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Production of marine algae methyl esters and evaluation of its engine performance and emission characteristics

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A number of critical factors influence the competitiveness of any biodiesel, including feedstock availability, production costs, byproducts produced, and government subsidies. In this situation, a cost-effective and environmentally acceptable supply of biodiesel is required. When compared to other non-edible oil sources, algal oil is a significant emerging non-edible biodiesel source. The current study includes tests on pure diesel and its three algae oil blends. When the properties of the biodiesel made from the oils were tested, the results were within the acceptable limits. The engine test results show that, aside from NO_X emissions, biodiesel blends emit very little carbon when compared to diesel. When biodiesel blends were used, the engine required more fuel. The results of the performance tests revealed that the biodiesel blends had better and more complete combustion. This research shows that biodiesel blends of up to 20 % can be a better substitute for pure diesel fuel and can be used in CI engines without modification.

[**Keywords**: Biodiesel, Emission, Engine performance, Macro algae, Micro algae]

Introduction

A variety of fuels have been tested so far for the use of combustion in IC engines; liquid fuels are used by the modern CI engines[1]. These liquid fuels are derived from crude oil. Diesel is a liquid fuel obtained after refining the crude oil. The ever increasing demand for the fossil fuels, limited number of oil reserves available and the stringent emission norms have created greater fascination among the researchers towards alternate fuel technology in India. Biodiesel may be defined as an alternate fuel source which can be derived from plant oils and animal fats. Apart from being used as a fuel for CI engines, biodiesel can also used as a low carbon alternative to heating oil. Biodiesel has the advantages of high lubricity and better cetane ratings[2] with better lubricity; it reduces wear in the fuel system and increases life of the high pressure diesel injection system. Biodiesel is normally produced from animal fats and vegetable oils through transesterification. Transesterification is the chemical reaction that produces biodiesel upon reaction of oil with an alcohol[2]. Transesterified biodiesel is a compound of long chain fatty acids composed with mono alkyl esters. These esters are known as Fatty Acid Methyl Esters (FAME) or Fatty Acid Ethyl Esters (FAEE). Methanol is used as the alcohol in the production of FAME. Methanol is preferred than ethanol because it is less expensive. The alternate fuel sources available to produce biodiesel include virgin oil feedstock like soybean, Jatropha, mustard, palm, Pongamia, Hemp, etc. Animal fats are also used as the biodiesel source which includes tallows, chicken fats, lards, yellow greases and the byproducts drawn during the production of omega-3 fatty acid from fish oil. There are many reports on the performance of these biodiesel blends in CI engine[3-5]. In India, plants like Jatropha and Pongamia are the leading biodiesel plant sources. In fact, several plans are to be executed to produce biodiesel from these plants. Large cultivating area, nutrition and cost of biodiesel production are the difficulties faced in using these plants. More suitable crops and improving the oil yield are current challenges and focus of research. It is never recommended to make biodiesel from edible oil because it has an impact on the food chain. More than half of the imported oil used in India is for cooking. Biodiesel production from algal biomass is still in its infancy in India. For the synthesis of biofuels, algae provides a cheap, sustainable, and renewable source of biomass. Because they do not compete with food crops on arable land and use less water to cultivate than other crops, microalgae could have substantial positive effects on society and the environment. Numerous studies have been conducted to convert algal oil into biodiesel[6-8]. Algae are biofuels that can effectively offset carbon emissions. According to the industries, algal biodiesel has a 93 percent lower impact than pure diesel. Compared to some of the conventional oil crops like soybean and jatropha, an alga can yield 200 times more oil per unit area[9]. Algae are photosynthetic organisms that range in size from micrometres to metres and can grow in any watery environment. Macroalgae are multicellular, massive (measured in inches) organisms found in bodies of water. Microalgae are unicellular organisms that grow in suspension in bodies of water and are extremely small (measured in micrometres). A number of companies developing algae fuel refineries, as well as a number of airlines, have successfully conducted flight tests using fuel blends containing up to 40 % algae biodiesel. Algae are a low-cost, environmentally friendly, and renewable source of biomass for the production of biofuels[10].

Marine algae

Aquatic biomass source marine macroalgae has the potential to be a significant source of renewable energy[11-13]. Macro algae are enormous aquatic photosynthetic plants that may be seen without a microscope. “Seaweeds” or macroalgae are multi cellular plants which grow in freshwater or salt water. Depending on their pigmentation, they can be classified into three broad groups[3,6] *viz*. (1) brown algae (Phaeophyceae); (2) green algae (Chlorophyceae) and (3) red algae (Rhodophyceae). Aquatic biomass’s average photosynthetic efficiency is 6 – 8 % which is much higher than the photosynthetic efficiency of terrestrial biomass (1.8 – 2.2 %). Macro algae are quickly growing freshwater and marine plants that grow considerably (upto length of 60 m). Marine macroalgae growth rate exceeds that of terrestrial biomass, majorly because of lack of water limitations[5]. Communities of higher plants and sea grasses are relocated due to the algal biomass accumulation[14]. Cleaning of macroalgal species from the coastal areas is necessary as it leads to eutrophication and causes environmental hazards[1]. Hence, it is crucial to study about macro algal biomass which can be used as a source and to protect the environment. Biodiesel production is one of the best ways to utilize hazardous marine macroalgae. In recent years, fuel produced out of algae has received worldwide attention. This is because it has a high annual production rate, growth rate and efficient carbon dioxide fixation of algae. Unlike the terrestrial crops, microalgae and macroalgae have a higher growth rate and strong photosynthetic capacities. Sometimes the growth rate of macroalgae is higher than that of microalgae. This result in dual benefits of utilizing marine macroalgae for biodiesel as it is used as biodiesels as well as prevents environmental pollution. Macroalgal oil is found to be more economical when compared to biomass from trees and crops[6]. Macro algae has an advantage over conventional crops are it offers a higher yield advantage for production of biodiesel.

Though there are many advantages can be derived, the detailed analysis on the performance and emission analysis of algae biodiesel by varying the engine parameters like load, type of blend etc., has not been addressed or very few only addressed. This article deals about investigation on operating CI engine biodiesel blends of algae oils with straight diesel. The objective of the present research is to extract oil from fresh water and marine water algae biomass for the production of biodiesel in South Indian condition and to evaluate its benefits and limitations on performance and emission through experiments.

Materials and Methods

Biomass collection

Biomass of two different types of sea algae was gathered. One is from Chennai's Kovalam, and the other is from the brackish water source in Pulicat.

Drying

Both the types of algae biomass were dried in open sun for 48 h to remove the moisture content in it.

Pulverizing

The dried algae biomass content was pulverized in to a fine powder to ease it for crushing.

Solvent extraction

To extract the oil, a 3:2 mixture of hexane and isopropanol was mixed with dried, ground algae powder. After that, the solvent biomass mixture was allowed to settle for 12 h. The biomass was filtered, collected, and weighed.

Oil extraction

Following filtering, the algae biomass was thoroughly mashed with a motor and pestle. The ground algae were dried in an incubator for 30 minutes at 80 °C to release the water content. The mass proportions of biomass and oil extracted are presented in Table 1.

Table 1 — Mass proportions of algae biomass

Particular	Fresh weight (kg)	Dry weight (kg)	Extracted oil after removal of residues (kg)	Biomass after removal of residues (kg)
Freshwater algae	15	4.75	1.6	2.1
Marine algae	24	7	1.9	2.5

Evaporation

A rotary evaporator was used to extract the oil after evaporating the hexane and isoproponal solvents.

The biodiesel production method

The complete biodiesel production processes followed the present study are explained here.

Mixing of alcohol and catalyst

Sodium hydroxide pellets were used as a catalyst in the work (caustic soda). There are also caustic flakes available. By mixing, dry caustic pellets were dissolved in methanol. 3.75 g NaOH pellets in 200 ml methanol, properly stirred for 20 min. To avoid the formation of clumps and an unfavourable impact on downstream processes, it was ensured that the dry caustic pellets did not absorb an excessive amount of water in storage.

Transesterification process

In a conical flask, the catalyst and methanol mixture was poured into the oil. A magnetic stirrer at 300 rpm was used to mix the solution in the conical flask uniformly for 3 h. Throughout the reaction, the temperature was kept at 65 °C. To obtain the methyl esters from both types of algae oils, the same reaction procedure was used. Methanol and sodium hydroxide pellets were obtained from Southern India Suppliers in Chennai, India.

Methanol recovery

Excess alcohol is recovered at this stage of the reaction after esters and glycerin have been removed via distillation or the flash process. Methanol can also be extracted after the esters and glycerin have been removed.

Separation

After the reaction was finished and the alcohol was removed, the solution was kept for 24 h to allow the biodiesel and sediment layers to settle clearly. Glycerin and biodiesel are produced as a result of the settling. Because of the density difference, gravity separates glycerin and methyl esters, and the higher density glycerin at the bottom is simply drained off. Two layers are visible in this study, and the bottom layer was separated using a conical separator. Because no other layers are discovered, it can be concluded that the only thing left are the methyl esters.

Table 2 — Properties of diesel and biodiesels

S. No.	Properties	Diesel	MAME	AME
1	Density @15 °C in gm/cc	0.82	0.792	0.795
2	Kinematic viscosity @40 °C in cst	2	3.51	4.84
3	Gross calorific value in Kcal/kg	9724	9432	9145
4	Calculated Cetane Index	48	51	49
5	Flash point by Pensky Martens in °C	66	90	132
6	Conradson carbon residue in %	0.03	Nil	Nil
7	Sulfur content	Nil	Nil	Nil
8	Acidity total mg of KOH/g max	0.2	Nil	Nil

Glycerin recovery

Soaps and left over catalysts in the resulting glycerin are to be neutralized. Hydrochloric acids or phosphoric acids are usually used to neutralize the glycerin to make them as crude glycerin. When hydrochloric acid is used to treat sodium hydroxide, which is utilised as a catalyst, sodium chloride is produced and retained in the glycerin. This glycerin is ready to use as crude glycerin because it is clean.

Methyl ester wash

A flask separator was used to carefully separate the methyl esters from the sedimentation. The amount of glycerin, pigments, and so on was measured. Biodiesel is washed with 5 % water until it is pure. Biodiesel is dried in a dryer before being exposed to an electric fan for 12 h. The yield of biodiesel was measured and saved for property testing. The biodiesel samples are named MAME (from the Pulicate Lake sample) and AME (from the Kovalam sample), and the efficiency of yield of biodiesel from algae oils is 88 and 70 %, respectively.

Fuel properties

The fuel properties of the prepared biodiesel samples were tested and confirmed with ASTM standards. Table 2 displays these values. The properties of the prepared biodiesel samples show that they are within the ASTM limits, and these types of fuel can be used in compression ignition engines.

Engine set up and procedure

A 4 stroke, single cylinder vertical engine with air cooling is used for the test. The layout for test rig is presented in Figure 1. The specifications of the test rig are presented in Table 3.

Every experiment was run in steady-state condition. Straight diesel, % biodiesel with 95 % pure diesel (B5), 10 percent biodiesel with 90 % pure diesel (B10), and % biodiesel with % diesel (B20) were the fuels tested in this study (B20). In the investigation, load characteristics tests were performed with an injection pressure of 210 bar and a constant speed of 1500 rev/min. Five sets of loads with percentages ranging from 0 to 100 % are employed in the experiment. The amount of time needed to burn through 10 cc of gasoline was calculated for each load scenario.

Results and Discussion

Algae biodiesel diesel blend experiments were carried out in consistent with the objectives and technique described, and the outcomes are shown in this chapter. For comparison, tests on pure diesel were also conducted under the same circumstances. The experiment's findings are presented and discussed using graphs. Among the performance metrics are exhaust gas temperature, brake specific energy consumption, and brake thermal efficiency. Among the emission criteria are carbon monoxide, unburned hydrocarbons, NO_X, and smoke opacity.

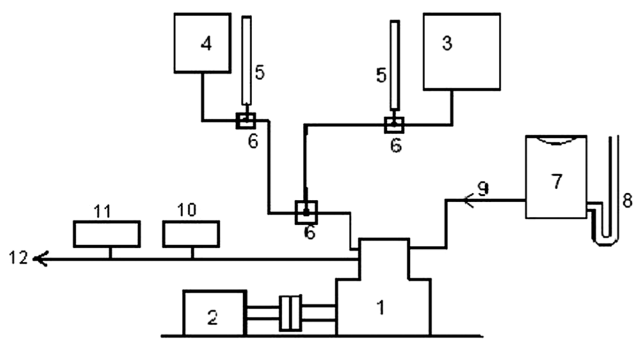

Fig. 1 — Layout of engine setup: 1) Engine setup; 2) Dynamometer for loading; 3) Diesel tank; 4) Biodiesel tank; 5) Burette for fuel consumption measurement; 6) Control valve; 7) Air box; 8) Manometer air consumption measurement; 9) Airline; 10) 5 Gas analyzer; 11) Smoke meter; and 12) Exhaust line

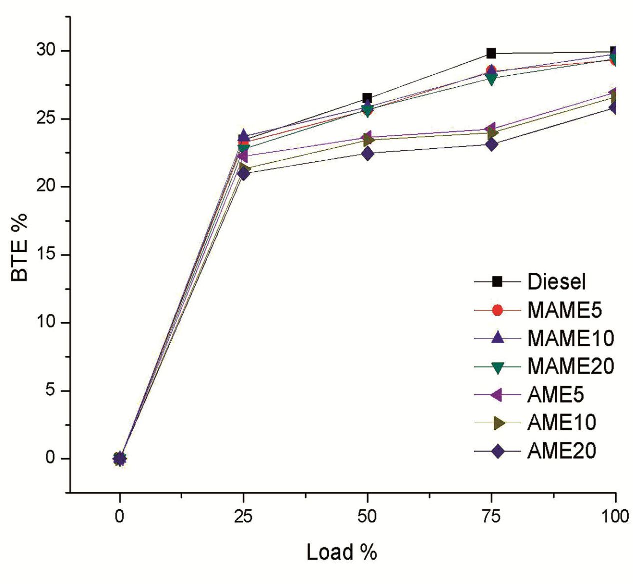

Fig. 2 — BTE of various blends

Brake thermal efficiency

Thermal efficiency is the ratio of a brake power output to the heat energy used to generate that power. Values for brake thermal efficiency are significantly influenced by fuel characteristics such as heating value and density. The differences in brake thermal efficiency values vs engine load for straight diesel, B5, B10, and B20 algal oil blends, respectively, are shown in Figure 2.

The graphs demonstrate that when compared to biodiesel blends, plain diesel has higher thermal efficiency values. Its high calorific value is the reason. At full load, the pure Diesel's average brake thermal values are 18.59 percent. As opposed to the biodiesel blends MAME and AME the average brake thermal efficiency at all loads are 18.96 and 17.75 %, respectively. When the blends' biodiesel content rises, the brake thermal efficiency increases as well. With increasing load, the brake thermal efficiency values for diesel and biodiesel blends rise until they reach a maximum at 75 % load before falling. Straight diesel outperformed biodiesel blends at lower loads in terms of efficiency values.

Brake specific energy consumption

Brake specific fuel consumption is the amount of fuel used for each unit of power produced for each unit of time. This parameter clearly shows the fuel efficiency. The differences in brake-specific energy

Table 3 — Engine specifications

Rated power in kW	4.4
Rated speed in rpm	1500
Cylinder bore	87.5 mm
Stroke length	110 mm
Compression ratio	17.5/1
Injection pressure	210 bar
Injection timing	23° bTDC
Orifice diameter in mm	13.4
Coefficient of discharge of orifice	0.6
Injector	Single 3 hole injector
Combustion	Direct injection
Injector nozzle diameter in mm	0.3 mm
Combustion chamber shape	Spherical shape
Loading type	Eddy current dynamometer

consumption figures for straight diesel, B5, B10, and B20 algal oil blends are shown, accordingly, vs engine load in Figure 3. The values for biodiesel blends' brake-specific energy consumption are higher than those for pure diesel under all circumstances. This is because they have a low heating value. The average brake specific energy consumption value for pure diesel at all loads is 9414.6 kJ/kW-h. Whereas for the biodiesel blends MAME and AME, the average brake specific energy consumption values at all loads are 10094 kJ/kW-h and 10411.46 kJ/kW-h, respectively. For all the biodiesel blends the BTE value increased gradually when the percentage of biodiesel level increases in the blend. During combustion, the MAME blends were consumed in slightly lower quantities by the engine. Similar findings were obtained by Jayaprabakar & Karthikeyan[15]. The energy consumption of all blends decreases as the engine load increases. At higher engine loads, the energy consumed is nearly identical for all blend types.

Exhaust Gas Temperature (EGT)

One of the output parameters that measure the utilization of heat energy is the temperature of the engine's exhaust gas. Figure 4 depicts the exhaust gas temperature values for straight diesel, B5, B10, and B20 algae oil blends.

The average EGT value for the pure Diesel at all loads is 267.4 °C. Whereas for the biodiesel blends MAME and AME the average EGT values at all loads are 282 °C and 289.77 °C, respectively. From all the EGT curves it can be observed that Diesel has less EGT values than the biodiesel blends at all load conditions. The higher EGT for biodiesel blends other way indicates its lower thermal efficiency. The MAME biodiesel blends recorded less EGT values than other biodiesel blends. All of the curves show that as the load increases, the exhaust gas temperatures for pure diesel and biodiesel blends rise. Since higher loads lead to higher combustion temperature, the full load condition in this study revealed higher EGT values for all the fuel types.

Emission characteristics

The emission characteristics of the tested fuels are explained below.

Nitrogen oxides

Figure 5 depicts the variations in nitrogen oxide emissions in ppm versus load for straight diesel, B5,

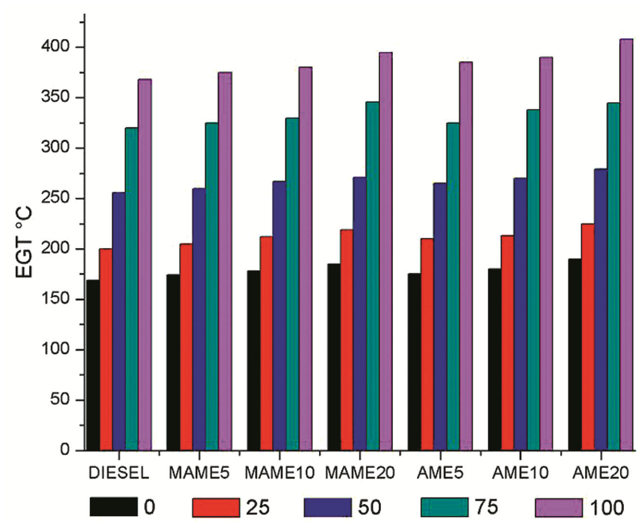

Fig. 4 — EGT of various blends

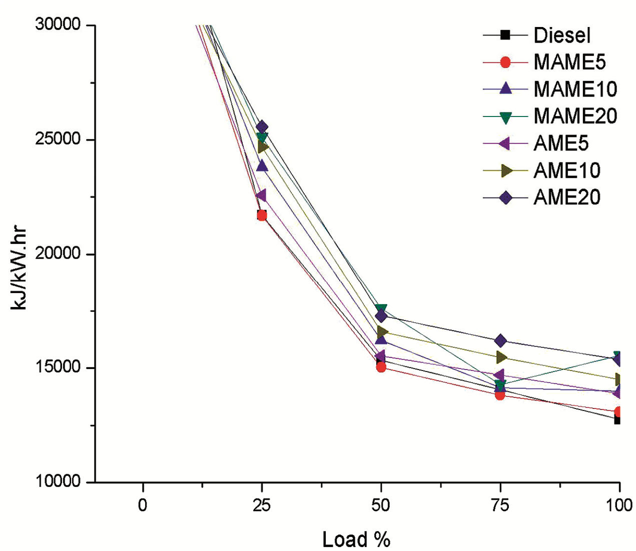

Fig. 3 — BSEC of various blends

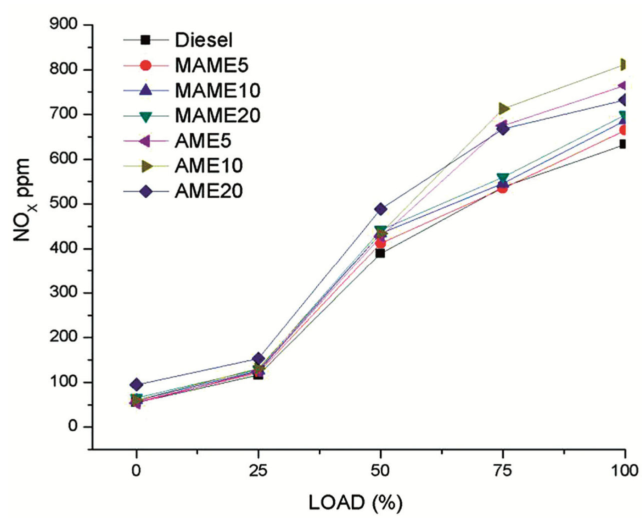

Fig. 5 — NO_X emission values of various blends

B10, and B20 algae oil blends. The average NO_X value in the engine for pure diesel at all loads is 316.67 ppm. Whereas the average NO_X values at all loads for the biodiesel blends MAME and AME are 362.8 ppm and 408.81 ppm, respectively. Compared to straight diesel the biodiesel blends in the study recorded high NO_X values as these biodiesel blends contains high oxygen content. The blends AME10 and MAME10 recorded higher NO_X values than other fuel types at all conditions. But the blends AME20 and MAME20 produced lesser NO_X values than their counterparts. The reasons for the reduced NO_X values of these blends are due to their comparatively reduced rate of premixed burning. When the load increases the NO_X emissions also increase gradually. At the initial load conditions, the NO_X emissions are lesser. Further increase in the load causes higher combustion temperature which significantly increases the NO_X values.

Carbon monoxides

Figure 6 depicts variations in carbon monoxide emissions as a percentage of engine load for straight diesel, B5, B10, and B20 algae oil blends. At all loads, the average CO emission value for pure Diesel is 0.078 percent. The average NO_X values at all loads for the biodiesel blends MAME and AME are 0.0673 percent and 0.086 percent, respectively. In comparison to straight diesel, biodiesel blends produced slightly lower CO emissions due to their high oxygen content, which leads to better oxidation. But in some cases, at lower loads the biodiesel blends MAME 10 and AME 10 recorded slightly higher CO emissions. The increase in CO is due to their poor spray formation characteristics because of higher viscosity compared to straight diesel. The blends MAME 20 and AME 20, on the other hand, resulted in lower CO emissions due to their complete combustion via high oxygen content. Similar biodiesel results were obtained by Costa *et al.*[16]. The CO emission gradually increases as the load increases. At lower loads, the difference in CO emission between the tested is negligible.

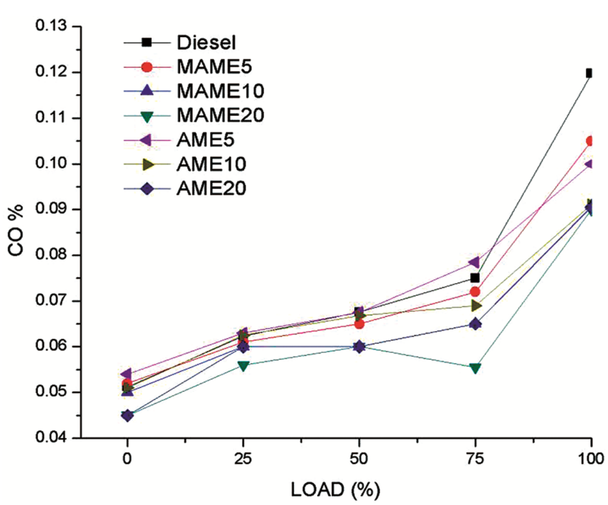

Fig. 6 — Carbon monoxide emission values of various blends

Smoke opacity

Fuel deposits on the cylinder walls produce a specific sort of emission particle known as smoke. Figure 7 shows the differences in smoke opacity for pure diesel, B5, B10, and B20 algal oil mixes in percent against load. The average smoke opacity for pure diesel is 38.98 % for all loads. For the biodiesel blends MAME and AME, the average smoke opacity values at all loads are 34.6, 36.67, and 39.59 %, respectively. The biodiesel mixes produced higher smoke opacity values when compared to pure diesel. This is caused by biodiesel blends' high viscosity, low volatility, and heavy molecules. The smoke opacity is shown to rise with increasing biodiesel content in the blends because biodiesel blends have poor atomization. The MAME biodiesel blends have slightly lesser smoke opacity values than their counterparts due its improved combustion because of light viscous nature. When the load increase the smoke opacity also gradually increases. At lower loads the differences in the values between the blends are little between all the fuels types tested here.

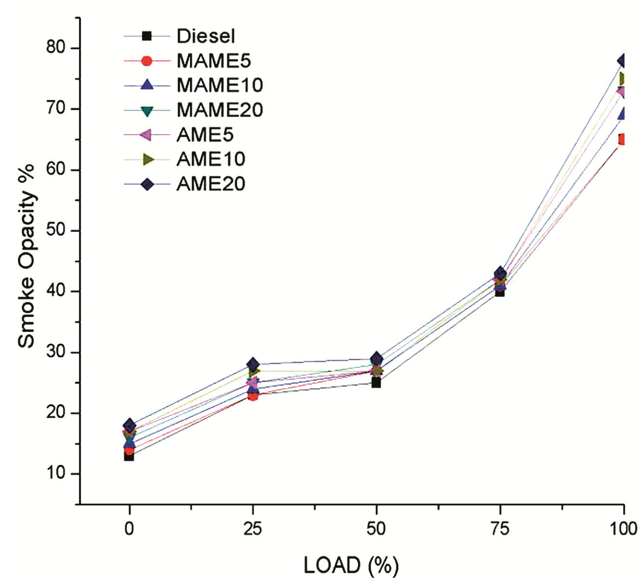

Fig. 7 — Smoke opacity values of various blends

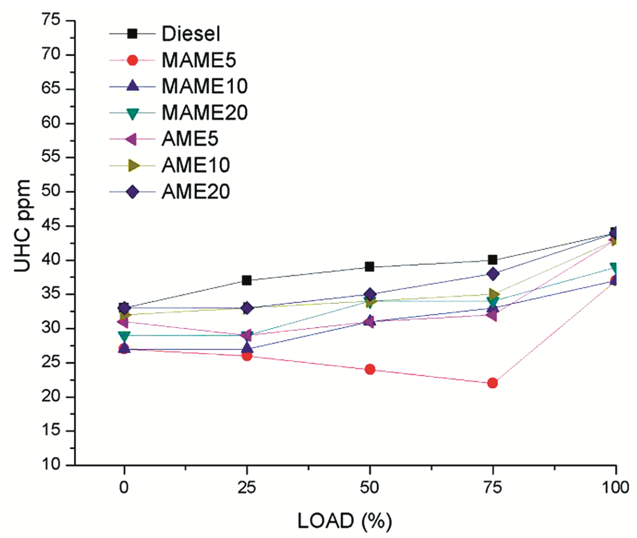

Fig. 8 — Hydro carbon emission values of various blends

Unburnt Hydrocarbons (UHC)

Figures 8 show the variations in unburnt hydrocarbon emissions in ppm versus load for straight Diesel, B5, B10, and B20 algae oil blends.

The average UHC value for pure diesel at all loads in the engine is 36.89 ppm. Whereas for the biodiesel blends MAME and AME the average smoke opacity values at all loads are 30.59 ppm and 34.29 ppm, respectively. The biodiesel blends record mixed variations of UHC emissions compared to diesel. Some cases, AME10 and AME 20 recorded higher UHC values. Higher viscosity and density values of these biodiesel types exhibits poor UHC emissions. The MAME blends show slightly lesser UHC values due their light viscosity and high oxygen content. The UHC values in blends decrease as the biodiesel content increases. When the load increases, so do UHC emissions for all fuel types. However, there is no significant increase in UHC emission values from no load to full load. It demonstrates that load variation has little effect on UHC formation. Hydrocarbon emissions are reduced when the combustion temperature is high. Because of the high oxygen content of biodiesel, better combustion occurs, resulting in fewer hydrocarbons released. It ensures that all biodiesel blends undergo complete combustion.

Conclusion

Transesterification was used to create two novel biodiesel blends with regular diesel derived from marine water. The prepared blends can be classified according to ASTM standards based on their fuel properties. The tests were carried out on a stationary, single-cylinder, CI engine using the three different types of fuel blends. Based on the results of the tests, it can be concluded that both algae oil biodiesel blends can be used in CI engines with minor modifications.

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Conflict of Interest

The authors declare no competing potential and financial interest.

Ethical Statement

This study is the author's original work and has not previously been published or is currently being considered for publication elsewhere.

Author Contributions

JJ: Conceptualization, writing - original draft & editing; AK: Methodology, review & validation; AP: Typesetting and review; MA: Editing and reviewing; and NJ: Software and validation.

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