

Full Length Article

Machine-learning-assisted optimization of alumina-enhanced *Citrullus lanatus* seed biodiesel combustion in a thermal-barrier-coated diesel engine

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ABSTRACT

The performance and emission characteristics of a thermal barrier-coated CI engine operating with watermelon seed oil methyl ester (WSOME) biodiesel blends with Al_2O_3 nanoparticles were investigated. The various biodiesel blends (B10, B20, and B30) were used with different concentrations of Al_2O_3 (25 ppm, 50 ppm, and 75 ppm) at different engine loads. Response Surface Methodology (RSM) has been used to identify optimal conditions to maximize brake thermal efficiency (BTE), minimize specific fuel consumption (SFC), and reduce CO, HC, NOx, and smoke emissions. The best condition was identified as B30 (75 ppm Al_2O_3) at 50 % load, with a desirability value of 0.757 based on RSM optimization results. Under these conditions, the predicted responses were SFC of 0.317 kg/kWh, BTE of 25.063 %, CO of 0.0219 vol%, HC of 30.75 ppm, NOx of 408.46 ppm, and smoke of 27.08 HSU. Optimized conditions yielded higher BTE and lower SFC, CO, HC, and NOx emissions than the baseline (uncoated diesel). Smoke increased slightly. Finally, an ANN-XGBoost stacking model was developed as a predictive modelling approach to estimate performance and emission responses as functions of blend ratio, engine load, and nanoparticle concentration. The ML results also agreed with the experimental and RSM trends, revealing that combustion in a TBC engine with Al_2O_3 can effectively enhance fuel economy and reduce major gaseous emissions within the engine's tested range.

1. Introduction

The accelerated growth in global energy consumption, the depletion of finite fossil fuel reserves, and the introduction of stricter environmental standards have intensified the quest for cleaner, more sustainable alternative fuels for internal combustion engines [1,2]. CI engines continue to dominate transportation, agriculture, power generation, and heavy-duty industries due to their high thermal efficiency and long lifespan [3]. However, traditional diesel engines are also significant contributors to greenhouse gas emissions and regulated pollutants, including carbon monoxide (CO), unburned hydrocarbons (HC), nitrogen oxides (NOx), and particulate matter, thereby causing serious environmental and human health issues [4,5]. This has led to the emergence of renewable fuels and sophisticated engine technologies that reduce emissions without affecting performance, making them a major research focus [6].

Because of its renewable nature, biodegradability, non-toxicity, and favourable combustion properties, biodiesel has become a promising substitute for petroleum diesel [7,8]. Biodiesel, which is a product of the transesterification of vegetable oils, animal fats, or waste cooking oils, can be used in CI engines with minor modifications [9]. Many studies have reported substantial reductions in CO, HC, and smoke emissions, attributable to biodiesel's oxygenated nature, which facilitates further combustion [10,11]. Nonetheless, its increased viscosity, low calorific value, and poor cold-flow characteristics adversely affect atomisation, fuel rate, and engine performance, while the rise in NOx emissions remains a significant weakness [12]. To address biodiesel fuel-related conflicts and sustainability concerns, current studies have placed increasing emphasis on non-edible and waste-based biodiesel feedstocks. Watermelon seed oil has been noted as an alternative, little-tapped source of biodiesel [13]. Watermelon (*Citrullus lanatus*) is commonly grown in tropical and subtropical areas, and its seeds are

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Table 1

Summary of literature findings and research gap.

Recent study	Fuel/additive/engine approach	Method used	Key findings	Specific research gap relevant to the present study
Modi et al. (2025) [40]	Milk scum biodiesel with Al ₂ O ₃ nanoparticles in a diesel engine	RSM and ML	Al ₂ O ₃ nano-addition improved biodiesel engine performance and emissions; the study used RSM and ML prediction.	Used Al ₂ O ₃ nanoparticles and ML, but did not investigate WSOME biodiesel or TBC-assisted combustion.
Kumar (2025) [41]	Moringa oleifera biodiesel doped with 1-hexanol and Al ₂ O ₃ catalyst in a single-cylinder CI engine.	Experimental performance, combustion, and emission analysis	The 90D7MO3H + 25 ppm Al ₂ O ₃ blend improved BTE, BSFC, HRR, and peak cylinder pressure, while selected blends reduced HC, CO, CO ₂ , and NOx emissions compared with diesel.	Used Al ₂ O ₃ nano-additive with biodiesel and alcohol ignition improver, but did not investigate WSOME biodiesel, TBC-assisted operation, RSM optimization, or ANN-XGBoost prediction.
Krishnamoorthi et al. (2024) [42]	Neat palm biodiesel with thermal barrier coating and nanoparticle additive	Experimental, statistical, energy, and exergy analysis	TBC and nanoparticle addition improved the performance and emissions of a DI diesel engine.	Focused on palm biodiesel; no WSOME biodiesel and no ensemble ML-based performance and emission prediction.
Krishnamurthy et al. (2025) [43]	Scum oil methyl ester blends in a mullite-coated diesel engine at different compression ratios	Experimental combustion and emission analysis	Mullite TBC improved BTE, BSFC, cylinder pressure, and HRR, and reduced CO, HC, and smoke, while slightly increasing NOx.	Focused on scum oil and compression ratio; did not include Al ₂ O ₃ nano-fuel, RSM optimization, or ML prediction.
Biberici et al. (2025) [44]	Waste cooking oil biodiesel/diesel blend	ANN and RSM optimization	ANN and RSM were used to optimize BTE, SFC, EGT, NOx, HC, CO, and smoke.	Included ANN and RSM, but not nanoparticle-enhanced fuel, TBC engine operation, or WSOME biodiesel.
Mylapalli et al. (2025) [45]	Sterculia foetida biodiesel with Fe ₃ O ₄ nanoparticles	Experimental and ML analysis	Fe ₃ O ₄ nanoparticles improved BTE and reduced SFC, CO, HC, NOx, and smoke; ML showed strong prediction capability.	Used Fe ₃ O ₄ nano-additive and ML, but did not examine Al ₂ O ₃ , TBC, or WSOME biodiesel.
Menda et al. (2025) [46]	Spirulina platensis biodiesel with DEE and CNT additives in a CRDI engine	Experimental and ML prediction	CNT and DEE improved BTE and reduced BSFC, HC, CO, NOx, and smoke; ML was used for prediction.	Focused on microalgae biodiesel, CNT, and DEE; did not address WSOME, Al ₂ O ₃ , or TBC-assisted combustion.
Bikkavolu et al. (2025) [47]	Pongamia biodiesel enhanced with nanoparticles in the CRDI engine	Diesel-RK simulation and ML	Nanoparticle-enhanced biodiesel improved BTE, BSFC, and emissions; SVR and RF predicted engine responses.	Considered nanoparticle biodiesel and ML, but not WSOME, TBC, RSM optimization, or ANN-XGBoost stacking.
Dhamodaran et al. (2026) [48]	Hydrogen-enriched nanoparticle-emulsified second-generation biodiesel	Experimental combustion and emission analysis	Showed that hydrogen enrichment and nanoparticles improve combustion but can affect NOx due to higher combustion temperature.	Addressed NOx mechanisms in advanced biodiesel combustion, but did not study WSOME biodiesel with TBC and Al ₂ O ₃ optimization.
Manikandan et al. (2025) [49]	Watermelon seed oil biodiesel with ferrous oxide nanoparticles	Experimental performance and emission analysis	Demonstrated the potential of watermelon seed biodiesel enhanced with metal oxide nanoparticles.	Closest to WSOME feedstock, but used Fe-based nanoparticles and did not include TBC, RSM, or ensemble ML prediction.

often discarded as agricultural waste [14]. However, they contain a significant amount of oil and have a favourable fatty-acid composition [15]. According to recent research, watermelon seed oil methyl ester (WSOME) meets the ASTM fuel requirements and can be efficiently blended with diesel for use in CI engines [16]. Still, the performance and emission restrictions associated with biodiesel blends require further improvements [17].

One way to address the shortcomings of biodiesel is to use nanoparticles as fuel additives. The presence of metal-oxide nanoparticles, including Al₂O₃, CeO₂, TiO₂, and ZnO, enhances combustion, attributed to their high surface area, catalytic properties, and enhanced thermal conductivity [18–20]. The nanoparticles have gained significant interest because aluminum oxide (Al₂O₃) is thermally stable, oxidation-resistant, and capable of carrying oxygen during combustion [21,22]. Recent experimental studies have shown enhancements in brake thermal efficiency (BTE), reductions in specific fuel consumption (SFC), and reductions in CO, HC, and smoke emissions in biodiesel-powered CI engines using Al₂O₃ nanoparticles [23,24]. However, the higher combustion temperatures resulting from the addition of nanoparticles could increase NOx emissions, thereby necessitating simultaneous engine modifications [25]. Over the past few years, thermal barrier coatings (TBCs) have become a promising engine-modification approach to minimize heat loss and increase in-cylinder combustion efficiency [26]. The application of ceramics, usually yttria-stabilised zirconia (YSZ), on piston crowns and combustion chambers enhances the fuel evaporation and thermal efficiency [27]. Recent studies have shown that CI engines operating on biodiesel and nanoparticle fuels with TBCs achieve higher efficiency and lower CO, HC, and smoke emissions [28,29]. However, higher peak burner temperatures once more can lead to high NOx emissions, requiring combined optimisation strategies [30].

Optimization and modelling are advanced methods required to analyse the complex interactions among fuel properties, engine

modifications, and operating conditions [31]. Response Surface Methodology (RSM) is a widely used approach for modelling non-linear relationships and optimising engine performance and emissions with minimal experimentation [32]. Simultaneously, recent progress in machine learning (ML) has been utilized to make predictive modelling in engine research [33]. Artificial Neural Networks (ANN) and Extreme Gradient Boosting (XGBoost) are also more accurate than traditional regression models in predicting CI engine performance and emissions [34,35]. In addition, the predictive power and robustness of ensemble learning methods, such as stacking models, have been improved. Table 1 summarizes the literature findings. Recent studies have shown that the use of nanoparticle additives and ML models significantly impacts the analysis of biodiesel engines. It has been reported that the use of nanoparticles such as SiO₂, CNTs, and Fe₃O₄ increases BTE, decreases BSFC, and reduces CO, HC, NOx, and smoke emissions in biodiesel-fuelled CI engines [36]. Concurrently, ML algorithms such as ANN, SVR, RF, DT, and XGBoost have been successfully employed to predict engine performance and emission responses with high accuracy [37]. However, the simultaneous use of WSOME biodiesel, Al₂O₃ nanoparticles, TBC-assisted combustion, RSM optimization, and ANN-XGBoost prediction has not been adequately investigated [38,39]. The present study aims to fill this research gap by implementing an integrated experimental–optimization–prediction framework.

The existing studies look at biodiesel fuels, nanoparticle additives, thermal barrier coatings, statistical optimization, and machine-learning prediction individually. The cumulative effect of watermelon seed oil methyl ester (WSOME), Al₂O₃ nanoparticles, TBC-assisted combustion, RSM optimization, and ensemble machine-learning prediction has, however, been understudied. Hence, the present study is novel in that it focuses on developing an integrated experimental–statistical–computational framework for a CI engine operating on alumina-enhanced biodiesel fuel derived from WSOME under both coated and uncoated

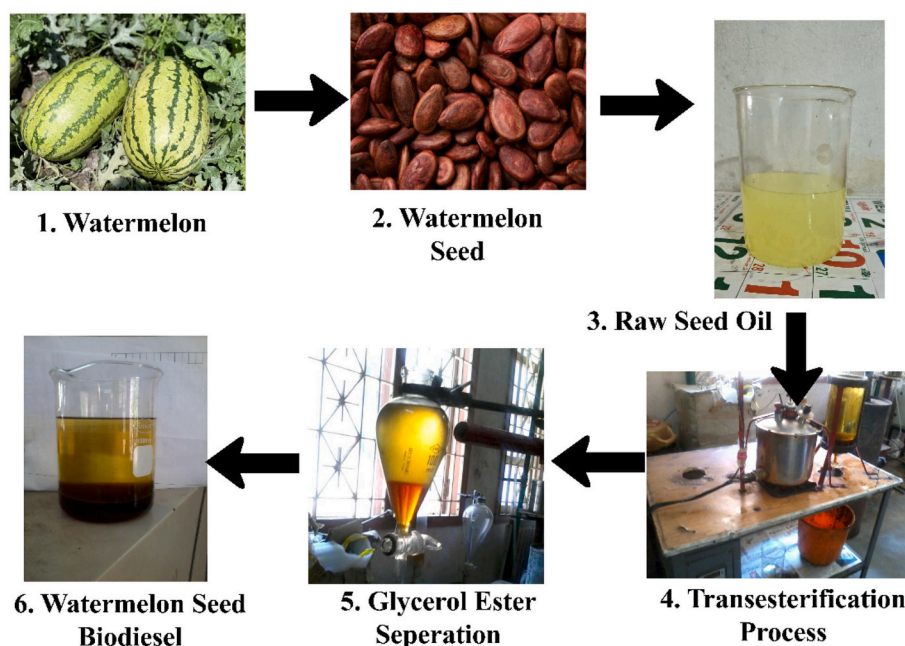


Fig. 1. Schematic representation of watermelon seed biodiesel production through base-catalyzed transesterification, and final WSOME collection.

conditions. In the present study, WSOME–diesel blends with Al_2O_3 nanoparticles were tested at various loads to investigate engine performance and emissions. The optimum operating condition was identified using a Taguchi L27-based RSM, and an ANN–XGBoost stacking model was developed to predict performance and emission responses. This is a combined approach that differs from previous studies, which focused only on parts of the problems: sustainable fuel utilization, nanoparticle-assisted combustion improvement, TBC-based heat-loss reduction, operating-condition optimization, and intelligent prediction. Hence, the study offers a more comprehensive route towards efficiency and emission characteristics of biodiesel-fuelled CI engine.

2. Materials and methods

2.1. Preparation of watermelon seed biodiesel (WSOME)

Watermelon (*Citrullus lanatus*) is a fruit in the family Cucurbitaceae and is well known for its nutritional value and health benefits. Its seeds, or pepitas, contain a high percentage of fatty acids, especially linoleic acid, and are a good source of oil that can be processed into biodiesel. The feedstock used in the present study is the commercially available filtered watermelon seed oil. The oil was filtered to remove solid impurities and heated to 60 °C to remove the moisture before transesterification. The measured acid value of the oil was 0.400 mg KOH g^{−1}, appropriate for base-catalyzed transesterification.

Sodium methoxide was prepared by dissolving sodium hydroxide in methanol to produce biodiesel. The reaction was carried out at a methanol-to-oil molar ratio of 6:1 and 1.0 wt% NaOH catalyst (based on oil weight). The prepared sodium methoxide solution was added dropwise to the preheated watermelon seed oil to initiate transesterification. The reaction was conducted at approximately 65 °C for 60 min under continuous stirring at 600 rpm. Fig. 1 shows the schematic representation of watermelon seed biodiesel production. The reaction mixture was then placed in a separating funnel and left to stand for 24 h after completion. At this time, two layers formed: an upper layer containing watermelon seed oil methyl ester (WSOME) and a lower layer containing glycerol. This methyl ester layer was separated and washed several times with warm distilled water (65 °C) to remove impurities such as soaps, methanol, and glycerol, as well as residual catalyst. The washed biodiesel was then gently heated to evaporate moisture. The final biodiesel

Table 2
Properties of Watermelon Seed Oil Biodiesel.

Property	Diesel	B10	B20	B30	B100	ASTM method
Density at 15 °C (kg/m ³)	838.1	844.6	851.1	857.6	903.0	ASTM D1298
Kinematic viscosity at 40 °C (cSt)	3.90	4.10	4.30	4.50	5.90	ASTM D445
Flash point (°C)	58.5	72.0	86.5	101.0	170.2	ASTM D93
Fire point (°C)	68.0	82.5	97.0	112.0	180.3	ASTM D93
Gross calorific value (MJ/kg)	43.4	43.0	42.7	42.4	40.1	ASTM D240
Cetane number	48.0	48.6	49.2	49.8	52.8	ASTM D613
Carbon content, C (wt.%)	86.2	—	—	—	77.2	CHNS/O analysis
Hydrogen content, H (wt.%)	13.6	—	—	—	12.0	CHNS/O analysis
Oxygen content, O (wt.%)	0.2	—	—	—	10.8	CHNS/O analysis
Nitrogen content, N (wt.%)	Trace	—	—	—	<0.01	CHNS/O analysis
Sulfur content, S (wt.%)	0.035	—	—	—	<0.005	ASTM D5453
Acid value (mg KOH/g)	0.05	0.09	0.13	0.17	0.40	ASTM D664
Water content (mg/kg)	80	110	140	165	290	ASTM D6304
Oxidation stability at 110 °C (h)	—	9.2	8.1	7.0	5.5	EN 14,112
Cloud point (°C)	−3	−1	1	3	6	ASTM D2500
Pour point (°C)	−12	−9	−6	−3	3	ASTM D97
Cold filter plugging point, CFPP (°C)	−8	−6	−4	−2	2	ASTM D6371

yield was ~92.5 %, and the ester conversion was 96.8 %, indicating efficient conversion of watermelon seed oil to WSOME [50]. The obtained biodiesel (B100) was then characterized and compared with conventional diesel fuel in accordance with ASTM test methods.

Table 2 shows the physicochemical properties of diesel, B100, and WSOME–diesel blends. In addition to density, viscosity, flash point, fire

Table 3Properties of Al₂O₃-doped WSOME–diesel nano-fuel blends.

Fuel blend	Al ₂ O ₃ concentration (ppm)	Density at 15 °C (kg/m ³)	Kinematic viscosity at 40 °C (cSt)	Gross calorific value (MJ/kg)	Flash point (°C)
B30A25	25	857.9	4.52	42.4	101.5
B30A50	50	858.2	4.54	42.3	102.0
B30A75	75	858.6	4.56	42.3	102.5

Table 4Physicochemical Properties of Aluminum Oxide (Al₂O₃).

Properties	Values
Molecular formula	Al ₂ O ₃
Molar mass	101.96 g/mol
Physical Appearance	White crystalline solid
Density	3.987 g/cm ³
Melting point	2,072 °C
Boiling point	2,977 °C
Water solubility	Insoluble
Average Particle Size	Less than 22 nm
Crystal structure	hexagonal crystal structure (α -Al ₂ O ₃)

point, and calorific value, important fuel-quality parameters included cetane number, acid value, water content, oxidation stability, cloud point, pour point, and cold filter plugging point. The properties are important because they influence the ignition quality, atomization, combustion stability, storage life, and low-temperature operability. Compared with diesel, blending WSOME increased density, viscosity, flash point, cetane number, and oxygenated fuel characteristics, while slightly reducing calorific value. Table 3 shows the properties of the fuel blends with Al₂O₃ nanoparticles (75 ppm alumina concentration), and only slight differences in density and viscosity were observed due to the low nanoparticle dosage.

2.2. Aluminum oxide (Al₂O₃) additive

The incorporation of Al₂O₃ nano-additives into biodiesel is reported to enhance combustion efficiency and reduce exhaust emissions [41]. These additives enhance fuel reactivity and thermal behaviour. The most important physicochemical characteristics of Al₂O₃ nanoparticles that render it suitable for high-temperature applications, including fuel additives and thermal-barrier materials used in compression-ignition engines, are available in Table 4.

Aluminum oxide is a thermally stable material that melts at 2072 °C

and boils at 2977 °C. Its density is 3.987 g/cm³, indicating a small, hexagonal (α -Al₂O₃) crystal structure. The nanoparticles are smaller than 22 nm in diameter, and thus have a high surface-to-volume ratio, which increases catalytic performance and heat-transfer rates during combustion. The desired amount of the Al₂O₃ nanoparticles was accurately weighed for each of the nano-fuel blends in this study, which are B10, B20, and B30 WSOME–diesel blends, to achieve the concentrations of 25, 50, and 75 ppm, respectively. The mixtures were stirred for 30 min at room temperature using a magnetic stirrer to ensure the initial distribution of nanoparticles in the fuel. The blends were then ultrasonicated for 45 min to minimize nanoparticle agglomeration and achieve a more stable dispersion [51]. The resulting nano-fuel samples were then placed in clear glass containers and left to rest for 48 h to assess potential sedimentation and/or phase separation. During this time-frame, no sedimentation or separation was seen, meaning that the WSOME–Al₂O₃ blends were reasonably stable before testing in the engine.

2.3. Thermal barrier coating (TBC)

The present work presents the development of a composite coating using a ceramic material to protect key engine components, such as the piston crown and cylinder liner, thereby reducing heat loss and enhancing in-cylinder combustion temperatures. The surface roughness and mechanical interlocking of the cylinder liner and piston crown surface were increased by grit blasting with alumina particles prior to the coating of the surface. To promote the bond between the metallic base and ceramic top coat, a NiCrAlY bond coat of $\sim 50 \pm 5 \mu\text{m}$ was first deposited. The 94 vol% YSZ, 2 vol% Al₂O₃, and 4 vol% CeO₂ ceramic top coat was then deposited using the Air Plasma Spray technique. The spray current was 500 A, and the voltage was 60 V; the spray distance was 100 mm; the powder feed rate was 30 g min⁻¹; the primary (Ar) gas flow rate was 45 L min⁻¹, and the secondary (H) and the carrier gas flow rates were 10 L min⁻¹ and 5 L min⁻¹, respectively. Images of the specimen cross-section were taken using SEM, and the coating thickness at five different positions was measured with image-analysis software. The thickness of the coating was $152 \pm 8 \mu\text{m}$ on the piston crown and $304 \pm 12 \mu\text{m}$ on the cylinder liner. The average porosity ($9.6 \pm 0.8\%$) obtained from SEM image analysis was acceptable for thermal barrier applications, as controlled porosity helps reduce heat transfer. The pull-off adhesion strength of the coating was $34.7 \pm 2.1 \text{ MPa}$, confirming a good bond between the substrate, bond coat, and ceramic top coat.

Fig. 2 shows that the TBC demonstrated outstanding stability following engine testing, with only slight peripheral cracking on the piston crown and no large-scale damage elsewhere in the coating. These observations affirm the toughness and dependability of the composite

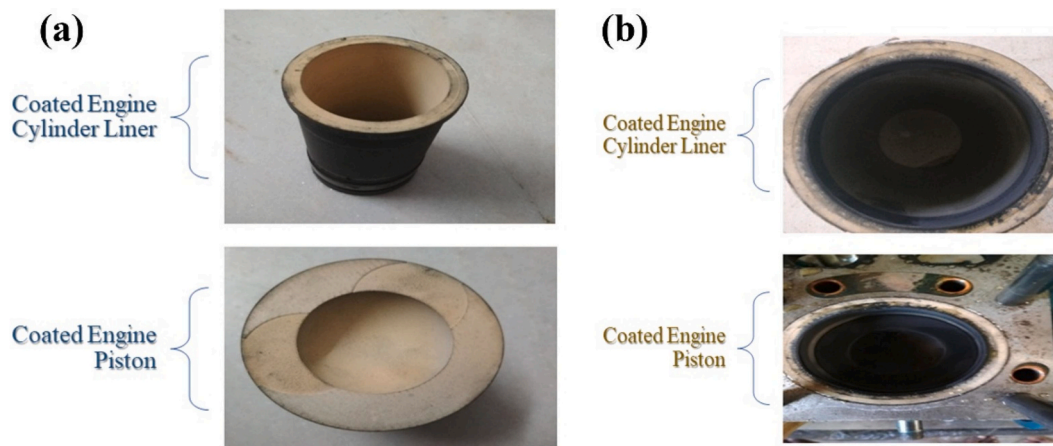


Fig. 2. Photographic view of TBC-coated engine components: (a) coated piston crown and cylinder liner before engine operation and (b) coated components after 100 h of engine operation, showing coating retention and minor surface deposits.

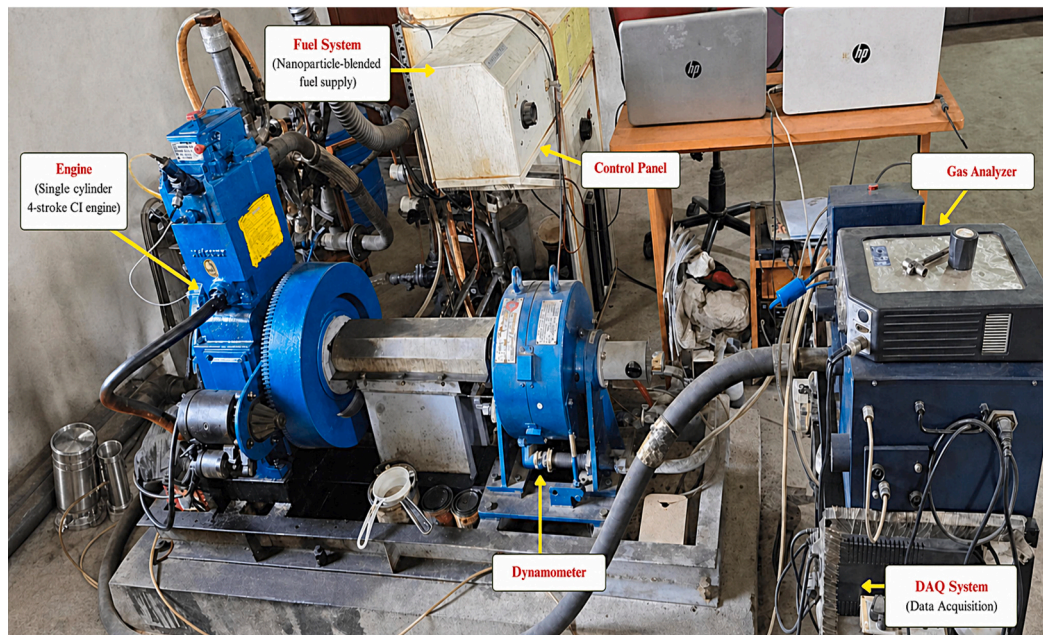


Fig. 3. Photographic view of the experimental CI engine test setup used for evaluating WSOME–diesel blends with Al_2O_3 nanoparticles under uncoated and TBC-assisted operating conditions.

Table 5
Specification of the engine.

Specification	Details
Engine Configuration	Single-cylinder, four-stroke, vertical, water-cooled CI engine
Make & model	Kirloskar TV-1
Maximum Rated Power	5.2 kW at 1500 rpm
Nominal Engine Speed	1500 revolutions per minute (rpm)
Total Number of Cylinders	1
Operation Cycle	Four-stroke
Compression Ratio	17.5:1
Bore Diameter	87.5 mm
Piston Stroke	110 mm
Mode of Ignition	Compression ignition

TBC under the conditions tested.

2.4. Experimental setup

Fig. 3 shows the schematic design of the experimental test rig used in this study. It was an experimental procedure using a one-cylinder, four-

stroke, direct-injection, water-cooled compression-ignition diesel engine directly coupled to an eddy-current dynamometer and a built-in data acquisition system. The eddy-current dynamometer was also used to apply the necessary load and to measure the brake power output. Engine operations were performed in standard operating conditions with a pressure of 215 bar of fuel injection, a fixed 26° before top dead centre of fuel injection timing, and a constant compression ratio of 17.5:1. The thermocouples of the type Chromel and Alumel (K type) were used to measure the temperature at the inlet and exhaust manifolds and at the cylinder wall at specific points. Carbon monoxide (CO), unburned hydrocarbons (HC), and nitrogen oxides (NO_x) in exhaust gases were measured using an AVL 444 di-gas analyser based on the non-dispersive infrared (NDIR) principle. The smoke emissions were measured using the AVL 437 °C smoke meter, and the readings were reported in Hartridge Smoke Units (HSU). Table 5 presents the test engine specifications in detail. All the measuring instruments were calibrated before engine testing to ensure that the experimental data are accurate and repeatable. Zero gas and standard span gases were used to calibrate the AVL gas analyser prior to the emission measurements. The smoke-opacity testing was preceded by checking the AVL smoke meter with the manufacturer-recommended calibration filter. The calibration

Table 6
Experimental uncertainty.

Parameter	Unit	Range	Instrument/method	Accuracy	Uncertainty
Engine speed	rpm	0–10,000 rpm	Magnetic pickup	± 10 rpm	± 0.10 %
Load	N	0–500 N	Strain-gauge load cell	± 10 N	± 0.20 %
Fuel volume	cm^3	0–50 cm^3	Burette/volume method	± 0.1 cm^3	± 1.00 %
Time	s	–	Stopwatch	± 0.1 s	± 0.20 %
Temperature	$^\circ\text{C}$	0–1200 $^\circ\text{C}$	K-type thermocouple	± 1 $^\circ\text{C}$	± 0.15 %
Pressure	bar	0–5000 psi	Pressure transducer	± 0.1 bar	± 0.10 %
CO	vol.%	0–10 % Vol.	Gas analyzer	± 0.02 vol%	± 0.20 %
HC	ppm	0–20,000 ppm.	Gas analyzer	± 10 ppm	± 0.10 %
NO _x	ppm	0–5000 ppm	Gas analyzer	± 12 ppm	± 0.20 %
Smoke	HSU	0–100 HSU	Smoke meter	± 1 HSU	± 1.00 %
Brake power	kW	0–20,000 ppm	Calculated	—	± 0.22 %
Fuel-consumption rate	kg/h	0–100	Calculated	—	± 1.03 %
SFC	kg/kWh	—	Calculated	—	± 1.05 %
BTE	%	—	Calculated	—	± 1.16 %
Overall experimental uncertainty	%	—	Root-sum-square method	—	± 2.28 %

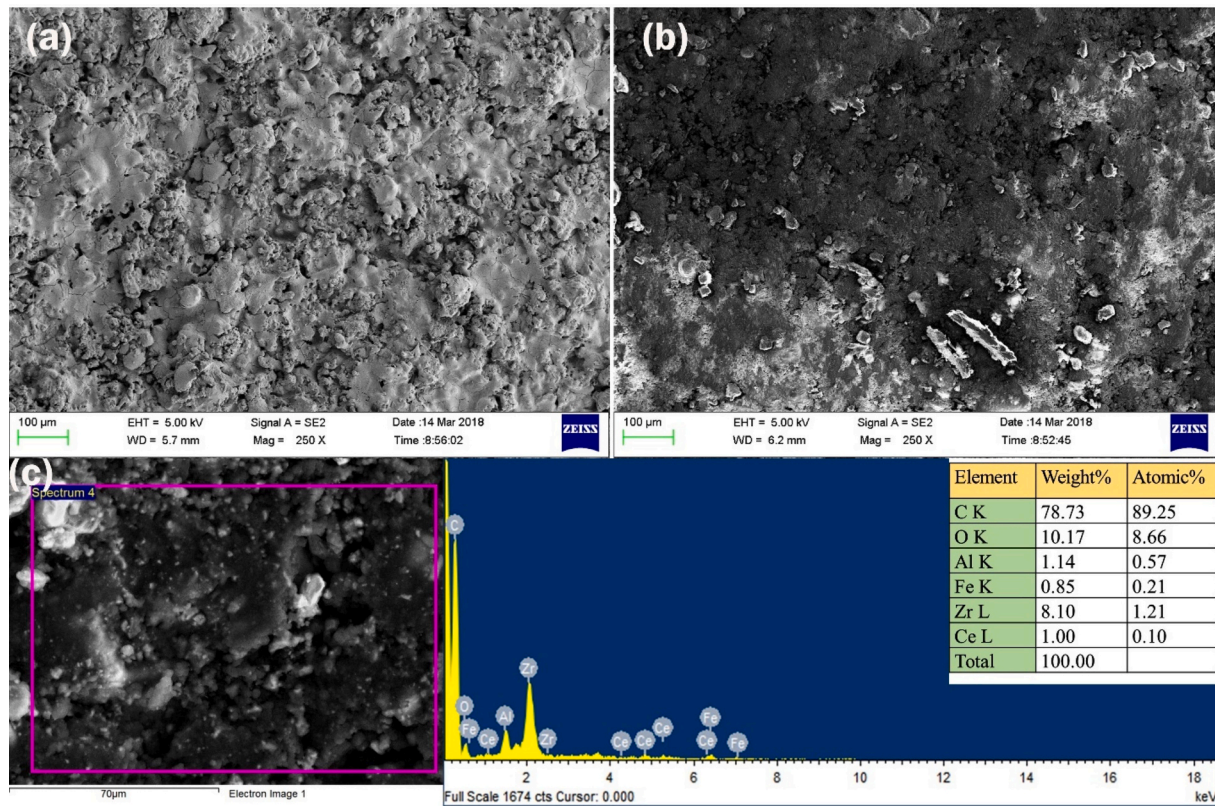


Fig. 4. SEM/EDX characterization of the thermal-barrier coating: (a) SEM surface morphology before combustion, (b) SEM surface morphology after 100 h engine operation, and (c) EDX spectrum of the post-combustion coating surface showing oxide coating elements and combustion-derived deposits.

of K-type thermocouples was performed over the operating temperature range using a standard temperature calibrator. The eddy-current dyna-

joint uncertainty without systematic errors in the experiment.

$$\text{Total Uncertainty} = \sqrt{[TFC^2 + Bp^2 + BSFC^2 + BTE^2 + CO^2 + HC^2 + NOx^2 + Smoke^2 + T_{ex}^2 + Pressuredrop^2]}$$

$$\text{Total Uncertainty} = \sqrt{(1.10^2 + 0.22^2 + 1.05^2 + 1.16^2 + 0.2^2 + 0.10^2 + 0.2^2 + 1.00^2 + 0.15^2 + 0.1^2)} = \pm 2.28\% \quad (1)$$

momenter load cell was calibrated with known dead weights, and the fuel-flow measuring system was checked by timing the flow of known volumes of fuel through a calibrated burette. Three repetitions of each test have been performed under steady-state conditions, and average values have been used for performance and emission analysis.

2.5. Uncertainty analysis

The uncertainty in the experimental measurements arises from variations introduced during the experiment, including environmental conditions, instrument accuracy, calibration procedures, and observational inaccuracies. To measure the cumulative effect of such factors, the error-propagation approach, as described by J. P. Holman, has been used to approximate the total uncertainty in the experimental results. Table 6 lists the individual uncertainties for the major measured and calculated parameters, namely fuel flow rate, brake power, brake-specific fuel consumption, brake thermal efficiency, CO, unburned HC, NOx, smoke opacimeter, and pressure pickup. The absolute uncertainty was determined through the root-mean-square method, in which the square root of the sum of the squares of the respective uncertainties would be the

The uncertainties in brake power, fuel-consumption rate, SFC, and BTE were estimated to be $\pm 0.22\%$, $\pm 1.03\%$, $\pm 1.05\%$, and $\pm 1.16\%$, respectively, using the above relations. The overall experimental uncertainty was calculated by adding the uncertainties of all major measured and calculated parameters using the root-sum-square method, yielding a total uncertainty of about $\pm 2.28\%$. This value is acceptable for demonstrating repeatability and reliability of the experimental measurements.

2.6. Experimental testing

In the current experimental study, the performance and emission properties of watermelon seed biodiesel blends, with or without Al_2O_3 nanoparticles, were investigated in both uncoated and TBC compression-ignition engines. The biodiesel blends (i.e., B10, B20, and B30) contain 10 %, 20 %, and 30 % biodiesel, respectively, in conventional diesel fuel. The B10, B20, and B30 blends were selected to represent low-to-moderate biodiesel substitution levels that can be used in practice in existing CI engines without major hardware modifications.

Higher WSOME fractions were not considered in the present study because B100 has a higher density and viscosity and a lower calorific value than diesel, which may affect spray atomization, evaporation, combustion stability, and fuel consumption. Therefore, the selected blend range was intended to balance renewable fuel replacement with stable engine operation. However, higher blends such as B40, B50, and B100 should be examined in future studies to identify the maximum usable WSOME fraction and its applicability limits under long-term engine operation.

Aluminium oxide nanoparticles were added at concentrations of 25, 50, and 75 ppm to assess their potential to improve combustion efficiency. Loads corresponding to 50 %, 75 %, and 100 % were applied to the engines to simulate different operating conditions. All biodiesel-nanoparticle blends were sonicated for 30 min prior to testing to ensure a homogeneous dispersion. The maximum cylinder pressure of the diesel-operated uncoated engine was 57.8 bar, the maximum heat release rate was 42.6 J/°C·A, the ignition delay was 11.8 °C·A, and the exhaust gas temperature was 318 °C. The optimized B30 + 75 ppm Al₂O₃ mixture in the TBC engine, on the other hand, resulted in a higher peak cylinder pressure (66.9 bar), a higher maximum heat release rate (52.7 J/°C·A), and a reduced ignition delay (9.7 °C·A). This is primarily due to the synergy of biodiesel-bound oxygen, Al₂O₃-assisted catalytic oxidation, enhanced heat transfer, and reduced heat loss from the coated combustion chamber. The exhaust gas temperature also rose to 382 °C due to the increased thermal energy stored in the cylinder by the TBC. The combustion improvements account for the observed increase in BTE and the reductions in SFC, CO, HC, and smoke emissions. But the higher combustion temperature could also contribute to the formation of thermal NO_x. Testing of the piston and cylinder liner integrity was also conducted during about 100 hrs of operation.

2.7. Optimization and prediction of engine performance analysis

Design-Expert V13 software was used to develop the regression model and optimize the performance and emission responses of a CI engine using Response Surface Methodology (RSM). The optimization goal was to maximize BTE and minimize SFC, CO, HC, NO_x, and smoke across biodiesel blend ratios, engine loads, and Al₂O₃ nanoparticle concentrations. Thus, the statistical optimization technique (RSM) was employed to determine the optimal operating conditions within the experimental range. Meanwhile, a stacked model combining an ANN and XGBoost was designed to predict engine performance and emissions. The Python implementation was done in Google Colab, where data preprocessing, model training, hyperparameter tuning, and five-fold cross-validation were performed. Linear regression and second-order polynomial regression were also considered as baseline models, using the same input and output variables, train-test split, and validation procedure, to verify the advantage of the proposed model. A simple linear regression reference proved inadequate for capturing this nonlinear response behavior, while polynomial regression with quadratic and interaction terms marginally improved predictive ability. ANN and XGBoost were chosen because nonlinear and interaction-based dependencies of engine responses on fuel blend, load, and nanoparticle concentration were observed. ANN can learn complex nonlinear patterns, while XGBoost is a regularized tree-based learning method that models feature interactions well and can control overfitting more than individual decision tree or random forest models. As a result, the ANN-XGBoost stacking model achieved higher prediction accuracy than the traditional baseline models across the experimental range.

3. Results and discussion

3.1. SEM and EDX analysis of coating samples

The SEM micrographs & EDS spectra of the TBC samples (Fig. 4), acquired before and after engine combustion, demonstrate the stability

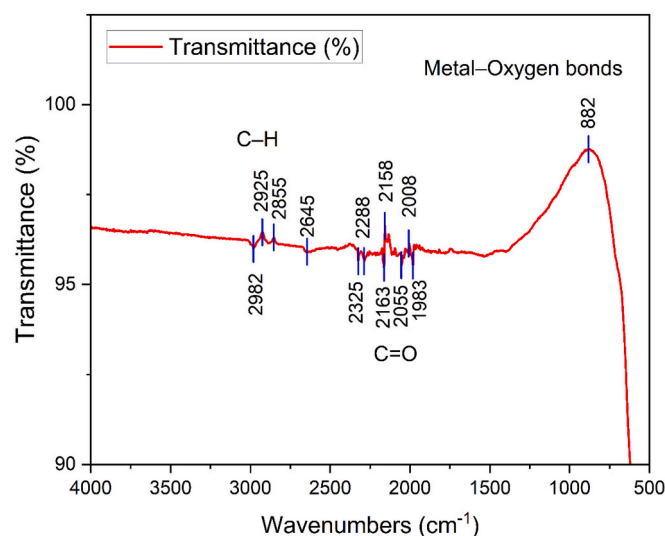


Fig. 5. FTIR spectrum of the TBC powder showing characteristic absorption bands associated with metal-oxygen bonds and minor surface functional groups, confirming the ceramic oxide nature of the coating material.

of the TBC morphology and elemental integrity under the challenging working conditions. The SEM image of the TBC-coated surface before combustion, at 250× magnification, is shown in Fig. 4(a). The coating exhibits a relatively uniform, continuous surface with a rough, porous morphology, which is common in plasma-sprayed and ceramic-based thermal barriers. The presence of fine pores and micro-cavities therefore has a positive effect, as they increase thermal insulation by attenuating heat transfer to the substrate and improve resistance to strain during thermal cycling. Strong coating adhesion and structural integrity before engine running are determined by the absence of noticeable cracks or delamination. The SEM image of the same coating after combustion is given in Fig. 4(b). The morphology of the post-combustion surface indicates localised particle aggregation and slight densification relative to the pre-combustion surface, attributable to prolonged exposure to high combustion temperatures and pressure fluctuations. Minor surface smoothing and minor micro-crack formation are evident; however, no severe spallation or coating failure is evident. These observations confirm that the TBC layer maintained its mechanical stability and withstood thermal stresses during engine operation, thereby demonstrating its suitability for CI engine applications.

The EDX spectrum of the post-combustion TBC surface is presented in Fig. 4(c). The high carbon content on the surface is primarily due to carbonaceous combustion deposits formed during engine operation and should not be considered a direct indicator of coating stability. The oxide-based ceramic coating and potential surface oxidation during combustion resulted in the detection of oxygen. The presence of zirconium indicates that the YSZ-based ceramic top coat was retained after engine testing. Aluminium is related to Al₂O₃ of the coating system and also to possible impurities from the nano-additive of Al₂O₃ in the fuel. Importantly attributed to the CeO₂ phase in the TBC composition and not the fuel additive. Low iron levels may be due to the metallic substrate or to exposure of the metallic substrate at surface defects. Overall, SEM/EDX results show that there were combustion deposits and minor surface changes after the engine run, but the major elements of the ceramic coating were still present, confirming that no major loss of coating or large-scale delamination occurred.

3.2. FTIR analysis of thermal barrier coating (TBC) powder

In the present investigation, the Fourier-transform infrared (FTIR) spectrum of the TBC powder was analyzed to gain in-depth insight into its chemical architecture and bonding characteristics. The FTIR

Table 7

Taguchi L27 experimental matrix and measured performance–emission responses for the TBC-assisted CI engine.

Run	WSOME blend	Blend ratio (%)	Load (%)	Al ₂ O ₃ (ppm)	SFC (kg/kWh)	BTE (%)	CO (vol.%)	HC (ppm)	NOx (ppm)	Smoke (HSU)
1	B10	10	50	25	0.38	20	0.027	40	430	16
2	B10	10	50	50	0.35	22	0.025	38	410	18
3	B10	10	50	75	0.34	24	0.024	36	395	22
4	B10	10	75	25	0.35	24	0.025	44	615	25
5	B10	10	75	50	0.33	26	0.023	41	600	29
6	B10	10	75	75	0.32	28	0.021	39	585	32
7	B10	10	100	25	0.37	28	0.035	47	700	30
8	B10	10	100	50	0.35	30	0.033	45	685	34
9	B10	10	100	75	0.34	31	0.032	44	670	38
10	B20	20	50	25	0.36	23	0.026	37	440	18
11	B20	20	50	50	0.34	25	0.024	35	420	20
12	B20	20	50	75	0.33	26	0.022	33	405	24
13	B20	20	75	25	0.36	27	0.024	40	640	30
14	B20	20	75	50	0.34	28	0.022	38	620	33
15	B20	20	75	75	0.33	29	0.021	36	600	36
16	B20	20	100	25	0.38	29	0.034	46	720	34
17	B20	20	100	50	0.36	31	0.032	43	705	37
18	B20	20	100	75	0.35	32	0.031	41	690	43
19	B30	30	50	25	0.35	22	0.025	35	440	21
20	B30	30	50	50	0.33	24	0.023	33	425	23
21	B30	30	50	75	0.32	25	0.022	31	410	28
22	B30	30	75	25	0.34	26	0.023	36	650	31
23	B30	30	75	50	0.32	27	0.021	34	630	34
24	B30	30	75	75	0.31	28	0.020	33	610	39
25	B30	30	100	25	0.37	29	0.032	42	725	36
26	B30	30	100	50	0.35	31	0.031	40	710	38
27	B30	30	100	75	0.34	32	0.030	39	695	42

Table 8

ANOVA for the BTE model.

BTE Model							
Source	Sum of Squares	df	Mean Square	F-value	p-value	Contribution	
Model	272.28	9	30.25	143.90	< 0.0001	Significant	
A-Biodiesel Blend	6.72	1	6.72	31.97	< 0.0001	Significant	2 %
B-Load	213.56	1	213.56	1015.77	< 0.0001	Significant	78 %
C-Alumina	40.50	1	40.50	192.64	< 0.0001	Significant	15 %
AB	0.3333	1	0.3333	1.59	0.2250		0 %
AC	0.7500	1	0.7500	3.57	0.0761		0 %
BC	0.0833	1	0.0833	0.3964	0.5373		0 %
A ²	9.80	1	9.80	46.60	< 0.0001	Significant	4 %
B ²	0.0741	1	0.0741	0.3523	0.5606		0 %
C ²	0.4630	1	0.4630	2.20	0.1561		0 %
Residual	3.57	17	0.2102				1 %
Cor Total	275.85	26					
Std. Dev.	0.4585		R ²	0.9870			
Mean	26.93		Adjusted R ²	0.9802			
C.V. %	1.70		Predicted R ²	0.9677			
			Adeq Precision	43.7005			

assessment (Fig. 5) showed several key absorption bands corresponding to distinct molecular bonds. Intense peaks at 2923, 2853, and 2642 cm⁻¹ were ascribed to C–H stretching vibrations characteristic of organic residues or hydrocarbon constituents that are on the surface of the powder. Additional significant peaks in the 2300–1980 cm⁻¹ interval were attributed to carbonyl (C=O) and other functional groups, suggesting minor organic contamination or residual components from the coating process.

The most prominent feature of the FTIR spectrum was a broad band at around 875 cm⁻¹ corresponding to metal–oxygen vibrational modes, specifically from metal–oxygen interactions in the TBC. This absorption is a definitive indication of the crystalline nature of the TBC material, which consists primarily of YSZ, Al₂O₃, and CeO₂. The discovery is consistent with the material's thermal stability and its use as a thermal insulator. These observations are consistent with the expected characteristics of the TBC, in which the ceramic matrix is expected to provide excellent thermal insulation, combustion efficiency, and high-temperature resistance during engine operation. The FTIR analysis of the TBC powder under optimized conditions confirms its robustness and

stability, which are imperative for preserving the coating's structural integrity and enhancing engine performance. These results highlight the importance of the TBC in reducing heat loss, enhancing combustion efficiency, and helping to reduce the overall emission of pollutants, especially carbon monoxide CO and hydrocarbons HC, and at the same time respond to the possible increase of NOx emissions due to the increase of combustion temperatures.

3.3. Engine performance analysis

The Taguchi orthogonal array L27 was adopted in this investigation to systematically study the interactions between the input variables, each of which was considered at three discrete levels. In this robust experimental design, the effects of three factors (biodiesel blend, engine load, and alumina nanoparticle concentration) were analyzed on the engine's performance indices and emission characteristics. To clarify the discussion, the experimental matrix (L27) in Table 7 was used for the TBC-assisted engine condition with WSOME-diesel blends of varying Al₂O₃ nanoparticle concentrations and engine loads. The uncoated

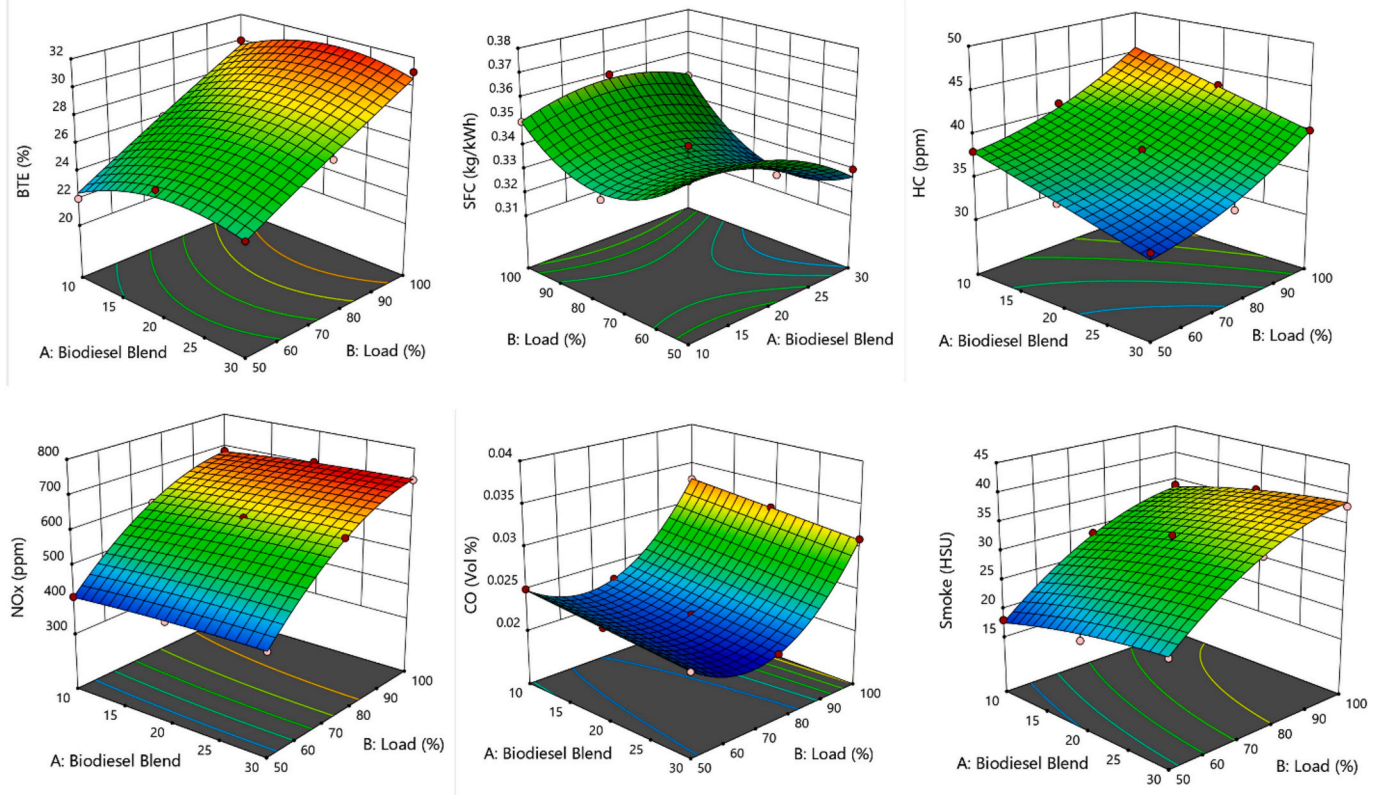


Fig. 6. 3D RSM surface plots showing the combined effect of biodiesel blend ratio and engine load on SFC, BTE, CO, HC, NOx, and smoke emissions at fixed Al_2O_3 nanoparticle concentration.

engine was tested separately under baseline/reference conditions to assess the effect of the TBC on engine performance and emissions. So the same L27 design was not repeated with the coated and uncoated engines; instead, the results obtained from the uncoated engine were used as benchmark data, and the coated-engine L27 data set was used for RSM optimization and machine-learning prediction.

The thermal barrier coating can affect volumetric efficiency because the coated piston crown and cylinder liner retain more heat in the combustion chamber. This higher wall temperature could raise the temperatures of the residual gases and the incoming air charge, slightly reducing air density during intake. Therefore, there may be a small drop in volumetric efficiency in the TBC engine compared with the uncoated engine. However, in the present study, this effect was not predominant because the engine was run at a constant speed under controlled-load conditions. Heat loss and increased combustion temperature led to improved fuel evaporation, oxidation, and combustion efficiency, more than offsetting the potential slight loss of volumetric efficiency.

3.3.1. RSM optimization

The main objective of this optimization is to maximize the BTE and minimize the SFC and emission characteristics. A quadratic model was fitted to the experimental data and provides a satisfactory representation of the relationship between the input variables and the responses. The independent variables considered were biodiesel blend percentage (B10, B20, B30), aluminum oxide nanoparticle concentration (25, 50, 75 ppm), and engine load (50 %, 75 %, 100 %). Optimization was performed by using Design-Expert version 13 software, and a user-defined model was applied to determine the best combinations of these factors. The equation given below represents the fitted quadratic model (Equation (2)–(7)):

$$\begin{aligned} SFC = & 0.548148 + 0.000639(\text{BiodieselBlend}) - 0.004422(\text{Load}) \\ & - 0.001678(\text{Alumina}) + 0.000023(\text{BiodieselBlend} \times \text{Load}) \\ & + 3.33333 \times 10^{-6}(\text{BiodieselBlend} \times \text{Alumina}) \\ & + 1.33333 \times 10^{-6}(\text{Load} \times \text{Alumina}) - 0.000078(\text{BiodieselBlend}^2) \\ & + 0.000028(\text{Load}^2) + 8.88889 \times 10^{-6}(\text{Alumina}^2) \end{aligned} \quad (2)$$

$$\begin{aligned} BTE = & 3.75926 + 0.672222(\text{BiodieselBlend}) + 0.184444(\text{Load}) \\ & + 0.134444(\text{Alumina}) - 0.000667(\text{BiodieselBlend} \times \text{Load}) \\ & - 0.001(\text{BiodieselBlend} \times \text{Alumina}) - 0.000133(\text{Load} \times \text{Alumina}) \\ & - 0.012778(\text{BiodieselBlend}^2) - 0.000178(\text{Load}^2) \\ & - 0.000444(\text{Alumina}^2) \end{aligned} \quad (3)$$

$$\begin{aligned} CO = & 0.071611 - 0.000108(\text{BiodieselBlend}) - 0.001287(\text{Load}) \\ & - 0.000149(\text{Alumina}) - 3.33333 \times 10^{-7}(\text{BiodieselBlend} \times \text{Load}) \\ & + 6.66667 \times 10^{-7}(\text{BiodieselBlend} \times \text{Alumina}) + 2.66667 \\ & \times 10^{-7}(\text{Load} \times \text{Alumina}) - 7.53815 \times 10^{-20}(\text{BiodieselBlend}^2) \\ & + 9.60000 \times 10^{-6}(\text{Load}^2) + 5.33333 \times 10^{-7}(\text{Alumina}^2) \end{aligned} \quad (4)$$

$$\begin{aligned} HC = & 49.35185 - 0.294444(\text{BiodieselBlend}) - 0.160000(\text{Load}) \\ & - 0.145556(\text{Alumina}) - 3.89939 \times 10^{-17}(\text{BiodieselBlend} \times \text{Load}) \\ & + 0.000667(\text{BiodieselBlend} \times \text{Alumina}) + 0.000133(\text{Load} \times \text{Alumina}) \\ & - 0.000556(\text{BiodieselBlend}^2) + 0.002044(\text{Load}^2) \\ & + 0.000444(\text{Alumina}^2) \end{aligned} \quad (5)$$

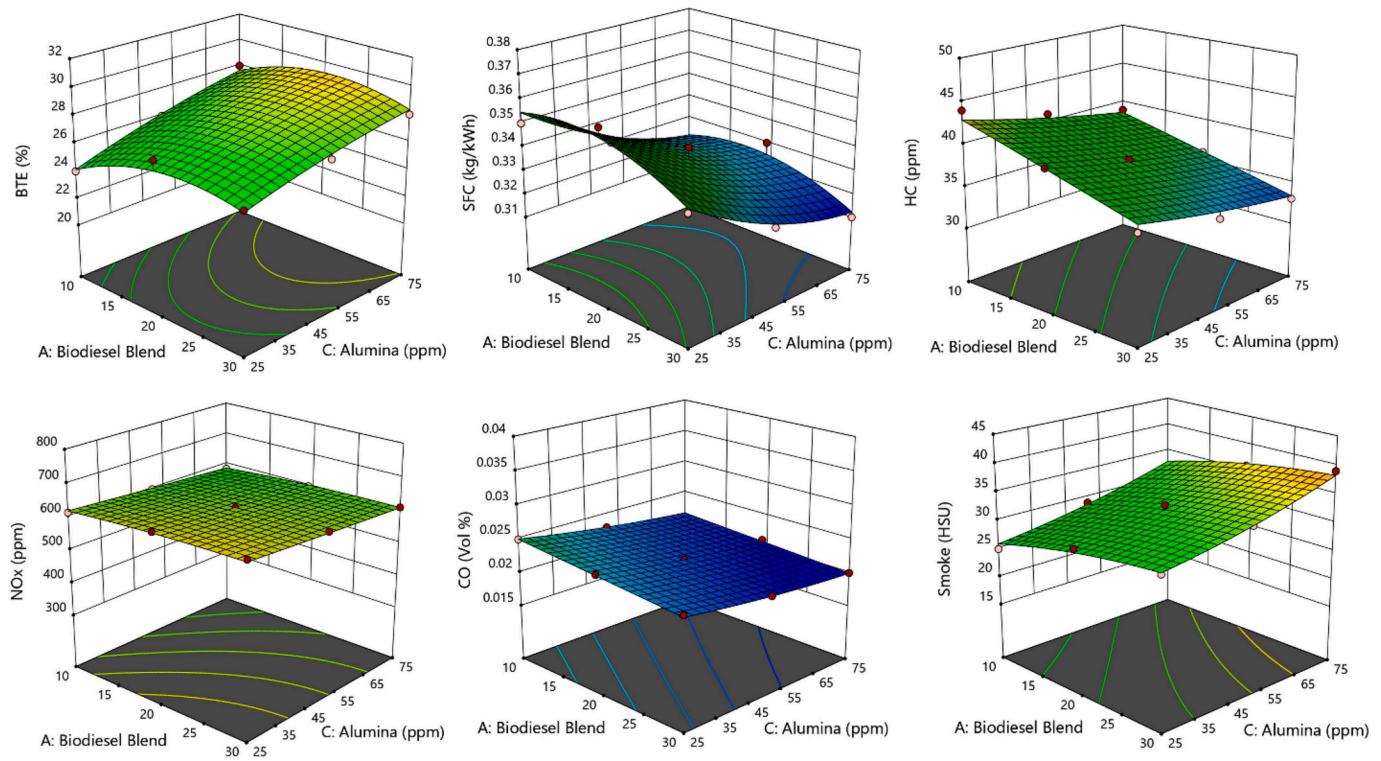


Fig. 7. 3D RSM surface plots showing the combined effect of biodiesel blend ratio and Al_2O_3 nanoparticle concentration on SFC, BTE, CO, HC, NOx, and smoke emissions at fixed engine load.

$$\begin{aligned}
 \text{NOx} = & -301.01852 + 2.45833(\text{BiodieselBlend}) + 18.97778(\text{Load}) \\
 & - 0.82222(\text{Alumina}) + 0.011667(\text{BiodieselBlend} \times \text{Load}) \\
 & - 0.001667(\text{BiodieselBlend} \times \text{Alumina}) \\
 & + 0.001333(\text{Load} \times \text{Alumina}) - 0.052778(\text{BiodieselBlend}^2) \\
 & - 0.091111(\text{Load}^2) + 0.000889(\text{Alumina}^2)
 \end{aligned} \quad (6)$$

$$\begin{aligned}
 \text{Smoke} = & -31.07407 + 0.627778(\text{BiodieselBlend}) + 1.04889(\text{Load}) \\
 & - 0.015556(\text{Alumina}) - 0.000667(\text{BiodieselBlend} \times \text{Load}) \\
 & + 2.94690 \times 10^{-17}(\text{BiodieselBlend} \times \text{Alumina}) \\
 & + 0.000533(\text{Load} \times \text{Alumina}) - 0.007778(\text{BiodieselBlend}^2) \\
 & - 0.004978(\text{Load}^2) + 0.001156(\text{Alumina}^2)
 \end{aligned} \quad (7)$$

3.3.1.1. ANOVA for all output models. The results of the analysis of variance (ANOVA) (Supplementary file) were obtained for multiple output models, which provide insight regarding the relative importance and contribution of the different factors and their interactions for the performance and emission characteristics of biodiesel blends produced from watermelon seed oil doped with Al_2O_3 nanoparticles. The result of the ANOVA table for the BTE model is shown in Table 8, while the results of the rest of the output models are in the supplementary file. For the SFC model, the results were highly significant, with an F statistic of 46.59 and a p-value less than 0.0001. This shows a strong association between the input variables and the SFC response. Among the factors evaluated, the most important variables in this study were the concentration of Al_2O_3 (C), which explained 53 % of the variance; engine load (B), which explained 8 %; and biodiesel blend proportion (A), which explained 8 %. The quadratic term for the biodiesel blend (A^2) was also statistically significant and accounted for 5 % of the variance. The coefficient of determination for the SFC model ($R^2 = 0.961$) shows that the factors considered and their interactions account for 96.1 % of the

variation in SFC.

In the BTE model, engine load (B) is the most important factor, accounting for 78 % of the explained variance, followed by Al_2O_3 concentration (C), which accounts for 15 %. The p-values for both factors are extremely low (<0.0001), indicating a statistically significant effect on BTE. In addition, the quadratic term of the biodiesel blend (A^2) also explains 4 % of the variance. The coefficient of determination, $R^2 = 0.9870$, indicates that the model explains 98.7 % of the variance in BTE. In the CO emissions model, both engine load (B) and aluminum oxide concentration (C) are considered very important, with F- and p-values of 2889.44 and 436.98, respectively, and $p < 0.0001$. Notably, biodiesel blend (A) has a negligible effect on CO emissions. The quadratic engine load term, B^2 , contributes 33.3 % to the model, and with $R^2 = 0.9970$, the model accounts for 99.7 % of the variance in CO emissions.

The HC emissions model also shows that engine load (B) is the most important contributor, accounting for 54 % of the total variance. Al_2O_3 concentration (C) and the biodiesel blend (A) account for 14 % and 30 %, respectively. Both the quadratic terms of engine load (B^2) and biodiesel mix (A^2) are large, with the engine load (B^2) contributing 2 %. The R^2 value is 0.9850, indicating that the model explains 98.5 % of the variance in HC emissions. Regarding NOx emissions, engine load (B) and Al_2O_3 concentration (C) were again the dominant factors, accounting for 93 % and 1 %, respectively. The quadratic component associated with engine load (B^2) is statistically significant, and it explains 5 % of the total variability. The model explains 99.95 % of the variability of NOx emissions with an R^2 of 0.9995. In the smoke emission model, engine load (B) explains 73 % of the variance, and Al_2O_3 (C) explains 14 %. The quadratic engine load term, B^2 , is also significant, contributing 4 % to the variance. An R^2 of 0.9911 indicates that the model explains 99.11 percent of the variance in smoke emissions. Overall, the analysis of variance results show that engine load and Al_2O_3 concentration are the most influential factors affecting engine performance and emissions. The consistently high R^2 values for all models confirm that the quadratic models provide an excellent fit to the experimental data and may be useful for optimizing engine performance with biodiesel blends.

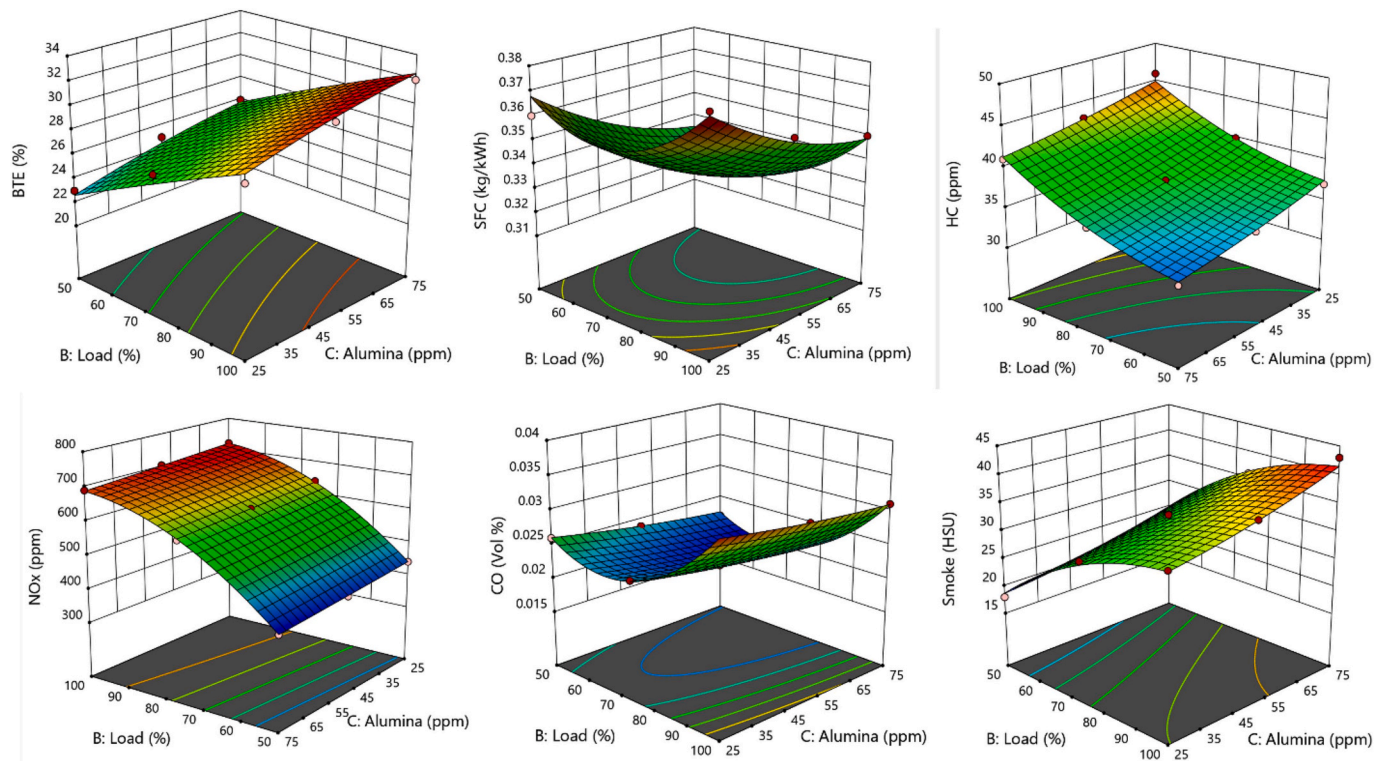


Fig. 8. 3D RSM surface plots showing the combined effect of engine load and Al_2O_3 nanoparticle concentration on SFC, BTE, CO, HC, NOx, and smoke emissions for WSOME–diesel blends.

3.3.1.2. Interaction contour plots. The 3D surface visualization will provide a comprehensive description of how the engine's output measures are modulated by the interplay between two key input parameters. Fig. 6 illustrates the variation of the output variables with the biodiesel blend-to-engine load ratio (A) and engine load (B), providing a comprehensive view of the interaction effect.

The surface plot indicates a monotonic increase in BTE with increasing biodiesel blend percentage and engine load. This trend implies that the oxygen-rich character of biodiesel will result in a higher combustion efficiency at higher loads and hence higher thermal efficiency. These observations are consistent with theoretical expectations, bearing in mind the structure of biodiesel, i.e., its inherent oxygen content, which promotes more complete combustion, especially under high-load conditions. The SFC trend shows a decrease as biodiesel blend and engine load increase, indicating improved fuel economy. Specifically, increased biodiesel loads at higher loads can yield more efficient fuel use; hence, the suggestion that biodiesel may offer more efficient fuel use at higher loads. With regard to HC emissions, the surface plot indicates an increase in HC at lower loads with higher biodiesel concentrations, whilst HC declines at high loads. The higher load at which the HC emission reduction becomes effective can be attributed to enhanced combustion, resulting in a greater proportion of the fuel being oxidized. On the other hand, the NOx surface plot shows an increase in NOx emissions as the biodiesel blend percentage and engine load increase. This trend is a common attribute of biodiesel combustion, where higher combustion temperatures, owing to increased loads and biodiesel mixing, are responses to increased loads. Hence, the trade-off between performance gains and NOx emissions is one of the most important factors in optimizing biodiesel utilization. The present findings are in line with earlier studies, such as Krishnamoorthi et al [52], who concluded that the higher the biodiesel content, the higher the engine performance, but the higher the engine NOx emissions. The surface plot of CO emissions reveals that CO concentration decreases with increasing biodiesel concentration and engine load. This decrease could be

attributed to biodiesel's better combustion properties, which enable it to be more oxidized and thus form less CO. Similarly, the smoke opacity plot analysis reveals a decrease with increasing biodiesel concentration and higher engine load, indicating reduced particulate matter formation. It is presumed that the reduction in smoke opacity is due to increased combustion efficiency observed at higher loads with biodiesel blends. These findings suggest that higher engine loads with biodiesel blends lead to improved engine performance, particularly in BTE and SFC. However, the increase in NOx emissions at high loads and biodiesel concentrations indicates that further optimization is needed to balance high performance and emission control. The incorporation of Al_2O_3 nanoparticles into biodiesel blends and TBCs is a feasible means of controlling smoke and particulate emissions while improving combustion efficiency. However, the continued increase in NOx emissions highlights the need for potential optimization strategies to reduce them.

The 3D surface plots in Fig. 7 show how the biodiesel blend (A) and the concentration of alumina nanoparticles (C) interact to alter various engine performance measures and emissions. BTE shows a weak positive dependence on the ratio of biodiesel blends and the concentration of alumina, as evidenced by increases in both. This improvement is likely due to the high oxygen content of biodiesel, coupled with the catalytic effect of alumina nanoparticles, which together contribute to more complete combustion. SFC decreases as biodiesel density increases and alumina loading decreases, indicating improved fuel economy, as the net energy per unit of fuel is higher due to higher combustion efficiency. Regarding HC emissions, the data show few differences across biodiesel and alumina concentrations and suggest that biodiesel is oxygenated and therefore undergoes complete combustion, producing lower HC emissions. These results are consistent with other studies, such as Dhinesh et al. [53], which demonstrated that the introduction of alumina nanoparticles and thermal barrier coatings increased thermal efficiency and reduced fuel consumption. The NOx formation trend is primarily attributed to the thermal NOx mechanism. The TBC engine reduces heat loss due to the rise in local in-cylinder temperature, and Al_2O_3

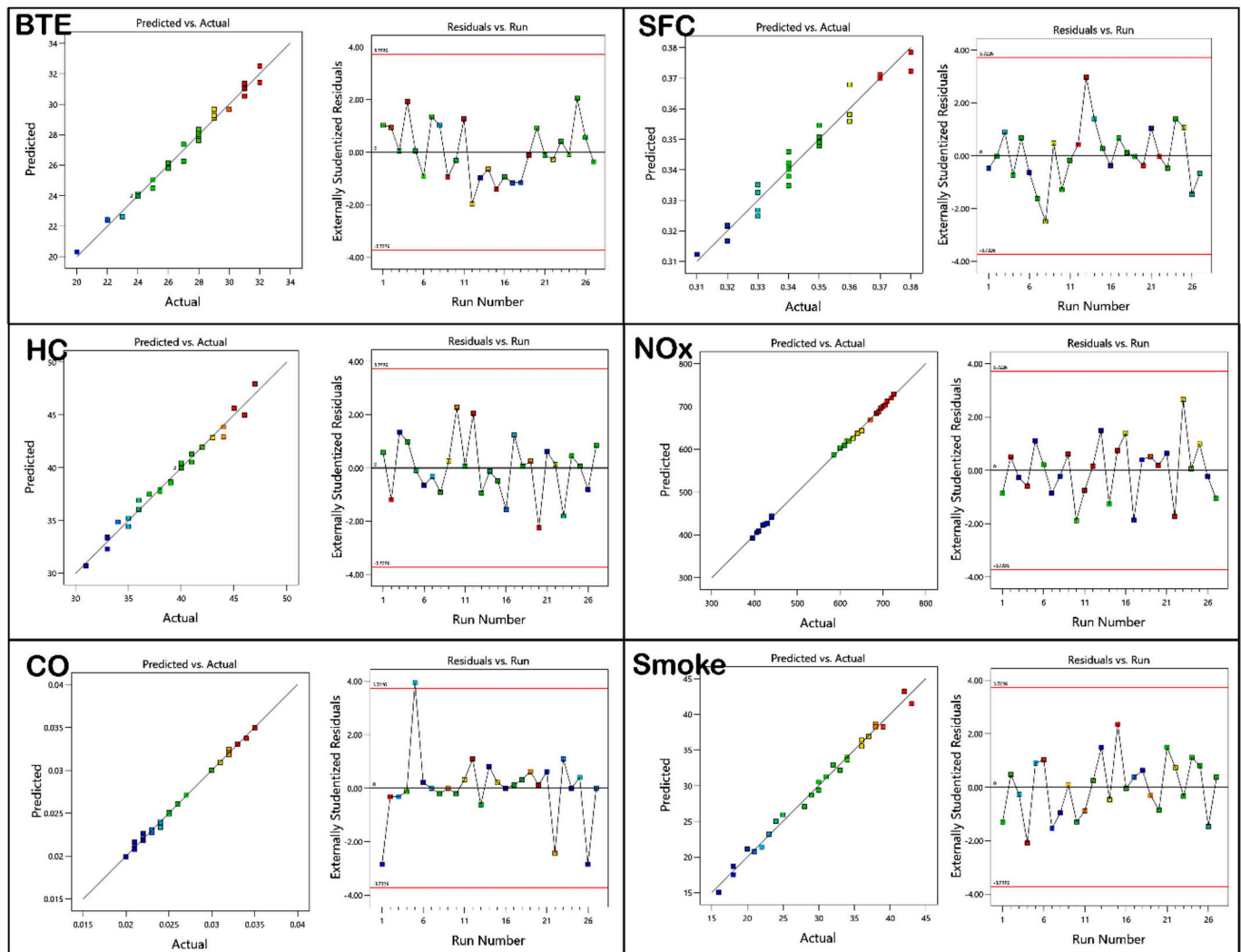


Fig. 9. RSM model diagnostic plots showing predicted versus actual values and residuals versus experimental run order for SFC, BTE, CO, HC, NOx, and smoke emissions.

nanoparticles enhance catalytic oxidation, heat transfer, and combustion intensity. Also, due to the oxygenation of WSOE, fuel combustion can be more complete. These combined effects lead to higher BTE and reduced CO, HC, and smoke emissions, but higher combustion temperatures and oxygen supply increase the potential for nitrogen oxidation and NOx formation. This same phenomenon was observed by Dharmadran et al. [48], who found that the use of hydrogen-enriched nanoparticle-emulsified biodiesel resulted in enhanced combustion but led to NOx formation owing to higher combustion temperatures. Finally, the smoke opacity test indicates that particulate matter emissions decrease with higher concentrations of biodiesel and alumina. This attenuation could be associated with the presence of oxygenates in biodiesel and the catalytic effect of alumina nanoparticles, which may act together to prevent soot formation [54,55]. Taken together, these plots demonstrate the positive effects of biodiesel-alumina blends on engine performance and emissions reduction, and indicate the need to further optimize these blends to control NOx levels without detracting from the overall benefits of improved combustion.

The surface plots in Fig. 8 illustrate the interaction between Engine Load (B) and Alumina Nanoparticle Concentration (C), providing insight into changes in various engine performance parameters and emission characteristics under their combined influence. The BTE surface shows a clear spike in efficiency with increasing engine load and alumina nanoparticle concentration, indicating that high-load conditions with

high particle loads yield more efficient combustion. The observed enhancement in thermal performance and combustion stability provided by alumina nanoparticles is likely to explain the rise in thermal performance. In line with this, the SFC surface shows a decline in fuel consumption as engine load and alumina concentration increase, owing to improved combustion dynamics at higher engine load and alumina concentration. According to the HC emission plot, there is a slight decrease in HC levels at higher engine loads and higher alumina nanoparticle levels, attributed to the complete oxidation of fuel in the presence of alumina nanoparticles, thereby reducing HC emissions.

The rise in NOx with increasing engine load and with increasing concentration of the alumina nanoparticle increases the amount of NOx formed, which in turn increases the catalytic activity of the alumina nanoparticle. Conversely, the CO emission surface decreases with increasing engine load and alumina concentration, which agrees with a near-complete oxidation process under these conditions and with the catalytic ability of the alumina particles. The smoke opacity surface shows a concomitant decrease as load and particle concentration increase, indicating lower particulate matter and soot emissions and improved combustion dynamics. These surfaces and their association give a fascinating reconsideration of the intricate interrelationships among engine load, alumina concentration, performance, and emissions. Although the concomitant rise in load and alumina nanoparticle concentration is typically advantageous for enhancing engine efficiency

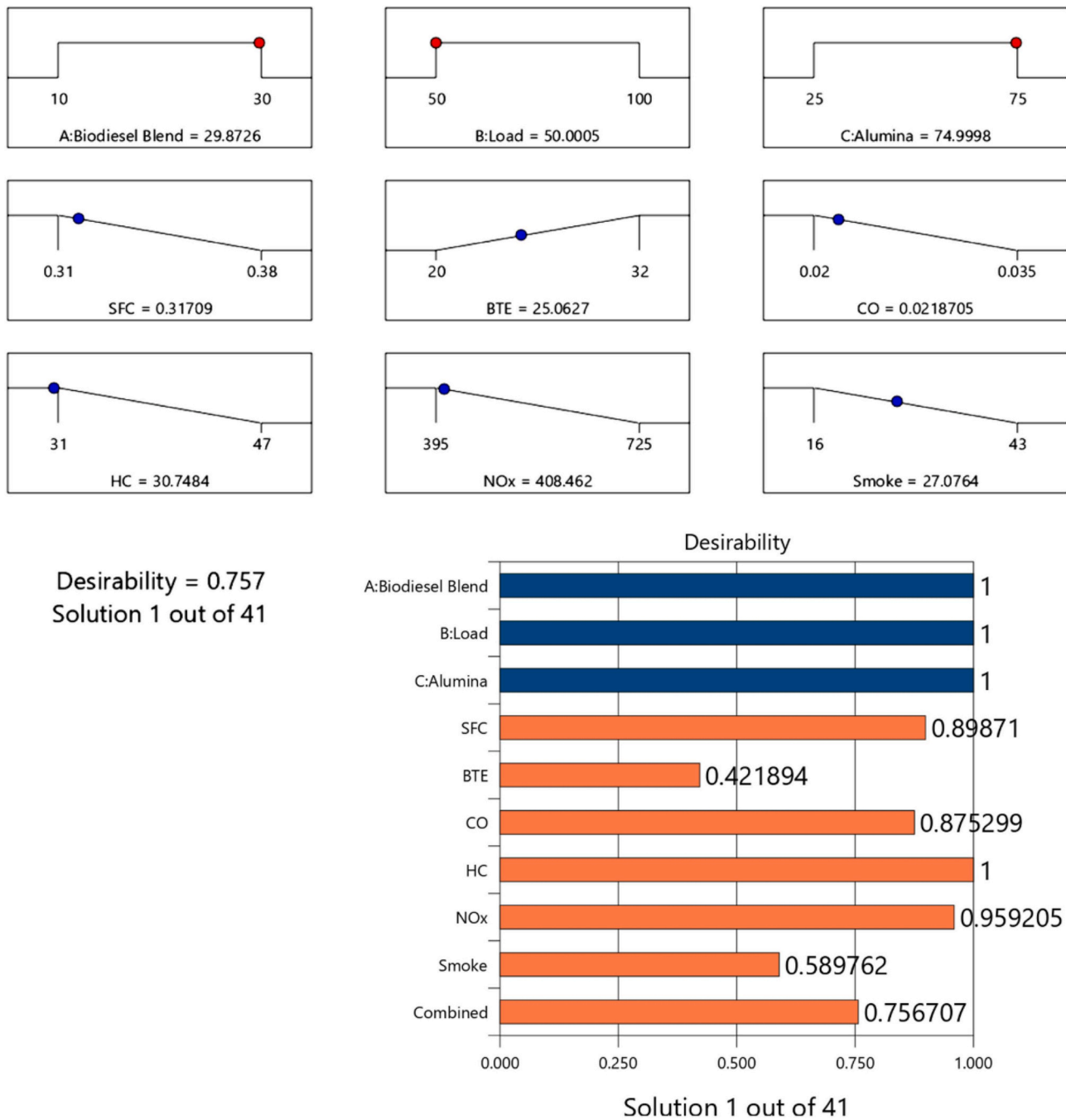


Fig. 10. Desirability-based RSM optimization plot showing the optimum operating condition for maximizing BTE and minimizing SFC, CO, HC, NOx, and smoke emissions.

(BTE) and SFC, and for reducing smoke opacity and CO emissions, it is also accompanied by higher NOx concentrations, which are driven by increased temperature. Therefore, a perfect balance must be struck between performance enhancement and NOx emissions regulation.

This result agrees with other studies, e.g., Khanam et al [56], which reported higher engine performance with alumina nanoparticle additives. BTE shows a similarly significant improvement when operating at higher load conditions based upon increasing nanoparticle concentration, which was attributed to the oxygen-rich nature of the nanoparticles, which would promote more efficient combustion; a conclusion which was supported by Vignesh Palani et al [57] who documented increased thermal efficiency for the nanoparticle-triggered biodiesel blends. CO emissions are reduced at higher nanoparticle concentrations,

particularly at higher engine loads, consistent with the findings of Dhinesh et al [53], who reported that nanoparticle additives improved oxidation reactions and decreased CO emissions. HC emissions also decrease with increasing alumina content, especially at full engine load, indicating more complete combustion. On the contrary, NOx emissions increase with higher alumina concentrations, particularly at higher loads, as reported by previous studies, including Reddy et al. [58]. Smoke opacity decreased with a higher alumina concentration, indicating a catalytic role of the nanoparticles in reducing particulate emissions. Notwithstanding the principal conclusions of the present investigation, the observed augmentation of NOx emissions at elevated nanoparticle concentration and high engine loads does not agree with the principal conclusions obtained herein. It is similar to those reported

Table 9

Benchmark comparison of the present optimized configuration with B0 and related literature.

Case/study	Engine condition	Key condition	Main reported result	Interpretation for the present study
Present study: B0 baseline	Uncoated	B0, 50 % load, 0 ppm	BTE = 18.4 %; SFC = 0.46 kg/kWh; CO = 0.048 %; HC = 39 ppm; NOx = 853 ppm; Smoke = 23 HSU	Practical baseline for direct comparison with the present optimized condition
Present study: optimized validation point	Coated	B30, 50 % load, 75 ppm Al ₂ O ₃	BTE = 25.0 %; SFC = 0.32 kg/kWh; CO = 0.022 %; HC = 31 ppm; NOx = 410 ppm; Smoke = 28 HSU	Relative to B0, BTE increased by 35.87 %, while SFC, CO, HC, and NOx decreased by 30.43 %, 54.17 %, 20.51 %, and 51.93 %, respectively; smoke increased by 21.74 %
Vinothkannan & Pushparaj [62]	Uncoated	B20 pumpkin-teak biodiesel + DEE, maximum load	BTE + 35.5 %, BSFC – 25.8 %, CO – 26.67 %, NO – 22.85 %, HC + 58.2 %, Smoke + 9.84 % vs diesel	Shows that strong efficiency improvement can be achieved in an uncoated engine, but with clear HC and smoke penalties
Dhairiyasamy et al. [63]	Uncoated	BSM20 with natural additives, full load	BSFC for BSM20-NLA = 0.488 kg/kWh (only 1.2 % above diesel); BTE for BSM20-PLA = 32.19 % vs diesel 33.04 %; CO – 36.84 %, HC – 22.22 %, NOx – 17.72 %, Smoke – 13.83 %	Indicates that substantial emission reduction is also achievable in uncoated biodiesel engines through fuel/additive design alone
Şahin & Torun [64]	Uncoated	Waste pumpkin biodiesel blends	PB2D98 showed the closest overall behavior to diesel; lowest SFC = 194.33 g HPh ⁻¹ for PB2D98; highest	Suggests that, in uncoated seed-derived biodiesel operation, closer-to-diesel behavior may require a lower biodiesel fraction

Table 9 (continued)

Case/study	Engine condition	Key condition	Main reported result	Interpretation for the present study
			BTE = 30.92 %	
			still occurred with diesel; average NOx was lowest for D100 (473 ppm) and highest for PB100 (1208 ppm)	
Paramasivam et al. [65]	Uncoated dual-fuel	Optimized at 82.71 % load and CR 18.5	BTE = 16.98 %, HC = 112 ppm, NOx = 306 ppm, CO = 172 ppm	Supports the use of RSM + ML for optimization in uncoated engines, but direct comparison is limited because of the dual-fuel configuration
Krishnamoorthi et al. [42]	Coated	BD100 + 200 µm TBC + 45 ppm CeO ₂	Average SFC reduction of 0.065 kg/kWh and BTE increase of 4.07 % vs uncoated diesel; CO = 0.0916 %, UBHC = 38.2 ppm, NOx = 132 ppm, Smoke = 10.52 %	Useful as an external coated-engine benchmark, but not equivalent to a controlled coated/uncoated comparison within the present study

by Sambandam et al. [59]. This phenomenon is conventionally attributed to the high combustion temperatures induced by nanoparticles, which facilitate NOx production, particularly at high load.

The accuracy and reliability of the models are supported by comparative analyses of differences between predicted and actual values and between residuals and the run plot (Fig. 9) for each response parameter in the RSM optimization results. The fact that the predicted-versus-actual plots are nearly linear across all parameters suggests that the RSM model captures underlying trends and interactions in the experimental data. The arguments are tightly clustered around the diagonal, which therefore counters the high accuracy of the model predictions. Conversely, the plots of residuals against run display random dispersion with no apparent pattern or systematic trend, indicating model strength and the absence of inherent bias. The residual distribution is symmetric about zero, which supports the validity of the model's assumptions and the predictive variance when the model is run repeatedly. Taken together, these visual diagnostics support the conclusion that the RSM optimization framework provides a sound representation of engine performance and emission dynamics, with insignificant differences between predicted and actual values, confirming the effectiveness of the RSM approach in optimizing engine performance and emissions when using biodiesel.

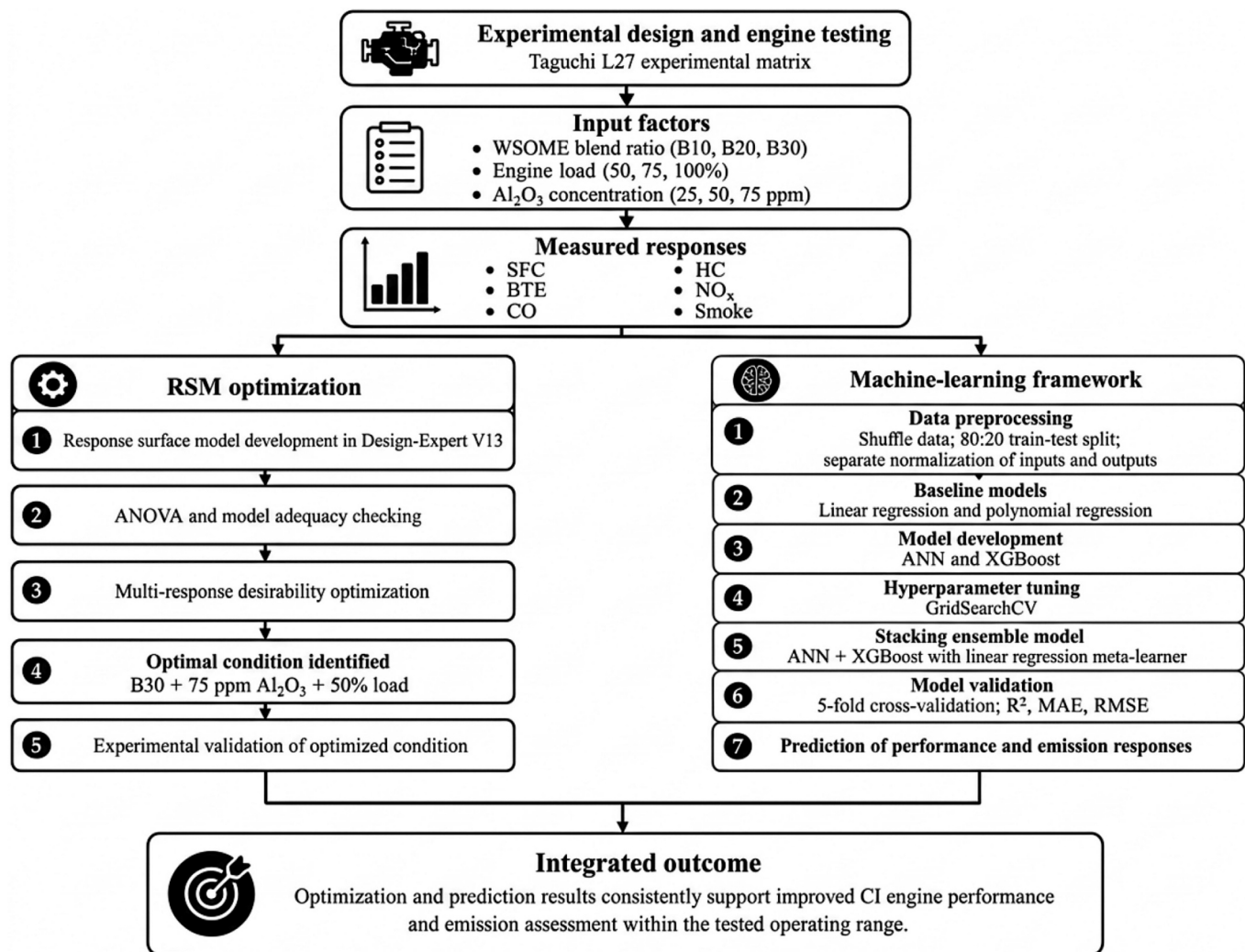


Fig. 11. Flowchart of the RSM optimization and ANN-XGBoost machine-learning framework used for modelling, optimization, validation, and prediction of CI engine performance and emission responses.

3.3.1.3. Optimization result. Fig. 10 shows the results of the desirability-based optimization obtained through the RSM model. The solution that optimized engine load was found at a B30 biodiesel blend, an engine load of 50 N, and a concentration of 75 ppm alumina nanoparticles. At this operating condition, the predicted response values were SFC = 0.31709 kg/kWh, BTE = 25.0627 %, CO = 0.0218705 % vol., HC = 30.7484 ppm, NOx = 408.462 ppm, and smoke = 27.0764 HSU.

The optimum performance obtained with B30 and 75 ppm Al₂O₃ can be explained by the balanced fuel-combustion characteristics of this combination. The B30 blend contains sufficient biodiesel-bound oxygen, which promotes better oxidation of the fuel during combustion and helps reduce CO, HC, and smoke emissions. At the same time, the diesel fraction in B30 maintains acceptable calorific value, volatility, and spray atomization, preventing the excessive viscosity-related penalties that may occur at higher biodiesel concentrations [60]. The addition of 75 ppm Al₂O₃ further improves combustion by providing a high-surface-area catalytic medium, enhancing heat transfer within the fuel spray, shortening ignition delay, and supporting more uniform fuel-air mixing. These effects increase the rate of complete combustion, resulting in higher BTE and lower SFC. The Al₂O₃ nanoparticles may also act as oxygen-buffering sites, promoting the secondary oxidation of unburned fuel fragments and thereby explaining the reduction in CO and HC emissions [61]. Therefore, B30 with 75 ppm Al₂O₃ represents a suitable compromise among biodiesel oxygen availability, diesel-like spray

behavior, and nanoparticle-assisted catalytic combustion, resulting in the highest overall desirability in the present optimization.

For the sake of consistency, the benchmark comparison in Table 9 is explained in the context of the uncoated neat diesel B0 state at 50 % load. Compared with this reference condition, the optimized B30 + 75 ppm Al₂O₃ TBC case increased BTE by 35.87 % and reduced SFC, CO, HC, and NOx by 30.43 %, 54.17 %, 20.51 %, and 51.93 %, respectively. However, smoke opacity was raised by 21.74 %. Thus, the optimized condition reduced most gaseous emissions and improved fuel economy, but it did not reduce smoke as compared to B0. The NOx result should also be understood in the context of the selected reference conditions: NOx decreased compared to the B0 reference, but increased combustion temperatures due to the use of TBC and combustion with nanoparticles can, under certain operating conditions, lead to a greater tendency to form thermal NOx.

3.3.2. Machine learning prediction

In this work, a machine learning technique was employed to predict engine performance and emission response to three input parameters: biodiesel blend ratio, engine load, and Al₂O₃ nanoparticle concentration. These three parameters were used as inputs for the 27-run Taguchi L27 experimental dataset, and the output responses were SFC, BTE, CO, HC, NOx, and smoke. The data was randomized and split into training (80 %) and test (20 %) sets, with a fixed random state of 42 to ensure

Table 10
Gridsearch result for ANN and XGBoost.

Model	ANN		XGBoost	
	Hyperparameters	R ²	Hyperparameters	R ²
SFC	Hidden layer1: 6 Hidden layer2: 6 Hidden layer3: 3	0.836	n_estimators = 1000, learning_rate = 1.985, max_depth = 8, subsample = 0.8, colsample_bytree = 0.8	0.886
BTE	Hidden layer1: 9 Hidden layer2: 5 Hidden layer3: 5	0.912	n_estimators = 1000, learning_rate = 0.5, max_depth = 8, subsample = 0.65, colsample_bytree = 0.65	0.935
CO	Hidden layer1: 8 Hidden layer2: 4 Hidden layer3: 4	0.953	n_estimators = 1000, learning_rate = 1.35, max_depth = 8, subsample = 0.65, colsample_bytree = 0.65	0.962
HC	Hidden layer1: 6 Hidden layer2: 3 Hidden layer3: 3	0.894	n_estimators = 1000, learning_rate = 1.97, max_depth = 8, subsample = 0.65, colsample_bytree = 0.65	0.957
NOx	Hidden layer1: 6 Hidden layer2: 5 Hidden layer3: 5	0.956	n_estimators = 1000, learning_rate = 0.35, max_depth = 8, subsample = 0.65, colsample_bytree = 0.65	0.982
Smoke	Hidden layer1: 6 Hidden layer2: 6 Hidden layer3: 3	0.963	n_estimators = 1000, learning_rate = 0.95, max_depth = 8, subsample = 0.65, colsample_bytree = 0.65	0.891

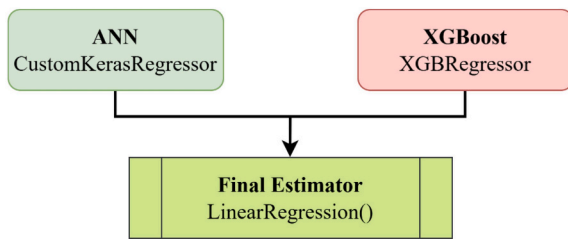


Fig. 12. Architecture of the ANN-XGBoost stacking ensemble model used for predicting engine performance and emission responses.

reproducibility. For model training, the input and output variables were normalized separately. To avoid larger numerical ranges overwhelming the training process, each output response was scaled individually, while the input variables were scaled using StandardScaler. Since the scaler was applied to the training data and used for the testing data, data leakage was avoided. The outputs from the prediction models were then inverse-transformed to their original units for R² calculation, MAE, and RMSE. To avoid model complexity, separate prediction models were developed for each response. Both ANN and XGBoost models had hyperparameter tuning using GridSearchCV. Then the optimized ANN and XGBoost models were integrated in a stacking regressor using the LR meta-learner. The dataset was small, but the model was used only for interpolation within the tested range. The reliability of the model was evaluated by R², MAE, RMSE, plots of predicted versus actual values, residual plots, and five-fold cross-validation. The overall RSM optimization and machine-learning workflow is shown in Fig. 11.

Step 1: Data Preparation and Normalization: In the first phase, data were prepared by selecting relevant features, namely biodiesel blend, load percentage, alumina particle, and the target variables, namely SFC, BTE, CO, HC, NOx, and smoke. The data was then standardized using the StandardScaler class to ensure all features were on a common scale, which is very important for good model performance.

Table 11
Comparison of ANN, XGBoost, and ANN-XGBoost stacking model prediction performance.

Output response	ANN R ²	XGBoost R ²	Ensemble Model R ²	Ensemble MAE	Ensemble RMSE
SFC (kg/kWh)	0.836	0.886	0.9756 ± 0.0124	0.5465 ± 0.0912	0.4407 ± 0.0745
BTE (%)	0.912	0.935	0.9926 ± 0.0041	0.0003 ± 0.0001	0.0002 ± 0.0001
CO (vol.%)	0.953	0.962	0.9784 ± 0.0136	0.5016 ± 0.0873	0.3841 ± 0.0694
HC (ppm)	0.894	0.957	0.9974 ± 0.0022	5.7010 ± 0.9365	4.1435 ± 0.7128
NOx (ppm)	0.956	0.982	0.9820 ± 0.0108	1.0725 ± 0.1846	0.8411 ± 0.1397
Smoke (HSU)	0.963	0.891	0.9756 ± 0.0124	0.5465 ± 0.0912	0.4407 ± 0.0745
Average	0.919	0.936	0.980	—	—

Step 2: Splitting Data into Training and Testing Datasets: The dataset was split into training and testing sets using scikit-learn's train_test_split function. 80 % of the data was used to develop the model, and the remaining 20 % was used for performance evaluation.

Step 3: Model Optimization Using GridSearchCV: The ANN and XGBoost models were optimized using GridSearchCV. For the ANN, parameters such as the number of hidden layers and neurons per layer were experimented. In the XGBoost configuration, the most important hyperparameters, such as the learning rate, maximum depth, and subsampling ratio, were optimized. GridSearchCV identified parameter settings that maximized the R² score; the results are shown in Table 10.

Step 4: Construction of Stacking Regressor Model Ensemble. After optimizing the two individual learners, ANN and XGBoost, the next step was to amalgamate them using a Stacking Regressor Ensemble, as shown in Fig. 12. This ensemble uses ANN and XGBoost as base regressors, with a linear regression estimator as the meta-regressor, leveraging the complementary capabilities of each model to improve prediction accuracy and robustness. The ANN model was trained using mean squared error (MSE) as the loss function because the prediction task involved continuous output responses. The Adam optimizer was used for weight updating due to its stable convergence behaviour for nonlinear regression problems. The maximum number of training epochs was fixed at 1000. During training, 20 % of the training data was used as the validation subset to monitor generalization performance. Early stopping was applied to avoid overfitting; training was stopped when the validation loss did not improve for 25 consecutive epochs. The model weights corresponding to the lowest validation loss were retained for final testing. This stopping criterion ensured that the ANN model did not continue learning noise from the limited experimental dataset.

Step 5: The Stacking Regressor Ensemble Model Construction. After optimizing the two constituents, i.e., ANN & XGBoost, the next phase was to integrate them using the Stacking Regressor Ensemble Model, as shown in Fig. 12. Within this architecture, ANN and XGBoost would act as base regressors, whilst a linear regression model would serve as the meta-learner. This hierarchical setup aims to increase the model's predictive accuracy and robustness by leveraging the complementary nature of the individual base learners.

Step 6: Training of the Ensemble model: The ensemble was then trained on the set of training data that had been designated. The Stacking Regressor was configured to predict performance and emission features by combining the predictions of ANN and XGBoost models.

Step 7: Evaluation of the Model: The fully-trained ensemble was tested and evaluated on an independent test data set using known performance frameworks in terms of the coefficient of determination (R²), Mean Absolute Error (MAE), and Root Mean Squared Error (RMSE). The performance of the prediction of the three models: ANN, XGBoost, and the ANN-XGBoost stacking model is compared to clearly show the advantage of the proposed ensemble approach, as presented in Table 11. The

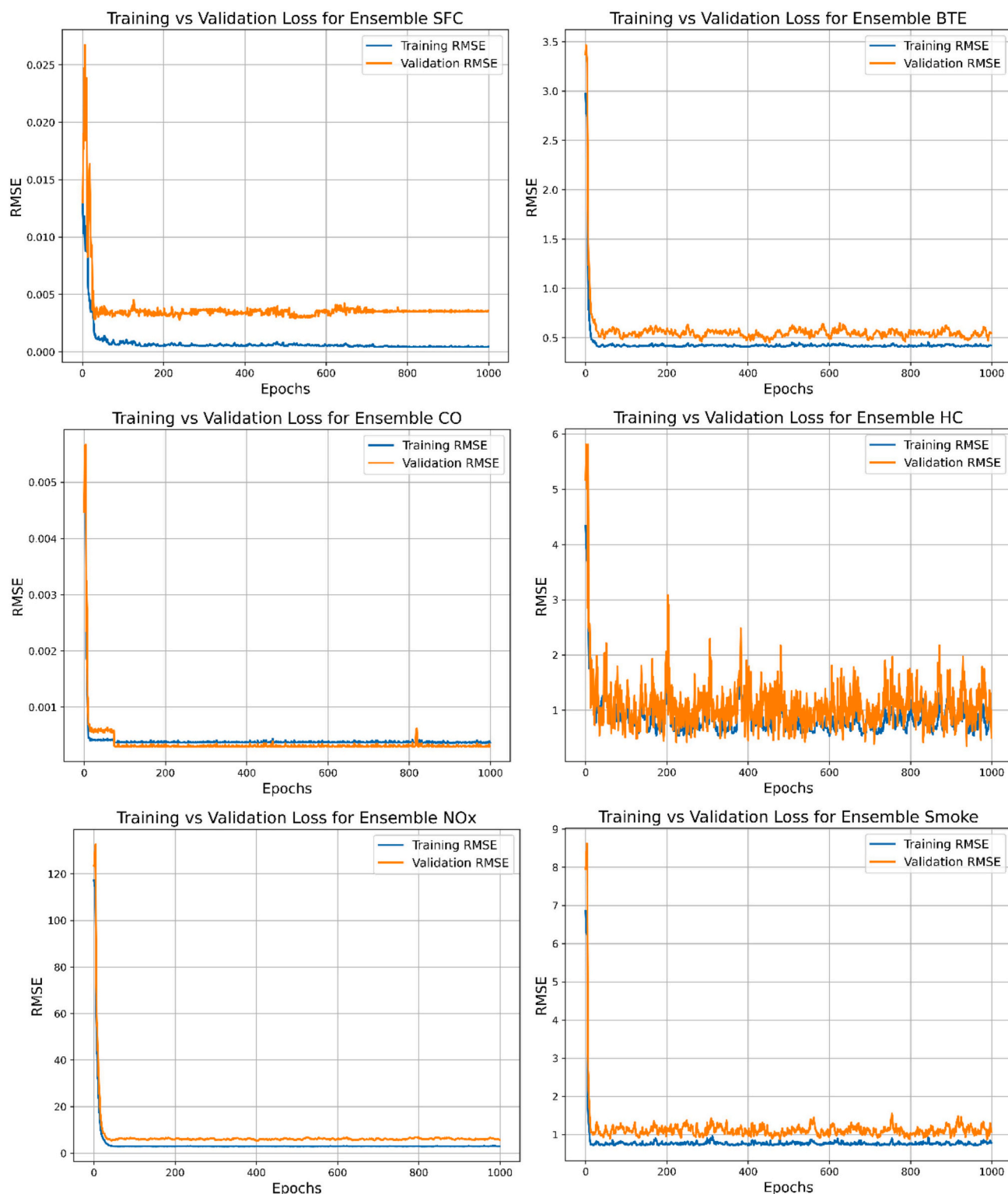


Fig. 13. Training and validation loss curves of the ensemble model for SFC, BTE, CO, HC, NOx, and smoke, showing model convergence and validation behaviour.

individual ANN model was used to capture the nonlinear relationship between the input variables and engine responses, and XGBoost was used to model feature interactions via boosted decision trees, thereby enhancing predictive performance. But the stacking ensemble achieved the best R^2 values for all responses because it fuses the nonlinear learning power of ANN with the strong feature-interaction power of XGBoost. The average R^2 values also improved from 0.919 for ANN and 0.936 for XGBoost to 0.980 for the stacking ensemble, indicating better

prediction stability of the proposed model.

The results show that the ANN–XGBoost stacking ensemble achieved better predictive performance than the individual ANN and XGBoost models. Hence, ensemble modelling was chosen to validate the experimental trend and to aid in optimizing the operating conditions using RSM.

Step 8: Cross-validation using KFold: To assess the model's generalizability and mitigate overfitting, KFold cross-validation was used. The

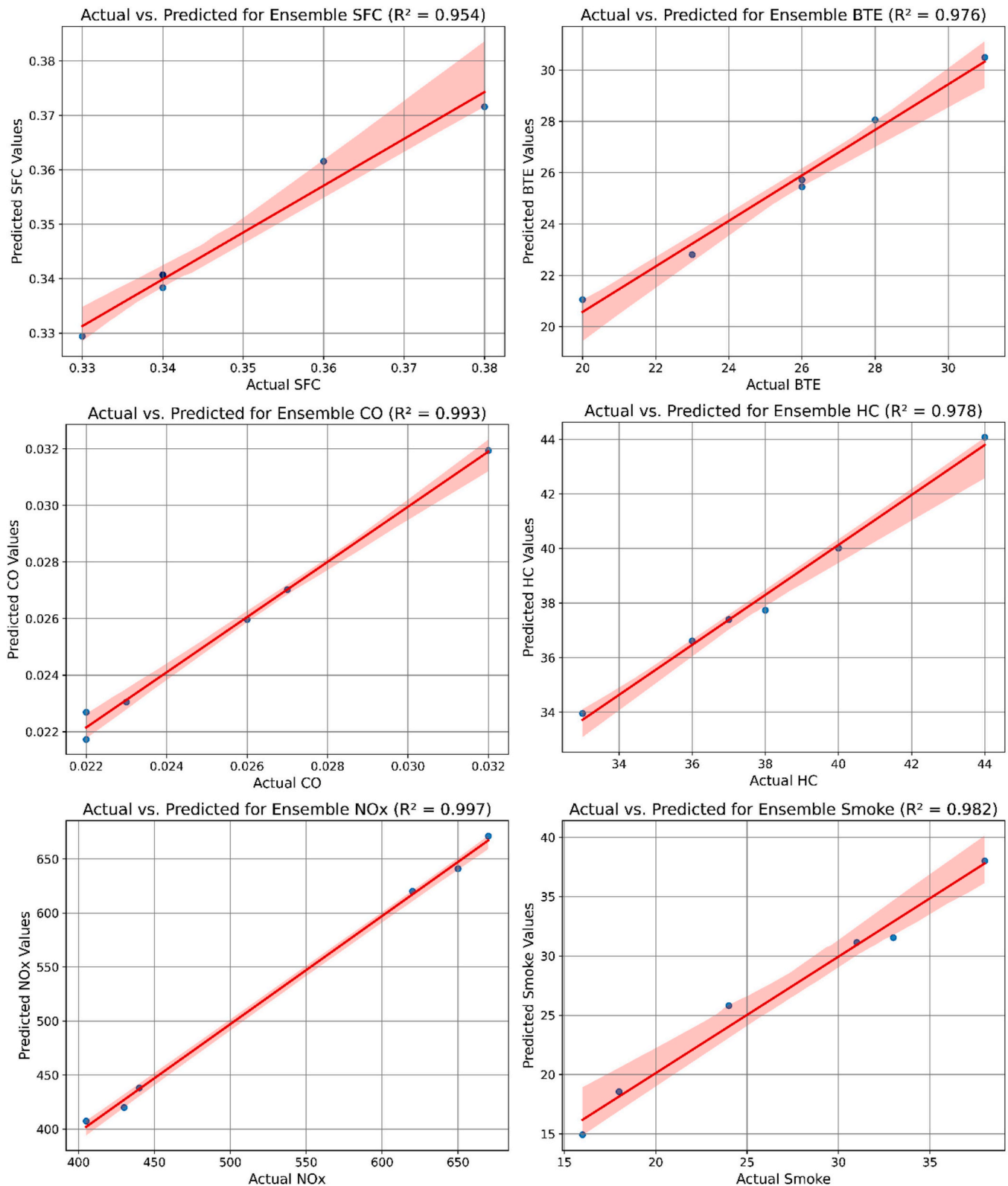


Fig. 14. Actual versus predicted plots for the ANN-XGBoost ensemble model, showing prediction agreement for SFC, BTE, CO, HC, NOx, and smoke emissions.

data set was divided into five folds, with the model trained on the other four folds and the held-out fold used for testing. This procedure allowed us to test the stability of the models across several data subdivisions.

Step 9: Visualization and Analysis of Results: Result visualizations were built for Actual vs. Predicted values and for trajectories for Training vs. Validation Loss. The Actual vs. Predicted plot showed a strong

correlation between the estimated and observed values, while the Training vs. Validation Loss plot indicated no overfitting. In addition, the cross-validation results provided further evidence of the model's robustness, with average R^2 values of 0.89, an MSE below 0.05, and an MAE of about 0.1.

Table 12

Five-fold cross-validation performance of the ANN-XGBoost stacking model. Values are reported as mean $\pm$ standard deviation across five validation folds.

Model/response	MAE	RMSE	R ²
SFC	0.0045 $\pm$ 0.0005	0.0054 $\pm$ 0.0007	0.8749 $\pm$ 0.0268
BTE	0.5474 $\pm$ 0.0615	0.6121 $\pm$ 0.0742	0.9393 $\pm$ 0.0186
CO	0.0003 $\pm$ 0.00004	0.0004 $\pm$ 0.00005	0.9907 $\pm$ 0.0042
HC	0.9525 $\pm$ 0.1187	1.0931 $\pm$ 0.1426	0.8759 $\pm$ 0.0294
NOx	4.4115 $\pm$ 0.5248	5.0870 $\pm$ 0.6135	0.9980 $\pm$ 0.0011
Smoke	0.9035 $\pm$ 0.1042	1.1497 $\pm$ 0.1368	0.9677 $\pm$ 0.0125

3.3.2.1. Ensemble model performance. The Training vs. Validation Loss plots (Fig. 13) for the ensemble model provide insight into the model's performance across multiple output variables. Concurrently, the validation RMSE decreases, albeit to a lesser extent, indicating satisfactory

performance on the training data and revealing some variance in the model's generalization to the validation set. Similarly, the plot of the combustion efficiency BTE indicates that the training RMSE decreases quickly but exhibits greater variation than for SFC.

The validation RMSE exhibits similar oscillations, suggesting that further improvement in the model's generalization is possible. For CO and HC, the validation RMSE is unstable and varies significantly across training runs, indicating that the model struggles to predict these emissions consistently. The NOx plot shows a dramatic reduction in the training RMSE; however, the validation RMSE exhibits substantial variation, indicating challenges with generalization. Finally, the smoke opacity plot shows high oscillations in both the training and validation RMSE values, indicating that although performance has improved over time, the model remains unstable in predicting smoke opacity. Collectively, these results indicate that although the ensemble model performs

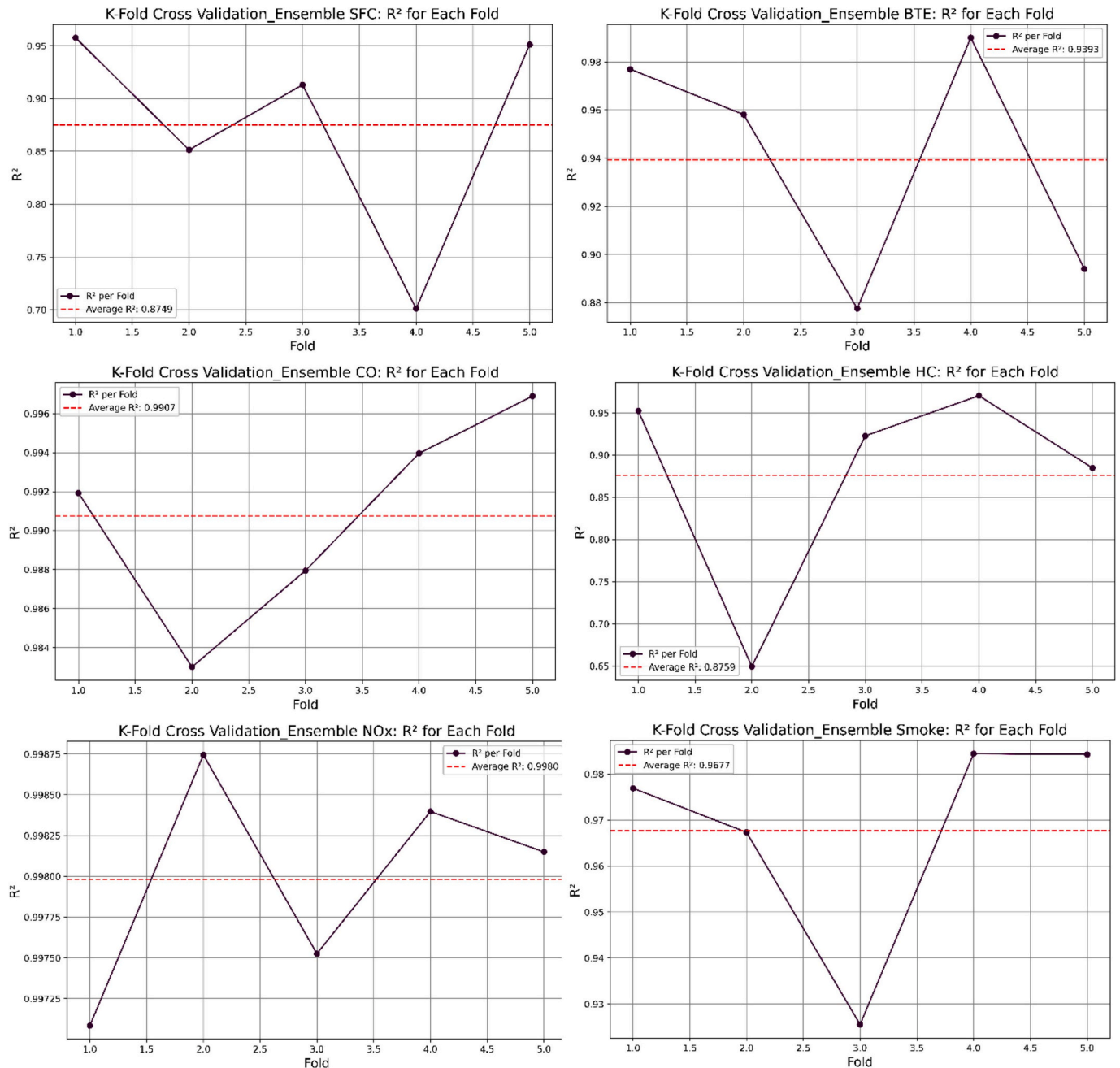


Fig. 15. Five-fold cross-validation R² scores of the ensemble model for SFC, BTE, CO, HC, NOx, and smoke, indicating prediction stability across different data partitions.

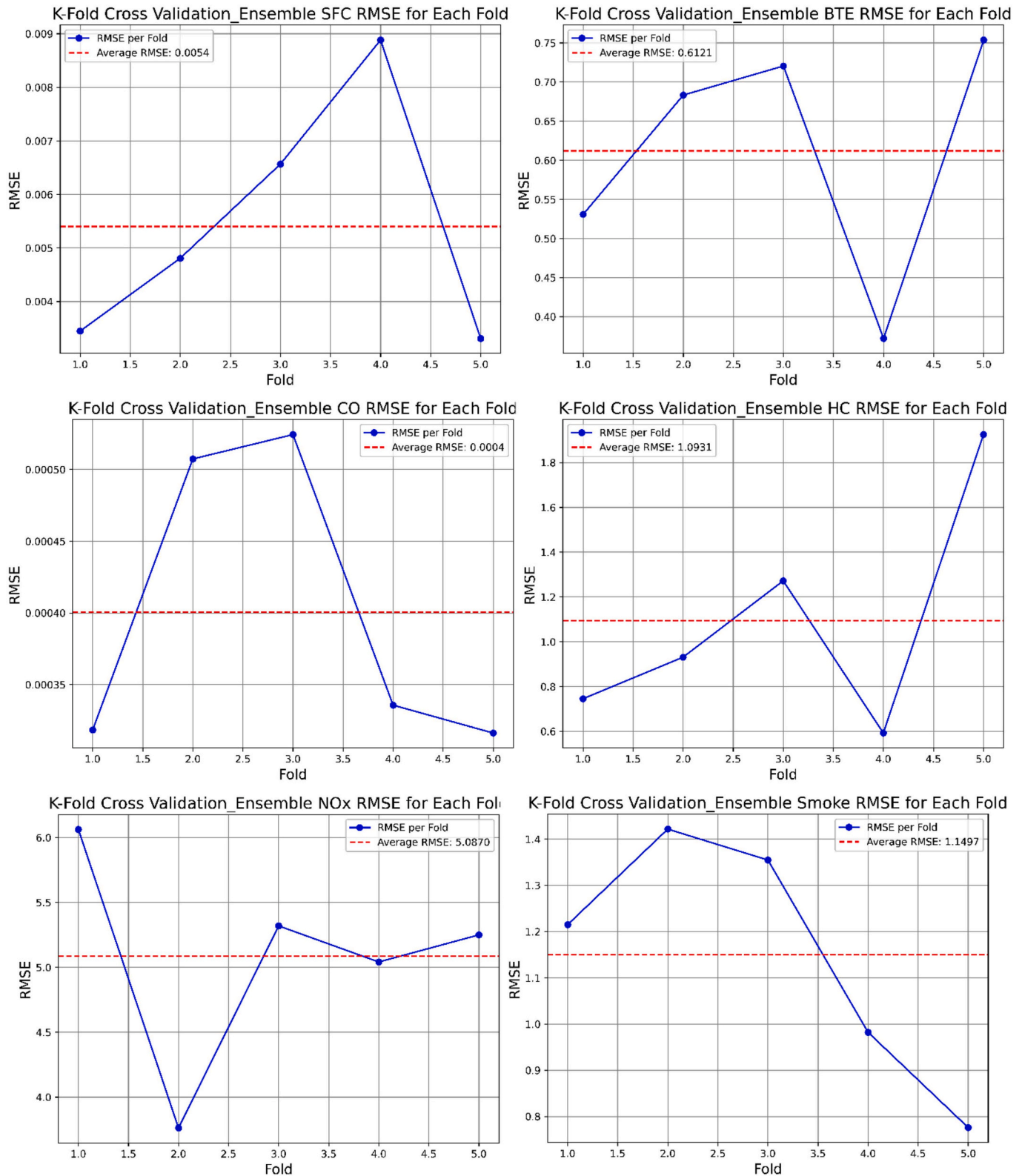


Fig. 16. Five-fold cross-validation RMSE values of the ensemble model for SFC, BTE, CO, HC, NOx, and smoke, showing prediction error variation among validation folds.

generally well, there is room to optimize it to achieve greater stability across all emission characteristics. The actual vs. predicted plots (Fig. 14) for the ensemble model demonstrate its ability to predict several engine performance and emission parameters. In each figure, a red regression line is compared with experimental actual values and the

ensemble model's predictions, thereby reflecting the model's predictive proficiency.

The R^2 scores for each plot measure the strength of the relationship between observed and predicted values. Regarding specific parameters, the SFC plot shows a strong linear relationship, with an R^2 of 0.954,

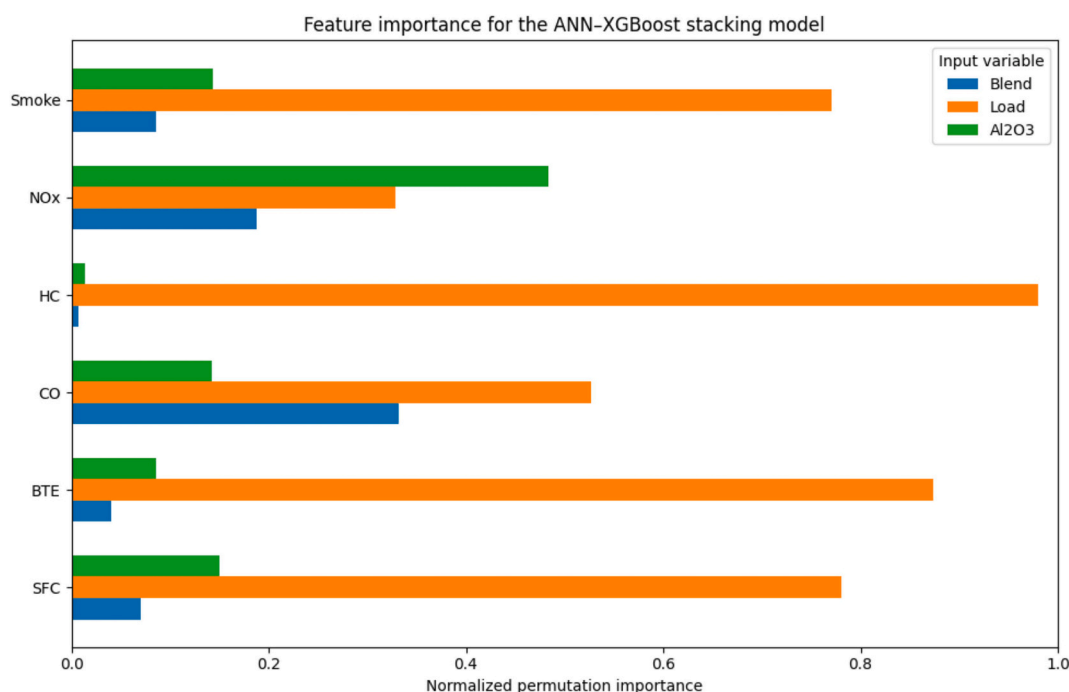


Fig. 17. Permutation-based feature importance of biodiesel blend ratio, engine load, and Al₂O₃ concentration for ANN-XGBoost predictions of SFC, BTE, CO, HC, NOx, and smoke.

indicating the model's accuracy in predicting fuel consumption across various engine operating conditions. Likewise, with BTE, the model achieves an R^2 of 0.976, indicating good agreement between predicted and actual values and therefore good performance in predicting thermal efficiency. The R^2 of 0.993 for the CO plot indicates that the model predicts carbon monoxide emissions with negligible error. For HC emissions, the plot shows an R^2 of 0.978, again showing a very good ability to predict. The NOx plot shows an R^2 of 0.997, the best observed for all variables tested, indicating that NOx emissions can be predicted almost perfectly. Lastly, the smoke opacity plot shows an R^2 of 0.982, indicating that the model has good predictive power for smoke opacity and, consequently, for overall emission forecasting. Viewed through the ensemble approach, these charts show that the ensemble consistently provides high R^2 values across all output variables, making it a reliable and accurate instrument for predicting engine performance and emissions.

3.3.2.2. Cross-validation of the ensemble model. Ensemble models were trained and evaluated using a five-fold cross-validation scheme (KFold) to improve robustness and reduce overfitting. The results of the cross-validation are shown in Table 12. Fig. 15 shows the R^2 coefficients for the ensemble model for the different output metrics SFC, BTE, CO, HC, NOx, and Smoke. Each panel shows the R^2 scores across all folds and the mean R^2 . For instance, the SFC model had an R^2 of 0.8749, while the CO and NOx models performed excellently, with R^2 values of 0.9907 and 0.9980, respectively, indicating better predictive accuracy for these emissions. Similarly, the BTE model's R^2 was 0.9393, indicating high predictive performance. HC emissions showed a slightly lower R^2 of 0.8759, suggesting room for improvement in HC prediction.

The RMSE of each fold is shown in Fig. 16, and a red dashed line shows the average RMSE. The low RMSE and high R^2 values indicate strong predictive agreement for CO and NOx within the tested experimental range, although the model's reliability outside this range requires further validation using a larger dataset. In contrast, HC emissions had a higher RMSE of 1.0931, indicating a more difficult task for accurate prediction. NOx exhibited a relatively high RMSE of 5.0870, indicating some difficulty in accurately predicting NOx emissions, even

though the R^2 value is high.

Table 12 summarizes the KFold cross-validation results, including MAE, RMSE, and R^2 for each model. The KFold cross-validation results, along with the associated R^2 , MAE, and RMSE, indicate that the ensemble model is highly effective in predicting engine performance and emission characteristics, particularly for CO and NOx. While the model performs well across most variables, there is still room for improvement in predicting more complex emissions such as HC and Smoke.

To enhance the interpretability of the ANN-XGBoost framework, a permutation-based feature-importance analysis was conducted in biodiesel blend ratio, engine load, and Al₂O₃ concentration (Fig. 17). The results indicated that engine load was the most dominant predictor of most responses with the normalized importance values of 0.7805 on BTE, 0.8742 on CO, 0.5267 on HC, 0.9800 on NOx, and 0.7705 on smoke. Conversely, the SFC value was most strongly affected by the concentration of Al₂O₃ (0.4838), then load (0.3289), and finally the percentage ratio of the blend (0.1873). The secondary but significant contribution was observed for the biodiesel blend ratio, especially for HC (0.3313) and SFC (0.1873). These findings suggest that the machine-learning model represented physically significant trends, and the ranking of the predictors was generally consistent with the experimental and RSM results, particularly the dominance of the load and the significant role of alumina in fuel-consumption behaviour.

3.3.2.3. Validation of experimental values with predicted values. To assess the ensemble machine learning model's performance, the model's predictions for a range of emission characteristics were compared with experimental measurements across multiple runs. The predicted values were obtained by plugging the experimental parameters into the trained ensemble machine-learning program in Python. These comparisons were visualized in Fig. 18 and summarized in Table 13, which reports the percentage error for each experimental configuration. The experiments chosen for validation include Exp 1, Exp 9, Exp 14, Exp 17, and Exp 27, along with the optimum values from the RSM optimization. The ensemble model's predicted values show strong concordance with experimental values across all parameters, indicating its efficacy in reproducing real-world engine behaviour. For example, both BTE and

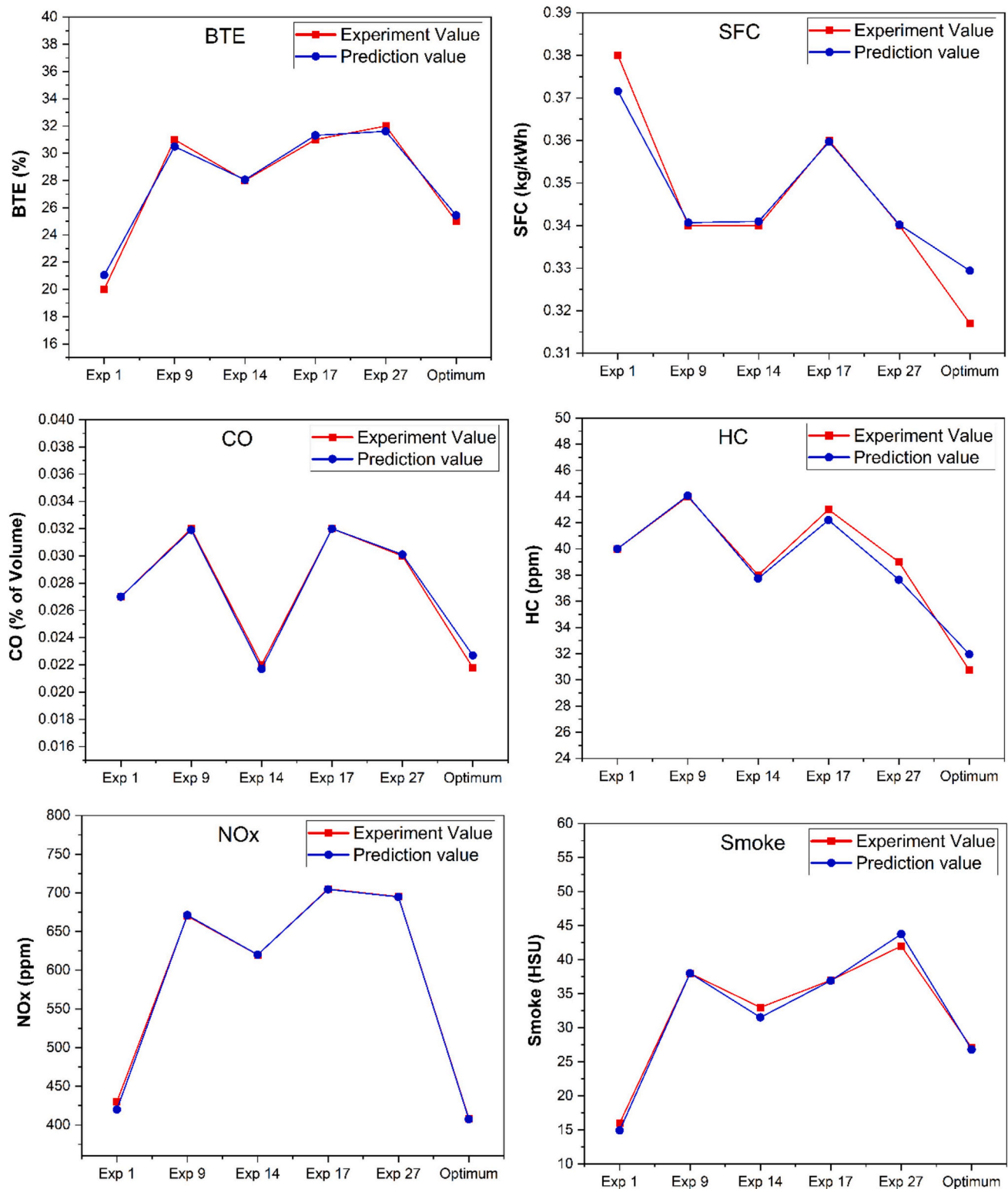


Fig. 18. Actual vs. Predicted Values for Various Parameters.

SFC show remarkably similar trends, highlighting the model's ability to accurately predict thermal efficiency and fuel consumption. Likewise, the predictions for CO, HC, NOx, and smoke are in close agreement with the experimental values, with small deviations observed only in some tests, particularly Exp 1 and Exp 9.

The percentage error between the experimental results and the values obtained from the ensemble model is shown in Table 13. For the

SFC metric, the error is small, with an average absolute error of -0.363 %, indicating good predictive reliability. Similar low errors are found for BTE and HC with mean absolute errors of -0.887 % and -0.464 %, respectively. Nonetheless, some experiments, i.e., Exp 9 and Exp 17, show a slight increase in error, particularly for NOx and smoke emissions, at 4.4115 % and 1.360 %, respectively. Despite these slight discrepancies, the model remains reliable overall; in Exp 1, the largest error

Table 13

Percentage of error for each experiment.

Exp No	Biodiesel Blend	Load %	Al ₂ O ₃ (ppm)	SFC (kg/kWh)	BTE (%)	CO (% of Volume)	HC (ppm)	NOx (ppm)	Smoke (HSU)
1	10	50	25	2.21	−5.25	0.00	−0.02	2.34	6.75
9	10	100	75	−0.21	1.65	0.31	−0.16	−0.17	−0.02
14	20	75	50	−0.29	−0.18	1.36	0.68	−0.02	4.45
17	20	100	50	0.08	−1.00	0.00	1.86	0.07	0.22
27	30	100	75	−0.06	1.22	−0.33	3.47	0.04	−4.21
Optimum	29.87	50	75	−3.91	−1.76	−4.13	−3.94	0.26	0.97
Average Absolute % of Error				−0.363	−0.887	−0.464	0.315	0.420	1.360

in NOx emission is 2.342 ppm relative to the control value. Consequently, the ensemble machine learning model has offered accurate predictions of engine performance and emissions under various experimental conditions. The good agreement between experimental and predicted results, along with low percent errors, verifies the model's validity in predicting real-world engine and emission behaviour, thereby optimizing the use of biodiesel-powered engines.

Despite the promising results, the present study has some limitations. Since the experimental dataset consisted only of Taguchi L27 runs for the three input variables, the developed ANN-XGBoost model can only be used for interpolation within the tested range and not for extrapolation to untested fuel blends, nanoparticle concentrations, or engine loads. The TBC durability assessment was conducted only over 100 h of engine operation, and longer-term endurance testing is needed to assess coating degradation, thermal-cycling damage, and long-term adhesion stability. The smoke opacity was higher in the optimized B30 + 75 ppm Al₂O₃ TBC condition, whereas BTE was higher and SFC was lower than the diesel baseline without TBC. CO, HC, and NOx were reduced in both the TBC conditions. Moreover, the present work did not include any advanced NOx-control technologies like EGR, injection-timing optimization or after-treatment systems. In general, the ANN-XGBoost stacking model corroborated the experimental and RSM results by effectively capturing the nonlinear relationships among the biodiesel blend ratio, engine load, and Al₂O₃ concentration, as well as the corresponding performance and emission responses. The model predicted trends of enhanced BTE, reduced SFC, and reduced CO and HC emissions for nanoparticle-assisted WSOME combustion, consistent with the experimental findings. The results from the feature importance analysis also indicated that engine load and Al₂O₃ concentration were the most significant factors, consistent with the RSM analysis. Thus, the developed ML model will serve as an additional tool to validate the optimized B30 + 75 ppm Al₂O₃ condition within the tested experimental range. The TBC durability assessment was conducted only over 100 h of engine operation, and longer-term endurance testing is needed to assess coating degradation, thermal-cycling damage, and long-term adhesion stability.

4. Conclusions

In the present study, the performance and emission characteristics of a TBC-assisted CI engine operating on WSOME–diesel blends containing different concentrations of Al₂O₃ nanoparticles were investigated. The results indicated that combining these three additives (WSOME biodiesel, Al₂O₃ nano-additive, and THC) increased combustion efficiency and affected emissions. Based on RSM optimization, the B30 operating condition, consisting of 75 ppm Al₂O₃ at 50 % engine load, was found to be optimal, with an overall desirability of 0.757. At this condition, the predicted responses were SFC of 0.317 kg/kWh, BTE of 25.063 %, CO of 0.0219 vol%, HC of 30.75 ppm, NOx of 408.46 ppm, and smoke opacity of 27.08 HSU.

The optimized B30 + 75 ppm Al₂O₃ TBC condition led to a 35.87 % increase in BTE and decreases in SFC, CO, HC, and NOx of 30.43 %, 54.17 %, 20.51 %, and 51.93 %, respectively, compared with the uncoated diesel baseline. However, smoke opacity increased by 21.74 %,

indicating that additional soot-control measures are needed. The improvement in BTE and decrease in gaseous emissions is primarily due to the biodiesel-bound oxygen, catalytic oxidation of Al₂O₃ nanoparticles, and the reduction of heat loss in the combustion chamber of TBC.

The results of the thin-film characterization and 100 h engine testing demonstrated acceptable structural integrity of the TBC layer, with no severe spallation or delamination. The experimental and RSM results were corroborated by the ANN-XGBoost stacking model, which captured the nonlinear relationships among the blend ratio, engine load, Al₂O₃ concentration, and engine responses within the investigated range. Unfortunately, however, given the small 27-run dataset, the model is only suitable for interpolating within the experimental domain. Future work should involve long-term TBC durability under prolonged engine operation, advanced NOx-control methods, larger experimental datasets to improve ML generalization, and real-time engine optimization based on ML for practical applications in biodiesel-fuelled CI engines.

CRediT authorship contribution statement

V.S. Shaisundaram: . **Saravanakumar Sengottaiyan:** Writing – review & editing, Validation, Software, Data curation. **D. Yogaraj:** . **Krishnamoorthy Natarajan:** Writing – original draft, Project administration.

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Generative artificial intelligence (AI)

During the preparation of this work, the author(s) used ChatGPT (version 5.2) exclusively for language refinement and grammar correction. No generative AI tools were employed in the development of scientific content, data interpretation, or any core research processes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

The ANOVA tables for all output models are provided in the supplementary file. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2026.140713>.

Data availability

Data will be made available on request.

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