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Review

Technical Implications of the Use of Biofuels in Agricultural and Industrial Compression-Ignition Engines with a Special Focus on the Interactions with (Bio)lubricants

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Abstract: The environmental sustainability of agricultural and industrial vehicles, as well as of the transportation sector, represents one of the most critical challenges to the sustainable development of a nation. In recent decades, compression-ignition engines have been widely used in on-road and off-road vehicles due to their better fuel economy, autonomy, compactness, and mechanical performance (spec. the high torque values). Due to the consistent environmental impact of fossil fuels, scientists are searching for alternative energy sources while preserving the beneficial features of diesel engines. The utilization of blends of diesel fuel, biodiesel, and bioethanol fuel (referred to as "ternary blends") is among the most promising solutions for replacing fossil fuels in the near term, allowing, at the same time, us to continue using existing vehicles until new technologies are developed, consolidated and adapted to the agricultural and industrial sector. These ternary blends can lower exhaust emissions without creating major problems for existing fuel-feeding systems, typically designed for low-viscosity fossil fuels. One of the concerns in using liquid biofuels, specifically biodiesel, is the high chemical affinity with conventional and bio-based lubricants, so the main parameters of lubricants can vary significantly after a long operation of the engine. The comprehensive literature review presented in this article delves into the technical challenges, the main research pathways, and the potential solutions associated with the utilization of biofuels. Additionally, it investigates the emerging application of nanoparticles as additives in lubricants and biofuels, highlighting their valuable potential. This study also discusses the potential implementation of bio-ethanol in ternary blends, offering a promising avenue for reducing reliance on fossil fuels while maintaining engine efficiency.

Keywords: compression-ignition engines; biodiesel; biofuels; alternative energy; lubricants; nanoparticles

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1. Introduction

There are three main issues that humanity is currently dealing with from the perspective of heavy-duty applications in the industrial and agricultural sector: (1) reduction in greenhouse gas (GHG) emissions and global warming; (2) individuation of renewable or sustainable energy sources; and (3) granting of energy security. As a result, in October 2014, "*the European Council adopted a binding target for the European Union (EU) of at least a 40% domestic reduction in greenhouse gas emissions by 2030 compared to 1990*". In addition, "*a binding EU target of at least 27% has been set for the share of renewable energy consumed in the EU in 2030; And an EU-wide target of at least 27% improvement in energy efficiency has been set by 2030, against future energy consumption projections based on current benchmarks*" [1].

This is an indication that the use of fossil fuels in the energy sector is not sustainable and alternative solutions have to be developed. Therefore, scientists are seeking alternative and renewable fuel sources that are acceptable to the environment. The most significant category of alternative fuels is biofuels, which are particularly aligned with the principles of a circular economy. This economic model emphasizes the importance of reusing and recycling materials, designing out waste, and extending the lifecycle of resources [2]. Currently, there is a great deal of potential because of new biofuel manufacturing techniques that adhere to these principles. The utilization of vegetable oils as a substitute fuel dates back to the 1930s, and research has shown that these oils are useful for short-term use because the high viscosity of these oils leads to thickening of the lubricating oil and excessive carbon deposition in the long term. Then, in 1980, sunflower oil ester experiments were conducted as a fuel in diesel engines. However, the recent energy crisis has again drawn attention to alternative fuels that can be produced locally, fostering a circular economy perspective. Vegetable oil-based biofuels seem to be a great replacement for fossil fuels. Their manufacturing is rather straightforward, and they embody the circular economy's goals by being less harmful, recyclable, biodegradable, and benzene-free [1,3–5].

The transesterification reaction significantly reduces the viscosity [6] and improves the physical properties of vegetable oils as a fuel in a compression-ignition engine. The research also showed that ester fuels increase the volume transfer by the injection pump and reduce internal pump leakage [5].

In 1983, some researchers investigated the dynamometer test of direct injection diesel engines with 100% soybean oil ethyl ester as fuel and six different lubricants. They showed that the degree of ester contamination of crankcase lubricants is inappropriately high, causing serious engine damage due to the consequent insufficient lubrication caused by the loss of viscosity. The corrosion of copper/lead bearing in the engine was also observed. When using 100% ester fuels commercially, the only way to ensure reliable lubrication is to reduce oil change intervals. The performance of soy esters in terms of power, smoke, and fuel economy is reasonable, but the negative effects on lubricants must be mitigated [5,7]. Some authors have mentioned that the presence of fuel in oil increases the risk of "crankshaft explosion". Depending on the kind of impurities, factors like the age of the lubricant, the progressive removal of additives, and the presence of pollutants like water, combustion products, heavy fuel oil (HFO), diesel fuel, or biodiesel may all affect how viscous the lubricant is [8].

Numerous nations, including those within the European Union, are markedly increasing their utilization of biodiesel in response to concerns about energy security, environmental regulations, and the escalating costs of fossil fuels [9]. Germany exported around 2.34 million metric tons (more than 700 million gallons) of biodiesel in 2022. EU nations made up the majority of German biodiesel's customers, with the Netherlands, Poland, and Belgium at the top of the list. The German government introduced new biofuel legislation in May 2021, requiring fuel producers to significantly increase the usage of biodiesel, bioethanol, and biomethane in the transportation sector to meet the law's carbon emission reduction targets. The Italian ENI biorefinery located in Porto Marghera (province of Venice, Veneto region, northern Italy) serves as a notable example of converting a traditional refinery into a biorefinery, marking a significant milestone in the world. ENI S.p.A. company (Rome, Italy), in 2022, furthered its commitment to the development of new decarbonization products and services, aligning with the growing focus on renewable energy sources and sustainability. As the pricing of petroleum products fluctuates, biodiesel is becoming increasingly cost-effective, indicating that it will likely comprise a larger share of transportation fuel in the future [10].

In contrast to its benefits, biodiesel has drawbacks for engines and lubricating oils. The two main problems of using biodiesel in compression-ignition (CI) engines are poor cold flow properties and thermal stability. The weak cold flow characteristic of biodiesels affects the engine startability at sub-zero temperatures [11]. Considering the effect of biodiesel on engine function and engine lubricant, its main disadvantages are its incompatibility with certain materials, the tendency to deposit in injector nozzles, corrosion, etc. When using biodiesel in concentrations below 20% in volume, the effects of the items mentioned above are significantly reduced. Due to its properties, it tends to accumulate in the crankshaft, which leads to a dilution of the engine lubricant. Oxidation processes that occur due to the presence of biodiesel in lubricant lead to deposition and corrosion of non-ferrous metals. Diluting the lubricant too much can cause engine performance problems. Biodiesel buildup in lubricant causes viscosity to decrease, oxidation products to accumulate, deposits to form, and low-temperature qualities to deteriorate [12].

The purpose of this study is to discuss the main challenges in internal combustion engines when using biofuels, in particular concerning the long-term effects on the lubricants. So, after a classification of biofuels and an explanation about the reasons for their utilization in heavy-duty agricultural and industrial engines, a general summary of the technical solutions provided so far to overcome the illustrated problems are provided and discussed. The disadvantages and consequences of the interaction of biofuels with lubricants are among the issues highlighted in this review together with some possible drivers for future research initiatives.

2. Global Trends in Scientific Publications on Biofuels

A comprehensive analysis of global scientific publications (NB: properly referred to as "scientific research articles") about biofuels, aimed at highlighting studies about their possible interactions, e.g., with lubricants/biolubricants, and modifications of them, e.g., by adding nanoparticles, was performed through Scopus search engine. Proper logical connectors (AND, OR) and curly brackets, in accordance with the syntax of that search engine, were used to put a chosen set of keywords in reciprocal relation and allow that search engine to scan within the abstracts, the titles, and the keywords of all the articles in its database. Specifically, four main searches were performed (reference periods were indicated by Scopus and started from the year of publication of the first document found):

(a) biodiesel OR {biodiesel blends} OR {biodiesel/diesel} OR bioethanol OR biofuel OR {ternary fuel blends}, obtaining 92,628 articles in the period 1974–2024 (i.e., 51 years);
(b) (lubricant OR biolubricant) AND (biodiesel OR {biodiesel blends} OR {biodiesel/diesel} OR bioethanol OR biofuel OR {ternary fuel blends}), obtaining 504 articles in the period 1995–2024 (i.e., 30 years);
(c) (nanoparticles OR nanofuels) AND (biodiesel OR {biodiesel blends} OR {biodiesel/diesel} OR bioethanol OR biofuel OR {ternary fuel blends}), obtaining 2578 articles in the period 2000–2024 (i.e., 25 years);
(d) (lubricant OR biolubricant) AND (nanoparticles OR nanofuels) AND (biodiesel OR {biodiesel blends} OR {biodiesel/diesel} OR bioethanol OR biofuel OR {ternary fuel blends}), obtaining 20 articles in the period 2011–2024 (i.e., 14 years).

The result of this analysis is represented through some graphs illustrating, respectively, the number of publications over the years and the absolute numbers of publications ascribable to the first 10 contributing countries at a world scale (Figure 1). Furthermore, a Venn diagram is also reported here (Figure 2) to allow for a better understanding of the numerousness of articles presenting specific sets of keywords (and combinations of these ones) in their abstracts, titles, or keywords.

As can be seen from the figures, the keywords "nanoparticles OR nanofuels" provide the highest number of articles, followed by "biodiesel OR {biodiesel blends} OR {biodiesel/diesel} OR bioethanol OR biofuel OR {ternary fuel blends}" (search "a"), underlining a high interest of the scientific community on the related topics (710,529 and 92,628 articles, with trends substantially constant over the last 8–10 years). If looking at the documents presenting both these two sets of keywords (search "c"), the magnitude order is, instead, much lower (by two orders of magnitude: 2578 articles), indicating that the possible interactions between nanoparticles and biofuels are only recently being investigated by scientists, but the interest is increasing quickly (as witnessed by the increasing trend in Figure 1c). Also, the interactions between lubricants and biofuels (keywords "(lubricant OR biolubricant) AND (biodiesel OR {biodiesel blends} OR {biodiesel/diesel} OR bioethanol OR biofuel OR {ternary fuel blends})"; search "b") have been investigated in relatively few studies (only 504 articles). Also, in this case, the trend is increasing, even if the slope is lower than the slope of search "c". Finally, the articles presenting all of the previously listed keywords ("(lubricant OR biolubricant) AND (nanoparticles OR nanofuels) AND (biodiesel OR {biodiesel blends} OR {biodiesel/diesel} OR bioethanol OR biofuel OR {ternary fuel blends})", search "d") are very few, only 20, indicating a subtopic that is only at its initial development. In all the illustrated cases, among the first five contributors, there are always the most populous countries, particularly (in decreasing order of population according to Wordometer) India, China, and the United States of America. It is worth noting that this fact is not particularly significant for the particular interest of these nations in these topics: due to their population, indeed, they have a large number of universities and scientists. Instead, if considering the population of those countries (India and China have about 4.25 times the population of the USA), with the publications normalized over the population, it seems that these topics are of major interest amongst USA academicians.

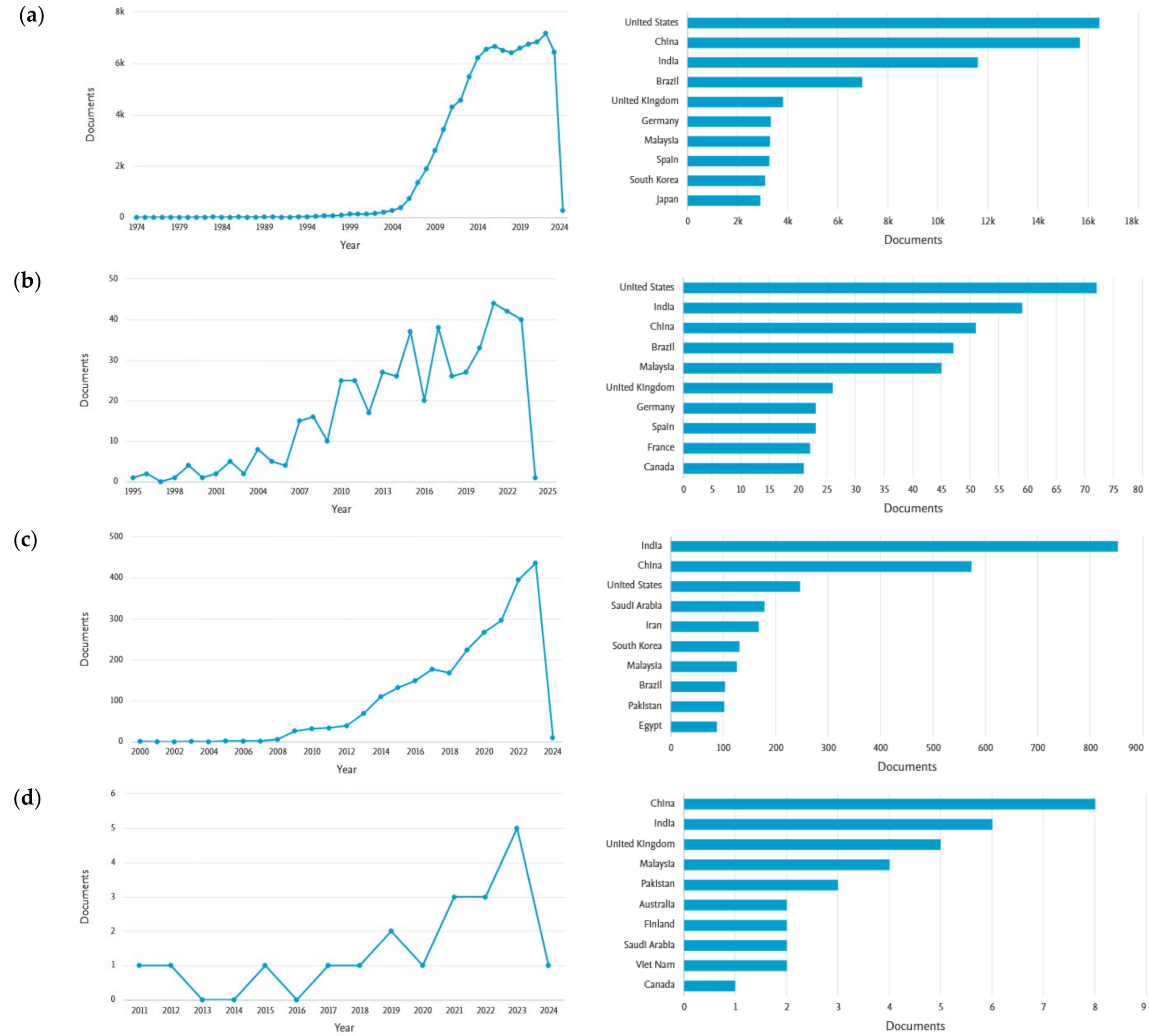


Figure 1. Results of the literature review. The two graphs in each row (left: global trend in publications; right: absolute number of publications from the first 10 contributors at the world scale) refer to the four enquiries presented in the text: (**a**) "biodiesel OR {biodiesel blends} OR {biodiesel/diesel} OR bioethanol OR biofuel OR {ternary fuel blends}"; (**b**) "(lubricant OR biolubricant) AND (biodiesel OR {biodiesel blends} OR {biodiesel/diesel} OR bioethanol OR biofuel OR {ternary fuel blends})"; (**c**) "(nanoparticles OR nanofuels) AND (biodiesel OR {biodiesel blends} OR {biodiesel/diesel} OR bioethanol OR biofuel OR {ternary fuel blends})"; (**d**) "(lubricant OR biolubricant) AND (nanoparticles OR nanofuels) AND (biodiesel OR {biodiesel blends} OR {biodiesel/diesel} OR bioethanol OR biofuel OR {ternary fuel blends})".

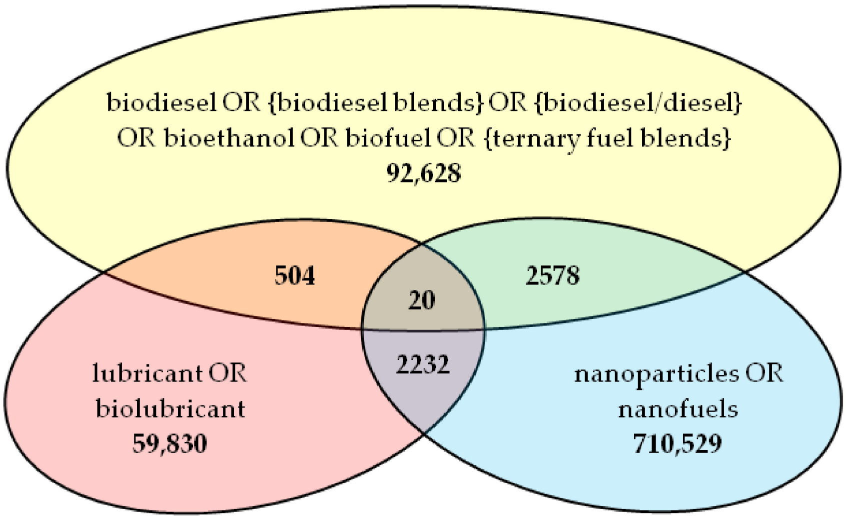


Figure 2. Number of scientific articles presenting specific sets of keywords in their abstracts, titles, or keywords. Intersecting areas can be inquired using the "AND" logical connector. With reference to the list in the text, the yellow domain corresponds to the (a) search, the intersection between yellow and red domains corresponds to the (b) search, the intersection between yellow and blue domains corresponds to the (c) search, and the intersection among yellow, red, and blue domains corresponds to the (d) search.

3. Why Biofuels Are Used in Agricultural and Industrial Heavy-Duty Engines

A viable alternative to liquid fossil fuels must manage the so-called "Energy trilemma" competitive features, which are defined based on three main dimensions: (a) energy security, (b) energy equity, and (c) environmental sustainability. The uninterrupted availability of energy resources at an affordable price is important from an economic point of view, which actually defines "energy security", so energy security means its availability, its compatibility with the environment, and its reasonable price, which leads to economic development [13–15]. Expanding the use of renewable resources, namely liquid biofuels for the application in Internal Combustion Engines (ICEs), also improves the energy autarchy and reduces the dependence on other countries [16]. The significance and consequences of using biofuel alternatives may be related to the following factors:

1. By employing more renewable fuels produced locally, concerns about the dependency on fossil fuels may be allayed [17].
2. It is possible to enhance the energy and environmental performance of the ICE, due to some superior physical and chemical characteristics of alternative fuels as compared to fossil fuels [1,18,19]. Notwithstanding some fossil fuels (e.g., diesel fuel) have a higher lower heating value than biodiesel and vegetable oil, this metric alone does not capture the full advantages brought by biofuels to engine performance and environmental impact. Biofuels, such as biodiesel, indeed, offer several advantages, including renewability, biodegradability, and lower emissions of greenhouse gases during combustion. These attributes contribute to a reduced environmental footprint and increased energy security, which are critical considerations in the transition towards sustainable energy sources.
3. Biodiesel and alcohols have higher oxygen content compared to diesel fuel. This characteristic ensures the promotion of complete combustion [20]. Unfortunately, this characteristic can also result in the faster degradation of some properties of lubricant and materials coming into contact with biofuels, due to an increased solvency characteristic of higher blending rates. The search for a trade-off highlights the need for ongoing research to optimize biofuel formulations and engine designs to mitigate these effects.

4. The maximum heat release rate (HRR) is kind of lower for biodiesel–diesel–ethanol blends and rises with the ethanol proportion in diesel–ethanol blends [1]. In diesel–ethanol blends, the ignition delay rises as the ethanol proportion rises, while it falls marginally in biodiesel–diesel–ethanol blends or when a cetane number (CN) improver is added [21–23]. In blends of diesel fuel and ethanol, cylinder pressure rises with increasing ethanol content, whereas it either slightly falls or remains similar in blends of biodiesel and diesel with ethanol [24,25].
5. In terms of engine performance, when compared to the use of fossil (diesel) fuel, the brake-specific fuel consumption is greater in all the investigated circumstances; the brake thermal efficiency increases or is comparable; and the expressed power is very similar to or slightly lower. Some changes in exhaust gas temperatures were noted; the indicated mean effective pressure also shows minor variations or decreases when fuel blends contain more than 35% ethanol [1,4,23–25].
6. Due to the increased demand for diesel fuel, renewable biodiesel from affordable sources, which can supply the need, is required. Realistically, the use of sustainable biodiesel in large quantities may immediately enhance engine performance and emission characteristics [26].
7. The use of biodiesel in diesel engines reduces GHG emissions, and more reductions are possible with the anticipated growth in biodiesel production and fuel consumption [27].

3.1. Classification of Liquid Biofuels Used in Agricultural and Industrial Heavy-Duty Engines

Biofuel is a sustainable fuel that, in general, may be either liquid or gaseous and is derived from biomasses [28]. Biofuels must be suitable for use with current engines and fuel specifications [29]. Biofuels used to replace non-renewable energy fuels mainly come from agricultural and vital crops, forests, and waste streams [30]. Liquid biofuels include ethanol, which may replace gasoline in many late-model vehicles, and biodiesel, which can replace diesel fuel in agricultural and industrial heavy-duty engines. For this reason, biofuels are particularly useful in supplying energy to the transportation sector [31]. Biofuels are classified into different generations based on the used feed stock and conversion method [32]. The classification of biofuels is shown in Table 1.

Table 1. Classification of biofuels based on their generation technologies [32–34].

Generation	Description	Used Feedstocks	Production Technologies	Examples
1st	Biofuels are produced using ingredients including grain, sugar, animal fats, and vegetable oils.	Sugarcane, corn, soybeans, wheat, barley	Fermentation and distillation for ethanol, transesterification for biodiesel	Ethanol, biodiesel, biobutanol, bioethanol
2nd	Often referred to as advanced biofuels, these are fuels that may be produced from several forms of (waste) biomass, including plant and animal resources.	Switchgrass, wood chips, agricultural waste, municipal waste, forest residues	enzymatic hydrolysis and fermentation for ethanol, transesterification for biodiesel	Cellulosic ethanol, biomethane
3rd	Biofuels are generated from aquatic autotrophic organisms. Microalgal organisms in particular have a superb capacity to produce important chemical and food products, which is primarily responsible for the manufacture of biodiesel.	Algae, cyanobacteria	Synthetic biology, metabolic engineering, and fermentation for hydrocarbons and biohydrogen	Algae-based biofuels
4th	It is created from modified algae even though it is still in the experimental laboratory stage. Algae are undergoing metabolic modification in this way to raise their oil content, boost their capacity to trap carbon, and improve the cultivation, harvesting, and fermentation processes. Additionally, certain species of algae biomass use metabolic engineering to increase the lipid content and accelerate growth.	Synthetic biology and genetic engineering, bioengineered cyanobacteria, yeasts, fungus, or algae	Biomethanation, and power-to-liquid technologies	Synthetic biofuels

3.1.1. Biodiesel, First-Generation Biofuels

Biodiesel is a biofuel derived from renewable sources, such as vegetable oils and animal fats. It is the result of a chemical process (transesterification of vegetable oils with ethyl or methyl alcohol) or other biological components [35]. The main issue with using bio-oils directly in conventional diesel engines is their excessive viscosity. Pyrolysis, microemulsion, dilution, and transesterification are techniques and processes that use different non-edible raw materials to reduce the viscosity of biodiesel. Transesterification is a viable process adopted so far for viscosity reduction [27]. Alkyl esters are created by the transesterification process, which involves mixing vegetable oils with alcohol to make alkyl esters in the presence of a catalyst. Methanol and ethanol are the alcohols in this process that are most readily accessible and affordable [34]. The process of transesterification to produce biodiesel is shown in Figure 3, and the physical–chemical properties of biodiesel from different feedstocks are briefly compared in Table 2.

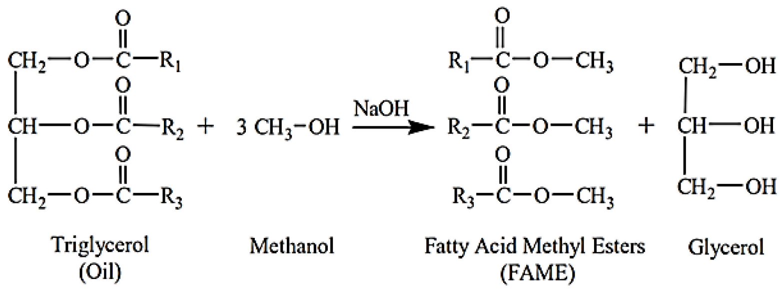


Figure 3. Process of transesterification to produce biodiesel [36].

Table 2. Physical–chemical properties of biodiesel from different feedstocks [1,37–43].

Property	Unit	Diesel (EN 590)	Soybean Oil	Canola Oil	Palm Oil	Jatropha Oil	Rapeseed Oil	Animal Fat (Tallow)	Used Cooking Oil	Sunflower Oil	SAF-Flower Oil	Yellow Grease	Coconut Oil	Corn	Cottonseed Oil	Rice Bran Oil
Density at 15 °C	[kg·L^{-1}]	0.82/0.84	0.88	0.87	0.87	0.86	0.87	0.87	0.87	0.86	0.88	0.89	0.86	0.86	0.88	0.88
Viscosity at 40 °C	[mm^2·s^{-1}]	2.0/4.5	4.1	4.4	4.5	4.5	4.4	4.2	3.6	4.2	4.1	4.8	5.5	4.1	4.1	5.1
Flash point FP	[°C]	>+55.0	+140.1	+172.3	+176.7	+175.5	+169.5	+124.0	+160.0	+180.3	+174.0	+161.0	+113.8	+171.0	+210.0	+161.0
Cloud point	[°C]	−5/+3	0	−3.25	+14.25	+5.66	−3.50	+13.00	–	+1.33	−4.00	+8.00	−1.60	−4.00	+1.70	+0.55
Cold filter plugging point (CFPP)	[°C]	−15/−5	−4	–	+9	–	−12	+13	–	−2	−6	+1	−5	−8	–	–
Cetane number, CN	[−]	>51.0	51.3	54.0	61.9	55.7	53.7	58.9	50.4	51.1	51.1	56.8	59.3	55.7	52.0	56.2
Iodine value	[g_{I2}·(100g)$^{-1}$]	–	125.5	113.6	54.0	109.5	116.1	65.9	–	128.7	141.0	89.9	18.5	101.0	120.0	102.0
Acid value	[mg_{KOH}·g^{-1}]	–	0.18	0.49	0.20	0.24	0.26	0.38	–	0.35	–	–	0.18	–	0.5	–
Sulphur content	[ppm]	<10	2	2	2	5	4	7	–	2	–	5	3	4	–	–
Pour point	[°C]	–	−3.2	−8.0	+14.3	+6.0	−11.0	+10.0	–	−2.0	−7.0	+3.0	−8.3	−2.0	−12.5	−6.8
Relative density	[−]	–	0.882	0.883	0.873	0.876	0.879	0.878	–	0.878	0.879	0.879	0.874	0.883	0.885	–
Lower heating value	[MJ·kg^{-1}]	42.7	37.0	38.9	37.3	37.7	37.6	37.2	–	35.3	–	37.6	35.2	39.9	37.5	38.7
Higher heating value	[MJ·kg^{-1}]	–	39.7	41.3	40.6	40.7	41.1	37.0	–	40.6	42.2	39.4	38.1	43.1	–	–
Average chain length	[−]	–	17.9	18.2	17.2	18.3	17.9	17.3	–	18.1	17.8	18.5	13.4	17.6	–	–
Average unsaturation	[−]	–	1.50	1.34	0.62	1.15	1.31	0.59	–	1.59	1.63	1.06	0.12	1.46	–	–
Boiling point	[°C]	–	–	–	–	–	–	–	–	–	–	–	–	–	+280/+400	–
Stoichiometric air-fuel ratio (AFR)	[−]	–	–	–	–	–	–	–	–	–	–	–	–	–	12.5	–

3.1.2. Alcohols Methanol, Ethanol, Butanol

Alcohols are typically produced chemically from coal (methanol, CH_3OH) or synthetically from plant waste (ethanol, C_2H_5OH), both of which may be made from non-petroleum sources. Due to the issue of combining alcohol with gasoline at high rates (phase separation, fuel watering, and corrosion on engine components), up to 10% to 15%, alcohol may be combined with gasoline without causing any damage to the engine. Additionally, alcohol blends boost volumetric efficiency by decreasing intake temperature as a consequence of eliminating heat from the aspired air since they have a greater latent heat of vaporization than gasoline. The characteristics of methanol, ethanol, butanol, and gasoline are summarized in Table 3 [44].

Table 3. Properties of methanol, ethanol, butanol, and gasoline [44–53].

Property	Measurement Unit	Fuel			
		Methanol (CH_3OH)	Ethanol (C_2H_5OH)	n-Butanol (C_4H_9OH)	Gasoline (C_8H15)
Density at 15 °C	[kg·m^{-3}]	791.3	789.4	809.1	750.0
Molecular weight	[kg·kmol^{-1}]	32.04	46.07	74.12	114.23
Vapor pressure	[mm$_{Hg}$]	127.0	55.0	7.0	562.5
Boiling point	[°C]	+65.0	+78.0	+117.5	+30.0/+190.0
Research octane number (RON)	[-]	110	119	–	97
Motor octane number (MON)	[-]	92	92	–	86
Cetane number	[-]	5	11	17	8
Stoichiometric AFR	[kg·kg^{-1}]	6.50	9.00	11.10	14.70
Lower heating value at 15 °C	[MJ·kg^{-1}]	19.80	26.40	33.09	41.30
Higher heating value	[MJ·kg^{-1}]	22.88	29.85	36.07	48.00
Flash point at closed cup	[°C]	+12	+13	+29	−45
Oxygen content by mass	[%]	49.93	34.73	21.58	0.00
Hydrogen content by mass	[%]	12.58	13.13	13.60	~14.00
Carbon content by mass	[%]	37.48	52.14	64.82	~86.00
Vapor density (STP)	[kg·m^{-3}]	1.42	2.06	2.60	3.88
Heat of vaporization	[kJ·kg^{-1}]	1100	838	585	180–350
Surface tension at 20 °C	[mN·m^{-1}]	22.1	22.3	24.6	21.6
Dynamic viscosity at 20 °C	[mPa·s]	0.57	1.20	2.80	0.60
Volumetric energy content	[MJ·m^{-3}]	15,871	21,291	26,795	31,746
Specific CO_2 emissions	[g·MJ^{-1}]	68.44	70.99	71.90	73.95
Auto ignition temperature	[K]	738	698	616	465/743
Adiabatic flame temperature	[K]	2143	2193	2262	~2275

One of the most popular chemical compounds employed as a hydrogen transporter is methanol (CH_3OH), which is a simple oxygenated hydrocarbon (also known as methyl alcohol and wood alcohol). Its symbol is MeOH and it is the simplest aliphatic alcohol [54–56]. ICEs and direct methanol fuel cells (DMFCs) may both utilize methanol, which is regarded as the most desired alternative fuel as a replacement for gasoline. M85 (85% methanol, 15% gasoline) and M10 (10% methanol, 90% gasoline) are common methanol blends [44,55]. The following is a summary of the issues raised by the usage of methanol in internal engines:

1. Strong corrosive effect on metal parts: Figure 4 summarizes the scanning electron microscopy (SEM) images taken of the engine components' surfaces before and after they were exposed to fuel samples for 180 days. The photographs demonstrate that the polished surface of the pistons has less corrosion damage than the surface exposed to fuel samples [57].
2. The formation of formic acid and carbonic acid due to the reaction of its wastes with carbon dioxide and water in the car exhaust [44,58].
3. Reduction in HC and CO exhaust, while NO_x emission and formaldehyde formation increase 5 times (when using M85 fuel) [44].

4. Because of its propensity to react with water and separate from petrol, it results in a heterogeneous combination.
5. It causes irregular operation of the engine if not properly regulated because this heterogeneous mixture has a different air-to-fuel ratio [44,55].

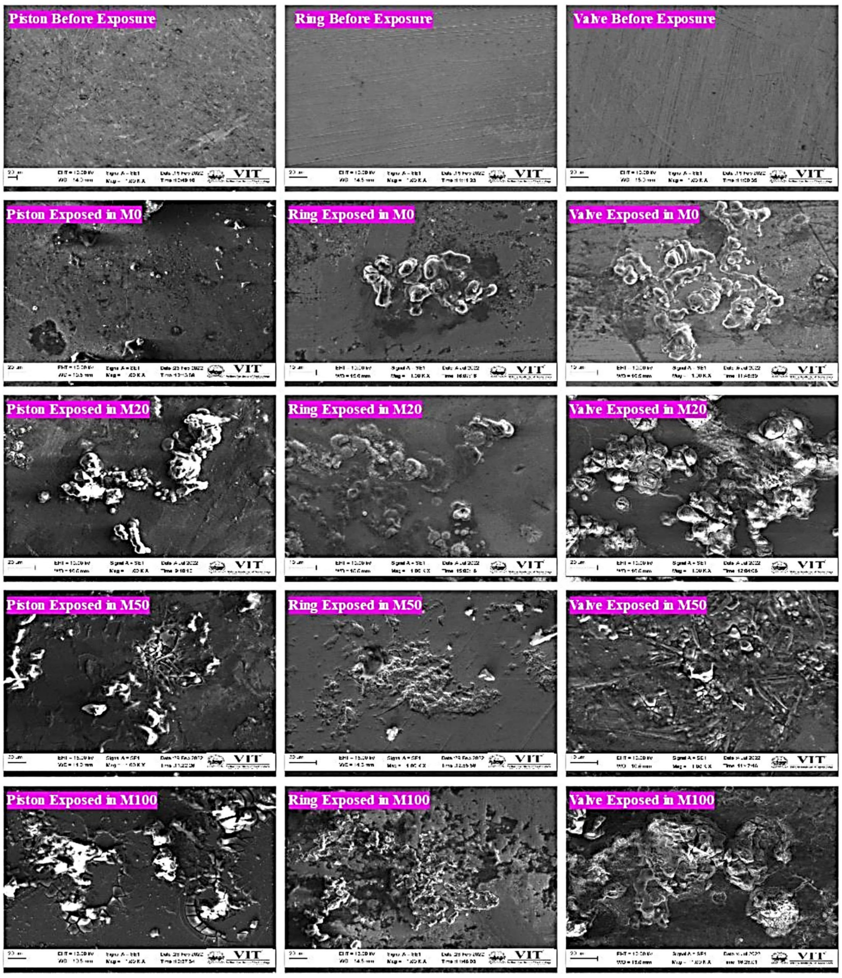


Figure 4. SEM images of metal samples before and after being exposed to fuels.

Ethanol with the chemical formula C_2H_6O (abbreviation of EtOH: ethyl alcohol, also called grain alcohol, drinking alcohol, or simple alcohol) is an organic compound. Ethanol is produced naturally through the fermentation process of sugars by yeasts or through petrochemical processes such as ethylene hydration [59]. The fuel blend of ethanol, e.g., E85 (85% ethanol, 15% gasoline) and E10 (10% ethanol, 90% gasoline), are broadly used. E10 fuel blend is also known as "gasohol" [44]. Butanol (C_4H_9OH), commonly known as butyl alcohol, is a four-carbon alcohol that is largely employed as a solvent and as an intermediary in chemical synthesis. It may also be used as a fuel. Biobutanol, which may be either n-butanol or isobutanol, is the term for butanol produced biologically. By fermenting biomass, particularly wood waste that is enriched in cellulose, butanol may be obtained [60]. The advantages of butanol compared to other alcohols (methanol and ethanol) are as follows [44]:

1. Higher cetane number;
2. Lower corrosion;
3. Lower ignition temperature;
4. Lower evaporation enthalpy [61].

3.2. The Main Fluid Dynamic and Thermodynamic Properties of Fuels for ICEs

Several fluid dynamic and thermodynamic properties of a fuel can significantly impact the performance of ICEs. One such property is viscosity, which affects the behavior of fuel injection. As the ambient temperature decreases, the viscosity increases, so measures must be taken to prevent a reduction in the engine performance. Higher viscosity of fuel leads to poor atomization and weak evaporation of fuel, larger droplets, and more penetration of fuel spray into the cylinder, in particular during cold starts at low temperatures. As the study [1] has shown, on the other hand, a high viscosity also reduces the fuel flow rate and causes insufficient fuel delivery. Very high viscosity has effects such as pump disturbance, bad combustion, more diffusion, and increased engine lubricant dilution, which were reported in this study.

Density is also one of the properties that increase with decreasing temperature. Higher density means that the same volume of injected fuel corresponds to a greater mass, which affects the air-to-fuel ratio and the total energy content inside the cylinder; all these phenomena happen at low ambient temperatures and during cold starts [1]. Cetane number is a measure of fuel ignition delay time in diesel engines and, hence, is related to the quality characteristics of fuel combustion and auto-ignition in the engine. It also affects the cold start of the engine [1]. Using fuels with a higher cetane number accelerates the ignition process, resulting in a shorter engine start-up and reduced cranking time. The volatile properties are described by the vapor and distillation pressure curves. Evaporation characteristics have an effect on the structure of the spray, which has consequences on the air–fuel mixture [62]. Distillation properties have a significant effect on fuel spray penetration and mixture formation [63]. The flash point (FP) temperature of a petroleum product is the lowest temperature (at a pressure of 101.3 kPa) in which the substance vapors (fuel) form a combustible mixture with air so that, by bringing a small flame close to it, it ignites and extinguishes almost instantaneously. The more volatile the fuel, the lower the FP [62]. Low FP is needed for safety and better fuel transfer. The three characteristics of fuel that affect the performance of CI engines in cold ambient temperatures are as follows: the cloud point (CP) is the lowest temperature at which the first crystals start to form, solid fuel particles start to emerge, and clear liquid begins to cloud. The term "Cold Filter Plugging Point" (CFPP) refers to the lowest temperature (°C) at which, under certain circumstances, a given amount of diesel fuel will still flow through a standardized filtration system at a given time [64]. The lowest temperature at which a liquid, particularly a lubricant, flows under certain circumstances is known as the pour point (PP) of that liquid (i.e., the temperature beyond which the oil can be easily pumped) [62]. Low-Temperature Flow Test (LTFT) was conducted in the United States and Canada to predict fuel performance at low temperatures. The type of fuel for an engine should be selected according to the seasonal characteristics and weather of that region. Lower and higher heating values of fuel (LHV and HHV) are the amounts of heat that are released from burning fuel at a certain temperature and pressure by considering or not considering the heat used to vaporize water [65,66]. It is very important to develop a model and technique to measure LHV and HHV of compounds. The water content of a fuel is an important factor that can lead to clogging the flow of fuel to the engine at low temperatures. It is highly suggested that the fuel must be free of water. Other disadvantages of water in fuel include increased corrosion, acceleration of oxidation, and strengthening of microbial growth [67].

4. Lubrication and Complications of Interaction of Biofuels with Lubricants

Lubrication is a method in which the use of chemicals (lubricants) reduces the wear of surfaces in relative movement with each other and improves pressure transfer between opposite surfaces. Lubricants, (anti-friction agents) whose quality and type play a key role in reducing friction, support better performance of the device and reduce frequent breakdowns [68]. An excellent lubricant should have features such as a high boiling point, a low freezing point, a high viscosity index, strong thermal stability, hydraulic stability, corrosion resistance, and high oxidation resistance. Furthermore, the lubricant reduces the temperature in the metal contact areas [69] and, therefore, also contributes to cooling the hot parts. One of the important uses of lubricants is as motor oil for gasoline and diesel engines. They mainly reduce the friction and wear of materials between moving parts, thus improving the efficiency of equipment and machinery and playing a significant role in saving fuel and energy. One of the factors that have a negative effect on lubricants is temperature. Increasing the temperature reduces properties such as viscosity and can degrade the lubricant [70–73]. Contamination agents and wear particles of metal parts are other factors that deteriorate the lubricant's performance. Lubricants lose their properties with increasing time and decreasing desirable properties, so they should be replaced periodically with new lubricants. The two main reasons why lubricants are unsuitable for further use include the accumulation of pollutants and their chemical changes, while their base oil does not deteriorate and is only contaminated [74].

Their base oil is mostly vegetable oils or synthetic liquids (hydrogenated polyolefins, esters, silicones, fluorocarbons, etc.). Lubricants generally include 90% base oil and 10% additives, i.e., components that are able to reduce friction and wear, increase viscosity, and improve their overall resistance to corrosion, oxidation, ageing, and pollution [75].

The classification of lubricants depends on the type of source and its properties, and they are generally synthesized from two different sources of base oil. As shown in Figure 5, biological and non-biological sources are two sources of base oil that have different properties and uses [76].

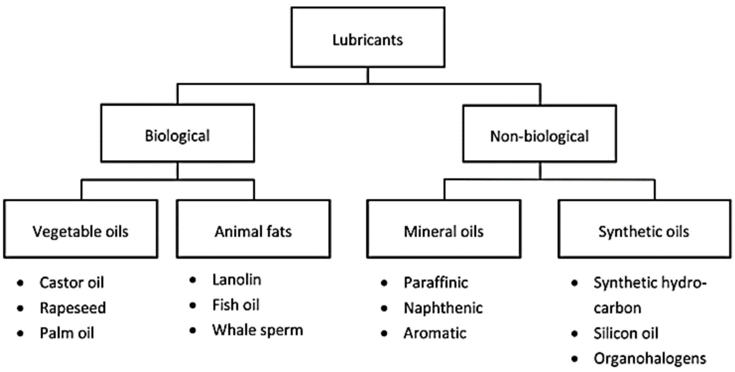


Figure 5. Classification of lubricant sources [77].

4.1. Non-Biological Lubricants

Non-biological or conventional lubricants are made from mineral or synthetic oils. In particular, mineral oil is a petroleum product used as a lubricant in the automotive, railway, and aviation industries, as well as cosmetic and health products [78]. Synthetic lubricant is a type of lubricant that is composed of chemical compounds (chemically modified petroleum components) that are synthesized artificially. Crude oil is the most common raw material, which is converted into a lubricant by distillation and then physically and chemically modified. Synthetic lubricants have an exceptional performance compared to conventional lubricants based on mineral materials [79]. In the comparison between synthetic and mineral lubricants, many advantages can be mentioned for synthetic lubricants, for example, better fluidity at low temperatures, oxidation stability, and thermal stability. The disadvantages of synthetic lubricants include higher prices (two to four times of mineral lubricants), as well as an increased risk of additive precipitation due to cold storage [80,81].

4.2. Biological Lubricants

Biolubricants represent a category of lubricants generated from renewable sources such as vegetable oils and animal fats, which may contain triglyceride esters but can also contain other bio-based chemicals. The most common oils for biolubricants are vegetable oils such as high oleic canopy oil, castor oil, palm oil, sunflower oil, canola oil, and so on [82]. Different applications of vegetable oils are shown in Table 4. As the studies reported in the cited table show, one of the most common applications of vegetable oils is lubrication. Biolubricants that have been synthesized from vegetable oils have higher levels of lubrication. Also, the flash point, volatility, and viscosity index show higher levels than conventional lubricants. Table 5 provides a general comparison between mineral oils and vegetable oils.

Table 4. Various vegetable oils and their applications [68,83–85].

Vegetable Oil	Major Applications in Industry
Soybean Oil	Lubricant, hydraulic fluid, plasticizers, printing inks, pesticides, disinfectants, and in the manufacture of soap, plastics, and synthetic rubber.
Canola Oil	The production of biodiesel and as a lubricant in the food industry. Hydraulic oils, tractor transmission fluids, metalworking fluids.
Palm Oil	The production of soaps, candles, and as a lubricant in the textile and machinery industries.
Sunflower Oil	The production of paints, varnishes, and as a lubricant in the machinery industry. Grease, diesel fuel substitutes.
Peanut Oil	Lubricant in the machinery and textile industries, and in the production of soaps and cosmetics.
Olive Oil	Automotive lubricants. The production of soaps and as a lubricant in the food industry.
Coconut Oil	The production of soaps, cosmetics, as a lubricant in the food industry, and engine oils.
Flaxseed Oil	The production of paints, varnishes, and as a lubricant in the machinery industry.
Corn Oil	The production of biodiesel and as a lubricant in the food industry.
Cottonseed Oil	The production of soaps and as a lubricant in the machinery and textile industries.
Rapeseed Oil	The production of biodiesel and as a lubricant in the machinery industry. Air compressor-farm equipment.
Sesame Oil	The production of soaps, cosmetics and as a lubricant in the food industry
Castor Oil	The production of soaps, cosmetics, and as a lubricant in the machinery industry. Gear lubricants, greases.
Grape seed Oil	The production of paints, varnishes, and as a lubricant in the machinery industry.
Rice Bran Oil	The production of biodiesel and as a lubricant in the food industry. Cosmetics, soap making.
Tallow oil	The production of candles, soaps, lubricants, plastics.
Cuphea oil	Used in cosmetics and personal care products, motor oil.
Crambe oil	Lubricant and industrial lubricant. Intermediate chemicals, surfactants
Jojoba oil	Used in cosmetics, personal care products, and as a lubricant.
Linseed oil	The production of paints, varnishes, stains, and lacquers.
Safflower oil	Used in cosmetics, personal care products, and as a lubricant.

Table 5. Comparison between mineral oils and vegetable oils [69,86–88].

Characteristics	Vegetable Oils	Mineral Oils
Source	Extracted from seeds, nuts, or fruits of plants	Derived from petroleum
Chemical structure	Complex mixtures of fatty acids, triglycerides, and other compounds	Complex mixtures of hydrocarbons
Density @ 20 °C ($kg\cdot m^{-3}$)	910–940	820–900
Viscosity index (-)	80–220	95–105
Pour point (°C)	−15 to −30	−15 to −60
Flash point (°C)	>150	>150
Oxidation stability	Neutral	Stable
Hydrolytic stability	Not stable; can break down in the presence of water	Stable
Cold flow behavior	May solidify or become thicker at low temperatures	Less affected by low temperatures
Solubility in water	Insoluble	Insoluble
Sludge forming tendency	Can form sludge when exposed to air and moisture	Minimal sludge formation
Seal swelling tendency	Slender	Slender
Shear stability	Stable	Stable
Environmental impact	Renewable, biodegradable, and less harmful to the environment	Non-renewable, non-biodegradable, and can have a negative impact on the environment

Biolubricants are biodegradable, have good thermal stability (higher heat content than mineral oil) and low pour and cloud points, and contain a large amount of unsaturated fatty acids and minimum sulphur content [89]. According to the literature [68,83,89,90], biolubricants can effectively replace mineral lubricants in many applications. Their applications include gearbox oil, hydraulic oils, engine oils, two-stroke engine lubricants, tractors, insulation oils, aircraft oil, grease, metal grinding oils, or multipurpose oils [88].

Environmental worries and constraints towards conventional lubricants have led to a wider use [91] of biological lubricants that are environmentally friendly and produced from non-edible plant resources. Furthermore, biolubricants are also potential candidates for automotive applications notwithstanding the severe service conditions they undergo in an internal combustion engine [69].

The experimental results in a research study showed that after comparing rapeseed-based biolubricant and synthetic lubricant, both of which were contaminated with biodiesel, in the same operating conditions, the performance of biolubricant was reported to be better in terms of wear and friction [92]. Vegetable oils can be a source of alternative lubricants. Among the advantages of biolubricants, we can mention renewability, compatibility with the environment, biodegradability, and less toxicity [93]. Transesterification may address the shortcomings of vegetable oils as biolubricants, particularly the higher viscosity if not processed as indicated. The most notable drawbacks of vegetable oils used as lubricants include poor performance at low temperatures, low oxidation, thermal stability, and gummy effect [94,95]. One of the technical issues and the most important features of biolubricants is their viscosity range, which should be improved, and for that improvement, environmentally friendly viscosity modifiers are suggested. Styrene–butadiene–styrene (SBS) and ethylene-vinyl acetate (EVA) copolymers were utilized to expand the range of viscosity in biolubricants, which improved and increased kinematic viscosity between 150–250 cSt and 26–36 cSt at 40 °C and 100 °C temperatures [96]. The tribological properties of a biolubricant formulated by jatropha oil (10–50% by volume) with base lubricant SAE 40 were investigated. The blend of jatropha oil with base lubricant performed very well as a biolubricant additive. The results showed that the addition of 10% jatropha oil in the base lubricant had the best performance in terms of reduction in wear, friction coefficient, viscosity, increase in temperature, wear scar diameter, and flash temperature parameter [97].

4.3. Important Properties for Lubricating Oil Performance

The performance of lubricating oil is affected by numerous crucial characteristics. These characteristics are necessary to guarantee efficient lubrication and protection of equipment and engines. Among the essential characteristics are the following:

- **Viscosity**. The most important characteristic of lubricants, which is measured as the fluid resistance to flow, directly related to the minimization of friction losses, is viscosity. The viscosity of the lubricating oil in an engine can decrease or increase due to the dilution operated by the fuel and according to the type of fuel used (diesel fuel causes it to decrease and heavy diesel fuel causes it to increase) [98]. Another factor that increases viscosity is oil aging due to progressive oxidation and thermal degradation [99]. One of the effects of too-high viscosity is an excessive resistance to flow, and one of the effects of too-low viscosity is the excessive wear of moving organs due to the lubricant film not being preserved between the moving surfaces [98,100]. In general, increasing the temperature of the lubricant leads to a decrease in viscosity [101], but, if the viscosity index is high (above 200), that lubricant has an outstanding advantage because, in this case, the viscosity will not be affected by temperature [102].
- **Thermal stability**. Thermal stability is another essential lubricant property, especially when vegetable oil is used as a lubricant under high-temperature conditions. The onset temperature, which can be defined as the temperature at which lubricant begins to decompose, determines thermal stability. Thermal stability is primarily determined by the chemical composition and fatty acid composition (FAC) of a hydrocarbon [103,104].

- **Oxidation resistance**. Oxidation is a chemical reaction that occurs when oil is exposed to oxygen and heat, resulting in thickening of the oil, sediment formation, and acidity. To preserve its efficacy and prevent engine or machinery damage, lubricating oil should have a high oxidation resistance [105].
- **Wear protection**. Strong film-forming lubricants can efficiently separate contact surfaces, resulting in minimal wear of interacting surfaces and low friction in mixed and boundary lubrication regimes. Therefore, the indicators of wear and friction are necessary to comprehend a lubricant's efficacy [106].
- **Corrosion and rust protection**. Metal surfaces should be protected by lubricating oil from rust and corrosion brought on by moisture or acidic combustion by-products. It ought to have additives that provide a barrier of defense against the development of corrosive chemicals [107,108].
- **Foam resistance**. One of the most fundamental physical properties of lubricants is their resistance to foam formation. In the formulation of a lubricant, detergent and anti-oxidation additives may contribute to the formation of foam. Foaming results in discontinuous lubrication, and the addition of anti-foaming agents prevents the formation of stable foam in oil. Antifoaming agents reduce the surface tension of air bubbles by breaking them into smaller bubbles or eliminating them on the surface, thereby promoting the rapid decomposition of foam [109].
- **Compatibility with seals and materials**. It is essential that lubricating oil is compatible with the seals and materials of the machinery. It should not cause seals, gaskets, or other components to expand, contract, or deteriorate [110].
- **Water content**. The presence of water [111] in the lubricant will cause many complications. It worsens the rheological properties, reduces the ability of lubrication and insulation, reduces the possibility of bearing load transfer, speeds up the oxidation process of the oil, rinses out the improvers, increases the amount of sediment, and causes corrosion [112]. According to the manufacturers' regulations, the source should be investigated for the limit of 0.2% [111], while remedial measures are necessary at 0.5%. Also, the presence of Na and Mg in the lubricant indicates contamination with salt water [98], which is another condition to be avoided.
- **Flash point**. The flash point is the lowest temperature at which a liquid may generate sufficient vapor to combine with air to ignite. Commercial products must comply with specific flash points to guarantee safe handling, transit, and use because this can pose a major fire risk. The precise flash point specifications, which might change depending on the product and how it will be used, are frequently set by supervisory authorities or organizations that develop industry standards [98,113,114].
- **Content of metal particles**. Metals, non-metals, and chemicals can belong to one of the main categories of wear metals, oil elements, pollutants, and additives. The limits of chemical components accepted in the industry for diesel engines are summarized according to Table 6. Due to the wear and tear of engine components, metal particles are discharged into the lubricant during engine operation. In addition to dust, dirt, and combustion by-products, lubricants can contain other contaminants. As a guide for monitoring the metal particle content of the lubricating oil, the limits presented in Table 6 are used. They represent the permissible maximum levels of each metal component in the lubricant, which can indicate abnormal engine wear or other problems. By frequently monitoring the metal particle content in the lubricant and comparing it to the limits presented in Table 6, engine operators can determine if the engine is experiencing abnormal degradation or other issues that may necessitate maintenance [100,115].

Table 6. Limits of metal content in the industry independently of the brand name and kilometers or working hours for diesel engines [100].

Metal Component	Normal (ppm)	Abnormal (ppm)	Critical (ppm)
Aluminum (Al)	<20	20–30	>30
Chrome (Cr)	<10	10–25	>25
Copper (Cu)	<30	30–75	>75
Nickel (Ni)	<10	10–20	>20
Iron (Fe)	<100	100–200	>200
Sodium (Na)	<50	50–200	>200
Lead (Pb)	<30	30–75	>75
Tin (Sn)	<20	20–30	>30
Silicon (Si)	<20	20–50	>50

- **Total Base Number (TBN).** TBN refers to a lubricant's capacity to neutralize acids, measured by the quantity of potassium hydroxide (KOH) needed to neutralize one gram of the lubricant sample, expressed in milligrams. TBN is a crucial parameter in petroleum products, and its value fluctuates based on the specific use case [116,117].
- **Total Acid Number (TAN).** TAN is a crucial parameter for evaluating the overall acidity of a substance, determined by the quantity of potassium hydroxide required to neutralize the acids present in one gram of lubricant. TAN testing plays a vital role in assessing additive depletion, acidic contamination, and oxidation in lubricants, contributing to the proactive preservation of equipment. This measurement encompasses both low-pH organic acids and high-pH inorganic acids within the lubricant. An increase in TAN indicates lubricant oxidation, which may result from factors such as time or operational temperature [118,119].

5. Possible Problems in Using Biofuels in Internal Combustion Engines

Utilizing biofuels in internal combustion engines can present a number of challenging circumstances and opportunities, e.g., they can present an approach to reduce greenhouse gas emissions and increase energy security, but they also have some restrictions to be kept in consideration. This section discusses the restrictions and concerns associated with biofuel use in internal combustion engines. The potential problems associated with using biofuels in internal combustion engines include the following:

1. In comparison to conventional fuels, biofuels often include more water [1] and oxygen [120], which can cause, for example, fuel system components to corrode [1]. Older engines that might not have been built to manage the increasing levels of water and oxygen of actual fuels may find this to be especially problematic. Fuel leaks and other issues brought on by corrosion can cause serious damage to an engine [121]. The high temperature of combustion leads to an increase in the acidity of biodiesel and the chemical reaction between biodiesel and the surface of the injection nozzle, and these processes of oxidation and corrosion increase the level of wear [122].
2. Compared to traditional fuels, biofuels have a larger potential for pollutant build-up, including dust, debris, and other impurities [123]. Due to chemical differences, biodiesel has a higher boiling point and a more limited range compared to diesel, which leads to accumulation in crankshaft oil [124]. These impurities may block diesel fuel filters [125,126] and injectors, thus reducing engine output and energy efficiency [127]. Biofuels may also be more susceptible to clogs and other issues with the fuel system [128–131].
3. In principle, biofuels have a lower energy content than conventional fuels, which can reduce engine performance and fuel efficiency [20,132–134]. Many researches showed that, when using 100% biodiesel as fuel in compression-ignition engines, the produced power decreases slightly [135,136].

4. If exposed to cold temperatures, biofuels could be more likely to gel or form wax, which might lead to fuel system clogging and engine stalling. In colder areas where winter temperatures can drop dramatically this can be very hazardous [137].
5. In comparison to traditional fuels, biofuels have the potential to minimize greenhouse gas emissions while maintaining equal engine power output; however, the actual emissions profile can vary greatly depending on the kind of biofuel, the method of production, and the engine technology. For instance, some types of biofuels may increase emissions of specific pollutants including nitrogen oxides (NO_x) [23,138,139] or particulate matter (PM) [140], which may be harmful to the environment and the general public health.
6. The ignition and combustion characteristics of biofuels may differ from those of conventional fuels, which can impact engine performance and emissions. Some biofuels, for instance, may have lower volatility [30,141,142] or higher boiling points [143] than conventional fuels. This can result in issues such as misfires [144], decreased power output, and even, paradoxically, increased NO_x emissions [145,146]. Pure biodiesel's enhanced viscosity and density have an adverse effect on fuel atomization, air-fuel mixing, and the combustion process in a diesel engine that has not been adjusted to use such fuels [147].

Impact of Biofuels on Engine Lubricant: Performance, Dilution, and Degradation

During long-term engine operation, fuel is considered to be a significant influencing factor for engine oil conditions [9]. Biofuels may contain higher levels of oxygen (10% to 45%) [148], which can increase lubricant oxidation and degradation, thereby diminishing their efficacy and lifespan [9,149,150]. In addition, certain types of biofuels may contain contaminants or impurities that interact with lubricants, resulting in additive depletion and viscosity changes [150,151]. For example, the physical properties of biodiesel, which are different from diesel, such as higher surface tension, lower volatility, and higher relative density, cause the formation of larger droplets downstream of the injector [152] and more collisions with the fuel wall during injection into the combustion chamber. They also lead to higher dilution of biodiesel than diesel [153]. Based on the studies and experiments [154,155], it is possible to conclude that biodiesel has other destructive effects in addition to changes in lubricating oil viscosity. Diluting lubricating oil with aged biodiesel and its degradation products (oxidized biodiesel) can cause interaction with zinc dialkyldithiophosphate (ZDDP) anti-wear additives in lubricating oil, which lead to increased engine wear [153]. Also, the presence of biodiesel increases TAN and decreases the TBN of the lubricant [150]. Researchers showed that the use of biofuels in long-term engine durability tests also leads to engine damage due to more carbon deposits and lubricating oil pollution [156].

6. Technical Solutions Proposed So Far to Handle Biofuels in ICEs

Numerous technical solutions have been proposed to address the obstacles posed by the utilization of biofuels in compression-ignition engines in agricultural and industrial settings. These solutions include modifications to the engine itself, fuel composition considerations, and strategic lubrication approaches. By implementing these solutions, it will be possible to overcome limitations and optimize the performance of biofuels in such engines.

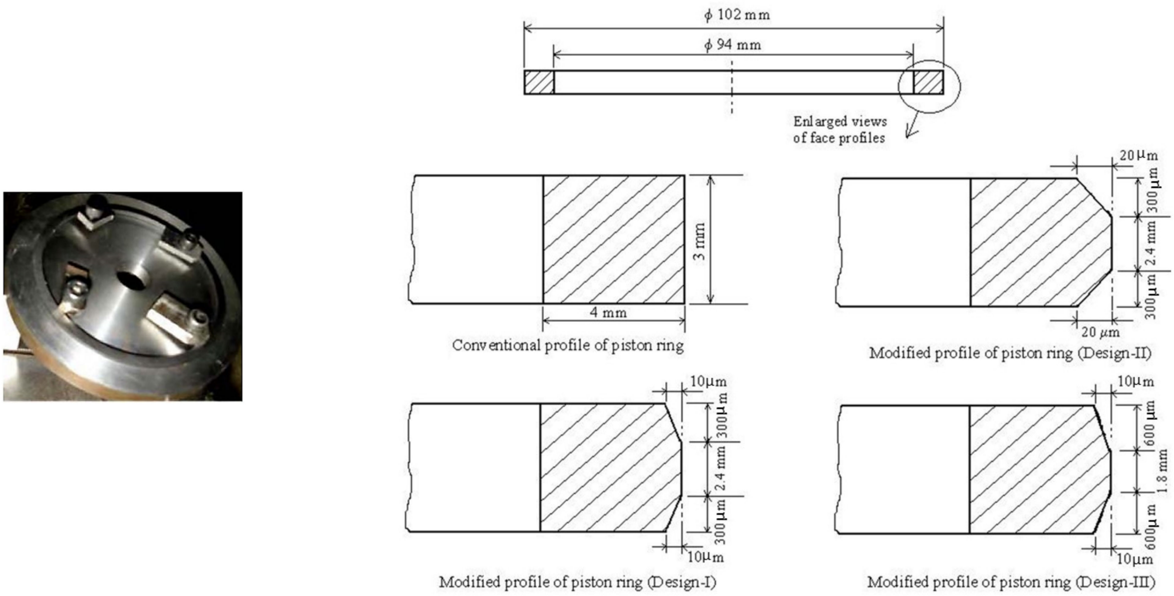
6.1. Modification of the Engine Design

The modification of engine design to accommodate the specific properties of biofuels is the first strategy for addressing the issues associated with the use of biofuels in agricultural and industrial compression-ignition engines. The fact that biofuels have distinct physical and chemical properties compared to conventional fossil fuels is one of the major obstacles, indeed. To resolve these issues, engine designers may modify engine design to accommodate biofuels' unique properties.

The first possible modifications concern the engine injection system. After many experiments on a single-cylinder, four-stroke direct injection diesel engine operating at a constant speed of 1500 rpm with several injection pressure and timing combinations, some scholars discovered that a higher injection pressure of 280 bar and an advanced injection timing of 25.5 °bTDC (before top dead center) significantly improved the brake thermal efficiency, cylinder gas pressure, and heat release rate. Smoke and nitric oxide (NO) emission reductions were also reported [157].

When using biodiesel fuel in an engine that was originally designed for fossil diesel, nitrogen oxide emissions typically increase (NO_x). As a result, the engine's injector nozzle bore and injection mechanisms could be modified to minimize the dangerous fuel emissions, as in [158]. The adjustments included employing two distinct injection strategies (double and triple) and altering the diameter of three injection holes in the nozzle [158]. Modern CI engines have recently shifted towards a multi-injection system design in an effort to lower emissions and boost engine performance [159,160]. Some researchers analyzed the impact of multiple injection strategy designs on the NO_x emissions levels of a single-cylinder diesel engine under various circumstances. Specifically, modified diesel engines employed double injection techniques. The first minor injection timing occurs when the piston is at the top dead center, in this new proposal, which is followed by the main injection. According to their findings, under a specific injection strategy with delayed main injections, it is feasible for B100 with low-temperature combustion mode to emit up to 34% less NO_x than B0 [161].

In a study conducted by Singh et al. [162], the researchers explored the impact of three novel piston ring face profile designs, denoted as Types I, II, and III, as shown in Figure 6, alternatively assembled on the same piston. The study was conducted on a commercial diesel engine fueled with diesel and Jatropha-based biodiesel (B100), and the engine was investigated at multiple loads (up to 100%). The results were compared with the conventional (standard) design for the same piston rings. Piston ring face profiles affected lubricating oil consumption and brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), and mass flow rate regardless of fuel. New piston rings with face profile III boost diesel engine BTE by 2–8% due to better lubrication inside the cylinder. Face profile design III piston rings also increase biodiesel-fueled BTE by 8–16%, so their adoption is strongly suggested, especially in concomitance with a change in engine fueling. BSFC (biodiesel) decreases by 28–34% with a BTE increase.



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

Figure 6. (**a**) Fixture with a clamped piston ring being created by turning at the lathe; (**b**) schematic diagrams of standard (conventional) and three new face profiles of piston rings [162].

The fuel-adaptable engine designed by ClearFlame Engine Technologies is another cutting-edge technology that deserves to be cited here. Indeed, this innovative engine design allows for the operation of existing diesel engines on a wide range of cost-effective, low-carbon, and readily available fuels, including biofuels. This achievement involves making various adjustments, such as customizing the engine's fuel systems and applying surface treatments to specific engine components. These modifications, along with the integration of an engine control unit, enable the engine to seamlessly adapt to different fuels and support their rapid auto-ignition. This flexibility provides an opportunity to decouple the engine-fuel pairing, allowing for the use of a diverse range of fuels without the need for major engine overhauls [163].

6.2. Advanced Fuel Injection Technologies

Some researchers have investigated the use of sophisticated and more recent fuel injection technologies, such as common rail fuel injection systems, which offer more precise control over fuel delivery and injection timing, thereby enhancing combustion efficiency and reducing emissions.

A diesel engine that has been retrofitted with a common rail direct injection (CRDi) system has been used to evaluate the performance, emission, and combustion characteristics of four low-viscosity biofuels (camphor oil, cedarwood oil, wintergreen oil, and lemon peel oil) [164]. This system allows for the modification of the injection duration and injected fuel quantity. All fuels were tested under the same conditions of 5% pilot injection at 600 bar injection pressure. According to the study, low viscous biofuels combined with diesel fuel constitute an effective replacement fuel, starting with an increase in brake thermal efficiency and a decrease in CO_2 and other emissions. Low viscous biofuels appear to primarily have increased NO emission. Among the other biofuels considered, wintergreen oil is one of the denser and relatively less viscous fuels; it shows a 6% improvement in brake thermal efficiency, a 3% decrease in brake-specific energy consumption, a 7% increase in peak pressure, a 20% reduction in CO_2 emissions, a 17% reduction in HC, and a 20% reduction in smoke [164].

6.3. Alternative Combustion Strategies

Some alternative engine designs, such as homogeneous charge compression-ignition (HCCI) engines or dual-fuel engines, may be more compatible with biofuels. These engine designs can benefit by enhancing fuel efficiency, decreasing emissions, and minimizing engine degradation [165–167]. In HCCI engines, biodiesel fuel can enhance engine performance and combustion characteristics, reduce detrimental emissions, and improve fuel economy and engine performance. Nonetheless, controlling combustion phasing and reducing excessive HC and CO emissions remain to be challenging. By adjusting parameters such as inlet air temperature, exhaust gas ratio, and injection pressure, biodiesel fuel in HCCI engines can enhance engine performance and reduce hazardous emissions [168].

6.4. Implementing Exhaust Gas After-Treatment Systems

Compression-ignition engines operating on biofuels may be equipped with exhaust gas after-treatment technologies such as diesel particulate filters (DPFs) [169–172] and selective catalytic reduction (SCR) [173–176] systems to reduce emissions. These technologies can assist in the removal of particulates, nitrogen oxides, and other pollutants from exhaust gas. Exhaust gas recirculation (EGR) systems are another potential solution that can reduce the formation of hazardous pollutants such as nitrogen oxides (NO_x). EGR systems can be incorporated into engine designs so that they are compatible with biofuels [177–179]. The use of Diesel Oxidation Catalyst (DOC) in the emission control system was effective and applying DOC to the diesel engine's exhaust pipe resulted in a 90% decrease in HC and an

85% reduction in CO [180]. In an experiment, waste soybean cooking oil (WSCO) biodiesel is used as an alternative fuel in an agriculture-based diesel engine. Response surface methodology (RSM) was applied to blends of WSCO biodiesel and ultra-low sulphur diesel (ULSD) at various EGR rates (a schematic of engine setup is shown in Figure 7) 20–35% v/v WSCO biodiesel was blended with ULSD to create binary compounds. The results indicate that the most desirable blend is 35% v/v WSCO biodiesel-ULSD with 15% EGR (B35EGR15). B35EGR15 can, therefore, reduce NO_x and particulate emissions by 59.04% and 17.46%, respectively, when compared to ULSDEGR0 with a brake thermal efficiency (BTE) limit that is acceptable. The cost comparison reveals that B35EGR15 is more cost-effective than ULSDEGR0. All WSCO biodiesel-ULSD mixtures have been shown to be effective at reducing emissions from diesel engines [181].

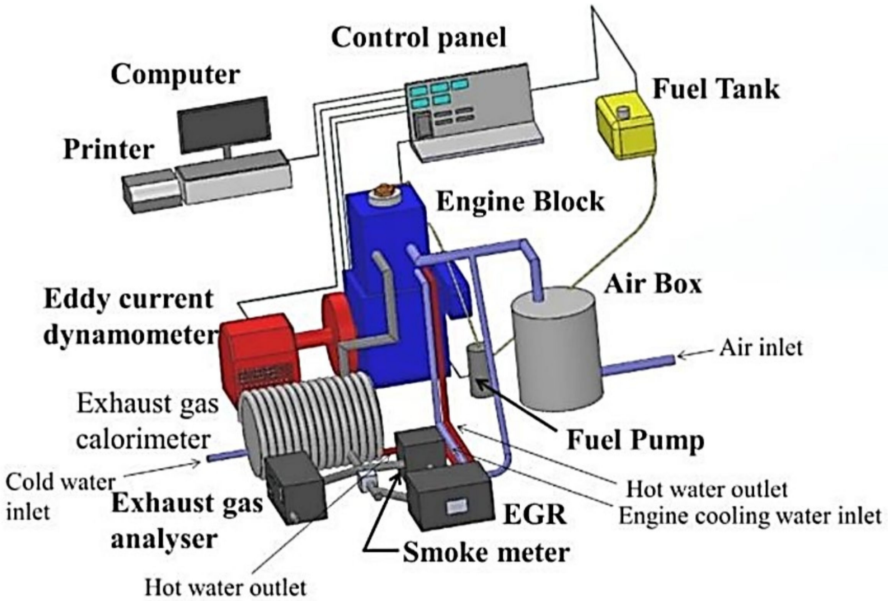


Figure 7. Schematic of engine setup [181].

6.5. Using Fuel Preheating Systems

The adoption of fuel-preheating systems is another potential remedy because it can enhance the flow characteristics of biofuels and lower the danger of engine damage due to fuel gelling at low temperatures. Engine designs can use fuel-preheating equipment to interact with biofuels and provide better compatibility [182,183]. Viscosity is the determining factor in spray formation and fuel combustion quality. A proposed solution to solve the viscosity difference in the fuel feed system when using biodiesel instead of pure diesel fuel is to install an additional preheater on the engine [184].

6.6. Using Advanced Sensors and Control Systems

Compression-ignition engines can be made to run more effectively and efficiently by utilizing sophisticated sensors and control systems. Predictive analytics, sophisticated feedback control systems, and other cutting-edge technology may be used in Electronic Control Units (ECUs) (a schematic of the engine test bench is shown in Figure 8) to optimize engine performance and raise fuel efficiency [185,186].

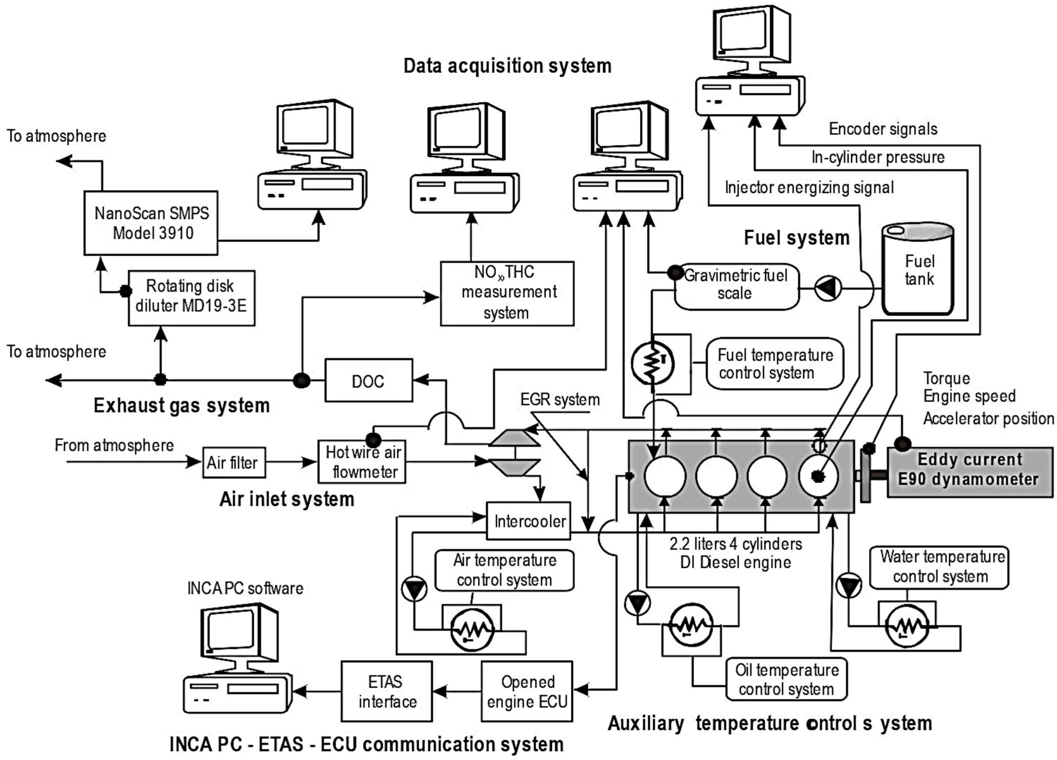


Figure 8. Schematic of engine test bench [187].

6.7. Using Biofuel-Specific Engine Calibration

To optimize engine performance and reduce emissions, engine calibration can be adapted to the specific properties of biofuels. This may involve modifying the injector timing, injection pressure, and combustion parameters to accommodate the biofuel's properties [188,189]. For example, to improve the dual-injection engines running on biofuels, a new and quick calibration method based on the sparse Bayesian extreme learning machine (SBELM) and metaheuristic optimization is suggested. For demonstration purposes, a dual-injection spark-ignition engine running on petrol and ethanol is used. SBELM is used to build an engine model after initially acquiring the engine response for various factors. The so-developed engine model allows for the determination of the ideal engine parameters using recently introduced metaheuristic optimization techniques. The application of machine learning and metaheuristic optimization for dual-injection engine calibration is effective and promising, according to experimental results that support the optimal settings produced with the suggested methodology [190].

In summary, there are several potential solutions that can be explored to improve the compatibility and performance of biofuels in agricultural and industrial compression-ignition engines. These solutions can involve advancements in engine design, fuel and lubricant formulations, materials, production processes, and supporting technologies such as after-treatment systems, preheating systems, thermal management systems, and advanced sensors and control systems.

6.8. Developing New and Innovative Biofuel Blends

The development of novel and inventive biofuel blends that are more compatible with compression-ignition engines is another potential solution. This may involve combining various types of biofuels or adding specific additives to enhance the properties and performance of the fuel. Utilizing fuel additives or fuel conditioners to enhance the efficacy of biofuels in compression-ignition engines is a viable solution. For example, the quality of biodiesel is improved by the use of metal-based additives [191,192], cetane number additives [193–195], antioxidant additives [196–198], and oxygenated additives [199–202].

Utilizing fuel additives is one of the effective approaches to enhance fuel quality, in particular in terms of viscosity, especially when dealing with oils fully derived from biomasses. For example, the findings of a study revealed that the characteristics of biodiesel fuel derived from exhausted cooking oil were significantly changed by the inclusion of viscosity- and pour-point-improving additives [203]. Some of the disadvantages of biodiesel and vegetable oils can be eliminated or improved by alcohols and ethers due to their different properties and increase the concentration of biofuel in the blend [106,204]. The viscosity, density, and cetane number of the blend are reduced by adding alcohols (e.g., ethanol, methanol, propanol, butanol, and pentanol) to biodiesel and vegetable oils, which causes better combustion and reduction in greenhouse gas emissions [204,205]. Ethers, when mixed with biodiesel, vegetable oils, and diesel, improve flow and ignition characteristics due to their higher cetane number and lower viscosity [206,207]. Ethers such as DME (Dimethyl Ether), DEE (Diethyl Ether), DBE (Dibutyl Ether), and DMM (Dimethoxy Methane) were recognized as an additive in recent studies and so they were investigated [106]. Studies have shown that ethers added in a small proportion can reduce the emission level and improve the combustion process [208,209]. Ternary or quaternary compounds with alcohols have been reported in many research studies, while reports on ethers are limited. The optimal triple blend of DEE10 in an unmodified diesel engine as fuel was reported. The developed ANN (Artificial Neural Network) model, which was used for testing and validation in this study, reported and predicted the engine characteristics of experimental fuels with an R^2 value of 0.98. In fact, this model finds the concentration of DEE for the combination of B40 and B60 [210]. Different environmental conditions are considered during the calibration of an internal combustion engine, which has an effect on fuels and is analyzed through physical and chemical properties. Analyzing the physical and chemical properties of the composition of different combustible materials is needed for use in ICEs. The addition of alcohols (methanol or ethanol) in biodiesel mixtures improves the physical and chemical properties of biodiesel; in other words, they reduce viscosity and density, which leads to improved combustion efficiency and reduced pollutants in the CI engine [1].

6.9. Using Nanoparticles to Empower Additives

In recent years, many researchers have investigated the use of nano additives in biodiesel to increase its properties. It has been claimed that nano-scale additions like aluminum oxide, barium oxide, and magnesium oxide not only increase complete combustion [211] but also decrease the emission of hazardous greenhouse gases [212]. Some authors, for example, individuated in the nanoparticles a possible way to enhance a diesel engine's behavior during the combustion of a biodiesel blend. For example, inorganic nanoparticles were added to diary scum oil methyl ester and producer gas (DiSOME-PG). In this case, Al_2O_3 [213,214] nanoparticles were used in biodiesel, as they may alter the combustion process due to their improved mechanical and thermal characteristics. Al_2O_3 particles mostly affect the respiratory system and are combustible and irritating. Instead, Al_2O_3 nanoparticles used properly improve engine performance and lower engine exhaust emissions [214–219]. Many studies showed that aluminum particles improve engine output power (brake output power) and reduce greenhouse gas emissions (HC, CO_2, NO_x) due to high energy concentration [220–223]. Another study showed that aluminum and Al_2O_3 particles reduce the delay period and improve the combustion quality of diesel [220,222,224]. The addition of Al_2O_3 particles to jojoba biodiesel (JB20D), for example, improved the performance characteristics and reduced emissions of CO gases by 80%, NO_x by 70%, and unburned hydrocarbons by 60% for 20 mg·L^{-1} Al_2O_3 particles concentration [225]. The addition of 75 ppm Al_2O_3 nano additive in the Silkworm Oil Methyl Ester (B30 SWOME) led to improved performance, increased braking thermal efficiency, increased combustion, as well as a considerable improvement in emissions [180].

The blend of biodiesel with octanol and suspension of multi-walled carbon nanotubes (MWCNT) was also investigated in 2020. The addition of MWCNT nanoparticles to cottonseed oil biodiesel demonstrated that, although it might enhance the thermal and mass transport characteristics of biodiesel, the combustion quality was not enhanced [226].

6.10. Blending Biofuels with Traditional Diesel Fuel

One of the possibilities to improve the fuel properties and make it more compatible with compression-ignition engines is blending biofuels with conventional diesel fuel [227–229]. The first and most important suggestion from many points of view for reducing greenhouse gas emissions and promoting sustainable energy practices is utilizing the optimum blend ratio of conventional fuels with biofuels [230–232]. For example, the percentage of biodiesel in the blends should not exceed a certain limit that varies depending on the type of engine and the intended use. If looking only at the engine performance derating due to biodiesel in the blend, automobile manufacturers advise using a maximum of 20% biodiesel (B20) with gasoline for automobiles [229,233]. The optimal combination for unmodified diesel engines is the combination of B20 (diesel–biodiesel), which has been shown in many research studies [229,234]. Ternary or quaternary compounds in diesel engines have been also studied in order to increase the concentration of biofuel in recent years [235,236]. These compounds can include biodiesel, vegetable oils, alcohols, and ethers with different proportions of diesel [236,237].

There are three primary outcomes that result from the utilization of ternary (diesel, biodiesel, and alcohol) blends as fuel:

1. The duration of combustion is diminished due to the difference in combustion characteristics compared to diesel fuels [1]. By raising the fraction of ethanol in the diesel-ethanol blends, the maximum rate of heat release increases, while it decreases slightly for biodiesel–diesel–ethanol blends [23]. In diesel–ethanol blends, the ignition delay increases [23] as the ethanol proportion rises, although it decreases marginally in biodiesel–diesel–ethanol blends when an improver is added. In diesel-ethanol blends, cylinder pressure increases [24] with increasing ethanol proportion, but it decreases somewhat or stays constant in biodiesel–diesel–ethanol blends.
2. Engine performance is modified when using blends of biofuels; in these cases, the specific fuel consumption is higher [4,25,238] compared to diesel fuel, and the brake-specific thermal efficiency increases [239] comparably, while the expressed power is slightly less or significantly comparable. The temperature of the exhaust gases shows small and minor changes. The mean effective pressure also showed minor changes [1].
3. Emissions of HC and CO are determined by the composition, type, and ratio of the fuel, as well as the performance characteristics of the engine. The emission of NO_x, smoke, and suspended particles is reported to be generally lower [239–241].

6.11. Emulsified Biofuels

Emulsified biofuels are manufactured from water, biofuel, and an emulsifying agent. The biofuel component, usually vegetable oil or animal fat, is blended with a small amount of diesel fuel to improve its quality. The emulsifier keeps biofuel and water from separating, stabilizing the combination. Emulsified biofuel can be used in diesel engines without considerable modifications [242] and may even outperform diesel [243]. Renewable sources may emit fewer particulates and nitrogen oxides. Although emulsified biofuel has a number of disadvantages, such as a high viscosity and the presence of larger, heavier molecules. These factors can reduce a substance's ability to atomize and effectively blend with fuel and air. Consequently, an appropriate surfactant and co-surfactant mixture is required [244]. The synthesis and stability of bio-oil in diesel emulsion fuels were investigated, and the optimum surfactant concentration ranged from 0.8 to 1.5% wt., depending on bio-oil concentration and power input. Centrifuged bio-oil had a third of diesel's heating value, lowering the emulsions' heating values. When emulsions formed, linear interpolation gave pyrolytic bio-oil a cetane number of 5.6. The cetane number was reduced by 4 per 10% bio-oil concentration. Emulsion fuels were easy to handle due to their lower viscosity than bio-oil, especially in the 10–20% concentration range. Emulsion fuels had half the corrosivity of bio-oil, as measured by steel weight loss [245]. Another researcher found that adding 5% water and 2% span80 surfactant by volume to Borassus Flabellifer Oil (BFO) emulsion fuel and using antioxidant L-ascorbic acid as an additive increased engine BTE and BSEC by 31.08% and 13.02 MJ·(kW·h)$^{-1}$ at the ultimate load condition. Raw BFO has 25.7001%, 15.70 MJ·(kW·h)$^{-1}$, while emulsified BFO has 28.70%, 14.71 MJ·(kW·h)$^{-1}$. Because of L-ascorbic acid, BFO additive emulsion had 34.92% and 22.22% lower HC and CO emissions than diesel. Nitrogen oxide emission dropped 20.08% for BFO additive emulsified fuel. Microexplosion and secondary atomization of BFO additive emulsified fuel reduced fall smoke by 20.83% compared to diesel fuel [242].

6.12. Improving the Quality and Consistency of Biofuels (Alternative Feedstocks)

One solution is to improve the quality and consistency of biofuels by implementing improved production and different quality control procedures. This can include enhancements to feedstock selection, processing methods, and monitoring and testing procedures to ensure that biofuels meet industry specifications. In addition, researchers have proposed using alternative feedstocks for biofuels, such as algae [246–248] and waste oils [249–254], which may have different properties than conventional biofuels and may be more compatible with existing engine designs and lubricants.

6.13. Developing Advanced Lubricants

Compression-ignition engines can be made more efficient and long-lasting with the help of advanced lubricants. This may involve the application of synthetic lubricants, nano lubricants, and other advanced lubrication technologies. In addition, the development of novel engine lubricants designed specifically for use with biofuels can enhance engine performance and longevity. These lubricants can be formulated with additives and properties that are better adapted for biofuels, thereby reducing engine wear and enhancing fuel efficiency.

High-performance lubricants depend significantly on additives [255–257]. When lubrication conditions are challenging, these additives, which are chemically active under friction, can produce thin solid or viscous films that separate surfaces [258,259]. The overall performance of the lubricant is greatly improved by these interactions [260,261]. Tribofilm is a thin film made of the results of these additive-induced reactions [258,262]. The discovery of this tribofilm was made with zinc dithiophosphates (ZDDP) [262]. ZDDP was first added to lubricating oil as a corrosion prevention measure [263]. But it was later found that the addition of ZDDP to the lubricant caused the lubricated surfaces to develop a thin coating. Despite having an average friction behavior, this layer significantly improved the surfaces' resistance to wear. Since ZDDP was the first lubricant additive to have its tribochemical process thoroughly studied, other chemically active lubricant additives like molybdenum dithiocarbamate (MoDTC) have also benefited from a better understanding of ZDDP's tribochemical process. A study showed that ZDDP is a powerful oxidation inhibitor for mineral oils, while Methyl Oleate (MO) is a powerful oxidation enhancer that is well-liked because of its innate chemical reactivity. When ZDDP and MO interacted chemically, it was evident that MO considerably increased ZDDP's antioxidant capacity while lowering its anti-wear capability [264]. Additionally, in the 2000s, ionic liquids (ILs) and nanoparticles (NPs), two new categories of lubricant additives, were developed [265]. The results of many investigations that were carried out to examine the impact of adding nanoparticles to mineral oils and biolubricants are summarized in Table 7.

Table 7. Overview of the research conducted using nanoparticle additives added to mineral oils and biolubricants.

Researchers	Reference Lubricant	Reference Nanoparticles	Test Method(s) and Condition(s)	Results
Sulgani and Karimipour (2019) [266]	Engine oil (10W40)	Hybrid nano-powder of aluminum oxide (Al_2O_3) and iron (III) oxide (Fe_2O_3)	The thermal conductivity coefficient of the hybrid nanofluid was measured using the assistance of the KD2-Pro (by Decagon devices Inc., Pullman, WA, USA) thermal analyzer. The thermal conductivity was measured in the concentration range of 0.25% to 4.00% and the temperature range of 25 °C to 65 °C.	Even at low mass concentrations, nano-lubricant improved the thermal properties of 10W40 engine oil throughout a wide temperature range. The highest boost in thermal conductivity (33%) was observed at 4% mass fraction and 65 °C as shown in Figure 9.
Celik et al. (2013) [267]	Engine oil (SAE 10W)	Nano hexagonal boron nitride (hBN) particles	Four distinct lubricant samples were made with engine oil containing 0–10% nano hexagonal boron nitride by volume spectroscopy and damaged substrate surfaces were examined (EDS). Ball-on-disc geometry was used to conduct wear testing. The worn surfaces of substrates were examined using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy.	The friction coefficient increased by 14.4% and the rate of wear was reduced by 65% when nano hBN was used as an oil additive as shown in Figure 10.
Jatti and Kumar (2015) [268]	Mineral-based multigrade engine oil (Castrol India Ltd., Mumbai, Maharashtra, India)	Titanium oxide nanoparticles (TiO_2)	Friction-reduction and anti-wear properties were investigated using a pin-on-disc tribometer. Tests were carried out with nanoparticle concentrations of 0.5% wt., 1% wt., 1.5% wt., and 2% wt., loads of 40 N, 60 N, and 90 N, and sliding speeds of 0.5 $m{\cdot}s^{-1}$, 1.0 $m{\cdot}s^{-1}$, and 1.5 $m{\cdot}s^{-1}$.	It has been proven that adding nanoparticles to lubricants may significantly enhance their lubricating capabilities. As the friction coefficient dropped, rolling friction replaced sliding friction as a consequence of the nanoparticles moving into the friction zone with the flow of lubricant.
Singh et al. (2021) [269]	Mongongo oil	SiO_2 nanoparticles	Nanoparticles were added to the oil at varying quantities of 0.2%, 0.4%, and 0.8% based on weight. For the investigation of the tribological characteristics of the nano lubricants, the pin on the disc machine was considered.	The outcomes were better under all circumstances when the nanoparticle concentration was up to 0.4%. The friction and wear of the components are reduced even more than at 0.4% concentration when the concentration is raised to 0.8%.

Table 7. *Cont.*

Researchers	Reference Lubricant	Reference Nanoparticles	Test Method(s) and Condition(s)	Results
Singh et al. (2019) [270]	Mineral oil	Al_2O_3 (Aluminum Oxide), CuO (Copper Oxide), TiO_2 (Titanium dioxide), ZnO (Zinc Oxide), molybdenum disulfide (MoS_2), graphene oxide dotted with nickel nanoparticles (Sc–Ni/GO)	It is investigated how different nanoparticles behave under various loading circumstances, concentrations, and RPM.	A 0.01 vol. fraction of titanium dioxide (TiO_2) can boost the load-carrying capacity of journal bearings by 40%, while paraffin oil containing 0.08% wt. of graphene oxide doped with nickel nanoparticles (Sc-Ni/GO) can decrease COF and wear scar width by 32% and 42%, respectively.
Padgurskas et al. (2013) [271]	Mineral oil (SAE 10)	Fe, Cu, and Co nanoparticles	In order to calculate the coefficient of friction, a four-ball tribotester was used. The experiments were placed at the usual room temperature.	Nanoparticles in oil reduced friction and wear by as much as 1.5 times compared to oil without them. The use of copper nanoparticles, either alone or in combination with other nanoparticles, was shown to be the most effective strategy in tribological testing to minimize wear and friction. They found that combining different nanoparticles improved performance over using them alone.
Wan et al. (2015) [272]	Lubricating oil (SAE 15W40)	Nanoparticles of boron nitride (BN)	The lubricating oil's rheological behavior was measured using a rheometer, and the nano-anti-wear lubricant's anti-frictional performance was examined using a tribo-tester. Nano-BN oils with concentrations of 0.1% wt., 0.5% wt., and 1.0% wt. were created and designated as BN01, BN5, and BN1.	A concentration of 0.1% wt. for nanoparticles was calculated based on the friction coefficient and line roughness of the weathered surface. Lubricating oil with a trace amount of boron nitride nanoparticles may perform well tribologically, as evidenced by atomic force microscopy and scanning electron microscopy analyses of wear track morphology and X-ray energy dispersive spectroscopy analyses of element distributions on the worn surface. With an increase in temperature, the viscosity of both the basic oil and nano-BN oils decreased significantly.

Table 7. *Cont.*

Researchers	Reference Lubricant	Reference Nanoparticles	Test Method(s) and Condition(s)	Results
Asnida et al. (2018) [273]	Engine oil (SAE 10W30)	Copper (II) oxide nanoparticles	Physical properties of dispersed lubricants were analyzed by checking their moisture content and viscosity. The piston skirt standard, aluminum 6061, was put to the test in a piston skirt-liner contact tester in order to determine the amount of wear and friction. RSM was used to construct the experimental design. To determine the optimal lubricant concentration, the effects of rotational speed (200, 250, and 300 rpm), volume concentration (0.005% and 0.01% of dispersed nanomaterial), and load (2 N, 5.5 N, and 9 N) were tested. Experimental wear was measured using Field Emission Scanning Electron Microscope (FESEM).	The results demonstrated that the base oil-dispersed CuO nanoparticles had effective friction-reduction and anti-wear capabilities. When a concentration of 0.005% wt. was employed, the resulting coefficient of friction was 0.06125, and the wear rate was 0.2482 $mm^3 \cdot (Nm)^{-1}$. The component element of the nanoparticles precipitated at the contact region, according to SEM data. The EDAX analysis revealed a protective layer. The optimal parameters were 291 rpm speed, 0.008% concentration, and 75.152 N load.
Raina and Anand (2018) [274]	Polyalphaolefin (PAO) oil	Diamond nanoparticle	The concentrations of the diamond nanoparticles utilized in the research range from 0–0.8% wt. The tests have been run at a constant load of 100 N and a constant sliding speed of 0.58 $m \cdot s^{-1}$. Evaluation of the concentration's impact on friction wear performance. For steel/steel contacts, frictional properties are measured using a pin-on-disc tribometer. To better understand how lubricants wear, scanning electron microscopy (SEM) has been used.	The study's findings showed that PAO oil with 0.2 weight percent of diamond nanoparticles had the lowest coefficient of friction (COF). The SEM photographs of the worn surfaces showed that there is little surface damage (0.2% wt.) and that the diamond nanoparticles' ploughing impact is primarily responsible for the wear.

Table 7. *Cont.*

Researchers	Reference Lubricant	Reference Nanoparticles	Test Method(s) and Condition(s)	Results
Zulkifi et al. (2013) [275,276]	Paraffin oil and Biolubricant. Biolubricant was derived from palm oil-based TMP (trimethylol-propane) ester	TiO_2 nanoparticles	Tribotester with four balls was used for the friction and wear investigations. A 10-min experiment with 40 kg, 80 kg, 120 kg, and 160 kg was run at 1200 rpm. The test temperatures were set to normal.	The results of the experiments show that the friction may be significantly reduced by mixing nanoparticles of TiO_2 with a TMP ester. The inclusion of TiO_2 nanoparticles at 160 kg reduced the friction coefficient by 15% and the wear scar width by 11% compared to TMP ester without TiO_2 nanoparticles.
Gulzar et al. (2015) [277]	Chemically modified palm oil (CMPO)	Molybdenum disulphide (MoS_2), copper(II) oxide (CuO) nanoparticles	To produce nanolubricants, CMPO was combined with 1% wt. CuO and MoS_2 nanoparticles. Nanoparticle-enhanced chemically modified palm oil (CMPO) was tested for its anti-wear (AW) and extreme pressure (EP) capabilities using a four-ball and sliding wear test. Wear surfaces were analyzed using scanning electron microscopy, energy-dispersive X-ray spectroscopy, and micro-Raman scattering spectroscopy.	The anti-wear (AW)/extreme pressure (EP) characteristics of the MoS_2 nanoparticles were superior to those of the CuO nanoparticles. Agglomerates could be reduced more easily when a surfactant with 1% wt. oleic acid content was added.
Gulzar et al. (2017) [278]	Bio-based lubricant (Palm TMP ester)	Modified CuO nanoparticle suspensions	Four-Ball Extreme Pressure (EP) testing and sliding wear tests were used to assess wear protection.	CuO-enriched suspensions with changed surfaces exhibited consistent and predictable behaviors. In experiments where piston rings and cylinders moved past one another, the inclusion of anionic surfactant not only assisted with nanoparticle suspension but also with wear reduction. The AW/EP properties of the surface-modified nano-CuO enriched TMP ester are significantly better than those obtained without surfactant.

Table 7. *Cont.*

Researchers	Reference Lubricant	Reference Nanoparticles	Test Method(s) and Condition(s)	Results
Shafi and Charoo et al. (2020) [279]	Biolubricant–hazelnut oil	Zirconium-dioxide (ZrO_2) nanoparticles	The studies are conducted using different shear rates of 1–4000 s^{-1} at low temperatures (20 °C to −10 °C) and high temperatures of 40 °C. The oil has three distinct weight percentages (% wt.) of nanoparticles added to it: 0.5, 1.0, and 1.5.	The mixture's viscosity was determined to be at its highest (5.8%) when 1.5% ZrO_2 by weight was added to hazelnut oil at 40 °C. Hazelnut oil also maintains its flowability at extremely low temperatures, showing outstanding resistance to the increase in viscosity at lower temperatures.
Singh et al. (2020) [280]	Modified Juliflora oil for bio-based lubricant	TiO_2 nanoparticles	Kinematic viscosity, viscosity index, flash point, and iodine value of the lubricants were all assessed. A scanning electron microscope (SEM) was needed to look at the worn surfaces. The oil's kinematic viscosity rises as a result of the chemical modification and the inclusion of the nanoparticles.	Nanoparticles raise the flash point, peaking at 0.6% TiO_2 nanoparticles. With this nanoparticle content, it was observed a reduced pin wear and COF during the tribological study. Due to effective surface lubrication, SEM images indicated better surfaces when nanoparticles were applied up to 0.6% at weight concentration. The best nanoparticle addition was 0.6% in chemically modified oil, which had a superior anti-wear mechanism. Oil that has been altered with nanoparticles showed higher viscosity, viscosity index, flash point, and lowest iodine and acid values.
Roselina et al. (2020) [281]	Palm oil biolubricant	TiO_2 nanoparticles	The TiO_2 nanoparticles were blended with lubricants using the ultrasonication technique for 30 min after being added at weight percentages of 0, 0.5, and 1.0 for each sample.	According to the experimental findings, at both 40 °C and 60 °C, samples of palm oil-based biolubricant with and without TiO_2 addition had viscosities that are equivalent to those of SAE 0W20 grade. When TiO_2 is added as an addition to palm oil, it improves the bio-viscosity lubricant's index, which may be related to how effectively TiO_2 disperses with ethylene glycol. Using TiO_2 as an addition, the viscosity index of the palm oil biolubricant was raised by 4.1%.

Table 7. *Cont.*

Researchers	Reference Lubricant	Reference Nanoparticles	Test Method(s) and Condition(s)	Results
Tang et al. (2020) [282]	Poly-alpha-olefin (PAO6) based oil	Silver nanoparticles (Ag/BP) "Black phosphorus (BP)"	An analysis of the tests was performed using a ball-on-disc tribometer.	According to the results, oil diluted with a negligible amount of Ag/BP nanoadditives functions effectively as a lubricant for steel-on-steel contact. Dispersing 0.075% wt. Ag/BP nanoadditives in PAO6 oil reduces friction by 73.4% and wear by 92.0% compared to using only PAO6 oil as the foundation.
Razak et al. (2019) [283]	Palm oil as a biolubricant, mineral oil CRB diesel 20W40	Nano-clay	The provider gave the size and true density of the nano-clay surface modified with 0.5–5% wt. Amino Propyl Triethoxy Silane 15–35% wt. An ultrasonic vibrator blended the nanoparticles to prevent agglomeration. The optimal amount of nano-clay addition in palm oil, ranging from 0.02% to 0.08% wt., was established by four ball testers using ASTM D4172-94 (2016) guidelines [284].	The optimum concentration was 0.04% wt. nano-clay additive in palm oil, with a coefficient of friction of 0.081, i.e., 16% lower than mineral oil (20W40), the reference lubricant. It reduced worn scars by 32%. Pressure, friction, and temperature. Modified palm oil with nano-clay has a lower coefficient of friction and temperature profile than mineral oil. Nano-clay increased pressure in palm oil, which had lower viscosity. Palm oil with nano-clay might replace mineral oil.
Gong et al. (2020) [276]	Polyalkylene glycol (PAG) base oil	Nanocomposites of MoS_2 nanoparticles (NPs) grown on carbon nanotubes (MoS_2@CNT), graphene (MoS_2@Gr), and fullerene C60 (MoS_2@C60)	The friction-reducing and antiwear properties of these nanoparticles were evaluated using an effective reciprocation friction monitor with a ball-on-disc setup.	Using the synergistic interaction between MoS_2 and carbon nanomaterials (CNMs), the nanocomposites can be effectively dispersed in polyalkylene glycol (PAG) base oil, and they are more stable than pure MoS_2 NPs. Suspensions of MoS_2@CNT, MoS_2@Gr, and MoS_2@C60 added to PAG show significantly improved friction reduction and antiwear (AW) behaviors at elevated temperatures compared to PAG and PAG containing CNTs, Gr, C60, and MoS_2 NPs, respectively.

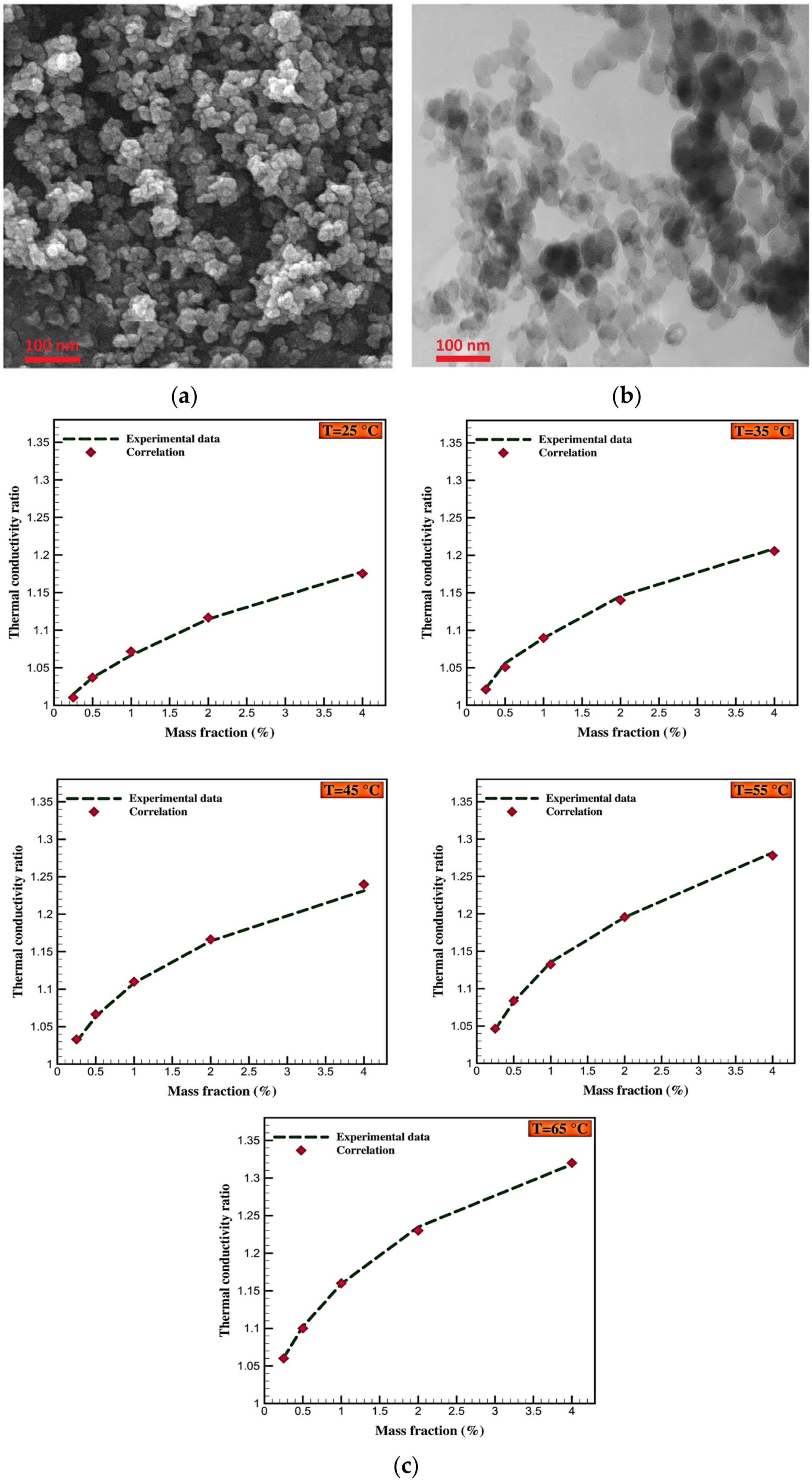


Figure 9. (**a**) SEM image of Fe_2O_3 nanoparticles; (**b**) SEM image of Al_2O_3 nanoparticles; (**c**) thermal conductivity ratios of nanolubricant "10W40/Al_2O_3-Fe_2O_3" at different temperatures.

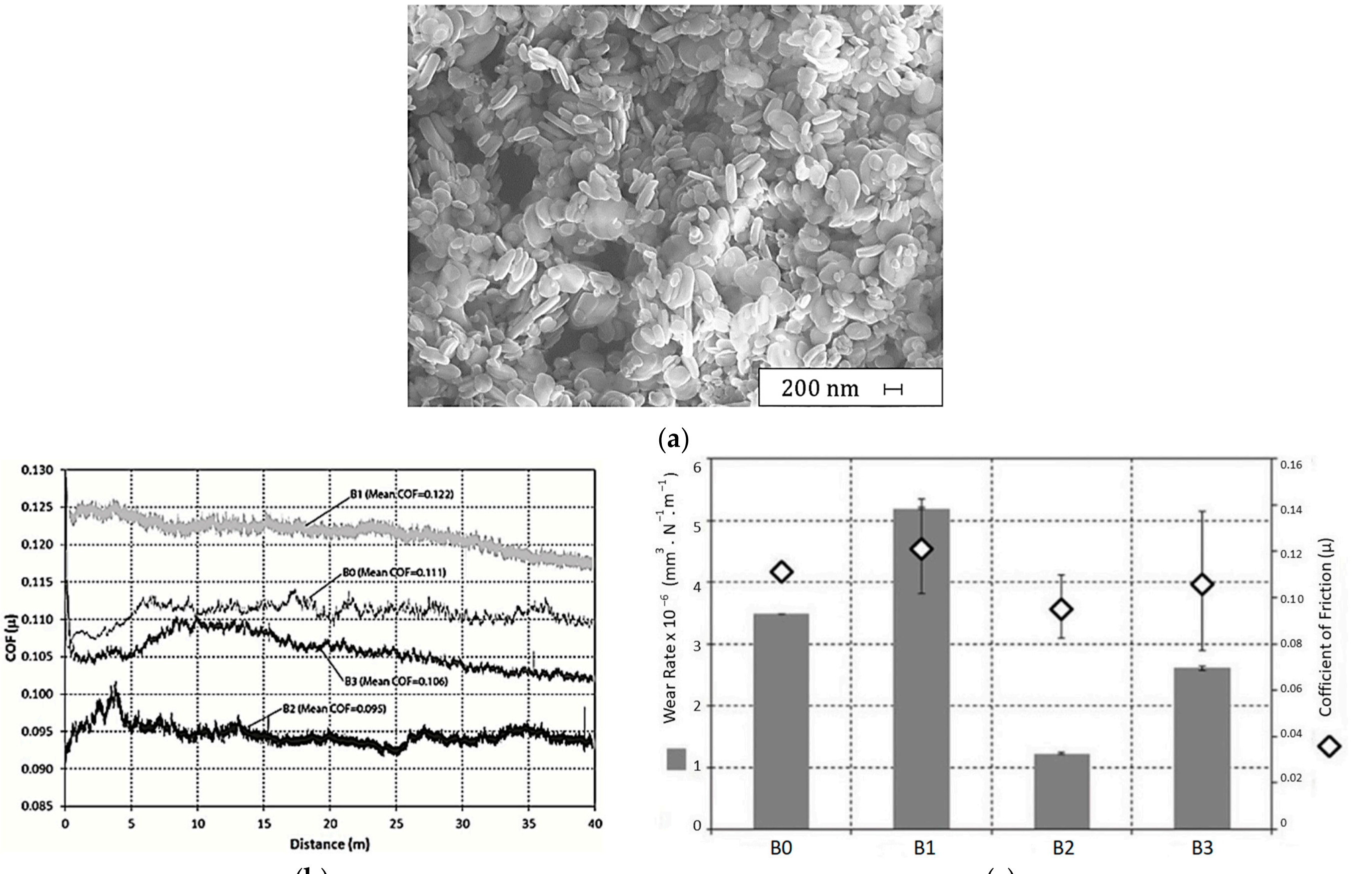


Figure 10. (**a**) SEM image of hBN nanoparticles; (**b**) coefficients of friction; (**c**) wear profiles, the specific wear rates, and the coefficient.

7. Conclusions and Recommendations

In the early 1900s, the concept of utilizing biofuels in diesel engines was originally proposed. Concerning energy usage and greenhouse gas emissions, transportation comes in third place behind industry and construction. Biodiesel and alcohols are recognized as the most viable alternatives to diesel fuel. However, they cannot be directly utilized as fuels without previously being blended with fossil fuels at low percentages, due to problems including variances in physical and chemical characteristics, poor low heating value of the resulting fuel, and corrosion issues in some components of the thermal engines. There are many studies on the effect of biofuels on vehicle engines and lubricants. Many researchers have shown that when pure biodiesel fuel is used, it has very negative aspects on components and lubricants. The idea of using blended fuels, diesel, biodiesel, and alcohols as biofuels was very promising. One of the greatest methods to enhance the qualities of biodiesel is to add alcohol; among the alcohols, butanol is the most promising additive.

Despite the demonstrated reduction in many negative aspects, biofuels still cannot seriously convince engineers because all technical problems consequent to use on existing ICEs (e.g., decreased engine efficiency, potential engine damage due to biofuel properties, the need for specialized engine modifications, and concerns about the availability and sustainability of biofuel feedstocks) have not yet been completely resolved.

The impact of biofuels on lubricants is another enduring issue that has involved many researchers in more research and experiments. The interaction between biofuels and lubricants can alter the viscosity, oxidative stability, and wear protection properties of the lubricant. These modifications may result in increased engine friction, decreased engine efficiency, and accelerated component degradation. In order to resolve these issues, extensive research and experiments have been conducted in order to comprehend the intricate relationship between biofuels and lubricants. Efforts are concentrated on the development of lubricant formulations that mitigate the negative effects of biofuels, guarantee optimal engine performance, and minimize engine damage.

Furthermore, the use of biolubricants has controversial challenges due to their difference in properties with respect to conventional lubricants. They have a shorter lifespan than conventional lubricants due to their inability to operate at high temperatures for long periods. Optimizing the formulation of the lubricant is one solution to address this issue due to its inability to operate at high temperatures for extended periods. This can be accomplished by incorporating additives that improve the bio lubricant's high-temperature stability, such as antioxidants, viscosity enhancers, and friction modifiers. In addition, the choice of base oil can have a significant effect on the biolubricant's high-temperature efficacy. By selecting the appropriate base oil and additives, it is possible to create biolubricants with improved high-temperature stability and a longer service life, making them more applicable to a broader range of applications.

Many studies have shown that additives such as nanoparticles can improve the properties of biofuels, as well as lubricants. Indeed, mineral oils and biolubricants may benefit from adding nanoparticle additions to enhance lubrication, decrease friction, and boost wear resistance, among other things. These advantages may lead to increased energy efficiency and longer lifespans of engine mechanical organs. To completely comprehend the possible implications of utilizing nanoparticles in lubricants, including any hazards or adverse effects, additional research is necessary. The type, size, and characteristics of the nanoparticles employed, as well as the characteristics of the lubricant they are added to, will all affect the precise consequences of utilizing nanoparticle additives.

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