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Exergetic and environmental life cycle assessments for waste cooking oil microemulsion biofuel in compression ignition engine

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ABSTRACT

Biofuels are considered as the alternative to petrofuels in Compression Ignition (CI) engines. However, investigations on combustion exergy, exergetic life cycle, and environmental impacts are imperative for understanding the sustainability of biofuel in engine applications. In the present study, the sustainability of Waste Cooking Oil (WCO) microemulsion biofuel in CI engines is validated by evaluating the life cycle performances, emission characteristics, and cogeneration potential. The life cycle assessment (LCA) analysis indicated that the environmental impact of fossil resource exploitation could be reduced up to 34% with WCO microemulsion biofuel-petrodiesel blends (WMBDs) in comparison to petrodiesel. Moreover, CO, CO₂, and NO_x emissions decreased for WMBDs at different load conditions. In addition, WMBDs exhibited higher cylinder pressure and the highest net heat release rate (NHRR_{max}) than petrodiesel. WMBDs showed the net system exergy output, relative shares of brake power, and exhaust exergy comparable to petrodiesel, justifying the cogeneration potential of the formulated WCO microemulsion blends. In addition, WMBDs exhibited higher utilization efficiency over petrodiesel in exergetic life cycle assessment analysis. Furthermore, the resource utilization efficiency and environmental sustainability could be increased up to 27.76% and 26.62%, respectively, with waste heat recovery (cogeneration) facility for WMBDs. CI engines (both with and without integrated cogeneration facility) fueled with WMBDs outperformed petrodiesel in terms of environmental sustainability.

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I. INTRODUCTION

The global reliance on fossil fuels for energy production diminishes its reserves and escalates greenhouse gas (GHG) emissions from end-use sectors. Replacing fossil fuels with advanced biofuels combined with technical and operational energy efficiency measures can, therefore, offer the least carbon-intensive technology options. Out of the different novel advanced biofuel production methods, microemulsion biofuel production using microemulsification presents multiple advantages in terms of process sustainability. Simple production methods, technology implementation with 100% product utilization, short production period without heat (energy) application or chemical reactions, requiring no product purification or separation, and the absence

of by-products characterize microemulsification processes.^{1,2} Thus, simple mixing of vegetable oil, surface active agents, and a polar solvent (e.g., ethanol), at an ambient temperature, can yield microemulsion biofuels with properties comparable to petrodiesel and biodiesel.²

The microemulsion fuel formulations are characterized by nano-sized fluid droplets (or colloidal dispersions) of size 1–150 nm. These are defined as the optically isotropic, thermodynamically stable, transparent, and homogeneous fluid medium. Microemulsion systems exhibit unique structural characteristics and dynamic behavior. Therefore, detailed investigation concerned with droplet formation, interaction, and aggregation is very much critical in investigating the fuel quality as well as for a better understanding of the formulated

system.² The phase behavior, droplet parameters, and thermodynamic stability were studied for a microemulsion biofuel from *Thevetia peruviana* seed oil.^{2,3} Ashikhmin *et al.*⁴ have recently investigated diesel fuel–rapeseed oil blends using distilled water as a polar solvent to define the temperature-dependent aggregate thermal stability and rheological properties. Liu *et al.*⁵ demonstrated the palm oil fractionations based microemulsion as a potential biomaterial feedstock, especially in terms of the viscosity characteristics or anti-shearing properties.

The surface active agents (surfactants and co-surfactants) stabilize the microemulsion system by reducing the interfacial tension, between the oil phase and the polar solvent.² Nonionic surfactants are generally preferred for microemulsion fuel formulations since they show superior phase behavior with polar organic solvents (e.g., ethanol and butanol). The possibility of fuel system destabilization and the occurrence of chemical reactions (during processing and storage) can be reduced with the utilization of nonionic surfactants.^{2,3} The thermal stability and phase behaviors of water-diesel microemulsion system prepared using the nonionic surfactants Neonol AF 9-6 and PEG-6 nonylphenyl ether and the cosurfactant 2-ethylhexanol were studied in two (2) recent studies.^{6,7} In addition, Kayali *et al.*⁸ interpreted the phase behavior of a water-diesel microemulsion system formulated using nonionic surfactant alkyl polyglycol ethers and alcohol carboxylates. Acharya and his coauthors investigated the phase behavior, cloud point, electrical conductivity, soot estimation, and density of water in the diesel based microemulsion system formulated using the nonionic surfactant Tween-80 and cosurfactant n-butanol/isobutanol.^{9,10} The microemulsion formulation with branched alkyl chain (isobutanol) cosurfactant exhibited superior fuel compatibility in comparison to the system formulated with straight alkyl chain (n-butanol) cosurfactant.¹⁰

However, subsequent cost escalation due to the addition of external surfactants has favored surfactant free microemulsion fuel systems^{11–13} even vs environmentally benign and nonionic surface active agents.^{2,14} Vegetable oils contain a significant amount of naturally occurring surfactants, such as mono-, di-glycerides, and free fatty acids (FFAs) or fatty esters. Consequently, the production of microemulsion biofuel from five different indigenous vegetable oil feedstocks was attempted without adding any external surfactants.¹⁴ Thus, crude vegetable oil could become the major feedstock for biofuel production as external surfactants are not required and it is economically viable.

At present, much emphasis is being placed on Waste Cooking Oil (WCO) as a feasible feedstock for microemulsion biofuel production, as humungous quantities of WCO generated annually from the global food market are raising serious environmental concerns.^{15,16} For instance, China, United States, India, and Japan generate 5.6, 1.2, 1.1, and 0.57 Mt of WCO per year, respectively.¹⁶ Therefore, recycling, effective repurposing, or efficient utilization of WCO for advanced biofuel production would aid ecosystem sustainability.¹⁷ Phasukarratchai¹⁷ studied the phase behavior and fuel properties of a WCO microemulsion biofuel blended with diesel fuel. WCO microemulsion biofuels were formulated using ethanol, 1-butanol, and nonionic surfactants. In one of the previous studies, microemulsion biofuel from WCO using ethanol as a polar solvent and butan-2-ol as a cosurfactant was formulated.¹⁵ It was reported that the gross calorific value (GCV) for pre-treated WCO (P-WCO) based microemulsion biofuel (39.01 MJ/kg) was comparable to the GCV of WCO biodiesel (39.3 MJ/kg).¹⁵ However, this study warrants further research into the sustainability of the engine application process. It is pertinent to mention that the

presence of nano-sized droplets in the microemulsion fuel systems can enhance microexplosions during combustion in compression Ignition (CI) engines, which improves engine performance and emission characteristics.¹⁸ However, since the GCV of WCO microemulsion biofuel is lower than petrodiesel, it enables investigations into engine performance, combustion, and emission characteristic studies with WCO microemulsion biofuel–petrodiesel blends (WMBDs).

In addition, it is vital that the environmental performance of WMBDs is evaluated using a structured tool such as life cycle assessment (LCA). The LCA approach analyzes the environmental impacts and energy consumptions patterns pertaining to the services of the entire life cycle of WMBDs from “cradle to grave.”^{19–21} In addition, the waste-heat and GHG generated at the CI engine exhaust for a particular fuel is crucial for energy conservation and environmental pollution, respectively. Therefore, cogeneration facilities equipped with a waste heat recovery unit, and integrated with the CI engine is a feasible option for maximizing the resource (fuel) utilization efficiency and environmental sustainability (ES) of the process. In addition, the undesirable GHG emission at the CI engine exhaust can be further combated with environmentally benign fuels like biofuels.

The waste heat recovery potential at the diesel engine exhaust can be evaluated using “exergy analysis,” which takes into account changes in quality or usefulness of different forms of energy (such as physical, chemical, thermal, etc.) as defined by the Second Law of Thermodynamics. The thermodynamic irreversibility is quantified as exergy destruction in exergy analysis, which is otherwise a wasted energy-production potential.^{22,23} Exergy analysis identifies the processes and as well as the components of a system that engender considerable destruction of exergy.^{22,24} It reflects the degree of deviation of the system or its components (of the system), with respect to a reference environment. It is a state function that can be defined with pressure, temperature, and chemical potential of a system or a fluid stream.¹⁹ The exergy concept has been extensively applied to several studies investigating diesel engines with diesel–biodiesel, and diesel–biodiesel–ethanol/methanol fuel blends in recent years.^{25–28} However, these studies are focused only on exergy analysis of the combustion processes.

Therefore, a comprehensive understanding of the cogeneration potential of CI engine based energy conversion systems with WMBDs must necessarily be derived from exergoenvironmental life cycle assessments in which exergy analysis is correlated with the environmental impact evaluations, in addition to conventional LCA. This implies that the thermodynamic performance of CI engine based energy conversion systems can be effectively assessed using the exergetic life cycle assessment analysis (ELCA), i.e., by integrating exergy analysis with the entire life cycle of WMBD or its service. The advantage of ELCA approach over conventional LCA is that the former takes into consideration the cumulative exergy consumption, attributed to the life cycle of WMBDs. Thus, ELCA includes the extensive system boundary to the CI engine under investigation.^{19,20} Moving ahead from the work of Peiró *et al.*²¹ on ELCA for production of biodiesel from WCO over a decade ago, the study by Hosseinzadeh-Bandbafha *et al.*²⁰ recently conducted in 2021, offers fresh insights into an ELCA study of a heavy-duty diesel engine with diesel–biodiesel–bioethanol fuel blends.

The present study is a novel effort toward investigating the sustainability of WCO microemulsion biofuel–diesel blends in a CI

engine, evaluated by using both ELCA and LCA approaches. Surfactant free microemulsion biofuels were prepared from WCO using ethanol as polar solvent and butan-2-ol as cosurfactant based on the previous studies. The engine performance and combustion characteristics of a CI engine, in addition to exhaust emissions, were evaluated for WMBDs and petrodiesel. Moreover, the physicochemical properties of all the WMBDs were determined and compared with petrodiesel and crude WCO. In addition, the combustion exergy analysis of exhaust gases has been undertaken to evaluate the cogeneration potential of the engine system.

II. MATERIALS AND METHODS

A. Materials

WCO was collected from various restaurants in Guwahati, Assam. Ethanol (<99.9%), synthesis-grade methanol ($\geq 99\%$ assay and $\leq 0.2\%$ water content), NaHCO_3 (99%), NaOH (99%), Na_2SO_4 (99.5%), and H_2SO_4 (98%) were procured from Merck India Limited, Mumbai. Butan-2-ol (Reagent PlusR $\geq 99\%$) was purchased from Sigma Aldrich. Petrodiesel (product name: High Speed Diesel, Manufacturer: Indian Oil Corporation Limited²⁹) was sourced from local filling stations at Guwahati, Assam. All chemicals and reagents were used without further purification.

B. Methods

1. Preparation and pretreatment of microemulsion biofuel

The collected WCO was filtered under vacuum for 2-3 times in order to separate the solid contaminants and other impurities. The filtrate was then allowed to settle under gravity for 72 h to remove further impurities (if any). The samples were again subjected to vacuum filtration, followed by drying over anhydrous Na_2SO_4 . The dried WCO samples were pretreated for 30 min to convert the FFAs to corresponding fatty acid methyl esters (FAMES).² After completion of the pretreatment process, excess methanol was recovered using a rotary evaporator. Unreacted catalysts (2 wt. % H_2SO_4) were neutralized with 1 M NaHCO_3 solution. The resulting pretreated WCO was dried in an oven maintained at 110°C . Microemulsion fuel formulations were prepared by mixing the pretreated WCO (P-WCO) with butan-2-ol and ethanol at ambient temperature. Three fuel formulations, as mentioned in Table I, were selected for engine performance, combustion, emission, exergy, LCA, and ELCA study, as per the best results obtained from the previous studies by Bora *et al.*¹⁵ and Kumar *et al.*³⁰ The microemulsion biofuel samples (as mentioned in Table I) were blended with petrodiesel fuel in 1:1 v/v ratios for further study.

TABLE I. Compositions of microemulsion biofuel samples.

P-WCO (vol. %)	Butan-2-ol (vol. %)	Ethanol (vol. %)	Petrodiesel (vol. %)	Sample name
30	15	5	50	Sample 1
27.5	16.5	6	50	Sample 2
25	20	5	50	Sample 3

2. Engine performance and emission characteristics analyses

The CI engine performance parameters, such as brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), brake power (BP), mechanical efficiency (ME), indicated thermal efficiency (ITE), exhaust gas temperature, along with combustion characteristics: Net Heat Release Rate (NHRR) and in-cylinder pressure, were determined for WMBDs and petrodiesel at varying load conditions. The emission levels of unburned hydrocarbon (HC), CO, NO_x , and CO_2 , from the engine exhaust, were also evaluated for the fuels, using a Testo 350 flue gas analyzer system. The 95% confidence level (or prediction band) was taken into account for these analyses. A detailed description of the experimental set up used for performance and emission characteristic analyses along with testing procedures is provided in the [supplementary material](#).

3. Exhaust exergy analysis

A significant quantity of harmful gases and waste heat is released into the atmosphere through the CI engine exhaust, at high pressure and temperature relative to the ambient conditions. The thermal energy content that manifests in the exhaust gas by virtue of the elevated pressure and temperature levels could be harnessed for useful energy applications. Additionally, the exhaust gases comprise of certain gaseous components, which might undergo further chemical reactions with the liberation of energy. This type of chemical reaction is caused due to the components' disequilibrium between the "exhaust emission condition" and the surrounding environment. Further, the concentration difference between the emission stream and the reference environment results in energy liberation by diffusion of the chemical species of the exhaust gases.^{19,20}

To quantify the overall high grade energy content extractable from the exhaust gas, an exergy analysis was performed for the petrodiesel as well as WMBDs. Following the study by Li *et al.*,³¹ the thermomechanical exergy, Ex^{th} (extractable from the exhaust gas' thermal energy content), was calculated with Eq. (1); and chemil exergy, Ex^{ch} (extractable from the chemical potential existing between exhaust gas components and surrounding reference environment), was calculated with Eq. (2),

$$\text{Ex}^{\text{th}} = \sum_{i=1}^k H_i(T_e) - H_i(T_o) - T_o \left[S_i(T_e) - S_i(T_o) - R \ln \frac{P_e}{P_o} \right], \quad (1)$$

$$\text{Ex}^{\text{ch}} = R T_o \sum_{i=1}^k \ln \frac{x_i^e}{x_i^o}, \quad (2)$$

where H_i and S_i represent the enthalpy and entropy of the i -th component of the exhaust gas. These values were calculated from the specific property values extracted using REFPROP software,³² for each component of the exhaust gas, at different pressure (p_e) and temperature (T_e), and under different load conditions on the engine. The ambient conditions were taken as 25°C (T_o) and 1 bar (p_o), with x_i^e and x_i^o being mole fractions of the i -th component of the gas at exhaust and ambient conditions, respectively. Further details about the compositions of gases and vapor at the engine exhaust are provided in the [supplementary material](#).

4. LCA

LCA analysis was performed in four steps in accordance with ISO 14040:2006¹⁹⁻²¹ principles and framework. The first step of LCA analysis is the selection of “goal and scope” of the investigation. The study aimed to analyze the environmental impact of WMBD production from (i) WCO, (ii) butan-2-ol, (iii) ethanol, and (iv) petrodiesel, which formed the four major components. The functional unit (FU) for this analysis was taken as 1 kg of the product (fuel). The system boundary consisted of procedures for WCO pretreatment (WCO collection, delivery to treatment plant, water removal, treatment of impurities, conditioning and storage of oil, effluent treatment steps, GCV of biomass, CO₂ credit in the process etc.), in addition to ethanol, butan-2-ol, and petrodiesel production processes, microemulsion fuel formulation with ethanol and butanol; and blending in petrodiesel. Inventory analysis constituted the second step, where the materials and energy incorporated in the fuel production were determined. Thus, the emissions to the air, water, and soil by the fuels over their entire life cycle were specified and environmental impacts were analyzed using the software program SimaPro 9.2.0 with databases EcoInvent (version 3) and Agri-footprint (version 5). Life cycle impact assessment

is the third step, where the end point damage categories (human health, ecosystem quality and resource scarcity) were obtained based on the inventory data. The contributions of different impact factors in the end point damage categories were also configured. The results obtained were then interpreted and evaluated in the fourth and final step of LCA analysis. The results obtained for WMBDs were compared with the environmental impacts of conventional petrodiesel.

5. ELCA

ELCA included the same system boundaries and steps, which were considered for the LCA approach. The cumulative exergy consumption values of WMBD and petrodiesel per kg of the fuels were computed from the EcoInvent databases in SimaPro software (version 9.2.0). The resource utilization efficiency (E_{ff}) and environmental sustainability (ES) were obtained for the fuels at different load operating conditions of CI engine following Hosseinzadeh-Bondbafha *et al.*²⁰ The resource utilization efficiency and environmental sustainability for CI engine (without cogeneration), i.e., E_{ff-Cl} and ES_{Cl} were calculated with Eqs. (3) and (4), respectively, as follows:

$$E_{ff-Cl} = \frac{\frac{BP}{\dot{m}_f}}{\text{Cumulative exergy consumption of fuel formulations}}, \quad (3)$$

$$ES_{Cl} = \frac{\frac{BP}{\dot{m}_f}}{\left(\text{Cumulative exergy consumption of fuel formulations} + \frac{Ex^{ch}}{\dot{m}_{ex}} \right)}, \quad (4)$$

where \dot{m}_f and \dot{m}_{ex} are the mass flow rates of fuel and exhaust gas in kg/s, respectively. The resource utilization efficiency and environmental sustainability for CI engine cogeneration system (CCS), i.e., E_{ff-CCS} and ES_{CCS} were similarly calculated with Eqs. (5) and (6), respectively, as follows:

$$E_{ff-CCS} = \frac{\frac{BP}{\dot{m}_f} + \frac{Ex^{th}}{\dot{m}_{ex}}}{\text{Cumulative exergy consumption of fuel formulations}}, \quad (5)$$

$$ES_{CCS} = \frac{\frac{BP}{\dot{m}_f} + \frac{Ex^{th}}{\dot{m}_{ex}}}{\left(\text{Cumulative exergy consumption of fuel formulations} + \frac{Ex^{ch}}{\dot{m}_{ex}} \right)}. \quad (6)$$

C. Characterization

The fatty acid compositions of WCO were determined using gas chromatography (GC). WCO microemulsion biofuels were also characterized by ¹H NMR and FT-IR spectroscopy. Details about the fatty acid compositions of WCO and spectra are provided in the [supplementary material](#). Moreover, the physicochemical properties of WCO, petrodiesel, microemulsion biofuel, and WMBDs, such as density, kinematic viscosity, GCV, cloud point, and flash point, were determined using standard test methods. The cloud point was analyzed according to ASTM D 2500-11. The flash point was determined in an open cup analyzer as per ASTM D 93, while density and kinematic

viscosity were measured by ASTM D1298 and Haake, type C falling-ball viscometer (as per ASTM D 445), respectively. GCV was determined in an oxygen bomb calorimeter (model: 6050, make: Parr Instruments, USA) according to ASTM D 4809. In all of the experimental investigations, uncertainty on measurements was taken into consideration, with triplicate measurements.

III. RESULTS AND DISCUSSION

A. Physicochemical properties of the oil

The physicochemical properties of microemulsion biofuel formulations and WMBD samples are presented in [Tables II and III](#),

TABLE II. Fuel properties of microemulsion biofuels.

Microemulsion composition (p-WCO:butan-2-ol:ethanol)	Density (g cm ⁻³) @15 °C	Viscosity (cSt) @ 40 °C	GCV (MJ Kg ⁻¹)	Flash point (°C)	Cloud point (°C)
60:30:10	0.892 ± 0.001	5.40 ± 0.01	38.87 ± 0.02	45 ± 1	-7 ± 2
55:33:12	0.878 ± 0.001	5.10 ± 0.03	39.21 ± 0.02	44 ± 2	-7 ± 1
50:40:10	0.866 ± 0.001	4.73 ± 0.01	37.94 ± 0.03	43 ± 2	-6 ± 1

respectively. These results of the physicochemical properties of the microemulsion biofuels are in accordance with a previous study.¹⁵ The fuel properties of WCO and petrodiesel are also presented in Table III for comparative assessment. Moreover, the specifications for petrodiesel as per the standard testing methods are mentioned in Table III for reference. WMBDs exhibited superior fuel quality in terms of viscosity, GCV, and cloud points in comparison to corresponding microemulsion biofuels (which were not blended with petrodiesel).

B. CI engine performance analysis

The engine performance parameters, such as BTE, BSFC, ME, ITE, and BP, under various load conditions with petrodiesel and WMBD are presented in Figs. 1(a)–1(e), respectively. As expected, BTE (η_{bte}) in Fig. 1(a) increased with the rise in load condition, though the overload flattens the BTE vs load curve slightly toward right or full load condition.³³ The phenomenon occurs when in comparison to part and full load conditions, when the time available for heat dissipation to the cylinder walls is reasonably high during zero loading conditions, resulting in significant heat loss. Though, at higher load conditions, the net heat release rate increases with load and causes high combustion pressure and equivalent rise in BTE.³⁴ The BTE of the CI engine at CR 17 for petrodiesel was greater than that for WMBDs by around 5%–8% under full load conditions. This might be due to the higher viscosity and density of the WMBDs in comparison to petrodiesel, which prevented atomization of the fuel up to a certain extent in the combustion chamber.³⁵

A significant increase in BSFC was observed at 1 kg load for both petrodiesel and WMBDs [Fig. 1(b)]. However, the increment in BSFC was distinctly higher for WMBDs than for petrodiesel. However, a drastic fall in BSFC was observed for petrodiesel and WMBDs on further increase in crank shaft load from 1 kg operating condition. This implies better combustion inside the engine cylinder under higher loading conditions, which results in efficient burning of fuel in the engine. BSFC of a CI engine mainly depends on amount of fuel

injected and fuel properties, such as density, kinematic viscosity, and GCV of the fuel.^{36,37} Generally, a fuel with lower GCV is predicted to have higher BSFC at a particular load to meet the output power demand.³⁸ However, in this investigation, BSFC for both the fuels (petrodiesel and WMBD) followed similar trends, with almost equivalent results at part and full loading conditions. It confirms that the sufficient degree of alcohol-microexplosion (of ethanol and butan-2-ol) forming a homogeneous air fuel mixture took place in the CI engine, fueled by WMBD, especially at higher load conditions, despite the lower GCV of the fuel samples.^{36,37} In addition, with respect to petrodiesel, no significant variation in ME (η_{mech}) was observed for WMBD under different loads [Fig. 1(c)]. ITE (η_{ite}) of an internal combustion engine depends on power developed during the power stroke inside the cylinder. At 3 kg condition, sample 2 exhibited highest ITE among all the tested fuel samples. ITE for WMBDs, in general, were lower than for petrodiesel by around 2%–6% [Fig. 1(d)]. The unusual data trends [observed in Figs. 1(c) and 1(d)] for ME and ITE at engine loads 9 and 3 kg, respectively, were due to the increase in the friction power to overcome the friction of mechanical components (e.g., bearings, piston, etc.) and drive the engine accessories. This increase in mechanical friction component, particularly at part load conditions is mainly caused by the higher cylinder gas pressure.³⁹ The BP increased from zero to full load condition [Fig. 1(e)]. Since petrodiesel exhibited highest GCV among all the tested fuels; therefore, it produced highest BP followed by sample 2, sample 1, and sample 3, respectively. At lower load (e.g., at 1 kg load condition), BP of WMBD was significantly less than that of petrodiesel. However, BP of WMBDs and petrodiesel was almost equivalent at higher load conditions. This is due to the fact that WMBD contains 20%–25% alcohol (ethanol and butan-2-ol), which increases the latent heat of vaporization and causes cooling inside the engine cylinder. This cooling effect creates a negative impact on thermal efficiency, which results in reduction of BP, though; this negative effect could be overcome with increase in engine load.⁴⁰

TABLE III. Fuel properties of WMBD samples, petrodiesel, and WCO.

Sample	Density (g cm ⁻³) @ 15 °C	Viscosity (cSt) @ 40 °C	GCV (MJ Kg ⁻¹)	Flash point (°C)	Cloud point (°C)
Sample 1	0.884 ± 0.001	4.56 ± 0.01	41.10 ± 0.02	51 ± 2	-10 ± 2
Sample 2	0.874 ± 0.001	4.14 ± 0.01	41.88 ± 0.03	50 ± 2	-11 ± 1
Sample 3	0.863 ± 0.002	3.98 ± 0.03	40.49 ± 0.02	49 ± 1	-11 ± 1
Petrodiesel	0.835 ± 0.002	2.56 ± 0.02	45.20 ± 0.01	65 ± 2	-12 ± 1
WCO	0.910 ± 0.002	33.31 ± 0.01	39.12 ± 0.03	>100	0 ± 2
Specifications for petrodiesel ²⁹	0.815–0.845	2.0–4.5

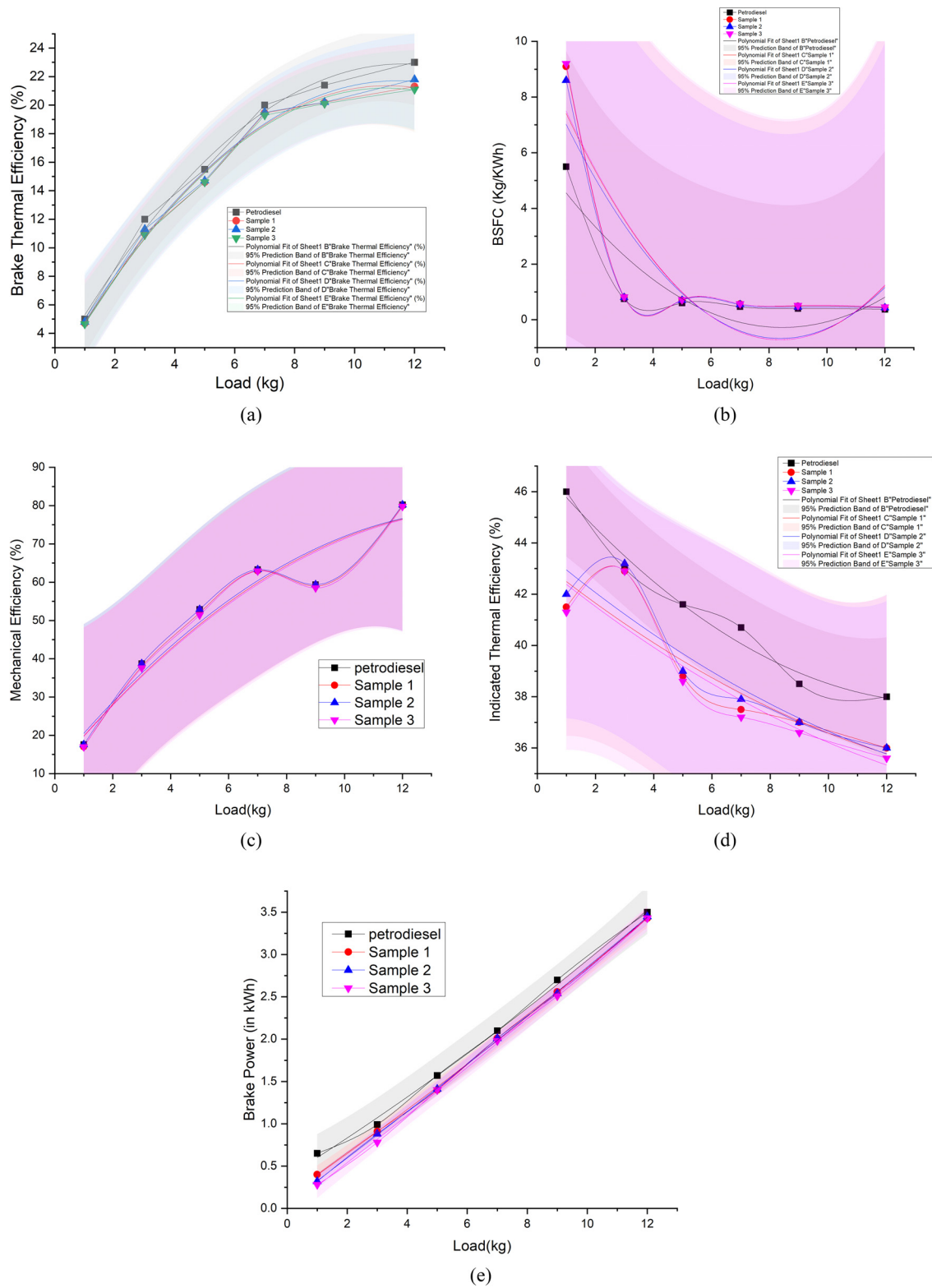


FIG. 1. CI engine performance for the WMBDs and petrodiesel under different load conditions: (a) BTE, (b) BSFC, (c) ME, (d) ITE, and (e) BP.

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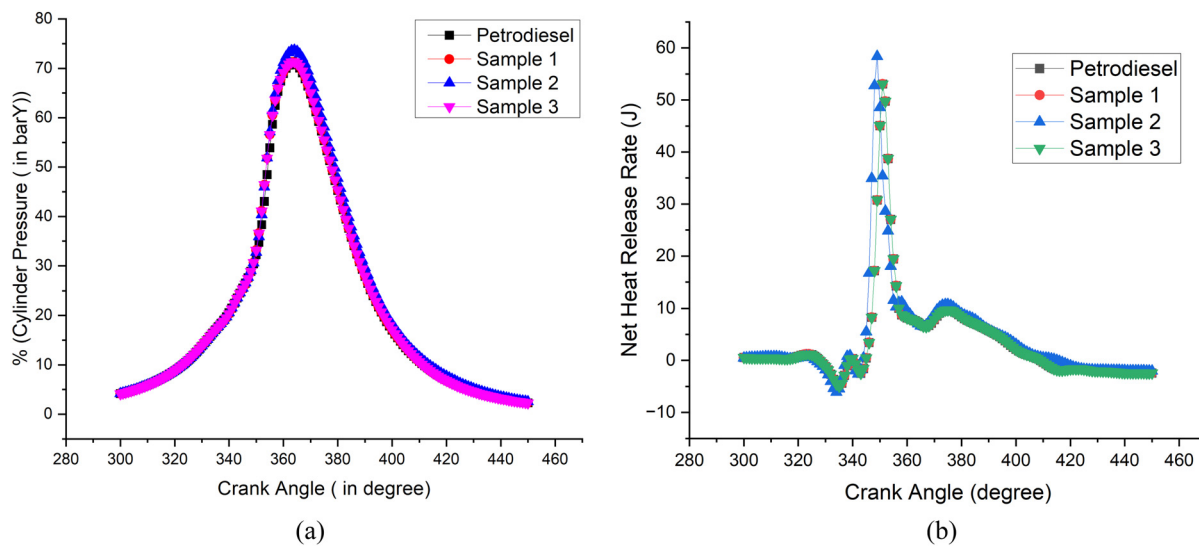


FIG. 2. CI Engine combustion characteristics for the WMBDs and petrodiesel under different load conditions: (a) cylinder pressure vs crank angle, and (b) net heat release rate vs crank angle.

C. CI engine combustion characteristics analysis

To investigate the combustion characteristics, cylinder pressure vs crank angle and net heat release rate vs crank angle for the tested fuel samples were plotted in Figs. 2(a) and 2(b), respectively. The engine cylinder pressure increased from compression to power stroke in CI engines, regardless of the fuel type. The highest value of peak cylinder pressure (CP_{max}) was obtained for sample 2 (73.7 bar), followed by petrodiesel (70.99 bar), and sample 1 (71.31 bar). CP_{max} was obtained at corresponding crank angles of 370° for all the tested fuel samples.

The greater CP_{max} values for WMBDs vs petrodiesel signifies the combustion-worthy abilities of WMBDs in CI engines. These values further indicate the occurrence of successful microexplosion inside the combustion chamber for WMBDs. The possibility of microexplosion in the combustion engine had been extensively studied for water-diesel and water-rapeed oil emulsion systems by Antonov and his co-researchers.^{41,42} One such research work demonstrated 40% probability of microexplosion for water in diesel and water in rapeed oil emulsion systems with a mean droplet diameter of $1.2 \mu\text{m}$.⁴¹ Another investigation with initial droplet radii in the range $0.62\text{--}1.34 \text{ mm}$ showed that the time to microexplosion increased with increasing water droplet sizes and decreased with increasing temperature, but was not much influenced by the volume fraction of fuel.⁴² However, in the present study, the microexplosion phenomenon is concerned with the reverse micellar microemulsion structure or nano-sized dispersed droplets, where the presence of surface active agents completely disperses the polar ethanol phase to the droplets in the oil continuum.³⁶ The presence of such reverse micelle (dispersed droplets) contributed to the formation of a fine and homogeneous microemulsion system, further enhancing the probability of the successful microexplosion phenomenon, which resulted in higher CP_{max} for WMBDs.

The NHRR of all the tested fuels followed a similar increasing trend from compression to power stroke. The $NHRR_{max}$ for sample 2 was 58.39 J (highest among all the tested fuels) at 350° CA (crank

angle). In general, NHRR followed a “delayed trend” for petrodiesel with respect to WMBDs, which is also in accordance with previous studies.³⁶ The improvement and earlier rise in NHRR for WMBDs are based on the following facts: The combustion process starts in-advance in the case of WMBDs because of its lower flash points (which is due to the incorporation of alcohols) than petrodiesel. The sudden and earlier combustion for the fuels with low flash points (such as WMBDs) materializes a premixed-combustion phase thereby partially advancing and improving the combustion process as well as increasing the NHRR.³⁵ Overall, optimum combustion for the CI engine with no ignition delay was obtained for the fuel samples at the crank angle in the range of $350^\circ\text{--}353^\circ$.

D. Exhaust emission characteristics analysis

The exhaust emissions (such as CO , CO_2 , NO_x , and unburned HC) from a CI engine, measured for the tested fuels at CR 17 under different loading conditions are presented in Fig. 3. CO emission from the incomplete combustion of fuel inside the engine cylinder was attributed to the poor air fuel mixture; consequently, the CO emission levels for petrodiesel and WMBD were almost equivalent under lower load conditions.³⁸ However, at maximum load conditions, petrodiesel CO emissions were three times greater than the WMBD; 50% decrease in CO emissions was noted in WMBD at maximal load in comparison to the lower load emission levels [Fig. 3(a)]. Conversely, CO emission percentage increased for petrodiesel particularly at higher load conditions. The formulated microemulsion biofuels comprised of 20%–25% alcohol, increased oxygen content in the WMBDs, enhanced the atomization and combustion of the fuels, and contributed to lower CO emission. Since alcohols cause cooling effect inside the engine cylinder; therefore, at low engine loads, it reduced the in-cylinder gas temperature leading to poor combustion. This resulted in the higher level of CO emission. However, when the in-cylinder temperature increased due to full engine load, the cooling effect caused by alcohol

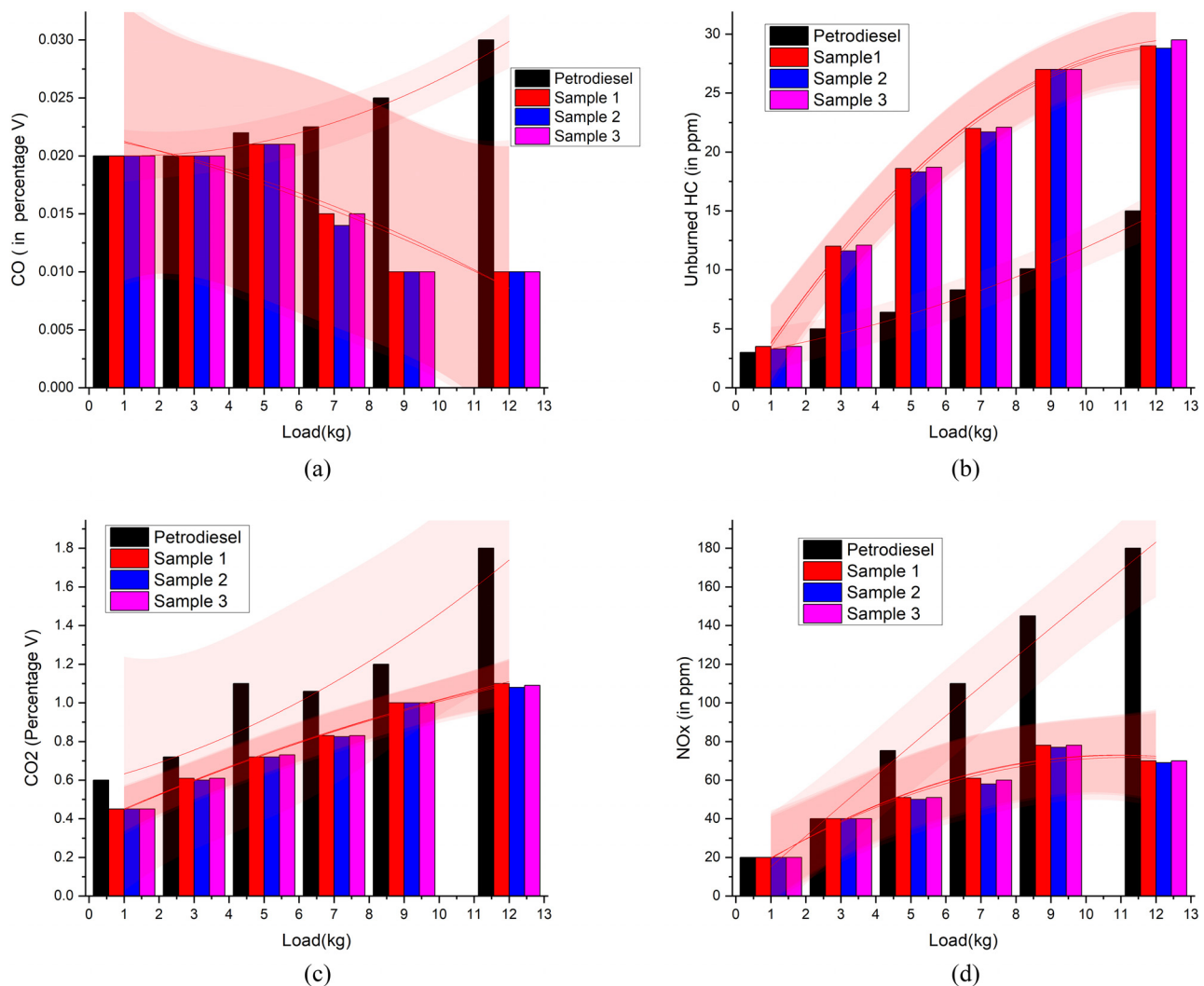


FIG. 3. CI engines exhaust emissions for the WMBDs and petrodiesel under different load conditions: (a) CO, (b) unburned HC, (c) CO₂, and (d) NO_x.

components was overcome. This resulted in complete combustion with the lower amount of CO emission.^{36,43}

Unburned HC results from incomplete combustion caused by insufficient air supply and inadequate combustion temperature.⁴⁴ Unburned HC emission at all loads was higher for WMBDs than for petrodiesel [Fig. 3(b)]. This might be due to incomplete combustion of high molecular weight triglyceride component of WMBD in CI engine.⁴⁵ The prolonged duration of combustion leads to increased accumulation of air-fuel mixture inside the CI engine combustion chamber. This, in turn, increases the unburned HC emissions caused by incomplete combustion inside the cylinder. In addition, incorporation of oxygenated compounds, such as alcohol and fatty acids (or fatty acid methyl esters), also contributed to higher unburned HC emission.³⁶ Under maximum load condition, the amount of unburned HC emitted by petrodiesel and WMBD (sample 3) were 15 and 29.5 ppm, respectively. However, the unburned HC levels were very

negligible in comparison to the emission levels of the major exhaust gases such as CO₂. Moreover, the incombustibility of high molecular weight triglycerides component of WMBDs was not much prevalent, and therefore, it did not have impact on the CI engine combustion characteristics, as evident from the above discussions in Sec. III C.

On the other hand, the presence of the significant amount of CO₂ at the exhaust of a CI engine signals proper combustion inside the engine cylinder. The CO₂ emission trend of all the tested fuels under varying loading conditions is presented in Fig. 3(c). These data endorse effective combustion at higher loads evinced by increased CO₂ emission. It is noteworthy, that at all loads, the CO₂ emission levels from petrodiesel were markedly higher vs WMBDs; the rapid evaporation of alcoholic compounds in WMBDs may have restricted conversion of CO₂ from CO.^{36,43} At maximum load, the CO₂ emission level for petrodiesel was 1.8%, while emission levels for sample 1, sample 2, and sample 3 were 1.1%, 1.08%, and 1.09%, respectively.

The NO_x emissions from the CI engine fueled with the tested fuels at various loading conditions are presented in Fig. 3(d). NO_x formation during combustion in a CI engine is primarily due to oxygen concentration, peak combustion temperature, and residence time. Thus, the oxygen content of fuels dictates the level of NO_x formation in CI engines, combined with atmospheric nitrogen, which constitutes the major component of air intake. Consequently, NO_x formation in engine exhaust results from the combustion of the fuel at high temperatures.³⁸ NO_x emission levels for WMBD followed an increasing trend up to 80% load (9 kg) and decreased slightly at full load condition. On the other hand, an exponential rise in NO_x emission was observed at full load for petrodiesel. NO_x emission of WMBDs was found to be significantly lower (70 ppm) than petrodiesel (170 ppm), particularly at higher load conditions. This is due to the higher latent heat of vaporization of ethanol and butan-2-ol in WMBDs that reduced the combustion temperature inside the engine cylinder.^{36,45}

E. Exhaust gas temperature analysis

The exhaust gas temperature for all the tested fuels at different engine loads is presented in Fig. 4. The exhaust gas temperature increased with an increase in engine load. Petrodiesel has the highest exhaust temperature of 433.33 °C at full load. The exhaust temperatures for WMBDs were much lower (350–360 °C) than that of the exhaust temperature for petrodiesel. The higher latent heat of vaporization of alcohol reduces in-cylinder temperature during combustion,³⁴ which is the major reason for lower exhaust temperature for WMBDs. However, the exhaust temperatures obtained for WMBD fuels are quite sufficient for useful energy generation through effective heat recovery system.⁴³

F. Exhaust exergy analysis

The Ex^{th} and Ex^{ch} of the exhaust gases [calculated from Eqs. (1) and (2) using Modelica software] for WMBDs and petrodiesel at

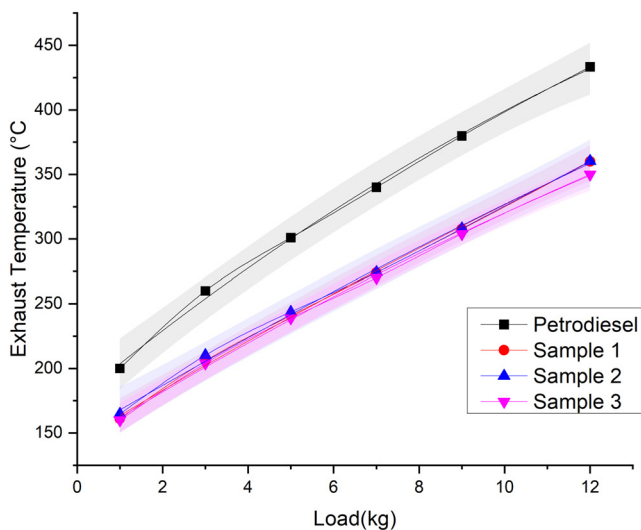


FIG. 4. Exhaust temperature for WMBDs and petrodiesel under different load conditions.

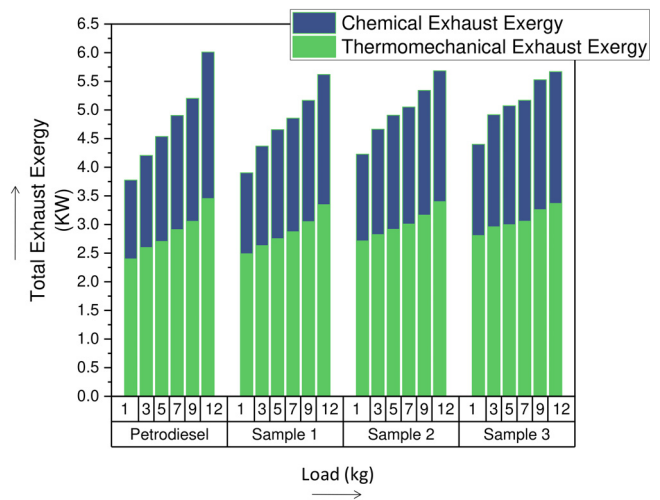


FIG. 5. The thermomechanical exergy (Ex^{th}) and chemical exergy (Ex^{ch}) of the exhaust gases for WMBD samples and petrodiesel at different load conditions.

different loads are presented in Fig. 5. Several inferences could be drawn from these results. The total exhaust exergy increased with increasing load. The pressure and temperature of exhaust gases increased for each load increment, which led to an increase in Ex^{th} . The surge of Ex^{ch} with increasing load for all the samples is attributed to the significant chemical potential between the exhaust and the surrounding ambient environment. This chemical potential existed between the “exhaust” and “ambient” mainly due to (1) concentration difference and (2) reactive nature of the exhaust gases.^{19,20} However, the pattern and nature of the exhaust gases (discussed in Sec. III D) suggest that the concentration difference is most likely to have the major impact on “chemical potential” as well as on Ex^{ch} . Moreover, at lower loads, both Ex^{th} and Ex^{ch} of the petrodiesel were lower in comparison to that of WMBDs. However, this trend was reversed at the highest load (i.e., 12 kg). This suggests that WMBD fuels could be successfully used at the proposed cogeneration system, particularly under low to medium load conditions. On the other hand, petrodiesel exhibited the highest cogeneration potential both in terms of Ex^{th} and Ex^{ch} at full load conditions.

A clear observation from Fig. 6 is that the total exergy of the system increased with increasing load for all the tested samples. It resulted from the steady increment of both BP and total exhaust exergy in relation to engine load for all the samples. Moreover, the share of BP in the total exergy content of the system increased with load increment; the latter also reduced the disparities in the BP at similar loads for different fuel samples (Fig. 7). A larger easily extractable BP share at lower loads from petrodiesel could easily furnish as compared to the WMBDs. However, operating the engine at higher loads will marginalize the exergetic performance variations across the tested fuels, where the net system exergy outputs, as well as the relative shares of BP and exhaust exergy, tend to become similar for each candidate.

G. LCA analysis

The variations in environmental impact factors, as well as end point damage categories namely, human health, ecosystem quality,

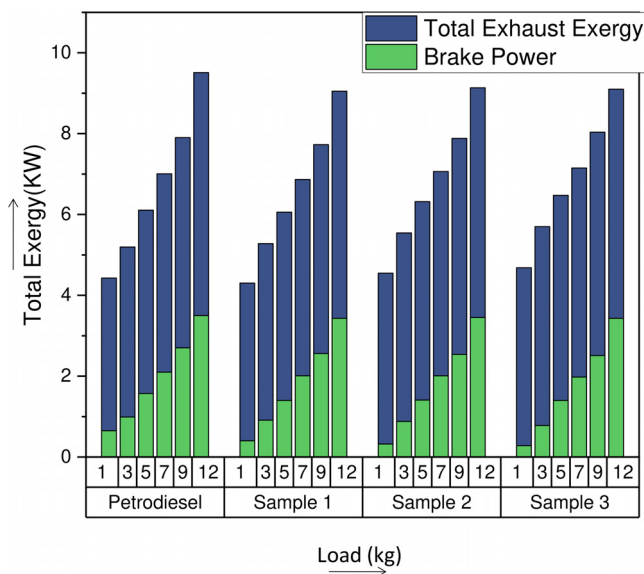


FIG. 6. The total exergy of the exhaust gases for WMBD samples and petrodiesel under different load conditions.

and resource exploitation for WMBDs and petrodiesel, are presented in Table IV. WMBDs indicated a greater impact in the human health damage category in comparison to petrodiesel. The major contribution of human health damage category arose from the impact of particulate matter formation for both WMBDs and petrodiesel. Although the percentages of increase were not widely divergent, it can be concluded that the incorporation of alcohols in WMBDs contributed to increased particulate matter formation. In addition, water consumption and global warming were the two predominant factors for the higher

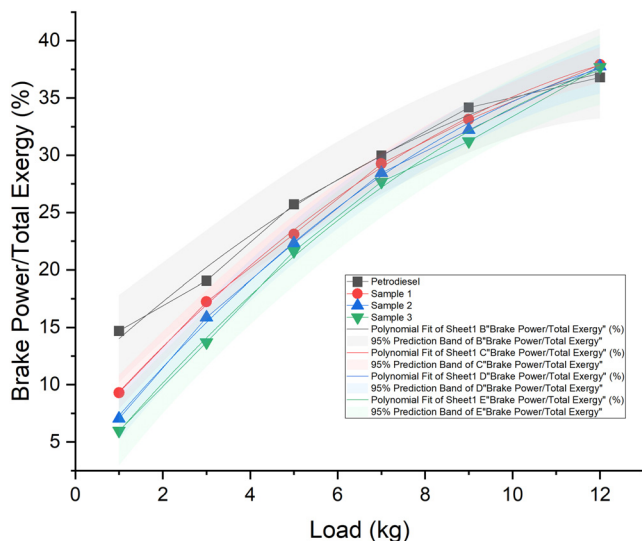


FIG. 7. The brake power (BP) share in the total exergy of the exhaust gases for WMBD samples and petrodiesel under different load conditions.

impact of WMBD in the human health damage category over petrodiesel. This might emanate from the alcohol manufacturing processes; especially the butan-2-ol, which requires higher water consumption for hydration, thus apprehending global warming. However, among the human health damage category impact parameters, the human non-carcinogenic toxicity, stratospheric ozone depletion, and ionizing radiation impacts were significantly lower for WMBDs than that of the petrodiesel.

WMBDs showed greater impact in the ecosystem quality damage category over petrodiesel. Global warming, terrestrial ecosystem ozone formation, and terrestrial acidification were the main impact factors, with the greatest contributions in the ecosystem quality damage category for WMBDs and petrodiesel. The terrestrial ecosystem ozone formation and global warming impact levels for WMBDs were higher than that of petrodiesel. The butan-2-ol production process might be responsible for increasing the impact of these two factors in the case of WMBDs. On the contrary, WMBDs showed a lower impact of terrestrial acidification and terrestrial ecotoxicity than petrodiesel, among the ecosystem quality impact assessment factors. The incorporation of alcohols and WCO in WMBDs contributed toward reducing the impact of terrestrial acidification and ecotoxicity.

WMBDs suggested a lower impact on resource depletion level in the damage category in comparison to petrodiesel. The present LCA analysis indicated that the impact of fossil resource exploitation or scarcity could be reduced up to 34% with the utilization of WMBD, instead of petrodiesel in energy applications. It confirms that WMBD fuels produced from WCO can play a significant role in combating the scarcity of fossil fuel reserves, as well as worldwide impending energy crisis.

The alcohol fraction in WMBD contributed toward increasing the impact of human health and ecosystem quality damage categories, attributed to hydration for conversion of ethene and butane to ethanol and butan-2-ol, respectively. This manufacturing process impacted water consumption, water eutrophication, freshwater toxicity, global warming, and ozone formation in LCA analysis. Therefore, the adoption of an alternative manufacturing process could bypass these significant and negative impacts on human health and ecosystem quality damages. The feedstock chosen for ethanol and butanol production is also crucial in this respect. Bioethanol produced from different biodegradable or renewable biomass is currently viewed as a feasible solution.⁴⁶ Similarly, biobutanol production from various second- and third-generation biomass feedstocks, such as sugarcane bagasse, rice straw, wheat straw, corn stover, and microalgal biomass, are part of the resources under consideration.⁴⁷ Methods for fermentative production of butan-2-ol (2-butanol) from various waste and bio-based materials have also received significant consideration in recent years.⁴⁸⁻⁵⁰ Bioethanol and bio-based butan-2-ol will possibly negate the human health and ecosystem quality damage impacts of WMBDs.

H. ELCA analysis

The cumulative exergy consumption of WMBDs and petrodiesel is presented in Table V. Cumulative exergy consumption of petrodiesel was greater than that of WMBDs. The major contribution in the cumulative exergy consumption was obtained from nonrenewable resources, whereas renewable resources exhibited a negligible share of the cumulative exergy consumption. Moreover, petrodiesel and

TABLE IV. Impacts of end point damage categories (and different factors associated with them) for the fuels.

Endpoint damage category	Impact factors	Unit	Impact quantity/points			
			Petrodiesel	Sample 1	Sample 2	Sample 3
Human health	Global warming, human health	Daily	4.93×10^{-8}	6.92×10^{-8}	7.4×10^{-8}	7.9×10^{-8}
	Stratospheric ozone depletion	Daily	1.74×10^{-10}	1.02×10^{-10}	1.03×10^{-10}	1.05×10^{-10}
	Ionizing radiation	Daily	1.39×10^{-10}	1.02×10^{-10}	1.03×10^{-10}	1.06×10^{-10}
	Ozone formation, human health	Daily	1.89×10^{-9}	2.39×10^{-9}	2.59×10^{-9}	2.62×10^{-9}
	Particulate matter formation	Daily	1.25×10^{-7}	1.33×10^{-7}	1.38×10^{-7}	1.5×10^{-7}
	Human carcinogenic toxicity	Daily	5.55×10^{-10}	6.24×10^{-10}	6.66×10^{-10}	6.93×10^{-10}
	Human non-carcinogenic toxicity	Daily	2.39×10^{-9}	2.2×10^{-9}	2.28×10^{-9}	2.48×10^{-9}
	Water consumption, human health	Daily	-7.22×10^{-10}	4.79×10^{-8}	5.27×10^{-8}	6.38×10^{-8}
Ecosystems	Global warming, terrestrial ecosystems	species.yr	3.23×10^{-10}	4.54×10^{-10}	4.55×10^{-10}	5.17×10^{-10}
	Global warming, Fresh water ecosystems	species.yr	8.8×10^{-15}	1.24×10^{-14}	1.32×10^{-14}	1.41×10^{-14}
	Ozone formation, Terrestrial ecosystems	species.yr	2.85×10^{-10}	4.2×10^{-10}	4.6×10^{-10}	4.6×10^{-10}
	Terrestrial acidification	species.yr	7.99×10^{-10}	6.4×10^{-10}	6.64×10^{-10}	7.0×10^{-10}
	Fresh water eutrophication	species.yr	2.8×10^{-11}	1.01×10^{-10}	1.14×10^{-10}	1.05×10^{-10}
	Marine eutrophication	species.yr	7.29×10^{-15}	1.07×10^{-14}	1.12×10^{-14}	1.21×10^{-14}
	Terrestrial ecotoxicity	species.yr	6.36×10^{-12}	4.11×10^{-12}	4.15×10^{-12}	4.34×10^{-12}
	Freshwater ecotoxicity	species.yr	3.72×10^{-12}	5.56×10^{-12}	5.84×10^{-12}	6.55×10^{-12}
	Marine ecotoxicity	species.yr	2.41×10^{-13}	2.87×10^{-13}	3×10^{-13}	3.31×10^{-13}
	Land use	species.yr	5.65×10^{-11}	8.96×10^{-11}	9.48×10^{-11}	1.07×10^{-10}
Resources	Mineral resource scarcity	USD2013	0.000 107	0.000 1	0.000 104	0.000 112
	Fossil resource scarcity	USD2013	0.528	0.348	0.358	0.365
Human health		Daily	1.79×10^{-7}	2.56×10^{-7}	2.7×10^{-7}	2.99×10^{-7}
Ecosystems		species.yr	1.5×10^{-9}	1.71×10^{-9}	1.83×10^{-9}	1.9×10^{-9}
Resources		USD2013	0.528	0.348	0.358	0.365

butan-2-ol had the greater exergetic influence in the entire life cycle of the WMBD fuels. The E_{ff} and ES at all loads for the fuel samples are presented in Figs. 8 and 9, respectively. E_{ff} and ES for the WMBDs were comparatively greater than that of petrodiesel at all loads. Moreover, E_{ff} and ES increased significantly with the integration of waste heat recovery (cogeneration) unit for all fuels. Generally, E_{ff} and ES increased with an increase in load conditions of the CI engine (without cogeneration facility) for each of the fuel samples. The highest E_{ff} in CCS was obtained for each of the WMBDs at full load conditions of the engine. At full loading conditions, E_{ff-CCS} for sample 1, sample 2, and sample 3 were 27.76%, 26.96%, and 24.57%, respectively. ES_{CCS} was maximum (26.62%) for the sample 1 at full load conditions, followed by sample 2 (25.94%), and sample 3 (23.72%). The ELCA analysis justifies that WMBD fuels exhibit superior utilization efficiency. Moreover, both CI engine (without cogeneration) and CCS,

possessed greater compatibility with WMBD fuels, than petrodiesel in terms of environmental sustainability.

The improvement in exergetic life cycle performance parameters after incorporation of oxygenated biofuel in petrodiesel was in agreement with the previous study by Hosseinzadeh-Bondbafha *et al.*²⁰ The engine performance and combustion exergy analyses indicated inferior performance for WMBDs with respect to petrodiesel particularly at the low engine loading conditions (discussed in Sec. III B). However, ELCA analysis suggests counterbalancing of such negative effects associated with BP and BSFC, and E_{ff} and ES values of WMBDs surpassed the values corresponding to petrodiesel. Although WMBDs exhibited lower GCV and viscosity than the petrodiesel, the former exceeds the latter in terms of exergetic life cycle performance indicators. Overall, the blending of WCO microemulsion biofuel with petrodiesel was proved to be a successful strategy from the perspectives of resource saving and environmental sustainability. E_{ff} and ES results obtained in the study can be important for practical applications of WMBDs for power production and in the transportation sector.

IV. CONCLUSIONS

The sustainability of WMBDs was investigated in the present study. The CI engine performance, combustion, and emission characteristics for WMBDs were evaluated and compared with petrodiesel. The engine performance parameters, such as BSFC, BP, and ME, of

TABLE V. Cumulative exergy consumption of the fuels.

Sample	Cumulative exergy consumption (MJ/kg)
Petrodiesel	54.1
Sample 1	38.2
Sample 2	39.5
Sample 3	40.4

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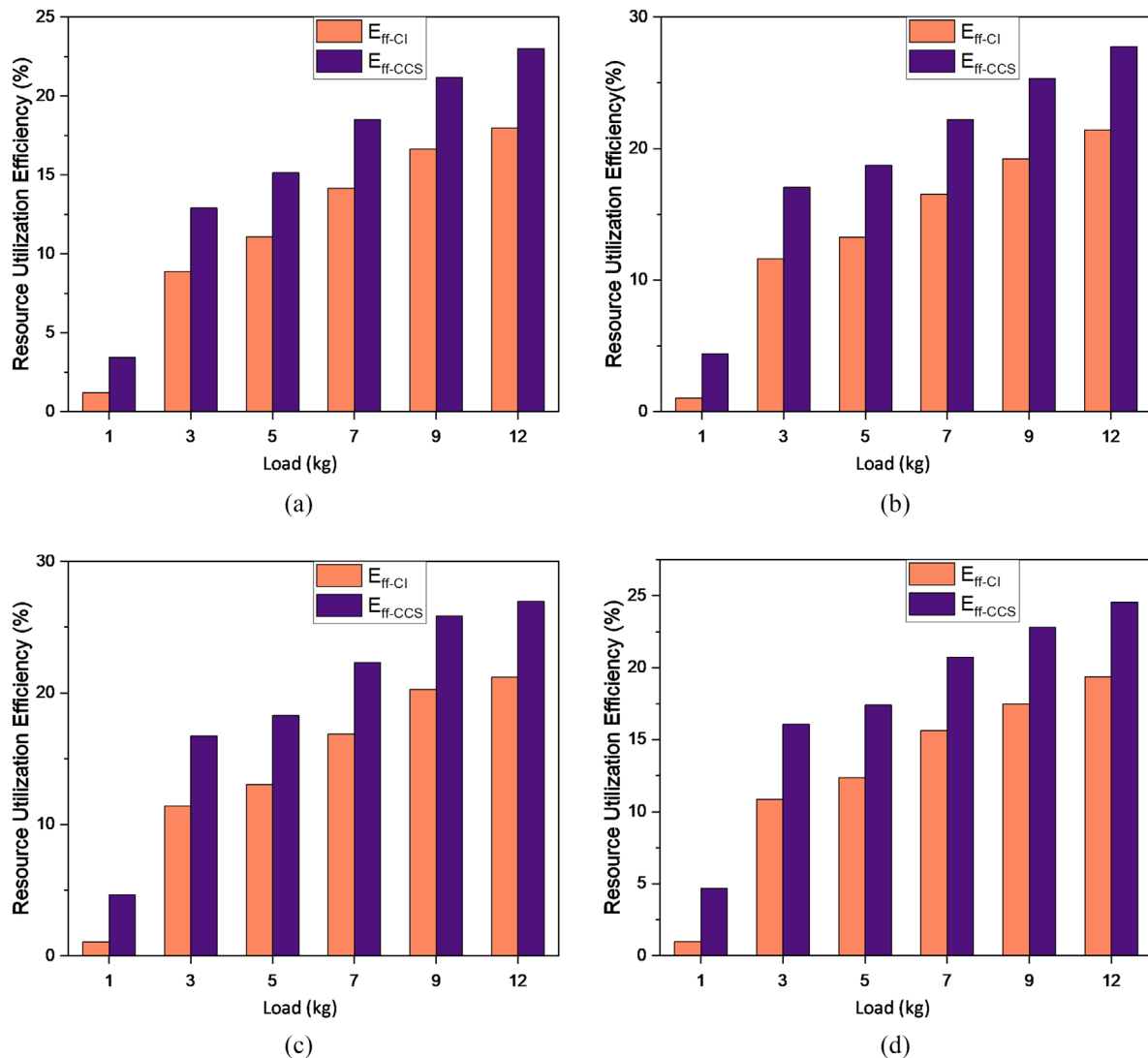


FIG. 8. Resource utilization efficiency WMBDs and petrodiesel at different load conditions (representing CI and CCS): (a) Petrodiesel, (b) sample 1, (c) sample 2, and (d) sample 3.

WMBDs were comparable to petrodiesel. WMBDs exhibited higher cylinder pressure and $NHRR_{max}$ than petrodiesel. However, BTE and ITE were lower for the WMBDs than that of the petrodiesel. WMBDs emitted a lower amount of CO , CO_2 , and NO_x in comparison to petrodiesel, particularly at intermediate, and higher loading conditions of the CI engine. The CO emission level for WMBDs reduced significantly, with an increase in load of the engine. Although the unburned HC percentage was higher for WMBDs in comparison to the unburned HC percentage of petrodiesel, the emission levels were insignificant with respect to the other exhaust gases.

LCA analysis indicated that the impact of fossil resource exploitation could be reduced up to 34% with WMBDs in comparison to petrodiesel. The alcohol fraction (ethanol and butan-2-ol) in WMBD contributed toward increasing the human health and ecosystem quality damage impacts in LCA analysis. However, the higher human

health and ecosystem damaging impacts for WMBDs most likely could be eliminated with the utilization of bioethanol and biobased butan-2-ol/biobutanol.

The thermomechanical exergy and chemical exergy analyses of the exhaust gases suggest that WMBDs exhibited cogeneration potential particularly at low and medium load conditions, while petrodiesel possessed the highest cogeneration potential under full load conditions. The net system exergy output, as well as the relative shares of brake power and exhaust exergy, tended to become similar for both WMBDs and petrodiesel at higher operating loads. The ELCA analysis proves that WMBD fuels exhibited superior utilization efficiency over petrodiesel. Moreover, the CI engine with and without cogeneration facility (or integrated waste heat recovery facility) showed better performance with WMBD fuels than petrodiesel in terms of environmental sustainability. The resource utilization efficiency (E_{ff}) and

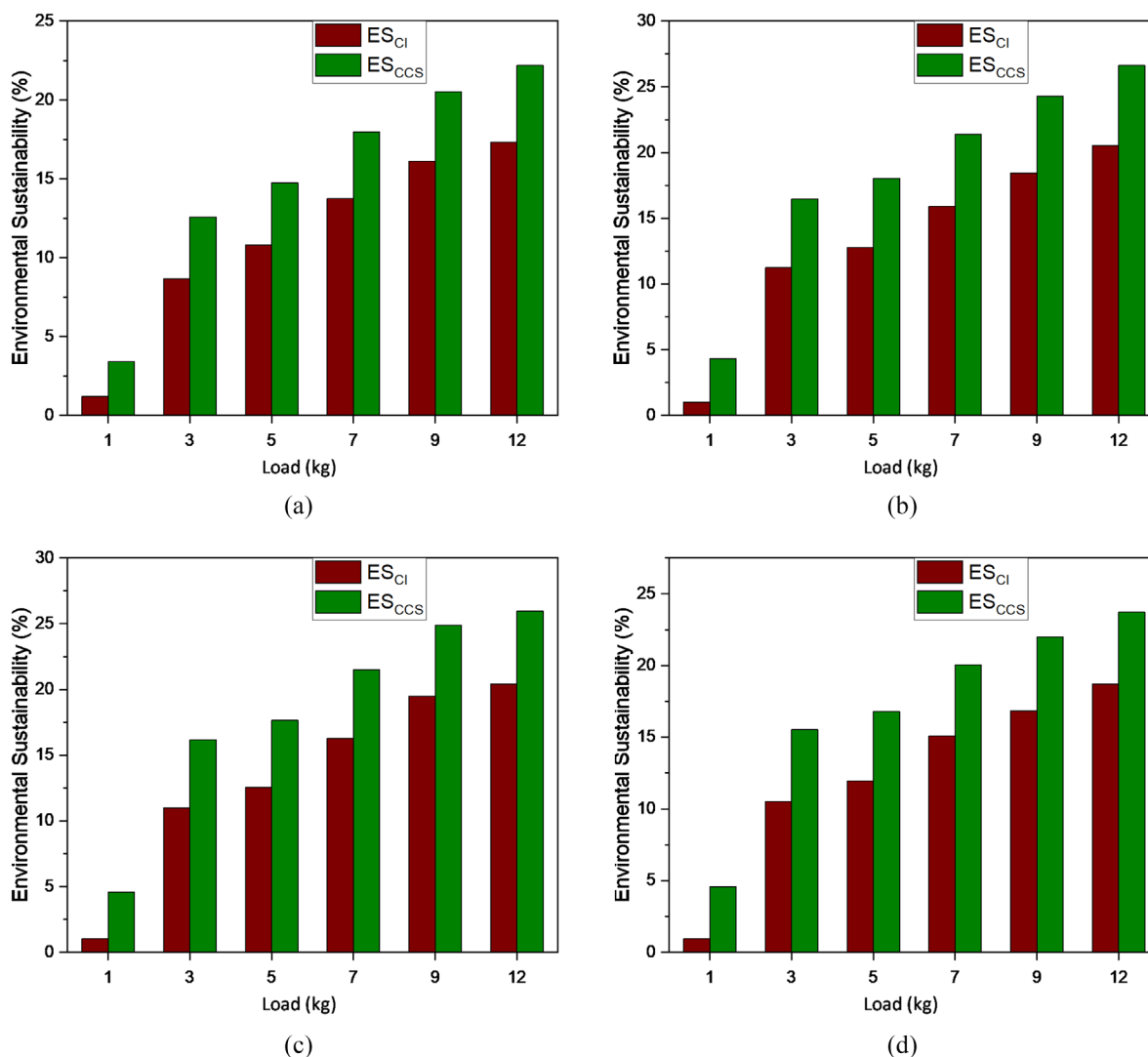


FIG. 9. Environmental sustainability for WMBDs and petrodiesel at different load conditions (representing CI and CCS): (a) Petrodiesel, (b) sample 1, (c) sample 2, and (d) sample 3.

environmental sustainability (ES) increased significantly with the integration of waste heat recovery unit (CCS) for all the fuels.

The combustion exergy and exergoenvironmental life cycle assessments along with engine performance and emission characteristic study suggests that WMBDs offer strong candidature as a sustainable environmentally benign alternative fuel for CI engine based power generation processes. Nonetheless, the sustainability of the surfactant free microemulsion biofuels from WCO can be further validated through extensive real-world based energy production applications.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for details on experimental setup and testing procedure for engine performance and emission

characteristics evaluation (Sec. S.I), compositions of gases and vapor at the engine exhaust (Sec. S.II), fuel characterization (Sec. S.III), technical specification of the CI engine set up (Table S.I), CRDI VCR engine measurement accuracies (Table S.II), measurement range, resolutions and accuracies of the gas analyzer (Table S.III), fatty acid compositions of WCO (Table S.IV), statistical data for confidence interval for Figs. 1, 3, 4, and 7 (Tables S.V–S.XVI), schematic representation of the experimental setup (Fig. S.1), ¹H NMR spectroscopy of microemulsion biofuel (Fig. S.2), and FT-IR spectroscopy of microemulsion biofuel (Fig. S.3).

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Plaban Bora: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Resources (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Jyotishmanyu Kakoti:** Formal analysis (equal); Investigation (equal); Methodology (equal); Validation (equal); Writing – original draft (equal). **Pranaynil Saikia:** Formal analysis (equal); Validation (equal); Writing – original draft (equal). **Nayan Jyoti Talukdar:** Formal analysis (equal); Validation (equal). **Mayur Mausoom Phukan:** Formal Analysis (equal); Investigation (equal); Writing – review & editing (equal). **Dibakar Rakshit:** Formal analysis (equal); Supervision (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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