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Reduction in environmental pollution by marine microalgae based biofuels blended with nanomaterials in diesel engines

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The current respiratory health issues caused by toxic emissions of automobiles and industrial processes are clear indicators of poor quality of life in cities worldwide. This situation emphasizes the need for further research on the improvement of fuel focussed on minimizing the direct impact on human health and avoiding the generation of long- or medium-term health problems caused by Particulate Matter (PM) emissions released through burning of fuels. The primary source of PM emissions is the internal combustion engines and industrial solid fuels. Certain biofuels, including those derived from *Schizochytrium* sp. green algae, produce chemical compounds that can serve as precursors to PM in its early stages. This study aims to assess the reduction in emissions achieved by using biodiesel derived from *Schizochytrium* sp. algae, both on its own and in combination with commercial-grade diesel. A comparative analysis is conducted between the results obtained from an existing mathematical model, which predicts the PM production from *Schizochytrium* sp. biofuels and their mixtures with commercial-grade diesel, and experimental data obtained under natural conditions in a laboratory engine. The engine operates at different rotational speeds for mixtures containing 10 %, 15 %, and 20 % biodiesel with a load below 25 % and an average load of 50 %.The findings reveal that the biofuels, specifically *Schizochytrium* sp. biodiesel, play an important role in reducing PM emissions. The emissions of particulate matter from a 20 % mixture of *Schizochytrium* sp. biodiesel are significantly lower compared to the 15 % and 10 % mixtures, based on the available data. However, it is worth noting that the 15 % mixture shows higher emissions at low loads and a speed of 1500, indicating the limitations of the predictive model in accounting for additional variables inherent to the engine.

[**Keywords**: Biodiesel, Combustion, Nano blends, Particulate material, Reaction kinetics]

Introduction

Air pollution has become a persistent issue, leading to respiratory illnesses and environmental deterioration in densely populated areas with high concentrations of vehicles and industrial activities. Particulate Matter (PM), primarily emitted by vehicle engines and industries, is a major contributor to this problem[1]. Numerous scientific studies have established a direct correlation between PM emissions and respiratory diseases.In the mining industry, which anticipates extensive use of biofuels, public policies have been implemented to encourage the adoption of biodiesel, incentivizing its production and commercialization. This presents an opportunity for reducing the impact of emissions in this sector[2]. This study focuses on the production and characterization of biofuels derived from *Schizochytrium* sp. algae (SAME) and their application in tests conducted under various operating conditions in an internal combustion engine[3]. The extraction and characterization of biofuels from *Schizochytrium* sp. algae were carried out as part of this research. The use of *Schizochytrium* sp. algae was explored as an alternative fuel for compression-powered engines[4]. The obtained results are compared with those derived from an existing mathematical model that simulates the production of particulate matter resulting from the combustion of the fuel in an internal combustion engine, considering factors such as temperature in the combustion chamber and volumetric fractions of input. To facilitate comparison, assumptions were made for different engine operating conditions: a rich mixture (50 % load) and a medium-poor mixture (50 % load) representing 50 % engine loads, and a poor mixture (25 % load) representing a 25 % engine load. It should be noted that due to the limitations of the predictive model, load conditions could not be considered directly, thus emphasizing the direct relationship between the experimental and theoretical aspects of the simulation[5]. According to the literature, the use of B100 (100 % biodiesel) results in a significant reduction of over 75 % in carbon dioxide emissions. When using B20 (20 % biodiesel), there is a 15 % reduction in carbon dioxide emissions. Figure 1 displays the image of *Schizochytrium* sp. algae.

Materials and Methods

Experimental description

Test engine

The core component of the system was a single diesel engine equipped with a 3.3 kW single-phase generator with a power factor. The system's configuration is illustrated in Figure 2. The load bank consisted of a purely resistive setup, featuring a panel of 4 kW incandescent lamps with a dissipative capacity. To establish baseline parameters such as power, torque, hourly consumption, specific consumption, as well as CO and CO_2 emissions; the engine was initially fueled with commercial diesel. Four different loads *viz*. 0, 1500, 1800 and 2100 were applied during testing. Fuel consumption measurements were taken every five minutes, and the volume of fuel consumed was calculated for each interval. The engine's rotational speed was maintained at a constant 3600 rpm throughout the tests. For each test, the mixtures utilized consisted of commercial diesel combined with a percentage of biodiesel, specifically 20 %. The densities of the different fuel blends were determined by establishing the relationship between weight and volume for each mixture[6].

Internal combustion engine ignited by compression

In this study, an engine equipped with a three-cylinder compression mechanism is utilized to assess the impact of different fuel types on particulate matter emissions. The power output of the engine is measured using an electronic torque meter connected to a National Instruments data acquisition system[7]. Specifically, a Kirloskar motor is employed, which is linked to an electric generator typically found in a power plant or generation unit. However, due to the specific operational speed range of the generator and its pole configuration, which only permits electricity generation within a restricted speed range (below 350 rpm), the generator was removed. In its place, a

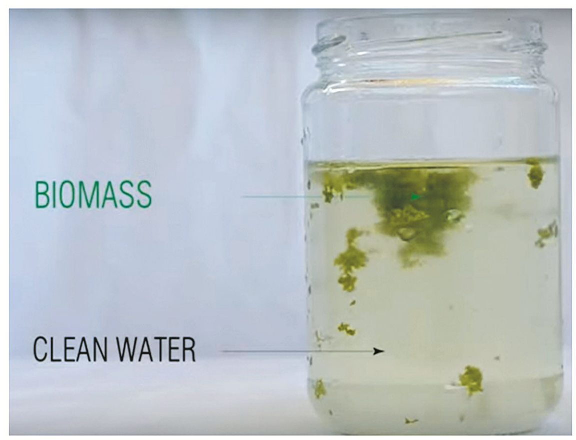

Fig. 1 — *Schizochytrium* sp. algae biomass

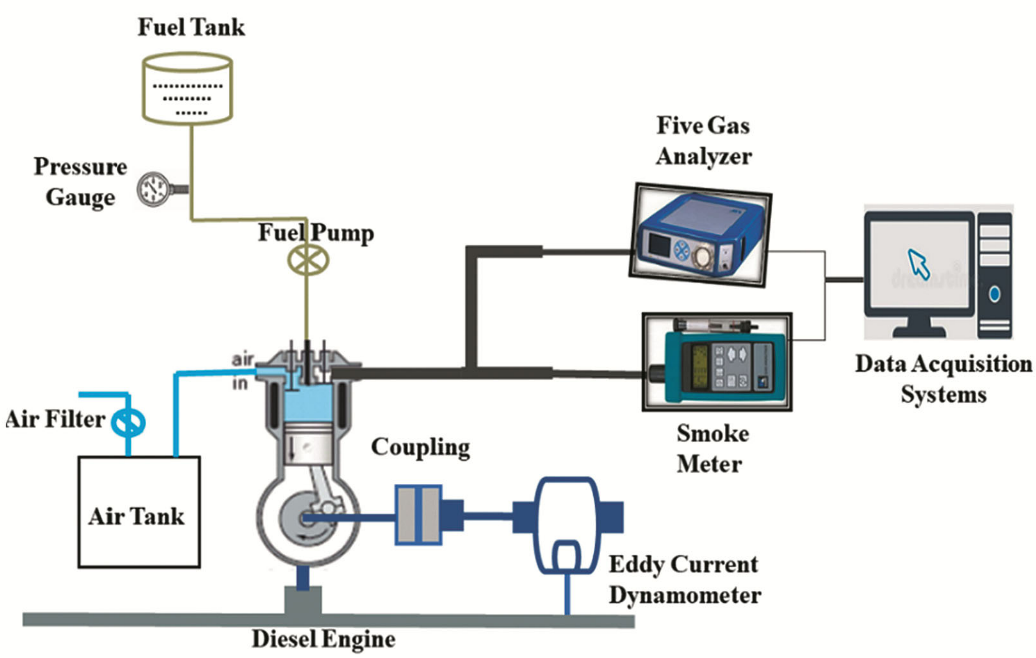

Fig. 2 — Experimental set-up

variable-speed hydraulic brake was installed, enabling the motor to operate at different speed ranges[8]. Despite this modification, the configuration of the injection system and fuel flow control in the engine remained unaltered. Consequently, the operating range of the engine was limited to its original design capacity of 1500 to 3000 rpm[9].

Formation model of particulate material and combustion

Several researchers have conducted studies on the formation of particulate matter emitted by internal combustion engines fueled by conventional petroleum-based fuels or biofuels. It has been observed that using biofuels derived from plant sources such as cottonseed, soybean, rapeseed methyl ester, and palm methyl ester can lead to improved engine performance in terms of reduced emissions of hydrocarbons and carbon monoxide (CO), but an increase in nitrogen oxides (NOx) emissions[10]. The behavior of these parameters is directly influenced by the interaction between the fuel and the oxidizer, which forms the basis for some existing models used to predict the formation of particulate matter[11]. These models consider properties such as molar concentration, mass density, and number of particles. The following model has been developed to work with input conditions including combustion chamber temperature, initial fuel concentrations, a rich air-fuel ratio (50 % charge), as well as mathematical parameters such as integration intervals, simulation time, time step, and computational time. These inputs are utilized to simulate and predict the formation of particulate matter[12].

Oxidation

The oxidation phenomenon is described using independent models; the first is for the oxidation of O_2 particles, and the second considers oxidation by the OH radical. The following describes each one of the models.

Oxidation model by O_2

$$PM + \frac{1}{2}Q_2 \rightarrow CO \qquad \ldots (1)$$

$$\dot{w}_{O_2} = 1.6\,X\,10^7 e^{\left(\frac{-14000}{T}\right)} T^{\frac{1}{2}} N^{\frac{1}{2}} N\left[MP^{2/3}\right] O_2 \qquad \ldots (2)$$

Oxidation model by OH

$$PM + OH \rightarrow CO + H \qquad \ldots (3)$$

$$\dot{w}_{OH} = \gamma OH \frac{3_n OH^n}{N_A}\left(\frac{8RT}{\pi M_{OH}}\right)^{\frac{1}{2}} \qquad \ldots (4)$$

Balance of particles

The global model establishes that the total formation of PM is the contribution of formation and oxidation phenomena. Thus the global model is expressed as follows:

$$\frac{d}{dt}[PM] = \dot{w}_n + \dot{w}_c - \dot{w}_{ox} \text{ (kmol/m}^3\text{)} \qquad \ldots (5)$$

The particle balance, determined by defining the N, the number of particle densities, is based on Smoluchowski's equation. The particle formation rate:

$$w_n^p = \frac{d}{dt}\frac{(PM)N_A}{C_{min}} \qquad \ldots (6)$$

Where, N_A is the Avogadro number, C_{min} corresponds to the minimum number of C atoms needed to form a particle; this variable has a value of 100 atoms.

On the other hand, the coagulation stage is described by:

$$\dot{w}_{coag} = \frac{5}{6} k_{coag} (Y_{PM})^{\frac{1}{6}} N^{\frac{1}{6}} \qquad \ldots (7)$$

Where, Y_{PM} is the volumetric fraction of particles (m^3 of particles / m^3 of mixture); y is given by:

$$Y_{PM} = \frac{M_{PM}[PM]}{\rho_{PM}} \qquad \ldots (8)$$

In this equation, M_{PM} is the molecular mass, [PM] is the molar concentration and ρ is the collision coefficient, given by:

$$k_{coag} = \frac{5}{12}\frac{3^{1/6}}{4\pi}\frac{6k_bT}{\rho_{PM}} G C_\alpha \qquad \ldots (9)$$

Kb corresponds to the Boltzman constant. Constant G takes a value of 2 and Cα takes a value of 6.55. In this way, the particle formation rate is obtained:

$$\frac{d[N]}{dt} = \dot{w}_n^p + \dot{w}_{coag} (particulas/m^3) \qquad \ldots (10)$$

Having these definitions, the global model of PM formation is described by the equations:

$$\frac{d}{dt}[PM] = \dot{w}_n + \dot{w}_c - \dot{w}_{ox} \text{ (kmol/m}^3\text{)} \qquad \ldots (11)$$

$$\frac{d[N]}{dt} = \dot{w}_n^p + \dot{w}_{coag} (particulas/m^3) \qquad \ldots (12)$$

Results and Discussion

Experimental results

By operating the Lister engine with various fuel mixtures, valuable results were obtained that highlight the impact of biodiesel on particulate matter emissions under constant load conditions. Generally, it was observed that the use of pure diesel fuel required less energy compared to any of the biodiesel blends examined[13]. Numerous studies have confirmed that the inclusion of biodiesel in fuel mixtures leads to an earlier combustion initiation and delayed ignition due to factors such as high cetane number, lower compression, and the unique composition of fatty acids present in these fuel oils[14]. Furthermore, researchers have discovered that the biodiesel component with the highest concentration in the blends exhibits a greater tendency to generate unburned hydrocarbons, which contributes to incomplete combustion within the biodiesel complex[15]. This finding helps explain the higher energy consumption observed with diesel fuel. By analyzing particulate matter emissions relative to the fuel mass consumed by the engine, important insights can be gained regarding the comparative effectiveness of biofuels in compression-ignition engines. In the case of the 50 % load condition, it was observed that the mixture containing 10 % biodiesel (with lower concentration) resulted in the highest emissions per unit of fuel across different speed ranges (Fig. 3). Conversely, the blend with the highest proportion of biodiesel exhibited the lowest levels of particulate matter emissions[16].

These findings align with the research conducted by Graboski[17], who investigated the effects of different diesel and biodiesel mixtures (at concentrations of 10 %, 15 %, 20 %, and 100 %) on an internal combustion engine. Graboski's study demonstrated a consistent reduction in particle emissions as the biodiesel concentration increased, following a linear trend. It was found that the engine's optimal operating point, resulting in the lowest particulate matter generation per unit of fuel, occurred at an engine speed of 2100 rpm when operating with pure diesel[18]. This value was consistent across the various fuel blends evaluated under the 50 % load condition, indicating the lowest PM emissions for all tested mixtures as depicted in Figures 4 – 5 of present study.

The engine speed of 2100 rpm and the 50 % load condition align with the recommended values provided in the engine's technical datasheet for

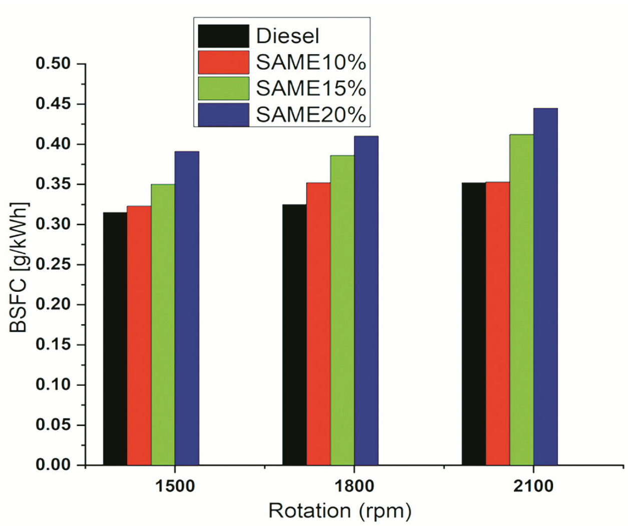

Fig. 3 — Specific fuel consumption for the engine ignited by compression at 50 % load

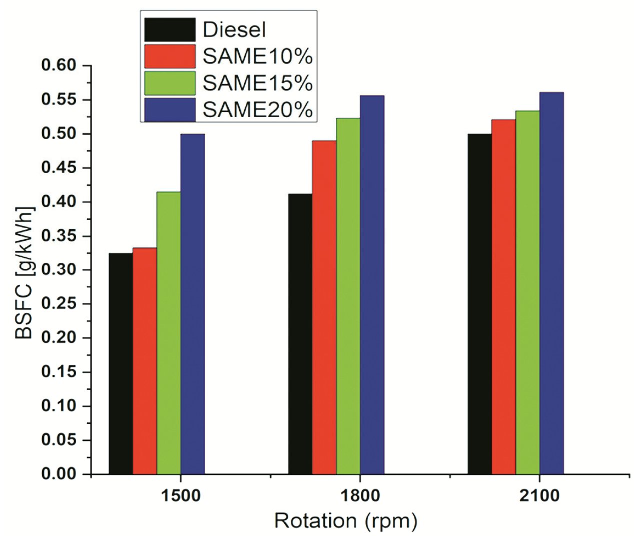

Fig. 4 — Specific fuel consumption for the engine ignited by compression at 25 % load

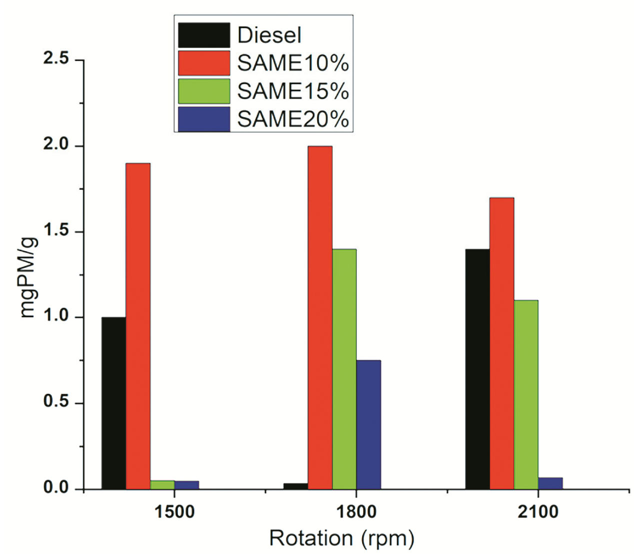

Fig. 5 — Emission of particulate material in bulk per unit of energy at 50 % charge percentage

achieving optimal efficiency. This suggests that the engine is specifically designed to operate efficiently at variable speeds and with the use of fuel management components[19]. Among the different fuel mixtures tested, the operation with 20 % biodiesel exhibited the lowest emissions across all three engine rotational speeds. It is noteworthy that the particulate matter emissions observed with the fuel mixtures containing biodiesel are directly related to the emission behavior exhibited when the engine runs on pure diesel fuel. Analyzing this phenomenon reveals that pure diesel operation results in high emissions at both low and high speeds, while the emissions are lower and more favorable at medium speeds, which is characteristic of a diesel cycle engine[20]. The behavior observed with biofuels may be influenced by factors such as the inability to adjust the injection system, injection times, and maintaining consistent fuel temperature across all four fuel types[7]. Further investigations with a larger number of repetitions are necessary to gather sufficient data and confirm these different observations. Operating the engine with a 10 % biodiesel blend resulted in the highest emissions and is considered the least favorable condition in terms of total particulate matter emissions. This behavior underscores the importance of conducting detailed studies on the reaction kinetics of fuel mixtures to better understand the combustion process and identify the reasons behind the less favorable results associated with lower biodiesel content compared to mixtures with higher biodiesel concentrations. Under high-load conditions, which correspond to 25 % of the rated engine load, different results were observed for engine operation. Lower speeds were found to yield less pollution for all fuel types tested, while the highest operating speed exhibited greater emissions across all fuels as shown in Figures 6 – 7.

Interestingly, the behavior of PM emissions for different biodiesel concentrations is contrary to the results observed under high-load conditions. In this case, the fuel mixture with the lowest biodiesel content exhibits lower emitted mass, while the highest contaminating emissions are present in the 15 % biodiesel mixture. This emission trend in relation to load variation aligns with a study conducted by Huang[21], which observed similar variations in PM emissions when operating an engine with B20 fuel. Both types of diesel fuel and biodiesel showed increased particulate matter emissions as the load increased. The mixture containing 15 % biodiesel exhibits the highest emissions, whereas the reference diesel fuel displays the lowest PM emission values[9]. This behavior emphasizes the importance of fine-tuning parameters such as injection timing, pressure, and fuel temperature in a specific manner for each fuel mixture. It highlights the need for meticulous adjustment and optimization of these parameters to mitigate particulate matter emissions effectively[22].

Predictive model results

This section presents the results obtained from the particulate matter formation model specifically developed for *Schizochytrium* sp. algae biodiesel. The simulations were conducted with various fuel

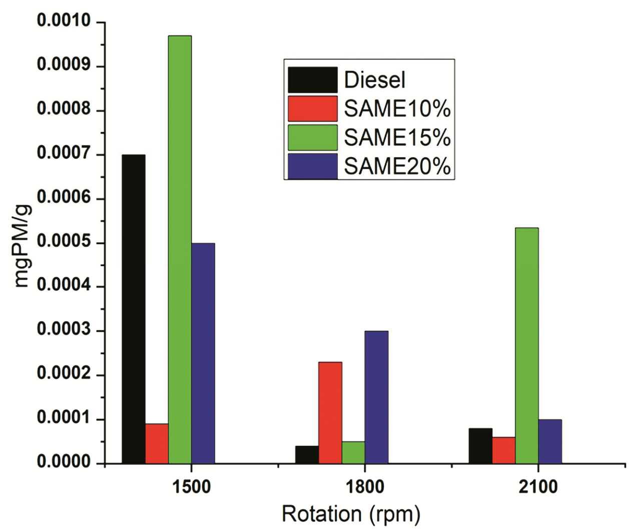

Fig. 6 — Emission of particulate material in bulk per unit of energy at 25 % charge percentage

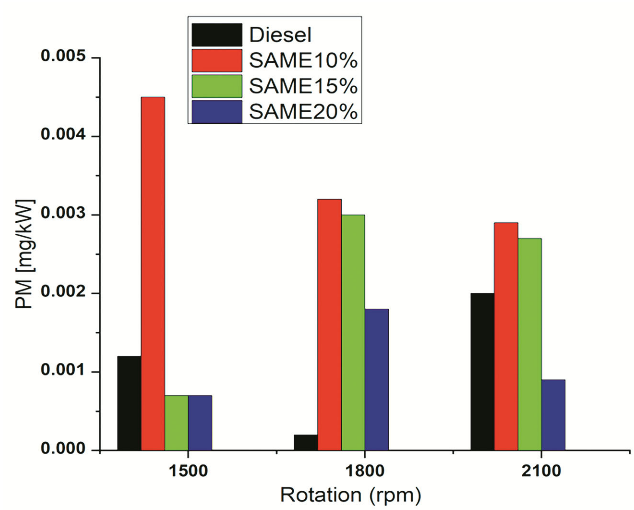

Fig. 7 — Formation of particulate material per fuel unit at 50 % charge

mixtures: Diesel 100 %, and 10 %, 15 %, and 20 % biodiesel concentrations. Two different air-fuel ratios were considered: a poor fuel mixture (assumed to represent a 25 % load in comparison to the experimental data) and a rich fuel mixture (representing a 50 % load in relation to the experimental conditions). The simulations were performed at a constant temperature of 1200 K.

Quantitative analysis of the results is challenging due to the need for more detailed information regarding the specific phenomena occurring in the combustion chamber[10]. The implemented predictive model in the comparisons accounts for these complexities, and therefore, the analysis is presented in terms of trends. Continuing with the investigation of the 20 %, 15 %, and 10 % fuel mixtures at rich (50 % load) and poor (25 % load) fuel ratios, it is observed that the significant area of PM production has been oxidized, resulting in a constant value thereafter. The predictive model indicates that the highest PM production occurs with the 10 % mixture for both the rich (50 % load) and poor (25 % load) fuel ratios, while the lowest production is observed with the 20 % mixture (Fig. 8). These findings align with literature studies that suggest a lower particulate matter formation with a higher amount of biofuel, specifically *Schizochytrium* sp. algae biodiesel[23]. The experimental results also support this observation, as the lowest particulate matter production was observed at a 25 % load regardless of the mixture considered[24]. The reduced production of PM can be attributed to the higher oxygen content within the biodiesel molecule, enabling complete combustion even in areas of the combustion chamber where a rich fuel mixture (50 % charge) is geometrically formed. Considering the greater oxygen content in the biodiesel molecule, it can be deduced that the stoichiometric air requirement for this biofuel is lower, reducing the likelihood of precursor species formation for PM. Figure 9 further supports this conclusion, as it demonstrates a higher concentration of PM for the all rich fuel mixture (50 % load), indicating that the proportion of air is insufficient for complete oxidation of all fuel components. Additionally, the 20 % mixture exhibits a higher PM production with the rich fuel ratio (50 % load) compared to the poor or lean mix fuel ratio (25 % load), which aligns with the expected results. Similar patterm of PM production is also highlighted by Mushtaq *et al.*[25] with 50 % and 25 % load.

In the case of the 15 % fuel mixtures, it is evident that the production of PM is approximately 20 % higher for the rich fuel ratio (50 % load) compared to the poor fuel ratio (25 % load) in the 15 % mixture. Similarly, the rich fuel ratio (50 % load) for the 10 % mixture exhibits a 36 % higher PM production than the poor fuel ratio (25 % load) as shown in Figures 10 – 12. Comparing the rich fuel ratio (50 % load) among the different mixtures, it is observed that the 20 % mixture has a 37 % lower production compared to the 10 % mixture and is 10 % lower than the 15 % mixture. Furthermore, the rich fuel ratio (50 % load) for the 15 % mixture is 11 % lower than

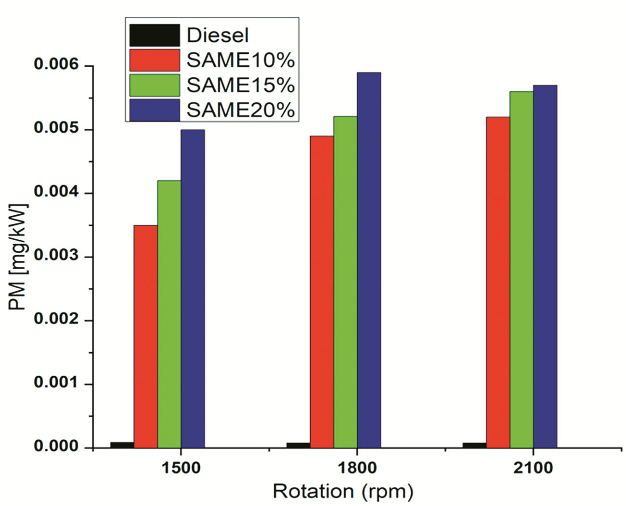

Fig. 8 — Formation of particulate material per fuel unit at 25 % load

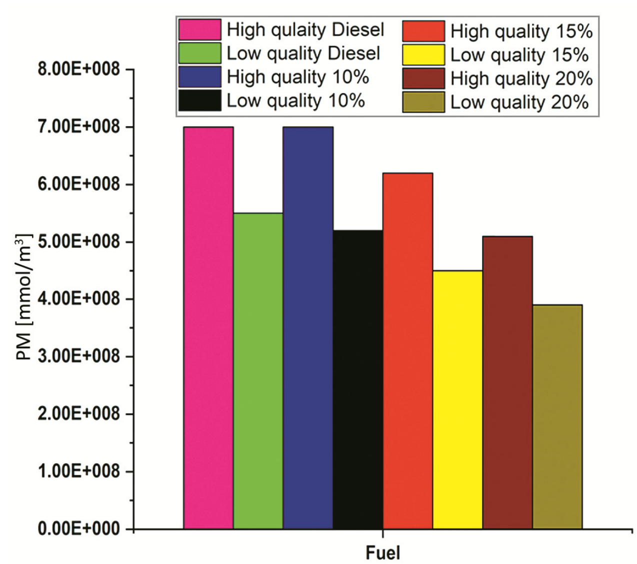

Fig. 9 — Production of particulate material for 100 % diesel and 10 %, 15 %, and 20 % biodiesel mixtures (Rich mix/high quality (50 % load), and lean mix/low quality (25 % load))

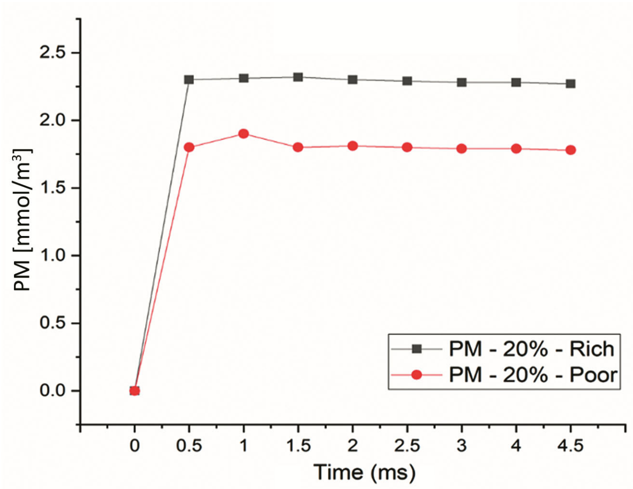

Fig. 10 — Concentration of PM emissions for 20 % mixture

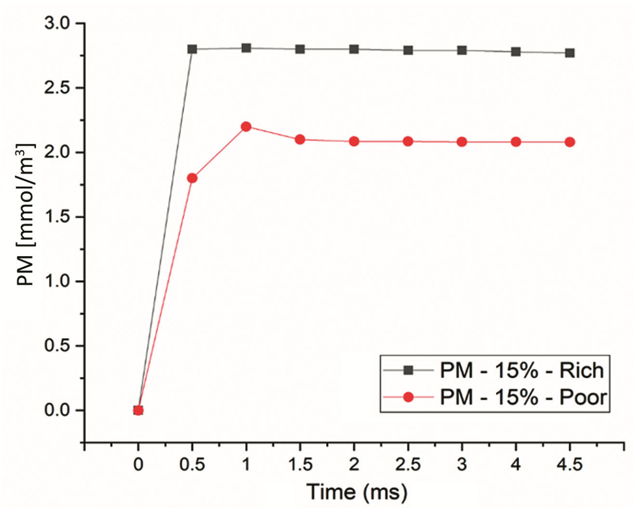

Fig. 11 — Concentration of PM emissions for 15 % mixture

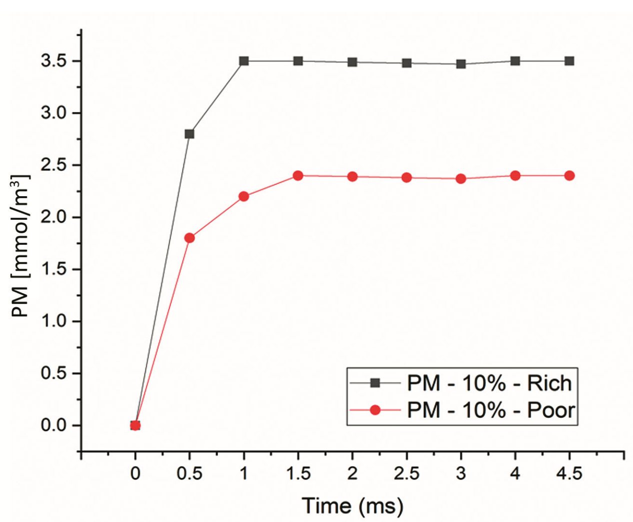

Fig. 12 — Concentration of PM emissions for 10 % mixture

the rich fuel ratio (50 % load) for the 10 % mixture. It is noteworthy that in all cases, PM production is more significant when the engine operates at a 50 % load (rich mixture) compared to a 25 % load (poor mixture) (Figs. 10 – 12). These results emphasize the direct relationship between fuel composition and the amount of emitted PM as reported by Shadidi *et al.*[26]. Various authors have noted that the use of biodiesel, including *Schizochytrium* sp. algae biodiesel, leads to a less delayed start of combustion and injection. This effect can be attributed to inherent properties of biofuel generation and higher cetane numbers in biofuels. The early start of combustion observed with biodiesel, in the case of *Schizochytrium* sp. algae biodiesel, promotes the faster oxidation of PM particles, irrespective of the air-fuel ratio[11].

Conclusions

The experimental results demonstrate that the generation of particulate matter is influenced by the engine's rotational speed and load. Specifically, for the engine used in this study, it was found that higher rotational speeds and average loads (50 %) corresponded to the highest emissions among the three considered fuel mixtures. However, for the 15 % mixture, it was observed that at medium load, the PM emissions were significantly lower compared to the reference fuel, diesel, with a reduction of more than 50 %. Similarly, for the 10 % mixture at average load, the rotational speed had a considerable effect on particle emissions, maintaining consistently low values across all three tested speeds. In the case of the 20 % mixture, there was an inverse relationship between high and medium loads. At medium load, the mixture exhibited emissions that were proportional to the rotational speed, while at low load, the emissions from this mixture were significantly reduced. The comparison conducted in this study provides a qualitative analysis of PM emissions for *Schizochytrium* sp. algae biodiesel blends with commercial diesel. However, to further enhance the analysis and obtain quantitative insights, it would be beneficial to incorporate a mathematical model that considers the interaction between rotational speed, load, and fuel properties. Such a model would provide a more robust understanding of the factors influencing the PM production or emissions.

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Data availability statement

The data used to support the findings of this study are included in the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

Ethical Statement

This material is the authors' own original work, which has not been previously published elsewhere.

Author Contributions:

SK: Writing- Original draft preparation, Supervision, Investigation, Software; and OAD: Conceptualization, Methodology, Visualization, Validation, and Writing- Reviewing.

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