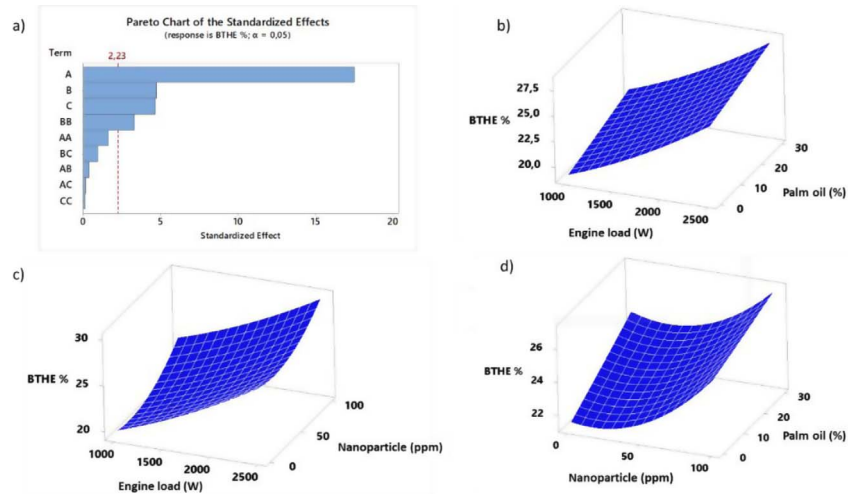


Fig. 5. Pareto chart (a) and simultaneous impacts of NP amount, engine load, and PO ratio on BTHE (b, c, d).

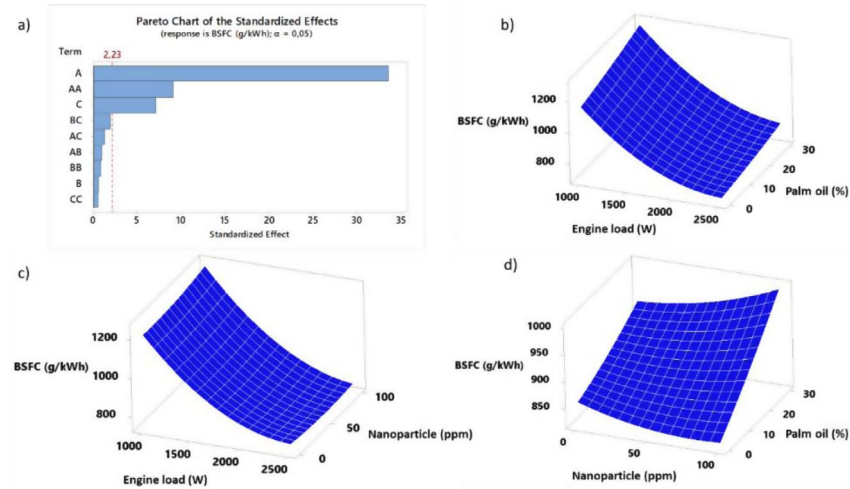


Fig. 6. Pareto chart (a) and simultaneous impacts of NP amount, engine load, and PO ratio on BSFC (b, c, d).

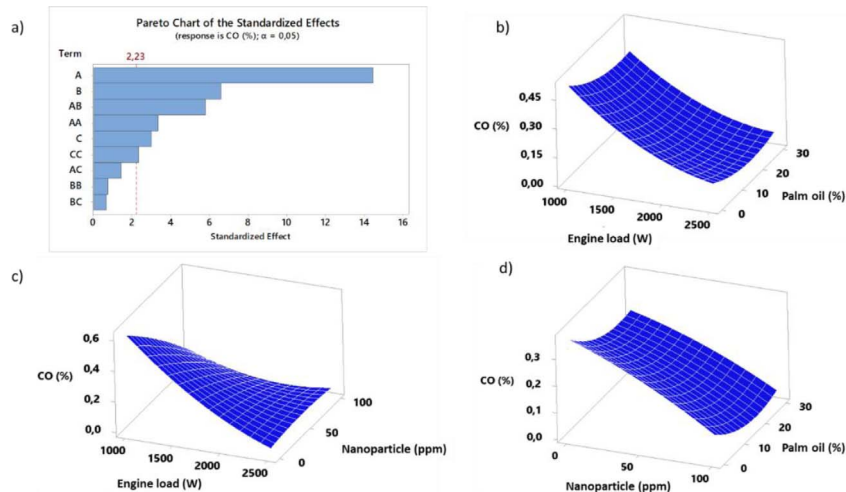


Fig. 7. Pareto chart (a) and simultaneous impacts of NP amount, engine load, and PO ratio on CO (b, c, d).

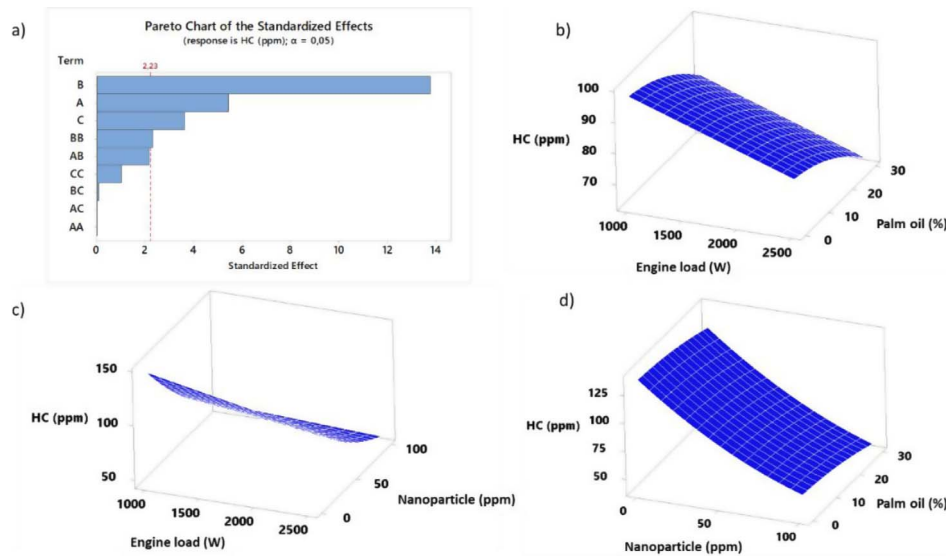


Fig. 8. Pareto chart (a) and simultaneous impacts of NP amount, engine load, and PO ratio on HC (b, c, d).

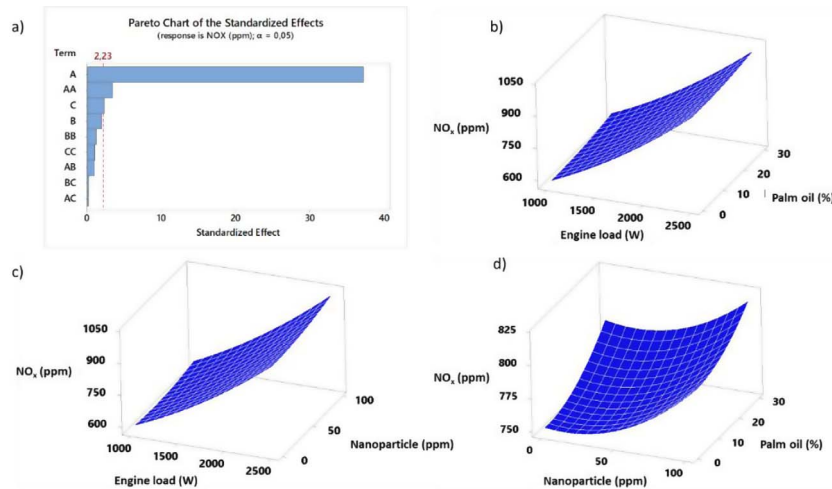


Fig. 9. Pareto chart (a) and simultaneous impacts of NP amount, engine load, and PO ratio on NO_x (b, c, d).

reaction of N₂ and O₂ in the air at high temperatures (1500 °C) during combustion [51, 56, 57]. Figure 9a shows the pareto chart of NO_x. The engine load on the right side of the vertical red line is the most influential variable on NO_x emissions. Additionally, ANOVA results support these results with *p*-values for NP amount and PO percentage higher than 0.05. Figures 9b–9d show the simultaneous effect of variables on NO_x emission. It is seen that increased engine loads resulted in increased NO_x emission. The adding Fe–Ni–TiO₂/AC NPs to the fuel blend increased the fuel's thermal conductivity, which promoted a decrease in ignition delay and enhanced combustion. Furthermore, the presence of O₂ in biodiesel can increase NO_x formation [56, 58]. Liu *et al.* [59] found a similar result that NO_x emission increased depending on both the increased engine load and the PO percentage.

Smoke emissions

Smoke emissions form from the oxygen-poor combustion of long-chain HC compounds under high temperatures [52, 54]. Figure 10 shows the pareto chart and 3D plots of smoke according to different NP amounts, engine loads, and PO ratios. As indicated in Figure 10a, the maximum impact on smoke emission is due to engine load. According to Table 10, where the ANOVA results are shown, the engine load has an effective rate of 46.85%, the amount of NPs 29.39%, and the PO percentage of 8.97%. Smoke emissions rise with increasing engine loads as a result of increased fuel consumption, rising combustion chamber temperature, and inadequate or incomplete combustion [56, 58]. The biodiesel added to the fuel mixture also contains more oxygen, which results in lower smoke emissions.

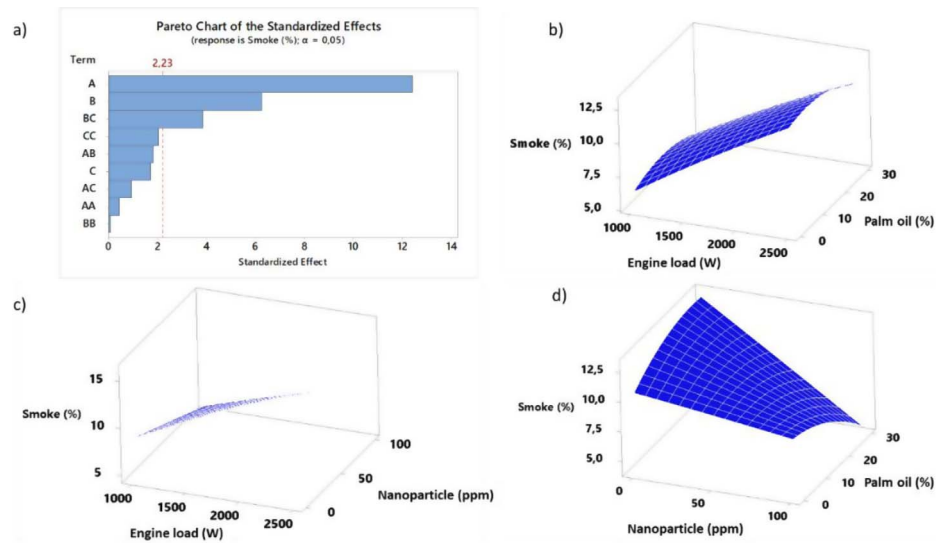


Fig. 10. Pareto chart (a) and simultaneous impacts of NP amount, engine load, and PO ratio on smoke (b, c, d).

Table 12. Details regarding optimization constraints.

Response	Goal	Lower	Target	Upper	Weight	Importance
Smoke	Minimize	2.8	2.8	13.66	1	1
NO _x	Minimize	590	590	1061	1	1
HC	Minimize	35	35	158	1	1
CO	Minimize	4.28	4.28	0.73	1	1
BSFC	Minimize	725	725	1323	1	1
BTHE	Maximize	18.05	30.55	30.55	1	1

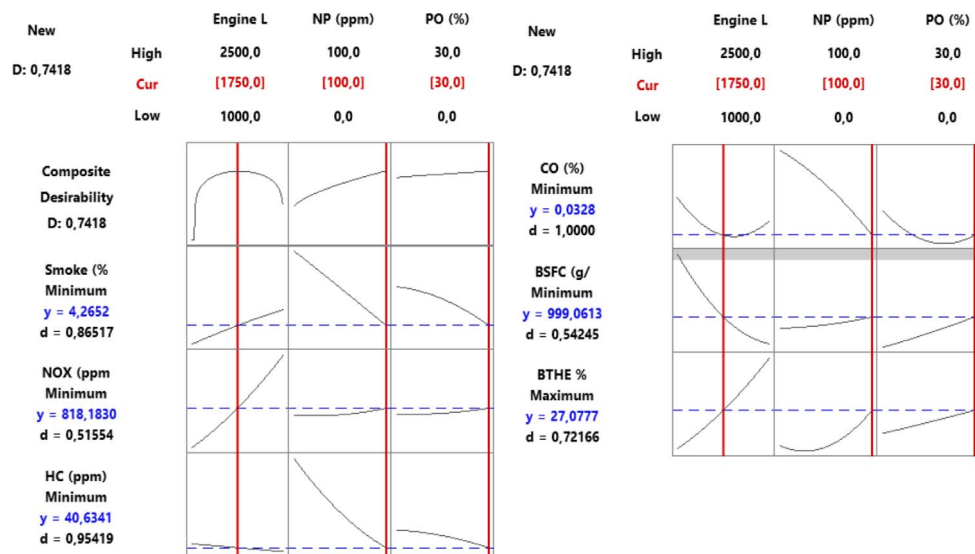


Fig. 11. Optimization results.

Table 13. Confirmatory test results.

Engine Load (W)	NP (ppm)	PO (%)		BTHE %	BSFC (g/kWh)	CO (%)	HC (ppm)	NO _x (ppm)	Smoke (%)	Desirability
1750	100	30	Optimum	27.07	999.06	0.032	40.63	818.18	4.26	0.7418
			Actual	25.89	1019.27	0.034	42.42	798	4.38	
			%Error	4.52	1.98	4.09	4.17	2.52	2.73	

Thiruselvam *et al.* [55] found a similar result. On the other side, it is observed that the addition of NPs causes the smoke emissions spurred on by the excess oxygen in the fuel to decrease. By increasing the blend percentage and decreasing the amount of unburned fuel in the combustion chamber, the addition of NPs decreased the generation of smoke precursors and reduced smoke emissions [60].

3.2.3 Optimization and validation studies

In this project, the engine performance and pollution levels were optimized using the RSM optimiser tool. The main purpose of optimization is to determine the optimum simultaneous working conditions for the variables while reaching the specified goals for the outputs. The goals for the optimization process are shown in Table 12. Figure 11 illustrates the optimization outcomes carried out according to the selected goals. According to optimization results, 1750 W engine load, 100 ppm NP amount, and 30% PO ratio were determined as optimum conditions. The best responses for the optimized operating conditions were 27.07% BTHE, 999.06 g/kWh BSFC, 4.26% smoke, 818.18 ppm NO_x, 40.63 ppm HC, and 0.032% CO.

Verification experiments have been done to validate optimized RSM results. Table 13 shows the results of the confirmation. When the optimization outcomes and test outcomes are compared, it is seen that the results are in high agreement with each other, and the highest error rate was obtained in BTHE with 4.52%. Results showed that optimization is successful.

4 Conclusion

In the present research, the performance and emission responses of the diesel engine were taken into account after adding Fe–Ni–TiO₂/AC NPs made as a new catalyst to the biodiesel–diesel combination. In order to determine the ideal NP amount, PO ratio, and engine load, RSM optimization was carried out. In RSM optimization BSFC, BTHE, CO, HC, NO_x, and smoke were selected as output factors. The main outcomes of the current research are as follows:

- According to results, BTHE and BSFC reply benefit from NP addition. Additionally, the addition of NP reduces CO, HC, and smoke emissions while increasing NO_x emissions, according to emission responses.
- The addition of PO positively affected BTHE and negatively affected BSFC. As with NP, the addition of PO reduced CO, HC, and smoke emissions, while increasing NO_x.

- Another input parameter, engine load, contributed to the performance improvement by increasing BTHE and decreasing BSFC. Moreover, it was effective in reducing CO and HC emissions. Conversely, it caused a rise in NO_x and smoke emissions.
- The R^2 values for BTHE, BSFC, smoke, NO_x, HC, and CO were determined as 98.24%, 99.38%, 97.21%, 99.41%, 98.62%, and 97.88%, respectively. The high R^2 values make the study meaningful.
- According to the RSM, optimum results were determined as 1750 W engine load, 100 ppm NP concentration, and 30% PO ratio. The optimum responses were 27.07%, 999.06 g/kWh, 4.26%, 818.18 ppm, 40.63 ppm, and 0.03% for BTHE, BSFC, smoke, NO_x, HC, and CO, respectively.
- The validation study showed that the optimization and experimental results were in good agreement with each other, with a 0.7148 desirability value. The error ratio was between 1.98% and 4.52%.

Consequently, the RSM approach has been effectively used to determine the optimum conditions for the diesel engine fuelled with diesel–biodiesel blends catalyzed with NP. This study has demonstrated under which conditions Fe–Ni–TiO₂/AC nanoparticles, a nanoparticle that has never been used as a fuel catalyst, can be used more harmoniously in a diesel engine. In the present study, it is anticipated that it will provide insight into subsequent research.

Authors' contributions

Rahman Çalhan: Conceptualization, Methodology, Writing, Editing.

Songül Kaskun Ergani: Investigation, Writing-Reviewing.

Samet Ushu: Software, Analysing the results, Editing.

All the authors read and approved the final manuscript.

Conflict of interest

The authors declare no competing interests.

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