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Economic Considerations on Nutrient Utilization in Wastewater Management

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Abstract: There is wide consensus that *Spirulina* can serve as a tool for wastewater management and simultaneously provide feedstock for biorefining. However, the economic aspects associated with its use remain a significant challenge. *Spirulina* cultivated in wastewater decreased the concentrations of both ammonia and nitrate and also served as a biodiesel source. The oil obtained in the feedstock was subjected to transesterification and turned into biodiesel. The biodiesel was subsequently analyzed in a test motor (water-cooled, four-stroke, single-cylinder compression ignition with injection). The tests were conducted at a constant 1500 rpm, and the output power was 3.7 kW. Mixtures of diesel and biodiesel were also enriched with carbon nanotubes (CNTs). The amount of CNTs added to the diesel was 30 mg L^{-1}. The algae and de-oiled biomass were characterized using XRD analysis, and an ultrasonicator was used to mix the CNTs with diesel and *spirulina* blends. A series of tests were conducted at different load conditions (25%, 50%, 75%, and 100%) for all fuel blends. Test results were compared with a neat diesel engine with a CR of 17.5:1. Among the fuel blends, the B25 reported improved brake thermal efficiency and reduced emissions. The outcomes are a reduction in thermal efficiency of 0.98% and exhaust gas temperature of 1.7%. The addition of *Spirulina* biodiesel blends had a positive impact on the reduction of greenhouse gas emissions, including reductions of 16.3%, 3.6%, 6.8%, and 12.35% of CO, NO_x, and smoke, respectively. The specific fuel consumption and CO_2 emissions were reduced by 5.2% and 2.8%, respectively, for B25 fuel blends compared to plain diesel and B50. Concerning cost competitiveness, vigorous research on microalgae for the production of biodiesel can cut production costs in the future.

Keywords: *Spirulina platensis*; biomass; algae biomass; wastewater; wastewater treatment; biofuel

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1. Introduction

Over the past few decades, fossil fuel consumption has grown tremendously, putting pressure on an alternate fuels [1]. Overall, 81% of world energy is derived from fossil fuels, used to cool or heat homes and other commercial places, generate electricity, run vehicles, and fuel industry [2]. Despite positive qualities, fossil fuels emit unwanted and environmentally harmful gases, which cause global warming [3]. The detrimental qualities of gas emissions and the depletion of fossil fuel resources urge researchers to find a replacement for conventional oil [4]. The research on biofuel as an alternative to fossil fuels is supported by many countries, since bioresources are perceived by policymakers as abundant in nature and environmentally as well as economically sustainable. However, there is still skepticism, especially regarding price competitiveness [5]. Targeted cultivation of biomass for the production of biofuels has been realized. Current efforts are focused on the use of waste biomass. Initially, researchers concentrated on combining petroleum fuels with biofuel in different proportions, because complete replacement brought various technical problems in combustion engines [6]. However, the use of biofuel in transportation would significantly reduce greenhouse gas emissions. Nevertheless, adding biofuel blends at percentages of 20% to 50% reduces harmful gas emissions, such as carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxide (NO_x), and unburnt hydrocarbon (UHC), by more than 50% [7,8]. The use of biofuel also reduces the break thermal efficiency (BTE) in combustion engines [9]. The usage of biomass should be increased to 35% and up to 50% by 2050 [10–12] to meet fossil fuel shortages in the future. In general, there is more than enough literature on the formation, qualities, and difficulties in biodiesel use. Extra investigation, effort, and attention are needed for research in the area of biomass production [13].

The idea of using *Spirulina* as the source of biofuel is comparatively new, and information and studies are limited, particularly for biofuel cultivated from wastewater [14,15].

The removal of nutrients such as ammonia and nitrate has been repeatedly and independently proven during multiple experiments on wastewater treatment [16]. The aim of this study was to examine whether biodiesel made of *Spirulina* oil, blended with conventional diesel with a concentration of 25 and 50%, decreases the effectiveness and performance of fuel in engine operation. The results of this study could significantly change the use of algae biofuels in the future.

2. Materials and Methods

2.1. Biodiesel Mixtures

In this study, biodiesel was produced from *Spirulina* cultivated in wastewater. Wastewater was obtained at a local municipal wastewater plant. The ammonium concentration was measured using the standard wastewater analysis [17]. The microalgae were grown in a 500 mL Erlenmeyer flask with Zarrouk liquid medium. pH levels were maintained below 9. The procured algae were grown in a 50 Hz photobioreactor. Every 48 h, the microalgae were harvested by centrifugation and dried for 60 min at 70 °C. Lipid extraction was done by mixing chloroform and methanol at 1: v/v by the Bligh and Dyers method [18]. The lipid extract was mixed with the 1:6 w/v methanol along with the catalyst 0.6 wt% NaOH and allowed to settle for at least 15 h. After transesterification, two typical layers were formed, one at the top and another at the bottom. Biodiesel and ethanol settled on the top layer, while the heavy phase glycerol settled at the bottom. The collected biodiesel was dried over anhydrous sodium sulphate [19–21]. FTIR analysis was performed for both conventional algae and de-oiled biomass using an IRAffinity-1s FTIR instrument, Shimadzu, Japan [22–27]. Fuel blends (conventional diesel mixed with biodiesel) were prepared by adding 25% (B25) and 50% (B50) of *Spirulina* biodiesel to neat diesel. Carbon nanotubes (CNTs) were subsequently added in the amount of 50 ppm by the ultrasonication process. The CNTs (2 nm diameter) were purchased from Light Mach Composites, India.

2.2. Test Engine Experimentation

The biodiesel mixtures were tested in a single-cylinder, four-stroke, water-cooled, compression ignition KIRLOSKAR AV1 diesel engine run by *Spirulina* microalgae at different proportions with 50 ppm carbon nanotubes. Tests were conducted for fuels such as D100 (neat diesel), B25 (25% biodiesel 50 ppm CNT) and B50 (50% biodiesel 50 ppm CNT) at different engine load conditions of 25%, 50%, 75%, and 100% at a speed of 1500 rpm. The combustion analysis and cylinder pressure were also analyzed in addition to the analysis of engine performance and emission characteristics. An illustration of the experimental setup is provided in Figure 1. The properties of different fuel blends are also shown in Table 1. While conducting all experiments, the engine speed was kept constant at 1500 rpm, with full load conditions and the compression ratio remaining the same at 17.5:1 [28,29].

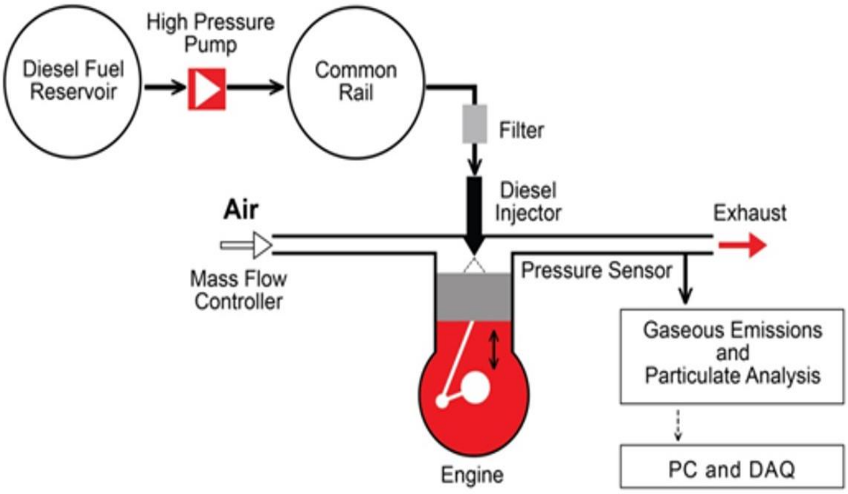

Figure 1. Experimental setup for fuel analysis.

Table 1. Properties of biodiesel and nano-additive blended fuel.

Properties	Diesel	B50	B25
Kinematic Viscosity at 40 °C (mm^2/s)	2.2	2.67	2.3
Cetane Number	54	50.5	55
Calorific Value (KJ/Kg)	43,324	44,350	44,700
Flash Point	46	41	40

The eddy current dynamometer was coupled with the engine setup for applying load. A separate control system monitored the load. The test fuels D100, B25 and B50 were used to test all the properties by maintaining a constant engine speed and compression ratio. A series of sensors were used to measure the air consumption rate and the orifice plate pressure. The location of the crank angle encoder was the opposite side of the eddy current dynamometer. The data acquisition system was equipped to measure fuel consumption with a burette-based optical sensor [30–33]. The combustion parameters, engine performance and combustion performance were calculated by keeping the engine at full load.

The considered error in the measurement of all properties of the diesel engine was taken as ±0.15. The exhaust gas emission parameters of NO_x, CO, HC and CO_2 were measured using the Testo-350 analyzer [34]. The uncertainty percentage and the accuracy while using the Testo-350 instrument were calculated and are listed in Table 2.

Table 2. Accuracy of measurements and uncertainties.

Device Used	Parameter	Measuring Range	Resolution	Accuracy	Maximum Uncertainty
Fuel measuring burette	Fuel flow (g/h)	0–100 mL	-	±1 ml	±0.5%
Electronic precision balance	Fuel consumption (g)	0–99 kg/h	-	±0.02 kg/h	±0.1%
Pressure sensor	In cylinder pressure (bar)	0–250 bar	-	±1 bar	±0.6%
Temperature indicator (K-Type)	Temperature (°C)	0–1200 °C	-	±1 °C	±1%
AVL DI	Smoke meter	0–100%	-	≤0.01	±0.1%
Testo 350 exhaust gas analyzer	CO	0–50 vol%	0.01 vol%		±0.3%
	CO_2	0–50 vol%	0.01 vol%		±0.3
	HC	0–40000 ppm	1 ppm	±10% of reading	±0.1
	NO_x	0–3000 ppm	1 ppm	±5% reading < 2000 ppm	±0.5%
Data acquisition system		National instruments (6218 DAS)—Equipped with one touch			

2.3. Analysis of Uncertainty

The uncertainty of measurements and possible errors were analyzed [35] 5 times during every measurement. The analysis of uncertainty was carried out to calculate the overall uncertainty percentage using the formula given below. The errors used for the calculation are listed in Table 2. The overall percentage of uncertainty was ±2.155% [36–38].

$$R_0 = R(X_1\,, X_2\ \ldots\ldots X_n) \tag{1}$$

$$\frac{U_R}{R} = \sqrt{\left(\frac{X_n \partial R}{R \partial X_n}\right)^2 \frac{U_{X_n}^2}{X_n^2}} \tag{2}$$

where

R_0—Independent variable functions
$\frac{\partial R}{\partial x_1}$—Sensitivity for a single variable

3. Results and Discussion

3.1. Production of *Spirulina platensis* Biomass and Nutrient Removal

The cultivation of *Spirulina* in wastewater showed that the efficient time of cultivation must be lower than six days (Figure 2) due to the decreasing concentration of nutrients. As the concentration of the wastewater increased from 0.03 v/v to 0.25 v/v, the biomass concentration decreased by 90%, which confirmed that *Spirulina* competed for the nutrients with other microorganisms in unsterilized wastewater, and the highest dilution is necessary for the successful growth of *Spirulina*.

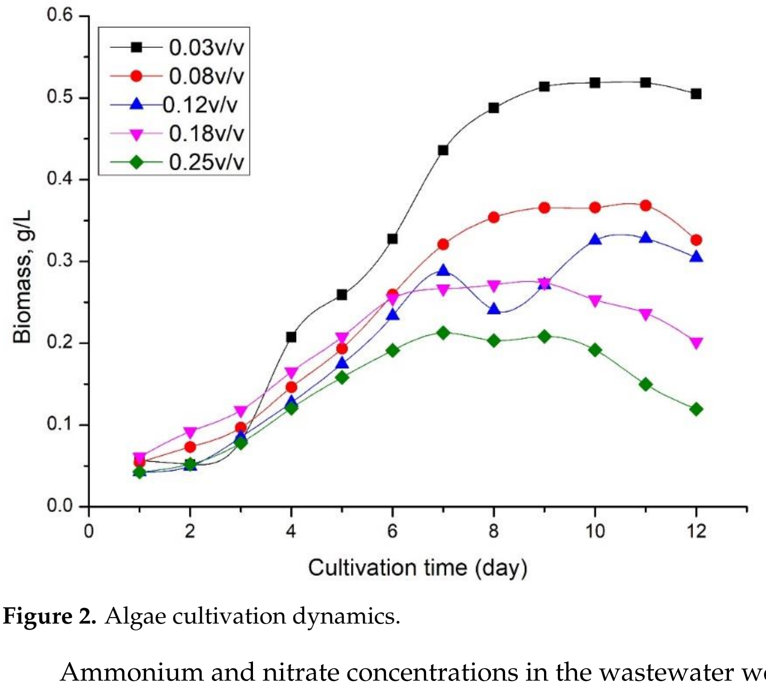

Figure 2. Algae cultivation dynamics.

Ammonium and nitrate concentrations in the wastewater were sufficiently removed during the *Spirulina* cultivation (Figure 3). Original ammonia and nitrate concentrations decreased from 0.75 and 0.8 to 0.15 and 0.52, respectively, after 75 h. The decrease of ammonia to half of its original concentration was recorded within 40 h of cultivation, and nitrate concentration decreased by the same amount in 75 h (Figure 3).

3.2. FTIR Analysis

FTIR analyses of *Spirulina* biomass, de-oiled biomass, Algae blends, and neat diesel were performed (Figures 4 and 5). The peaks from 3100 cm^{-1} to 2800 cm^{-1} denote the presence of lipids [39]. Due to the formation of high concentration lipids, the quality of the bio-oil was impacted, with reduced calorific value. Notably, peaks of 2943.23 and

1723.56 cm^{-1} were responsible for the stretching of -CH_2- groups [40,41]. The drop in the peaks clearly emphasize the exaction of the lipid content from the biomass. The highest peak of 3462.13 cm^{-1} and the lowest peak of 1050.13 cm^{-1} were observed for the *Spirulina* blends and neat diesel due to the stretching of the double bond and C-O bond. The peaks in the algae were different from neat biodiesel (Figure 5) due to the presence of aliphatic hydrocarbon content in the neat diesel.

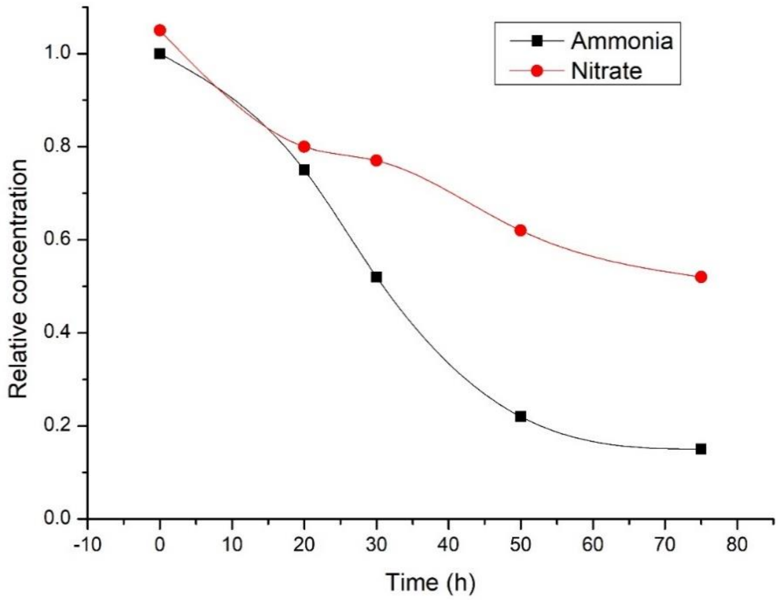

Figure 3. Nitrogen dynamics.

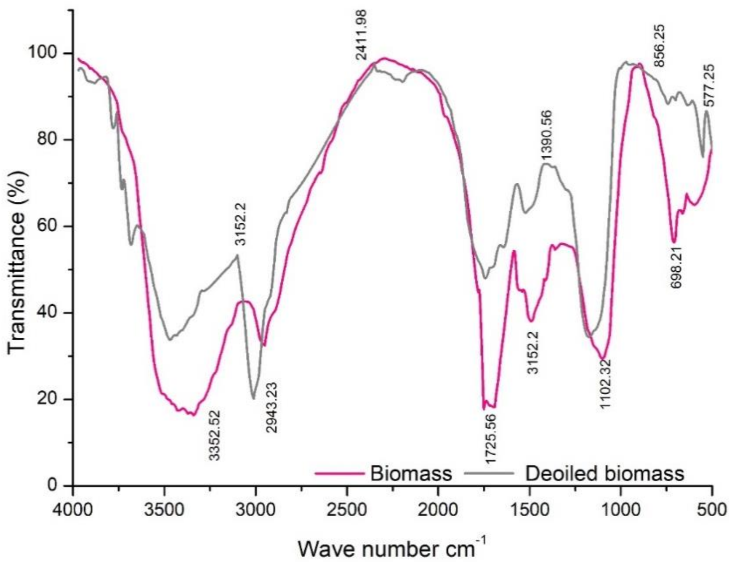

Figure 4. FTIR analyses.

3.3. Combustion Analysis Parameters

The main parameters that determine combustion chamber performance are chamber pressure, heat release rate (HRR) and cylinder peak heat release rate (CPHRR), ignition delay (ID), and maximum rate of pressure rise (MRPR). These parameter values were measured load conditions of 0 % to 100 % for the fuel blends of B25 and B50.

3.3.1. Cylinder Pressure

Cylinder pressure directly affects exhaust gas emissions. The variation in cylinder pressure for different crank angles at the compression ratio of 17.5:1 for the D100, B25 and B50 fuels is shown in Figure 6. Biodiesel made of *Spirulina* and enriched with CNT showed characteristics similar to D100 at the crank angle of 369.9. Moreover, the cylinder pressure was 88.0 MPa, and for the blends B25 and B50 the cylinder pressure was 863 kPa and 855 kPa, respectively, under the same conditions. The cylinder pressure was lower in the CNT B25 blend; however, NO_x emissions were higher. The rate of combustion depends mainly on the cylinder pressure. The type of fuel used also plays a significant role. The cylinder pressure variation for different fuel blends of *Spirulina* and CNTs as well as plain diesel fuel is shown in Figure 6. Cylinder pressure was consistently high for plain diesel D100, which was 2% higher than B25 and 5.4% higher than B50.

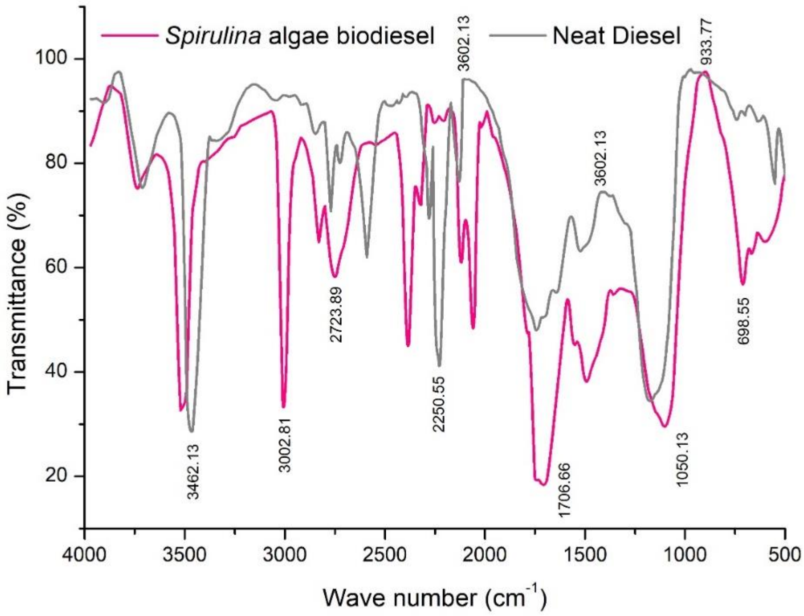

Figure 5. FTIR analyses.

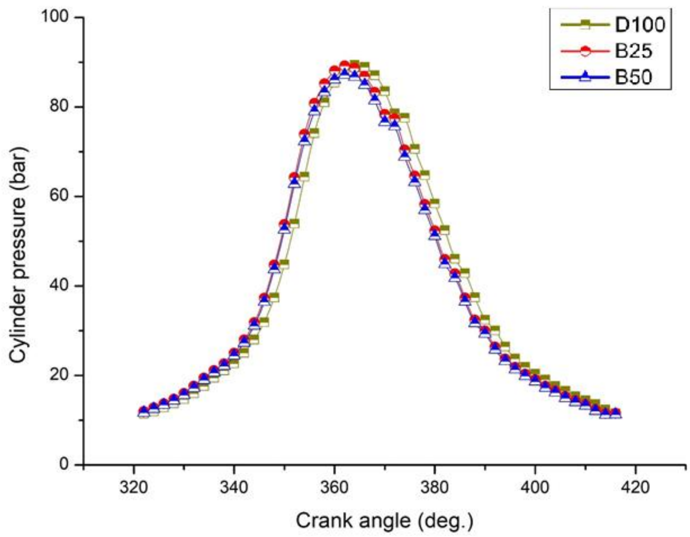

Figure 6. Analysis of cylinder pressure variations.

3.3.2. Heat Release Rate

The factors determining heat release rate are the viscosity of the fuel, air–fuel mixing and the heating value of biofuels. The highest heat release was observed in D100, with lower rates in the *Spirulina* fuel blended with CNT (Figure 7). B25 and B50 showed a reduced heat release rate compared to D100 [26]. This was caused by the higher viscosity of the diesel, longer ignition delay, and the difficulties in mixing the fuel with air. As the spray formation rate increases in all *Spirulina* CNT fuel blends due to a decrease in viscosity, the heat release rate for all fuel blends is lower than for the diesel. As the blend ratio increases, the viscosity increases simultaneously with the oxygen content. Due to the increment in the viscosity, the fuel blends show a reduced heat release rate. The higher ignition delay results in an increased heat release rate in the D100. The heat release rates at 25% and 75% loads were expressed as 39.2 J/CA, 38.51 J/CA and 77.3 J/CA, 74.6 J/CA, respectively. The B25 and B50 blends were found to produce a heat release rate of about 5.8% at CR17.5. The values of maximum heat release rate were 88.51 J/CA for B25 and 87.3 J/CA for B50.

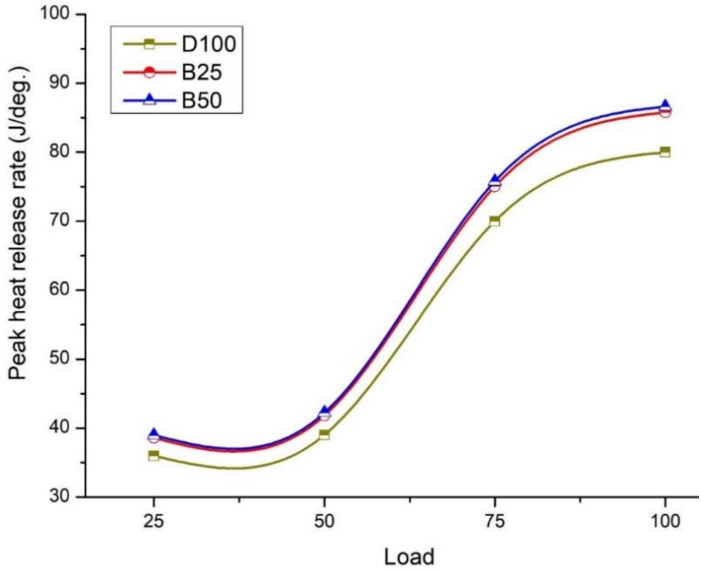

Figure 7. Analysis of heat release.

3.3.3. Rate of Pressure Rise

The measurement of pressure rise (MRPR) with different loads of 25%, 50%, 75%, and 100% for neat diesel and CNT-mixed B25 and B50 revealed peak pressure that was observed near the top dead center and that increased the power output (Figure 8) [42,43]. The determination of MRPR is crucial since it is one of the main reasons for NO_x emissions and the cause of knocking. The peak pressure values were 8.09, 7.55, and 7.5 for D100, B25, and B50, respectively [44–46]. At 100% load, the rate of MRPR was 2.8% higher in D100 fuel than the B50 fuel blend at the compression ratio of 17.5. The lower rates of MRPR for D100 and B50 were 3.15 bar/deg and 2.4 bar/deg. Considering the knocking effect, the peak pressure level was above 0.8 MPa. The permissible level of pressure is from 6 to 7 bar [47,48]. When comparing the results, dispersion of CNT with the conventional diesel improved the compression ratio. Further, the blends with CNT had better anti-knocking quality than other fuel blends.

3.3.4. Ignition Delay

Ignition delay refers to the time gap between the time of injection of the fuel and its ignition, and it rises with the amount of injected fuel. Higher ignition delay leads to higher NO_x emissions, higher heat release rate due to over consumption of fuel, and higher air–fuel mixing rate. The ignition delay for D100 was lower than for B25 and B50 (Figure 9). The ignition delay for D100 was 12.02°, and it was 12.65° for the fuel blends of

CNT, pre biodiesel, B25 and B50, which is lower due to a CR of 17.5 [49–53]. Emissions are reduced by maintaining the pressure and temperature, resulting in the stable operation of the engine.

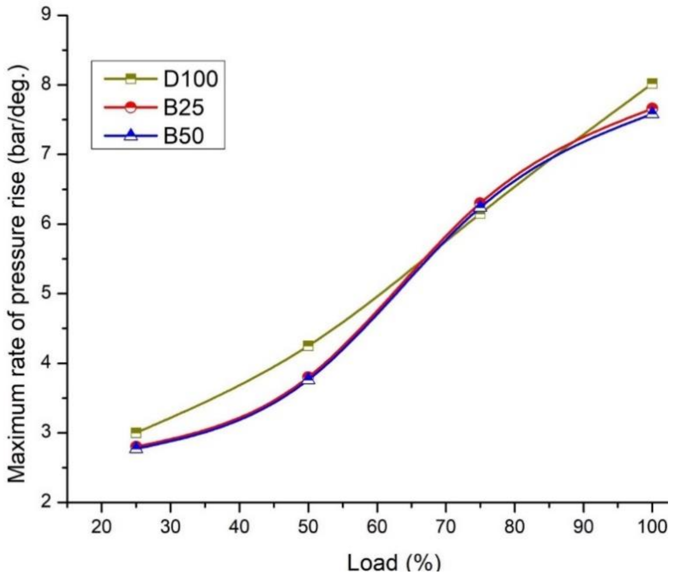

Figure 8. Analysis of maximum rate of pressure.

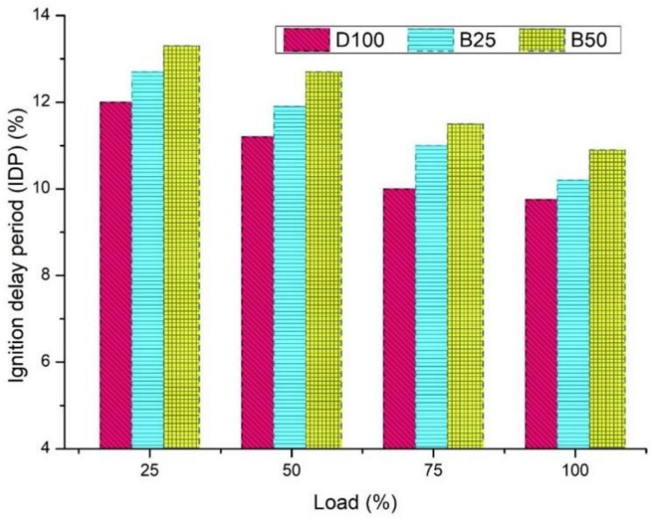

Figure 9. Analysis of ignition delay.

3.4. Analysis of Engine Performance

3.4.1. Specific Fuel Consumption

Density and viscosity of the fuel are the influencing factors for specific fuel consumption. The calculated SFC [54] of B25 was the lowest (Figure 10). On the other hand, the fuel consumption rate of other blends was higher due to the deficit in the heating release rate. Initially, at 25% engine load, the BSFC was 599 g/kWh, 556.3 g/kWh and 576.4 g/kWh for D100, B25 and B50, respectively. Surprisingly, the performance value of B25 was 8.6% higher than D100. On the other hand, at full load conditions, the respective BSFC values were 295 g/kWh, 248 g/kWh, and 278 g/kWh. Typically, this is 17.3% and 59% lower than neat diesel [55].

3.4.2. Brake Thermal Efficiency

The factors affecting the BTE are the volatility, viscosity, density, and heating value of fuel. BTE is reduced due to a decrease in the calorific value of fuel. The calorific value of B25 and B50 was low due to the additional consumption of fuel. The brake thermal efficiency of B50 was lower than the BTE of B25. The BTE values of D100, B25, and B50 were 28%, 26.5%, and 32.1%, respectively, at 80% load condition of the engine [56]. At full load, there was a drastic drop in BTE (Figure 11). The total reduction in BTE of B50 was 5.3% when compared to B25.

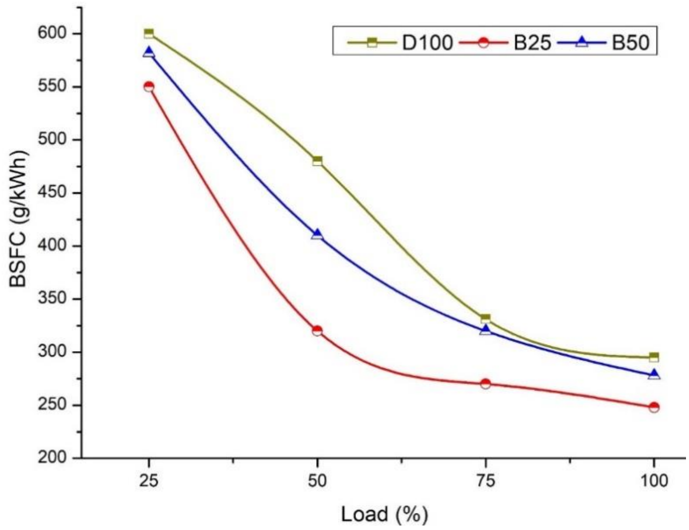

Figure 10. Analysis of BSFC.

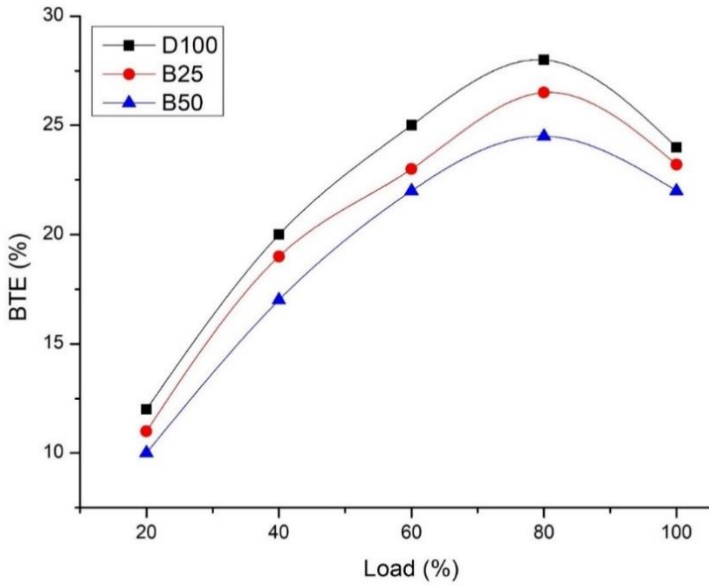

Figure 11. Analysis of BTE.

3.4.3. Exhaust Gas Temperature

With a higher amount of fuel injected into the engine, the engine's temperature increases, which consequently increases EGT. The combustion process timing also affects the EGT [57]. However, due to the lower calorific value and higher oxygen content present in the biodiesel blends, the EGT value is lower than in diesel because of the short complete combustion. The EGT of B50 was 7.5% lower than the EGT of B25 (Figure 12). The EGT values of D100, B25, and B50 at CR17.5 were 620 K, 663 K, and 635 K, respectively. On the other hand, B50 reported a temperature 4% lower than B25. The biofuels had lower heating value and lower EGT due to early combustion, allowing them to increase the crank angle and the ignition time. From these results, it is clearly seen that there is a partial combustion of the biofuels, thus providing better combustibility than diesel [58].

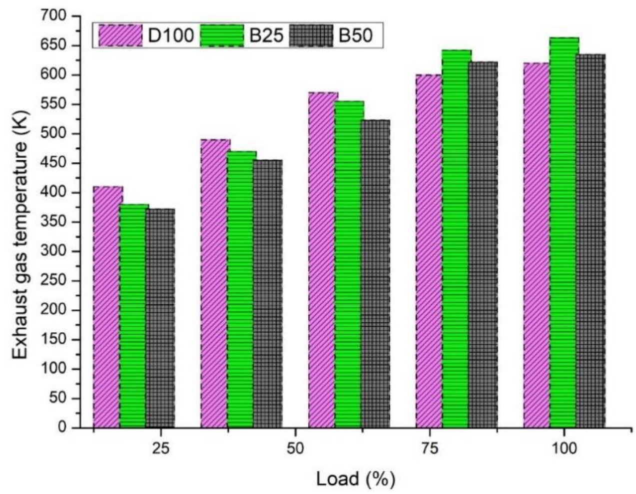

Figure 12. Analysis of exhaust rate temperature.

3.5. Emission Analysis

3.5.1. Carbon Dioxide (CO_2) Emissions

CO_2 emissions were higher in the biodiesel blends, especially in B50 (Figure 13). Early combustion and blend ratio play an important role, and these parameters are interrelated. Moreover, the addition of Carbon Nanotubes to the fuel mix increases the CO_2 emissions. The CO_2 emission rate of B25 and B50 was 940 g/kWh and 980 g/kWh, respectively [59,60]. The net increment in CO_2 emissions in the fuel blend B25 was around 3% compared to neat diesel.

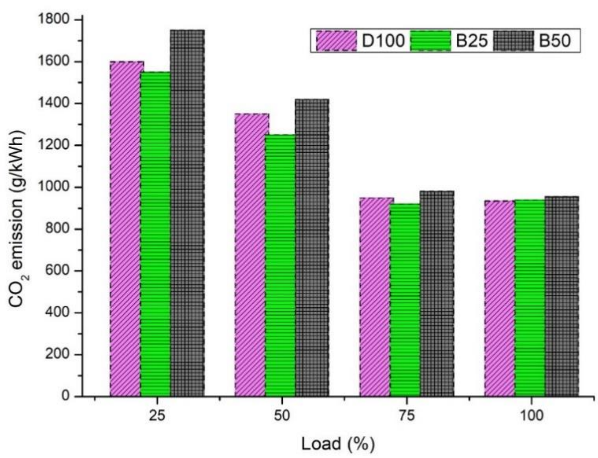

Figure 13. Analysis of CO_2 emissions.

3.5.2. NO_x Emissions

The nitrous oxide emission variation based on different load conditions for algae-based biodiesel blends is depicted in Figure 14. The linear increment in emissions of nitrous oxide is clearly seen in Figure 14 for all the blends. Oxygen content and combustion temperature in the combustion product determines the nitrous oxide formation. In general, increments in load conditions leads to linear increases in NO_x emissions, resulting in an increase of the average gas temperature and fuel to air ratio. Algae-based biodiesel showed lower nitrous oxide emissions and high heat release rates. Shorter combustion duration reduces the biodiesel blends' NO_x emissions. In addition, the shorter duration available to form nitrous oxide from nitrogen reduces the NO_x emissions. This process decreases the gas temperature, which ultimately reduces NO_x emissions. From Figure 14, it is evident that biodiesel blends showed lower NO_x emissions from 25% to 100% load conditions. The B25 blend showed more than 100% reduction in NO_x emissions compared to conventional fuel. The reason behind the lower NO_x emissions is that biodiesel fuel has improper spray properties, due to an increase in density and viscosity, along with improper combustion.

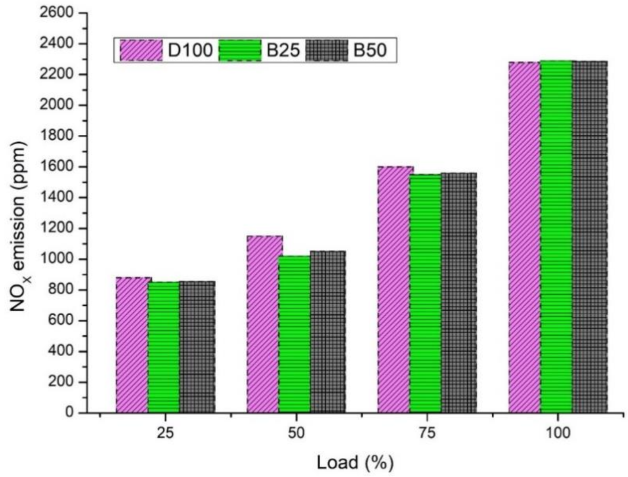

Figure 14. Analysis of NO_X emissions.

3.5.3. Hydro Carbon (HC) Emissions

The unburned HC emissions of biofuel were lower than for diesel (Figure 15). The higher amount of oxygen present in the biofuels improves the combustion process, thus decreasing the HC emissions [61]. The HC emissions are directly opposite to the NO_x emissions. As the HC emissions decrease, the NO and NO_x emissions increase [62,63]. The amount of NO_x emissions was 0.058 g/kWh, 0.057 g/kWh, and 0.038 g/kWh for D100, B25, and B50, respectively.

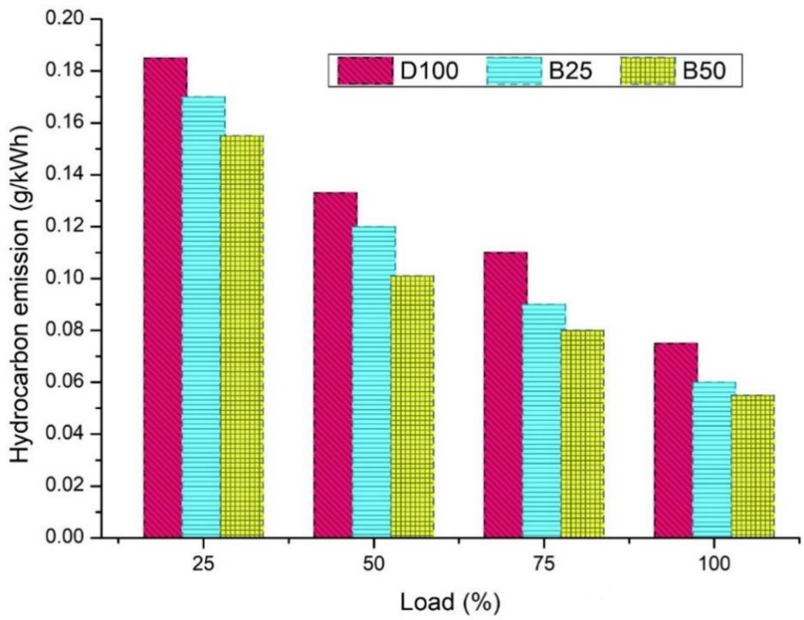

Figure 15. Analysis of HC emissions.

3.5.4. Carbon Monoxide (CO)

Owing to the complete combustion of biofuels, the emission rate of CO is lower in all biofuels (Figure 16). The rate of CO emissions for the D100, B25, and B50 was 3.56 g/kWh, 3.43 g/kWh, and 2.92 g/kWh, respectively, at CR17.5 and at full load conditions [31,39]. The reduced CO rate for B25 was about 2.8%, which is comparatively lower than diesel.

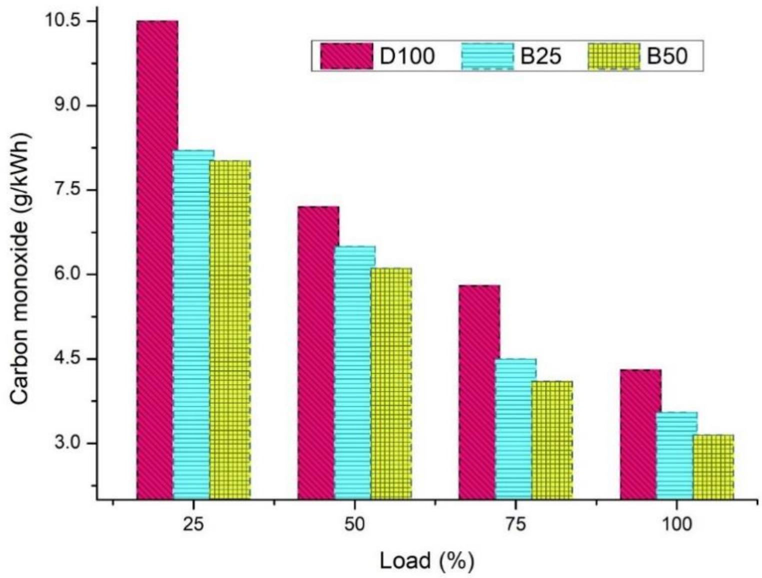

Figure 16. Analysis of CO emissions.

3.5.5. Smoke Emissions

The smoke emission rate of biofuels is lower than diesel (Figure 17). The higher amount of oxygen present in the CNT-added *spirulina* microalgae biofuel helps achieve the complete burning of the fuel, which results in reduced smoke [64]. The quality air-fuel mixture also plays an important role in the emission of smoke. Rather than increased load resulting in increased smoke emissions, the increased blend ratio reduced the smoke emissions. The smoke emission for D100 at full load condition was 12.35%, while the smoke emission of B25 was 3.5%. This proves the positive properties of the B25 and B50 biofuels.

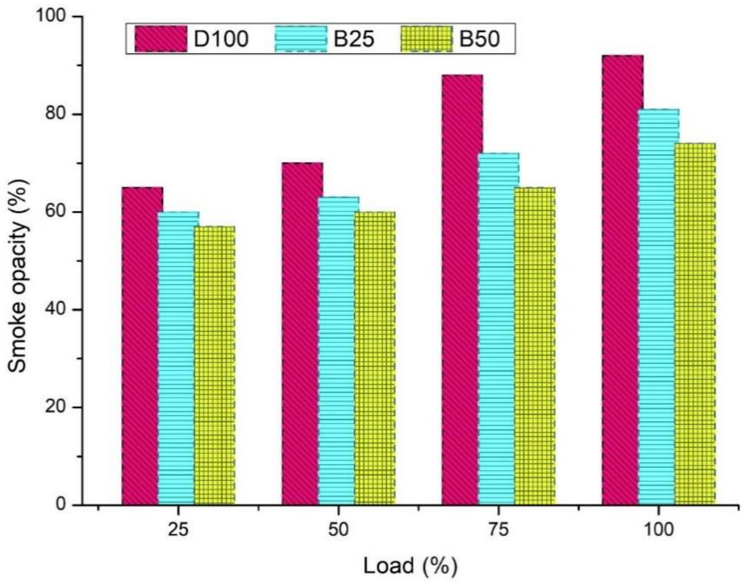

Figure 17. Smoke analysis.

3.6. Economic Considerations

A decade ago, the biodiesel derived from purpose-grown algae was considered as a potential third generation fuel, and the technological concept attracted policymakers and investors. Many industrial firms had great confidence that biofuels would replace fossil fuels. However, the production cost of the biodiesel obtained (3–7 € L^{-1}) was far from competitive with existing fossil diesel fuels. Following these observations, many policymakers and investors realized that such expensive fuels would significantly reduce the competitiveness of key products to an extent they could afford. As a result, policies were tuned down, and many corporations went bankrupt. Most efforts to produce biofuels from purpose-grown biomass ended in a similar way, and despite much effort, production of cheap fuel from purpose-grown algae remains a distant dream. Production of inexpensive fuel from algae is currently impossible due to the high cultivation and harvesting costs. To produce 1 kg of biodiesel from algae costs more than €2, which is 50% higher than corn or soybean biodiesel [65]. Reducing the chemical conversion burden in the transesterification process cuts processing costs. Although technologies like the usage of CO_2 for harvesting algae cuts 25% of production costs, there is still a long way to go before algae can be seen as a usable fuel. In a nutshell, from this study we can confirm the possibility of the usage of algae fuel in conventional diesel engines [66]. However, sustainability is questionable due to production costs [67]. By strengthening the economic sustainability of microalgae production and harvesting, the production biodiesel can be made viable [68,69].

4. Conclusions

Experimental analysis was done for D100, B25, and B50 fuels, and the following conclusions were drawn. *Spirulina* could be cultivated only in highly diluted wastewater at the advance of nutrient removal. The biodiesel extracted from the biomass was effectively utilized by blending with neat diesel. The ignition delay was reduced in all biofuel blends due to the higher cetane number, caused by the addition of carbon nanotubes and oil extracted from *Spirulina* biomass.

In the performance characteristics, the BTE was reduced slightly for all fuel blends. For diesel, the BTE gradually increased at different load conditions. A slight increment in the SFC was noticed in the case of biofuels. The peak pressure reached for D100, B25, and B50 fuel blends was 86 bar, 84.3 bar, and 81.4 bar, respectively. The peak pressure for B25 was close to the peak pressure value of B50.

The heat release rate for D100, B25, and B50 was 93.54 J/CA, 87.1 J/CA, and 63.2 J/CA, respectively. Considering the emission characteristics, for all biofuels, NO_x was lower than for diesel; however, as the load condition increased, NO_x emissions also increased because of the improved compression. Similarly, CO emissions were lower than for diesel. To conclude, the attempt to use the B25 and B50 blends as an alternative fuel was successful, as they produced lower emissions of harmful greenhouse gases. However, the sustainability of algae-derived biodiesel was questionable due to the higher production and harvesting costs. Compared to conventional diesel, the algae-derived fuels were 60% more expensive. Thus, finding optimized inexpensive methods are essential to replace conventional fuels.

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