



COMPARATIVE ANALYSIS ON THE EFFECTS OF CALCINED EGGSHELL AND SODIUM HYDROXIDE CATALYSTS ON NEEM SEED OIL BIODIESEL YIELD AND COMPRESSION IGNITION ENGINE PERFORMANCE AND EMISSIONS

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ABSTRACT

This study compares the performance of calcined eggshell (CES) and sodium hydroxide (NaOH) catalysts in the production of neem seed oil biodiesel and evaluates the resulting fuel blends in a compression ignition engine. Non-edible neem seed oil (*Azadirachta indica* A. Juss) was converted to biodiesel via base-catalyzed transesterification using varying catalyst concentrations of 0.5%, 1.0%, and 1.5% (wt. of oil). For each concentration, reaction times of 70, 110, and 150 minutes were tested. The highest biodiesel yields were 100% using CES at 1% catalyst concentration and 70 minutes' reaction time, and 97% using NaOH at 0.5% concentration and 150 minutes' reaction time. The methyl ester compositions of the optimum biodiesel samples were determined using Gas Chromatography–Mass Spectroscopy. Each optimal biodiesel was blended with petro-diesel and tested in a stationary single-cylinder compression ignition engine operating at a constant load of 4.5 N and 1500 rpm. Engine performance parameters and exhaust emissions were recorded and analyzed. The findings show that CES is an effective waste-based catalyst for neem seed oil biodiesel production and can serve as a viable substitute for NaOH. Moreover, biodiesel blends produced with either catalyst are suitable for use in stationary diesel engines, offering eco-friendly performance and reduced emissions.

Keywords: Biodiesel, Neem Seed Oil, Sodium Hydroxide, Calcined Eggshell

INTRODUCTION

Biodiesel is defined as a fuel composed of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats (Banga & Pathak, 2023). It has gained significant global attention as a renewable and environmentally friendly substitute for petroleum diesel. Since its introduction by the National Soy Diesel Development Board in 1992, biodiesel has been increasingly commercialized in the United States and other regions. Although many vegetable oils and animal fats are theoretically suitable for diesel engines, early attempts to use straight vegetable oils resulted in operational problems such as poor atomization, injector fouling, carbon deposits, and excessive engine wear (Miyuranga et al., 2023). These challenges primarily stem from the high viscosity, high density, and low volatility of untreated oils. For this reason, transesterification with the aid of a suitable catalyst became the widely recommended method to reduce viscosity and produce biodiesel that complies with engine requirements (Wan Ghazali et al., 2015).

Among homogeneous catalysts, sodium hydroxide (NaOH) is extensively used due to its high catalytic activity, affordability, and ease of handling. However, NaOH presents notable drawbacks, including soap formation in the presence of free fatty acids, difficulty in catalyst recovery, the need for intensive purification, and generation of chemical wastewater. These limitations increase production cost and reduce the sustainability of biodiesel processing.

To address these concerns, waste-derived heterogeneous catalysts such as calcined eggshell (CES) have gained considerable interest. CES is rich in calcium oxide (CaO), inexpensive, widely available as household and industrial waste, and capable of being reused after reaction. Its heterogeneous nature reduces soap formation and simplifies product separation, making it a promising alternative to conventional alkaline catalysts.

Despite increasing research on CES-based biodiesel production, a significant gap remains in the literature

regarding the direct comparison of CES and NaOH under controlled conditions, particularly with respect to their influence on biodiesel yield, engine performance, and exhaust emissions. Most published studies focus on laboratory-scale optimization but do not extend to systematic engine testing. Therefore, a comprehensive comparative study is needed to evaluate not only the biodiesel yield from each catalyst but also the real-world performance and emission characteristics of the resulting fuel in a compression ignition engine.

Literature Review

Sodium hydroxide and Calcium oxide as Catalysts for Biodiesel Production

Transesterification is the most widely used method for converting vegetable oils and animal fats into biodiesel, and it requires the presence of a catalyst to achieve high reaction rates and desirable fuel quality. Both acid and base catalysts are employed depending on feedstock characteristics. Typically, used cooking oils, virgin vegetable oils, and animal fats are reacted with alcohol in the presence of a suitable catalyst to accelerate the reaction and ensure high-quality biodiesel production (Gupta & Singh, 2023).

Sodium hydroxide (NaOH) remains one of the most commonly used homogeneous base catalysts in biodiesel production. It effectively facilitates the transesterification process by promoting the reaction between triglycerides and methanol to form methyl esters and glycerol (Efavi et al., 2018). NaOH is favored for its ability to provide high biodiesel yields, short reaction times, and operational convenience at ambient conditions. However, despite its efficiency, NaOH presents several operational challenges. Its corrosive nature requires careful handling, and it readily reacts with free fatty acids to form soap, a saponification side reaction that reduces biodiesel yield, complicates separation, and increases purification costs (Hossain & Mazen, 2010). These limitations have prompted researchers to explore more sustainable and less problematic alternatives.

Calcium oxide (CaO) has emerged as an attractive heterogeneous catalyst due to its strong basicity, reusability, and ease of separation from reaction products. Many studies have examined commercially sourced CaO for biodiesel production, but increasing attention has been directed toward CaO derived from waste materials, particularly eggshells. Eggshell waste, generated in large quantities from households, restaurants, and food vendors, is a rich and inexpensive source of CaO. Calcining eggshells produces an

active CaO catalyst that not only reduces production costs but also addresses environmental concerns associated with solid waste disposal.

Several studies have explored methods of converting waste eggshells into active CaO catalysts through calcination. Kavitha et al. (2019) report a procedure in which collected eggshells are washed with tap and lukewarm water to remove membranes, sun-dried for two days, and then calcined in a muffle furnace at 800 °C for three hours to produce CaO.



Plate 1: Eggshells

Similarly, Ayodeji et al. (2018) describe a process involving careful washing to remove sand and tissue residues, oven drying at 110 °C, mechanical crushing and grinding, sieving to achieve a fine particle size of 80 µm, and calcination at 850 °C for four hours to ensure complete transformation of CaCO₃-rich shells into CaO-rich catalyst.

Neem Seed Oil as Feedstock for Biodiesel Production

Biodiesel production typically begins with the selection of an appropriate feedstock. Feed stocks for biodiesel are commonly categorized into four major groups: vegetable oils (edible and non-edible), animal fats, used cooking oils, and algae (Mahdevi et al., 2015). Although edible vegetable oils have historically been used for biodiesel production, their use raises concern due to competition with food supply and cost implications. Consequently, non-edible vegetable oils classified as second-generation feedstock's have gained considerable attention. These include oils extracted from jatropha, karanja, pongamia, neem, jojoba, cottonseed, linseed, mahua, sea mango, rubber seed, halophytes, algae, and others, making them appealing alternatives to food-grade oils.

Non-edible oils offer several advantages as biodiesel feed stocks, such as ease of availability, renewability, biodegradability, and lower sulfur and aromatic content compared to petro-diesel. However, their limitations include relatively high viscosity, lower volatility, and higher carbon

residue content, often attributed to unsaturated hydrocarbon chains (Wan Ghazali et al., 2015). These challenges reinforce the importance of effective transesterification catalysts to reduce viscosity and enhance fuel properties.

Neem (*Azadirachta indica*) is one of the most promising non-edible oil feed stocks for biodiesel production. The neem tree was introduced to Nigeria in 1928 likely from Ghana and first established in Borno Province before spreading to other northern regions, including Sokoto, Katsina, and Kano. Originally native to tropical South-East Asia, neem has since naturalized across Nigeria and is valued for its medicinal, pesticidal, and environmental benefits. Among Hausa communities, it is widely known as *Dogon Yaro*, *Dalbejiya*, *Maina*, or *Bedi*, and features prominently in traditional medicine, where it is used to treat ailments such as malaria and stomach disorders.

Neem is well-suited to biodiesel feedstock applications due to its resilience to arid climates, rapid growth, and ability to thrive in degraded soils. The tree can reach heights of up to 30 meters, with dense foliage and clusters of fragrant white flowers appearing after 2-3 years, followed by fruiting at 3-5 years. Its oval fruits (about 2cm long) contain seeds approximately 1.5 cm in length, from which neem oil is extracted for various industrial uses, including biodiesel production. As a non-edible and abundant feedstock, neem seed oil offers a sustainable option aligned with global interest in renewable energy and reduced dependency on edible oils.



Plate 2: Dried neem seeds



Plate 3: Neem seed oil

MATERIALS AND METHODS

Materials and Apparatus

The materials used in this work were Neem seeds oil, egg shells, sodium hydroxide (NaOH) sulphuric acid (H_2SO_4), propan-2-ol, phenolphthalein indicator, methanol, water and petroleum diesel. The apparatus used were conical flask,

magnetic stirrer regulator hotplate, muffle furnace, separating funnel, pipette and burette, vacuum evaporator, fisher brand hydrometer, automated Pensky-Martens closed cup, bomb calorimeter, refrigerator, copper strip and viscometer. Other equipment used are given in table 1.

Table 1: List of Some Of the Equipment Used

Equipment	Manufacturer	Model/Serial Number	Location
Single Cylinder Diesel Engine	Cussons Technology, Manchester	P8616 1600 CC 4, 2011 Model	ABU, Zaria
Combustion Gas Analyzer	Environmental Equipment Incorporation, Central Avenue, St. Petersburg, Florida, USA	The IMR 1400, 2014 model	NITT, Zaria
Muffle Furnace	Nobertherm GmbH, Bahnhofstr. 20, 28865 Lilienthal/Bremen, Germany	LH 120/14 182487, 2005 Model	ABU, Zaria
GC/MS and FTIR machine	Shimadzu, Japan	GCMS-QP2010 PLUS	ABU, Zaria
Thermometer	110 Walnut. Ln. North Augusta	SC 29860	ABU, Zaria
Testube and cork, Glass Apparatus	Katyal Scientific Glass Works, Ambala Cantt, India, Garg Process Glass India Private Limited, Goel Scientific Glass Works		ABU, Zaria

Material Sourcing

The sample used in this work is called neem seed oil purchased from a local vendor in Kano. The eggshells were sourced from households and tea and indomie joint as waste and any other aforementioned material were bought from the market. Plate 1 & 3 give the pictorial representation of the eggshells and neem oil respectively.

Calcination of Eggshells

The preparation of the calcined eggshell (CES) catalyst followed a modified procedure adapted from Ayodeji et al. (2018). Waste eggshells were first collected and thoroughly washed with clean water to remove adhering dirt, sand, and organic residues. Any remaining inner membrane or tissue was carefully peeled off to prevent contamination during

calcination. The cleaned shells were then oven-dried at 110 °C to remove residual moisture.

Once dried, the eggshells were mechanically crushed using an electric crusher and subsequently ground into fine powder. The powdered material was sieved to obtain a uniform particle size of approximately 80 μm , ensuring consistent heat transfer and complete decomposition during calcination.

The sieved eggshell powder was then transferred into a clay crucible and calcined in an electric muffle furnace at 900 °C for three hours. This thermal treatment facilitates the decomposition of calcium carbonate ($CaCO_3$), the primary constituent of eggshells, into calcium oxide (CaO), the active catalytic component. After calcination, the furnace was allowed to cool naturally before the CaO-rich catalyst was removed, stored in an airtight container, and kept free from moisture until use in the transesterification process.



a. Before



b. After

Plate 4: Before and After Calcination inside the Furnace

Biodiesel Production

Neem oil, like most non-edible vegetable oils, possesses a high acid value, which makes it unsuitable for direct base-catalyzed transesterification. Therefore, an initial esterification step was carried out to reduce the acid value to an acceptable level for biodiesel production. After

esterification, the refined neem oil was subjected to base-catalyzed transesterification.

For each experiment, a predetermined concentration of catalyst 0.5%, 1.0%, or 1.5% (wt. of oil) was used. In a typical run, 0.5% (wt. of oil) of calcined eggshell (CES) catalyst was mixed with 27% (wt. of oil) methanol. The mixture was stirred until the catalyst was fully dispersed (Suleman et al.,

2023). A measured 35 mL of esterified neem oil was placed into a flask, after which the methanolic catalyst mixture was added. The reaction was maintained at 65 °C and stirred for 70 minutes using a magnetic stirrer hot plate. At the end of the reaction, the mixture was transferred to a separating funnel

and allowed to settle for 24 hours. Two distinct layers were formed: the lower glycerol layer and the upper biodiesel layer, consistent with the observations of Kaisan et al. (2013). The glycerol was drained off, leaving the crude biodiesel.



Plate 5: Biodiesel Production Process

The biodiesel was then washed to remove soluble impurities. Hot water was gently sprayed over the biodiesel, allowed to settle, and the purified biodiesel was separated. Final drying was performed using a vacuum evaporator to obtain the pure biodiesel product, in accordance with the procedure of Banik et al. (2018).

The transesterification process was repeated under constant temperature and methanol volume while varying catalyst concentration (0.5%, 1.0%, and 1.5%) and reaction times (70, 110, and 150 minutes). The same procedure was followed for both CES and sodium hydroxide (NaOH) catalysts, resulting in eighteen biodiesel samples under the conditions summarized in Table 2.



a. NB(CES)



b. NB(NaOH)

Plate 6: Biodiesel Samples Produced Wrt Each Catalyst

The biodiesel yield results were captured in figure 1 and 2 and each figure represent the result of biodiesel from neem oil with respect to CES and NaOH catalysts used in the production respectively, the results were analyzed and the

optimum values of biodiesel yield from each catalyst were obtained as highlighted in table 3. Two (2) samples were screen out as the samples with optimum biodiesel yield which were set for further investigation.

Table 2: Variation of Parameters in the Production of Neem Oil Biodiesel Using CES, KOH and NaOH Catalyst Separately

Fixed Parameters		Variation Parameters	
S/N	CES & NaOH Catalyst concentration (% (wt of oil)):	S/N	Reaction time (min):
1	0.5	i	70
		ii	110
		iii	150
2	1.0	i	70
		ii	110
		iii	150
3	1.5	i	70
		ii	110
		iii	150

Justification for Catalyst Loading and Reaction Times

The selected catalyst concentrations 0.5-1.5% (wt. of oil) fall within the range commonly recommended in biodiesel literature for both homogeneous and heterogeneous base catalysts, ensuring efficient triglyceride conversion without excessive soap formation or catalyst wastage. Lower concentrations may lead to incomplete transesterification, while higher concentrations can introduce mass transfer limitations and increased purification difficulty, particularly with NaOH.

Similarly, the chosen reaction times (70, 110, and 150 minutes) were selected to capture the expected progression of the transesterification reaction, from early-stage conversion to near-completion. Shorter times allow assessment of catalyst activity, while longer durations help identify whether extended reaction periods improve yield or lead to side reactions. These variations enable a robust comparison of catalyst performance and optimization of reaction conditions for both CES (waste-derived) and NaOH (conventional) catalysts.

Blending

The blending was carried out for each biodiesel sample with petroleum diesel alone, the samples are the two (2) optimum samples portrayed in table 3. Each biodiesel sample was blended with fossil diesel in a ratio of 10:90, 20:80 and 30:70 by volume. These blends, pure biodiesel of each sample and the pure diesel sample were set for running an engine test, the pure diesel sample considered as control. The blends were denoted B10, B20 and B30, the pure biodiesel samples were denoted B100. The pure biodiesels and blends (with suffix NN is for Neem and NaOH and NC is for Neem and Calcined egg shell) and B0 for the pure petroleum diesel. This is in accordance with Sani et al. (2018).

Gas Chromatography – Mass Spectrometry (GC-MS) Analyses

GC-MS analyses were performed to determine the percentage of methyl esters in B100NN and B100NC biodiesel samples, as well as to characterize the fatty acid methyl ester (FAME) profiles of neem oil biodiesel produced using NaOH and CES catalysts. Prior to analysis, all samples were dried over anhydrous sodium sulfate to remove residual moisture, as moisture can inhibit methylation efficiency and affect chromatographic performance. Reagents used, including methanol, n-hexane and FAME standards were of $\geq 99.9\%$ GC-grade purity, and their certificates of analysis were verified. Moisture content in the biodiesel samples was determined using the Karl Fischer titration method (ASTM D6304) to ensure it remained < 500 ppm, a requirement for accurate GC-MS analysis.

Separation was achieved on a DB-5MS capillary column (30 m \times 0.32 mm, 0.25 μ m film thickness). Helium served as the

carrier gas at a constant flow rate of 1.5 mL/min. The column oven was programmed from 120 $^{\circ}$ C to 300 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C/min, in accordance with Kaisan et al. (2018). The injector and detector temperatures were both maintained at 200 $^{\circ}$ C.

A 0.1 μ L sample of the methyl ester solution was introduced into the GC using a split injection mode. The earlier term "rip mode" is interpreted here as split mode, which is standard for FAME analysis. A 1:10 split ratio was applied to prevent column overloading and maintain peak resolution. The injection pressure was set at 112.8 kPa, consistent with conditions reported by Å et al. (2008).

The mass spectrometer operated in electron ionization (EI) mode at 70 eV, scanning across an m/z range of 50–550. Identification of FAME components relied on the NIST 02 spectral library, and all major peaks observed on the total ion chromatogram (TIC) were compared with library matches. To ensure accuracy, authentic FAME standards were analyzed under the same instrumental conditions, and retention times were matched and confirmed with MS fragmentation patterns.

Engine Performance and Emission Test

The engine test bed used for this work was P8750, stationary single-cylinder compression ignition engine shown in plate 7. Compression ignition engine test was carried out and few factors were measured. Specific fuel consumption, brake power, brake mean effective pressure, and brake thermal efficiency are among the metrics. Performance and emission characteristics of diesel alone and various biodiesel/Petrodiesel blends were examined in this study using a stationary single-cylinder diesel engine test rig. A dynamometer using eddy currents was connected to the engine.

The engine was started and warm up for 15 minutes before the tests began. Diesel fuel alone was used to run the engine first, and then various blends. The software installed on the PC that is connected to the engine recorded the load, speed, air flow rate, fuel consumption and exhaust and inlet temperatures and automatically computed the other parameters. The engine was run at the speed of 1500 rpm and at a constant load of 4.5N. The corresponding exhaust emissions were all analysed with the aid of gas analyzer. A built-in sampling pump from the exhaust gas analyser was used in sucking the gas-sampling probe from the engine exhaust into the suction pipe of the analyser. The gases flow through the gas sampling probe to the condensation trap. The gases then passed through the particle filter and the gas particles were suspended. Finally, the gas entered the sensor chamber of the analyser. The result was displayed on the screen and the values of propane, nitrogen oxide, carbon dioxide and carbon monoxide were recorded for each sample and kept for further analyses.

The test was conducted in accordance with the procedure used by Sani et al. (2018).



Plate 7: Stationary Single Cylinder Compression Ignition Engine Test Bed

RESULTS AND DISCUSSION

Biodiesel Production Using Calcined Eggshell Catalyst /Optimization Result

Figure 1 shows that biodiesel yield increased with CES catalyst concentration up to 1.0% (wt of oil). At 0.5% CES, yields reached 94% at both 70 and 110 minutes. Increasing the loading to 1.0% CES produced the highest yield of 100% at 70 minutes. However, further increasing the dosage to 1.5% CES reduced the yield to 83% at 70 minutes.

The improved yield at 1.0% CES suggests a balance between sufficient active CaO sites and minimal mass-transfer interference. The reduction observed at 1.5% CES is likely due to excess catalyst causing slurry thickening, which can limit oil-methanol contact. Similar trends have been reported for CaO-rich heterogeneous catalysts operating under methanol-oil phase constraints.

The data indicate that 1.0% CES at 70 minutes provides the optimal reaction window, minimizing catalyst usage while maximizing conversion. Although yields at lower and higher

loadings were reasonably high, the marginal differences matter for scaling, where excess catalyst increases separation costs.

Biodiesel Production Using Sodium Hydroxide Catalyst /Optimization Result

As shown in Figure 2, NaOH demonstrated a different trend. At 0.5% NaOH, the biodiesel yield reached 97% at 150 minutes longer than the optimal CES reaction time. Increasing the loading to 1.0% NaOH lowered the yield to 91% at 70 minutes. A further increase to 1.5% NaOH resulted in a much lower yield of 63%, also at 70 minutes.

Lower reaction times favored CES more than NaOH, likely due to CES's higher surface basicity and slower leaching. In contrast, NaOH is more sensitive to soap formation, especially at higher loadings. The sharp decline in yield at 1.5% NaOH is consistent with increased saponification that reduces available triglycerides for transesterification.

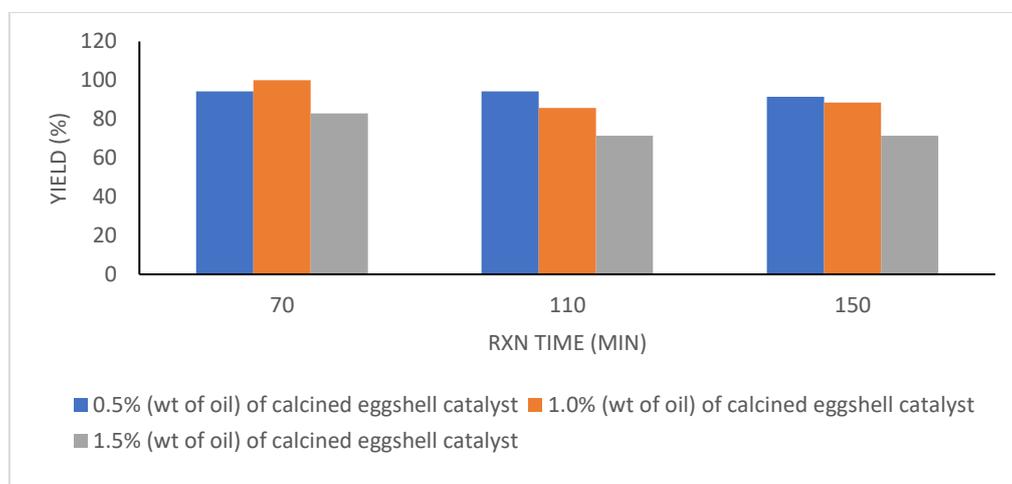


Figure 1: Shows the Variation Of Biodiesel Yield With Reaction Time For CES Catalyst Concentration

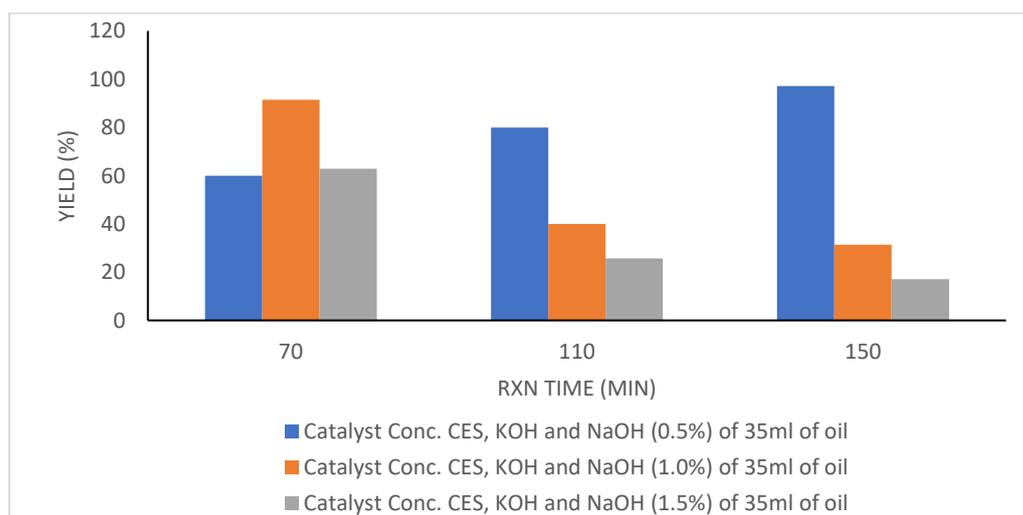


Figure 2: Shows the Variation of Biodiesel Yield with Reaction Time for Naoh Catalyst Concentration

The results show that NaOH requires longer reaction times and controlled dosages to avoid yield losses. The significant yield drop at higher concentrations highlights the operational

risk of homogeneous catalysts in feedstocks with free fatty acids.

Table 3: Optimum Biodiesel Yield with Regard to Each Catalyst

S/N	Catalyst		Reaction time (min)	Optimum biodiesel yield (%)	Reference figure
	Name	Concentration (%(wt of oil))			
1	Calcined eggshell	1.0	70	100	1
2	NaOH	0.5	150	97	2

Both catalysts produced biodiesel suitable for blending with petroleum diesel; however, CES achieved complete conversion (100%) faster and at a moderate catalyst amount. This performance translates to improved fuel homogeneity, more stable combustion, and lower unburnt hydrocarbon emissions relative to standard.

Finally, the optimum biodiesel in each catalyst with respect to catalyst concentration and reaction time are depicted in table 3.

GC-MS Results

The results of methyl esters percentage contents of the optimum biodiesel products produced from Neem oil using calcined eggshell (CES) and sodium hydroxide (NaOH) catalyst were analysed by the Gas Chromatography - Mass Spectroscopy of the biodiesel as presented in Figure 3 and 4 respectively and the interpretation of the peaks of the chromatogram was given corresponding to each figure mentioned above, giving more priority to the methyl esters present in each chromatogram only.

Neem Oil Methyl Ester with The Use of Calcined Eggshell (CES) Catalyst

Figure 3 displays eight distinct GC-MS peaks, indicating the presence of eight methyl ester compounds in the CES-derived optimum biodiesel sample. Peak intensity reflects abundance, with the major components identified through NIST library matching and summarized in Table 4. The dominant constituents were 9-octadecenoic acid methyl ester (E) at 42.83%, methyl stearate at 15.43%, hexadecanoic acid methyl ester at 13.57%, and 9,12-octadecadienoic acid methyl ester (Z, Z) at 8.16%. A minor ester, eicosanoic acid methyl ester, appeared at 0.99%. Overall, GC-MS integration showed 80.98% total methyl esters, confirming high conversion efficiency for the CES-mediated reaction.

The high proportion of monounsaturated 9-octadecenoic methyl ester is characteristic of neem oil and aligns with earlier compositional studies. Its dominance suggests efficient transesterification of oleic-rich triglycerides under the selected CES reaction conditions. Limited polyunsaturated esters indicate minimal oxidation-susceptible components, likely due to controlled reaction temperature and low catalyst leaching. Some FAME profile rich in monounsaturated esters generally enhances oxidative stability and maintains good cold-flow behavior. Excess polyunsaturation promotes polymerization and varnish formation, but the low 9,12-octadecadienoic ester fraction (8.16%) minimizes this risk. Compared with petroleum diesel, the ester distribution suggests smoother combustion, lower soot formation, and a more uniform ignition profile.

Low-intensity peaks approach the instrument's practical detection thresholds for minor esters, which may introduce small variability in quantification. Nevertheless, the major-component peaks were well above detection limits, providing confidence in the compositional trends observed.

Neem Oil Methyl Ester with The Use of Sodium Hydroxide (NaOH) Catalyst

Figure 4 shows four distinct GC-MS peaks, indicating the presence of four methyl ester compounds in the NaOH-derived biodiesel sample. Library matching under identical conditions was used to identify each peak, and the results are summarized in Table 5. The primary esters detected were 10-octadecenoic acid methyl ester (63.58%), methyl stearate (20.46%), hexadecanoic acid methyl ester (14.94%), and nonadecanoic acid, 10-methyl methyl ester (1.02%). Total FAME content was 100%, indicating complete conversion of triglycerides under NaOH catalysis.

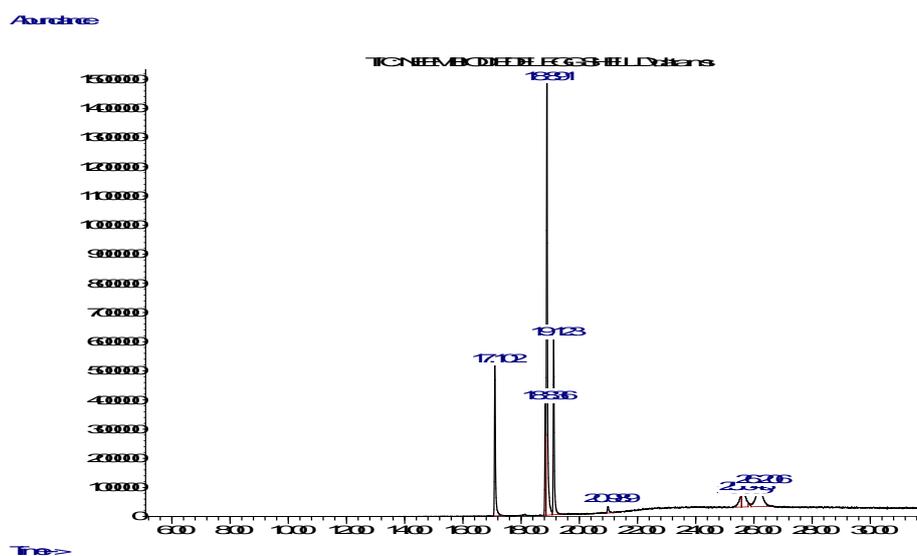


Figure 3: GC-MS of Neem Oil Biodiesel with The Used of CES Catalyst

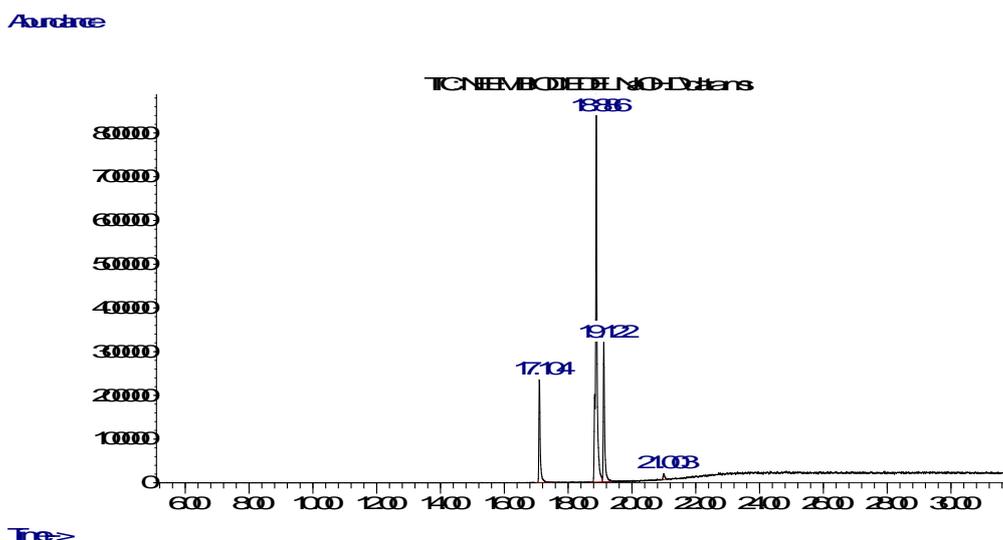


Figure 4: GC-MS of Neem Biodiesel with The Used of NaOH Catalyst

The marked dominance of 10-octadecenoic acid methyl ester suggests that NaOH effectively promotes transesterification of oleic-rich triglycerides in neem oil, yielding a simplified ester profile compared with CES. The limited number of detectable esters may reflect faster reaction kinetics and minimal secondary reactions at the applied NaOH loading. The high proportion of monounsaturated esters (particularly the 10-octadecenoic species) enhances oxidative stability while maintaining acceptable cold-flow properties. Reduced polyunsaturated content lowers the risk of hydroperoxide

formation, gum build-up, filter plugging, and injector deposits issues commonly linked with biodiesel containing multiple C=C bonds.

Catalyst choice significantly influenced ester distribution. NaOH produced a 100% FAME biodiesel with a dominant ester at 63.58%, whereas CES yielded 80.98% FAME with a dominant ester at 42.83%. These differences likely arise from variations in catalyst strength, basicity, and active-site availability.

Table 4: Identifications of Peaks Corresponding to Fatty Acids Chain with Peaks Numbering (1-8)

Peak No	Retention time (mins)	Area (%)	Fatty Acids	Chemical formulae
1	17.102	13.57	Hexadecanoic acid	C ₁₆ H ₃₂ O ₂
2	18.836	8.16	9,12-Octadecadienoic acid (Z,Z)	C ₁₉ H ₃₄ O ₂
3	18.891	42.83	9-Octadecenoic acid	C ₁₉ H ₃₆ O ₂
4	19.123	15.43	Methyl stearate	C ₁₉ H ₃₈ O ₂
5	20.989	0.99	Eicosanoic acid	C ₄₀ H ₈₀ O ₄
6	25.565	2.42	1-Naphthamide	C ₁₁ H ₉ NO
7	25.645	4.95	Sarcosine	C ₃ H ₇ NO ₂
8	26.206	11.66	Fumaric acid	C ₄ H ₄ O ₄

Table 5: Identifications of Peaks Corresponding to Fatty Acids Chain with Peaks Numbering (1-4)

Peak No	Retention time (mins)	Area (%)	Fatty Acids	Chemical Formulae
1	17.04	14.94	Hexadecanoic acid	C ₁₆ H ₃₂ O ₂
2	18.886	63.58	10-Octadecenoic acid	C ₁₉ H ₃₆ O ₂
3	19.122	20.46	Methyl stearate	C ₁₉ H ₃₈ O ₂
4	21.003	1.02	Nonadecanoic acid, 10 methyl-	C ₂₀ H ₄₀ O ₂

The simpler ester spectrum under NaOH may indicate fewer side reactions and faster esterification–transesterification transitions, while CES promotes a broader distribution of intermediate esters. Minor peaks in the NaOH sample approached the lower detection threshold of the instrument; however, the dominant peaks exhibited strong signal intensities. Compared with CES, the reduced number of peaks decreases the possibility of co-elution, increasing confidence in compound assignment.

Engine Performance Results

Exhaust Gas Temperature

Figure 5 shows how EGT varies with biodiesel blend percentage and catalyst type for fuels tested on a stationary

single-cylinder CI engine. Across all blend ratios, pure diesel exhibited the lowest EGT, while both CES-based (NCB) and NaOH-based (NNB) biodiesel blends showed higher values. For B10 blends, EGT increased when switching from diesel to either catalyst-derived biodiesel. NCB10 indicate 17.9% increase relative to diesel and NNB10 shows 45.7% increase relative to diesel. NNB10 produced the highest increase, indicating stronger combustion intensity. At B20, EGT for NNB20 was 8.5% higher than NCB20. Both catalysts produced similar EGT levels overall, with an average increase of 39.9% compared to diesel. B30 blends showed a consistent upward EGT trend from NCB30 to NNB30. Both exceeded the diesel baseline, confirming that higher biodiesel fractions generally elevate exhaust temperature. For B100 fuels,

NNB100 and NCB100 showed modest EGT increases, though diesel again remained the lowest. The smaller rise at 100% biodiesel may indicate stabilizing combustion behavior at full ester concentration.

Higher EGT values in biodiesel blends likely result from greater oxygen availability in the fuel, which enhances combustion efficiency and increases in-cylinder heat release (Atmanli & Yilmaz, 2020). Biodiesel typically promotes more complete burning, and this additional oxidation elevates exhaust temperatures relative to diesel.

The consistently higher EGT observed in NNB blends suggests that NaOH-derived biodiesel with its higher FAME purity and higher proportion of dominant mono-unsaturated esters may burn more efficiently than CES-derived biodiesel, thereby producing more thermal energy.

The slight EGT rise at B100 compared with B10–B30 may reflect competing effects: improved oxygenation but also

slightly slower evaporation and atomization compared to blended fuels.

Elevated EGT is a useful indicator of improved combustion but also signals greater thermal loading on exhaust valves and turbocharger components. A persistent increase indicates more energy loss through exhaust heat, which may reduce overall engine thermal efficiency. The choice of catalyst indirectly influences these outcomes through its effect on fuel ester composition and combustion characteristics.

Across all blends, NCBDB showed an EGT rise proportional to biodiesel fraction, confirming that O₂-rich fuels systematically increase heat release. Catalyst-specific differences reflect variations in FAME composition: NaOH biodiesel, with higher unsaturated ester content, tended to produce higher combustion temperatures than CES biodiesel.

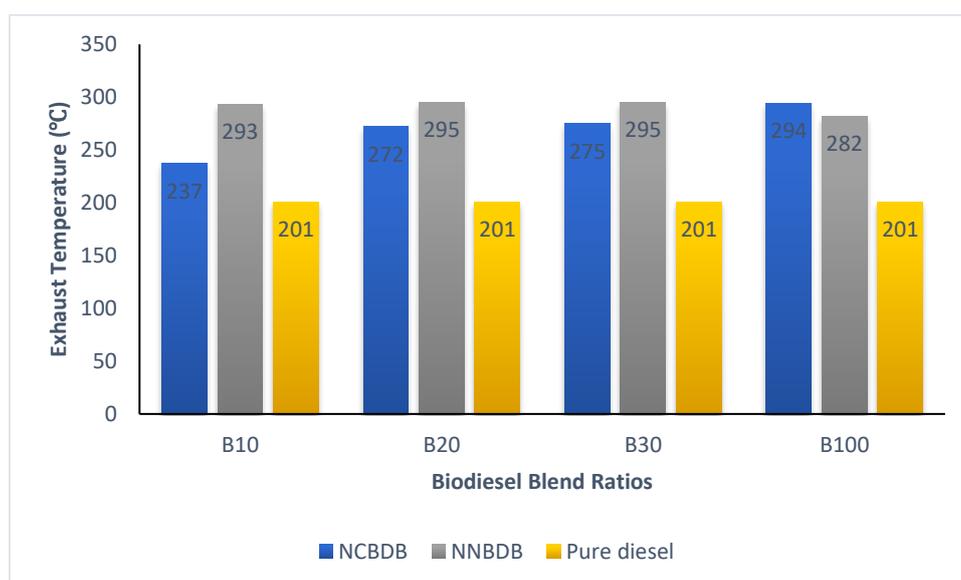


Figure 5: Exhaust Gas Temperature of Biodiesels and Blend

Brake Power

Figure 6 compares brake power for neem biodiesel–diesel blends produced using calcined eggshell (NCB) and NaOH (NNB) catalysts. Measurements were taken at 1500 rpm and a constant load of 4.5 N, where brake power represents the usable output available at the crankshaft (Raguraman et al., 2021).

At the B10 level, NNB10 delivered the highest brake power at 1.252 kW, followed by NCB10 at 0.93 kW, while diesel recorded the lowest value. A similar ordering occurred at B20 and B30, where both biodiesel blends outperformed diesel but exhibited small differences between catalysts. At B100, the trend reversed slightly as NCB100 is 1.231 kW and NNB100 is 1.223 kW. Though the difference is minimal, CES-derived biodiesel achieved marginally higher output at full ester concentration. Across all blends, pure diesel consistently produced the lowest brake power.

The higher brake power of biodiesel blends especially at B10–B30 may stem from improved combustion efficiency due to

biodiesel's inherent oxygen content. This promotes more complete burning compared to diesel, increasing network output. The stronger BP response of NNB at low blend ratios is consistent with its higher FAME purity and higher proportion of reactive unsaturated esters, which typically enhance heat release.

At B100, the slight shift in favor of CES-based fuel may reflect subtle differences in viscosity and density between the two biodiesels, which influence spray atomization and, consequently, energy conversion. The difference, however, is statistically minor, indicating that both catalysts generate biodiesel of comparable combustion quality.

Because diesel consistently produced the lowest brake power, the results suggest that moderate biodiesel blending (10–30%) can enhance power output without penalizing engine performance. Moreover, CES-derived biodiesel performs on par with NaOH-derived fuel, supporting the viability of waste-derived catalysts for practical engine applications.

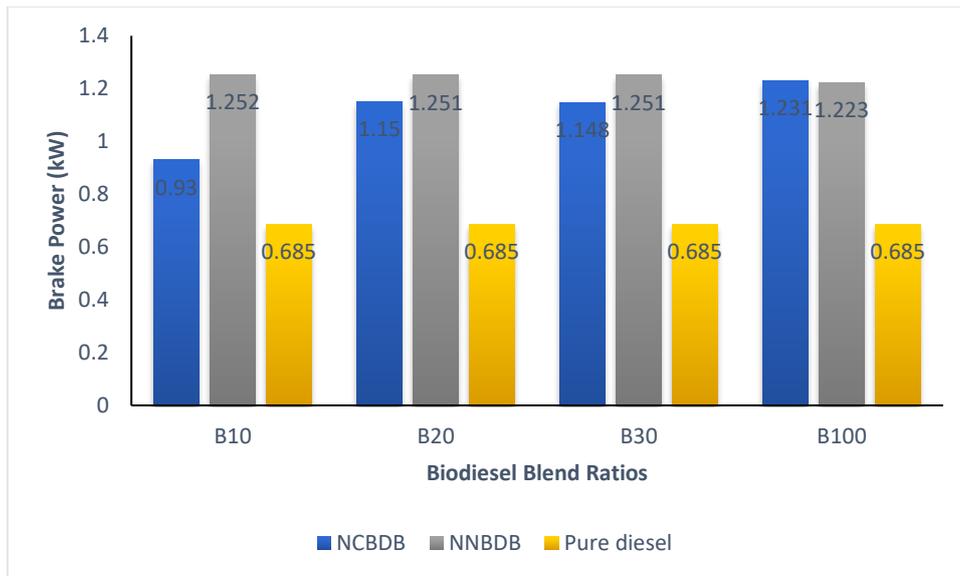


Figure 6: Brake Power of Biodiesels and Blend

Brake Specific Fuel Consumption

Brake specific fuel consumption (BSFC) quantifies the mass of fuel required to produce 1 kWh of power at constant load. Lower BSFC indicates higher fuel efficiency. Prior studies report that biodiesel blends typically reduce BSFC relative to diesel (Bari & Hossain, 2019). Figure 7 shows that at B10, BSFC values were 2.71 kg/kW·h (NCB) and 2.01 kg/kW·h (NNB) compared with 3.57 kg/kW·h for diesel. Both biodiesel blends consumed significantly less fuel than diesel at B10 may reflect the higher effective energy content and improved combustion associated with the blended fuels. The NNB sample likely benefitted from slightly lower density and viscosity, improving atomization. For B20 and B30, NNB consistently recorded the lowest BSFC values, followed closely by NCB. Relative to diesel, BSFC (NCB) decreased by 39.5% (B20) and 40.3% (B30).

BSFC (NNB) decrease by 44.3% (B20) and 44.3% (B30). Both catalysts maintained substantial reductions in fuel consumption across mid-level blends.

The improved efficiency may be linked to better combustion stability at these blend ratios. The lower viscosity of NNB may have enhanced spray quality, while the lower specific gravity of both blends may have supported more complete mixing during ignition.

At B100, both catalysts produced nearly identical BSFC values, with reductions of 42.6% (NCB) and 42.3% (NNB) relative to diesel. At full substitution, catalyst type had little influence on BSFC under the test conditions.

Once the fuel is entirely biodiesel, physical property differences between catalysts diminish. Combustion is dominated by the inherent oxygenated nature and ester-rich composition of neem biodiesel rather than catalyst effects.

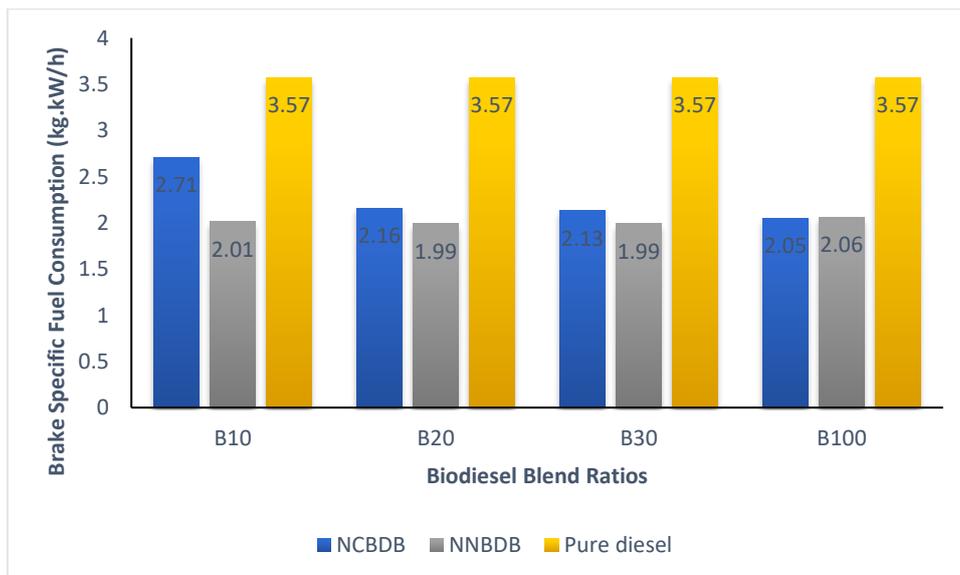


Figure 7: Brake Specific Fuel Consumption of Biodiesels and Blend

The relatively low BSFC values are consistent with the ester profile of neem biodiesel. Saturated and monounsaturated methyl esters typically burn more efficiently, producing stable

flame fronts and reducing the mass of fuel required for equivalent output. This supports the observed reductions relative to diesel. Across all blends, BSFC values were

significantly lower than diesel, indicating that neem biodiesel regardless of catalyst offers strong efficiency advantages for CI engines. Small differences between catalysts at some blend levels were within typical experimental variation and may not reflect meaningful real-world performance differences.

Brake Mean Effective Pressure

In figure 8, BMEP increased consistently with higher biodiesel fractions for both CES-based (NCBDB) and NaOH-based (NNBDB) neem biodiesel. Across all blends, diesel showed the lowest BMEP (2.74 bar), while NCBDB and NNBDB produced higher and relatively stable pressures (3.78-4.96 bar and 5.03-4.94 bar respectively). NNBDB maintained the highest BMEP at every blend ratio. At B10, BMEP was 3.78 bar for NCBDB and 5.03 bar for NNBDB, compared to diesel's 2.74 bar. At B20 and B30, NCBDB increased slightly (4.58 bar and 4.67 bar), while NNBDB remained constant at 5.03 bar. At B100, NCBDB reached 4.96 bar and NNBDB remained high at 4.94 bar, both still well above diesel's unchanged 2.74 bar. Across all blends, diesel did not exceed 2.74 bar.

The higher BMEP in both biodiesel samples may relate to their higher oxygen content, enhancing combustion efficiency and increasing the pressure developed during the power

stroke. NNBDB consistently showed the highest BMEP, possibly due to its higher ester purity (100% in GC-MS results) and slightly lower viscosity, which improves fuel-air mixing. In contrast, the lower BMEP from diesel reflects its lower oxygen concentration, leading to less complete combustion. Although the difference between NCBDB and NNBDB is small (e.g., 4.96 vs. 4.94 bar at B100), this variation is not practically significant for engine performance. However, both biodiesel types outperform diesel substantially (+38% to +85% BMEP across blends), indicating their strong potential as performance-enhancing alternative fuels.

The dominance of monounsaturated methyl esters in both biodiesel types supports more stable combustion, reducing ignition delay and promoting uniform pressure rise. The high concentration of 10-octadecenoic acid methyl ester in NNBDB aligns with its consistently higher BMEP, since monounsaturated esters generally burn cleaner and release heat more evenly. Small fluctuations in BMEP particularly between 4.94 bar and 4.96 bar at B100 may fall within normal experimental variability of the test engine. Measurement precision limits may influence these minor differences, but the observed diesel-biodiesel gap is large enough to remain statistically meaningful.

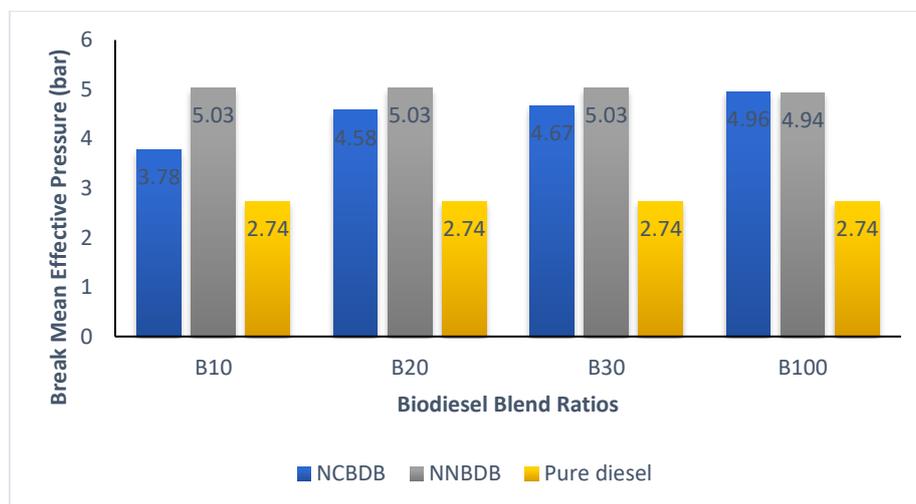


Figure 8: Brake Mean Effective Pressure of Biodiesels and Blend

Brake Thermal Efficiency

Figure 9 explain that, Brake thermal efficiency increased for all biodiesel blends relative to pure diesel, with the highest efficiencies recorded for the NaOH-based biodiesel (NNBDB). At B20 and B30, NNBDB reached 4.28%, which is nearly double the diesel baseline of 2.21%. CES-based biodiesel (NCBDB) also exceeded diesel values across all blends, though with slightly lower magnitudes compared to NNBDB.

BTE increased from diesel (2.21%) to 3.28-4.19% for NCBDB and 4.17-4.28% for NNBDB across B10-B100. B10 NCBDB is 3.28%, NNBDB is 4.18% and Diesel is 2.21%. B20 NCBDB is 3.84%, NNBDB is 4.28% and Diesel is 2.21%. B30 NCBDB is 4.00%, NNBDB is 4.28% and Diesel is 2.21%. B100 NCBDB is 4.19%, NNBDB is 4.17% and Diesel is 2.21%. These results show consistent improvement over diesel and a narrow performance gap between B30 and B100 for both catalysts. Higher BTE values for both biodiesel types likely stem from enhanced oxygen availability, which improves combustion efficiency relative to diesel. The

slightly higher performance of NNBDB suggests better fuel-air mixing due to its lower viscosity and higher calorific value. At higher blend ratios (B100), the minimal difference between NCBDB and NNBDB indicates that catalyst-specific variations in ester composition become less influential once diesel is fully displaced.

Across all blends, NNBDB showed 89-94% improvement over diesel's BTE (2.21%), whereas NCBDB showed 48-89% improvement. Even the lowest biodiesel performance (NCBDB at B10) still exceeded diesel by 48%, indicating robust thermal efficiency enhancement regardless of catalyst. Differences between NCBDB and NNBDB at higher blends (B30-B100) are small (<3%), suggesting that both catalysts produce fuel of comparable thermal performance. These differences are operationally minor and may not translate into meaningful real-world efficiency variation within typical measurement uncertainty ranges for engine tests.

The improved BTE values align with the GC-MS results from earlier sections.

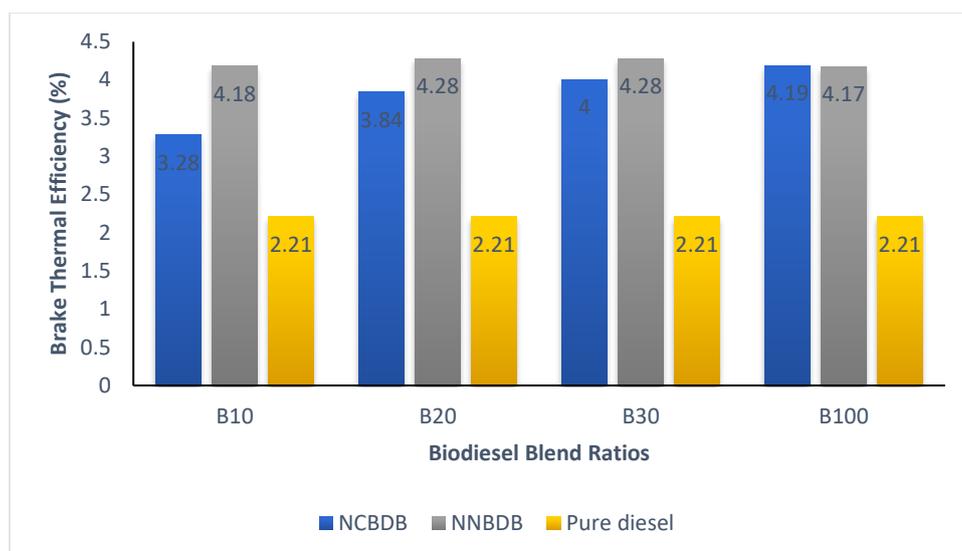


Figure 9: Brake Thermal Efficiency of Biodiesels and Blend

Both fuels contain high proportions of monounsaturated methyl esters (e.g., octadecenoic acid methyl ester), which promote cleaner and more complete combustion due to moderate ignition quality and favorable volatility. This ester profile supports efficient energy conversion and explains the superior BTE compared to diesel.

Analysis of Variance for the Performance Characteristics

Table 6-10 provides an over view of the performance characteristics of a diesel engine on biodiesels and blends. The analysis of variance is based on the two hypotheses:

- i. Null hypothesis (H_0); There is no significant difference between the two samples of biodiesel within their respective blends in addition with diesel
- ii. Alternalte hypothesis (H_a); There is a significant difference between the two samples of the biodiesel within their respective blends in addition with diesel.

The level of significance is taken to be 0.05. The test statistics factor (F) is defined as the ratio of mean square between the groups and mean square within the groups

$$F = \frac{MS (between\ groups)}{MS (within\ groups)} \tag{1}$$

Table 1: Analysis of Variance For Exhaust Gas Temperature (EGT)

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	434.25	3	144.75	0.060556	0.979141	4.066181
Within Groups	19122.67	8	2390.333			
Total	19556.92	11				

Table 2: Analysis Of Variance For Brake Power (Bp)

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.014573	3	0.004858	0.05385	0.982367	4.066181
Within Groups	0.721646	8	0.090206			
Total	0.736219	11				

Table 3: Analysis Of Variance For Brake Specific Fuel Consumption (BSFC)

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.0883	3	0.029433	0.040699	0.988228	4.066181
Within Groups	5.7856	8	0.7232			
Total	5.8739	11				

Table 4: Analysis Of Variance For Brake Mean Effective Pressure (BMEP)

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.229367	3	0.076456	0.051561	0.983433	4.066181
Within Groups	11.8626	8	1.482825			
Total	12.09197	11				

Table 5: Analysis of Variance for Brake Thermal Efficiency (BTE)

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.1673	3	0.055767	0.047292	0.985372	4.066181
Within Groups	9.433667	8	1.179208			
Total	9.600967	11				

The decision taken is in consideration of the P value or statistical and critical factor which is based on the following conditions:

H_0 is rejected and H_a is accepted if P is less than or equal to 0.05 ($P \leq 0.05$) and vice versa i.e. H_0 is accepted and H_a is rejected if P is greater than 0.05 ($P > 0.05$). On the other hand, H_0 is rejected and H_a is accepted if $F_{\text{statistic}}$ is greater than F_{critical} and vice versa i.e. H_0 is accepted and H_a is rejected if $F_{\text{statistic}}$ is less than or equal to F_{critical} .

From Table 6, the value of P is 0.979141, which is greater than 0.05, so the null hypothesis (H_0) is accepted and hence applicable and it may be concluded that there is no significant difference among the four categories of exhaust gas temperature of the diesel engine on biodiesel and blend including diesel. Hence the four categories contribute equally and no further analysis is needed. It can also be observed that from table 7-10, in all the analysis P is greater than 0.05 thus the same conclusions can be drawn as in the previous section.

Emissions Characteristics Results

Exhaust Emissions Results Using two samples of Neem Biodiesel (each produced with different catalysts i.e. calcined eggshell and sodium hydroxide catalysts) binary blends are presented in the figures 10 to 14.

Unburnt hydrocarbon (HC)

Unburnt hydrocarbon (HC) emissions decreased for all biodiesel blends relative to diesel, except for the NNBDDB B10 blend, which showed equal HC levels. The lowest emissions across all blends were consistently produced by the CES-based biodiesel (NCBDB). Figure 10 presents HC emissions for B10, B20, B30, and B100 blends from two neem biodiesels NCBDB (CES catalyst) and NNBDDB (NaOH catalyst) compared to conventional diesel. Diesel recorded the highest HC emissions (4 units) at all conditions except for NNBDDB B10, which matched this value. Across all blends, NCBDB produced the lowest HC emissions, ranging from 1.0-2.0 units, representing a 50-75% reduction relative to diesel. NNBDDB blends showed moderate reductions (2-3 units) except at B10.

The lower HC emissions from biodiesel blends are likely linked to their higher inherent oxygen content, which enhances oxidation during combustion—an observation consistent with Atmanli & Yilmaz (2020). The strong performance of NCBDB in particular may be attributed to improved fuel atomization and better air-fuel mixing, possibly due to its slightly higher cetane number and volatility. A shorter ignition delay, as described by Raguraman et al. (2021), could also explain why NCBDB achieves more complete combustion.

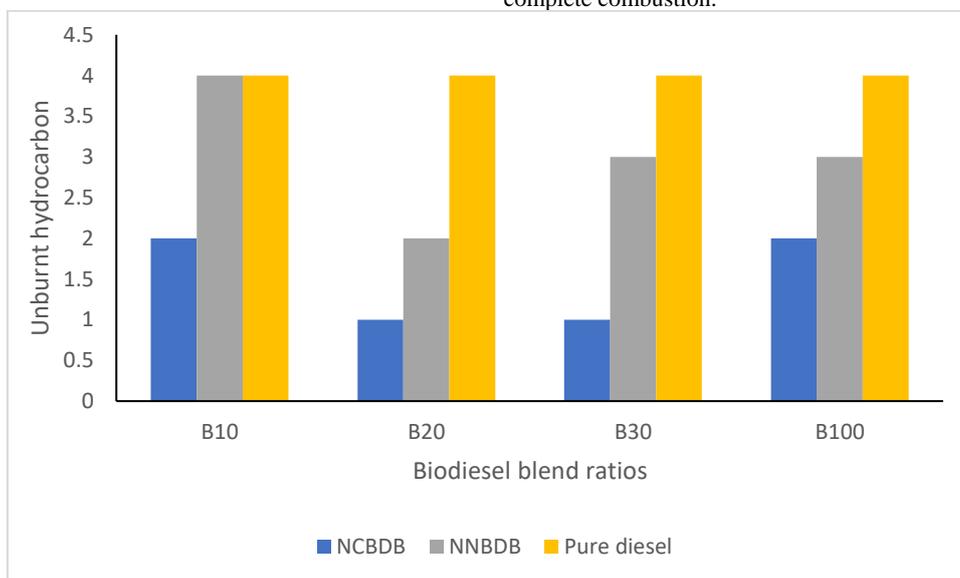


Figure 10: Variation of Unburnt Hydrocarbon with Biodiesel Blend Ratios

The higher HC levels of NNBDDB at B10 may suggest incomplete atomization at low blend ratios, where diesel-like properties dominate, limiting the combustion improvement typically introduced by biodiesel oxygenation. Although the difference between NCBDB and NNBDDB narrows at higher blend ratios, the consistently lower HC emissions of NCBDB highlight its potential environmental advantage in reducing unburnt hydrocarbons, especially in low-blend applications (B10-B30). Even where differences appear small, the reductions remain meaningful for emissions regulation and urban air-quality goals. Small variations in injector

temperature, fuel spray behavior, and environmental humidity could influence HC measurements. However, the consistent directional trend, diesel highest, NCBDB lowest, suggests robust behavior across operating conditions.

Nitric oxide (NOx) Emissions

All biodiesel blends, both NCB and NNB produced lower NOx emissions than diesel, with blend-dependent trends that differed between catalysts. Figure 11 compares NOx emissions for biodiesel blends (B10-B100) produced using CES catalyst (NCBDB) and NaOH catalyst (NNBDDB),

alongside diesel as the baseline. Diesel recorded the highest NO_x levels across all operating conditions. For NCBDB, NO_x decreased steadily from B10 to B30, then increased again at B100 to approximately the same level observed at B10. For NNBDB, NO_x increased from B10-B30 (60, 62 and 71 ppm), then dropped at B100 to 51 ppm. This pattern is the opposite of NCBDB. All blends, regardless of catalyst, remained below diesel's NO_x level, confirming consistent improvement under constant-load conditions.

The lower NO_x emissions relative to diesel align with reports by Atmanli & Yilmaz (2020), who linked reductions to higher biodiesel oxygen content and lower combustion temperatures associated with unsaturated fatty acid profiles. Neem biodiesel contains substantial monounsaturated methyl esters, which tend to suppress peak flame temperatures and reduce thermal NO_x formation.

The opposite response patterns between NCB and NNB blends may be influenced by their differing ester compositions. NNB shows a higher proportion of

monounsaturated FAME (63.58%), which may elevate combustion temperature at moderate blend ratios (B20–B30) and thus slightly raise NO_x before dropping at B100 when volatility and ignition delay shift again. NCB, which has lower overall methyl ester concentration (80.98%) may exhibit cooler combustion over B10-B30, thereby reducing NO_x progressively until full-strength biodiesel alters spray and ignition behavior at B100. These explanations remain consistent with temperature-dependent NO_x pathways described by Ashok et al. (2019).

Even though NCB and NNB follow opposite trends, both catalysts provide NO_x advantages over diesel at all blend ratios. The blend-dependent fluctuation is relatively small compared with diesel's baseline, meaning the statistical effect is likely minimal for real-world operation at constant load. This suggests that neem biodiesel, especially blends up to B30 can serve as a cleaner alternative fuel without the commonly reported NO_x penalty associated with some biodiesels.

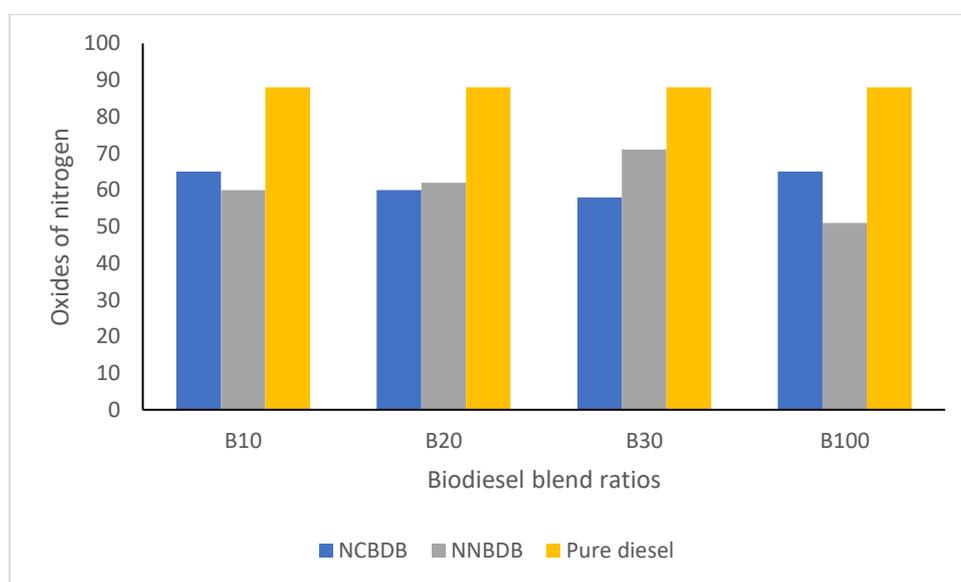


Figure 11: Variation of Nitric Oxide with Biodiesel Blend Ratios

Some studies (Demirbas, 2005; Raguraman et al., 2021) report increased NO_x when biodiesel is tested under varying load. The lower NO_x observed in the present study may be attributable to the constant 4.5 N load, which limits peak temperature excursions normally responsible for NO_x rise. Differences between studies reinforce that NO_x behavior is load-sensitive, feedstock-sensitive, and catalyst-dependent. Small variations in exhaust temperature measurement, injector spray temperature, and humidity may influence NO_x readings. However, the consistent trend, lower NO_x for all biodiesel blends relative to diesel suggests robust behavior across test conditions.

Carbon monoxide (CO) Emissions

Carbon monoxide emissions typically arise from incomplete combustion, especially in zones where the air-fuel mixture becomes fuel-rich. CO formation is strongly influenced by the air-fuel ratio, as insufficient oxygen prevents the full oxidation of carbon to CO₂ (Ashok et al., 2019). Diesel fuel generally exhibits higher CO emissions than biodiesel

because diesel is a purely hydrocarbon-based fuel, whereas biodiesel contains inherent oxygen, which promotes more complete combustion.

Figure 12 illustrates the CO emission behaviour of the two biodiesel samples and their respective blends under constant load (4.5 N) and constant speed (1500 rpm). Notably, no carbon monoxide emissions were recorded for all test fuels, including diesel, biodiesel, and their blends. This outcome suggests that the combustion conditions within the CI engine strongly favoured complete oxidation. The absence of CO across all samples indicates that sufficient excess air was supplied during combustion, ensuring that adequate oxygen was available to convert carbon into CO₂ rather than CO. This finding aligns with the observation of Abed et al. (2019), who reported similarly negligible CO emissions when oxygen availability was sufficiently high. Thus, under the operating conditions of this study, both biodiesel fuels and their blends demonstrated efficient combustion performance, with no measurable CO formation.

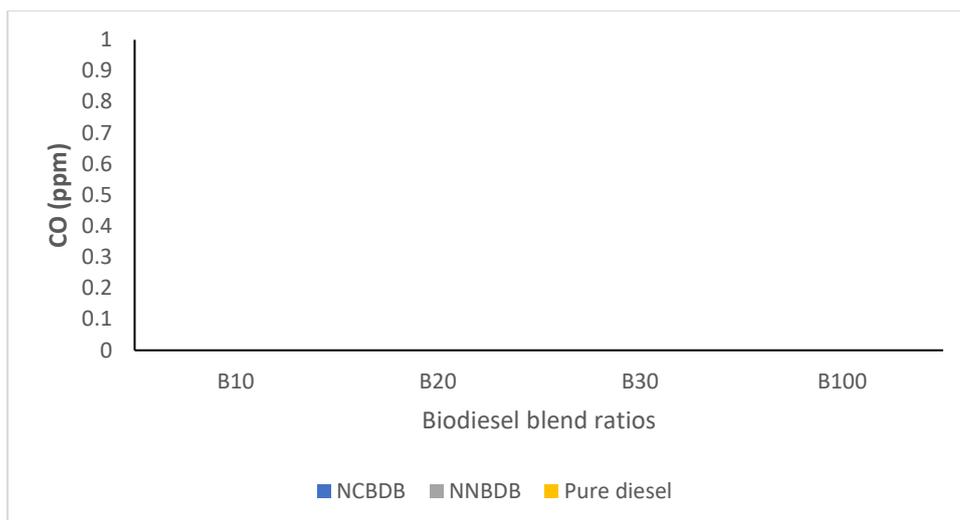


Figure 12: Variation of CO with Biodiesel Blend Ratios

Carbon dioxide (CO₂) Emissions

Carbon dioxide formation in internal combustion engines is primarily associated with complete oxidation of carbon-based fuels. The presence of additional oxygen molecules within biodiesel enhances oxidation efficiency, thereby promoting the conversion of carbon monoxide (CO) to CO₂ through reactions involving hydroxyl radicals during combustion. As a result, fuels with higher inherent oxygen content often exhibit varying CO₂ emission trends depending on combustion characteristics and the specific biodiesel feedstock used.

Figure 13 presents the CO₂ emission profiles of neem oil biodiesel produced with two different catalysts across various biodiesel-diesel blend ratios. The results show a non-linear increase-decrease pattern for both biodiesel samples as blend percentage increases. When compared to pure diesel, the biodiesel produced using calcined eggshell catalyst (CEC) displayed CO₂ emissions identical to diesel at B10 and B20. At B30, CO₂ emissions decreased by 8.3%, while neat biodiesel (B100) generated 12.5% higher CO₂ than diesel.

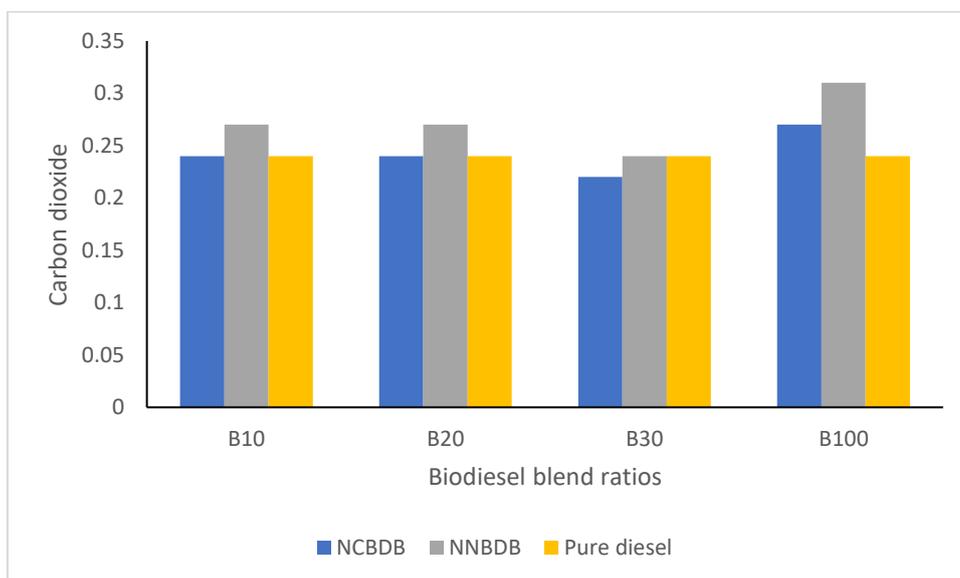


Figure 13: Variation of CO₂ with Biodiesel Blend Ratios

For biodiesel produced using sodium hydroxide (NaOH) catalyst, CO₂ emissions increased by 12.5% at both B10 and B20 relative to diesel. At B30, the emissions were similar to diesel, whereas B100 showed a more substantial increase, producing 29.2% higher CO₂ than pure diesel. These findings highlight that biodiesel may either increase or decrease CO₂ emissions depending on the biodiesel type, catalyst used, and blend ratio, in agreement with the observations of McCarthy et al. (2011).

Overall, this study demonstrates that neem oil biodiesel synthesized with CEC exhibits higher CO₂ emissions at

higher blend levels, a trend consistent with the results reported by Abed et al. (2019). The increased CO₂ output at elevated blend ratios further reflects the enhanced oxygen content and improved combustion completeness associated with biodiesel fuels.

Analysis of Variance for the Emission Characteristics

Table 11-13 show that all the emissions from biodiesel, diesel and their various blends running on CI engine at constant load and speed of 4.5 and 1500rpm respectively which were subjected to a single factor analysis of variance with two

samples of fuels and their blends. The analysis conducted at 0.05 significance level and hence all effects were discovered to be statistically insignificant as $f_{\text{statistic}}$ is less than f_{critical} which serve as the governing condition as stated in section 3.4.6 above.

This analysis implies that the mean of all the samples and their blends were statistically insignificant to variation of fuels during engine's operation.

Table 6: Analysis Of Variance For Unburnt Hydrocarbons (HC)

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.666667	3	0.555556	0.31746	0.812674	4.066181
Within Groups	14	8	1.75			
Total	15.66667	11				

Table 7: Analysis Of Variance For Oxide Of Nitrogen (Nox)

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	30	3	10	0.038375	0.989191	4.066181
Within Groups	2084.667	8	260.5833			
Total	2114.667	11				

Table 8: Analysis Of Variance For Carbon Dioxide (CO₂)

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.002433	3	0.000811	1.649718	0.253777	4.066181
Within Groups	0.003933	8	0.000492			
Total	0.006367	11				

But for carbon monoxide as there is no recorded values for its emissions, analysis of variance cannot be enhanced for the computation of the p-value among the various fuels and their blends.

These analyses explain that the mean hydrocarbon, nitric oxide and carbon dioxide were statistically not significant to variation of fuels during engine's operation.

CONCLUSION

This study evaluated the production and performance of neem oil biodiesel using two catalysts, calcined eggshell (CES), derived from waste materials, and conventional sodium hydroxide (NaOH). The results provide important insights into biodiesel production efficiency, fuel quality, engine performance, and emissions behavior.

Both catalysts demonstrated high biodiesel yields, with CES achieving an optimum yield of 100% at 1.0 wt% concentration and 70 minutes' reaction time, while NaOH achieved 97% at 0.5 wt.% and 150 minutes. Although NaOH required lower catalyst loading, CES was more advantageous in terms of reaction speed and cost-effectiveness, especially considering its origin from waste eggshells. Using CES highlights the relevance of waste-derived heterogeneous catalysts, which enhance sustainability, reduce waste disposal burdens, and lower overall biodiesel production costs.

Fuel characterization revealed that biodiesel produced with NaOH contained 100% methyl esters, while CES-based biodiesel contained 80.98%. In both cases, the dominant fatty acid methyl esters, methyl oleate, methyl stearate, and methyl palmitate indicate the suitability of the produced biodiesel for compression ignition engines. This confirms that neem oil biodiesel, regardless of catalyst type, is a renewable, combustible, and engine-compatible alternative fuel.

Engine performance tests across B10, B20, and B30 blends showed varying strengths for each catalyst. CES-based biodiesel blends generally exhibited lower exhaust gas temperatures (EGT), reflecting cleaner combustion and reduced thermal stress. NaOH-based biodiesel blends,

however, delivered higher brake power (bp), brake mean effective pressure (bmep), brake thermal efficiency (BTE), and lower brake specific fuel consumption (bsfc), indicating superior overall engine performance. Emission results further demonstrated that CES biodiesel blends produced the lowest unburnt hydrocarbons, while both catalysts yielded lower NO_x emissions than diesel, with no carbon monoxide detected. Carbon dioxide emissions varied, with most blends performing comparably to diesel.

Overall, both biodiesel samples show strong potential as viable diesel alternatives, with CES offering added value in terms of sustainability and environmental circularity, and NaOH performing strongly in engine metrics.

This research has certain limitations that were considered when interpreting the findings:

- Tests were conducted on only one compression ignition engine, limiting the generalizability of results to other engine types or displacement categories.
- All experiments were performed at a fixed load (4.5 N) and engine speed (1500 rpm). Real-world operating conditions involve variable loads and speeds, which may influence performance and emission characteristics differently.
- The quality of CES depends on waste eggshell availability, calcination conditions, and particle uniformity. These factors may introduce batch-to-batch variability that could affect biodiesel yield and fuel properties.

The outcomes of this study suggest that waste-derived catalysts such as CES can significantly reduce biodiesel production costs, making large-scale biodiesel manufacturing more affordable and environmentally responsible. Lower EGT and emission reductions demonstrate clear environmental benefits, while superior engine performance metrics from NaOH catalyzed biodiesel blends highlight promising real-world applicability. These findings provide a foundation for future optimization and potential commercial

adoption of neem oil biodiesel, particularly in regions with abundant neem resources and agricultural waste stream.

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