



Review Article

Comprehensive review of algae biodiesel: production, engine performance, and emission characteristics with additives

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ABSTRACT

The combustion of petro-diesel fuels in internal combustion engines is one of the contributing factors to increased environmental air pollution. The combustion byproducts are toxic exhaust emissions, which are dangerous to human health and the environment. Therefore, the need for sustainable and renewable fuels, like biodiesels, is gaining significant attention to regulate the toxic exhaust emissions from compression ignition engines. Biodiesels are popular due to their biodegradable, renewable, eco-friendly, non-toxic factors and their ability to be employed in diesel engines without major modifications. These features have attracted researchers to investigate different biodiesels and their performance and emissions compatibility with existing engines. In this systematic review, research findings from the year 2009 to 2024 on biodiesel production from second and third-generation feedstocks, their significant fuel properties, and fatty acid compositions are critically reviewed. In addition, combustion performance and exhaust emission characteristics of different diesel and biodiesel blends are discussed. Similarly, additives are gaining popularity for improving the significant biodiesel properties and enhancing combustion performance with regulated emissions. Therefore, the influence of additive blending in biodiesel is also highlighted. Further, a comprehensive review was conducted on the emergence of algae biodiesel processing methods of algae to meet the future energy requirements in engines. The findings from the literature confirmed that the presence of high saturated fatty acid composition in green algae biodiesel mitigated the upsurge in nitrogen oxide emissions and suggested that green microalgae biodiesel is best suited as a potential source of biodiesel production. Finally, this review reported that compared to non-edible biodiesel, algae biodiesel resulted in enhanced combustion propensity, engine performance, and reduced nitrogen oxide emissions, a prominent source of green, sustainable fuel to replace fossil fuel.

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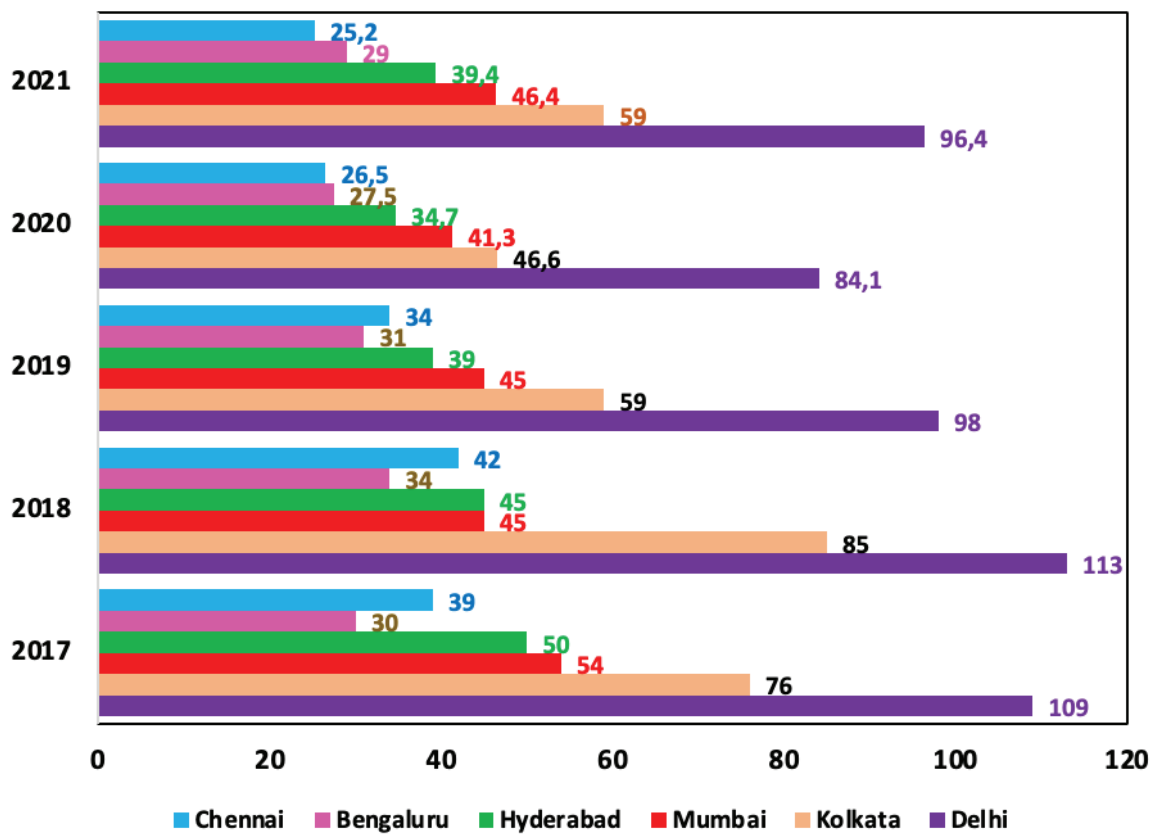


Figure 1. Annual average ($\mu\text{g}/\text{m}^3$) of PM 2.5 in Indian major cities (2017 – 2021).

the practical applications of internal combustion engines are growing gradually due to their high-power output and marginally low fuel consumption. In addition, they found almost all industrial applications, from small to large scales, in today's world.

The primary concern of these combustion engines is their toxic exhaust emissions[14]. In the present situation, the dangerous pollutants exerted by automobile engines, including carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxide (NO_x), particulate matter (PM), unburned hydrocarbons (UHC), and smoke, are considered as a severe threat to humankind. Different research groups have made various proposals to regulate this issue. Replacing internal combustion engines with electric motors and replacing existing fossil fuels with renewable and sustainable fuels are attractive proposals that are gaining wide attention. In addition, the entry of 17 sustainable development goals into the force has motivated the researchers to achieve *Affordable and Clean Energy* by 2030. Within this limited time frame, burning and using sustainable alternative fuels to replace fossil fuels are considered feasible solutions compared to replacing existing engines with other technology like electric motors. However, the fossil-derived petro-diesel fuels presently used in compression ignition (CI) engines are at

the exhaustion phase, which led to a focus on a sustainable energy source known as biodiesel.

EMERGENCE OF BIODIESELS

Biodiesels are widespread for their clean burning, high oxygen levels, and low carbon content[15] and are famous for producing less emissions than conventional diesel fuels [16]. Biodiesels are used in the CI engines as neat biodiesel or blended. They have been proven to be one of the emerging sources for replacing fossil fuels. Raman et al. [17] used rapeseed biodiesel to estimate the engine behavior of a conventional DI diesel engine. The investigation concluded that the B25 biodiesel blends enhanced engine performance, resulting in high BTE and reduced engine exhaust emissions. Similarly, Chozhavendhan et al. [18] discussed various parameters influencing biodiesel production, like lipid/fat content, catalyst, molar ratio, and purification process, to reduce the unit and operation cost to produce biodiesel. The study reported that biodiesel from lignocellulose, edible, non-edible oils, and micro and macroalgae emits less pollution than fossil fuels. Prasada Rao et al. [19] conducted an experimental investigation using palmyra biodiesel blends of POME10, POME20, POME30, and

POME40 to estimate the engine performance and emissions. The findings reported that the exhaust emissions for the blend POME20 are reduced for CO by 15.86 %, UHC by 18.5%, and smoke emissions by 14.28 % compared to diesel.

BIODIESEL GENERATIONS

Biodiesels are extensively categorized into first-generation (IG), second-generation (IIG), third-generation (IIIG), and fourth-generation (IVG). A detailed overview of the four-generation biofuels and their latest developments were highlighted [20], and various feedstocks, oil, and biodiesel yield percentages, and characterization of biodiesel fuel properties for the production of biodiesels were reviewed [21]. The first-generation biodiesels (IG) come under edible oils; these crops produce biodiesel and are used for food consumption. Gradually, the utilization of IG biodiesels has raised concerns about food vs. fuel. Hence, to overcome the drawbacks associated with biodiesel, IIG biodiesels exist; these are linked to the non-edible oil category, such as seed oil, waste vegetable oils, and animal fats [22]. Rezanian et al. [23] reviewed different non-edible sources (IIG) for biodiesel production using the transesterification method as these are economical, and there is no issue or debate on food vs. fuel, likewise in edible sources. However, various second-generation biodiesel feedstocks are tested on the CI engine to observe the performance characteristics and emission levels. Correspondingly, experimental studies are conducted by mixing additives [24–26] into the biodiesel blends.

Aruna Kumari et al. [27] tested the engine emissions using lemon peel biodiesel blends of 10%, 20 and 30% vol.% and trailed on the CI engine. The test observations revealed that CO, HC, and smoke emissions were recorded at 20% of lemon peel oil blend by 25%, 25.6%, and 15.44%, and an increase in NO_x was observed when compared with diesel. With this motivation, Enweremadu et al. [28] used canola and sunflower biodiesel feedstocks and simulated the engine behavior using C++ software on a Mercedes Benz DI engine. The output indicated that biodiesel possesses higher Specific fuel consumption (SFC), brake power (BP), and thermal efficiency than diesel. Further, high NO_x and low smoke emissions were recorded compared to diesel. Thus, several researchers extended their investigations to mitigate emissions by employing additives in IIG biodiesels [29–31].

Accordingly, Ahmad S et al. [10] mixed oxygenated additives, methanol or diethyl ether in Neem biodiesel, a second-generation biodiesel, due to the rise in NO_x emissions. The engine experimental test showed that BSFC was reduced by 10%, CO and HC were decreased by 25%, and NO_x emissions lowered when Neem biodiesel was tested with diethyl ether. In a similar form, the addition of heptane butanol and diethyl ether was mixed in *Jatropha* biodiesel, and the output results showed that there is an enhancement in BTE and an increase in BSFC by 5–20% and a reduction in engine emissions by 3–12%. Similarly, *Calophyllum inophyllum* biodiesel enhanced engine efficiency and lowered

emissions by adding oxygenated additives butanol, pentanol, decanol, and hexanol. Thus, overcoming a few shortcomings in biodiesels, such as higher density, kinematic viscosity, lower calorific value, and rise in NO_x, has instigated researchers to add oxygenated additives in different biodiesel generations.

Based on the investigations contributed by enormous numbers of researchers, it is understood that biodiesels can replace fossil fuels. Though IIG biodiesels such as waste cooking oil gained positive attention as this feedstock is obtained at low cost and readily available, the main set back observed over WCO biodiesel was the filtering and processing of WCO [32]. Thus, the hitches raised in IG and IIG biodiesels have directed the approach towards sustainable, clean, and green fuels, known as third-generation algae biodiesels (IIIG).

Algae are ubiquitous photosynthetic organisms on the earth, identified as the fastest-growing biomass. Algae are known for their abundant availability, require less land space, rapid growth, use of natural resources such as sunlight CO₂, and use as food supplements [33]. The processing of algae is a crucial agent in the preparation of algae oil for biodiesel [33]. In particular, algae cultivation is significant for growing and harvesting algae. However, a slight increase in economic viability is a setting concern during harvesting [34], and separating algae layer by layer [35] consumes more time in algae processing. Hence, algae are the best source of biodiesel, producing clean-burning renewable fuel. In recent years, several researchers [36–38] have turned their interest toward fuel production from one of the oldest living creatures on the earth, known as algae, serving as a biofuel source.

With this motivation, an experimental investigation was performed on one cylinder, 4-stroke, at a speed of 1500 rpm, for the algae biodiesel blends of 5%, 10%, 20%, and 30% [39] to estimate the engine combustion performance and emission characteristics. The tested results reported that at blend up to 5%, the BTE decreased, and the reduction in CO and UHC was observed up to 28%. Finally, a gradual increase in NO_x emission (up to 13%) was shown in the experimental tests. And a volume fraction of 20% exhibited better results compared to other blends. However, additive mixing in biodiesel plays a significant role in overcoming the rising NO_x emissions. Based on this, Sekharraj K et al. [40] conducted an experimental study on green microalgae biodiesel blends for 80–20 (80% diesel and 20% biodiesel) mixed with Bi₂O₃ nanoadditives to determine the performance and emission characteristics. The engine test results reported that using nano additives enhanced the engine's performance and reduced the engine emissions. The schematic representation of the biodiesel production based on different generations is represented in Figure 2 [22].

The fourth-generation biodiesel (IVG) deals with the genetic modification of microalgae, fungi, yeast, and cyanobacteria [1], [22]. The primary benefit of employing IVG biodiesel was its ability to grow microalgae and collect significant

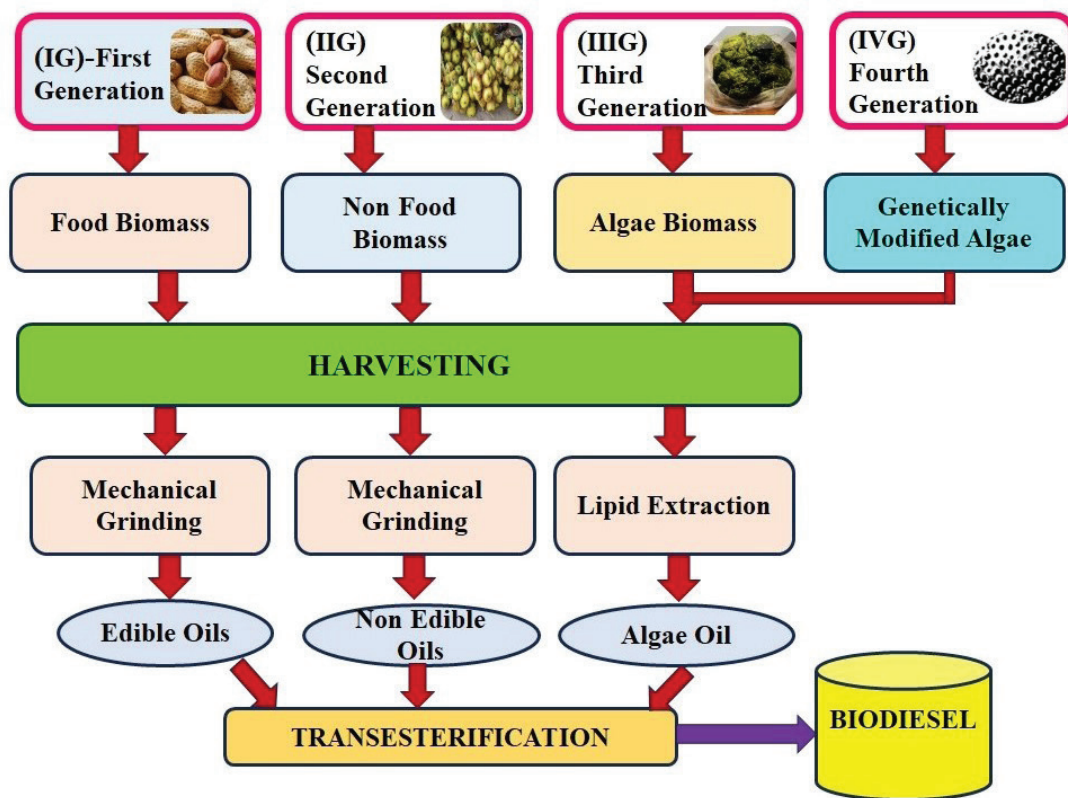


Figure 2. Different generations and their process of production of biodiesel.

amounts of CO₂ by boosting productivity and availability by incorporating modern technologies. However, this technology cannot be employed with all microalgae species due to a lack of gene and biological understanding [41]. Therefore, third-generation algae are recognized as the most significant potential to produce algae biodiesel and are considered one of the emerging sources of fuel to run and test on existing diesel to replace fossil fuels.

The observations from the biodiesel generations revealed that the IG edible oils created a debate on food vs. fuel, which hinders using fuel for transportation. Though IIG biodiesel (non-edible oils) play a vital role in improving efficiency and reducing emissions, the limiting factors, such as the availability of land to cultivate the non-edible oil crops and high fatty acid profiles, led to opt for IIIG algae biodiesel as one of the better options for replacing conventional fuels in CI engines since the land area required to cultivate the algae [36] is significantly less and reported high oil yields compared to the IG and IIG.

However, the rise in NO_x emissions in second-generation [27-28] and third-generation biodiesel [29] confirmed an increase in NO_x emissions. Thus, to mitigate emissions, several researchers extended their investigations by employing additives in IIG biodiesels [29-31] and IIIG biodiesels [41], resulting in improvements like complete combustion in ignition chambers and reduction in temperature,

leading to enhanced engine performance and lowers engine emissions.

Sustainable fuels like biodiesel are compact with existing engines, and their application doesn't require any major modifications in the existing engine designs, which made them attractive and popularly investigated by different research groups [42]. Therefore, in this review article, a clean burning and sustainable biodiesel from the 3rd generation oils is critically reviewed, highlighting its significance at different stages, such as its production process, significant properties, and applications in diesel engines in terms of performance and emissions. In addition, various additives that improve the overall properties with their addition to biodiesels are also reviewed. To further strengthen the readership of this review article, a bibliometric analysis [44] is carried out to understand the past and current research trends on this topic. For this purpose, the keywords "Algae Oil" AND "Production" are taken from the Scopus database, and their results as network graphs are highlighted in Figure 3, which clearly indicates that research on IIIG oils is emerging.

THIRD-GENERATION ALGAE OIL

Algae are living organisms primarily found in different breeds of aquatic environments and can reproduce faster than land-grown plants. These can survive in freshwater resources, ponds, rivers, lakes, rocks, marine, brackish,

requirement of various biodiesel feedstocks are presented in Table 2 and Figure 4.

Thus, it is observed from Table 2 that algae species are recorded with high oil yields. Figure 4 shows less land area required to cultivate the algae than second-generation biodiesel.

ALGAE PROCESSING METHODS

The selection of the site for algae cultivation is one of the basic requirements for algae biodiesel production. The four main processing methods of algae are cultivation, harvesting, oil extraction, and biodiesel preparation. Chowdhury et al. [46] demonstrated the importance of microalgae site selection for algae, reviewed different microalgae cultivation, harvesting, oil extraction, and biodiesel production methods, and reported that green algae possess a high growth rate. In an ideal environment, green algae can double their biomass in less than a day and possess massive lipid content (more than 50%), an excellent biodiesel production source.

ALGAE CULTIVATION

The essential factors required to absorb and convert natural sunlight into chemical energy are CO_2 and H_2O . The Algae can be cultured in two processes: natural cultivation and artificial cultivation process [26]. In the natural cultivation process, the algae are grown in open ponds,

Table 2. Oil yield produced by various biodiesel feedstocks

No.	Feedstock	Oil Yield (L/hect./year)
1	Camelina	915
2	Castor oil	1413
3	Corn	172
4	Cotton	327
5	Canola	1190
6	Coconut oil	2689
7	Jatropha oil	1892
8	Hemp oil	364
9	Mustard Seed	570
10	Maize	172
11	Palm oil	5950
12	Peanut oil	1057
13	Safflower	776
14	Sunflower	1090
15	Soybean oil	448
16	Microalgae biomass with 30 % oil (L/wt.)	58,700
17	Microalgae biomass with 70 % oil (L/wt.)	136,900
18	Algae Species	100,000

Source: [21], [45]

raceway ponds, and freshwater tanks, whereas in artificial cultivation, algae growth is initiated in closed reactors

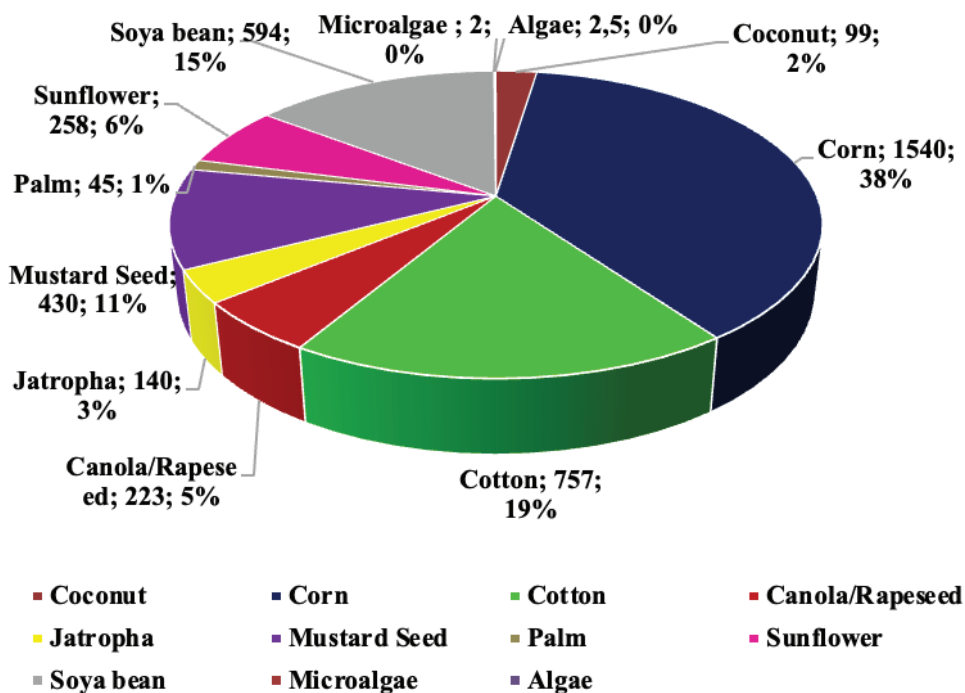


Figure 4. Land area required to produce oil (Mha).

(photobioreactors). Subsequently, the naturally-grown algae can be cultivated in freshwater tanks, directly collected from lakes, rivers, and ponds, and found as vats [45].

Kalyani et al.[35] cultivated the naturally grown green algae in the freshwater tank without chemical fertilizers; only sunlight, CO₂, and temperature are required to produce the algae. The basic parameters needed to maintain the algae growth and reproduction are temperature (20 °C to 30 °C), salinity, light intensity (33 μmol m⁻²s⁻² to 40 μmol m⁻²s⁻²), and pH value (5.5 to 7.5). Another researcher [47] collected the naturally grown green algae from open ponds and reservoirs without constructing a water tank for cultivation. Further, algae processing methods such as harvesting, oil extraction, and biodiesel production were processed using algae collected from open ponds.

HARVESTING

After algae growth, the wet algae biomass is harvested using various techniques [48], such as centrifugation, sedimentation, flocculation, and filtration. V. Ananthi et al.[48] studied the merits and demerits of several harvesting techniques and suggested that magnetic separation and chemical coprecipitation are the most commonly used methods. Thus, based on the above harvesting methods, the amount of processed dried algae biomass acquired can be further processed for algae oil extraction. J. Sen Tan et al.[49] provided information on microalgae culturing, harvesting, and extraction methods using advanced ionic liquids. Thus, using various algae harvesting methods, the algae is ready to extract the algae oil and determine the fuel properties.

OIL EXTRACTION PROCESS

The extraction process involves transferring the solid dried algae powder into a liquid phase. The oil extraction techniques were classified into chemical and mechanical methods [50]. Chemical methods include solvent extraction, Bligh and Dyer's, Ionic liquid extraction, Supercritical CO₂ (S-CO₂) techniques, and mechanical methods include oil expeller process, Osmotic shock, microwave-assisted and

ultrasonic assisted process[51],[52]. The oil yield is estimated using Equation 1.

$$\text{Oil Yield Efficiency (wt. \%)} = \frac{\text{Mass of the Algae Oil Extracted (grams)}}{\text{The total mass of the dried algae}} \times 100 \quad (1)$$

Studies from various methods have reported that supercritical CO₂, solvent extraction, and oil expeller techniques are viable methods to extract. Among these, the solvent extraction method is most efficient and recovers the oil up to 40 – 78%[45],[52],[53]. This method is economical, suitable for small scale, and has high extraction efficiency. However, to extract maximum oil, this method requires more time and a massive amount of algae powder [50].

Transesterification Process

Transesterification is the most widely adopted method to produce biodiesel at the micro and macro levels. The raw oil recovered from the crop seed and algae oil extraction process is converted into biodiesel using various preparation methods such as mixing raw oil, pyrolysis, dilution, microemulsions, and transesterification process[23],[51]. Among these methods, the transesterification method is the most appropriate method, as it reduces the high viscosity of the raw oil [53], and 98% of the methyl ester can be produced using this method [54].

The influence of different types of catalysts, such as homogeneous and heterogeneous catalysts used in the transesterification process, yielded high-purity biodiesel and glycerol, which depends on the long-chain fatty acids. Kalyani et al. [35] used homogeneous catalyst sodium hydroxide (NaOH) and methanol (CH₃OH) to initiate the transesterification reaction process for the algae biodiesel, and the saturated FFA was 73.95 wt.%. [55] used a waste chicken eggshell as a heterogeneous catalyst and obtained 1.9 wt.% FFA using the titration method. In a similar approach, Kalyani et al. [47] used chicken egg shell waste and methanol as a heterogeneous catalyst to prepare the algae biodiesel and obtained a saturated composition of FFA of 68.39 wt.% and an unsaturated composition of 29.3 wt.%.

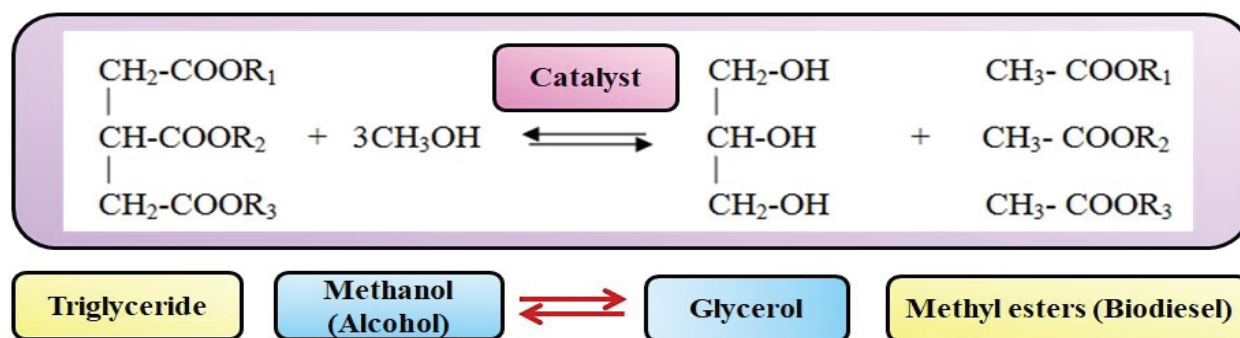


Figure 5. Transesterification reaction of triglycerides with alcohol.

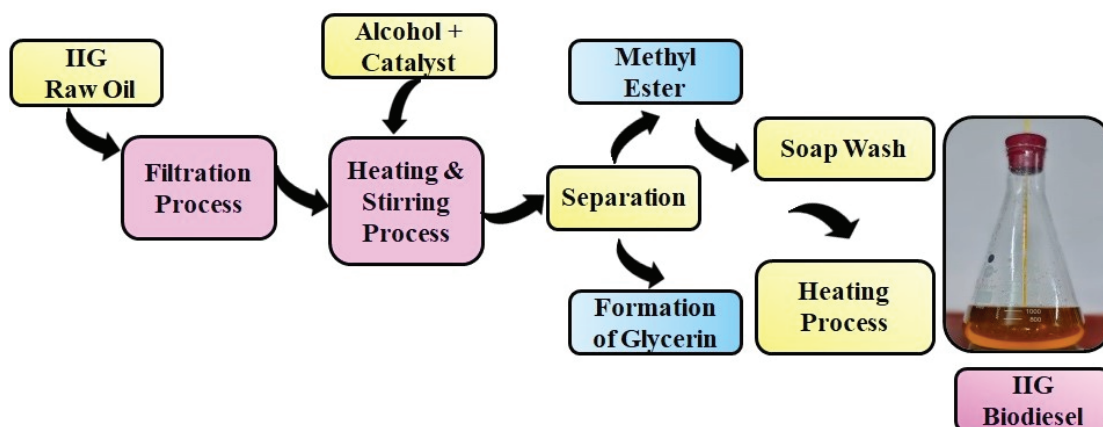


Figure 6. Preparation of second-generation biodiesel using transesterification process.

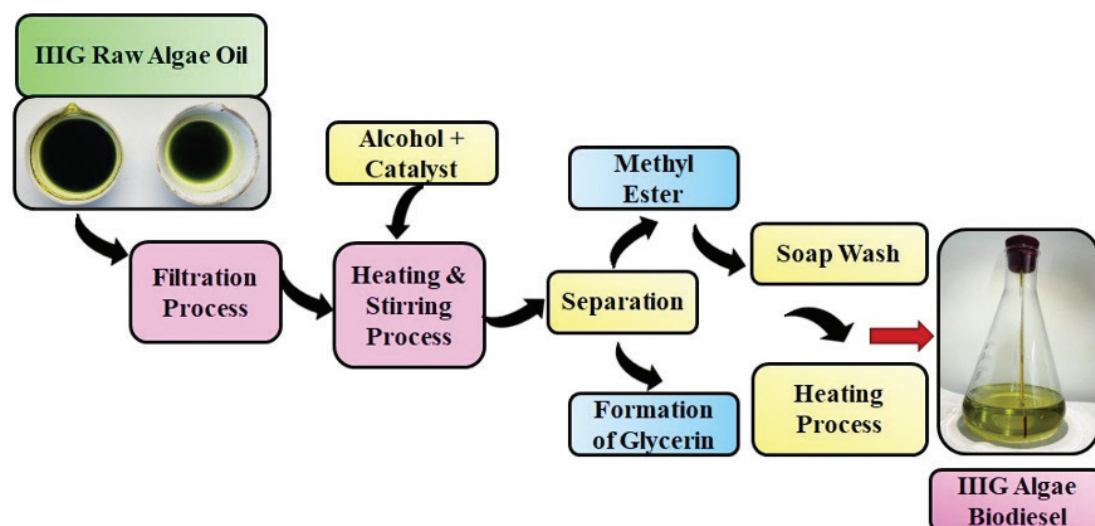


Figure 7. Preparation of third-generation biodiesel using the transesterification process.

Furthermore, If the FFA > 2.5 wt.%, the esterification process follows acidic treatment, i.e., a two-step transesterification process, and if the FFA < 2.5 wt.%, the base treatment is sufficient [42]. The influencing parameters that are used for acid and base treatments are molar ratio (MR), catalyst concentration (CC), reaction time (Time), and reaction temperature (Temp.) [41],[56]. Figure 5 shows the transesterification reaction of triglycerides with alcohol.

D.Singh et al. [41] have extensively assessed several biodiesel feedstocks, production methods, and biodiesel yield estimation. Therefore, a pictorial representation for preparing the biodiesel using the transesterification process for second and third-generation oil is shown in Figures 6 and 7 below [35],[47],[57].

The observations from the review suggested that third-generation (IIIG) algae biodiesel is better than second-generation (IIG) biodiesel because algae possess high

oil and energy content and emit less pollution. Thus, among all biodiesel production methods, transesterification is one of the most effective processes for turning raw oil into biodiesel. Further, the biodiesel was tested for its thermophysical properties and fatty acid compositions using the test apparatus. Therefore, the biodiesel is blended with diesel to meet future energy requirements and estimate the CI engine performance and emission parameters. The flow chart representing the algae processing methods and algae biodiesel as a fuel in diesel engines is depicted in Figure 8.

BIODIESEL BLENDING

Biodiesel of various feedstock obtained using a transesterification process was blended with diesel using a high-speed stirring device and whisked continuously for half an hour (30 mins.) from 10% to 90% with a 10% volumetric

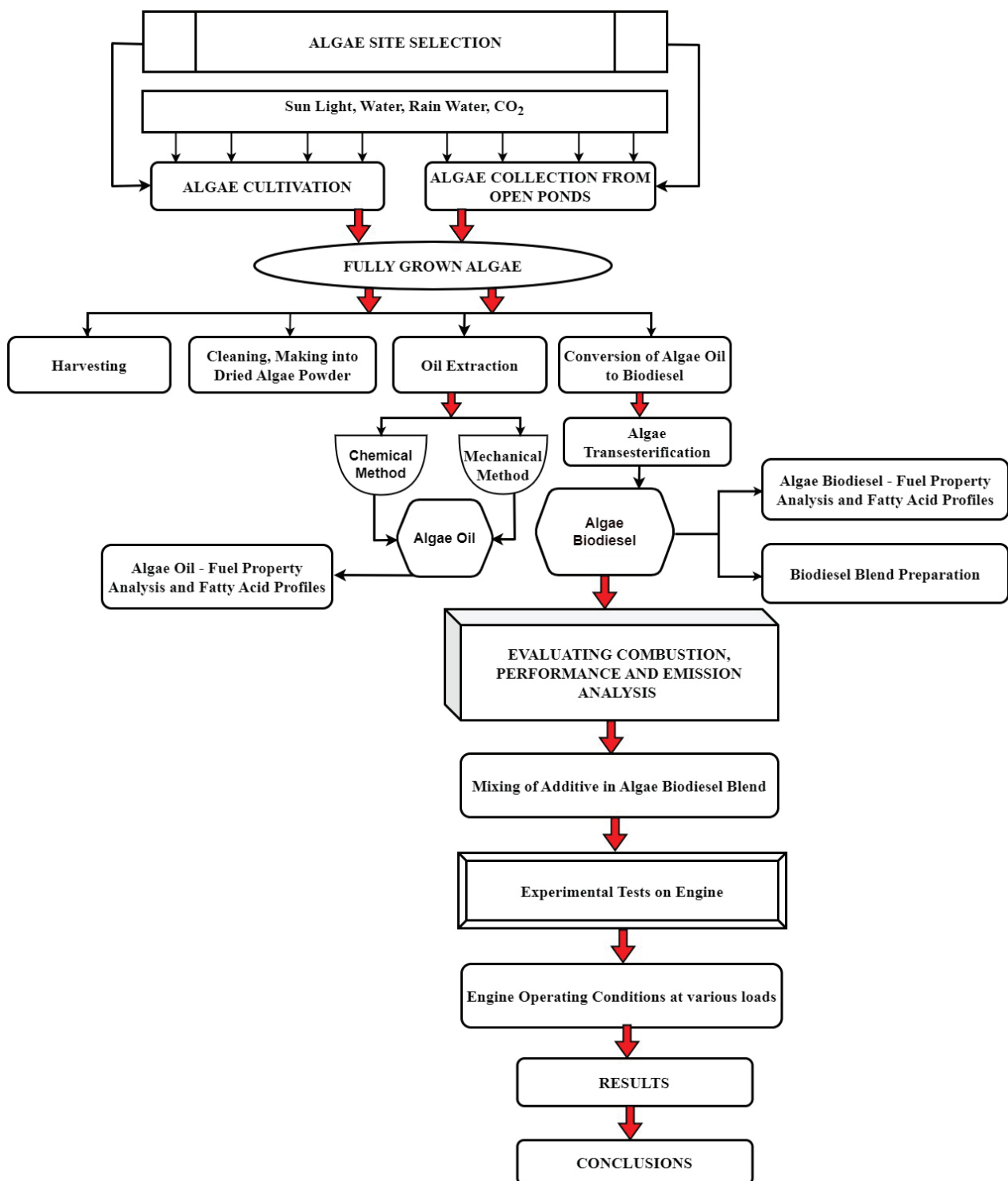


Figure 8. Flow chart representing the algae processing methods and engine experimentation.

increment of B10 to B100 [35]. The pictorial representation of the preparation of blends is shown in Figure 9. Biodiesels have significant benefits, including the technical viability of blending in any ratio and proportion with petroleum diesel fuels. Several investigators continued their research by testing both IIG and IIIG biodiesels for B10 and B20 [48], and

the test results were compared with the established international standards [58], [59], [60].

Several studies on the fuel refinement policies and experimental investigations [19], [61,62,63,64] were conducted on various biodiesel blends (i.e., B5 to B100) to determine the vital fuel properties and fatty acid compositions to

improve the engine performance characteristics. Hence, these draw a significant interest in mitigating the environmental problems to meet the future energy requirements in CI engines.

BIODIESEL FUEL PROPERTIES

One of the significant features of biodiesel is its ability to compete with diesel. These biodiesels are vital in storing, handling, transporting fuel, and commercialization. Studies revealed that fuel properties, such as flash and cloud points [65], are more excellent than diesel, representing a favorable sign to store the fuel. The literature suggests that engine performance depends upon the physicochemical fuel properties, and the vital fuel property values were compared with internationally recognized biodiesel fuel standards (ASTM). Several researchers [18], [65], [66] tested the biodiesel fuel properties of a few IIG and IIIG feedstocks and compared them with diesel are presented in Table 3.

Kinematic Viscosity (mm²/sec)

The kinematic viscosity (KV) of the working fluid plays a crucial part throughout the fuel injection process. Fuels with less viscosity were suggested to achieve improved fuel atomization during combustion and avoid blockage problems associated with fuel injectors. The kinematic viscosity was determined using a Redwood Viscometer according to ASTM D445 for the biodiesel blends. It is evident from Table 3 that the kinematic viscosity value of Spirogyra green algae biodiesel [36] is less than algae, canola, olive,

and cotton seed biodiesel. However, the KV values are higher than diesel KV values and fall within the range of ASTM D6751 standards. This change is due to the large size of triglyceride molecules in oils and the low volatility of biodiesels. Therefore, raw oils with high viscosity are not recommended to run on CI engines as they will cause incomplete combustion and could observe a high rise in engine exhaust emissions. In addition, some researchers tested using neat biodiesel on the CI engine running at a high compression ratio, and the results showed that the engine efficiency was enhanced [21]. Thus, increasing the diesel percentage can reduce the kinematic viscosity of the biodiesel.

Density (kg/m³)

The fuel density (D) is one of the key characteristics that mark its effects on the fuel performance, atomization quality, and combustion. The density was measured using a relative density meter, and ASTM D1298 standards were followed. Like kinematic viscosity, the density is higher for neat biodiesel fuels than diesel. This variation is due to the high molecular weight; however, the limit range is within the standard range. Similar to kinematic viscosity, the density of the neat biodiesel was reduced by adding a high percentage of diesel. The fuel's density influences combustion, atomization quality, and fuel performance, as the CI engines employ the fuel injection pump system to allow the fuel into the combustion chamber. The presence of FFA, H₂O content, and molar mass are the prime determinants of density in methyl or ethyl esters [47], [67].

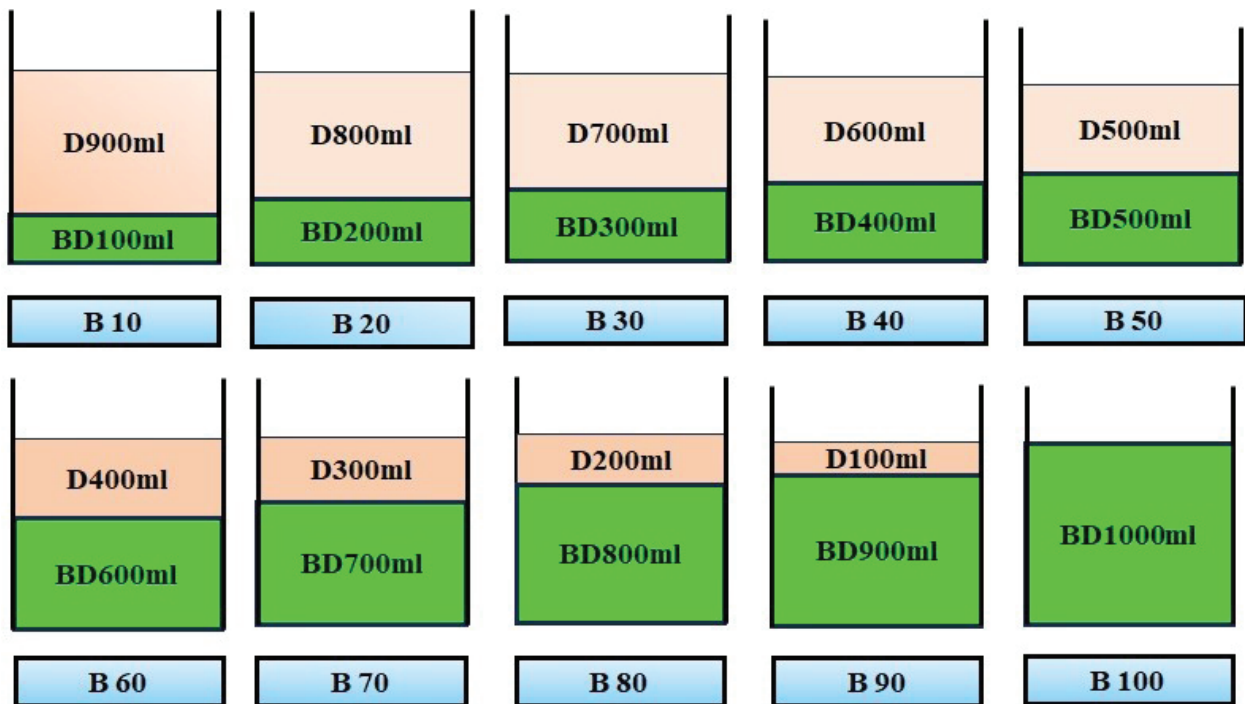


Figure 9. Biodiesel blending with diesel.

Cetane Number (CN)

Fuels with high cetane number (CN) are always preferred in diesel engines to improve combustion and engine performance. The fuel quality and combustion characteristics primarily depend on the cetane value as they can reduce the ignition delay period [66]. It is noted that the CN of biodiesel is higher than that of diesel because of the fatty acid composition of the fuel. An ignition quality tester was used to test the cetane number following ASTM D613 guidelines. The cetane number range for the biodiesel feedstocks was 48-67, depending on many significant factors, such as oil extraction and biodiesel preparation. However, the cetane number in biodiesels increases with the percentage of the blend mixed in diesel. Therefore, to run the engine efficiently and restrict the delay period during combustion, it is endorsed to maintain the cetane number in increasing order; however, in some algae biodiesel, the decrease in cetane number was observed because of the zero Sulphur and significantly less hydrocarbons [66].

Calorific Value (kJ/kg)

One of the most vital fuel characteristics is the calorific value (CV), which determines how much gasoline is used and how much power the engine produces. It provides data on the amount of heat released per fuel unit. Biodiesel from several terrestrial crops and animals has a lower heating value than diesel. Thus, biodiesels might vary due to the chemically attached oxygen (O_2) molecules. In addition, the CV of biodiesel increases when the amount of carbon molecules rises and lowers with the number of double-chain bonds [59]. The calorific value is determined using a Bomb Calorimeter of Make Widson following the ASTM D240 standard.

Flash Point ($^{\circ}C$)

Biodiesels have improved characteristics, such as less volatile and high flash point (FP) temperatures. These are well suited for safe storage and transportation, which are most important for fuel commercialization. Compared to diesel, the flash point of biodiesel is around 150% higher and guarantees a lower risk of a flammability hazard. The flash point for biodiesel was determined using a Pensky Martin closed-cup apparatus that adhered to ASTM D93 requirements [66]. Several aspects, such as the amount of carbon atoms, chemical composition, number of double bonds, and alcohol content, influence the flash point of biodiesel fuel. Most significantly, raising the level of fatty acid saturation in biodiesel fuels may raise their flash point; it is observed from Table 3. that the temperature of flash point for IIIG algae biodiesel and IIG terrestrial crop biodiesel was recorded more than diesel. This change was due to the high rise in carbon from fatty acids in a saturated state. However, this change benefits the storage and safe handling [47].

Pour Point and Cloud Point ($^{\circ}C$)

Particularly at lesser temperatures, the fuel's physico-chemical characteristics may change and can substantially

Table 3. Physicochemical fuel properties of some IIG and IIIG biodiesel feedstocks compared with diesel as per ASTM Standards

Fuel Properties	Test Apparatus [35]	Diesel [4], [68]	Spirogyra Algae Oil BD [35],[37],[63],[47]	Microalgae Oil BD [35],[63],[67]	Algae Oil BD [65]	Waste Cooking Oil (WCO) BD [2],[69]	Palm Oil (PO)BD [66][70][71]	Pongamia BD (PME) [4]	Mahua (MME) BD [4]	Jatropha (JME) BD [4]
Kinematic viscosity at 40 $^{\circ}C$ (mm^2/sec)	Redwood Viscometer	2.97 – 3.96	4.23	2 – 5.2	4.55	4.29	4.12 – 4.54	3.82	4.39	4.21
Density (kg/m^3)	Relative Density Meter	830 – 837	887	850 to 870	881	880	860 – 880	878	873	864
Cetane Number	Ignition Quality Tester	45-60	53.49	37 – 72	59	52	58-65	38559	38293	39455
Calorific Value (kJ/kg)	Bomb Calorimeter	44800 – 45700	41,243	37000 41000		38.08	38050 – 38540	55	52	58
Flash Point ($^{\circ}C$)	Pensky Marten Closed Cup	72-87	146	115	140	170	152	147	130	180
Fire Point ($^{\circ}C$)	Cleveland Apparatus	96	153			178	168			

impact the temperature change, which might be high or low. In biodiesels, the low temperature is observed because of the saturated and unsaturated fatty acid composition (FAC), which plays a major role in this transformation. Also, these biodiesels most likely react to atmospheric conditions. The pour point (PP) and cloud point (CP) are identified as low-temperature fuels and are measured using the PP and CP devices following ASTM D97 for the pour point and ASTM D2500 standards for the cloud point. The cloud point provides data near the lowest temperature at which cooling fuel helps the crystals of wax start to develop. Likewise, the fuel begins to take on gel forms for the pour point and loses its capacity to flow. Hence, the two fuel properties of the biodiesel blends are within the permissible bounds of international biodiesel fuel regulations. Thus, it is clear from various literature studies [36], [37, 47, 60, 63, 65, 67, 68] that the test outcomes of the significant fuel property values of all the diesel-biodiesel blends, mainly algae biodiesel compared to the fossil fuels falls within the acceptable ranges established standards (ASTM) and are suitable to operate in the existing CI engine.

Free Fatty Acids (FFA)

After obtaining the biodiesel, the fatty acid composition is tested using gas chromatography (GCMS) [44] to identify the saturated and unsaturated fatty acids in the biodiesel. The biodiesel fuel properties, such as density, kinematic viscosity, cetane number, and calorific value, significantly impact the FAC. Fevzi Yaşar [65] has comprehensively studied the vital fuel properties and fatty acid contents of 10 different IIG and IIIG biodiesel feedstocks. The test results suggested that cottonseed, olive, and algal

oil had the highest cetane numbers (58 for olive oil and 59 for algae biodiesel) and reported the highest saturated fatty acid composition concentration. The presence of rich oil in saturated fatty acids is more desirable because it will have better thermal efficiency and reduce NO_x emissions.

Saeed A. et al. [37] tested on green algae *S. Elongata*, which grows in freshwater. The experiments were conducted to extract algae oil and produce biodiesel, the catalyst KOH and zeolite. The highest fatty acids identified were oleic, lauric, myristic, and palmitic, and the results suggested that the freshwater green algae *S. Elongata* is a suitable algae feedstock to replace conventional fuels. Therefore, the comparison of the fatty acid composition tests of some second and third-generation biodiesel feedstocks gathered from literature studies is presented in Table 4 and Figure 10 (a – f).

The observations from Table 4 and Figure 10 (a – f), reveal that the unsaturated FAC in biodiesel fuels stimulates the increase in kinematic viscosity and lowers the calorific value. Simultaneously, FAC, with a highly saturated component, controls the increase in NO_x emissions during combustion [72] [73], proving that the third-generation algae biodiesel enhances engine performance and reduces emissions. With this motivation, a comprehensive review was conducted using several IIG and IIIG biodiesel fuels and tested on the CI engine to estimate the engine performance and emission characteristics. Further, studies related to various additives mixed in IIG and IIIG diesel – biodiesel blends were compared, and the findings were presented in Tables 5 & 6.

Table 4. Comparison of fatty acid composition for different second and third-generation biodiesels

Fatty Acid & Structure	Status	Spirogyra Algae Oil BD wt.% [35]	Algae Oil BD wt.% [66]	Palm Oil (PO) BD wt.% [66] [71]	Pongamia Oil (PME) BD wt.% [4]	Mahua Oil (MME) BD wt.% [4]	Jatropha Oil (JME) BD wt.% [4]
Behenic acid (C22:0)	Saturated	1.39	0.33				
Arachidic acid (C20:0)	Saturated	1.28	2.24	0.97	0.8	0.66	0.2
Stearic acid (C18:0)	Saturated	4.86	2.1	3.13	10.9	18.9	7.1
Palmitic acid (C16:0)	Saturated	28.63	15.64	37.48	14.1	21.53	15.2
Myristic acid (C14:0)	Saturated	15.29	-	1.97	0.1	0.08	0.1
Lauric acid (C12:0)	Saturated	21.9	-	0.79	-	-	-
Capric acid (C10:0)	Saturated	0.3	-	-	-	-	-
Caprylic acid (C8:0)	Saturated	0.3	-	0.39	-	-	-
Linoleic acid (C18:2)	Poly-unsaturated	2.5	19.56	9.17	17.3	19.55	32.7
Oleic acid (C18:1)	Mono-unsaturated	21.62	54.89	44.32	53.2	39.1	44.5
Palmioleic acid (C16:1)	Saturated	-	0.32	-	-	-	-
Linolenic acid (C18:3)	Mono-unsaturated	-	4.88	1.78	3.6	0.18	0.1
Others			0.04				0.1
Total Composition		100	100	100	100	100	100

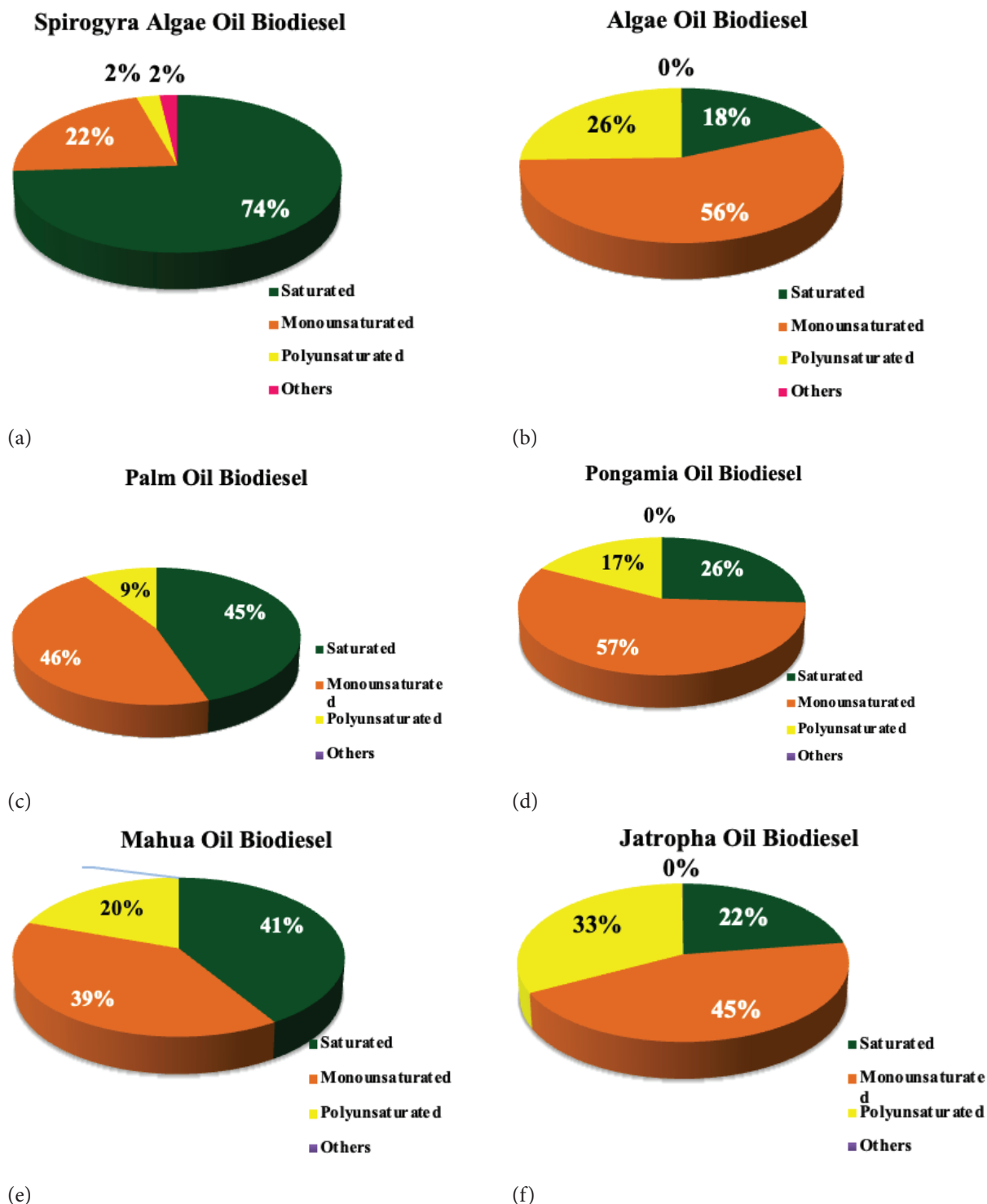


Figure 10 (a – f). Saturated and unsaturated fatty acid composition of different second and third-generation biodiesels.

EVOLUTION OF ALGAE TRANSPORTATION

Algae-derived biofuels can improve the world's transportation fuel and lower global GHG emissions. This renewable energy is expected to switch the world's energy supply by 2070 [74]. The control of emissions plays a pivotal role

when selecting the fuel/biodiesel. Due to increased global environmental pollution, stringent rules were imposed on the transportation industry, and several emission reduction measures such as exhaust gas recirculation [19], mixing of metallic, oxygenated additives [63], [75] mixing of nanoparticles [31], etc., were implemented.

Engine Emissions

The rising concerns about internal combustion engine exhaust emissions are due to their toxic nature. The main byproducts from the combustion of petro-diesel fuels are Unburnt hydrocarbons (UHC), carbon dioxide (CO₂), carbon monoxide (CO), sulfur oxide (SO_x), nitrogen oxide (NO_x), particulate matter (PM), soot and black smoke, which are dangerous to human health and also causes environment air pollution. Some of the human health issues like respiratory problems, cardiovascular diseases, cancer risks, neurological effects, irritation, and allergic reactions are witnessed in patients when they are exposed for a prolonged period to these exhaust gases [63].

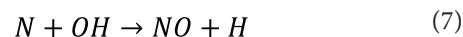
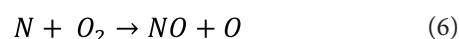
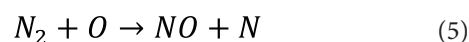
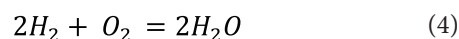
Different factors like fuel properties, air-fuel ratio, injection timing, engine speed, engine load, turbulence, and mixing play a significant role in the combustion of injected fuel and its byproducts of exhaust emissions. For instance, incomplete combustion of fuel will lead to the formation of carbon monoxide emissions, and this incomplete combustion is due to the unavailability of oxygen, poor mixing of air-fuel mixtures, and dissociation effects [76]. The chemical reaction, as shown in Equation 2, is a clear indication that a lower quantity of oxygen participation during the combustion reaction led to CO formation. It is also known that diesel engine combustion is heterogeneous combustion [77] and involves both liquid and gas phases. The hydrocarbon molecules react with available oxygen during the combustion process as a result of the formation of CO₂ and water (H₂O), which is also considered complete combustion, and the chemical reaction is shown in Equation 3 & 4.

The unburnt hydrocarbons are formed due to the incomplete oxidation process. Sometimes, the fuel does not receive enough oxygen to oxidize completely into CO₂ and H₂O during the combustion process; as a result, the unanticipated fuel remains unburnt hydrocarbons [78]. This phenomenon occurs particularly in fuel-rich areas where less air is available. Another significant contributing factor to harmful exhaust emissions is the combustion temperatures. High combustion temperatures result in high thermal NO_x formation, one of the most dangerous exhaust emissions.

The NO_x formation during the combustion process is governed by the *Zeldovich* mechanism [63], which describes the reaction of nitrogen with oxygen at elevated temperatures. At high temperatures (above 1200°C) the nitrogen molecule (N₂) in the air reacts with the available oxygen (O₂), and the chemical reactions are shown in Equations 5 to 7. Different studies [79] show that biodiesel combustion increases NO_x emissions, which may be true due to the inherent property of available oxygen in biodiesel being more than any other fuel, which helps increase combustion temperatures during its combustion. However, this case is applicable to neat biodiesel combustions.

To control the NO_x formation from biodiesel combustion, different techniques like low-temperature combustion, such as injecting the alcohols to maintain controlled

combustion temperatures and also with the implementation of different additives like oxygenated additives, nanoparticles regulate this NO_x formation to a greater extent [31],[64],[76],[81]. The Table 5 reveals the trends of exhaust emissions from biodiesels investigated by different research groups.



From Table 5, the above reference studies observed a positive incline toward the increase in engine performance and reduction in emissions. Interestingly, a drastic improvement in reducing emissions was observed using third-generation algae biodiesels (IIIG). However, an upsurge in NO_x emissions was reported as the signifying issue in most of the experimental tests [47,85,88,89]. Hence, to mitigate this raising concern, mixing additives in biodiesel feedstock is considered an alternate option to mitigate NO_x emissions.

INTRODUCTION TO ADDITIVES

Mixing additives in biodiesels is crucial in increasing the fuel's durability and decreasing the hazardous pollutants produced during fuel combustion. Also, the option to substantiate these issues was additive to avoid limitations of biofuel properties like auto-ignition, flash point, temperature, and cetane number. Additives primarily depend upon the selection, concentration ratio, fuel solubility, and physicochemical properties such as viscosity, density, toxicity, ignition quality, etc.

Various types of additives, such as metallic-based additives, oxygenated additives [25], metal-based additives, cold flow improver additives, cetane number improver additives, water, antioxidants, lubricity improvers, polymeric-based additives, and nanoparticles additives [24,26], are employed to blend with fuels used in diesel engines to achieve total fuel combustion, which further improves the performance of CI engines during combustion and reduce the engine emissions. Therefore, mixing additives in diesel - biodiesel blends result in improvements like complete combustion and temperature reduction, enhancing engine performance and reducing engine emissions [75], [89]. Many researchers have investigated various additives mixed in some IIG and IIIG biodiesel blends and tested them in

Table 5. Review on engine performance and emission characteristics of different second and third generation biodiesel feedstocks (continued)

Ref.	Biodiesel & BlendsEngine Test Condition	Performance Characteristics			Emission Characteristics			
		Performance and emission characteristics compared with diesel						
		BTE	BSFC	NOx	CO	CO2	UHC	Smoke, PM, PN
Kolakoti A.[73]	Palm oil biodiesel (POBD), Waste cooking biodiesel (WCBD), and Animal fat indirect injection biodiesel (AFBD) Diesel	↑ An increase in BTE was achieved for WCBD of (32.22%) followed by AFBF (31.99%) and POBD (30.93%) at 75% load.	↑ Increase in BSFC by 9.72% for POBD, 5.48% for AFBF & 4.90% for WCBD compared to diesel fuel.	↑ Increase in NOx by 2.52% for POBD, 17.16% for WCBD, and 8.09% for AFBF compared to diesel fuel at 100% load. And observed even at 75% and 50%	↑ Increase in CO ₂ by 11.23% for WCBD, 13.28% for AFBF, and decrease in CO ₂ for POBD	↓ Decrease in CO At 100% load 50% reduction is observed for POBD and 10.14% for WCBD and a 25% reduction in AFBF recorded compared to diesel fuel	↓ Decrease in UHC by 40.57% for POBD, 10.14% for WCBD and 37.68% for AFBF at 100% load compared with diesel fuel	↓ Decrease in smoke at 100% load by 38.18% for POBD, 63.63% for WCBD and 58.18% for AFBF
CA Rinaldini et al.,[81]	Chlorella Blends: B20	↓ Slight reduction (5-7%) of torque at high speed, full load	-----	↑ Increase up to 20% at high load, low speed (N<1500 rpm)	-----	↑ Increase up to 10% at full load, mid-low speed.	↓ Decrease in soot at high load (about 30%)	-----
Chand SM et al., [82]	Eureka Sativa (Taramira) seeds oil Blends: B10, B15, B20, and B25.	↓ Decrease in BTE at 100% load	↓ Decrease in BSFC by 0.29 kg/kw at B20 blend than all blends	↓ Decrease in NOx emission levels 1282 for B20, which is 5.78% higher than diesel.	↓ Decrease in CO for B20	↑ Increase in CO2 for B20.	↑ Increase in UHC for B20 blend	-----
	N= 1500 rpm and CR: 17.5.	↓ Decrease in BTE by 26.87% at B25 than B20.		Compared to diesel, B20 emits a 5.75% rise.	Compared to diesel, B20 emits 8.33% less	Compared to diesel, B20 emits 0.86% less	Compared to diesel, B20 emits 5.55% less.	
Rangasamy K et al., [83]	Chlorella emersonni methyl ester (CEME) Blends: B10, B20, B30 B100 and D100	Compared to diesel, B30 exhibited better results than other blends.	Compared to diesel, B30 exhibited better results than other blends.	Compared to diesel, B30 exhibited better results than other blends.	Compared to diesel, B30 exhibited better results than other blends.	Compared to diesel, B30 exhibited better results than other blends.	Compared to diesel, B30 exhibited better results than other blends.	Compared to diesel, B30 exhibited better results than other blends.
	Stationary single-cylinder diesel engine.	↑ Increase in BTE	↓ Decrease in BSFC	↑ Increase in NOx for B100, B30, B20	↓ Decrease in CO by 50%	-----	↓ Decrease in UHC by 24%	↓ Decrease in smoke by 56%

Table 5. Review on engine performance and emission characteristics of different second and third generation biodiesel feedstocks (continued)

Ref.	Biodiesel & BlendsEngine Test Condition	Performance Characteristics		Emission Characteristics					
		Performance and emission characteristics compared with diesel							
		BTE	BSFC	NOx	CO	CO2	UHC	Smoke, PM, PN	
Bradley D Wahlen et al., [84]	Chaetoceros gracilis (microalgae strain), a yeast (Cryptococcus curvatus), and a bacteria (Rhodococcus opacus) Blends: B100	Kubota Z482-ES04 naturally aspirated, 2 cylinders, indirect injection Power: 7.9 kW	Compared with soybean oil						
		↓ Decrease in power output by about 93% for microalgae biodiesel, whereas 96% for soybean oil	↑ Increase in BSFC for microalgae	↓ Decrease in NOx	↓ Decrease in CO	↓ Decrease in CO ₂	↓ Decrease in HC	↓ Decrease in power output by about 93% for microalgae biodiesel, whereas 96% for soybean oil	
SSS Satputaley et al., [85]	Microalgae Chlorella vulgaris Blends: Algae oil Algae Biodiesel (B 100) Diesel	Kirloskar TV1 model single cylinder, DI, water-cooled, CI engine Operated at 17.5 CR, 1500 fixed speed Power at 5.2 kW Variable load	↓ Decrease in BTE of 5.2% and 6.4% @ 5.15 kW brake power (BP) for Algae oil and Algae Biodiesel (B 100)	↑ Increase in BSFC for Algae oil and Algae Biodiesel (B 100) compared with diesel at all loading conditions.	↓ Decrease in NOx by 19 ppm at 5.15 kW BP for Algae oil.	↓ Decrease in both Algae oil and Algae Biodiesel (B 100)	-----	↓ Decrease in both Algae oil and Algae Biodiesel (B 100)	
Upendra Rajak et al., [86]	Spirulina microalgae biodiesel Blends: AB100	DI, CI engine Full load	↓ Decrease in BTE by 2.73 %	↑ Increase in SFC by 6.4%	↓ Decrease in NOx by 0.5%	↓ Decrease in CO ₂ by 6.1%	-----	↓ Decrease in PM by 60%	
G Ospina et al., [87]	Jojoba, Algae, and chocolate waste methyl esters	VCR, IDI engine.	-----	-----	↓ A decrease in pollution levels was identified using Algae methyl ester. &				
					A drastic ↑ increase in emissions was recorded in jojoba methyl ester. (Tested in two phases: First Set : N, CR, IT, P = constant Second Set varied IT (20° to 45°) bTDC, keeping N, CR, Loads = constant).				

↓ A decrease in pollution levels was identified using Algae methyl ester.

&

A drastic ↑ increase in emissions was recorded in jojoba methyl ester.

(Tested in two phases: **First Set:** N, CR, IT, P = constant

Second Set varied IT (20° to 45°) bTDC, keeping N, CR, Loads = constant).

Table 6. Review on engine performance and emission characteristics of mixing additives in different second and third generation biodiesel feedstocks (continued)

Ref.	Biodiesel + Additive & Mixing of Blends	Engine Test Conditions	Performance Characteristics					Emission Characteristics				
			Additive mixed in biodiesel and compared with diesel					Additive mixed in biodiesel and compared with diesel				
			BTE	BSFC	NOx	CO	CO ₂	UHC	Smoke, PM, PN			
B Aisosa Oni et al., [90]	Algae <i>Botryococcus</i> Braunii + Acetylene Induced at a mass flow rate of 100, 150, 200, and 300 g/hr.	4-stroke (Kirkoskar AV1), dual fuel CI engine with enhanced IT	↑ Increase in BTE by 3, 4, 3.6 and 5%	-----	↑ Increase in NOx	↓ Decrease in CO	↓ Decrease in CO ₂	↓ Decrease in UHC	-----			
Gökhan Tüccar et al., [91]	Microalgae + Butanol Blends: Diesel D80B20 D70B20But10 D60B20But20	Mitsubishi Canter 4D34-2A, direct injection, 4-stroke, 4-cylinder diesel engine. Power 89 kW 1200 - 2800 rpm at full-load	With the addition of butanol for all the blends									
			↓ Decrease in Power output with the addition of butanol	↑ Increase in BSFC about 10.9%, 17.1% and 29.7% for D80B20 D70B20But10 and D60B20But20 compared with diesel fuel	↓ Decrease in NOx with the addition of butanol for all the blends	↓ Decrease in CO with the addition of butanol for all the blends	-----	All test fuels are less than diesel fuel D80B20 reduced by 3.1% D70B20But10 by 27.3% and D60B20But20 by 49.5%	↓ Decrease in smoke with the addition of butanol for all the blends			
Ali Zare et al., [92]	Waste cooking biodiesel + Triacetin Blends: D100, B100, T100, T4B96, T8B92 T10B90 D60B35T5	6-cylinder turbocharged diesel engine Power 162 kW Speed 2000 rpm CR17.3:1 Friction Power	↑ Increase in BTE for BD100 compared to diesel.	↑ Increase in BSFC, BTE	↑ Increase in NOx by 31%.	↑ Increase in CO up to 82% at higher loads	↓ Decrease in CO ₂ up to 2.5 %	↓ Decrease in HC up to 64%	↓ Decrease in PM and PN both up to 90%			
John Kennedy Mwangi et al., [93]	Chlorella vulgaris and Chlorella Sorokiniana + Butanol & Water Addition Blends: B2, B2But20 and B2But20W0.5 (water addition)	Mitsubishi 4M40-2AT1, 4-cylinder, direct injection CR 20.1:1 Power 109 kW at 3700 rpm	↑ Increase in BTE for B2-But20-W0.5 compared to diesel.	↑ Increase in BSFC for B2-But20-W0.5 compared to diesel	↓ Decrease in NOx by 25.0% and 28.2% for B2But20 and B2But20W0.5	↑ Increase in CO for B2-But20-W0.5 compared to diesel.	↓ Decrease in CO ₂	↑ Increase in HC by 18.9% and 69.8% with water addition and ↓ Decrease by 50.2% for B2 blend compared to diesel	↓ Decrease in PM by 22.0%, 57.2%, and 59.5% - for B2, B2-But20 and B2-But20-W0.5 compared to diesel			

Table 6. Review on engine performance and emission characteristics of mixing additives in different second and third generation biodiesel feedstocks (continued)

Ref.	Biodiesel + Additive & Mixing of Blends	Engine Test Conditions	Performance Characteristics						Emission Characteristics			
			Additive mixed in biodiesel and compared with diesel						Additive mixed in biodiesel and compared with diesel			
			BTE	BSFC	NOx	CO	CO ₂	UHC	Smoke, PM, PN			
Talamala V et al., [94]	Rice bran methyl ester (RBME) + Isopropanol as an additive. Blends: 2/98%, 3/97%, 4/96% and 5/95%, by volume	IDI engine test rig, Bajaj RE100 diesel engine with an engine displacement of 447.3 cc operated at varying loads	↑ Increase in BTE by 4.3% at 2% additive at maximum engine-operated load	↓ Decrease in BSFC by 2.63% at 2% additive for 2.7kW load	↓ Decrease in NOx by 36.5% reductions were observed at 2% additive at maximum engine-operated load	↓ Decrease in CO by 14% reductions were observed at 2% additive at maximum engine-operated load	↑ Increase in CO ₂ with the increase in additive in percentage.	↓ Decrease in HC for 2% additive at maximum engine-operated load	↓ Decrease in smoke by 27.5% reductions were observed at 2% additive at maximum engine-operated load			
Ilipilla M et al., [95]	TiO ₂ nano particles + dispersant (QPAN80) Blends: BD20+ TiO ₂ at 50, 75, 100 mg/L+ dispersant (QPAN80) 1:1 ratio.	Diesel engine Injection pressures of 200, 225, and 250 bar	↑ Increase in BTE	↑ Increase in BSFC	↓ Decrease in NOx by 846 ppm	↓ Decrease in CO by 0.02%	-----	↓ Decrease in HC by 33 ppm	↓ Decrease in PM by 37.58%			
			The experimental reports revealed that BD20+ TiO ₂ at 75 mg/L+ dispersant (QPAN80) @ 250 bar pressure exhibited superior stability compared to the other combinations.									

diesel engines to analyze the engine performance and emission characteristics.

In this approach, [28] tested the engine using waste oil biodiesel mixed with various volume proportions of 1-pentanol additive. The ternary blends prepared for testing were DB, D75B20Pen5, D70B20Pen10, and D60B20Pen20, and conducted experiments at 0.1, 0.5, 3 kW load conditions running at 2000 rpm. Therefore, the results suggested that the increase in additive ratio resulted in the rise of brake-specific fuel consumption (BSFC), exhaust gas temperature (EGT), carbon monoxide (CO), unburned hydrocarbons (UHC), and nitrogen oxides (NOx) emissions, where a slight reduction in brake thermal efficiency (BTE) and combustion efficiency was observed. Thus, a minimum quantity of additive mixing in biodiesel is preferable.

In a similar case [30], the sunflower biodiesel was mixed with pentanol to estimate the engine characteristics. The blends prepared for testing are B20, B20P, B20P10, B20P15, and B20P20, and they are operated on four loads at a 3000-rpm fixed speed. The results showed a decrease in BTE and an increase in BSFC of 13.90% compared to diesel. Also, the increase in pentanol addition observed a reduction in NOx and an increase in CO₂ emissions, and the heat release rate and ignition delay were lowered by 15%. Therefore, the study summarized that if the alcohol percentage (pentanol) increases, there can be an improvement in engine behavior.

Another researcher [80] mixed Al₂O₃ nano additive 50ppm and 100ppm in waste cooking oil and neem biodiesel with diesel and tested for the blends B10 and B20. The experimental investigation was carried out on a single-cylinder, four-stroke diesel engine at a fixed speed of 1500rpm. The observed results confirmed that 50ppm in the B10 blend improves the combustion with high exergetic efficiency and low exergy destruction. Also, at 100% load, the blend B20 with 50 ppm of useful work increases by 33.1% more than other blends. Also, the study quoted that at 100% load, the B10+ 50 ppm Al₂O₃ nano additive-observed high exergetic efficiency of 38.69%, enhanced engine combustion performance, and engine emissions such as UHC, CO, and NOx reduced after the addition of nano additives. In spite of all the changes with nano additives, a similar approach was observed with the oxygenated additive. Some researchers investigated oxygenated additives in IIG and IIIG biodiesel, which is continued in the discussion below.

An experimental investigation was conducted using the oxygenated additive Triacetin (T) mixed in coconut oil methyl ester (COME) [75] for the determination of the engine characteristics. Diesel, COME, and COME mixed with Triacetin in the vol.% of 5 %, 10%, 15 %, 20%, and 25% were tested on the DI engine without any change. The output results reported that exhaust emissions lowered positively, near the blend of 10% triacetin mixed with 90% COME. Correspondingly, better engine performance results of BSFC and BTE were achieved with the oxygenated additive mixed in the biodiesel blend. Therefore, the

study concluded that adding oxygenated additives to biodiesel resulted in a favorable agreement to replace with conventional fuels.

In a similar approach, Kalyani et al. [63] mixed oxygenated additive triacetin in an algae biodiesel blend (ABD40) to estimate the engine combustion, performance, and emission characteristics. The oxygenated additive Triacetin was mixed in ABD40 at various percentages of 2%, 4%, 6%, and 8% by volume and conducted experimental tests on a cylinder, water-cooled, four-stroke diesel engine operated at constant speed and varying loads. The observations confirmed that at full operating load (100%), it was revealed that at 4% Triacetin in ABD40 achieved high combustion pressure compared to diesel and other blends. and a high BTE of 30.39%. Also, at 100% load, lower engine exhaust emissions of CO (25.51 %), NO_x (12.81 %), UHC (70.53 %), and smoke (14.85 %) were recorded for the 4 % triacetin in ABD40, recorded with low exhaust emissions compared to diesel. Thus, the investigation proved that the addition of oxygenated additive Triacetin in algae biodiesel enhanced the engine performance and emissions. A detailed literature review conducted by enormous researchers on the IIG and IIIG biodiesel mixed with additives is presented in Table 6 below.

CONCLUSION

The studies contributed by the enormous number of researchers on various second and third-generation biodiesel feedstocks, fuel properties, fatty acid composition, and mixing of additives in diesel-biodiesel of various blends suggested that third-generation green microalgae biodiesel is one of the best sources of green fuel to enhance engine performance and mitigate the emissions in compression ignition engine.

The findings revealed that:

- Third-generation green microalgae biodiesel is an emerging renewable energy source, as these species can be cultivated in open and closed ponds.
- Besides natural and artificial cultivation, the green algae can be collected from rivers, lakes, and reservoirs as these species double every 3-4 hours.
- The microalgae species have higher oil content and can extract algae in large quantities.
- The solvent oil extraction process is the best-suited method to extract algae oil compared to other extraction techniques. Though the extraction process of the algae cellular components consumes more time, it can recover 40 – 50% of the algae oil.
- The cultivation of algae requires less land space compared to second-generation biodiesel. Though second-generation biodiesels play a significant role in improving efficiency and reducing emissions, the prevailing limiting factors, such as the availability of land to cultivate the non-edible oil crops and high fatty acid profiles, led to opt for third-generation algae biodiesel

as one of the better options for replacing conventional fuels in compression ignition engines.

- Fatty acid composition in green algae biodiesel was reported with high saturated fatty acid composition percentage of 74%wt.% followed by second-generation palm oil biodiesel with 46%wt.%. Thus, this observation indicated that third-generation biodiesel plays a significant role in controlling the generation of NO_x emissions during combustion.
- The engine experimentations using second- and third-generation biodiesel stated that the third-generation algae biodiesel operated in diesel engines and observed enhancement in engine combustion, performance, and efficiency. These improvements reduced engine emissions such as carbon monoxide, carbon dioxide, unburnt hydrocarbons, smoke, and particulate matter, and a slight increase in NO_x emissions was observed.
- Mixing of additives in second and third-generation biodiesel improved the vital fuel properties, regulated the combustion issues formed inside the engine cylinder, and controlled the escalation in nitrogen oxide emissions.
- Reduction in maintenance cost is the foremost important aspect of microalgae biodiesel, making them commercially viable.
- Finally, the review studies elucidated that third-generation algae biodiesel is one of the emerging sources of fuel to run and test on existing diesel engines. Thus, algae biodiesel is considered one of the best alternatives to replace fossil fuels, and it holds great potential as a feedstock for future economically sustainable production.

NOMENCLATURE

IG	First-Generation Biodiesel
IIG	Second-Generation Biodiesel
IIIG	Third-Generation Biodiesel
IVG	Fourth-Generation Biodiesel
BD	Biodiesel
BSFC	Brake Specific Fuel Consumption
BMEP	Brake Mean Effective Pressure
CI	Compression Ignition
CR	Compression ratio
DI	Direct Injection
FAC	Fatty Acid Composition
GHG	Green House Gas
IDI	Indirect Direct Injection
IT	Injection Timing
IMEP	Indicated Mean Effective Pressure
VCR	Variable Compression Ignition

AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

STATEMENT ON THE USE OF ARTIFICIAL INTELLIGENCE

Artificial intelligence was not used in the preparation of the article.

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