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Experimental Investigation of energy, exergy and emission characteristics of Croton macrostachyus biodiesel blends in CI engine

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Abstract

The growing global energy demand and depletion of fossil fuels have intensified pollution, motivating the search for renewable and sustainable alternatives such as biodiesel. This study evaluates the energy, exergy, and emission characteristics of a compression ignition (CI) engine fueled with Croton macrostachyus methyl ester (CMB) biodiesel blends. The biodiesel was produced through transesterification using a novel hybrid calcium–aluminum oxide heterogeneous catalyst. Five fuels—pure diesel (B0) and blends CMB10, CMB15, CMB20, and CMB25—were tested on a single-cylinder, four-stroke diesel engine under full load at speeds of 800, 1400, 2000, and 2600 rpm. Results showed that CMB20 achieved the best overall balance among the blends, with a 5.85% lower brake thermal efficiency (BTE) and 3.86% higher brake specific fuel consumption (BSFC) than diesel. CMB25 reduced CO₂ emissions by 1.55%, though NO_x emissions increased by 8.6%. At 2600 rpm, CMB20 slightly raised the exhaust gas temperature (EGT) by 6.14%, while CMB25 exhibited 18.02% and 13.1% higher exhaust energy and exergy losses, respectively. Cooling water energy and exergy losses rose by 19–31.6% and 6.67–23.8% at lower engine speeds. CMB20 demonstrated 15.4% lower exergy destruction, and the maximum exergy efficiency (20%) was observed for CMB15. Overall, Croton macrostachyus biodiesel blends exhibited higher exhaust energy losses but lower exhaust exergy losses than diesel. At low to moderate speeds, CMB20 delivered improved thermodynamic performance and reduced emissions, indicating its potential as an environmentally favorable diesel substitute requiring optimization at higher speeds.

Keywords: Croton macrostachyus; Biodiesel; Exergy, Energy, Exergy destruction, Performance; Emission.

1. Introduction

Energy drives socio-economic growth, but rising demand from population and technology is depleting fossil fuels and increasing emissions [1,2]. Renewables like solar, wind, tidal, biomass, and geothermal offer cleaner alternatives [2]. Global energy demand is expected to rise 60% by 2030, with China and India contributing 45% [3]. Fossil fuels, especially in transport, still dominate, with consumption projected at 109.4 million barrels/day by 2040 and diesel use up by 5.7 million barrels/day [4–6]. Fossil fuels accelerate global warming and are depleting, driving the need for renewable, clean energy to cut CO₂ and other emissions [7]. With energy demand projected to rise over 50% from 2018 to 2040, interest in alternatives like biodiesel has grown. Made from plant oils, animal fats, or waste cooking oils via transesterification, biodiesel is renewable, biodegradable, low-toxicity, and reduces HC, CO, particulate matter, and sulfur oxide emissions [8,9].

Feedstock choice influences biodiesel cost, environmental impact, and quality. Biodiesel feedstocks broadly classified as edible oils (first generation), non-edible oils (second generation) [10–13] waste cooking and algae oils (third generation) [14], with fourth- and fifth-generation feedstocks using solar energy or genetically engineered crops. Since edible oils compete with food, non-edible sources are preferable [15]. Ethiopia has abundant non-edible options, including jatropha, castor bean, palm, cottonseed, croton macrostachyus, moringa, neem, sugarcane, animal fat, waste cooking oil, and microalgae [5].

This study focuses on Croton macrostachyus seeds, a non-food Ethiopian plant recognized for its high oil yield, favorable cold flow properties, and low production costs [16–19]. Known locally as Besana, Bakkanniisa, and Tambush, it serves multiple uses fuel, medicine, dyes, and soil enrichment and is identified by the Ethiopian Biodiversity Institute as a promising biodiesel source [16,17]. Growing 3–25 m tall, it thrives in 150–1200 mm rainfall, secondary forests, and poor soils, showing strong adaptability [20]. Native to Ethiopia and tropical Africa, it outyields Jatropha per hectare. Despite traditional medicinal uses, research on biodiesel from its leaves, kernels, and seeds is limited; seeds were chosen here for their abundance, affordability (low cost), and high oil content. After selecting feedstock, oil extraction is key, using drying (below 15% moisture) for

optimal mechanical, solvent, or enzymatic methods [5,21]. Transesterification is preferred to convert Croton macrostachyus seed oil into high-quality biodiesel with improved engine performance.

Catalysts are essential for accelerating the transesterification process, which in turn significantly enhances biodiesel yield [22]. Recent literature emphasizes the application of diverse catalysts for biodiesel production across various feedstocks, including homogeneous, heterogeneous, and composite heterogeneous catalysts. From the literature review the croton macrostachyus seed were produced with homogeneous and heterogenous catalysts still today. Mohammed et al. [23] achieved a 98.3% biodiesel yield from Croton macrostachyus seed oil using methanol and CaO catalyst from eggshells. Solomon et al. [18] reported a 91% yield with CaO catalyst and ethanol. Zamba and Reshad [24] reached 95% conversion using NaOH, while Aga et al. [17] obtained 96% yield with KOH catalyst. Bayisa et al. [20] used KOH to extract 45.9% oil. The composite heterogeneous catalyst hybrid from CaO/Al₂O₃ was used for different feedstocks for algal oil [25], waste cooking oil [26,27] yielded 95% and 96.56% respectively. As seen from the literatures there are few studies that utilized homogeneous and heterogeneous catalysts for croton macrostachyus seed oil, also the algal oil and waste cooking oil were used the hybrid heterogeneous catalysts. This study used the transesterification process for croton macrostachyus seed oil using hybrid heterogeneous catalyst (CaO/Al₂O₃) with methanol as solvent.

The literatures related to engine performance, emission, energy, and exergy characteristics of biodiesel blends in CI engine were investigated by several researchers were Morosukb et al. [28] found jatropha biodiesel-diesel blends reduced BTE by 21% and increased BSFC by 32%, but lowered CO₂ emissions at higher biodiesel levels. Garcia Mariaca et al. [29] reported a 37.5% rise in BSFC, 10% drop in BTE, and increased CO, HC, and PM emissions with jatropha biodiesel blends. Singh and Paul [30] evaluated diesel blends with up to 30% waste cooking oil and pyrolysis oil. The D90P10 blend showed the highest energy (33.6%) and exergy (30.3%) efficiency but a 25.6% increase in NO_x emissions. All blends outperformed pure diesel but had higher CO₂ costs. Rajendran et al. [31] found that a 20% Juli flora biodiesel blend (JF20) closely matches diesel's performance, with slightly higher BSFC, EGT and BT efficiency, lower NO_x, and reduced smoke, CO, and HC emissions. Kabudke et al. [32] reported that cottonseed biodiesel blends (CB20, CB30, CB40) improved BTE and fuel consumption compared to diesel.

Zamba and Reshad [24] tested Croton macrostachyus biodiesel blends (B5–B20) in a diesel

engine, observing decreased BTE, increased BSFC and EGT, reduced UHC, NO_x, and CO emissions, but higher CO₂ emissions versus pure diesel. Mohammed et al. [33] recent study showed that advancing injection timing improved BTE by 31%, lowered BSFC by 42.85%, and cut NO_x by 19.06% with Croton biodiesel. Higher blends and lower speeds raised CO₂ emissions, while higher engine speeds increased BSFC by 27.3% but reduced NO_x by up to 44.4%.

Recent studies using energy and exergy analysis show biodiesel blends improve CI engine efficiency and reduce exergy loss compared to diesel [34,35]. Gnanamani et al. [36] assessed a diesel engine running on cottonseed oil blends (CB5, CB10, CB15) and pure diesel. They found that with increasing engine speed, fuel exergy rose while thermal exergy fell. Compared to diesel, the blends reduced energy loss, heat release, exergy percentage, and exergy in exhaust gas. Shahnaz et al. [37] studied a DI diesel engine using diesel, soybean biodiesel (B100), and blends (B20, B40) at full load and 1200 rpm. B100 showed higher efficiency than diesel and B20, while B20 had greater total and work availability, heat loss, burned fuel availability, and irreversibility. Rath et al. [34] analyzed a CI engine using diesel and Karanja oil blends (K10, K20). K10 improved thermal efficiency by 6.08% and exergy efficiency by 5.76% over diesel. Exergy losses of 65–70% of fuel chemical energy were observed for all fuels.

Many biodiesel engine studies focus on improving efficiency and reducing fuel consumption using first-law (energy) analysis based on experimental data. While energy analysis measures performance metrics like power, BTE, and fuel consumption, it cannot assess energy quality or usability. Exergy analysis addresses this by identifying irreversibility and including factors such as exhaust emissions, cooling water, and engine temperatures. It quantifies losses from combustion, gas expansion, pressure drop, friction, and heat transfer, making it crucial for alternative fuel selection. However, it may overlook some system irreversibility causing losses.

Exergy analysis, based on the second law of thermodynamics, is essential for quantifying losses and identifying their sources in compression ignition engines [38]. Energy and exergy analyses are key tools for understanding and improving CI engine performance: energy analysis examines input, output, and losses, while exergy assesses maximum useful work by evaluating input, output, and destruction [34,35,39]. Exergy analysis considers exhaust emissions, cooling water, and engine temperatures, aiding fuel selection. This study uses both first and second law analyses to enhance CI engine performance and design. Biodiesel-diesel blend ratios affect engine performance and emissions; higher biodiesel from non-edible oils like *Jatropha* and *Karanja*

reduces particulates and NO_x but may lower calorific value and energy output.

This study examines the energy, exergy, and emission characteristics of *Croton macrostachyus* biodiesel blends in a CI engine, comparing them with conventional diesel to address a key research gap. The biodiesel was produced via transesterification using a composite heterogeneous catalyst from calcium and aluminum oxides, enhancing efficiency, quality, and cost-effectiveness. Existing research lacks comprehensive energy and exergy analyses of CI engines running on these blends and has largely been limited to homogeneous or single-metal heterogeneous catalysts for biodiesel production. The novelty of this work lies in two main aspects. First, it investigates the energy and exergy characteristics of *Croton macrostachyus* biodiesel blends across various blend ratios and engine speeds under constant full-load conditions. Second, it introduces the synthesis of a composite (hybrid) heterogeneous catalyst from two different metal oxides calcium and aluminum oxide for biodiesel production from *Croton macrostachyus* seed oil.

2. Materials and Methods

2.1 Materials

2.2 .1 Chemicals and Equipment

The *croton macrostachyus* seed were collected from Sibu Sire District/Wereda, East Wallaga, Oromia. The solvents and chemical reagents used were sourced from local chemical suppliers and included: methanol (CH₃OH, 99.8%), hexane (99%), ethanol (C₂H₅OH, 99.8%), phenolphthalein indicator, potassium hydroxide (KOH, 85%), aluminum oxide (Al₂O₃), calcium oxide (CaO) nanoparticles, iodine solution, chloroform, starch indicator, and acetic acid.

A variety of equipment was used in this study. Catalyst synthesis involved a muffle furnace and oven dryer, while oil extraction was performed using a solvent auto-extractor (SER158). Functional groups were analyzed with an FTIR spectrometer, chemical composition with GC-MS (Agilent 7890), surface area with a Horiba SA-9600 analyzer, and calorific value with a bomb calorimeter. For biodiesel production, key apparatus included a mechanical screw press, conical flasks, separating funnels, beakers, measuring cylinders, PPE, thermometers, hotplates with magnetic stirrers, a three-neck reactor, and digital balance. The engine employed was a TM8-04 model a single-cylinder, four-stroke, water-cooled diesel engine fully compatible with the TBMC8 test bench configuration. Exhaust emissions were quantified using a Seitron S500 exhaust gas analyzer (Seitron Americas Inc., Trevose, PA). TBMC-CG unit exhaust gas calorimeter. All

instruments were calibrated, and analyses were conducted in triplicate to ensure accuracy.

2.3 Methods

2.3.1 Composite heterogeneous catalysts preparation and characterization

Recent literature emphasizes the application of diverse catalysts for biodiesel production across various feedstocks with composite or hybrid heterogeneous catalysts as a promising source for biodiesel production, it's developed from different metal oxides. These composite heterogeneous catalysts carried out by calcination process both catalysts were used to evaluate the biodiesel yields of CMS oil by transesterifications.

In this study, a composite heterogeneous catalyst was synthesized from CaO and Al_2O_3 powders via calcination, typically in a 2:1 ratio to balance basicity and structural support. The ratio can be adjusted, though CaO-rich compositions are preferred for high-basicity uses like transesterification. Both oxides were first pre-dried at 110 °C for one hour to eliminate adsorbed moisture, with CaO handled under controlled conditions due to its high hygroscopicity. After cooling in a desiccator to prevent CO₂ and moisture uptake, the powders were combined in a dry mortar at a 2:1 ratio (CaO: Al_2O_3) and manually ground for 15–20 minutes to ensure uniform dispersion and deagglomeration. The homogenized blend was transferred to a porcelain crucible and subjected to calcination in a muffle furnace, heated at 5 °C/min to 600 °C and held for five hours to promote solid-state interaction and improve catalytic stability and activity. Following natural furnace cooling to ambient temperature to avoid thermal shock. After calcination, the catalysts were stored in a desiccator to prevent oxidation and contamination, ensuring their structural and chemical integrity for the transesterification reaction.

The calcinated CaO with Al_2O_3 were characterized using FTIR, XRD, and BET. FTIR spectroscopy was used to identify and characterize functional groups in each catalyst, providing qualitative and quantitative analysis by measuring infrared absorption spectra that reveal chemical bonds. For FTIR analysis, samples were prepared and subjected to a wavenumber range of 4000-400 cm^{-1} to capture all characteristic absorbance peaks of CaO/ Al_2O_3 . The infrared beam passing through the CaO/ Al_2O_3 sample was absorbed at specific wavelengths, corresponding to its molecular vibrations. The presence of CaO was confirmed within the particles. X-ray diffraction (XRD) analysis was conducted on the catalyst samples to determine their mineralogical

composition and crystalline structures. The Brunauer–Emmett–Teller (BET) method was used to measure specific surface area, pore size distribution, and porosity of the synthesized materials. Nitrogen adsorption-desorption at 77 K was conducted with a Horiba SA-9600 analyzer to generate isotherms for detailed porous structure characterization

2.3.2 Seed preparation

For this research, Croton Macrostachyus fruit was collected from Sibu Sire wereda, East Wallaga, Oromia. Following collection, the fruit was sun-dried, and the decortication process shown in Fig. 1a and Fig 1b was performed. Decortication of the Croton macrostachyus fruit yields the seeds. After seed collection completed, the quantity of effective seed from the dried fruit was measured. The overall process, from seed collection to oil extraction is illustrated in Fig. 2.

2.3.3 Oil extraction from croton macrostachyus seed

Oil extraction was performed at AASTU’s chemical engineering lab using a Soxhlet Solvent Auto Extractor SER158. 10 grams of crushed Croton macrostachyus seed kernel powder were placed in a thimble with 100 ml of n-hexane solvent as shown in Fig 1c. Extraction used the “Total fat in oily seeds and nuts” program for 2.5 hours at 70°C with 3.3 L/min water flow for hexane condensation. Hexane refluxed through the biomass, efficiently extracting oil. Solvent was removed by rotary evaporation, and oil yield was calculated using Eq. (1); as extracted oil weight divided by seed weight.

$$\text{Oil yield(\%)} = \frac{\text{Mass of the CMS oil}}{\text{Mass of the CM seed powder}} \times 100 \quad (1)$$

After extraction, crude CMS oil undergoes purification to remove impurities like gums, moisture, and waxes that affect biodiesel quality as shown in Fig. 1d. Degumming, chosen for its simplicity and cost-effectiveness, effectively eliminates these contaminants to produce high-quality oil.

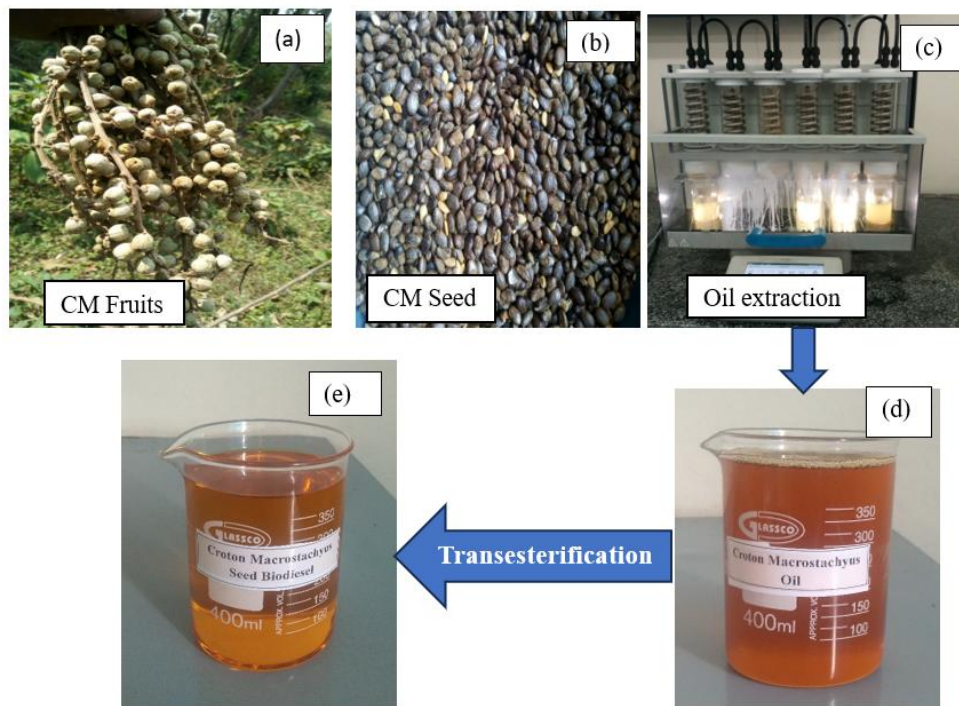


Fig. 1 Overall process up to biodiesel (a) CM fruits (b) CM seed (c) Soxhlet auto extractor (d) CMS oil (e) CMS biodiesel produced via transesterification

2.3.4 Croton macrostachyus seed biodiesel production

Transesterification process utilized for easy, quality and to obtain high yields, Croton macrostachyus seed oil was carried out using methanol and a calcined $\text{CaO-Al}_2\text{O}_3$ composite catalyst to produce biodiesel and glycerol as illustrated in Fig 1d and Fig. 2. The following procedures followed for biodiesel production of CMS oil. 300 ml Croton macrostachyus seed oil was heated to 60°C . A solution of 5 g calcined $\text{CaO/Al}_2\text{O}_3$ catalyst dissolved in 100 ml methanol (20:1 ratio) was added. The mixture was stirred at 600 rpm, 60°C for 1 hour with a cover to reduce methanol loss. After 24 hours of settling, glycerol separated from biodiesel, which was collected. The biodiesel was washed with hot water until clear and dried at 140°C for 1 hour. Purified biodiesel yield was then measured.

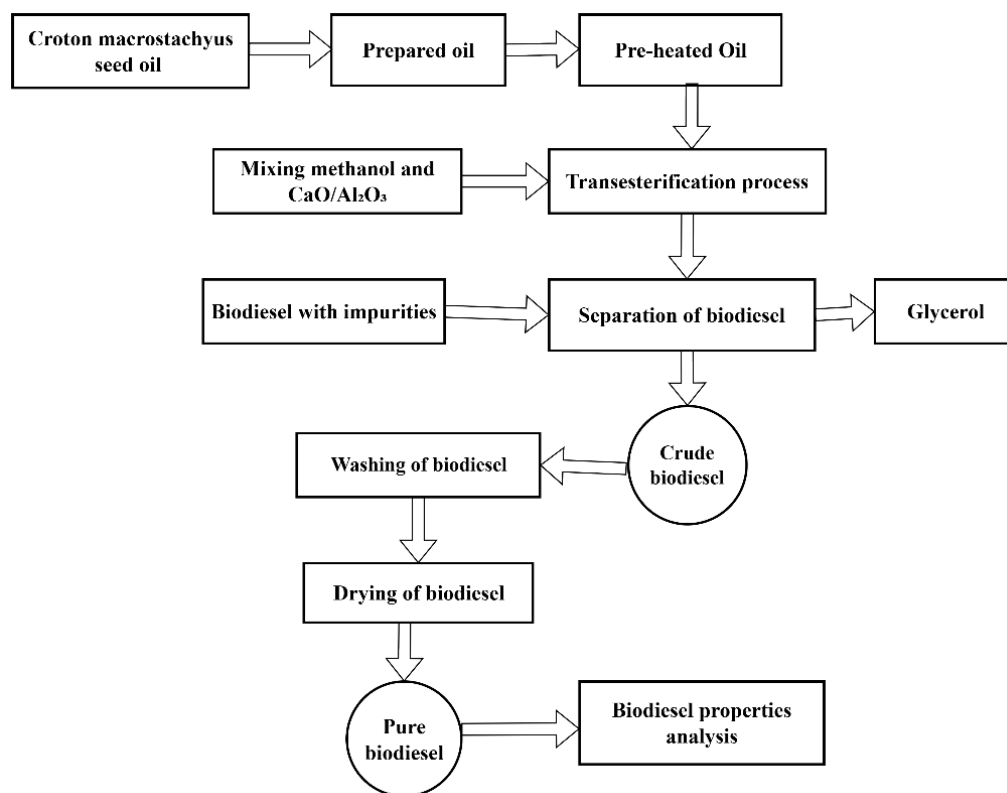


Fig. 2 CMS biodiesel production process from CMS oil

2.3.5 Croton macrostachyus seed oil and biodiesel characterization

The physicochemical properties of Croton macrostachyus (CMS) oil and biodiesel such as specific gravity, iodine value, saponification value, kinematic viscosity, moisture content, FFA percentage, acid value, density, calorific value, and viscosity were measured to evaluate fuel quality. Testing followed ASTM D6751 and EN 14214 standards, which set global benchmarks for biodiesel quality, ensuring proper storage and commercial viability. The titration method was used to determine the acid, iodine, and saponification values of the CMS oil and biodiesel separately. Viscosity was evaluated using a rheometer. Density was calculated by measuring the mass and volume of the oil at a specified temperature. The flash point and fire point of the biodiesel was determined using a closed-cup Pensky-Marten's apparatus (model: PMA 5; M/s Anton Paar, Germany) in accordance with the ASTM D93 method. The calorific value was determined using a bomb calorimeter.

Assessing CMS biodiesel against these standards is crucial before use, as factors like feedstock quality, fatty acid profile, production methods, and handling significantly affect fuel quality [40].

GC-MS analysis of Croton macrostachyus biodiesel identified key saturated and unsaturated fatty acid methyl esters, detailing features that influence viscosity and calorific value. Molecules were separated by gas chromatography based on chemical properties, then ionized and detected by mass spectrometry. The analysis used an Agilent 7890B GC and 5977B MS with an HP-5MS column, helium carrier gas at 1 ml/min, 5:1 split, injector at 250°C, oven ramping from 70°C to 280°C, and mass spectra scanned at 70 eV over 45–550 m/z. Fourier Transform Infrared (FTIR) spectroscopy was also utilized to analyze CMS oil and its derived biodiesel, enabling the identification of functional groups and verifying the successful conversion of the oil into biodiesel. All instruments were meticulously calibrated, and all measurements were conducted in triplicate to ensure accuracy and minimize experimental uncertainty.

2.3.6 Test fuel preparation/ Croton macrostachyus biodiesel blend preparation

Significant study has used vegetable oil as fuel, either neat or in blends. While neat vegetable oil can be used directly, blends with diesel are preferred. Biodiesel is commonly blended with petroleum diesel at various blend ratio. In this study, the diesel fuel was acquired from local fuel stations in Ethiopia. The biodiesel was synthesized from croton macrostachyus (CM) seed oil, which was selected as the feedstock due to its abundant availability. Five fuel samples were prepared by mixing pure diesel and biodiesel in specified proportions. Fuel samples were prepared at B0 (pure diesel), CMB10 (10% CMS biodiesel and 90% diesel), CMB15 (15% CMS biodiesel and 85% diesel), CMB20 (20% CMS biodiesel and 80 diesel), and CMB25 (25% CMS biodiesel and 75% diesel) as shown in Fig 3. Each blend was continuously mixed with a magnetic stirrer for 15 minutes to ensure homogeneity, then checked for component separation before testing. The properties of the CMS biodiesel and its blends were determined including density, energy content, flash point, and fire point. In summary, the test results for all five fuel samples indicates that the properties of each blend meet the requirements set by both ASTM D6751 and the EN 14214.



Fig. 3 Prepared biodiesel blends for test samples

2.3.7 Experimental setup

In this experimental study, a computer-controlled test bench tailored for single-cylinder internal combustion engines with a maximum power output of 7.5 kW was utilized. The engine employed was a TM8-04 model a single-cylinder, four-stroke, water-cooled diesel engine fully compatible with the TBMC8 test bench configuration are described in the line diagram Fig. 4. This apparatus incorporates a naturally aspirated, water-cooled, single-cylinder diesel engine. The TBMC8 setup exerts braking torque via an asynchronous motor governed by a variable frequency drive, which is linked to the engine shaft via an elastic coupling. Before conducting experiments, the engine was stabilized by running on pure diesel for 10 min. Testing was performed at variable engine speeds. Exhaust emissions of CO_2 and NO_x were measured using a Seitron S500 exhaust gas analyzer (Seitron Americas Inc., Trevose, PA). The TBMC-CG Exhaust Gases Calorimeter is specifically utilized to measure heat content via exhaust gases emitted from combustion engines. Detailed engine specifications are provided in Table 2, exhaust gas analyzer specification were provided in Table 1, and exhaust gas calorimeter specification detailed in Table 3.

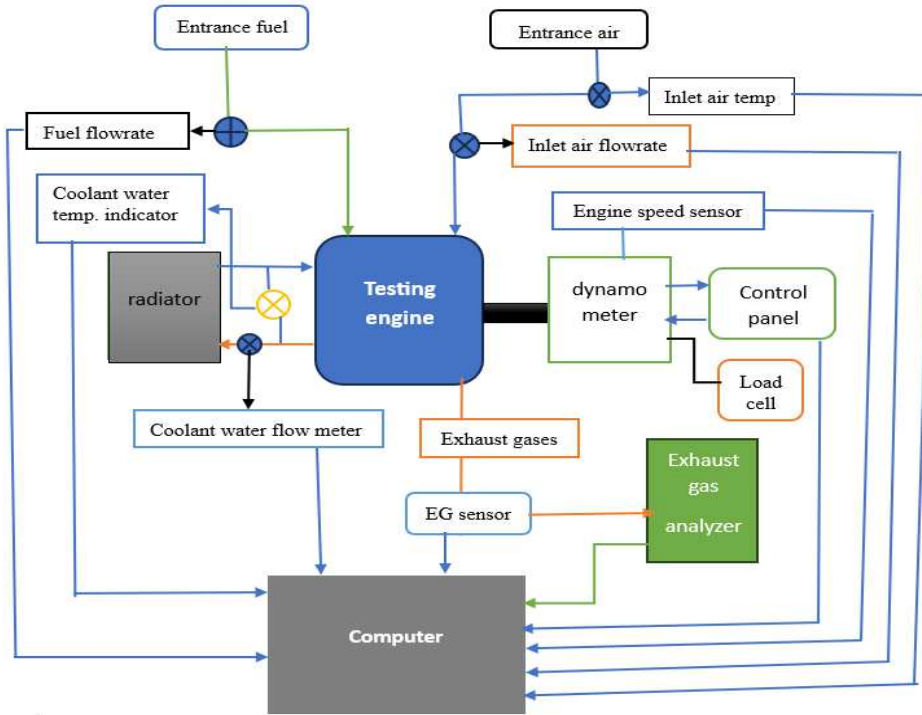


Fig 4

General

view of the engine experimental setup in a line diagram

Table 1 Exhaust gas analyzer specifications

Parameter	Resolution	Accuracy	Unit	Range
CO ₂	0.1 %	+/- 5	%	0–16
O ₂	0.1%	+/-5	%	0-25
CO	1 ppm	+/- 0.06	Ppm	0–4000
NOx	1 ppm	+/- 5	Ppm	0–2000
Lambda	0.001	-	-	0.8–1.2

Table 2 Engine test specifications for TM8-04

Engine parameters	Specifications
Model	Kubota Corporation, E300-ES01
Engine type	4-stroke direct injection, single-cylinder CI
Bore (mm) x stroke (mm)	77 x 70
Type of air intake	Naturally aspirated
Compression ratio	24:1
Displacement (cc)	309
Injection timing	27°C BTDC
Injection pump	Bosch K type
Lubricating system	Forced lubrication with trochoid pump
Rated power	5.2 kW@3000 rpm
Maximum torque (N.M)	~30 N.M.
Maximum power (kW/rpm)	7.5/1860
Type of cooling	Water cooling
Engine oil capacity	1.3L
Startup	Electrical
Starter	12V 0.8kw

Table 3 Exhaust gas calorimeter specifications instrumentation

Specifications	Descriptions
Type J thermocouples	Exhaust gases temperature at the input
	Gases temperature at the calorimeter output.
	Water temperature at the calorimeter input
	Water temperature at the calorimeter output
Flowmeter sensor	to measure the cooling water flow
Pressure sensor	Indicates gases pressure from 0 – 1 bar range
Measuring ranges	
Exhaust gas temperature	0 – 600 °C.
Water temperature	0 – 600 °C.
Flow rate	0 – 600 l/hour

2.3.8 Engine performance parameters

Brake Thermal Efficiency (BTE) indicates how efficiently an engine converts fuel's chemical energy into brake power. It is the ratio of brake power to total fuel energy input, normalized by the fuel's calorific value. BTE was calculated using Eq. (2). Brake Specific Fuel Consumption (BSFC) is an engine performance metric that represents the fuel consumption rate in kilograms per hour required to produce one kilowatt of brake power (BP) at a specific engine speed (N). BSFC was determined using Eq. (3). Where as $\dot{m}_f$ (mass flow rate of the fuel), Bp (brake power), and LHV (lower heating value of the fuel).

$$\text{BTE} = \frac{\text{BP} * 3600}{\dot{m}_f * \text{LHV}} \times 100 \% \quad (2)$$

$$\text{BSFC} = \frac{\dot{m}_f}{\text{BP}} \text{ (Kg/KW hr)} \quad (3)$$

Where each parameter units are expresses as BTE in %, BSFC in g/kWh, $\dot{m}_f$ in kg/h, Bp in KW.

2.4 Uncertainty Analysis

Experimental uncertainty can arise from instrument selection, measurement techniques, environmental conditions, and experimental configuration. To reduce variability, measurements were taken after a 5-minute stabilization at the specified load and speed, with each fuel sample tested three times. Uncertainties were evaluated using the propagation of uncertainty (root mean square) method [33], integrating individual errors to estimate total uncertainty based on each variable's contribution and sensitivity using Eq. (4). The function's total uncertainty U_R arises from the individual uncertainties $u_1, u_2, \dots, u_n$ of independent variables $x_1, x_2, \dots, x_n$, weighted by their sensitivity coefficients $\frac{\partial R}{\partial x_1}$.

$$U_R = \left[\left(\frac{\partial R}{\partial x_1} u_1 \right)^2 + \left(\frac{\partial R}{\partial x_2} u_2 \right)^2 + \dots + \left(\frac{\partial R}{\partial x_n} u_n \right)^2 \right]^{\frac{1}{2}} \quad (4)$$

2.4.1 Energy and exergy analysis

The experiment was conducted under controlled room temperature and pressure. The different parameters measured with the degree of accuracy and instruments incorporated are represented in Table 2. The test for energy and exergy analysis was carryout out with engine. speed of 800 rpm, 1400 rpm, 2000 rpm, and 2600 rpm. To control uncertainty in the measurement parameters, the test was conducted completely for each fuel sample with sufficient time interval of 30 minutes.

Energy analysis was performed using the first law of thermodynamics through energy balance and efficiency. The engine was treated as a steady-state open system and control volume for both energy and exergy analyses, with fuel and air entering, and mechanical work, heat loss, and exhaust gases exiting. For both the energy (First Law) and exergy (Second Law) analyses, the engine was modeled as a steady-state open system as shown in Table 4. The entire engine was designated as the control volume as shown in Fig. 5. It was assumed that fuel and air enter this volume, while mechanical work, heat losses, and exhaust gases leave at constant rates.

In order to simplify the calculation, the following assumptions were considered:

1. The engine runs at a steady state.
2. The entire system is considered as the control volume.
3. The composition of air and exhaust gas forms an ideal gas.
4. Potential and kinetic energy effects of the fuel mixture and outgoing exhaust gases are ignored.
5. Reference test conditions are $P_0 = 1$ atmosphere, $T_0 = 25$ °C.
6. Combustion is complete.

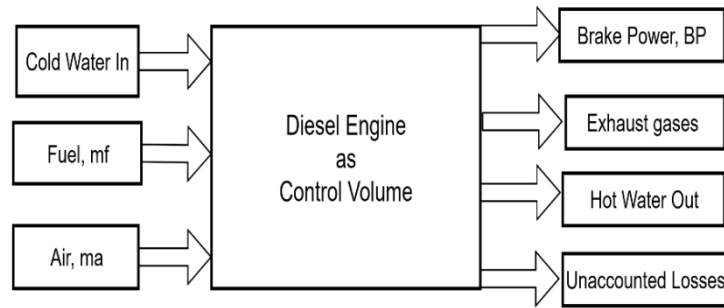


Fig. 5 Input parameter and out parameter from the engine test

Energy analysis

The energy analysis for a diesel engine involves the application of the First Law of Thermodynamic. These analyses were performed in accordance with the conservation of mass and energy principles, as detailed in Eq. (5) and (6). Where m_{in} = inlet stream mass, m_{out} = outlet stream mass, Q = net heat input, and h = enthalpy.

$$\sum m_{in} = \sum m_{out} \quad (5)$$

$$Q - W = \sum m_{out} h_{out} - \sum m_{in} h_{in} \quad (6)$$

Exergy analysis

Exergy analysis considers the irreversibility in the system when determining energy's capacity to carry out useful work. It involves exergy change of a system in thermodynamic process. This analysis helps to identify the optimal operating conditions of the engine and provides a more comprehensive understanding of energy losses, which energy analysis alone cannot accurately determine. These exergy terms of these fundamental equations for exergy analysis, derived from the 2nd law of thermodynamics as shown in Eq. (7) and (8).

$$E_{Xin} = E_{Xout} + E_{Xdest} \quad (7)$$

$$E_{Xair} + E_{Xfuel} = E(m_{out} + \epsilon_{out}) + E_{Xexh} + E_{Xwork} + E_{Xcw} + E_{Xdest} \quad (8)$$

Governing equations for calculating exergy and energy summarized in Table 4.

Table 4 Equations for calculating exergy and energy analysis

Calculations	Descriptions
Energy analysis [35,39,41]	
$E_{in} = E_{bp} + E_{exh} + E_{cw} + E_{un}$	Energy balance equation
$E_{in} = \dot{m}_f \times LCV$	Input fuel energy
$E_{bp} \text{ or } BP = \omega \times T$	shaft work (brake power) energy
$E_{cw} = \dot{m}_w \times C_{pw}(T_{cw,out} - T_{cw,inlet})$	Energy loss in cooling water
$E_{exh} = (\dot{m}_{exh}) \times C_{p,exh} \times (T_2 - T_{amb})$ or	Energy loss in exhaust gas
$E_{ex} = \frac{m_{cw} \cdot C_{pw}(T_{cw,out} - T_{cw,inlet})}{T_5 - T_6} \times (T_2 - T_{amb})$	
$E_{un} = E_{in} - (E_{bp} + E_{cw} + E_{exh})$	Unaccounted energy losses
$\eta_{Energy} = \frac{(\text{work done})BP}{E_{in}}$	Energy efficiency
Exergy analysis [42–44]	
$E_{Xin} = \dot{m}_f \times \phi_{fuel} \times LCV$	Input fuel exergy
$E_{Xwork} = B_p$	Exergy of shaft work

$E_{X_{cw}} = m_{cw} \times C_{p_{cw}} \times (T_{cw,out} - T_{cw,inlet}) - T_{amb} \times \ln\left(\frac{T_{cw,out}}{T_{cw,inlet}}\right)$	Exergy loss in cooling water
$E_{X_{exh}} = (\dot{m}_f + \dot{m}_{air}) \times C_{p_{exh}} \times \left[(T_2 - T_{amb}) - T_{amb} \ln\left(\frac{T_2}{T_{amb}}\right)\right]$	Exergy loss in exhaust gas
$Ex_{dest} = E_{Xin} - (E_{Xwork} + E_{Xcw} + E_{Xexh})$	Exergy destruction
$\eta_{exergy} = \frac{E_{Xwork}}{E_{Xin}}$	Exergy efficiency

3. Results and discussion

3.1 CaO/Al₂O₃ characterization

The FTIR spectrum of CaO/Al₂O₃ composite material presents some characteristic absorption bands, which are corresponding to the functional groups and bonding environments in the material. The results of FTIR shows various absorption peaks are shown in Fig. 6a. The vibrations of composite heterogeneous catalyst of CaO/Al₂O₃ were observed between 4000 cm⁻¹ up to 500 cm⁻¹ wave number. Peak at 3637.37 cm⁻¹ corresponds to hydroxyl (-OH) stretching from adsorbed moisture or surface hydroxyl on alumina (Al₂O₃) and calcium (CaO), contributing to basicity and reactivity. Peak at 1796.67 cm⁻¹ relates to carbonyl (C=O) stretching from carbonate species or adsorbed CO₂; CaO reacts with CO₂ to form calcium carbonate (CaCO₃). Peak at 1397.32 cm⁻¹ is from symmetric stretching of carbonate (CO₃²⁻) groups, indicating surface carbonates. Peak at 869.44 cm⁻¹ suggests Al–O–Al bending in alumina. It also overlaps with out of plane bending vibrations of carbonate species. The low frequency at 424.18 cm⁻¹ band reveals the characteristics of Al-O stretching vibrations in octahedral or tetrahedral coordination environments, indicates the presence of Al₂O₃ as the support structure. The co-existence of Ca-O and Al-O in these structures is thus confirmed. This results consistent with findings reported by [45,46].

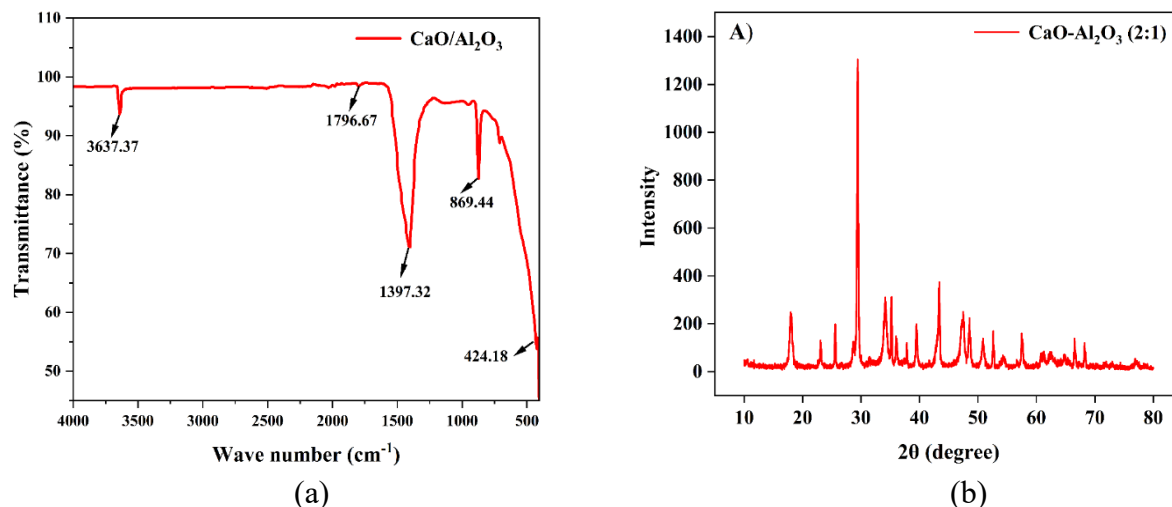


Fig. 6 Characterized result of CaO/Al₂O₃ catalyst: (a) FTIR analysis, (b) XRD results

BET analysis was conducted for the calcinated heterogeneous catalysts at different ratios of CaO and Al₂O₃ for 2:1 ratio. The result of BET surface area analysis shows the values for both samples of 2:1 ratio of calcium oxide to aluminum oxides. The sample 2:1 exhibited a much higher surface area (84.25 m²/gm). The 2:1 sample's higher surface area indicates increased porosity due to a higher CaO ratio. These results suggest that the material's textural characteristics are significantly impacted by changes in the CaO/Al₂O₃ ratio, which could have an impact on its catalytic or adsorption uses.

Fig. 6b shows XRD patterns of the CaO–Al₂O₃ (2:1) composite, calcined and synthesizing the heterogeneous catalyst. Based on the analysis, characteristic diffraction peaks were observed within the 2θ range of 10° to 80°. The XRD pattern of synthesized CaO–Al₂O₃ (2:1) catalyst defines its crystalline structure. The most intense peak at 2θ = 29.4° is attributed to CaO, indicating it is the dominant phase. Other sharp peaks between 2θ = 20° and 60° indicate multiple crystalline phases. The pattern shows separate peaks for CaO and Al₂O₃ phases, indicating coexistence and possible improved catalytic performance through synergistic interaction. Sharp peaks at ~29° indicate good calcination and crystallinity, while absence of broad peaks indicates no significant amorphous content and successful synthesis without hindering side products. According to previous studies [45], addition of Al₂O₃ to CaO enhances thermal stability and surface area while maintaining high basicity, which is important for transesterification in biodiesel production.

3.2 CM seed oil yields

The CM seed oil extracted via Soxhlet extraction achieved a yield of 47.64%, as shown in Fig. 1c. The analysis revealed a 47.64% crude oil yield from CM seeds through Soxhlet extraction, indicating their significant potential as a competitive industrial feedstock. The experimental results obtained in this study shows a higher oil yield percentage from CM seed compared to existing literature values reported by [18,23] from the CM seed; whereas *Croton macrostachyus* seeds oil yield was lower than kernels of the same species, as stated by [23]. As stated in previous studies by [23] the *croton macrostachyus* seed oil have the potential to yield an oil content between 40% to 53.35%. The CMS oil yield was comparable to *Jatropha* seed (52.96%) and Castor seed (45–50%) yields, yet higher than that of Cotton seed (15–25%) [47][48]. The results obtained were validated with different researchers results with these feedstocks of non-edible feedstocks (second generation).

3.3 *Croton macrostachyus* seed Oil and Biodiesel characterization

The acid value of CMS oil was assessed via titration. As a critical parameter, FFA influences biodiesel production. The titration was conducted three times to calculate an average value. The acid value (AV) and % of FFA content in the *Croton macrostachyus* seed oil were determined to be 2.50 mg KOH/g and 1.25%, respectively. These outcomes correspond with those documented in the studies of [17,23,24]. The study found that *Croton macrostachyus* seed oil, with a FFA level below 2.5%, is suitable for biodiesel conversion using a single-step transesterification process. The properties of CMS oil were compared with those of *jatropha* oil were found too comparable as shown in Table 5.

Table 5 Comparison of physiochemical property of CMS oil with *jatropha*.

Properties	Croton macrostachyus		Jatropha	
	Current study	Ref [18]	Ref [23]	Ref [47]
Oil yield (%)	47.64	46.85%	50.86	47.16-51.61%
Density of oil at 15°C (kg/m ³)	920	892	904.08	-
Density of oil at 40°C	0.898	-	0.895	-
Kinematic viscosity at 40°C (mm ² /s)	36.29	42.37	40.85	39.3

Specific gravity at 40 °C	0.92	-	0.895	-
Moisture content (%)	0.19	1.68	0.096	-
Acid value (mg KOH/g oil)	2.50	2.36	4.374	2.8
Free fatty acid content	1.25	1.18	2.18	1.5
Saponification value KOH/g oil)	178.89	198.03	187.935	186.5
Iodine Value (mg Iodine/g)	-	64.0	102.64	110.5

Additionally, the produced biodiesel was characterized to assess its physicochemical properties against ASTM standards, verifying its compatibility with diesel engines. Key parameters evaluated included density, viscosity, moisture, acid value, FFA, flash and fire points, pour and cloud points, iodine, and saponification values. Similarly, the produced biodiesel was tested for the acid value after transesterification and the croton macrostachyus biodiesel produced showed acid value of 0.478 mg of KOH/g and FFA value of 0.239 mg KOH/g. These values of AV and FFA CMS biodiesel meets ASTM and EN standards. The kinematic viscosity of CMS oil and biodiesel was measured at 40°C using a rheometer and obtained 36.26 mm²/s and 4.25 mm²/s respectively. The device first measured the dynamic viscosity, which was then converted to a kinematic viscosity. The viscosity was reduced to 4.4 mm²/s after glycerol removal through transesterification, aligning with standard specifications. The study exhibits a density 920 kg/m³ for CMS oil whereas the density of CMS biodiesel minimized to 885.8 kg/m³. The calorific value of the CMS biodiesel was determined to be 19197.8 BTU/LB. Its high calorific value makes it suitable for blending with diesel fuel in IC engine applications. The cetane number of the CMS biodiesel was also obtained 50.87. The flash point and fire point of Croton macrostachyus biodiesel were measured at 197 °C and 242 °C, respectively. The flash and fire points of the fuel were determined using an HFP380 Pensky-Marten's apparatus in accordance with the ASTM D93 standard. The CP and PP value are measured according to ASTM D6752 and EN 14214. The results showed for CMS biodiesel are -0.9°C and -19.9°C for CP and PP respectively. The result obtained in this study fits the standards and the findings of this study align with those reported in previous research by [18,23,24]. The result of CMS biodiesel obtained was summarized in Table 6. with comparing to Jatropha, and cottonseed.

Table 6 Physiochemical property of Croton macrostachyus biodiesel compared to Jatropha, and Cotton seed with standards specification of biodiesel

Parameter	Units	Croton macrostachyus				Cotton seed	Jatropha	Biodiesel standard	
		Current study	Ref [23]	Ref [18]	Ref [24]	Ref [49]	Ref [50]	ASTM D6751	EN 14214
Specific gravity at 24.8 °C	-	0.855	0.865	—	—	—	—	0.85-0.90	0.85
Density at 15 °C	Kg/m ³	885.8	846.30	878	872	887	865.7	820–900	860–900
Kinematic viscosity at 40°C	mm ² /s	4.25	4.43	4.87	4.58	4.19	4.73	1.9-6.0	3.5-5.0
Acid value	mg KOH/g of oil	0.478	0.22	0.48	0.462	—	0.05	min. 0.80	min 0.50
Free fatty acid	mg KOH/g of oil	0.239	0.11	0.24	0.231	—	0.025	≤ 0.4	≤ 0.25
Saponification value	KOH/g of oil	196.67	192.77	120	—	—	202	≤ 215.99	≤ 218.79
Moisture content	Vol %	0.048	0.051	0.027	—	—	—	min 0.05	min 0.02
Lower Calorific value	MJ/Kg	41.7	40.04	40.2	40.017	39.75	39.82	Min 38	Min 35.00
Cloud point	°C	-0.9	-9	—	—	1.7	3	-15 to 5	-3 to 12
Pour point	°C	-19.9	-15	—	—	-12.5	3	-35 to-15	-15 to 16
Flash point	°C	197	175	198	218	210	184.5	min100–170	min 120
Fire point	°C	242	180	—	—	—	—	—	—
Iodine value	Mg Iodine/g of oil	105.45	105.45	102.1	107.61	—	99	—	120
Cetane number		50.89	50.89	56	50.78	48.1	51	min 47	min 51

FTIR spectroscopy was used to analyze the functional groups of Croton macrostachyus seed oil and its biodiesel. Spectra were recorded at room temperature from 4000 to 400 cm⁻¹ Fig. 7. shows key peaks confirming the conversion of triglycerides to FAMES via transesterification. The 3500–3000 cm⁻¹ band in both Croton macrostachyus oil and biodiesel (FAME) reflects -OH stretching from hydroxyl-containing compounds. Peaks at 2922.73 and 2854.55 cm⁻¹ indicate CH₃ stretching of long hydrocarbon chains, unchanged after conversion, confirming the hydrocarbon backbone is retained. The 1745.45 cm⁻¹ band in CMS oil and biodiesel indicates C=O ester stretching, confirming ester linkage. Bands at 1454.55 cm⁻¹ (oil) and 1440.91 cm⁻¹ (biodiesel) correspond to

–C–H and –CH₃ vibrations, confirming methyl ester formation. A decrease in intensity at 1236.36 and 1154.55 cm⁻¹ in the biodiesel spectrum confirms glyceride removal. Peaks at 1745.45 cm⁻¹ (C=O) and 1168.18 cm⁻¹ (C–O) indicate ester formation, typical of fatty acid methyl esters, confirming successful transesterification. The 1154.55 cm⁻¹ band in both oil and biodiesel corresponds to C–O and C–O–C stretching, indicating ester and ether groups. The 718.18 cm⁻¹ peak in CMS oil and biodiesel reflects –CH₂– vibrations, showing the fatty acid framework is retained. Shifts from 1454.55, 1236.36, 1134.55, 718.18 cm⁻¹ (oil) to 1440.91, 1245.45, 1168.18, 718.18 cm⁻¹ (biodiesel), along with the loss of glycerol peaks and emergence of ester peaks (1745.45, 1168.18, 1245.45 cm⁻¹), confirm successful transesterification, consistent with prior studies.

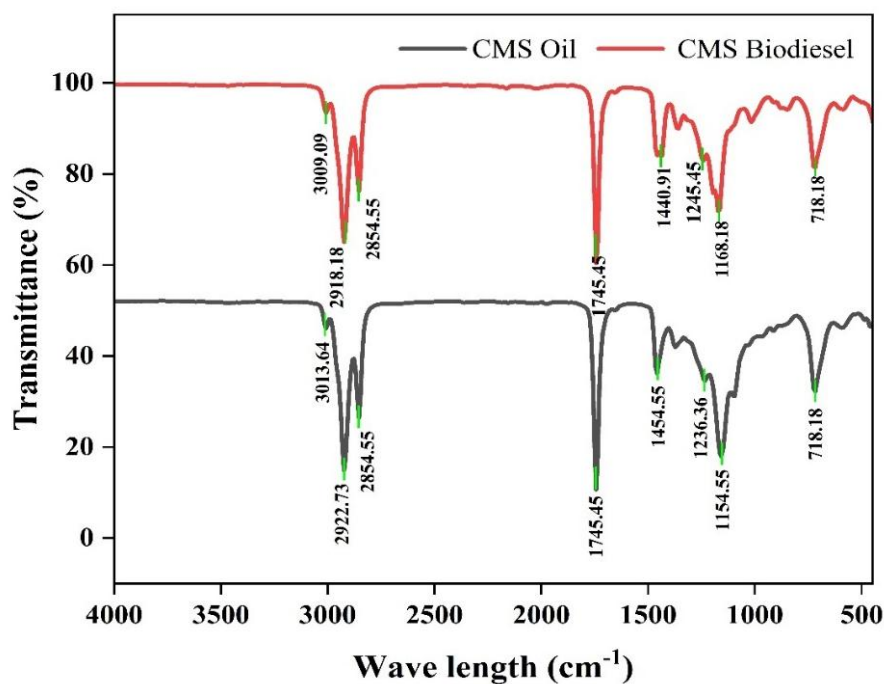


Fig. 7 FTIR result of the CM seed oil and biodiesel (methyl ester)

The FAME composition in the biodiesel of croton macrostachyus seed oil (CMS) was analyzed using GC-MS. The fatty acid methyl ester (FAME) profile of CMS biodiesel was determined via Gas Chromatography–Mass Spectrometry (GC-MS) to evaluate its essential physicochemical properties. Ten (10) major fatty acid methyl esters (FAMEs) were revealed in Croton macrostachyus seed oil biodiesel through GC-MS analysis. The three different kinds of molecules were identified by the analysis polyunsaturated (Cn:2,3), monosaturated (Cn:1), and saturated

(C_n:0) fatty acids. The results of fatty acid compositions of croton macrostachyus methyl esters contain Lauric acid (0.109%), Myristic acid (3.34%), 13-Methyl tetra decanoic acid (0.052%), Palmitic acid (14.71%), Margaric acid (0.3%), Oleic acid/13-octa decanoic acid (33.72%), Linoleic acid (41.83%), Stearic acid (3.78%), Cis-13-Eicosenoic acid (1.15%), Eicosanoic acid (0.79%), Behenic acid (0.118%), and Lignoceric acid (0.1%). The GC-MS analysis of FAME in the CMS biodiesel reveals a dominance of saturated fatty acid, while unsaturated fatty acids (monounsaturated and polyunsaturated). The CMS biodiesel FAME profile consists of 23.13% saturated fatty acids, mainly palmitic acid (C16:0, 14.71%) and stearic acid (C18:0, 3.78%), with minor myristic (C14:0) and margaric (C17:0) acids. Monounsaturated fatty acids account for 34.87%, dominated by oleic acid (C18:1, 33.78%) and minor cis-13-eicosenoic acid (C20:1, 1.15%). Polyunsaturated fatty acids are mainly linoleic acid (C18:2, 41.83%). The highest and lowest FAME percentages are linoleic acid (41.83%) and 13-methyl-tetradecanoic acid (0.052%). Overall, CMS biodiesel is rich in unsaturated fatty acids (mainly C18:2 and C18:1) with a balanced saturated content (C16:0 and C18:0). GC-MS analysis of CMS biodiesel confirms linoleic acid as the dominant unsaturated fatty acid, consistent with previous studies [17,23,24]. In this study, total unsaturated fatty acids account for 76.70%, lower than rubber seed (78.9%), soybean (81.14%), olive (84.4%), mustard (86.18%), and Jatropha (79.56%) oils, while CMS leaf oil contains 39.34% saturated and 60.65% unsaturated fatty acids, mainly palmitic acid (38.91%) [51].

3.4 Engine Performance

3.4.1 Brake thermal efficiency

Fig. 8a. displays the BTE of all tested diesel and biodiesel blend samples under full load conditions across different engine speeds. The findings indicate that BTE is lower biodiesel blends relative to B0. In contrast, diesel consistently shows is higher BTE at all tested engine speeds. The increase in BTE for pure diesel up to 2000 rpm suggests that it resulted from high calorific value, lower viscosity, better atomization, and finer droplets [52]. The lower BTE of biodiesel–diesel blends compared to B0 is mainly due to biodiesel's higher viscosity, density, oxygen content, and lower calorific value [52,53]. The highest BTE achieved for diesel fuel, CMB10, CMB15, CMB20, CMB25 were recorded 31.12%, 28%, 27.1%, 29.3%, and 26.4% respectively. Beyond 2000 rpm, BTE progressively reduced along with engine speed increasing, reaching its minimum value for each of the investigated fuels. CMB20 (20% biodiesel, 80% diesel) shows the highest brake thermal efficiency among the blends, due to optimal oxygen content and balanced fuel properties,

which enhance combustion, unlike higher blends that face reduced energy density or higher viscosity.

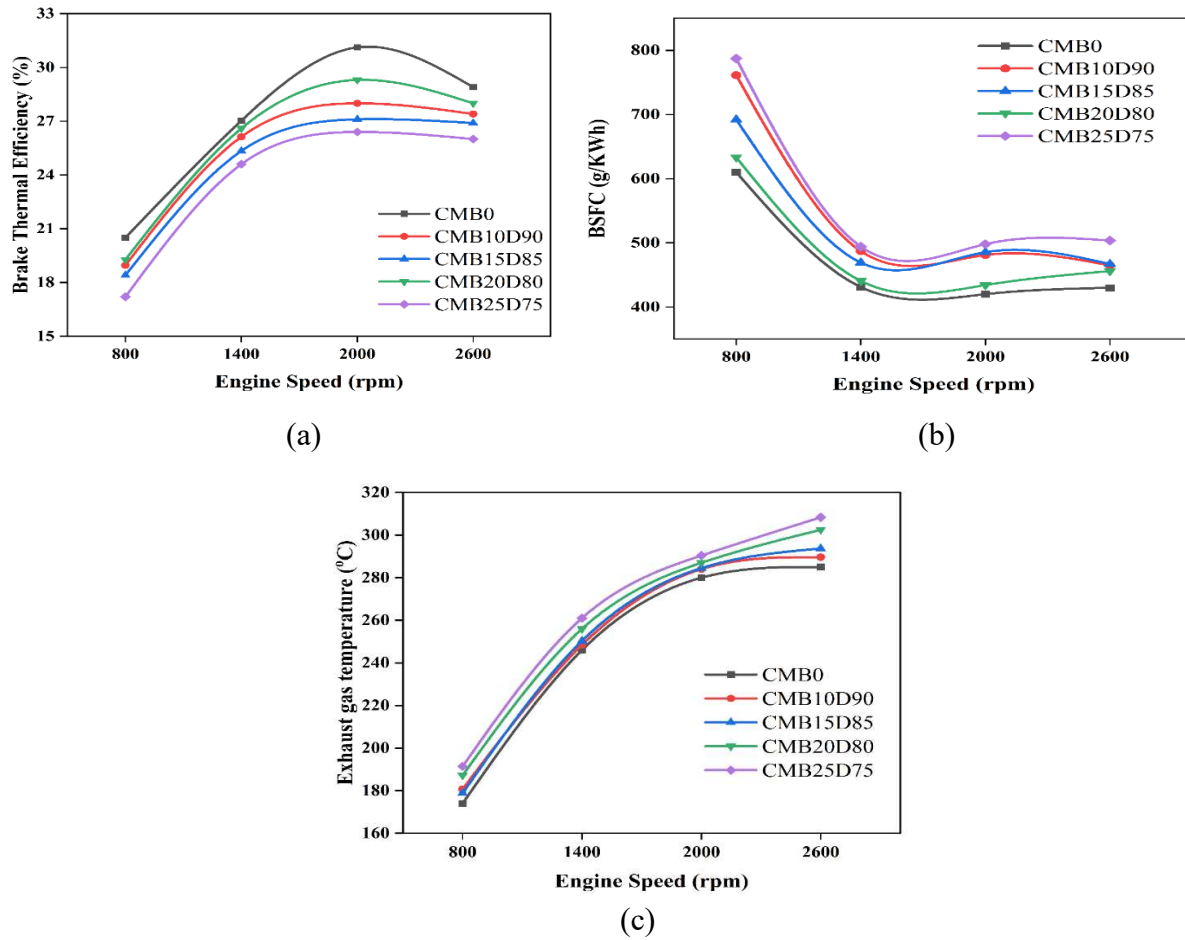


Fig. 8 BTE, BSFC, and EGT with varied speed: (a) BTE, (b) BSFC, (d) EGT

3.4.2 Brake specific fuel consumption (BSFC)

Brake specific fuel consumption quantifies the fuel consumption necessary to deliver a unit of engine power, serving as a critical indicator of engine efficiency. Fig. 8b shows that BSFC for CMS biodiesel blends decreases with engine speed to a minimum, then rises at higher speeds compared to standard diesel. Due to its lower calorific value and density, CMS biodiesel requires higher mass flow rates than diesel at all engine speeds to deliver equivalent power. The maximum BSFC occurred at 800 rpm, due to poor combustion efficiency and higher frictional losses. The lowest BSFC for all fuel types occurred at 1400 rpm. However, beyond 2000 rpm, BSFC began to rise gradually. The results indicate that biodiesel blends have higher BSFC than pure diesel under full load conditions, due to the combined effects of biodiesel's greater density, lower calorific

value, and higher viscosity [54]. The lowest BSFC values for each fuel sample were observed at different engine speeds. For B0, CMB10, CMB15, CMB20, and CMB25, the minimum BSFC were 420, 437.1, 469.13, 434.2, and 494 g/kWh, respectively, which is higher when compared to pure diesel. Because of biodiesel lacking proper atomization and spray pattern, which causes poor combustion and higher fuel consumption. In this study, the tested fuel across all blend ratios, the averages of BSFC at CMB20 are lower than CMB10, CMB15, and CMB25. In contrast, CMB25 shows a higher BSFC than both pure diesel and blends, mainly due to its increased viscosity, LCV, and higher proportion of croton macrostachyus seed biodiesel. Similar trends were observed in biodiesel blends from sunflower, rapeseed, soybean, and cottonseed [55], and Croton megalocarpus biodiesel [56], validating the findings of the present CMS biodiesel study

3.4.3 Exhaust gas temperature (EGT)

Exhaust gas temperature (EGT) indicates fuel combustion efficiency and thermal behavior, influencing engine performance, emissions control, and post-combustion treatment effectiveness. Fig. 8c shows that EGT increases with engine speed for all tested fuels, including diesel and CMB0, CMB10, CMB15, CMB20, and CMB25 biodiesel blends. The maximum EGT was achieved at 2600rpm for all fuel blends. The higher EGT obtained for CMB25 at 800rpm, 1400rpm, 2000rpm, and 2600rpm were 191.4 °C, 261 °C, 290.4 °C, and 308.3 °C, respectively obtained were engine runs at full load conditions due to high biodiesel concentrations. As a result, pure diesel fuel (CMB0) had the minimum EGT values, while CMS biodiesel blend fuels had the maximum EGT values. EGT rises with engine speed due to higher cylinder temperatures and shorter combustion durations [56,57]. Increased CMS biodiesel concentration further raises EGT across all speeds, as its oxygen content enhances combustion efficiency and fuel characteristics. There is an increase in exhaust temperature with increasing in the percentage's blends and vice versa. Similar trends were reported by [56] and [24], showing EGT rises with engine speed and blend percentage under full-load conditions.

3.5 Exhaust emission characteristics

3.5.1 Carbon dioxide Emission

The higher percentages of CO₂ are due to complete combustion, and excess oxygen (O₂) contents in the blended fuels result in easy conversion of CO into CO₂. As illustrated in Fig. 9, CO₂

emissions fluctuate with changes in engine speed under full load conditions. It is evident petrol diesel fuel produces more CO₂ than that of all CMS biodiesel blends. The highest CO₂ emission is observed for CMB0, whereas biodiesel blends with higher biodiesel proportions, such as CMB25, exhibit reduced emissions. Furthermore, CO₂ emissions decline with rising of engine speed across all biodiesel blends. The decrease is mainly due to the blend's higher oxygen content and preheating effects, along with its lower carbon-to-hydrogen ratio compared to diesel, all of which enhance combustion efficiency [53,58]. CO₂ emissions slightly rise with engine speed for all fuels tested [59], indicating more complete combustion in biodiesel blends than in diesel.

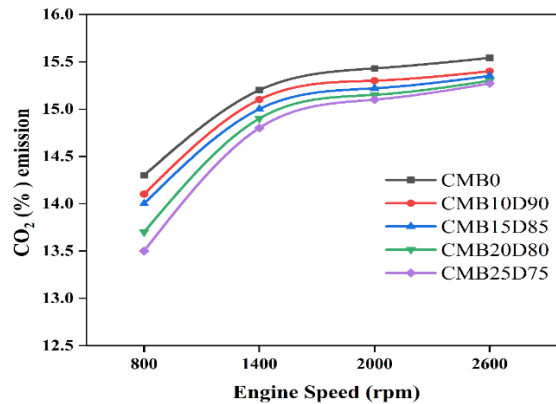


Fig. 9 CO₂ emission with varied speed

3.6 Oxides of nitrogen (NO_x)

Fig. 10 shows that NO_x emissions increase with rising engine speeds for both biodiesel blend and pure diesel. Maximum NO_x emission for all the fuels tested was obtained at 2600 rpm, while minimum was obtained at 800 rpm. When compared to pure diesel (CMB0), average NO_x emission increased by 1.8%, 4.66%, 7.24%, and 8.6% for CMB10, CMB15, CMB20, and CMB25, respectively. The NO_x increases are directly proportional to biodiesel ratios in the blend, primarily reason high oxygen level in the biological nature of biodiesel. CM biodiesel blends produce higher NO_x emissions than pure diesel, because of increased oxygen content, higher combustion temperatures, and greater viscosity. These factors enhance combustion intensity and thermal NO_x formation while reducing atomization efficiency.

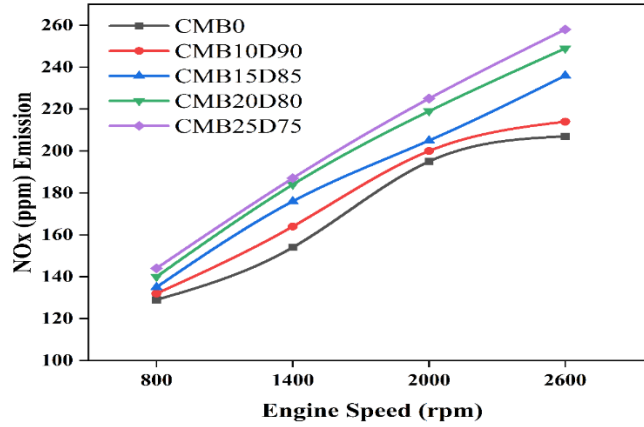


Fig. 10 NO_x emission with varied speed

3.7 Energy analysis

3.7.1 Input fuel energy

As shown in Fig. 11a, the highest input fuel energies for B0, CMB10, CMB15, CMB20, and CMB25 were recorded at 2600 rpm under full load, with values of 20.25, 17.85, 15.68, 18.12, and 19.2 kW, respectively. The lowest values occurred at 800 rpm, measuring 3.9, 3.86, 3.83, 3.5, and 3.72 kW, respectively. The finding reveals that the CMB10 blend bring better input fuel energy in contrast to other blends of biodiesel, owing to the lower blend ratios (CMB 10% and diesel 90%), which have better LCV compared to diesel fuel.

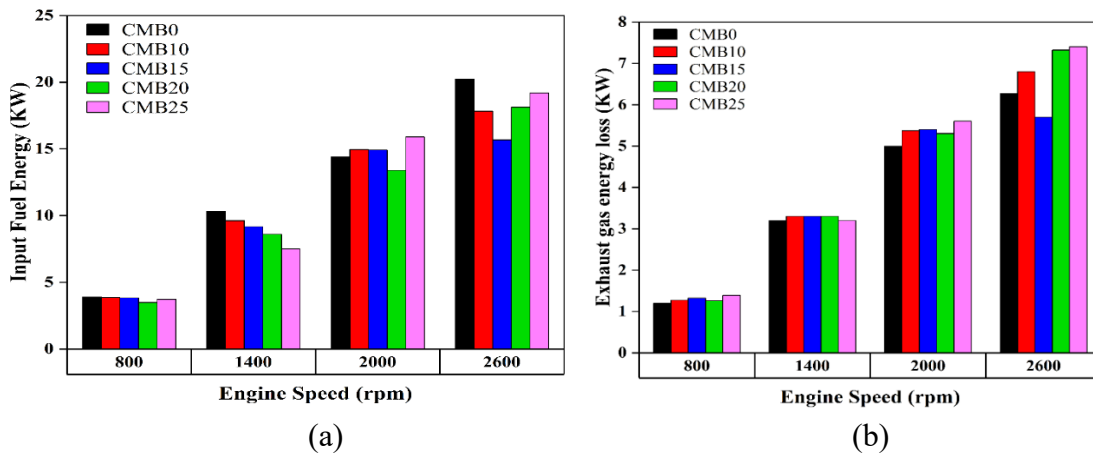


Fig. 11 Input fuel energy and Energy lost in exhaust gas variation with speed: (a) Energy loss in exhaust gas, (b) Input fuel energy

3.7.2 Exhaust gas energy loss

Fig. 11b illustrates the variation of exhaust gas energy loss with engine speed for various blends of biodiesel and pure diesel fuel. As noted, energy loss in exhaust gas grow with rising speed at full load operations. Pure diesel shows the lowest exhaust energy loss compared to biodiesel blends. At 2600 rpm, losses are 6.27, 6.8, 5.7, 7.32, and 7.4 kW for B0, CMB10, CMB15, CMB20, and CMB25, respectively, with CMB25 having the highest loss. This is attributed to higher biodiesel ratios, greater oxygen content, increased viscosity, lower calorific value, and the impact of fuel energy consumption on the engine, all of which promote exhaust heat loss.

3.7.3 Energy loss in cooling water

Fig. 12a shows the energy lost through cooling water for different biodiesel blends and pure diesel fuels at varying engine speeds under full load conditions. The findings show that at full load and varied engine speeds, the energy passed to cooling water for all fuel samples increases with the rise of speed. The results generally show biodiesel blends result in lower cooling water energy losses than pure diesel (CMB0), especially at lower and moderate engine speeds. However, in this study at 2600 rpm, particularly for CMB25, higher energy loss in cooling energy results from higher overall heat generation from complete combustion, and friction transfers more energy to the cooling water circulated in the water jackets.

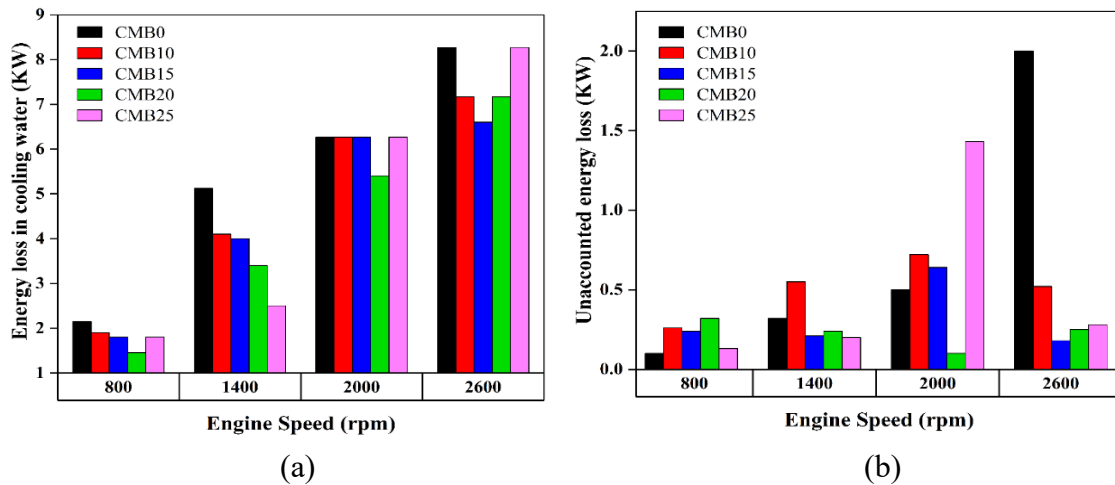


Fig. 12 Energy loss in cooling water and Unaccounted loss variation with speed: (a) Energy loss in cooling water, (b) Unaccounted loss

3.7.4 Unaccounted energy loss

Fig. 12b shows unaccounted energy losses for CMB0, CMB10, CMB15, CMB20, and CMB25 at engine speeds of 800, 1400, 2000, and 2600 rpm. The study reveals that the impact of fuel blending on unaccounted energy loss is highly dependent on engine speed. The maximum and minimum unaccounted energy losses occur at 800 and 2600 rpm, respectively, with values of 0.1 kW and 2 kW, for pure diesel. For the blends, the maximum and minimum energy loss was observed for CMB10 at 2600 rpm and CMB25 at 800 rpm, respectively. However, CMB25 shows maximum unaccounted energy losses at 2000 rpm are 1.43 kW, which is very close to the results of pure diesel at 2600 rpm because the fuel contains more oxygen, resulting in complete combustion. As the temperature of combustion rises, high heat transfers are formed.

3.7.5 Energy distribution in percentages

Fig. 13 demonstrates the energy distribution across different fuel samples at various engine speeds. The findings show how different biodiesel blends (CMB0 to CMB25) distribute energy at varying engine speeds (800, 1400, 2000, and 2600 rpm). The energy efficiency typically peaks at 2000 rpm, and the CMB20 blend achieves the highest energy efficiency of 20%. Energy efficiency is relatively low at low speeds (800 rpm) and ranges between 11% and 13%. Overall, cooling water energy loss (CWEL) percentages generally decreases with increased engine speed for all fuel blends, leveling out around 40–43% at 2600 rpm, suggesting that heat losses to the cooling system are much less significant at high speeds and full loads. Exhaust energy losses rise with engine speed and biodiesel content percentage. The highest exhaust loss percentages achieved is 43% for CMB25 at 2000 rpm and indicates more thermal energy lost with exhaust because of change in combustion dynamics or characteristics of biodiesel fuel. Unaccounted energy losses in percentages, while typically small, rise moderately with engine speed and with proportion of blend, up to a maximum of 10% for CMB20 at 2600 rpm. These losses are likely due to friction, radiation, and other small inefficiencies not include in the main energy categories.

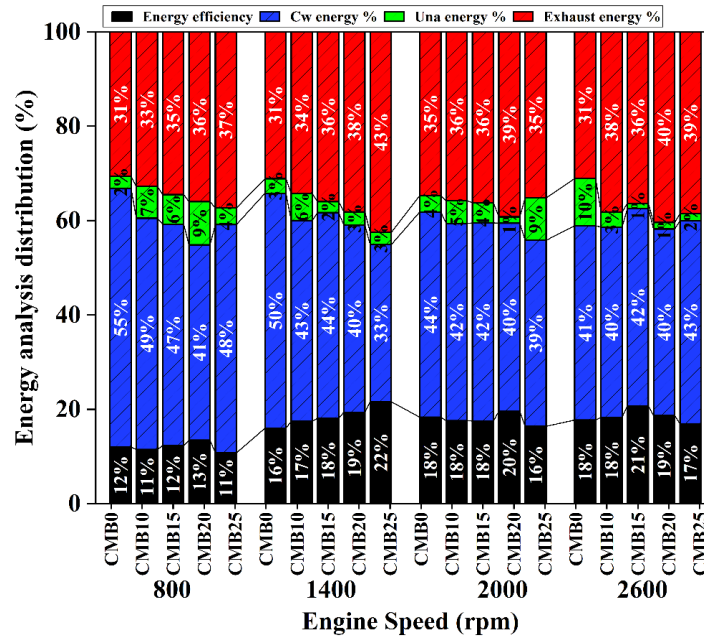


Figure 13. Energy distribution for various fuel samples at varied engine speed

3.8 Exergy Analysis

3.8.1 Input fuel exergy

The input fuel exergy of pure diesel is higher than Croton macrostachyus biodiesel fuel blend, as shown in Fig. 14a. The result indicates that as volume % of biodiesel increases, the input fuel exergy and engine speed also increase due to more fuel injections. As engine speed increases, fuel mass flow rate and incoming exergy rise. Higher biodiesel content further boosts fuel exergy due to its oxygen content, which enhances exergy properties [122]. The input fuel exergy value of B0 (pure diesel) is 4.17 kW which indicates higher input fuel exergy at 800 rpm compared to the biodiesel blends. Maximum input fuel exergy from the biodiesel blends at 800 rpm is 4.12 kW for the CMB10 (10% CM biodiesel and 90% diesel) blend, whereas the CMB20 biodiesel blend possesses the value of 3.76 kW, the lowest input fuel exergy among other blends at 800 rpm of engine speed. At maximum engine speed of 2600 rpm, pure diesel has a maximum exergy input of 21.67 kW, while the maximum exergy amount for biodiesel blend is observed for the CMB25 biodiesel blend, and the minimum pertains to CMB15 biodiesel.

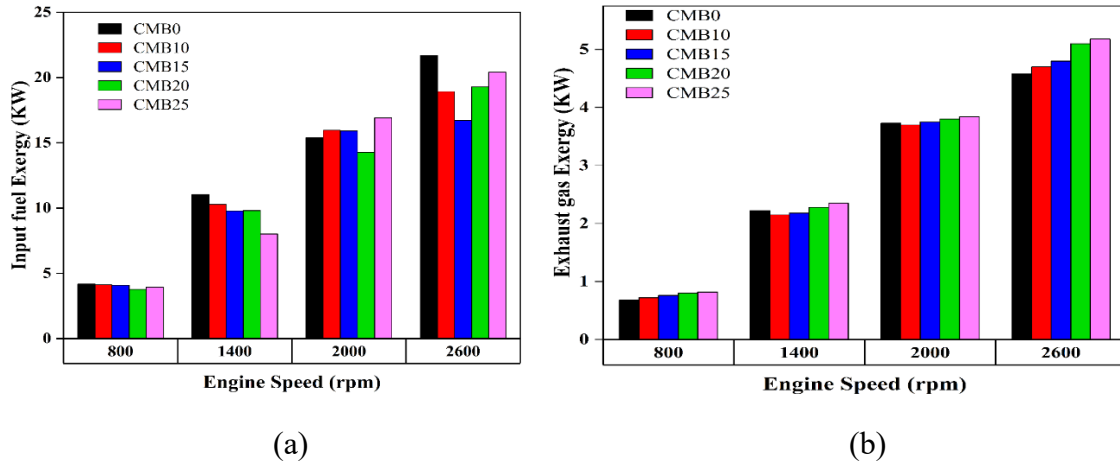


Fig. 14 Input fuel exergy and exhaust gas exergy variation with speed; (a) Input fuel exergy, (b) Exhaust gas exergy

3.8.2 Exhaust gas exergy

As illustrated in Fig. 14b, the biodiesel blends examined exhibit greater exhaust energy losses in contrast to pure diesel. The maximum loss of exergy due to exhaust gas observed at CMB25 is 5.18 kW, while the minimum loss via exhaust gas for diesel is 4.58 kW at 2600 rpm of the engine speed. Biodiesel blends have higher EGT due to oxygen in them, larger biodiesel volume fractions, lower heating value, and more fuel entering for producing power. Exhaust gas exergy increases with engine speed due to more intense combustion, raising EGT and air fuel flow rates. The lowest losses occur at 800 rpm for B0 (0.68 kW) and CMB10 (0.72 kW), while the highest is 0.82 kW for CMB25. At low speeds, reduced air–fuel volume and lower temperatures result in minimal exhaust exergy, even under full load.

3.8.3 Exergy loss in cooling water

Fig. 15a illustrates the variation in cooling water exergy loss for the test fuels under full-load engine speed conditions. The exergy loss in cooling water observed at 800 rpm and 1400 rpm engine speeds slightly increase for diesel relative to the biodiesel blends of CMB10, CMB15, CMB20, and CMB25. This indicates that pure diesel may be less efficient at converting fuel energy to useful work at low speeds, with more energy lost as heat through the cooling system. The bar graph shows that at 2000 and 2600 rpm, exergy losses to cooling water for all biodiesel blends are comparable to diesel. Higher engine speeds increase fuel injection and peak temperatures, leading

to greater heat rejection. Minimizing cooling water exergy losses requires selecting an optimal biodiesel blend ratio, consistent with findings by [123].

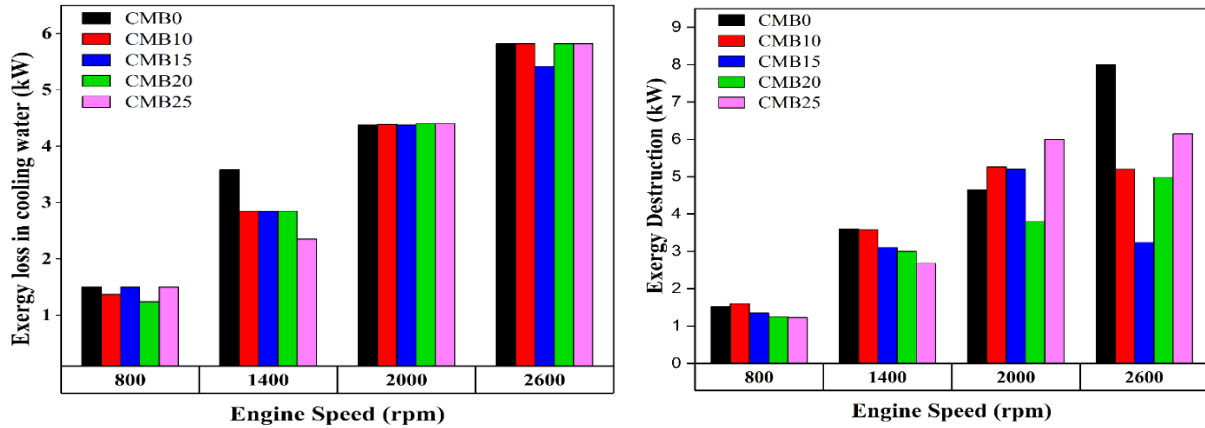


Fig. 15 Exergy loss in cooling with varied speed: (a) Exergy loss in cooling water, (b) Exergy destruction with varied speed

3.8.4 Exergy destruction

Fig. 15b illustrates exergy destruction (kW) for CMB0, CMB10, CMB15, CMB20, and CMB25 at engine speeds of 800, 1400, 2000, and 2600 rpm. Exergy destruction rises with engine speed due to higher fuel consumption, elevated combustion temperatures, and increased irreversible engine processes. At 800 rpm, the lowest tested speed, exergy destruction is minimal for all fuel blends, measuring 1.52, 1.6, 1.35, 1.25, and 1.23 kW for B0, CMB10, CMB15, CMB20, and CMB25, respectively. CMB20 and CMB25 exhibit the lowest exergy destruction, while CMB10 is slightly higher than diesel. Biodiesel blending improves thermodynamic efficiency at low speeds by reducing irreversibility. At 1400 rpm, all blends reduce exergy destruction, with B0 highest and CMB20 lowest. At 2000 rpm, CMB25 peaks at 6 kW, CMB20 remains lowest. At 2600 rpm, B0 is highest (8 kW), and CMB15 shows the best performance (3.24 kW). At higher engine speeds, base fuel (CMB0) shows increasing exergy destruction with the highest value at 2600 rpm

3.8.5 Exergy distribution in percentages

Fig. 16 shows the exergy distribution of biodiesel-diesel blends at 800, 1400, 2000, and 2600 rpm, divided into exergy efficiency, cooling water exergy, exhaust gas exergy, and exergy destruction percentages. Exergy efficiency generally rises with engine speed for all fuels, starting low at 800

rpm (10–13%) and peaking at 20% for CMB15 and CMB25 at 2600 rpm and 1400 rpm, respectively, showing higher useful exergy output, especially with low- to mid-level biodiesel blends. Cooling water exergy remains fairly consistent across speeds, ranging from 26% to 38%, and slightly decreases at higher engine speeds due to reduced heat rejection. Exhaust gas exergy increases with blend ratio and engine speed up to CMB20, while CMB25 shows inconsistent results. Values range from 16% for CMB0 at 800 rpm to a maximum of 30% for CMB25 at 1400 rpm, indicating more exergy loss at higher blends and speeds, which could be recovered via waste heat recovery. The exergy destruction is greatest at 800 rpm reveals 39% for the CMB10 blend ratio. At 2600 rpm, it is considerably lower, with the lowest being 19% for the CMB15 blend.

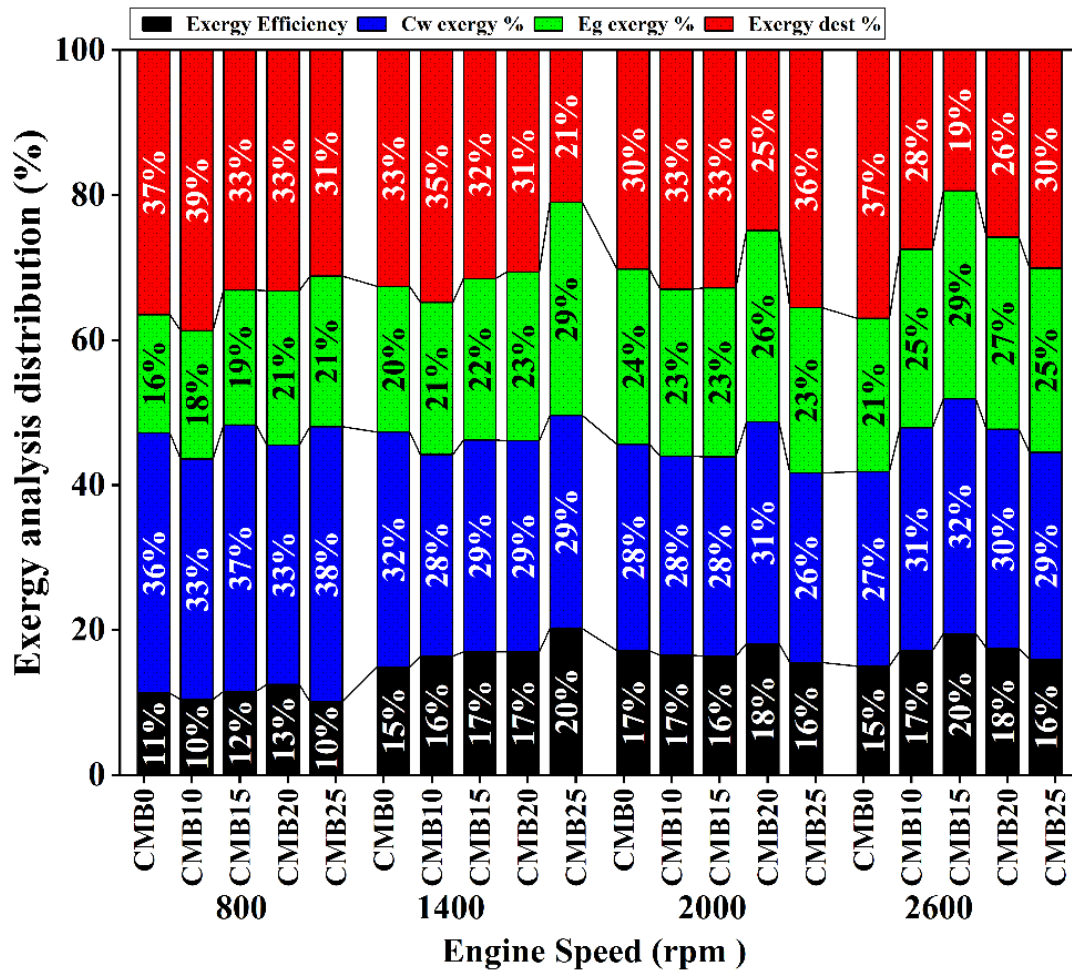


Fig. 16 Exergy distribution for various fuel samples different engine speed

4. Conclusion

This study experimentally investigates the engine performance, energy, exergy, and emission characteristics of biodiesel blends derived from *Croton macrostachyus*, tested in a compression ignition engine. As a novelty, this study observes the energy and exergy characteristics of *Croton macrostachyus* seed biodiesel blends. Also, this study demonstrates the emission and engine performances CMS biodiesel blends. Tests were conducted at constant load and variable engine speeds of 800, 1400, 2000, and 2600 rpm. The study evaluates fuel energy and exergy input rates, exhaust energy and exergy rates, energy and exergy losses in cooling water, unaccounted energy losses, exergy destruction, along with energy and exergy efficiencies. Therefore, the following conclusions are drawn from results and discussion part:

- *Croton macrostachyus* seed oil was extracted using solvent methods, yielding 47.64% crude oil, which was then purified and characterized.
- Composite heterogeneous catalysts were synthesized via calcination of a 2:1 CaO–Al₂O₃ hybrid in a muffle furnace and characterized by FTIR, XRD, and BET analyses. The catalyst's abundant basic sites confer high activity, enhancing transesterification efficiency for biodiesel production.
- *Croton macrostachyus* biodiesel was produced from CMS oil via transesterification, achieving a 93.73% yield using CaO/Al₂O₃ catalyst under conditions of 11.91:1 methanol-to-oil molar ratio, 53.78°C, 3.19 wt.% catalyst, and 82.5 minutes reaction time.
- Brake thermal efficiency (BTE) of *croton macrostachyus* biodiesel blends showed lower BTE compared to (B0) pure diesel. From the blends, CMB20 achieved maximum BTE of 29.3%, though this was reduced by 5.85% than B0. This improvement of BTE for CMB20 resulted due to optimal oxygenations and balanced fuel properties, which promote more complete combustion, efficient atomization and ignition.
- Brake specific fuel consumption (BSFC) increased with higher biodiesel blending ratios, owing to the lower energy density, reduced heating value, and higher viscosity of biodiesel. Compared to B0, CMB25 showed an 8.2% increase in BSFC, while CMB20 recorded a 3.86% increase and the lowest in BSFC among the blends.
- The exhaust gas temperature (EGT) rises with increased biodiesel concentrations, and engine speeds for all tested samples. At 2600 rpm, EGT rose by 1.6% for CMB10, 3.05% for CMB15, 6.14% for CMB20, and 8.24% for CMB25 compared to pure diesel. This rise

is attributed to high in-cylinder temperatures and shorter combustion durations, further supported by the additional oxygen content of CMS biodiesel.

- CO₂ emissions were lower for biodiesel blends compared to pure diesel (B0). Pure diesel emitted 0.7%, 0.76%, 1.23%, and 1.55% more CO₂ than CMB10, CMB15, CMB20, and CMB25, respectively. NO_x emissions increase with engine speed for biodiesel blends and pure diesel. This implies that at low speed the NO_x emission was minimum and vice versa. The average NO_x emission increased by 1.8% for CMB10, 4.66% for CMB15, 7.24% for CMB20, and 8.6% for CMB25 in contrast to pure diesel. O₂ in emissions percentages for blends are higher relative to pure diesel.
- The input fuel energy and exergy analysis show similar trends: both increase with engine speed due to higher injection rates. At 2600 rpm, CMB25's input fuel energy and exergy are 2.6% and 3% lower than pure diesel, indicating higher biodiesel ratios require more fuel at high speeds. At 800 rpm, CMB10's input energy and exergy are slightly lower than B0 by 0.52% and 0.6%, respectively, showing that reducing biodiesel content minimizes differences.
- Exhaust energy losses increased with both engine speed and biodiesel blend ratio. At 800 rpm, CMB25 exhibited 15.83% higher exhaust energy loss than diesel, whereas at 2600 rpm, B0 showed an 18.02% reduction compared to CMB25. This trend is attributed to the higher oxygen content of biodiesel, which promotes more complete combustion and higher exhaust gas temperatures. Exhaust gas exergy also increased for biodiesel blends, with CMB25 showing rises of 20.5% and 13.1% at 800 and 2600 rpm, respectively, while CMB10 recorded a 5.8% increase at both speeds compared to B0.
- Cooling water losses increased with engine speed due to higher injection rates and combustion temperatures. Biodiesel blends showed lower losses than diesel at low and moderate speeds, but maximum losses occurred at higher speeds. On average, energy and exergy losses by cooling increased by 19% and 6.67% at 800 rpm, and by 31.6% and 23.8% at 1400 rpm, while both fuels exhibited similar cooling water exergy at 2000 and 2600 rpm.
- Unaccounted energy loss depends strongly on engine speed. Biodiesel blends reduce this loss compared to pure diesel (B0), with CMB25 showing the minimum at 800 rpm and

CMB10 the maximum at 2600 rpm, due to diesel's lower oxygen content causing incomplete combustion.

- Exergy destruction rises with engine speed due to higher fuel consumption, combustion temperatures, and irreversible processes. At low speeds (800–1400 rpm), blends show lower exergy destruction than diesel; at 2000 rpm, biodiesel blends' exergy destruction increases, while at high speeds, diesel exhibits high exergy destruction from friction, heat, and poor combustion. CMB20 shows lower exergy destruction reduced by 15.4% than diesel.
- Exergy efficiency was recorded 20% at 2600 rpm for CMB15, but CMB20 shows 13% and 18% at 800 and 2000 rpm respectively and at 1400 rpm CMB25 achieved 20% exergy efficiency.
- Generally, calcinated composite heterogeneous catalysts of $\text{CaO}/\text{Al}_2\text{O}_3$ is recommended for biodiesel production via transesterifications enhanced biodiesel yield.
- Experimental results show that CMB20 achieves the highest BTE and BSFC, offering superior energy and exergy efficiency. This blend is recommended for minimizing losses and irreversibility across varying engine speeds.
- Based on this thesis, the future studies should investigate the energy and exergy characteristics of croton macrostachyus biodiesel blends at CMB20 with different nanoparticle proportions and dosages.

Contributions

Bona Birhanu Chemed: Conceptualization, Methodology, Validation, Writing - Original Draft; **Samson Mekbib Atnaw:** Supervision, Project Management, Visualization, Writing - Review & Editing, Validation; **Adem Siraj Mohammed:** Supervision, Writing - Review & Editing.

Declarations

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Abbreviations and Nomenclature

The following abbreviations and nomenclatures are used in this manuscript:

Bp = brake power	T = torque developed in Nm
BT = brake torque	φ_{fuel} = chemical exergy factor
BTE = Brake thermal efficiency	T_{amb} = ambient temperature in K
BSFC = Brake specific fuel consumption	T_2 = Exhaust gas temperature at engine in K
$\dot{m}_f$ = mass flow rate fuel	T_3 = is the calorimeter water inlet in K
LCV = lower calorific value	T_4 = is the calorimeter water outlet in K
TBMC= Test bench mobility controlled	η_{Energy} = energy efficiency
CI = compression ignition	η_{exergy} = Exergy efficiency
μ = dynamic viscosity	EGT = Exhaust gas temperature
ν = kinematic viscosity	CO ₂ = Carbon dioxide
ρ_{oil} = density of oil	NO _x = Oxides of nitrogen
$\dot{m}_{\text{in}}$ = mass flow rate at the inlet	O ₂ = Oxygen
$\dot{m}_{\text{out}}$ = mass flow rate at the output	C_{pw} = specific heat of water in kJ/Kg. K
E_{in} = input fuel energy	T_5 = temperature of exhaust gas entering to calorimeter in K
E_{bp} = shaft work energy	T_6 = temperature of exhaust gas leaving from calorimeter in K.
E_{exh} = Exhaust gas energy loss	NO _x = Oxides of Nitrogen
E_{cw} = Cooling water energy loss	CaO = Calcium oxide
E_{un} = Unaccounted energy	WCO =Waste cooking oil
E_{Xin} = input fuel exergy	Al ₂ O ₃ = Aluminum oxide
E_{Xwork} = shaft work exergy	XRD = X-Ray Diffraction
E_{Xexh} = Exhaust gases exergy	BET = Brunauer-EmmettTeller
E_{Xcw} = exergy loss in cooling water	FTIR =Fourier transform infrared ray
E_{Xdest} = Exergy destruction	EN = European Standard
$\dot{m}_f$ = mass of fuel supplied, kg/s	CI = Compression Ignition
$\dot{m}_{\text{air}}$ = mass of air	FFA = Free Fatty Acids
$\dot{m}_{\text{exh}}$ = mass of exhaust gas (mass of air plus mass of entering fuel)	FAME = Fatty acid methyl esters
$\dot{m}_w$ = mass of cooling water	BTE = Brake thermal efficiency
$\dot{m}_{\text{cw}}$ = mass flow rate of calorimeter cooling water (kg/s)	CM = Croton macrostachyus
N = engine speed (rpm)	

$C_{p_{exh}}$ = specific heat at constant pressure of exhaust gas in kJ/Kg. K
 $T_{CW,inlet}$ and $T_{CW,out}$ = Water temperature entering and when rise passing through the cooling jacket in the engine in K
 CMSO = Croton macrostachyus seed oil
 CMKO = Croton macrostachyus kernel oil
 CMB10 = 10% croton macrostachyus biodiesel and 90% diesel
 CMB15 = 15% croton macrostachyus biodiesel and 85% diesel
 CMB20 = 20% croton macrostachyus biodiesel and 80% diesel
 CMB225 = 10% croton macrostachyus biodiesel and 75% diesel

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