Effect of Dominant Fatty Acid Esters on Emission Characteristics of Waste Animal Fat Biodiesel in CI Engine

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This present study aims in understanding the influence of dominant fatty acid esters of waste animal fat biodiesel on its emission characteristics in CI engine. Biodiesel was produced from waste animal fat by means of base catalyzed transesterification; and Ethyl oleate (40.21%), ethyl palmitate (25.36%), and ethyl stearate (16.87%) were characterized as dominant fatty acid esters using GC spectra. Test samples were prepared for these ester molecules based on their availability, in addition to biodiesel blend and plain diesel and were tested for their emission levels in single cylinder four stroke CI engine using flue gas analyser. High exhaust gas temperature was contributed by Ethyl oleate (1.15% lesser than biodiesel), as a result of low cetane number due to unsaturation; and high viscosity. Likewise, the increased carbon chain length and unsaturation of ethyl oleate (2.55% lesser than biodiesel) resulted in high concentration of CO emission for biodiesel whereas high CO$_2$ emission concentration was because of ester molecules with increased carbon chain length (stearate and Oleate esters). Reduced NO$_X$ emission for biodiesel was as a result of higher cetane number from ethyl stearate (CN = 86.83) and ethyl palmitate (CN = 86.55), which reduced its ignition delay thereby moderating the heat release rate. In addition, long carbon chained ester molecules (oleate and stearate esters) in biodiesel consumed more oxygen content for improving overall rate of combustion while increased HC emission was explained by unsaturation in biodiesel because of ethyl oleate (on average, 50 PPM).

Keywords: animal fat biodiesel, fatty acid esters, cetane number, unsaturated double bonds, emission characteristics

INTRODUCTION

Increase in use of biodiesel as a viable supplement and alternate for fossil diesel fuel to meet the energy demand has made many researchers to focus on improvising its properties and engine characteristics with minimal energy and capital consumption. This renewable biofuel is highly regarded for combustion based applications because of its reduced emission characteristics owing to zero sulfur and aromatic content; and improvised engine performance due to higher oxygen content and cetane number (Srinivasan and Jambulingam, 2018).

Traditionally, Biodiesel is processed from different feedstocks like waste vegetable oil (Ray and Prakash, 2019), animal fat (Kirubakaran and Selvan, 2018), non-edible seeds oil (Hosseini and Wahid, 2012; Palani et al., 2017), waste oils and greases (Tran et al., 2018) and is converted into low viscous biofuel by means of catalyst assisted transesterification reaction using short chain primary alcohols like methanol, ethanol as solvent. Among these, waste animal fats are regarded as an ideal feedstock for low cost biodiesel production on account of its easy availability as discarded wastes, no "food over fuel" conflicts; in fact, using these wastes for energy production serves as an effective technique for reducing the environment threats caused by them. Apart from environmental concern, these waste fats are widely chosen as most promising feedstock because of its high energy density. In general, these waste animal fats are rendered from discarded fleshing wastes in leather tanneries and discarded fat wastes in slaughter houses and meat processing industries (Srinivasan et al., 2018a); and was found to be unsuitable for edibility but rich in triglyceride content, thereby making it as an ideal option for biodiesel production. Indeed, numerous studies related to its optimized production (Aboelazayem et al., 2018), properties study and their prediction using mathematical modeling (Jambulingam and Srinivasan, 2019), comprehensive engine characteristics (Nabi et al., 2019) and economic analysis (Subramanian et al., 2005) have been carried out to commercialize this biofuel in global market. However, for being a viable replacement for existing fossil fuel, which causes higher pollution, these biofuels must be evaluated thoroughly for its engine characteristics to determine their maximum range of efficiencies and emissions in exhaust gas and factors influencing them. In like manner, numerous experimental works have studied the performance and emission characteristics of biodiesel in compression ignition engine.

In relevance to that, Srinivasan et al. (2017) carried out the preliminary engine characteristics study on waste suet biodiesel and found higher brake-specific fuel consumption (BSFC) for biodiesel and its blends when compared to plain diesel as a result of low calorific value and high viscosity. In addition, the reduced thermal efficiency of biodiesel than plain diesel was because of high viscosity which reduced its atomization, vaporization and combustion. Interestingly, reduction in CO and NO_X emission for biodiesel and its blends was noticed by reason of high oxygen content and reduced ignition delay.

Similarly, Emiroğlu et al. (2018) carried out engine characteristics study on turkey fat biodiesel in CI engine by preparing 3 different blends in 10, 20, and 50% (v/v) with plain diesel. The maximum Heat Release rate and cylinder pressure for biodiesel blends was because of low cetane number which prolonged the ignition delay thereby making the accumulated fuel to undergo rapid combustion. Along with lower cetane

number, higher rate of density and viscosity of biodiesel increased its NO_X emissions and was found to be higher for B50 upon accounting its lowest cetane number. However, lower heating value of biodiesel blend resulted in reduced brake thermal efficiency (BTE) than compared to diesel despite its higher oxygen content.

Following this, Jayaprabakar et al. (2019) carried out the process optimization and engine characteristics study of biodiesel produced from sheep skin in CI engine by blending with plain diesel in varying concentrations: 5, 10, 15, and 20%. Here, CO_2 emission increased with blend% for biodiesel because of high oxygen and carbon content whereas high NO_X emission from biodiesel was the outcome of its high Cetane number and degree of unsaturation. However, high C/H ratio and low oxygen content resulted in higher hydrocarbon (HC) emission for diesel.

Apart from conventional CI engine, engine characteristics study was carried out in Common Rail Direct Injection (CRDI) engine for animal fat biodiesel by preparing five different blends in varying concentrations of 10–50% with plain diesel and concluded 30% blend as the most optimal blend. Interestingly, lower HC emission was noted for B30 blend because of abundant availability of oxygen and optimum blend which also helped in reducing its BSFC. Apparently, NO_X emission was found to be reducing for oxidized biodiesel as compared with unoxidized biodiesel owing to higher cetane number in case of former; and the same was reported by Monyem and Van Gerpen (2001) whose study concluded that both oxidized and unoxidized biodiesel demonstrated identical engine performance (Shahir et al., 2017).

Furthermore, Hazrat et al. (2019) carried out a significant study of emission characteristics in CI engine by employing a heterogeneous blend of waste tallow and cooking oil biodiesel blended with extra low sulfur diesel for varying biodiesel in concentration of 5, 10, and 15% and found that higher CO_2 emission concentration for biodiesel blends was on account of high oxygen content and elevated temperature inside combustion chamber. Similarly, NO_X emission was found reduced for plain diesel whereas increased for biodiesel, owing to surplus oxygen content from the binary biodiesel itself, which reacted with nitrogen present in the intake air; however, this oxygen content was responsible in reducing the HC emission as it helped in proper mixing and combustion of fuel. In contrast, CO emission was found to be very low for all the blends but higher emission was noted during the start of combustion owing to rapid acceleration resulting in improper oxidation of fuel.

Even though, previous literatures explained the possibility of reduced emission upon using biodiesel in CI engine; the causes and effects of these reduced emission can be explained by studying the role of fatty acid esters in deciding the emission characteristics for biodiesel on combustion. Inspite of its importance, only few studies related to the influence of ester molecules in emission characteristics have been carried out and reported.

Following that, Gopinath et al. (2010) compared the engine characteristics of 13 different biodiesels using single cylinder DI diesel engine and numerous conclusions were derived from this study. Preliminary results concluded that biodiesel with high unsaturated fatty acid content resulted in higher NO_X

Abbreviations: BSFC, Brake Specific Fuel Consumption; BTE, Brake Thermal Efficiency; C/H, Carbon-Hydrogen Ratio; CI, Compression Ignition; CO, Carbon monoxide; CO_2, Carbon dioxide; CRDI, Common Rail Direct Injection; EGT, Exhaust Gas Temperature; HC, Hydrocarbon; ITE, Indicated Thermal Efficiency; N_{air}, Air Quantity (in mols); NOx, Nitrogen Oxide; PM, Particulate Matter; SFC, Specific Fuel Consumption; $V_{overall}$, Overall volume of sample (in ml); ϕ_E, Ester Factor; ψ_B, Blend Factor.

emission and reduced thermal efficiency. The study indicated that the ignition delay increases with fuel density, degree of unsaturation and its iodine value but deceases with high cetane number whereas ignitability of fuel was based on cetane number, fatty acid ester composition, residual methanol, glycerides, and water content. Also, increase in unsaturation and density decreased maximum heat release rate, BTE but increased specific fuel consumption, maximum gas pressure, and exhaust gas temperature, CO and HC (since unsaturation decreases oxygen content) and NO_X emission. Interestingly, the dynamic injection timing was found to be faster for high density and high unsaturated fuels.

Similarly, Srinivasan et al. (2019) studied the role of fatty acid esters in influencing the engine characteristics of waste beef tallow biodiesel. Based on characterization, ethyl oleate, ethyl palmitate, and ethyl stearate were characterized as the dominant fatty acid ethyl esters and played a significant role in deciding the engine characteristics of biodiesel. Increased fuel consumption, reduced thermal efficiencies and elevated exhaust gas temperature, for biodiesel blends, were on account of higher viscosity for long carbon chained oleate and stearate esters. Even more, the presence of long chained stearate and oleate molecules in biodiesel blend resulted in high CO_2 emission concentration while the unsaturated double bond in fatty acid moiety of oleate molecule led to high CO emission concentration. Despite the fact, NO_X emission concentration reduced on account of higher cetane number from palmitate and stearate ester molecules which reduced its ignition delay. Furthermore, high cetane number along with surplus oxygen content contributed by individual fatty acid esters accounted for maximum cylinder pressure and high instantaneous heat release rate.

Moreover, Hellier et al. (2012) investigated the influence of alcohol moiety present in fatty acid ester molecules on engine characteristics. This study proposed that ester molecules released larger proportion of energy upon combustion owing to longer combustion duration and the ignition delay was decided based upon the chain length of fatty acid moiety instead of alcohol moiety. Even so, increase in carbon at alcohol moiety reduced the ignition delay but also increased the mass of particulates by double upon adding single carbon atom to chain of alcohol moiety. Consequently, increased NO_X emission was a consequence of unsaturation which increased the adiabatic flame temperature.

In addition, Schönborn et al. (2008) studied the influence of molecular structure of fatty acid esters in NO_X and particulate matter (PM) formation during combustion. This study proposed that ignition quality and early ignition increased with length of fatty acid chain length and helped in achieving better HRR. Longer chained molecules had longer combustion duration along with lower peak HRR and peak pressure. Also, long chained fatty acid esters ignited quickly thereby moderating the HRR resulting in peak temperature followed by reduced NO_X. Likewise, saturated fatty acid esters had reduced NO_X emissions where the emission was directly proportional to FA chain length but increases with addition of double bond in carbon chain. Moreover, increase in carbon atom at alcohol moiety by 1 or 2 atoms has the ability to reduce NO_X but increases PM slightly.

In this present work, a novel approach has been attempted in understanding the influence of dominant fatty acid esters in deciding the exhaust gas concentration of waste animal fat biodiesel by comparing emission characteristics of biodiesel from animal fat with characterized dominant fatty acid esters. Upon understanding their substantial role in engine characteristics, this work might act as a platform for redefining the combustion of biodiesel and achieve desired power output along with reduced emission by modifying the ester molecules in biodiesel through suitable techniques.

MATERIALS AND METHODOLOGY

Processing and Production of Biodiesel

Waste animal fat was rendered from discarded leather fleshing and meat processing wastes collected from tanneries and animal slaughterhouses; and were refrigerated to evade microbial infection and oxidation (rancidification). Rendering of waste fat was carried out using autoclave operated at 120°C and 2 Bar and; were filtered and degummed using orthophosphoric acid (Srinivasan et al., 2018b). The refined fat was subjected for ethanol based transesterification at stoichiometric molar ratio (1:6) and optimal catalyst: (0.5% wt. of fat) KOH concentration and reaction temperature of 60°C under continuous stirring. The reaction products were separated into biodiesel and glycerol by decantation under the influence of gravity and the resultant biodiesel was water washed successively followed by drying. All the chemicals used for biodiesel production and emission testing were procured from Sigma Aldrich Chemicals Company.

Characterization and Volumetric Blend Calculation of Fatty Acid Esters

Fatty acid esters in produced biodiesel were characterized from Gas chromatography spectra based on their respective peaks obtained at their corresponding retention time, whereas the area % occupied by the obtained peaks signified their composition. Accordingly, ethyl oleate, ethyl palmitate, and ethyl stearate were regarded as dominant fatty acid esters based on their availability % and are summarized in **Table 1** along with their retention time and molecular weight. **Figure 1** illustrates the GC spectra of waste animal fat biodiesel.

For emission characteristics study, a set of test samples namely: Biodiesel Blend, Oleate Blend, palmitate blends, and stearate blend, were prepared by blending waste fat biodiesel, ethyl oleate, ethyl palmitate, ethyl stearate with plain diesel, which was also taken as reference blend. The volume of ester/biodiesel sample for preparing the necessary blend was calculated using Equation 1(Srinivasan et al., 2019):

$$\text{Amount of Ester Sample (ml)} = V_{overall} * \{1 - [\varphi_E * \psi_B]\} \quad (1)$$

Where, $V_{overall}$-Required Sample Volume, ψ_B-Blend Factor, φ_E-Ester Factor and $\varphi_E = 1$, in case of biodiesel.

TABLE 1 | Availability of characterized dominant fatty acid esters along with their retention time and molecular weight.

Fatty acid ester	Common name	Molecular formula	Retention time (min)	Availability %	Molecular weight (g/mol)
Tetradecanoic acid ethyl ester	Ethyl myristate	$C_{16}H_{32}O_2$	17.486	10.79	256.2
Hexadecanoic acid ethyl ester	Ethyl palmitate	$C_{18}H_{36}O_2$	19.574	25.36	284.3
Oleic acid ethyl ester	Ethyl oleate	$C_{20}H_{38}O_2$	20.647	40.21	310.2
Octadecanoic acid ethyl ester	Ethyl stearate	$C_{20}H_{40}O_2$	21.354	16.87	312.3
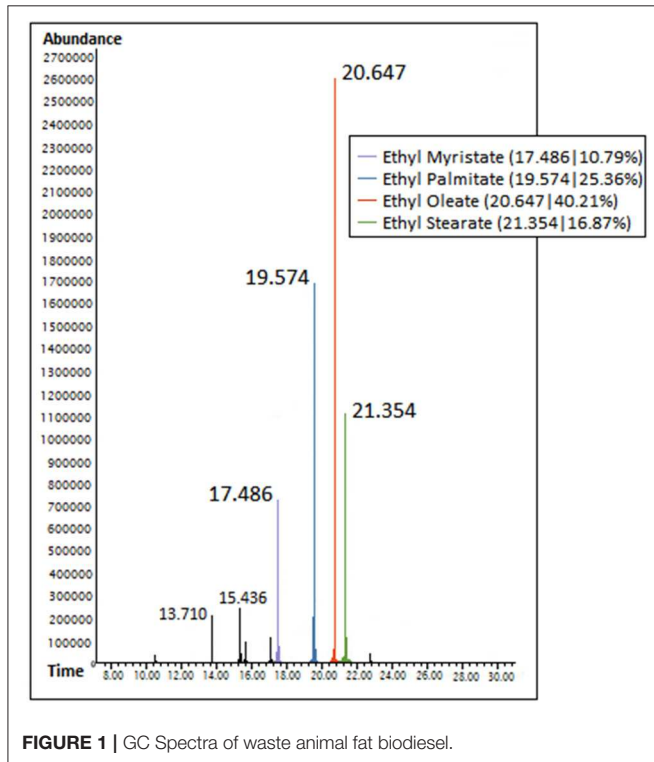
FIGURE 1 | GC Spectra of waste animal fat biodiesel.

TABLE 2 | Physico-chemical properties of waste animal fat biodiesel.

Properties	Unit	Waste fat biodiesel	Plain diesel	Limits	Standard
Density	Kg/m^3	870	790	–	–
Specific gravity	–	0.87	0.79	0.86–0.90	ASTM D1298
Flash point	°C	157	90	130 min	ASTM D93
Fire point	°C	168	100	–	ASTM D93
Kinematic Viscosity	mm^2/s	4.7	3.6	1.90–6.0	ASTM D445
Cetane number	–	74.45	47	47 (min)	ASTM D976
Calorific value	MJ/Kg	37.6	42.5	35 to 43	ASTM D240
Acid number	mg/KOH	0.1	0.07	0.80 max	ASTM D664
Iodine value	$(gI_2/100\ gm)$	33.47	–	120 max	ASTM D5554
Saponification value	(mg KOH/gm)	192.64	–	–	ASTM D5558
Chemical formula	–	$C_{19}H_{37}O_2$	$C_{16}H_{28}$	–	–
Carbon content	(wt.%)	76.77	85.16	–	ASTM D5291
Hydrogen content	(wt.%)	12.46	14.26	–	ASTM D5291
Oxygen content	(wt.%)	10.77	–	–	ASTM D5291
Sulfur content	(wt.%)	–	0.152	–	ASTM D5291

Properties and Engine Characteristics Evaluation

The suitability of waste animal fat biodiesel for commercialization and engine applications were analyzed by studying their thermal and physico-chemical properties determined as per ASTM standards and was found to be a viable supplement upon comparing with plain diesel. Properties like density, kinematic viscosity were determined to understand its physical behavior whereas flash point, cetane number, calorific value defined its thermal behavior. In addition, acid value, saponification, and iodine value explained its chemical behavior. **Table 2** consolidates the physico-chemical properties of waste animal fat biodiesel.

The exhaust gas was analyzed for oxides and dioxides of carbon and nitrogen along with residual oxygen content and particulate matter concentration for test samples using a four stroke single cylinder Diesel engine to understand the role of fatty acid esters in producing these emissions while undergoing combustion. Besides, engine performance characteristics like specific fuel consumption and thermal efficiencies were also studied to understand the fuel behavior in operating engine. The emission levels were determined based on undiluted measurement by passing the engine exhaust gas inside the flue gas analyser directly from exhaust manifold, where IR sensors sensed the concentration of oxides of carbon, nitrogen and Hydrocarbon emissions in it as electrical signals and were manipulated into numerical data using suitable software. **Table 3** outlines the technical specifications of Kirloskar Engine TV1 and AVL DI GAS 444 N (five gas analyser) (Srinivasan et al., 2019). **Figure 2** portrays the schematic diagram of test engine setup.

RESULTS AND DISCUSSIONS

Waste Animal Fat biodiesel was produced by means of ethanol based transesterification using optimized parameters as follows: molar ratio- 1:6 (Ethanol: waste animal fat); potassium hydroxide (KOH) as base catalyst for 0.5% wt. of fat; reaction temperature −60°C; reaction time-2 h; and maximum yield of 94% was achieved using these parameters. Especially, KOH was chosen for this study owing to its effectiveness as homogeneous catalyst for transesterification of animal fats (Carraretto et al., 2004). Besides, moderate reaction temperature

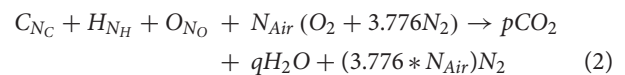**TABLE 3 |** Technical Specification of Kirloskar Engine TV1 & AVL DI GAS 444 N.

Kirloskar engine TV 1 specifications		AVL DI GAS 444 N (five gas analyser)	
Type: Four stroke, single cylinder water cooled		Measurement	Resolution
Rated power	5.2 KW	CO [0–15% Vol]	0.0001% Vol
Rated speed	1,500 rpm	HC [0–20,000 ppm Vol]	1 ppm/10 ppm
Bore diameter (D)	87.5 mm	CO_2 [0–20% Vol]	0.1% Vol
Stroke (L)	110 mm	O_2 [0–25% Vol]	0.01% Vol
Compression ratio	17.5:1	NO_x [0–6,000 ppm Vol]	1 ppm Vol

TABLE 4 | Blend factor and Ester factor for various blend and ester samples.

S. No	Sample name	Blend factor (ψ_B)	Ester factor (φ_E)	Diesel factor $[1-(\varphi_E{}^*\psi_B)]$
1	Diesel	0	0	1
2	Biodiesel blend	0.2	1	0.8
3	Ethyl oleate	0.2	0.4021	0.91958
4	Ethyl palmitate	0.2	0.2536	0.94928
5	Ethyl stearate	0.2	0.1687	0.96626

FIGURE 2 | Schematic diagram of test engine setup. Source: Apex innovations (Research equipment supplier in India).

was maintained throughout the process to avoid any thermal decomposition of fatty acids present in the waste fats as well as processed biodiesel.

From Equation (1), it was clearly noted that volume of ester samples was a function of blend factor (ψ_B) and ester factor (φ_E); and was entirely based on the % availability of fatty acid esters. In particular, the ester factor was maintained as 1, in case of biodiesel blend sample, indicating the summation of all characterized fatty acid esters. Since, the maximum permissible blend for commercial usage of biodiesel and enhanced performance exhibited by animal fat is for 20% blend, the blend factor was maintained as 0.2 for all the ester blends (Öner and Altun, 2009). **Table 4** tabulates the blend factor and ester factor for prepared samples.

Stoichiometric Air-Fuel Ratio

Based on availability of characterized fatty acid esters, the numbers of carbon, hydrogen and oxygen molecules were calculated and molecular formula of waste fat biodiesel was formulated as $C_{19}H_{37}O_2$. Following that, Stoichiometric air-fuel ratio was calculated from the quantity of air, N_{AIR} (in terms of mols), required for completely combusting of one mol of biodiesel, determined using Equation (3) (Srinivasan et al., 2019), derived from balanced equation (Equation 2) of Carbon, hydrogen and oxygen molecules available in the fuel (Sarkar, 1974):
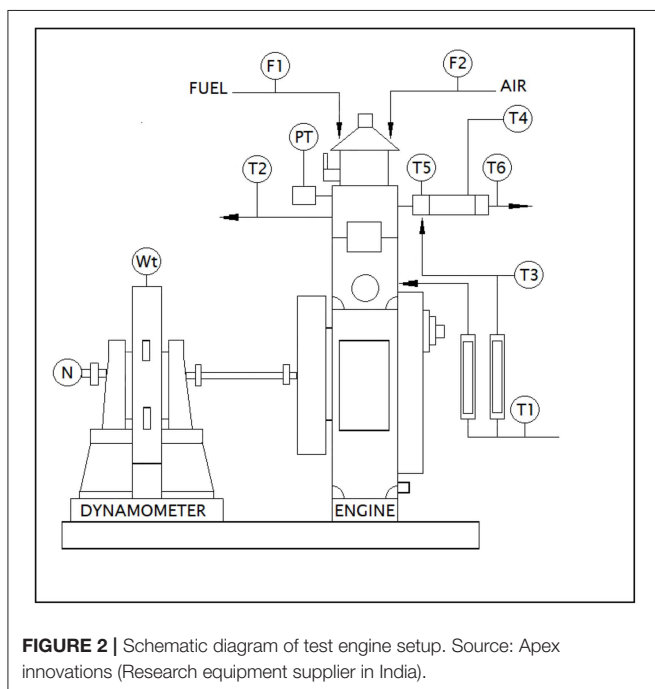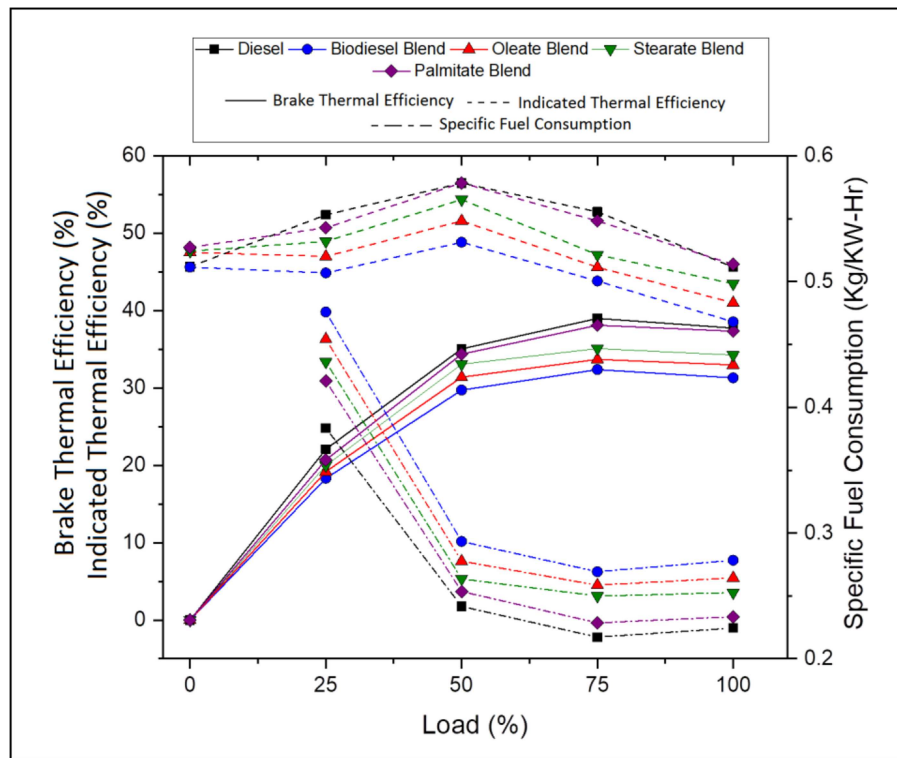
$$C_{N_C} + H_{N_H} + O_{N_O} + N_{Air}\left(O_2 + 3.776N_2\right) \rightarrow pCO_2 + qH_2O + (3.776*N_{Air})N_2 \tag{2}$$

$$N_{AIR} = \frac{4N_C + N_H - 2N_O}{4} \tag{3}$$

Using Equation (3), the required air quantity was calculated as 27.25 mols and Stoichiometric air-fuel ratio for the formulated molecular formula was computed and found to be 12.86:1. Since, a surplus amount of air (excess by 1.5 times than the calculated amount), is required for fuel to get completely combusted in engine, the actual stoichiometric air to fuel ratio was calculated as 19.29:1.

Performance Characteristics

Performance characteristics brief about the behavior of fuel during engine operation and propose the maximum work that can be derived from the fuel for any given running condition. In general, it explains the amount of fuel consumed for delivering the required work and maximum work that can be derived for that load condition. **Figure 3** portrays the specific fuel consumption, brake and indicated thermal efficiencies of various blends at various load conditions. **Table 5** tabulates the average specific fuel consumption, brake and indicated thermal efficiencies of various blends at various load.

Accordingly, Specific fuel consumption (SFC) specifies the fuel requirement for producing 1 unit of power and decreases with increasing load owing to increasing brake power (Ray and Prakash, 2019). The SFC was found to be 18.93% lesser, in case of neat diesel and 4.71, 8.73, and 14.07% lesser, in case of oleate, stearate, and palmitate, respectively, compared to biodiesel blend. To emphasize, increase in SFC for biodiesel

FIGURE 3 | Specific fuel consumption, brake and indicated thermal efficiency of diesel and blend samples for varying load conditions.

TABLE 5 | Average specific fuel consumption, brake and indicated thermal efficiency of diesel and blend samples.

Blend	Density	Calorific value	Average specific fuel consumption	Average brake thermal efficiency	Average indicated thermal efficiency
	Kg/m^3	MJ/Kg	Kg/KW-hr	%	%
Diesel	832	42.50	0.266666	26.77913	50.59036
Biodiesel blend	839.6	41.52	0.329149	22.34786	44.34434
Oleate blend	835.39	42.33	0.31368	23.45481	46.55681
Stearate blend	832.96	42.50	0.300509	24.4835	48.34043
Palmitate blend	833.59	42.44	0.284134	26.11162	50.59411

and its blends was on account of its low calorific value which increased its volumetric fuel consumption so as to sustain the energy demand of the engine. Infact, SFC was found to be higher for oleate and stearate blends because of their high viscosity on account of increased carbon chain length and; hence, the presence of these esters influenced the increased SFC for biodiesel blend.

On the contrary, Brake thermal efficiency (BTE) increased with load due to its high power demand and; on average; it was found to be 15.9% greater, in case of neat diesel and 3.96, 7.63, and 13.14% greater, in case of oleate, stearate, and palmitate, respectively, compared to biodiesel blend. Indeed, the reduced BTE for ester and biodiesel blends were because of their low calorific value and high viscosity (Hasan and Rahman, 2017; Prabu, 2018); however they tend to produce high BTE using the

fuel bound oxygen in them at higher loads (Debbarma and Misra, 2017). Relative to SFC, the BTE of waste animal fat biodiesel was on account of stearate and oleate molecules present in it.

Similarly, Indicated thermal efficiency (ITE) defines the ratio between power developed to energy given as input through fuel injection and on average, was found to be 14.26% greater, in case of neat diesel and 5.02, 9.09, and 14.25% greater, in case of oleate, stearate, and palmitate blends, respectively, on comparison with biodiesel blend. Low ITE for biodiesel blend was a consequence of high viscosity (imparted by long carbon chain length) which reduced its atomization and vaporization inspite of its increased Heat Release Rate. In fact, the marginal difference in the ITE between biodiesel and oleate was because their higher rate of viscosity and the influence of latter were reflected in ITE of biodiesel blend.

Emission Characteristics

Exhaust Gas Temperature (EGT)

Exhaust gas temperature helps in reporting the progress of combustion in engine and is influenced by the thermal properties of fuel used and operating parameters of the engine. In general, it tends to be higher for any long duration combustion process with a delayed start and subsequently results in higher concentration of NO_X emission. On average, the exhaust gas temperature was found to be 1.74% lesser, in case of neat diesel and 0.87, 0.78, and 1.71% lesser, in case of oleate, stearate, and palmitate, respectively, on comparing with biodiesel blend. Increase in EGT for biodiesel blend counter to diesel was accounted by its high cetane number, which also reduced the pre-mixing time (Abu-Hamdeh and Alnefaie, 2015). Besides, the marginal difference in the EGT for biodiesel blend and oleate and stearate blends were because of high oxidation rate of long chain ester molecules and abundant availability of fuel bound oxygen in it (Hellier et al., 2018) in addition to their high cetane number. The similarity in EGT for biodiesel and oleate blend was because of its unsaturation content which increased its ignition delay and viscosity, thereby producing higher NO_X emission upon long combustion duration due to high viscosity. **Figure 4** illustrates the exhaust gas temperature of diesel and blend samples for varying load conditions.

Carbon Monoxide (CO) Emissions

Carbon monoxide is a resultant by-product produced during incomplete combustion of fuel and is greatly influenced by nature of fuel and its degree of unsaturation and C/H ratio and engine cylinder temperature. On average, the CO emission was found to be 38.89% lesser, in case of neat diesel and 6.15, 20.04, and 28.54% lesser, in case of oleate, stearate, and palmitate, respectively, as compared with biodiesel blend. The reduction in the level of CO emission for biodiesel and ester samples was because of molecular oxygen available in the structure of ester molecules, which favors the complete oxidation of carbon and hydrogen molecules in the fuel (Hellier et al., 2018); however, their higher CO emission came by a reason of their high viscosity which reduced their atomization and hindered complete combustion. Also, the increased CO emission for biodiesel blend and oleate blend was due to presence of unsaturated double bond (C = C bond) in their carbon chain (Chukwuezie et al., 2017). Above all, higher CO emission at full load condition for all test samples was on account of higher fuel consumption rate to satisfy the higher energy demand. Hence, it can be concluded that concentration of CO emission will be higher for biodiesel with higher concentration of ester molecules having both long carbon chain and unsaturation. **Figure 5** shows the CO emission concentration of diesel and blend samples for varying load conditions.

Carbon Dioxide (CO_2) Emissions

Carbon dioxide is regarded as principal product obtained on complete combustion of fuel and is also deeply affected by type of fuel used and its degree of unsaturation and C/H ratio and engine cylinder temperature. On average, the CO_2 emission was 17.83% lesser, in case of neat diesel and 5.36, 3, and 12.34% lesser, in case of oleate, stearate, and palmitate, respectively, than biodiesel blend. Here, the closer margin between CO_2 emission concentration for diesel sample and palmitate blend is explained by their reduced carbon chain length and lower C/H ratio which tends to produce less CO_2 emission than compared to other blends (Adler and Bandhauer, 2017). Highest CO_2 emission concentration was noted for biodiesel blend owing to its adequate oxygen content and increased rate of viscosity that endows sufficient time to complete the combustion during expansion stroke (Abdul Malik et al., 2017). Moreover, increase in CO_2 emission concentration for oleate and stearate blend was because of their long carbon chain length corresponding to the fatty acids in their structure. On the other hand, drastic reduction in CO emission was noticed for increasing concentration of CO_2 emission. It can be concluded that biodiesel having long chained fatty acid esters tends to produce higher concentration of CO_2 emission. **Figure 6** depicts the CO_2 emission concentration of diesel and blend samples for varying load conditions.

Nitrogen Oxide (NO_X) Emissions

In general, NO_X emission is a temperature dependent phenomenon governed by the peak combustion temperature and is directly influenced by fuel with high cetane number and fuel bound oxygen content apart from longer residence time. Besides, higher NO_X emission rate for biodiesel fuel at higher temperature is because of the oxidation of hydrocarbons at fuel rich zones by means of fuel bound oxygen present in it (Prabu, 2018). Further, NO_X emission increased with availability of biodiesel owing to their high viscosity and oxygen content along with increased cetane number. In contrast, the NO_X emission of neat diesel was found to be 7.76% greater than biodiesel blend; and because of its increased ignition delay and reduced air-fuel mixing time that resulted in high cylinder pressure and combustion temperature on account of rapid combustion of fuel that were accumulated during premixed combustion phase. In the same way, the NO_X emissions of oleate and stearate blend were found to be 2.4 and 0.8% greater than biodiesel blend due to their reduced cetane number that tends to produce better combustion heat release rate. On the contrary, reduction in NO_X emission for palmitate blend was because of reduced Cumulative Heat Release Rate (CHRR) during combustion owing to its reduced carbon chain length which increased its ignition delay slightly (Coniglio et al., 2013) in addition to its high cetane number. Despite the fact, the NO_X emission of biodiesel blend remained below that of diesel because of its reduced degree of unsaturation and also slightly higher viscosity rate which hinders perfect atomization. **Figure 7** pictures the NO_X emission concentration of diesel and blend samples for varying load conditions.

Exhaust Oxygen (O_2) Concentration

Generally, the oxygen in exhaust gas describes about the completeness of the combustion reaction and explains the amount of oxygen consumed for oxidation of the fuel. On average, the exhaust Oxygen concentration was found to be 14.11% greater, in case of neat diesel and 2.6, 4, and 13.66% greater, in case of oleate, stearate, and palmitate, respectively, comparative to biodiesel blend. Reduced O_2 emission for
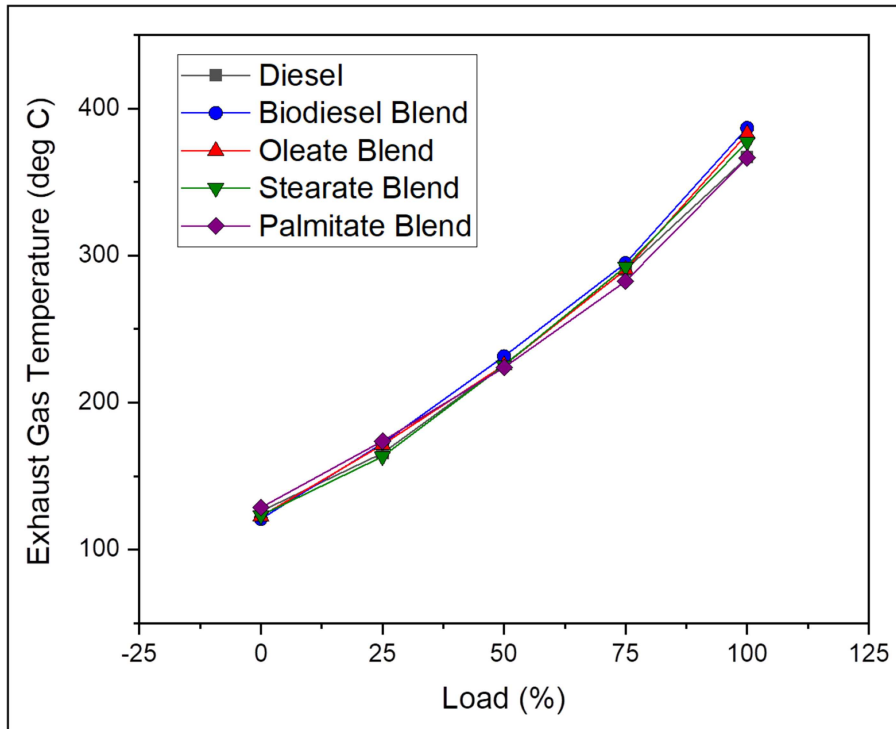
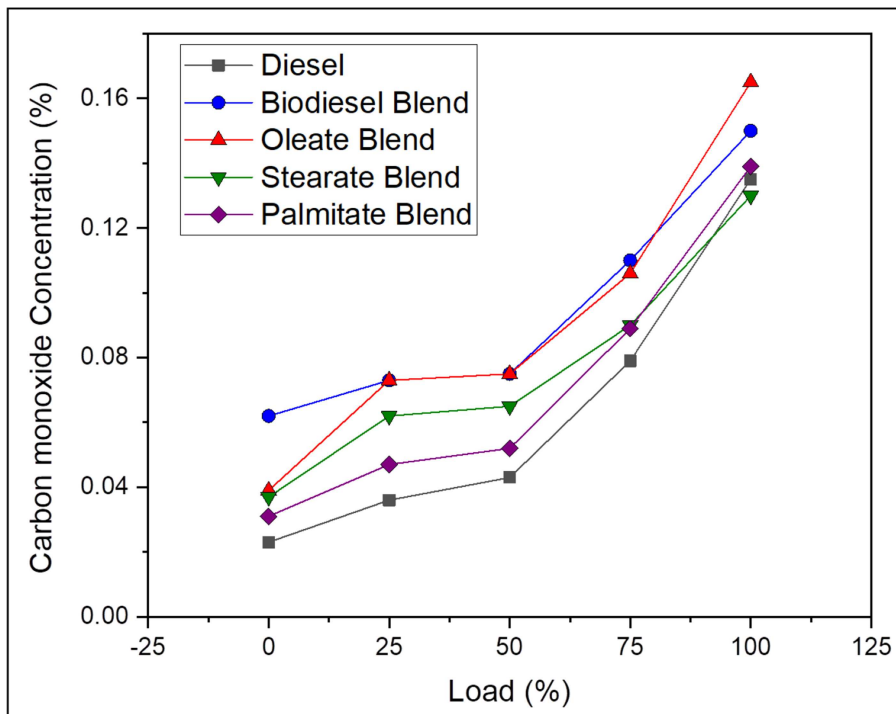**FIGURE 4 |** Exhaust gas temperature of diesel and blend samples for varying load conditions.

FIGURE 5 | CO emission concentration of diesel and blend samples for varying load conditions.
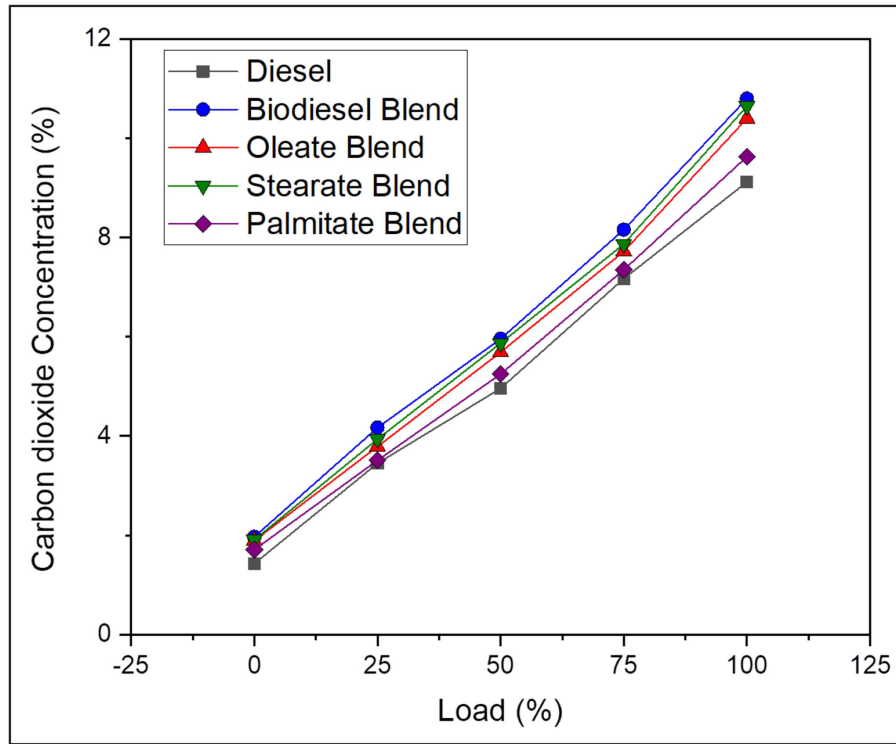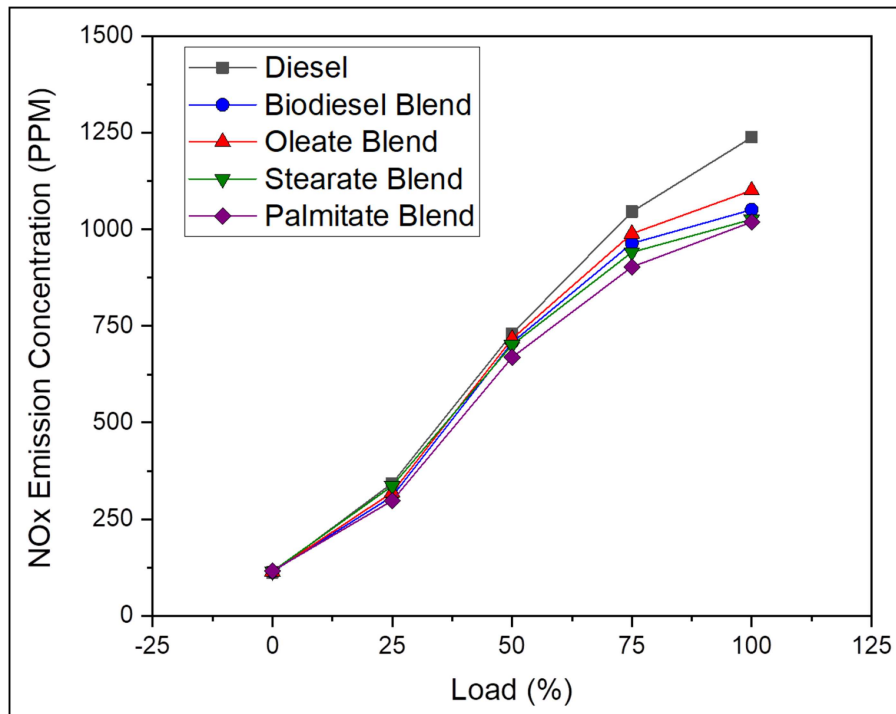
FIGURE 6 | CO_2 emission concentration of diesel and blend samples for varying load conditions.

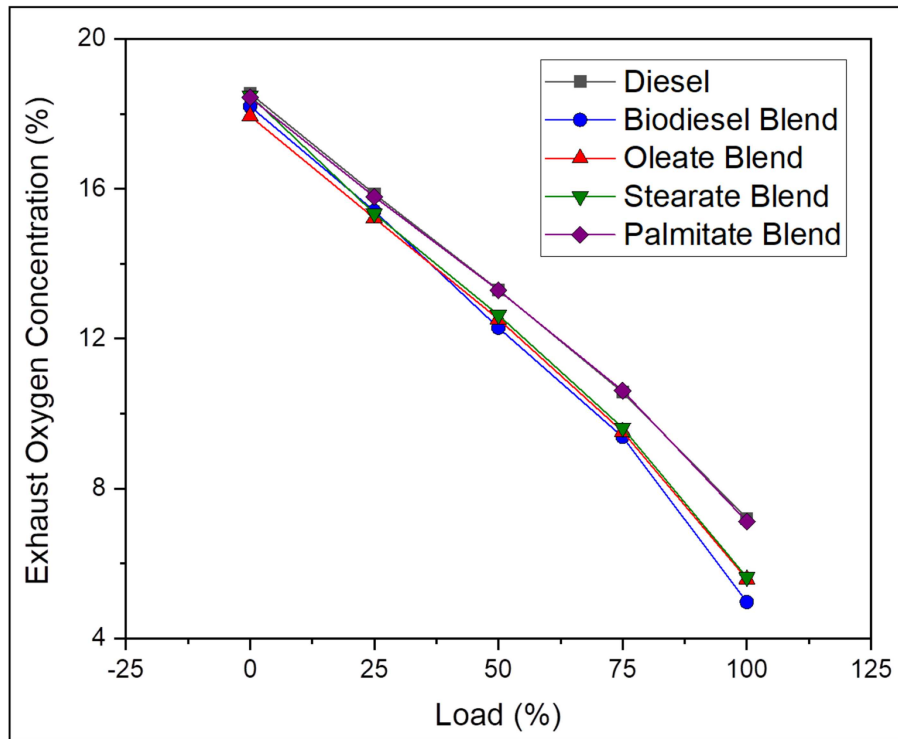**FIGURE 7 |** NO_x concentration of diesel and blend samples for varying load conditions.

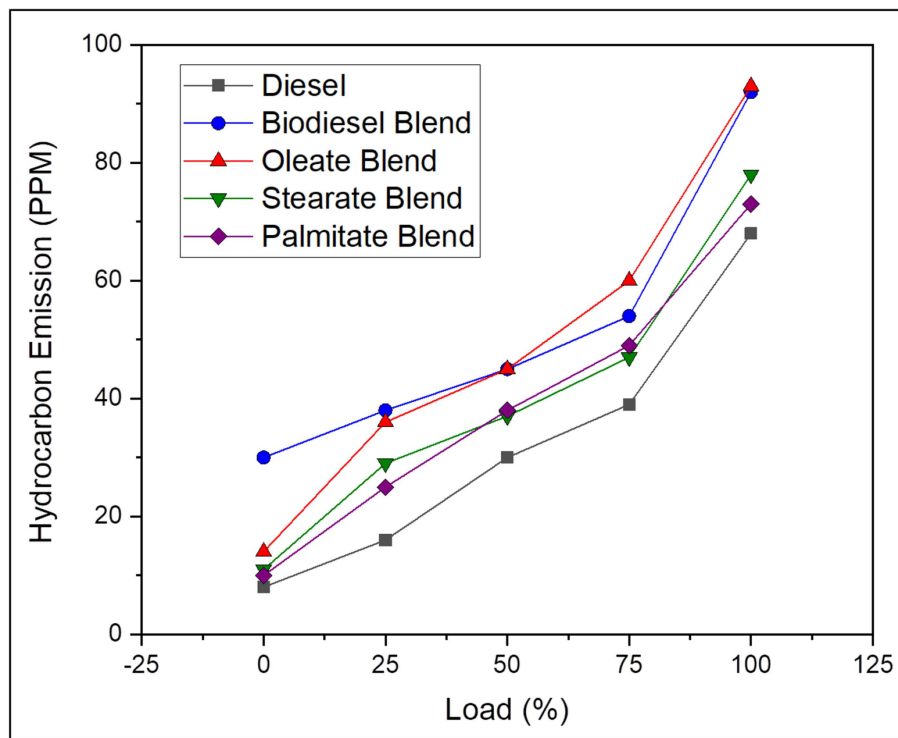**FIGURE 8 |** Exhaust Oxygen concentration of diesel and blend samples for varying load conditions.

FIGURE 9 | Hydrocarbon emission of diesel and blend samples for varying load conditions.

biodiesel blend was due to presence of long carbon chained ester molecules (oleate, stearate, and palmitate) which requires large amount of oxygen for complete combustion and extract maximum work from it (Hellier et al., 2012). In contrast, palmitate blend exhibited higher concentration of O_2 by reason of reduced carbon chain length which consumed less amount of oxygen than compared to other ester samples. To emphasize, the oxygen concentration reduced drastically with increase in load for all samples owing to higher consumption of oxygen for combusting the large amount of fuel to meet the power demand. In conclusion, biodiesel with long chained ester molecules consumed more oxygen content which improves the overall rate of combustion and also reduces the concentration of CO emissions. **Figure 8** represents the exhaust oxygen concentration of diesel and blend samples for varying load conditions.

Hydrocarbon (HC) Emissions

Hydrocarbon emission arises due to the unavailability of sufficient temperature for the air-fuel mixture found closer to the cylinder wall to undergo complete combustion thereby leading to unburnt fuel in exhaust gas (Correa and Arbilla, 2008). On average, the hydrocarbon emission was found to be 43.69% lesser, in case of neat diesel and 9.28, 26.6, and 29.27% lesser, in case of oleate, stearate, and palmitate, respectively, when compared to biodiesel blend. Above all, the lower concentration of HC emission for diesel blend was because of its high calorific value

and reduced viscosity rate, which upon combustion provided enough temperature for fuel to get combusted at wall surface. Besides, reduced HC emission for stearate, and palmitate blend was because of its higher oxygen content in its molecular structure; however, slight variation in the HC emission was result of difference in carbon chain length (Benjumea et al., 2010). Conversely, for oleate blend, HC emission was found to be higher than compared to other two ester blends owing to its unsaturation Inspite of its higher carbon chain length and good fuel bound oxygen content; and was reflected in the HC emission of biodiesel blend. Very likely, the HC emission inside cylinder is always greater than in exhaust tail pipe as there is a possibility for these unburnt fuels to undergo combustion, if sufficient oxygen and high temperature is available (Faiz et al., 1996). **Figure 9** outlines the hydrocarbon emission of diesel and blend samples for varying load conditions.

From these results, it was clearly evident that the emission characteristics of waste animal fat biodiesel were deeply influenced by the dominant fatty acid esters present in it. Properties like density, viscosity, cetane number, and calorific value played a substantial role in deciding the emission concentrations which are in turn depends on molecular weight (length of carbon chain) of the ester molecule along with its unsaturation content. Hence, this study provides sufficient evidence that biodiesel emissions and their concentration are dependent on the fatty acid ester molecules and their availability

TABLE 6 | Comparison of Engine characteristics from present study with existing literatures.

Parameters	Gopinath et al., 2010	Srinivasan et al., 2019	Benjumea et al., 2010	Schönborn et al., 2008	Present study
Specific Fuel Consumption (SFC)	Unsaturation and high density of fatty acid esters increased SFC	Long carbon chained oleate and stearate esters in biodiesel increased SFC	Degree of unsaturation has no significant effect on SFC	–	Long carbon chained oleate and stearate esters increased SFC
Brake Thermal Efficiency (BTE)	Unsaturation and high viscosity of fatty acid esters reduced BTE	Long carbon chained oleate and stearate esters in biodiesel reduced BTE	–	–	Long carbon chained oleate and stearate esters reduced BTE
Indicated Thermal Efficiency (ITE)	Unsaturation and high viscosity of fatty acid esters reduced ITE	Long carbon chained oleate and stearate esters in biodiesel reduced ITE	–	–	Long carbon chained oleate and stearate esters reduced ITE
Carbon monoxide emission	Unsaturation and high viscosity of fatty acid esters increased CO emission	Unsaturated fatty acid esters in biodiesel increased CO emission	–	–	Long chained fatty ester molecules with unsaturation increased CO emission
Carbon dioxide emission	–	Long carbon chained fatty acid esters in biodiesel increased CO_2 emission	–	–	Long carbon chained fatty acid esters Increased CO_2
Nitrogen oxide emission	Unsaturated fatty acid esters had lower cetane number which increased NO_X emission	Higher concentration of saturated fatty acid esters reduced NOx emission	Presence of double bond in fatty acid ester molecule enhanced NOx formation	Short chained Fatty acid esters and unsaturation produces high NOx emission due to long ignition delay	Higher concentration of saturated fatty acid esters reduced NOx emission
Exhaust oxygen emission	–	–	–	–	Long chain fatty acid esters consumed had reduced O_2 emissions
Hydrocarbon emission	Unsaturation and high viscosity of fatty acid esters increased HC emission	–	Hydrocarbon emission increased with higher degree of unsaturation	–	Unsaturated fatty acid esters increased HC emissions
Exhaust Gas Temperature (EGT)	Unsaturation and high viscosity of fatty acid esters increased EGT	Long carbon chained oleate and stearate esters in biodiesel increased EGT	–	Higher cetane number and long carbon chain enhanced EGT	Long carbon chained oleate and stearate esters in biodiesel increased EGT

in it. **Table 6** summarizes the key conclusion deduced from this present study along with other similar studies.

CONCLUSIONS

Thus, the effect of fatty acid esters of waste animal fat biodiesel in deciding its emission characteristics have been carried by comparing their emission concentration of waste animal fat biodiesel, diesel along with fatty acid esters. Following this, major conclusions deduced from this experimental work related to comparative study in emission characteristics are as follows:

(i) Ethyl oleate (40.21%), ethyl palmitate (25.36%), and ethyl stearate (16.87%) were characterized as dominant fatty acid esters present in waste animal fat biodiesel.

(ii) High exhaust gas temperature was caused by ethyl oleate due to its low cetane number and high viscosity leading to prolonged ignition delay.

(iii) High CO and CO_2 emission concentration was on account of increased carbon chain length (stearate and Oleate esters); however, unsaturation in fatty acid moiety (Oleate ester) had an adverse effect in CO emission.

(iv) Reduced NOx emission was because of high cetane number from saturated fatty acid esters (stearate and Palmitate esters), which in turn reduced its ignition delay thereby moderating the HRR.

(v) Likewise, long carbon chain fatty acid esters (stearate and Oleate esters) consumed more oxygen content for undergoing complete combustion whereas increased HC emission was owing to its increased unsaturation content (Oleate ester).

On the whole, the emission characteristics of any biodiesel are intensely based on carbon chain length (C/H ratio), cetane number, degree of unsaturation and density and viscosity of individual fatty acid esters constituting it. In conclusion, this experimental work serves as a precursor for understanding the influence of fatty acid esters on emission characteristics during combustion of biodiesel, which could help in developing modified biofuel aimed for reduced emissions to develop sustainably toward future.

DATA AVAILABILITY

The datasets generated for this study are available on request to the corresponding author.

AUTHOR CONTRIBUTIONS

GS: proposal of idea, literature survey, sample and chemical collection, fat extraction and biodiesel production, engine testing data collection and calculation, drafting of article, final approval. SP: literature survey, sample preparation for spectral analysis, GC testing data collection and interpretation, chemical equation calculations, drafting of article, and verification of typo errors. RJ: project supervision, evaluation of spectral data and chemical equations, critical review of finalized article, final approval, administrative, and technical support. VS: project supervision, fat extraction and handling, biodiesel preparation, Evaluation of spectral data and chemical equations, review of finalized article, final approval, administrative, and technical support.

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