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Review

A Review of the Emulsification Method for Alternative Fuels Used in Diesel Engines

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Abstract: Diesel engines are one of the most popular reciprocating engines on the market today owing to their great thermal efficiency and dependability in energy conversion. Growing concerns about the depletion of fossil resources, fluctuating prices in the market, and environmental issues have prompted the search for renewable fuels with higher efficiencies compared with conventional fuels. Fuel derived from vegetable oils and animal fats has comparable characteristics to diesel fuel, but is renewable, despite being manufactured from various feedstocks. Nevertheless, the direct use of these fuels is strictly prohibited because it will result in many issues in the engine, affecting engine performance and durability, as well as emissions. To make biofuels as efficient as fossil fuels, it is essential to alter their characteristics. The use of emulsification techniques to obtain emulsified biofuels is one of the many ways to modify the fuel characteristics. Emulsification techniques allow for a decrease in viscosity and an increase in atomisation during injection. To date, emulsification techniques have been studied less thoroughly for use with vegetable oils and animal fats. This article will discuss the preparation and characterisation of emulsified biofuels made from vegetable oils and animal fats. This current paper reviewed research studies carried out on different emulsification techniques for biofuels used in diesel engines.

Keywords: emulsified biofuel; neat biofuel; surfactant; alternative fuels; microemulsion

1. Introduction

Diesel engines are one of the most popular reciprocating engines and are used for diverse purposes such as in transportation, power production, agriculture, military, offshore drilling, and generator sets, among other fields. These power producers are the foundations of a country's economy, particularly in developing countries. Certain advantages of employing diesel engines, such as their high thermal efficiency, reliability, robustness, and lower maintenance, are the reason for their diversity of applications and their widespread use compared with other engines [1]. However, with the increasing use of diesel engines, diesel stockpiles are rapidly depleting and increasing pollution levels. Among them are nitrogen oxide (NOx), carbon dioxide (CO_2), carbon monoxide (CO), sulphur oxide (SOx), hydrocarbons (HC), soot, and particulate matter (PM) [2]. The formation of NOx via several mechanisms involves both premixed and diffusion burning, contributing to the high combustion temperature. Therefore, researchers worldwide are investigating potential methods to lower the peak combustion temperature without lowering the engine performance.

Conversely, the adverse effects of global warming on the environment have accelerated the search for sustainable alternatives that provide increased energy security, decreased emissions of greenhouse gases and PM, rural progress, upgraded vehicular performance, and decreased petroleum requirements [3]. Furthermore, the demand for fossil fuels is increasing on a daily basis all over the world. Energy consumption is projected to rise by almost 55% by 2030, as reported by the International Energy Agency. Worldwide, energy consumption continues to rise in lockstep with global population growth. Ashraful et al. implied that the world's energy consumption and demand are following a rising trend [4]. For example, in the early 1980s, fuel consumption was about 6700 million metric tonnes of oil equivalent (Mt), and in 2012, fuel consumption had risen by more than two-fold. As a consequence, one of the twenty-first century's new era challenges is to find solutions to decrease emissions and lower the reliance on fossil resources.

Animal fats and vegetable oils are regarded as possible substitute fuels as their physicochemical characteristics are equivalent to those of standard petro-diesel, as Vafakish [5] and Chozhavendhan [6] demonstrated. These alternative fuels can be obtained from a variety of sources, such as non-edible feedstock. Feedstock oils resultant from non-edible oils are natural liquids and are unsuitable for regular food consumption because of specific poisonous components in the oils. According to Melo et al., biofuel has several advantages, namely its renewability, availability, lower sulphur content, biodegradability, and low aromatic content [7]. Yet, the drawbacks of biofuels include their high viscosity, low grade, low volatility, and higher carbon residue percentage. In addition, non-edible cultivation tends to use land that is mainly unproductive and in impoverished areas.

The direct use of biofuels in diesel engines cannot be recommended as several engine complications may occur in the long run, such as carbon deposited built-up, piston ring sticking, injector chocking, less efficient combustion performance, lubricating oil thickening, poor atomisation, change in ignition delay, and reduced engine lifespan. Maher et al. described that the direct use of biofuel in the diesel engine without modification would result in the deposition of biofuel in the combustion chamber as a result of improper vaporisation and inadequate combustion [8]. The biofuel's unfavourable burning behaviour may be attributed to its characteristics, which include a high viscosity and lower volatility. In addition, the properties of biofuel are associated with a higher molecular mass and large triglyceride molecules in the chemical composition.

In the last decades, researchers, scientists, and vehicle manufactures have focused on the attention to advanced combustion modes such as premixed charge compression ignition (PCCI), homogeneous charge compression ignition (HCCI), and reactivity controlled compression ignition (RCCI) [9]. The results indicate a greater thermal efficiency, improved flame propagation, and low hazardous emissions, for instance NOx, soot, and PM. Although all the advance combustion modes are improving and there is high adaptability to the different kind of fuels applied in this type of engine, the controlling and timing phase are the two major factors that will affect the sudden high pressure rise, knocking, and noise, limited operation range, high CO, and HC emissions [10]. There is no direct control mechanism for this advanced combustion technology, such as auto-ignition fuel timing and eventually combustion effects. Whereas the auto-ignition fuel timing strongly depends on temperature and pressure during the intake stroke and physicochemical properties of fuel.

To create an economically feasible and environmentally acceptable engine fuel from sustainable feedstocks such as animal fats and vegetable oils, biofuels' physicochemical characteristics, such as surface tension, viscosity, moisture content, odorant, and free fatty acids, must be changed. For the above reasons, several methods have been introduced for instant preheating, such as blending biofuel with petro-diesel fuel, double blending dual biofuel (with dissimilar viscosity and cetane number), dual fuel operation, pyrolysis/cracking, and emulsification techniques. Blending and dual fuel operation with petro-diesel are among the popular methods previously mentioned, but they only partially solve the problems associated with physicochemical attributes and the negative impact they have on the engine [11]. Moreover, additional modifications to the engine may also be required for dual fuel systems [12]. Studies have reported higher emissions HC and CO with dual fuel operation with alcohol induction [12] and a lower performance [13].

The preheating technique has been assessed by several researchers [14]. The technique is more practical and easier to subject to higher viscosity fuels fed to the pipeline system and the combustion chamber without any modifications to the engine. Additionally, the study found that preheated animal fats and vegetable oils increased the thermal efficiency of the brakes and reduced the particle emissions in diesel engines [15]. Nonetheless, the preheating method is not a preferable practice due to the involvement of a complicated external auxiliary heating system, sensitivity fuel tank, and safety hazard design tank. The additional cost of installation and maintenance are required in this system. For this reason, it is recommended only for stationary engines.

Another technique that can be used in biofuel is pyrolysis of triglycerides to obtain physicochemical properties comparable to petro-diesel fuel [16]. Nevertheless, the thermal breakdown of triglycerides has the tendency to be complicated due to numerous structures and a multitude of potential triglyceride responses. Moreover, thermal cracking and pyrolysis equipment are considered costly for moderate throughputs [17]. They are chemically identical to gasoline and diesel fuel produced from petroleum, but the oxygen is removed during thermal processing, negating any environmental advantages associated with the use of an oxygenated fuel [18]. On the other hand, transesterification is a popular technique for producing environmentally friendly diesel fuel (biodiesel) from animal and vegetable oils. Transesterification is a complicated and time-consuming process [19], as it requires many different stages depending on the feedstock's quality. In addition, compared to petrol-diesel fuel, producing biodiesel has been a major impediment to its commercialisation due to its cost. The cost of producing biodiesel is influenced by the price of the catalyst (which is expensive) as well as specialised equipment such as separators, pumps, reactors, mixers, pipelines, and heaters. Similar limitations were observed and reported by Atmanli [20] and Agarwal [21]. Furthermore, certain products such as glycerol are produced during the transesterification process, which are unfit for use as an engine fuel [22,23].

The preparation of emulsified biofuel could be a probable resolution to inefficiency issues related to the high surface tension, the viscidness of animal fats, and vegetable oils. The physicochemical properties of emulsified fuel also significantly impact engine performance and exhaust emissions [24]. Numerous studies [25–27] have highlighted a substantial reduction in emissions (e.g., NOx) using biofuels in diesel engines rather than petro-diesel fuels. In addition, with the micro explosion phenomenon, as shown in Figure 1, it is also possible to compensate for the decrease in combustion efficiency in certain circumstances.

The emulsification technique can be preferred as it is an inexpensive method as it does not require modifications to the original engine design or involve any specialised and sophisticated equipment. Similarly, the preparation of an emulsion does not necessitate a complex chemical reaction or produce by-products, unlike the transesterification process. The emulsification process usually involves low quantities or volumes of surfactant, co-surfactant, and water. Previous studies have shown that using emulsified petro-diesel fuel can reduce massive toxic emissions, such as PM, smoke, and NOx, while most studies have also reported an improvement in engine combustion [28–31]. So far, only a few researchers have reported on emulsification techniques using vegetable oils or animal fats. The current paper aims to compile the information from the previously reported experiments to improve on knowledge regarding the different techniques and methods related to their formulation and application directly to the diesel engine.

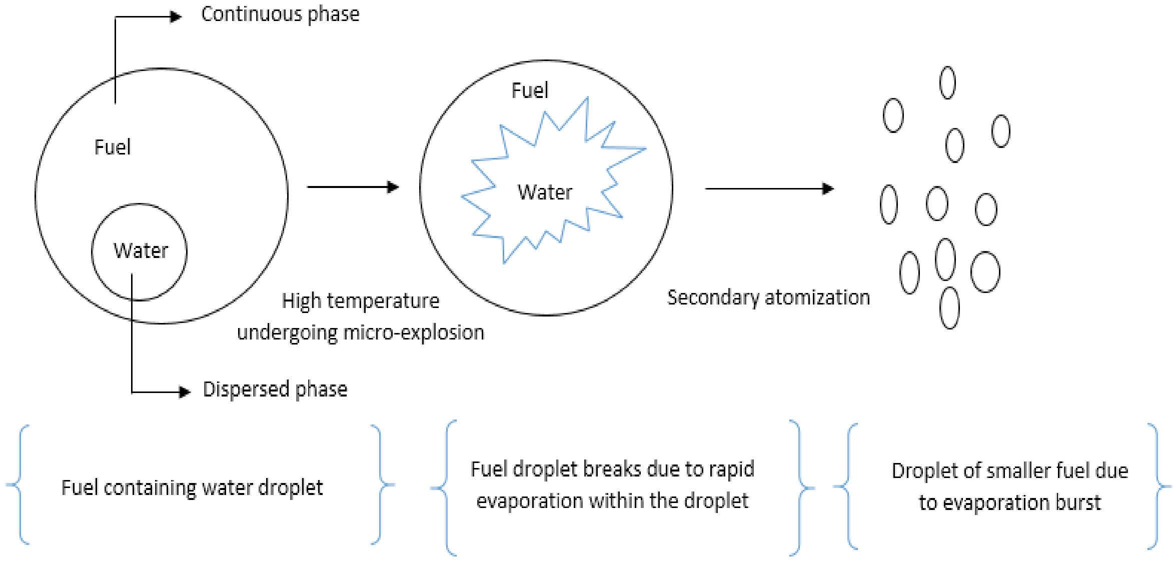


Figure 1. Fundamental concept of micro-explosion.

2. Biofuel Future and Present

The unexpected global pandemic of COVID-19 that plagued the world in 2020 has considerably impacted the transportation and automotive industries. The transportation system has played an important role in stimulating the economy worldwide. Nowadays, the main critical issue for the global transportation sector is energy supply, which is met by fossil fuels, namely gasoline and diesel fuel. Overall, the growth of the motorization industry has resulted in an annual increase of 1.1% of the worldwide energy consumption [32]. According to previous reports, only the transportation sector would account for 63% of the increase in the total worldwide liquid fuel use between 2010 and 2040 [33]. Furthermore, the rapid expansion of the global motorization sector has led to an increase in dangerous pollutant emissions to the environment.

According to the IEA, the transportation sector accounts for around 22% of the global GHG (greenhouse gas) emissions. In addition, the IEA predicts about 8.6 billion metric tons of CO_2 will be released into the atmosphere from 2020 to 2035. Vehicle emissions, such as PM, soot, HC, CO_2, CO, and NOx, are all major contributors to air quality deterioration. As a result, numerous researchers and specialists in the field are attempting to find new alternative resources that have a minimal environmental impact. Figure 2 depicts the distribution of the global energy supply and renewable energy contribution.

On the other hand, the side effect of environmental concern due to global warming has accelerated the search for a substitute for fossil fuels and the potential for alternative fuels that offer greater energy security, reductions in the emissions of greenhouse gases and particulate matter, rural development, and better vehicle performance, as well as reduce the demand for petroleum [3]. In addition, the demand for fossil fuels is continuously increasing worldwide. According to the IEA, the expected energy demand by 2030 is approximately 53%. As the world population grows, the global energy demand is growing. As reported by Ashraful et al., the world's energy consumption demand is on a rising trend, e.g., in early 1980, fuel consumption was about 6630 million tons of oil equivalent (Mt), whereas, in 2012, it nearly doubled to 12,239 Mt [4]. Consequently, one of the twenty-first century's new era challenges is to find solutions to reduce emissions and reliance on fossil fuels.

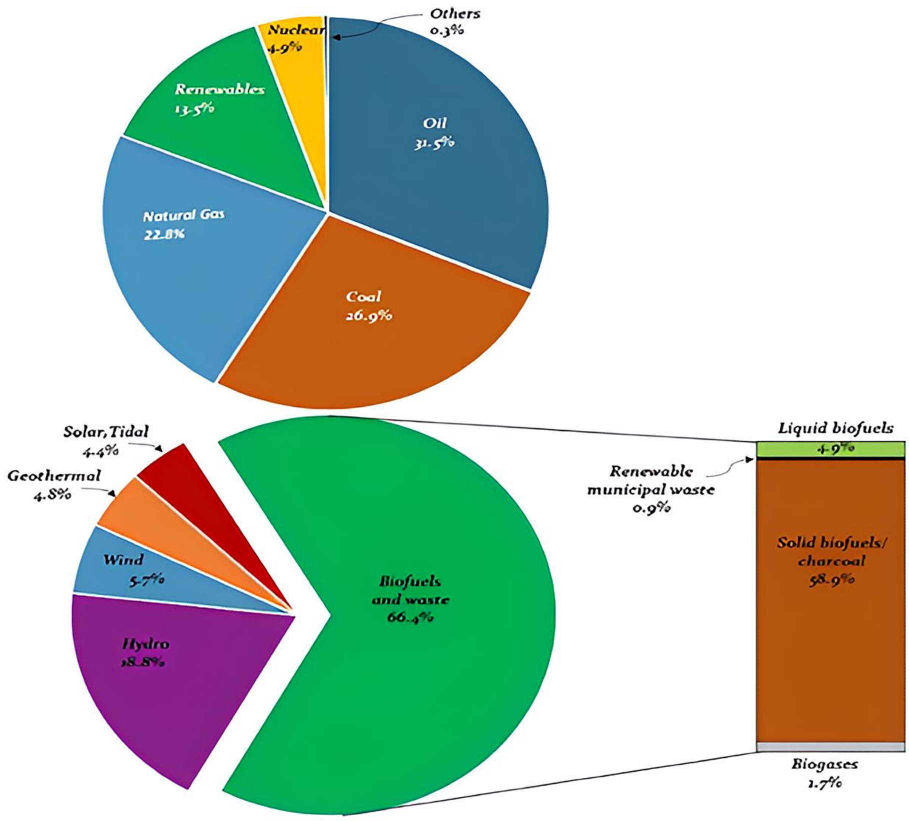


Figure 2. Distribution of global energy and renewable energy contribution [33].

Due to strict law enforcement in many European countries, fluctuating fossil fuel prices in the global markets, the current scarcity of fuel resources, and pollution of the environment have prompted research programs to instigate new methodologies and techniques that not only ensure that fuel consumption is met, but also that emissions are kept to an absolute minimum from different combustion devices [23]. This situation has motivated scientists, researchers, and automotive manufacturers to investigate alternative fuel sources, specifically biofuels. Biofuel will only be beneficial if it is cultivated in a sustainable manner that considers both diversity and the debate in mind, namely, "fuel verse food" [34]. Thus, direct research must be conducted on biofuels derived from edible vegetable oil, non-edible vegetable oil, non-edible corps, and waste vegetable oils products.

2.1. The Use of Biofuel in Internal Combustion (IC) Engines

Engine development in the past century was entirely focused on the utilization of fossil fuels as a primary fuel. However, the use of alternative fuels was also possible after certain modifications, according to certain local special needs. Alternative fuels are required by countries that have experienced difficulty securing crude oil supplies. In this context, flexible fuel engines are extremely prevalent in countries such as Brazil, allowing for the use of ethanol and gasoline in any proportions [35]. Alternative fuels made from biofuels can provide rapid assistance because they have similar heating values and qualities to liquid fossil fuels.

The extensive reliance on fossil fuel as a primary source of fuel in the internal combustion engines has led to a great sense of concern due to several factors, such as its future extraction, long-term availability, and discovery of new oil sources. In addition, the use of underground carbon as engine fuel increases CO_2 emissions and has significant environmental consequences, prompting the acceleration of a renewable energy research programme. In this regard, biofuels were able to provide immediate assistance as they have comparable heating value and physicochemical properties to liquid fossil fuels, making them a convenient replacement option [36].

There are four distinct generations of biofuels that can be highlighted as viable alternative fuel sources. The first generation is edible biomass biofuel. Edible biofuel is relatively closer to the characteristics of physicochemical fuel in terms of carbon balance with fossil fuels. Edible biofuels are also important for sustainability and economic growth because they can be produced locally. Nevertheless, its prices are prone to fluctuations in the global grain economy. Following this, the price of biofuel production increases globally similar to the prices of soybean, corn, and sugar, up to 21%, 27%, and 12% around the world, respectively. In addition, the ethical debates over the production of transportation fuels from food sources have increased.

As a result, the second generation of biofuel is to reduce reliance on edible oil resources, which comes with the drawbacks of technical complexity and production cost. The third generation of biofuel is focused on producing biofuel made from the properties of microorganisms, particularly algae. Growing algae requires a flexible environment and it has a significant capacity to absorb atmospheric CO_2. The fourth generation concentrates on modifying the genetic engineering model to improve their microorganism properties characteristics to enhance biofuel production, as well as further carbon emission reductions, particularly by changing the H/C ratio.

Biofuels use greatly reduces emissions and soil exploration as it evolves. However, the conversion of food-producing croplands to bioenergy may result in significant CO_2 emissions. Serrano et al. suggest that instead of vehicles intensifying air pollution, it is possible to manage the use of advanced biofuels and modern motors to create CO_2 carbon capture vehicles [37]. This new generation of sustainable vehicles is able to absorb CO_2 emissions via extrapolating the concept of net carbon neutrality. The first automobile fuels included vegetable oils, ethanol, and biodiesel, nevertheless, were ignored due to the discovery of petroleum deposits, which led to economical fuels and energy efficiency for internal combustion engines.

Currently, in the United States, blended fuels of fossil fuels and biofuels have been used since 2019 [38]. As shown in Figure 3, the total biofuel consumption made up approximately 5% of the total energy sources. Because of the existing environmental concern, several government incentives and studies indicate that biofuel use will increase, whether blended with fossil fuels or used exclusively. In this regard, it should be noted that biofuels policies have emphasised the volume of biofuel production, which benefits the productivity of biomass. Future policies should encourage crops with a high soil C storage potential, resulting in carbon-negative biofuels.

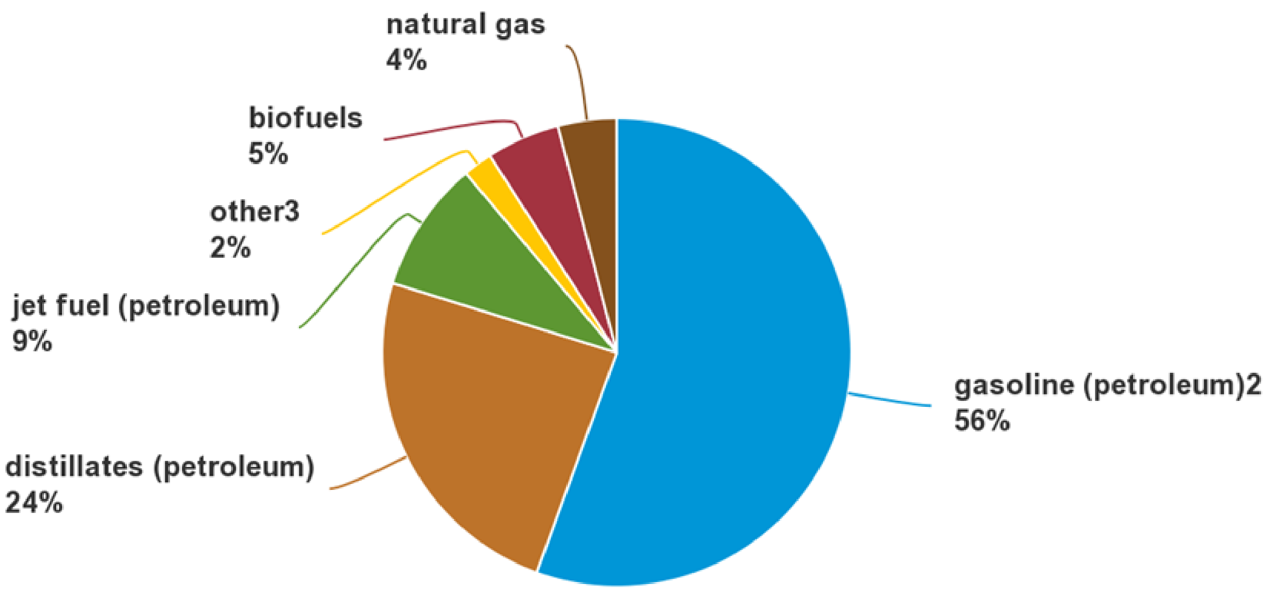


Figure 3. Transportation energy sources in the United States [38].

Alcohol and biodiesel can be mixed in small percentages in fossil fuel, for example biodiesel and diesel blends referred to B20 (20% biodiesel and 80% diesel). Engine modifications are required to use such fuels to make engine power that would have a comparable run with the fossil fuel. The flexible engines are an alternative to diesel-fuelled engines [35], even though their current design is less efficient than engines designed for a specific fuel. As an example, the chosen compression ratio is not in favour of the highest cetane number rated fuel. In this regard, the use of diesel-type fuel for ignition in low amounts combined with alcohol is a good alternative for use as a low-grade fuel, such as alternative fuels to reduce operating costs and exhaust emissions.

2.2. Alternative Fuels Performance and Emissions Behaviour in CI Engines

Nabi et al. [39] investigated the performance and emission of diesel engines run with cottonseed oil methyl ester (CSOME) blend compared with conventional petro-diesel. The findings revealed that BTE was slightly reduced and BSFC increased significantly. The emission results showed that CO, PM, and smoke opacity were reduced. Nevertheless, there was a slight increase in NOx emissions. According to Altaie et al., they discovered that enriched biodiesel blended fuel resulted in a lower brake torque and higher BSFC due to the lower calorific value [40]. However, because of the poor combustion quality, emissions such as NOx, HC, and CO had higher emissions from the exhaust to the environment.

Shaheed and Swain reported the performance and exhaust emissions using a small diesel engine fuelled with coconut oil methyl ester (COME) at various load conditions and found a lower BTE and higher BSFC [41]. They found that the lower BTE was due to a higher viscosity, and lower density and heating value compared with diesel fuel. They also reported that running with COME in an IC engine produces lower HC and CO emission, but a higher NOx emission. Agrawal et al. investigated the effect of several Karanja biodiesel blends (10%, 20%, and 50%) on the CI engine single-cylinder with a constant speed of 1500 rpm and analysed the dissimilar injection pressure sets (300, 500, 700, and 1000 bar) [42]. They discovered that increasing the injection pressure raised the maximum cylinder pressure in all of the fuel blends. Lower biodiesel blends had shorter combustion durations than diesel fuel, whereas B50 had a longer combustion duration. Table 1 summarises the various trial results on alternative fuels that run on CI engines.

Table 1. Summary of the experimental works on alternative fuels that run on CI engines.

Type of Alternative Fuel	Engine Type	Test Setup	Performance	Combustion	Emission	Reference
Cottonseed oil methyl ester (CSOME) blend	4 strokes, 1 cylinder, CR: 16.5:1 RP: 4.48 kW	Constant Speed (850 rpm) Variable load	BTE ↓ BSFC↑	-	CO ↓ PM↓ NOx↑	[39]
Jatropha Oil	1 cylinder, 4 Stroke, CR: 17.5:1 RP: 7.4 kW	Constant Speed (1500 rpm)	BSFC ↑ BTE↓	-	CO CO_2 HC Smoke Opacity Close to diesel fuel	[42]
Jatropha methyl ester	1 cylinder 4 strokes CR: 17.5:1 RP: 3.5 kW	Constant Speed (1500 rpm)	BSFC ↓ (after ↑ CR) BTE↑	-	PM↓ HC ↓ NOx↓ Smoke Opacity ↓ PM↓	[43]

Table 1. *Cont.*

Type of Alternative Fuel	Engine Type	Test Setup	Performance	Combustion	Emission	Reference
Jatropha biodiesel	1 cylinder, 4 strokes CR: 18:1 DI	Variable speeds (1000–2000 rpm)	Engine power ↓ Torque ↓	Peak cylinder pressure ↑	CO ↓ NOx↑ PM↓	[44]
Coconut	1 cylinder, DI, AC	Full Throttle at variable speeds (1200–3600 rpm)	BTE ↓ BSFC ↑ EGT↓	Almost similar	CO ↓ HC↓ Soot and PM↓	[41]
Sunflower	4 strokes 4 cylinders DI	Full load Variable speeds	BSFC ↑ BTE↓ Power (↓ 5%)	Peak cylinder pressure ↑	CO ↓ HC↓ PM↓	[45]
Palm oil	Multi cylinder, IDI	Full load at different speeds	Power (↓ 2.5%) BSFC↑	Lower than diesel	CO ↓ HC ↓ NOx ↑ Smoke↓	[46]
Poon	1 cylinder, 4 strokes	Speed 1500 rpm	Power (↓ 23%)	-	CO ↓ HC ↓	[47]
Tobacco	4 cylinders, DI, NA	Speed (1500–3000 rpm)	BSFC ↑	-	CO ↓ HC ↓ NOx↑ PM↓	[48]
Karanja	2 cylinders DI	Speed (1500 rpm)	BSFC ↑ Power (↓ 24.87%)	-	CO ↓ HC ↓ NOx↑ PM↓	[49]
Rapeseed	1 cylinder DI	Speed (1500 rpm)	BSFC ↑ BTE↓	-	CO ↓ HC ↓ NOx↑	[50]
Mahua Oil	4 strokes 1 cylinder	Speed (1500 rpm)	BSFC ↑ BTE↑ at low load	-	Smoke↓	[51]
Olive kernel	4 strokes DI engine	Speed (2000 rpm)	BSFC ↑	-	CO ↓ HC ↓ NOx↑	[52]
Canola oil	2 cylinders 4 strokes Naturally aspirated DI engine	Speed (1200–1800)	BSFC ↑ BTE↓	-	CO ↓ HC↓ at low rpm HC↑ at high rpm NOx↑	[53]
Crude Palm Oil	4 cylinders 4 strokes DI engine	Variety of load and rpm	Engine power ↓ Torque ↓ BTE ↓ BSFC ↑	-	CO ↓ HC ↓ at low rpm HC↑ at high rpm NOx↑	[54]

3. Background of Emulsified Biofuel

3.1. Dispersed System in the Emulsified Biofuel

A dispersed system is a homogeneous system in transition between a heterogeneous macroscopic and a molecular solution. The dispersed phase may be formed in two ways: by condensing the actual solution (fabrication by condensation) or by dispersing the macroscopic phase (fabrication by dispersion). Emulsified biofuel originates from a dispersed system and is described as a combination of two or more incompatible liquids that form a scattered droplet [55]. Dispersed droplets are made up of two liquids with non-miscible stabilities, in both internal and external phases. The development of the dispersed phase is reliant on the surfactant agent's hydrophilic–lipophilic balance (HLB) value, which determines whether the formation is oil-soluble or water-soluble, more often referred to as water in oil (W/O) and oil in water (O/W). (W/O) denotes the dispersed phase of water and the continuous oil phase, whereas (O/W) denotes the reverse [56]. Emulsified biofuels utilised in engines are distributed through (W/O) systems.

(W/O) is formed when water is present in the internal phase and appears as a scattered droplet, while oil is present in the exterior phase, which is referred to as the continuous phase. As a consequence, the (O/W) operating principle is different from that of (W/O) owing to the existence of water in a significant quantity in the exterior phase that would evaporate initially and the inability of the internal phase to break down the oil composition into ultra-fine droplets [57]. Because of the rapid initial combustion, the formation of an ultra-fine-sized droplet becomes critical. Additionally, it facilitates the transmission of heat to the molecular size composition through convection and radiation methods of thermal energy transfer [57]. Although classified as dispersed systems, emulsion and microemulsion are technically distinct.

The differences between microemulsion and emulsion not only depend on the size of the droplets, but also on their distinct thermodynamic stabilities [58]. The stability, viscosity, density, and specific gravity of an emulsion are highly reliant on the droplet and distribution size [59]. By and large, emulsions are thermodynamically unstable and need energy to form [58]. This is due to the fact that their Gibb free energy solution (ΔG_f) is greater than zero ($\Delta G_f > 0$). A positive Gibb free energy solution indicates that they have a natural tendency to separate into phases. Numerous techniques have been applied to raise the emulsion's thermodynamic constancy, with the most popular being the addition of emulsifier agents. The scattered phase generated by this method is usually greater than 0.1 µm in diameter (between 1 and 10 µm). Additionally, the bulk of such emulsions appear cloudy and chalky in colour.

As highlighted earlier, an emulsion is a thermodynamically unstable system. For this reason, emulsions tend to break down easily. Surfactants and solvents can be used to delay this procedure by improving the mixture's stability. The breakdown progression of the emulsion consists of various stages, such as the free energy change of the systems, a decrease in the interfacial area, and gravitational setting. Each breakdown involves a complicated physical process that necessitates a thorough examination of the different surface forces involved, as shown in Figure 4. Tadros has analysed and summarised the specifics of each process and its preventive measures [60]. Microemulsions are systems that form spontaneously and display nano-dispersed structures. Microemulsions have unique characteristics: large interfacial area, thermodynamically stable isotropic liquid, and ultralow interfacial tensions. The droplet size of microemulsions is tiny compared with the emulsion. The Gibb free energy of the solution is between zero and negative ($\Delta G_f < 0$).

3.2. The Micro-Explosion Phenomenon

In the phenomenon of micro-explosions, water acts as the main component in the emulsified fuels. In contrast, the presence of water in the engine system negatively impacts performance, and, as a result, emulsified fuel must be stabilised before use. The limitation of water-containing emulsified fuels is that they can produce rust and hydroperoxides from the oxidising fuel, leading to corrosion [57]. The issue needs to be addressed as water contains salt. Natural salts are present in tap water, bottled water, and dietary reference intake, which may impact on the emulsifier agent's function and the properties of the emulsified fuels. The dispersed system was affected by the inorganic salt content in water compounds, which was then stabilised with various surfactant agents, according to a number of researchers [61–63]. According to Anghel et al. [63], an electrolyte containing 0.5 wt% NaCl in water is ineffective in systems that contain ethoxylated surfactant. Consequently, to enhance the stability of a dispersed system, the appropriate surfactant and co-surfactant characteristics must be chosen.

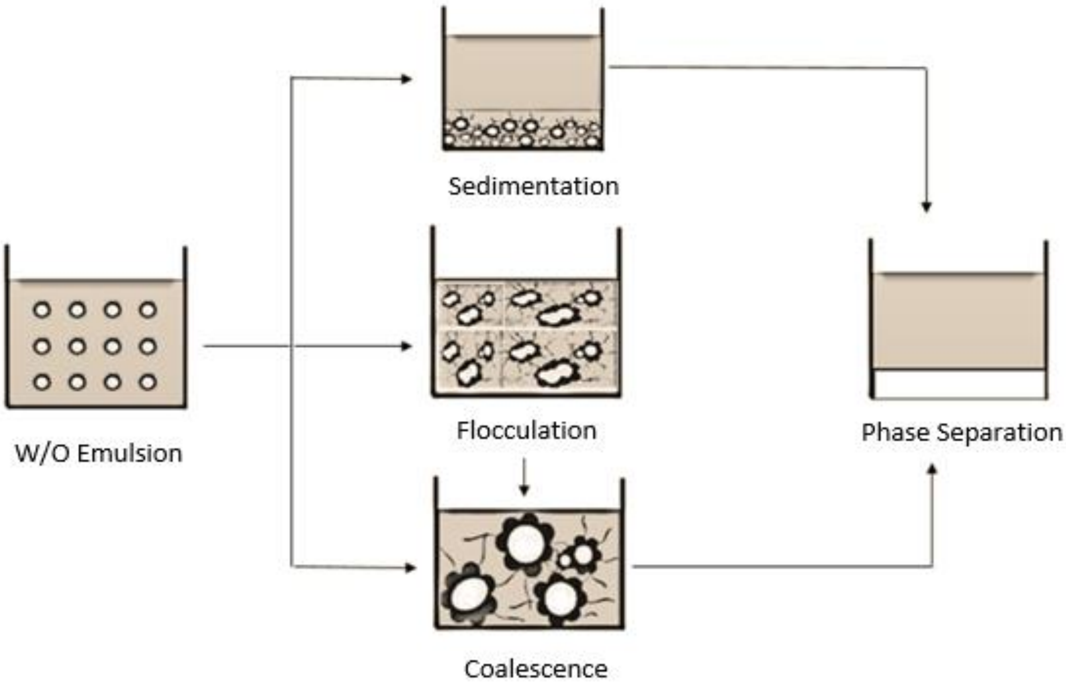


Figure 4. The sequence of the breakdown process in (W/O) emulsions [7].

Various researchers have suggested using demineralised water to improve the emulsified biofuel because it has a higher level of stability in an emulsion than regular tap water [64,65]. Thus, water treatment is required to remove the salt content from the water used in preparing the emulsion. Nevertheless, it is essential to consider the use of additional energy consumption required for water treatment, increasing costs, and the resources used to develop emulsified fuels. The presence of water in emulsified fuels should replace some amount of fuel. Its presence increases fuel injection and atomisation processes in the cylinder before combustion. The heating value of the fuel and the total energy per unit mass of fuel can also be lowered. It inhibits the production of NOx within the combustion chamber as a result of water abundance in the hot combustion setting by means of radiation and convection. In addition, it also shows that water presence in emulsified fuel has also improved the engine performance, bringing it closer to that of conventional petrol-diesel [66].

The improved engine performance is attributed to the water dispersed phase in the fuel's enhanced atomisation and mixing properties. According to Roy et al. [53], fuel is atomised into small droplets during injection by spraying it through the nozzle inside the combustion chamber of the cylinder. There is a dissimilarity between the boiling points of water and fuel, so it was observed that the water had reached its boiling point first and absorbed enough heat to cause the reaction. Additionally, this emulsified fuel method may be extended to include applications using vegetable oils and animal fats. There are differences in the volatility of water and fuel in emulsified fuel combustion, as described by Tran and Ghojel [67]. Due to heat transmission through convection and radiation, the droplet becomes severely superheated in the confined cylinder environment. A rapid bubble nucleation effect occurred within the droplet, followed by the internal formation of vapour bubbles. The vaporisation process, which began with water, blew up the oil layer, resulting in fine atomisation or volume ratio of the oil droplet. This occurrence is termed a micro-explosion by Crookes et al. [68].

The micro-explosion phenomenon was noticed in early 1965 by two researchers named Ivanov and Nefedov [69]. The micro-explosion effect in combustion has several advantages for the environment and engine performance. The micro-explosion caused primary and secondary explosions, according to Selim and Ghanam [70]. Mura et al. [71] discovered that secondary explosions were very fast and spread over a wide region, resulting in increased fuel/air premixing and overall combustion efficiency. Additionally, Jiao and Burgess [72] found that this process is critical for decreasing PM emissions from medium and heavy oils during atomisation. Figure 5 depicts the atomisation of a dispersed system before the combustion process.

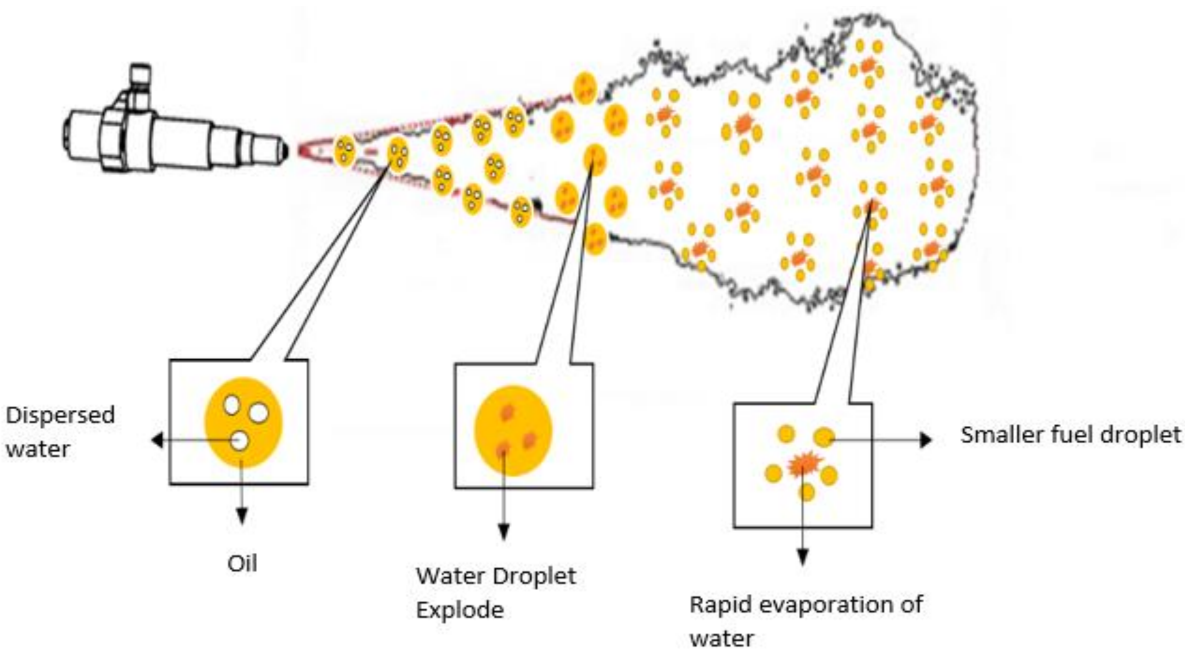


Figure 5. Atomisation of a dispersed system in sequence.

Alahmer et al. [73] asserted that the presence of water may also help decrease NOx gas emissions through a micro-explosion effect. Using emulsified fuel allowed the combustion reaction to be shortened, as described by Wang et al. [74]. This technique of enhancement resulted in less soot, PM, CO, and HC being produced. For regions with less oxygen, water vapour aids in forming particulates, which produce CO and H_2. As a result, the amount of particulate emitted was lower than expected [75]. According to Attia and Kulchitskiy [76], the discrepancy is still being debated, particularly concerning CO and unburnt hydrocarbon emissions. Leung et al. [77] discovered that the engine RPM and load determine the emission of CO in engines fuelled by emulsified fuel. In addition, the subsequent reduction in temperature within the combustion chamber results in increased viscosity. According to Lif et al. [78], emulsified fuels demonstrated an overall improvement, particularly at the beginning of injection and at the beginning of combustion (ignition delayed period).

Numerous studies have demonstrated that water in emulsified fuel decreases the temperature of a superheated environment via heat absorption by water vaporisation over the fuel jet [69,71,72]. As reported by Zhang et al. [79], endothermic vaporisation (the process by which water absorbs heat energy through vaporisation) in the combustion chamber significantly reduced the localised temperature. Additionally, in comparison with conventional petro-diesel fuels, it extends the ignition delay and improves combustion efficiency. The experimental method has made a significant contribution to the scientific understanding of the micro-explosion phenomenon. Califano et al. confirmed that the occurrence of the micro-explosion phenomenon was dependent on several parameters and did not occur in normal conditions all the time [80]. Coalescence or phase separation was discovered by Samec et al. as a key component affecting water droplets dispersed into the continuous phase [81]. To be more specific about flame temperature reduction, heat release rate, and chemical composition changes, water in the fuel had an indirect consequence on the physical and chemical dynamics. This resulted in a higher OH radical concentration and it dilutes the rich zone in the combustion chamber.

4. Formulation of Emulsified Biofuels: Materials and Procedures

4.1. Preparation of Emulsified Biofuels

It is difficult to develop a precise technique for emulsifying biofuels due to the diversity of feedstocks (animal fats and vegetable oils) and preparation methods (mechanical and physicochemical), for example, mechanical stirring or membrane emulsification [82]. Among these methods, dispersion is the most widely used. Ultrasonic vibration has been considered as an exceptional technique for the effective preparation of tiny particles in a high-speed solution. Numerous studies found that employing a mechanical stirrer and increasing the rotating speed was required to disperse the water to the smallest droplet size feasible [83–85]. Kerihuel et al. investigated this by fluctuating the stirrer RPM ranging from 500 to 1500 rpm; nevertheless, no difference in water droplet size was observed in their experiments [86].

The properties of emulsified biofuels can be enhanced by considering a variety of determinants throughout the preparational procedures, including physical properties (viscosity, density, surface tensions, and specific gravity), surfactant and co-surfactant attributes, the emulsified biofuel's preheating effect, and others. By choosing the proper heating temperature, it may be feasible to decrease the energy required to distort the contact. According to Anghel et al., at normal temperature, water is a more superior solvent for non-ionic amphiphiles than oil, but becomes a poor solvent as the temperature rises, while the reverse is true for ionic surfactants [63]. Adding surfactants will lower the surface tension of the oil and water, stimulate their surface layers, and increase the surface interaction area to obtain emulsions or microemulsions. The capacity of surfactant agents to stabilise dispersed systems (emulsions and microemulsions) is determined by the molecular structure of the surfactant and the energy released during system contact (polar and non-polar). The hydrophilic end of the surfactant faces the water, while the hydrophobic end faces the oil. Kerihuel et al. mentioned that the surfactant used to create emulsified biofuels needs to be completely liquefied in the oil (continued phase) in order to produce consistent emulsified biofuels [86]. Table 2 shows the characteristics of the surfactant agents that are commonly applied as emulsifying agents.

The surfactant can be categorised on the basis of formulation by the HLB variant number. Necati et al. mentioned that the HLB number is typically between 0 and 20, and has a non-dimensional value [87]. Hydrophilic compounds that contact or dissolve in water and other polar constituents must be considered. "Fats, oils, and lipids are lipophilic molecules" that dissolve in them, according to Debnath et al. [88]. Another report by researchers emphasised the importance of selecting a surfactant agent based on the HLB number when preparing dispersed systems [89]. Kerihuel et al. concluded that using lipophilic rather than hydrophilic surfactants in (W/O) dispersed systems is highly recommended, and the HLB number should be in the range between 4 and 6 for the (W/O) formations [86]. Anghel et al. demonstrated that combining hydrophilic and hydrophobic surfactants produces more stable emulsions [63]. As a result, a mathematical equation developed by Mollet and Grubenmann may be used to generate a combination of surfactants with HLB values based on previously suggested intervals [90]. Additionally, this equation may be used to determine the mass proportion of surfactants present in a combination.

Moreover, to increase the quantity of water or enhance the constancy of the emulsified biofuel, a cosurfactant may be added. Mollet and Grubenmann elucidated that a cosurfactant is a minor amphiphile with a decreasing head and tail size, such as alcohol, phenol, acid, or anime [90]. In this case, quaternary systems are used to describe dispersed systems (animal fats or vegetable oils/water/surfactant/cosurfactant). Table 3 shows the physicochemical properties and characteristics of these emulsified biofuels.

Table 2. Type of surfactants used in the preparation of emulsified biofuel.

Chemical Name	Molecular Formula	HLB Number	Reference
Sorbitan monooleate (Span 80)	$C_{24}H_{44}O_6$	4.3	[91]
Sorbitan monooleate (Span 80)	$C_{64}H_{124}O_{26}$	15.0	[91]
Sorbitan monostearate (Span 60)	$C_{24}H_{46}O_6$	4.7	[92]
Tetraethylene glycol dodecyl ether (Brij 30)	$C_{20}H_{42}O_5$	9.7	[93]
Sorbitan monopalmitate (Span 40)	$C_{22}H_{42}O_6$	6.7	[94]
Sodium bis-[2-ethylhexyl] sulfosuccinate (AOT)	$C_{20}H_{37}O_7SNa$	10.2	[93]
Sorbitan sesquiolate (Span 83)	$C_{66}H_{130}O_{18}$	3.7	[95]
Oleic acid	$C_{18}H_{34}O_2$	1.0	[92]
Sorbitan trioleate (Span 85)	$C_{60}H_{108}O_8$	1.8	[91]

Table 3. Physicochemical properties of biofuels [96–98].

Biofuel	Iodin Value	Cetane Number	Heating Value (kJ/kg)	Viscosity (mm^2/s (C))	CP	Density (kg/L)	Sulphur (%)	Carbon Residue (%)	Ash(%)
Mahua	-	44.0	30,182	15.5	-	-	0.01	-	-
Karanja	-	-	37,200	122	-	-	0.01	-	-
Neem Seeds	-	46.8	38,279	29.0	-	-	0.01	-	-
Jatropa	-	41.8	38,998	48.8	-	-	0.01	-	-
Soybean	121–134	36.7	38,893	31.9	−3.7	0.87	0.01	0.25	0.010
Sesame	114–130	39.6	38,829	34.7	−3.7	0.81	0.01	0.24	0.010
Sunflower	120–153	36.3	37,983	36.8	6.9	0.88	0.01	0.22	0.010
Cotton seed	95–145	42.4	38,864	32.8	2.1	0.89	0.01	0.19	0.010
Palm	40–65	39.0	37,241	38.5	30.0	0.82	0.01	-	-
Olive	85–96	-	-	-	-	-	0.01	-	-
Coconut	8–10	-	-	-	-	-	0.01	-	-
Sunflower	134–161	40.8	38,915	30.8	17.2	0.89	0.01	0.24	0.006
Castor	79–89	-	38,920	289	-	-	0.01	-	-
Corn	113–130	37.6	38,920	33.8	−1.2	0.87	0.01	0.23	0.011
Peanut	79–104	40.1	38,972	38.5	11.4	0.91	0.01	0.25	0.004
Rapeseed	92–132	36.8	38,909	36.4	−3.8	0.89	0.01	0.28	0.063

4.2. Physicochemical Characteristics of Stability

4.2.1. Stability

One of the essential considerations in making emulsified biofuel commercially viable is its stability. The engine may fail if the emulsified biofuel becomes destabilised while in storage or during engine operation. The sustainability of this mixable condition is a significant challenge in the long-term. The destabilisation of an emulsion depends on the viscosity of biofuel, surfactant volume amount, temperature affected, the density of fuel, specific gravity, and the water volume content [99].

4.2.2. Stability Classes

Water and oil can coexist in four different states: entrained water, stable, meso-stable, and unstable [100]. All of these states depend on the characteristics of the emulsions. Some emulsions can be stored for several months and are highly stable. These emulsions' viscosity and elasticity increase over time. Mesostable emulsions exhibit characteristics of both stable and unstable emulsions. It is assumed that these emulsions include a greater proportion of stabilising than destabilising elements. These emulsions have the potential to degrade into oil layers and stable emulsions. An unstable emulsion decomposes rapidly after mixing with oil and water within a few hours, with a viscosity twenty-fold less than that of the starting oil. Consequently, the viscidness of an emulsion could be used for determining its stability.

4.2.3. Factor Affecting Biofuel Emulsion Stability

Numerous variables affect the stability of emulsions, including the kind of emulsifier used, the emulsifier's HLB value, the water concentration, the type of emulsifier produced, and the emulsifier concentration. The most critical element to take into account throughout preparation is the water concentration, as it has the potential to alter the fuel characteristics of emulsified biofuel. Numerous researchers have used co-surfactants and additives to enhance stability [1,101,102]. A co-surfactant is used to increase surfactant transfer to the (O/W) emulsion, resulting in better stabilisation. The following sub-sections will discuss various factors that influence the emulsion's stability period.

HLB Value Effect on the Emulsion Stability

A biofuel emulsion with a broad range of HLB values may be prepared. The optimum HLB number that offers the greatest physicochemical stability must be chosen, which changes depending on the emulsion's production method. Lin and Lin discovered that using Span 80 and Tween 80 together caused the most constant emulsion with HLB 13 [103]. By increasing the hydrophilic emulsifier Tween 80, the scattered water phase may be better covered by the inner biodiesel phase. In contrast, Span 80 is a lipophilic emulsifier that improves the adherence of the external biodiesel phase to the (O/W) phase. Hence, an HLB value of 13 provided the best stability when preparing a three-phase emulsion. Raheman and Kumari prepared the emulsifier with HLB values of 4.3, 5, and 6, and found that the emulsifier with an HLB of 5 showed the most stable emulsion using 93% of Span 80 and 7% of Tween 80 [102]. The following equations are used to determine the mixture of the two surfactants:

$$\mathrm{HLB_{AB}} = [(\mathrm{H_A} \times \mathrm{W_A}) + (\mathrm{H_B} \times \mathrm{W_B})]/(\mathrm{W_A} + \mathrm{W_B}) \quad (1)$$

where A and B are the two dissimilar surfactants, H represents the HLB value, while W signifies the surfactant's precise mass.

Effect of Additives

The additives are used to improve the biofuel emulsion with regard to the physical and thermal attributes of the fuel. This will be beneficial for improving the engine's performance and reducing emissions [104]. The following table (Table 4) summarises the many additives used to enhance the features of the emulsified fuel. Using a diglyme/additive application consisting of 35.8% oxygen compound (by weight) increases the viscosity of the two-phase (O/W) emulsion more than the two-phase (W/O) emulsions. This is due to the considerable increase in the interfacial contact area between the diglyme additive and the emulsion type. This leads to an increase in friction and static electricity energies in the emulsion, which are the governing determinants for improving viscosity.

Table 4. Numerous emulsion preparation additives and their quantities.

Additive	Quantities	References
Dimethyl Ether,	12	[100]
Diethyl Ether (%)	12	[101]
H_2O_2 (%)	12	[100]
Alumina	25, 50, 100	[102]
Carbon Nanotube (CNT)	25, 50	[103]
Aqueous Ammonia (%)	5, 10	[104,105]

Effect of Emulsifier Type Used on Emulsion Stability

The selection of surfactant agents and their concentration is essential for the desired stability of the emulsified biofuel. The kind of emulsifier used may differ according to the source fuel. Therefore, for emulsion preparation, the emulsifier with the optimum function ought to be utilised to prevent unstable emulsions resulting from an improper surfactant concentration. Awang and May investigated seven different kinds of possible emulsifiers and discovered that the volume ratio/amount of surfactant employed during emulsion must be within a certain range as it has a significant consequence on the emulsion's constancy [105]. Because of the polydispersity surfactant micelles at (W/O), the emulsion is volatile at low surfactant dilutions because of oil droplet accumulation [106]. Therefore, an optimal surfactant level of concentration will result in a better emulsification process. Kerihuel et al. conducted another study in which they used a surfactant dosage of 2–8% to stabilise the emulsion of biofuel with animal fat as a fuel [94]. Lin and Lin discovered that the highest stability for palm oil in a range of surfactant dosage was approximately 1–2% surfactant concentration [103]. Furthermore, their research discovered that forming an emulsion with 1% surfactant increased the constancy of the emulsion when the magnetic stirrer's mixing speed was amplified from 500 to 1300 rpm. Thus, the study discovered that another critical factor affecting the stability of an emulsion is the mixing speed of the magnetic stirrer.

Co-Surfactant Effect on the Emulsion Stability

The selection of surfactant agents and their concentration is essential for the desired stability of the emulsified biofuel. The kind of emulsifier used may differ according to the source fuel. Therefore, for emulsion preparation, the emulsifier with the optimum function ought to be utilised to prevent unstable emulsions resulting from an improper surfactant concentration. Awang and May investigated seven different kinds of possible emulsifiers and discovered that the volume ratio/amount of surfactant employed during the emulsion must be within a certain range as it has a significant consequence on the emulsion's constancy [105]. Because of the polydispersity surfactant micelles at (W/O), the emulsion is volatile at low surfactant dilutions because of oil droplet accumulation [106]. Therefore, an optimal surfactant level of concentration will result in a better emulsification process. Kerihul et al. conducted another study in which they used a surfactant dosage of 2–8% to stabilise the emulsion of biofuel with animal fat as a fuel [94]. Lin and Lin discovered that the highest stability for palm oil in a range of surfactant dosage was at an approximately 1–2% surfactant concentration [103]. Furthermore, their research discovered that forming an emulsion with 1% surfactant increased the constancy of the emulsion when the magnetic stirrer's mixing speed was amplified from 500 to 1300 rpm. Thus, the study discovered that another critical factor affecting the stability of an emulsion is the mixing speed of the magnetic stirrer.

The Effect of WATER Concentration on the Stability of the Emulsion

The selection of surfactant agents and their concentration is essential for the desired stability of the emulsified biofuel. The kind of emulsifier used may differ according to the source fuel. Therefore, for emulsion preparation, the emulsifier with the optimum function ought to be utilised to prevent unstable emulsions resulting from improper surfactant concentration. Awang and May investigated seven different kinds of possible emulsifiers and discovered that the volume ratio/amount of the surfactant employed during emulsion must be within a certain range as it has a significant consequence on the emulsion's constancy [105]. Because of the polydispersity surfactant micelles at (W/O), the emulsion is volatile at low surfactant dilutions because of oil droplet accumulation [106]. Therefore, an optimal surfactant level of concentration will result in a better emulsification process. Kerihul et al. conducted another study in which they used a surfactant dosage of 2–8% to stabilise the emulsion of biofuel with animal fat as a fuel [84]. Lin and Lin discovered that the highest stability for palm oil in a range of surfactant dosage was approximately 1–2% surfactant concentration [103]. Furthermore, their research discovered that forming an emulsion with 1% surfactant increased the constancy of the emulsion when the magnetic stirrer's mixing speed was amplified from 500 to 1300 rpm. Thus, the study discovered that another critical factor affecting the stability of an emulsion is the mixing speed of the magnetic stirrer.

The Effect of the Type of Emulsion Used

The (W/O) emulsion is widely used in various industries, including pharmaceuticals, cosmetics and beauty, food, and fuel. While (O/W) emulsions, on the other hand, are used in the oil recovery method [107]. Nonetheless, the role of emulsion stabilisation is distinct, with steric and electrostatic aversion stabilising the (O/W) emulsion and solely steric force stabilising the (W/O) emulsion owing to the continuing phase's poor electric conductivity [108]. In general, the emulsion stability of (W/O) is lower because the emulsion contains highly mobile water droplets and has a proclivity to quickly flocculate, sediment, and coalesce [97]. In the meantime, (O/W) emulsion is inappropriate as a combustible fuel owing to its greater water content, as contact with water in the combustion chamber causes corrosion, and insufficient oil supply results in poor combustion or non-combustion. The (W/O) emulsion is recognised and commonly used in alternative fuels. Moreover, diesel emulsion is preferred over water in gasoline because of its different boiling points [99]. In another study, the pyrolysis process can generate (W/O) and (O/W) emulsions and depends on the pyrolysis ratio of oil and diesel [109]. Table 5 lists the period of stability among various emulsified biofuels derived from various feedstocks. As shown in the table, the most stable emulsion type is a microemulsion, which exhibits greater stability than other types of emulsion. To achieve commercial acceptability, biofuel emulsions must have characteristics similar to diesel fuel and satisfy all applicable requirements. The following sections will discuss the performance assessment and the effect of emulsified biofuels on diesel engine components.

Table 5. The stability of various types of emulsified biofuels.

Fuel	Surfactant	Type of Emulsion	HLB Value	Stability Time	References
Palm oil emulsion	Laboratory prepared surfactant	(W/O)	-	1 week	[105]
Palm oil methyl ester + water 5%	Span 80 and Tween 80	(W/O)	4.3, 5, 6	3 h almost no deposition	[88]
Waste cooking oil (WCO) + 15% water	Span 80 + Ethanol	(W/O)	4.3	2 weeks	[110]
Waste cooking palm oil (B70) + 0.5% water	Span80 + Ethanol	Microemulsion	4.3	2 weeks	[111]
Soybean biodiesel + 0.5% water	Span 80 + Ethanol	Microemulsion	4.3	Stable	[101]
88.4% Canola oil + 9.8% methanol + surfactant	Span 80 + Tween 80	(W/O) (in this case methanol in oil)	7	7 h	[95]
93% Jatropha methyl ester + 2% surfactant + 5% water	Span 80 + Tween 80	(W/O)	10	5 days	[112]

5. Evaluation of the Performance of Diesel Engines Running on Emulsified Biofuels

5.1. Emission and Overall Engine Performance

Emulsification is not a novel technique; it has been used for a protracted length of time to enhance the combustion process and emission attributes of diesel fuel (e.g., HC, soot, PM, NOx, CO, and SOx). Several studies [3,20,94,113] have been conducted using emulsified biofuels as engine fuel in various operating conditions. Nonetheless, the impact of emulsified fuels on engine functionality varies, based on the research type [114]. The obtained result is highly dependent on the mode of operation of the engine, type of injection spraying and fine-tuning, and the optimised configuration of the combustion chamber [115]. Additionally, the physicochemical attributes of the emulsified fuel have a substantial effect on the engine's functionality and discharge emissions.

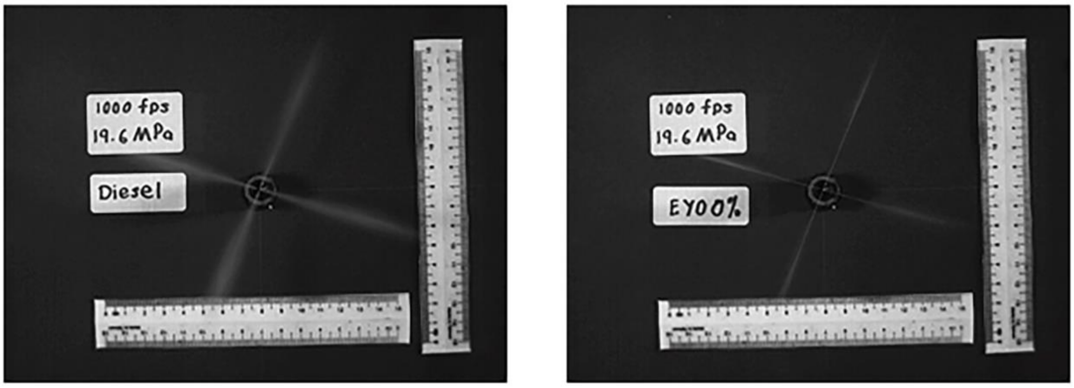
Emulsified biofuel is a blend of animal fats and vegetable oils, together with an emulsifier ingredient that has an inferior heating value and cetane number compared with traditional diesel fuel. As a consequence, engine functionality and discharge emissions will vary between emulsified biofuels, plain biofuels, and diesel fuel. Alcohol may be utilised as a cosurfactant to decrease the viscosity and surface tension of emulsified biofuels. It should be noted that previous research has indicated that a greater concentration of short-chain alcohol will lower the quality of fuel ignition because of the lower cetane number [116]. Accordingly, inferior engine functionality is observed when the engine does not deliver a comparable performance when fuelled with diesel. Taking this into consideration, Kumar and Khare explored the supplementation of additives in emulsified biofuels, for instance, cetane improvers, to boost engine performance nearer to that of the diesel injection [117].

Under various test conditions, it has been reported that emulsified biofuels have longer ignition delays [3,92,94]. However, the delays were shorter when compared with those of conventional diesel fuel [92]. Moreover, Crookes et al. did not continuously experience an increased delay in ignition as the water content increased in the emulsified biofuel [118]. According to another study, ethanol-emulsified animal fat-based biofuel has an extended ignition delay than methanol-emulsified animal fat-based biofuel [13]. This a typical behaviour may be explained by the physical characteristics of these emulsified biofuels and their effect on the premixed combustion phase and response rate. Additionally, as formerly stated, it is imperative to consider the type of engine operation mode employed. Crookes et al. discovered that the delay in ignition was shorter at moderate and high speeds [118].

To recompense the lower heating value of emulsified biofuel, the injection duration must be increased to achieve a similar engine power output to diesel fuel. In fact, there has been an upsurge in the particular fuel utilisation when running with emulsified biofuel compared with running with diesel fuel operation [3,20,94]. In addition, using the emulsified biofuel in the diesel engine has decreased the flame temperature of combustion due to water components present in the emulsified biofuel. This is a predicted outcome of the distributed water in the fuel's thermal action. In a study with Crookes et al., it was found that the water has a dual thermal consequence during combustion: the liquid is heated and the evaporation yields more enthalpy energy [118]. In general, high temperature in the combustion chamber led to the creation of NOx. Lower NOx emissions were expected as an outcome of the thermal impact of the water on the combustion temperature. Nonetheless, the NOx production in the combustion chamber is complicated, as many intermediary varieties are released in the exhaust [119].

Sangeeta et al. reported a reduced NOx emission and a slight increase in the power output after running the experiment using emulsified biofuels [120]. In a separate research study, different investigations concluded that the research confirmed that emulsified biofuel formulations from vegetable oil and animal fats produced the lowest NOx emissions in diesel engines [121]. Crookes et al. observed a lower NOx emission when running diesel engines on emulsified biofuels than conventional diesel and neat biofuels [118]. Nevertheless, comparable levels of NOx emission were observed by Jin et al. [116].

HC emissions are primarily caused by a lean air–fuel mixture, engine design, and erratic operating circumstances in diesel fuel combustion. There is lower flame speed to complete combustion during the power stroke, leading to high HC emissions in lean air-fuel mixing. In the diesel engine, factors such as messy injection, high nozzle cavity volumes, and injector needle bounce were found to contribute to HC emissions, as shown in Figure 6. In erratic operating circumstances, a significant degree of instantaneous engine speed variation has been shown to have an effect on the generation of HC emissions [122]. In comparison with diesel, emulsified biofuels possess a lower heating value and cetane number, implying an increase in hydrocarbon emissions. Numerous studies have shown that operating on emulsified biofuels rather than straight biofuels and diesel fuel causes a reduction in HC or CO emissions [122–124].



(**a**) (**b**)

Figure 6. Injection spray pattern between (**a**) diesel fuel and (**b**) palm oil biofuels.

Furthermore, when running the engine fuelled with emulsified biofuel, a higher ignition delay may be experienced. Consequently, the stages of combustion, heat release rates, peak pressure of the cylinder, and the fraction of air–fuel mixture distinctly vary. The variations of this phenomenon have a significant impact on the formation of CO and HC in diesel engines. Figure 7 depicts the relationship between the emulsion constituent indicators.

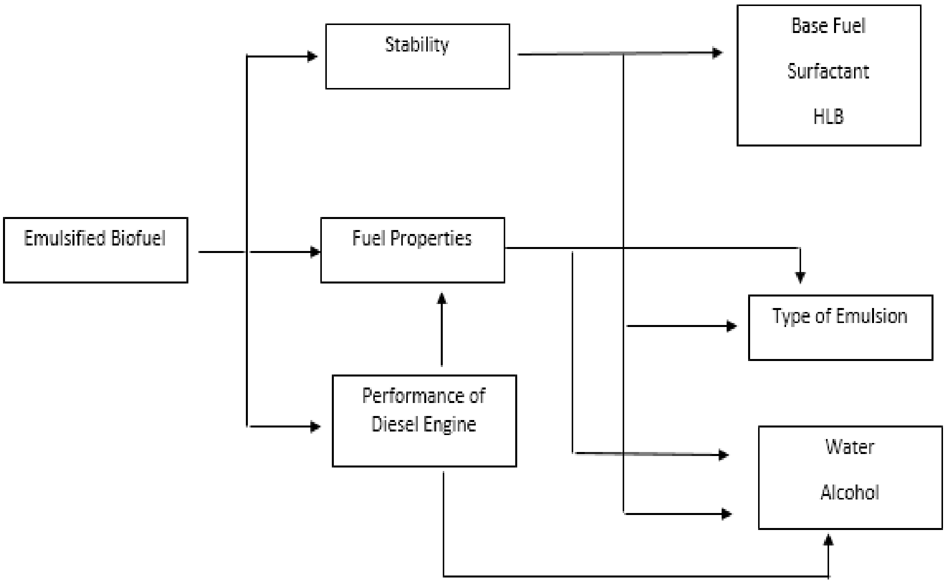


Figure 7. The interrelationship between the emulsion constituent indicators.

5.2. Effect of Emulsified Biofuels on Friction and Wear, Lubricant, and Endurance of Engine Components

The friction and wear method has been applied to the majority of diesel engine compartments, including the piston, piston ring, bearing, crankshaft, camshaft, rocker arm, intake valve, exhaust valve, and valve spring [54]. Generally, the usage of vegetable oils and animal fats as a substitute fuel source for diesel engines has created enduring problems inside the engine due to the components' physicochemical characteristics being different. According to Mofijur et al., a significant portion of these restrictions may be overcome by emulsifying the biofuels, i.e., lowering their viscosity and surface tension to facilitate the atomisation process [125]. Nevertheless, the effect of emulsified biofuels on engine wear and friction must be investigated at both stages of engine operation, namely before and after combustion.

The chemical structure of biofuels derived from vegetable oils and animal fats comprises long-chain triglycerides and polar fatty acids. According to researchers [125–128], the chemical structure of triglycerides in biofuel has the desirable properties for a boundary lubricant. Additionally, it produces high-strength lubricant films that exhibit a strong interaction with metallic exteriors and reduce both friction and wear on the wall. Furthermore, the polarity of fatty acids aids in molecular films that provide oiliness and anti-wear protection [127]. Hence, many engine compartments that come into direct contact with emulsified biofuels may exhibit an increased lifespan. Additionally, the emulsified biofuel may serve as a lubricant for components inside the combustion chamber, such as the cylinder liner, piston ring, and gears. Nevertheless, compatibility issues need to be considered for different components as they may be made up of different materials, such as elastomers, copper, and iron. The adverse impact on components composed of various materials may result in significant wear and corrosion as a result of incompatibility or change in the emulsified biofuel's characteristics, including breakdown, pH, oxidation, and formulation quality.

When using emulsified biofuel, adverse effects on the engine such as moving piston sticking, injector chocking, filter clogging, carbon deposit formation, lubricating oil degradation, and dilution may be expected because of the biofuel's continuous phase characteristics (vegetable oil and animal fats). Despite advancements in spray features due to micro-explosion effects, specific attributes that matter when using emulsified biofuel are ignition delay, diffusion phase of combustion, vaporisation, and premixed phase. The use of blended biofuel with alcohol in an emulsified biofuel formulation is one strategy for reducing the negative effects on engines. Kumar et al. explained that when alcohol is combined with emulsified biofuels, the latent heat of vaporisation is increased, allowing for fast cooling in the combustion chamber [128]. Another investigation was conducted by Schwab et al. who discovered that after using an improper cetane number in the emulsified biofuel during formulation, carbon accumulated around the injector holes and heavy deposits formed on the exhaust valves during engine operation [129]. Another study, conducted by Liaquat et al., discovered that after a 250 h endurance test with diesel fuels and Jatropha biodiesel JB20 (20% Jatropha biodiesel with 80% diesel), some carbon deposit developed on the injector tip surface, as shown in Figure 8, and JB20 was found to increase the amount of lead deposits that accumulate in the injector nozzle [130].

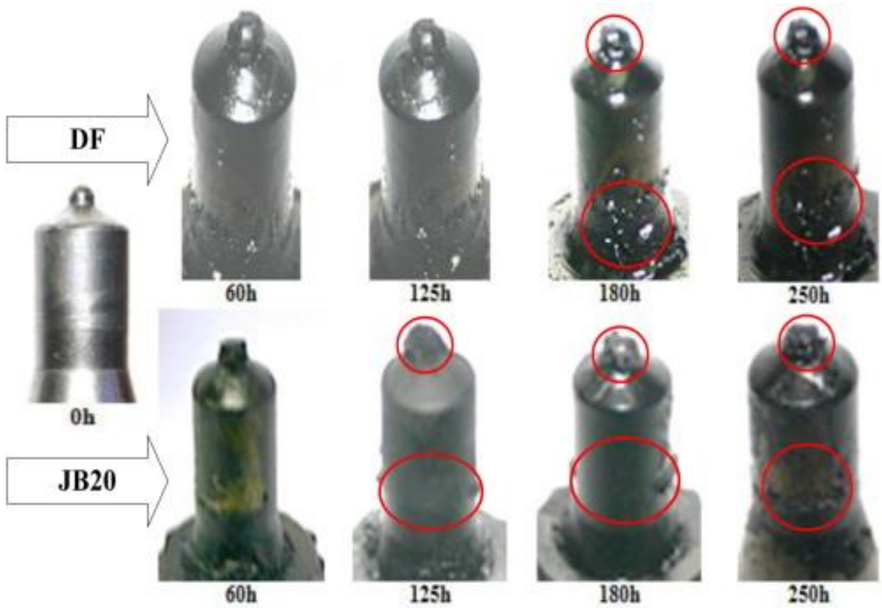


Figure 8. Image of Injector Nozzle showing carbon deposition (red circle) during an endurance Test [130].

The Engine Manufacturer Association (EMA) tested some of the emulsified biofuels [131]. In this test, the EMA recommended running the engine for 200 h and examining the engine component wear. Crookes et al. stated that engines run on emulsified biofuel were observed for surface changes caused by the engine components by means of scanning electron microscopy (SEM) [118]. They found that after running for almost one hour, the formation of carbon built up in the injector tip was considered lower than the neat biofuel. Georing and Fry inspected the consequence of biofuels on the wear of the engine before and after the run and disassembled the engine components for further examination [132]. They found that the engine produced a massive amount of carbon and lacquer on the top of the cylinder head, intake valves, and injector holes.

6. Conclusions

Biofuel has become one of the potential alternatives for the near future due to its similar physicochemical characteristics as fossil fuels and its environmentally friendly nature. However, the higher NOx, viscosity, and PM emissions associated with biofuel must be reduced by formulating emulsions. This review article discussed emulsified biofuels and the many emulsification processes used to process vegetable oils and animal fats, as these approaches are yet to be extensively assessed. The formulation and characterisation methods of emulsified biofuel investigation were the main focus of the paper. The need to stabilise the emulsified biofuel and obtain a suitable alternative fuel while minimising the adverse implications on engine functionality, discharge emissions, the engine compartment's wear and tear, and long-run engine operation has been highlighted. The following points are some of the significant findings from the review:

1. Despite the various feedstocks, emulsified biofuels are possibly formulated from vegetable oils or animal fats. Some factors affect emulsified biofuel stability, such as base biofuel, surfactant, co-surfactant, HLB value of surfactant, and alcohol. A surfactant, co-surfactant, and water composition optimised for a particular base biofuel may result in the greatest stability, as has been documented. Additionally, microemulsions have a greater degree of stability than other kinds of emulsions.
2. The viscosity, density, and cetane number of an emulsified biofuel system increase as the water concentration increases. On the other hand, amplified water concentration decreases the heating value and flash point of emulsified biofuel. Nevertheless, emulsified biofuel is capable of improving characteristics such as the combustion rate and emission levels.
3. The reduced calorific value of emulsified biofuel results in a rise in BSFC, BP, and torque, although the gain is not substantial in comparison to diesel.
4. As a result of water presence in emulsified biofuel, ignition is delayed. At low loads, this effect reduces the peak pressure of combustion.
5. The water vaporisation in the combustion chamber operates as a heat sink. Consequently, the combustion chamber's temperature will be decreased, and accordingly, NOx will be reduced.
6. The phenomenon of micro-explosion has been found to lower the BSFC and improve the engine brake thermal efficiency (BTE).
7. Using emulsified biofuel improves injection and atomisation due to the micro-explosion effect the instant emulsified biofuel droplets make their way into the combustion chamber.
8. The emulsified biofuel reduced the emissions of HC, CO, PM, CO_2, and NOx in comparison to conventional diesel fuel.

7. Recommendations

Comprehensive application-oriented studies in this potential area of research need to be carried out to enhance the emulsified biofuel's stability properties. Focus-oriented and concentrated studies into emulsified biofuels could assist in improving their applicability in commercial vehicles. Emulsified biofuel can be a viable alternative to conventional diesel, and its development indirectly contributes to environmental and economic progress. The following suggestions for further research on emulsified biofuel are recommended.

- The method and procedure for making emulsified biofuel ought to be cost-effective, simple to manage, efficient, and stable in formulation.
- The major drawback of emulsified biofuel lies in its reduced calorific value. This problem needs to be addressed by an extensive study on additional additives to improve energy efficiency.
- The advantages and disadvantages should be clearly emphasised in the areas of ignition delay and heat sink effectiveness.
- Additional research is needed to overcome the constraints associated with reduced BP and torque with regard to emulsified biofuels.
- Despite the emulsified biofuel being irrelevant to engine corrosion, further explanation is still needed regarding the phenomenon of water vapour formation when it condenses in the combustion chamber. Thus, corrosion analysis must be performed on the cylinder wall.
- Due to differences in the density of water and biofuel, emulsified biofuels result in better injection. Thus, an in-depth review of the findings is required to estimate the improvement in the extent of injection.

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Nomenclature

Abbreviations	**Description**
CI	Compression ignition
BTE	Brake thermal efficiency
HRR	Heat release rate
HC	Hydrocarbon
CO	Carbon monoxide
CSOME	Cottonseed oil methyl ester
NOx	Nitrogen oxides
PM	Particulate matter
SOx	Sulphur oxides
HC	Hydrocarbons
CO_2	Carbon dioxide
CR	Compression ratio
COME	Coconut oil methyl ester
BSFC	Brake specific fuel consumption
HLB	Hydrophilic-lipophilic balance

Abbreviations	Description
W/O	Water in oil
O/W	Oil in water
G_f	Gibb free energy
EMA	Engine manufacturer association
GHG	Greenhouse gas
IEA	International energy agency
EGT	Exhaust gas temperature
MRPR	Maximum rate of pressure rise
IC	Internal combustion

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