

Review Article

A Review on the Impact of Bio-Additives on Tribological Behavior of Diesel Fuels

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Automobile engines require lubrication to lessen the impact of friction due to the high levels of wear and frictional heat generated by the sliding parts. Wear and friction will cause engine parts to endure for less time, be less reliable, and require more maintenance. Diesel fuel can potentially be replaced with biodiesel among other fuels. Diesel engines have a serious problem with equipment that is lubricated by the fuel itself. This study's goal is to assess the influence of bio-additives on the diesel fuel tribological behavior and energy balance during the car's idle running, acceleration, constant speed, and braking. Lubricity issues with reformulated diesel and lubricity test procedures are explained. The relationship between tribology and bio-additives is also briefly illustrated. According to the literature, adding bio-additives to fuel boosts its lubricity. Biodiesel has long been considered an additive with excellent lubricant properties. Even in small amounts, adding biodiesel to diesel fuel can increase its lubricity without the need for conventional lubricity additives. This is especially true for diesel fuel with ultralow sulfur. Diesel fuel characteristics determine the precise blending percentage needed to provide the proper lubricity of maximum 520 μm testing wear scars with a high-frequency reciprocating rig (HFRR), although 2% biodiesel nearly invariably imparts adequate lubricity to biodiesel blends. Tall oil fatty acid (TOFA) was one of the bio-additives investigated by HFRR. When the additive concentration was raised from 0 to 500 g/g, the wear scar diameter (WSD) of nonadditive diesel fuel was lowered by 60.3%, from 630 to 250 μm , and the coefficient of friction (COF) was lowered by 95.7%, from 0.47 to 0.02.

1. Introduction

Today's fast changing automotive industry depends on fuel not only to run the vehicle but also to lubricate it with less impact on the environment and emit fewer pollutants [1]. Possible alternatives to petroleum-based products need to be investigated in light of the global energy crisis. As exhaust gases are released into the atmosphere during the production process, pollution from petroleum fuel is becoming an increasing environmental protection concern. Development of environmentally friendly and renewable fuels is, therefore, a major objective [2–4].

Biodiesel has physicochemical properties similar to regular diesel fuel, which makes it suitable for use as an energy source in diesel engines [5]. Animal fats, vegetable oils, oils produced by microorganisms, and frying oils can all be used

to make biodiesel. These sources allow biodiesel to be both a biodegradable fuel and a renewable resource [6, 7]. Biodiesel is also considerably more environmental friendly due to the fact that it contains little sulfur. Essential elements of fuel are reduced emissions and lubricity [8].

Transesterification is the process of using an acidic or alkaline catalyst to sequentially and reversibly react raw materials containing triglycerides, such as animal fat, vegetable oil, recycled cooking oil, and algae mixed with alcohols, in order to produce glycerol, the primary component of biodiesel, and monoalkyl esters [9]. Figure 1 shows a typical process for making biodiesel.

The fuel supply line lifetime and the lubricity of biodiesel are related from a tribological point of view. The capacity to lessen wear and friction on surfaces that are subject to load and relative motion defines lubricity [9]. Because friction is a

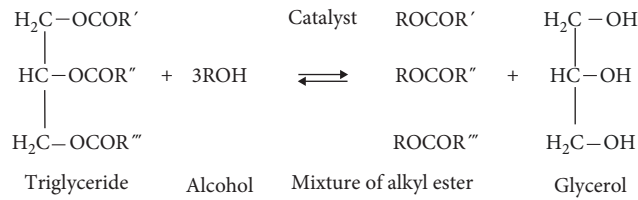


FIGURE 1: Transesterification of triglycerides.

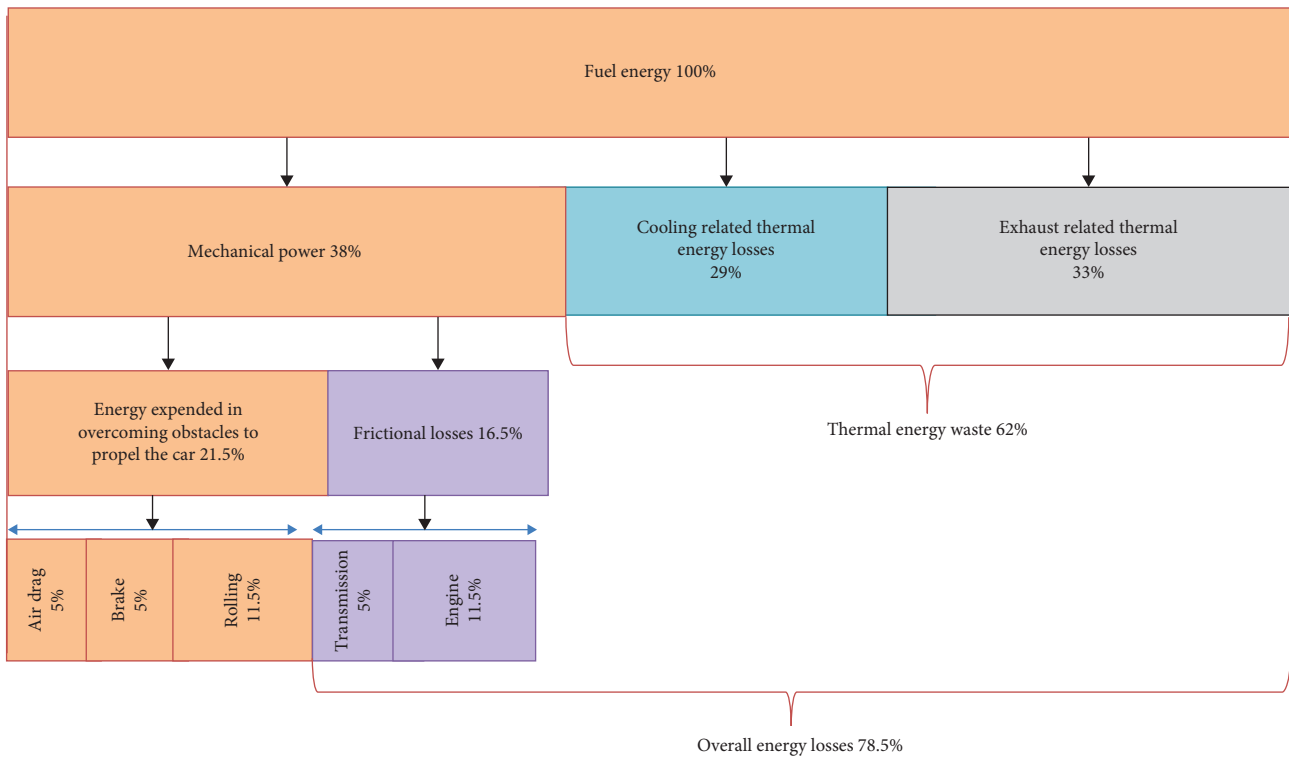


FIGURE 2: Breakdown of energy use for ICE driven passenger cars, tank-to-wheel calculations.

major problem with internal combustion engines, one of the most important qualities of biodiesel is its lubricity [10]. Fuel flow lubricates important parts of a diesel engine, including the injector and diesel injection equipment. The lubrication that the fuel provides is primarily responsible for the decreased friction and wear of such parts [11].

The obvious precondition for wear and friction/traction is the movement of one material over another. The engine fuel system's related parts encounter friction during fuel flow operations. Reducing CO₂ emissions and increasing energy savings are two major effects of tribological design [12]. Engines can only do useful work when their energy output is sufficient to overcome the friction created by their moving components. Friction in the engine and other moving parts of the car wastes more than 30% of the mechanical energy, or approximately 38% of total energy [13, 14].

Figure 2 illustrates the energy distribution resulting from fuel combustion [14]. The vehicle only uses 18%–25% of its fuel energy to move on the road, the remainder being lost due to mechanical losses in the engine and transmission caused by friction, exhaust gases, cooling, and other factors [15].

Consequently, there is a substantial opportunity to increase fuel efficiency through the application of modern technologies.

Tribological tasks that reduce wear and friction can increase output while lowering maintenance costs. Accurate and swift movements are possible with these tasks [16]. The vehicle's moving mass temporarily stores the potential loss of energy as kinetic energy while it travels from one place to another, while the remaining energy released is changed into energy loss as a result of friction [17]. Without accounting for energy losses from cooling and exhaust gases, the balance of mechanical energy losses during this time can be divided into four stages, as shown in Figure 3.

1.1. Idle Running. In this situation, the engine and a portion of the transmission parts are the only things operating and the car is stationary. To overcome friction resistance in this instance, fuel energy is only being used by the engine and the transmission.

1.2. Acceleration. The car is accelerating in this situation, and because of its kinetic energy, it needs more fuel to overcome

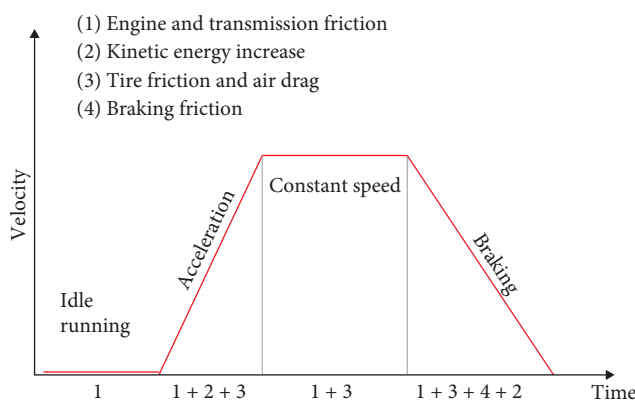


FIGURE 3: Energy balance during four stages of car operation.

air drag as well as friction in the tires, transmission, and engine.

1.3. Constant Speed Driving. The car is moving at a constant speed in this situation and fuel is utilized to overcome air drag and friction in the tires, transmission, and engine.

1.4. Braking. Fuel is used to overcome resistance from the tires, brakes, transmission, and engine in addition to the energy released by the car's decreased kinetic energy when its speed is lowered.

Diesel engines have larger mechanical frictional losses than petrol engines due to the presence of high-pressure pumps in the fuel delivery system (for example, piston–crank pin journal, piston ring–cylinder wall, fuel pump element, and several auxiliary assemblies) [18]. It is also possible to reduce fuel consumption by 1.5%–2.5% if mechanical friction losses are reduced by 10% [19].

In addition to reducing fuel consumption, tribological advancements can increase an engine's power output, improve durability, and reduce emissions [20]. Reducing the frictional energy loss will improve overall performance since it is equal to the quantity of exhaust emissions lost.

Conversely, the lubricity of a fluid indicates the degree to which two mating surfaces are shielded from damage or abrasion caused by movement between these two mating bodies. Engine parts require fuel lubrication to reduce mating part friction. A fuel is deemed dry if it does not contain enough lubricant materials to lubricate parts such as cylinder liners, the fuel delivery and injection system, and so forth [21].

Lubricity levels of diesel fuel vary greatly. The origin of the crude oil, the techniques employed during the refining process, and the use of lubricity enhancing additives alone or in combination with other performance enhancing additives are just a few of the many factors that affect it. In the 1980s, diesel fuel did not have a major lubricity problem because of a higher percentage of naturally occurring polar molecules that function as lubricant agents. However, the refineries were required to produce highly refined diesel fuel in the 1990s in order to prevent atmospheric pollutants that resulted in low lubricity issues

Lubricity additives have been widely used as a low-cost method of achieving the requisite level of performance Since

the inclusion of lubricity protection in the EN 590 diesel standard in Europe [22]. It is well recognized that the intrinsic lubricating qualities of fatty acid esters, regardless of the feedstock, are the reason for the lubricity benefit of biodiesel fuels. To improve fuel lubricity, FAMES from any source are thought to have a substantial impact if they have high unsaturation levels, long alkyl chains, and fatty acid concentrations [23]. Improvements in lubricity can therefore be measured for their positive effects on decreased friction loss and greater brake power [24].

2. Regulation of Diesel Fuel Sulfur Content

Because the combustion byproducts of diesel fuel's high sulfur content can produce hazardous oxide gases that can lead to acid rain and air pollution, the fuel's high sulfur content can be harmful to the environment [25]. Most regulations pertaining to exhaust emissions were implemented during the 1980s [26]. Due to the release of NO_x and SO_x emissions from internal combustion engines, vehicles that run on hydrocarbon fuels have a major impact on air pollution, which is known to be hazardous to human health. The best way to reduce NO_x and SO_x emissions is to develop ultraclean refinery fuels [27].

Diesel fuel cannot be used in its original form; in order to mitigate its harmful effects on the environment, it must go through one or more treatment processes, such as hydro treatment, solvent extraction, and caustic treatment. Because of various national restrictions and stricter quality standards, diesel fuel has a strong trend toward having less sulfur in it [28]. Reformulated diesel fuels are another name for low-sulfur diesel fuels. Additionally, some or all of them go through heavy hydrogenation during their industrial production. Each refinery stream will add something to the final fuel.

According to European regulations, in 1995 India limited diesel fuel sulfur content to 1%. This gradually decreased in 1996 to 0.5% and then in 2001 to 0.05%. The specifications for decreasing the sulfur level to 350 ppm (0.035%) and then to 50 ppm (0.005%) in 2010 became more stringent than in 2005. In 1993, the United States (US) Environmental Protection Agency (EPA) mandated the use of low-sulfur content diesel fuel with sulfur levels <500 ppm. However, since 2006,

TABLE 1: Requirements for sulfur content in diesel fuels for on-road transportation [29].

Fuels	USA		Australia	
	Sulfur content	Year	Sulfur content	Year
Diesel fuel	5,000 ppm	Until 1993	5,000 ppm	Before 2002
Low-sulfur diesel fuel	≤ 500 ppm	1993	≤ 500 ppm	2002
Ultralow-sulfur diesel fuel	≤ 15 ppm	2006	≤ 50 ppm	2006
—	—	—	≤ 10 ppm	2009

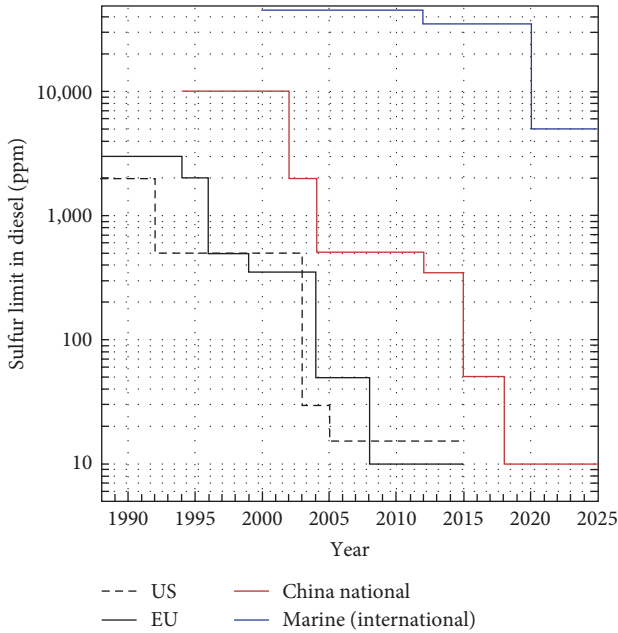


FIGURE 4: Sulfur in diesel in the United States, the European Union, China, and marine fuel.

the most recent EPA requirements have mandated that refineries producing ultralow-sulfur diesel (ULSD) fuel must generate <15 ppm of sulfur [18].

Since 2007, ULSD has been mostly used in Europe and America, so they are reported to have the world's lowest lubricity diesel fuel. Reduced sulfur content diesel fuel requirements for on-road transportation to minimize environmental pollution, as shown in Table 1.

To meet ever-stricter air quality criteria, engine and after-treatment hardware requirements have changed over the past 60 years, mostly driving changes in the fuel mix. The reduction of sulfur in gasoline and diesel fuel has been the most significant compositional fuel modification. Figure 4 illustrates how diesel fuel's sulfur content has decreased across several nations [27].

Diesel fuel is vital because it provides sufficient lubrication, especially for high-pressure pumps as well as injectors, which reduces wear on the fuel delivery system. Conventional high-sulfur content diesel fuel often has sufficient lubricating capacity to meet these active parts' requirements [30]. In the process of removing sulfur compounds, due to rigorous rules, techniques such as hydrodesulfurization and many others to reduce the quantity of diesel fuel's sulfur content are particularly beneficial for environmental protection, but they also

eliminate lubricity-imparting chemicals such as polyaromatics and oxygen-containing compounds [31] which results from the decline in fuel lubricity [32, 33].

Despite the common usage of fuel viscosity as a metric of a fuel's capacity to reduce wear, some higher viscosity fuels have been shown to induce wear by the introduction of low-sulfur diesel fuels because they lose their lubricity [34]. When the viscosities of two fluids are equal, the fluid with higher lubricity is the one that leaves a less obvious wear scar. Because of this, lubricity is also referred to as a substance's antiwear properties.

ULSD fuel is renowned for being extremely dry and unable to lubricate crucial fuel delivery components. As a result, a rapid decline in fuel lubrication performance and failures of numerous components of injection systems in diesel fuel devices [35]. The use of low lubricity poses some serious problems. Diesel fuel-related problems include faster wear, erosion or corrosion of the injection nozzles, instability of engine rpm, hard start, engine smoke, and limited power [36]. In the USA and Europe, it has been found that utilizing highly refined fuels can decrease distributor pump lifespans by up to 95% [34, 37].

The growth of passenger vehicle emissions restrictions over the past 2 decades is depicted in Figure 5. In addition to these, fuel cell applications require sulfur levels that are nearly nil for fuels like fuel cells with proton exchange membranes. Sulfur emissions should be zero or almost nil in the future.

3. Tribology

The field of tribology studies the relative motion of interacting surfaces. It addresses the application and exploration of the ideas behind friction, wear, and lubrication. In terms of roughness, hardness, flexibility, brittleness, and various impurities, the interacting surfaces may differ greatly, all of which have an important impact on the tribological process [38]. Since tribology is a subject that touches practically every part of our lives today, it has been and will continue a pertinent science. Another measure of how crucial these features are is the significant amount of today's worldwide energy consumption that is connected to friction, lubrication, and wear [39, 40].

In recent years, both the scope and depth of research in the discipline of tribology have expanded dramatically. As a result, practical and theoretical research has been published in numerous scholarly journals, like mechanical and manufacturing engineering, biomedical engineering, materials science and

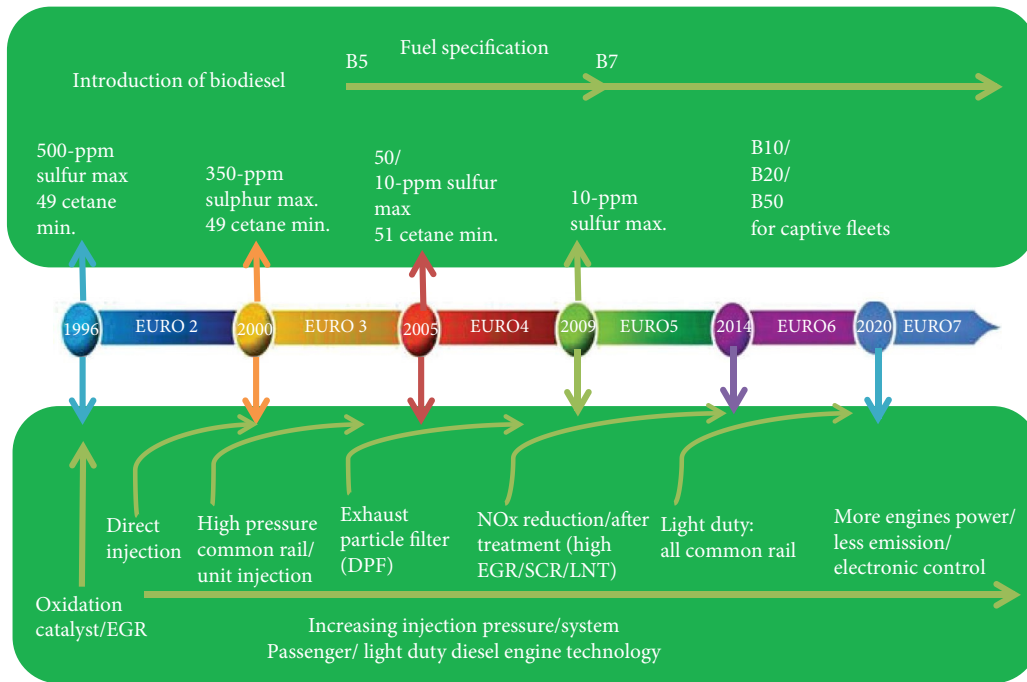


FIGURE 5: Vehicle emissions regulations development during last two decades [22].

engineering, surface science, nanotechnology, physics, and chemistry, which have increased significantly [41].

3.1. Fundamental Tribological Parameters. It is possible to measure the underlying material's surface properties separately. Key performance and dependability involve the component shape with contact type, i.e. static or dynamic. The loading type, sliding, and working environment are the main determinants of the material's wear resistance; however, the phenomenon is more complicated in the surface wear qualities, which are influenced by several tribological factors, such as the type of slide, loading method, and operating environment [42].

The most important factor to take into account when choosing a lubricant is ensuring that it meets the application's lubricating needs, particularly regarding tribological features. Lubricity, wear, and friction are all aspects of tribological performance in lubrication [43]. On sliding surfaces, lubricity is associated with the creation of a tribofilm, or lubricating layer. By minimizing direct contact between surface asperities, high lubricity decreases energy loss and friction. Three different forms of mechanical wear can happen when a sliding surface makes contact with an asperity: fatigue, adhesion, as well as abrasion. Abrasive wear (such as grooves) on sliding surfaces is caused by harsh asperities that remove a specific volume of surface material. Strong binding between the contact materials and plastic deformation are the main causes of adhesive wear, which includes the attachment of wear debris. Surface materials that are repeatedly exposed to high local stress for an extended period will eventually cause fatigue wear (e.g. cracks, fractures) [44, 45].

3.2. A Tribosystem's Mechanical Properties. A tribological system or tribosystem exists when two or more contacting

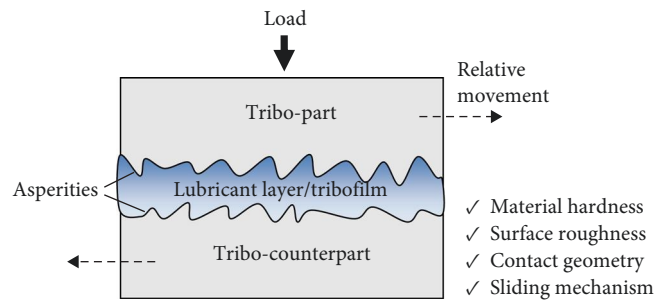


FIGURE 6: Mechanical characteristics of a tribosystem.

bodies interact with any external factor influence. The mechanical features of a tribosystem are fundamentally determined by the surface roughness, material hardness, sliding mechanism, and contact geometry of the interacting part and its complement, as seen in Figure 6.

In terms of a mechanical component or piece of equipment's performance, service life, and operating expenses, wear and friction are two highly important factors [46]. Many typical binary coatings have been used in the past two decades to reduce wear and friction where sliding or mating parts meet, like chrome nitride (CrN), titanium carbide (TiC), and titanium nitride (TiN).

Yet, because of their superior tribo-mechanical qualities, ternary nitride coatings have displaced binary coatings. These days, ternary nitride coatings are widely employed in a variety of industries, including those that produce decorative goods, naval equipment, microelectronics, orthopedic implants, cutting tools, and machinery components, the automobile sector, and the aerospace industry [47].

Most sliding materials have a surface roughness of $0.01\text{--}1.0\mu\text{m}$ and a Rockwell C hardness (HRC) of 30–64,

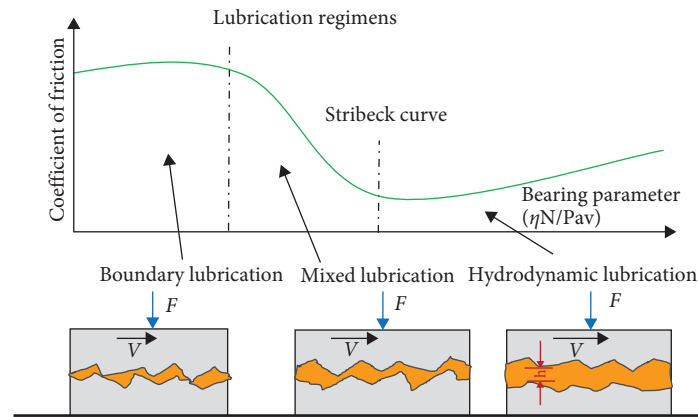


FIGURE 7: Lubrication regimes and conditions.

depending on the kind of material (like copper, steel, magnesium, etc.), hardening method (carburizing and nitriding), and coating (like polythene with an ultrahigh molecular weight), carbon-based coating, etc. [48–51]. In general, a greater hardness value means less wear, whereas more lubricity results from lower roughness values [52, 53].

3.3. Lubrication Conditions and Regimes. Lubrication is the practice or technique of applying a lubricant between two surfaces in contact to reduce wear and tear as well as friction. Tribology includes the discipline of lubrication.

Applying a lubricant between two touching bodies minimizes wear and friction is known as lubrication. Shearing action and interaction between two surfaces are avoided, which is in charge of the material's resistance to stress and motion. Surface layer lubrication and fluid pressure lubrication are the two groups of lubrication mechanisms.

Rheology and fluid dynamics govern the fluid pressure that is created inside the lubricant during fluid pressure lubrication, which keeps the separation of material surfaces. A protective thin film that adheres to the surface keeps surfaces partially separate from one another. This type of lubrication mechanism is known as surface film lubrication. This protective coating is mostly formed by chemical or physical bonding between surfaces, with the chemistry of lubricants playing a key part [54].

The type of lubrication film formed under particular operating conditions is explained by lubrication regimes. They are determined via the degree of contact among surfaces. Three categories exist for lubrication regimes: boundary, mixed, and hydrodynamic. Direct contact among the asperities is critical for boundary lubrication, and only a thin coating of the lubricant can be maintained. Choosing the appropriate lubricant is critical to the lubrication process [55, 56].

The operational parameters of any tribosystem have a significant impact on its tribological behavior. A detailed understanding of the operational lubrication regimes for the targeted machine part is necessary to provide an efficient lubricant [57]. Under strong load or startup conditions, the film thickness and roughness are of the same order of magnitude, changing the hydrodynamic lubrication into mixed

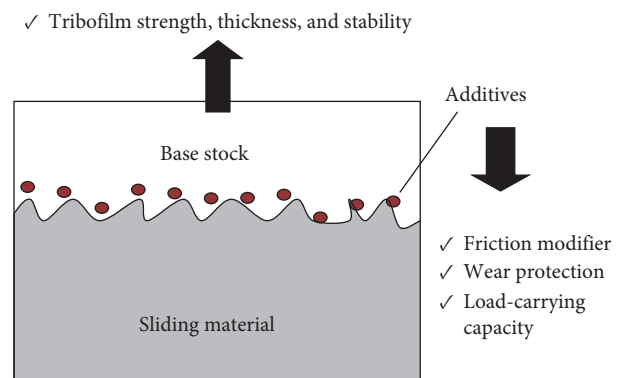


FIGURE 8: Physical and tribochemical properties of a lubricant.

lubrication [58]. In Figure 7, lubrication regimes and conditions are described.

It was found that lubrication difficulties arise in the regime of boundary lubrication situations under practical operating settings. These conditions often arise at high loads and low speeds when a very thin fluid coating adheres to the moving surfaces, separating them from one another. In these circumstances, the bulk properties of the lubricant are unimportant, and viscosity is not a friction-controlling parameter.

The most essential parameter is how the lubricant interacts with the solid surfaces both chemically and physically. Chemical reactions, physical bonding (forces of Van der Waals), and chemisorption are the processes that form boundary films. Lubricity determines the antiwear behavior of the lubricant under these conditions [26].

3.4. Lubricant Physical and Tribochemical Characteristics. Separating the contacting surfaces of moving parts is the greatest way to minimize friction and avoid wear. At sufficiently high speeds and light loads, fluidic forces or a tribochemical-produced film can perform this separation [59].

As shown in Figure 8, the most significant parameters influencing tribological performance are the lubricant's physical and tribochemical characteristics. The primary component affecting tribofilm thickness is viscosity, as well as its relationship to pressure and temperature, as a result of the

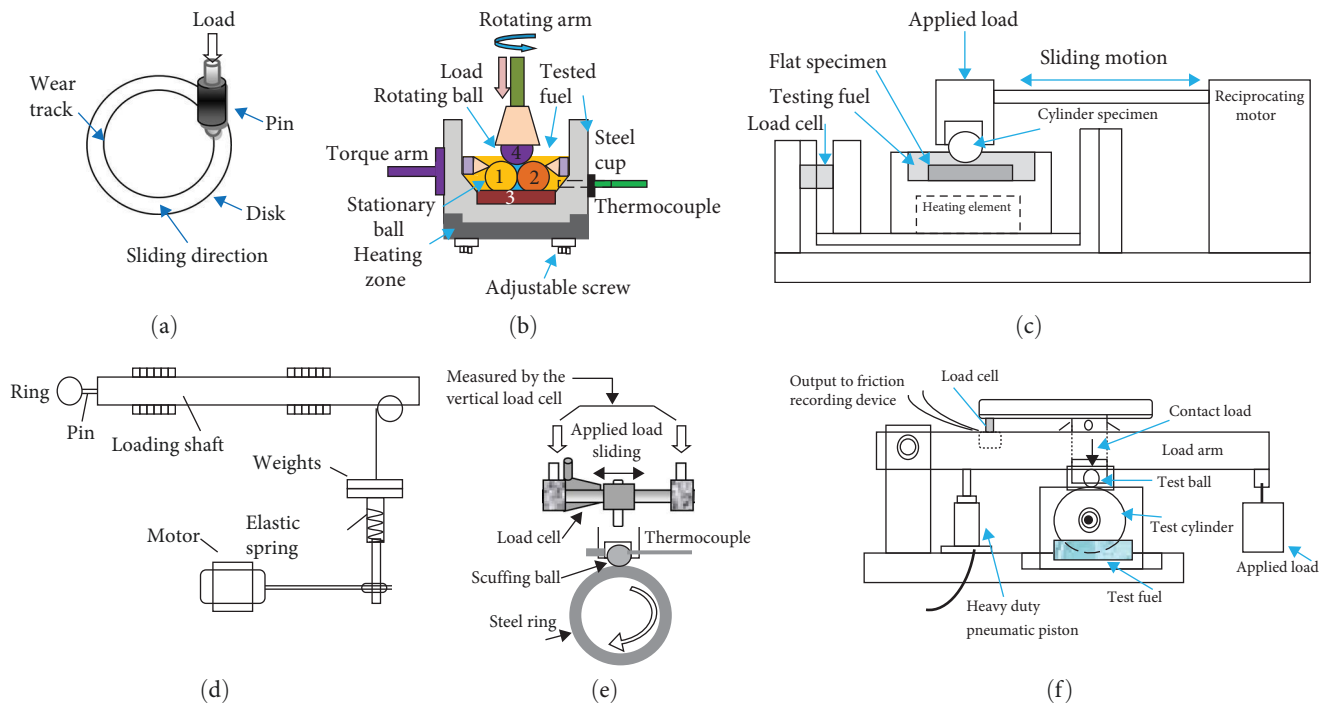


FIGURE 9: (a) Pin-on-disk tribometer, (b) four-ball wear tester, (c) high-frequency reciprocating wear rig, (d) pin-on-ring tribometer [66], (e) ball-on-cylinder (BOCLE) lubricity tests, and (f) scuffing load ball-on-cylinder (SLBOCLE).

base stock's physical characteristics, and also ultimately of tribological performance.

In the choice of lubricant viscosity for a given application, one must balance energy performance against lubrication. A more viscous lubricant that forms a thicker tribofilm however delivers poorer efficiency because of increased flow resistance. High viscosity index and pressure-viscosity coefficient lubricants ensure a stable tribofilm at high temperatures and contact loads. Further characteristics include volatility, oxidative stability, pour point, and temperature of thermal deterioration.

Surface-active materials exhibit lubricity, load carrying, and wear prevention capability in terms of a lubricant's tribochemical properties. These surface-active materials' main purposes are as friction modifiers, antiwear additives, and additives for severe pressure. In general, friction modifiers encourage protection layers that are softer and more easily sheared to decrease sliding friction, but to reduce wear, a protective sacrificial layer is created on the sliding surface using antiwear and severe pressure additives [52].

The best way to restore ULSD's original lubricating characteristics is to blend it with biodiesel. Biodiesel is used to minimize friction and encourage the formation of films. Organic compounds are routinely added to ULSD fuels to recover their lubricating qualities [60].

According to earlier research, the primary components of biodiesel, such as fatty acid methyl ester, and a few other chemicals, such as glycerides, antioxidants, and sterols, which can improve the lubricity of the fuels, are responsible for improved lubricity [36]. This finding can be attributed to the existence of oxygen-type heteroatoms, which provide the

molecule polarity and, as a result, increase its adhesion to metal surfaces. The following list of lubrication-enhancing oxygenated components is listed in descending directions: $\text{COOH} > \text{CHO} > \text{OH} > \text{COOCH}_3 > \text{C}=\text{O} > \text{C}-\text{O}-\text{C}$ [61].

4. Lubricity Test Methods

Good lubrication is critical to the reliability of an internal combustion engine [62]. Lubricity cannot be measured directly because it is not a material property. Finding out how effectively a lubricant works in a particular system is the goal of testing. This is often achieved by computing the wear that a surface experiences over a given time from a particular wear-inducing object. There is also information on other elements including surface area, temperature, and pressure. Tribometers are mechanical instruments frequently used to examine the properties of the friction contact between a specific set of material models, either in the presence or absence of lubricants [63].

The majority of the work has been done using the HFRR and the ball-on-cylinder lubricity evaluator (BOCLE). However, laboratory assessment techniques, like four-ball testers, pin-on-disc systems, high-temperature oscillating machines (HiTOM), roller-on-flat reciprocating testers, and scuffing load ball-on-cylinder lubricity evaluator (SLBOCLE), have also been developed for the several checks on the bench and in the field.

Using a tribometer has several advantages over performing experiments on actual-size components, including the ability to obtain test outcomes before producing the desired component and friction substance, as well as resource and time savings from using the same equipment for multiple tasks. A tribometer is often identified by the specific contact arrangement or original

equipment manufacturer that it simulates. The following section describes the various tribometer configurations.

4.1. Pin on Disk Tribometer. Pin-on-disk testing is a frequently used method to characterize wear and friction in materials, usually wear resistance and wear rates [64, 65]. Because it is a comparative testing method for managing wear and detecting friction in a wide range of materials, from biological implants' lubricated contacts to dry bolt screw contacts. The volume of the wear loss can be used to compute the wear rate of the material.

The pin was securely fastened to the pin support before being linked to the revolving plain disk with the necessary load. The lubricant was then injected into the machine continuously. At the start of the experiment, a hemispherical pin was employed and directly touched the disk surface [44]. Figure 9(a) shows a schematic representation of the pin and plate disc [67].

4.2. Four-Ball Wear Tribometer. In the oil industry, the four-ball wear tester is the most popular wear tester for analyzing lubricant chemistry [68]. Oil lubrication and lubrication techniques are essential for reducing wear and friction losses in machinery. The efficacy of the frictional system depends on the lubricant (oil, grease, and solid lubricants). The four-ball tester, often called the shell four-ball tester, is a tool used to describe lubricant properties such as frictional behavior, wear prevention (WP), and extreme pressure (EP) [69, 70].

Figure 9(b) shows the experimental setup of four balls. The four-ball setup is used to determine the wear scar qualities and coefficient of friction (COF) of lubricating grease. The tester is made up of four balls arranged in an equilateral tetrahedron. The bottom three balls remain stationary as the upper ball rotates and makes contact with them. The goal of this test is to determine a lubricant's wear-prevention properties [71, 72].

According to ASTM D-4172 or ASTM D-2266 (grease), over a given period and temperature, the rotation of a steel ball is against stationary lubricated three steel balls. The three stationary balls will show less wear scarring the better the lubricant avoids wear. After the test, the three wear scars are averaged and reported. During the 60 min test, the COF is also measured, and the average is provided.

4.3. High-Frequency Reciprocating Rig. A HFRR is used to measure the lubrication of heating oil or diesel fuel. Through HFRR testing, the fuel samples' lubricity was evaluated [11]. To estimate the lubricity, this standard measures the wear scar diameter (WSD) in μm along the x and y axis that are generated on the ball surface when it slides against the pressure plate, both of which are submerged in fluid. The value is stated in μm , with lower being better [9].

Even with a small amount of fuel, the HFRR allows for the detection of lubricant film generation for various additives in the lubricant region. Furthermore, at a lower sliding velocity, it is possible to assess fretting and adhesive wear. This approach can also be used to assess oil lubricity and fuels that contain lubricating additives [73]. The testing equipment allows you to change the load, temperature,

frequency, and length of the wear test. Linearly variable resistance transducer (LVRT) is used to measure wear depth [74]. Figure 9(c) shows the experimental setup of the HFRR [75].

4.4. Pin on a Ring. One of the often-used setups for tribology research on materials, coatings, and lubricants is the pin-on-ring tribometer [76]. The pin-on-ring tribometer experimental setup is depicted in Figure 9(d).

4.5. Ball on Cylinder (BOCLE). For the boundary lubrication tribological studies, a BOCLE was conceived and built in-house [77]. The US-based Ball-on-Cylinder machine and the UK-based Pin-on-Disc tester, both of which Esso created, were the first test apparatuses to exhibit sensitivity to aviation kerosene's lubricating properties. Both of these can distinguish between fuels with good lubricity and those with poor lubricity as well as look for additives [26]. Figure 9(e) shows the BOCLE [52].

4.6. Scuffing Load Ball-on-Cylinder (SLBOCLE). The SLBOCLE (ASTMD 6078-04) method is used to determine fuel lubricity [78]. To calculate how much wear has happened, the SLBOCLE method weighs down the metal ball that is in contact with the roller and measures the friction. The SLBOCLE result is expressed in grams of load, which describes the load-carrying capacity. The greater the rating, the better the fuel's scuffing load capacity. Figure 9(f) depicts the schematic representation of the SLBOCLE.

The choice of a tribotest is heavily influenced by the application being modeled and the contact conditions desired. It is not possible to say that this is the best tribometer test, but rather that it is possible to identify the optimum solution for a certain purpose. The SLBOCLE and HFRR methods are approved for diesel fuel lubricity testing per ASTM [79] standards.

Due to the various sliding geometries such as four-ball, pin-on-disk, and ball-on-disk and the unique sliding mechanism, tribological data cannot be compared between different types of tribometers like unidirectional or reciprocating, sliding to rolling ratio. A comparable machine and procedure such as ASTM D5183, ASTM D4172, ASTM D5001, ASTM 6078, and ASTM D6079 should be used for the measurements to allow for relevant comparison. To assure accuracy, even in cases where all these variables are nearly identical, researchers need to replicate the measurements in their instruments.

5. Diesel Fuel Bio-Additives

Diesel engines are widely employed in vehicle manufacture and agriculture today due to their increased operational life and tractive force [80]. To improve the quality and performance of the fuels used in automobiles, chemicals known as fuel additives have been produced [81]. Because of environmental concerns, vegetable oils have been identified as a viable biolubricant to replace present mineral oil [82].

Vegetable oils have great lubricating qualities, like high lubricity, low volatility, and a high viscosity index, making them prospective replacements for petroleum-based lubricants. Additionally, they are also renewable, less toxic, and environmentally benign [83]. Plant-based oil lubricants have

TABLE 2: Common fatty acids found in vegetable oil.

Fatty acid composition	Vegetable oils				
	Cottonseed oil [88]	Castor oil [89, 90]	Jatropha curcas [89, 91]	Neem oil [89]	Sugar cane mud [92]
Myristic acid (C14:0)	0.7	—	0.1	—	0.7
Palmitic acid (C16:0)	21.6	1.3	14.2	18.1	20.2
Palmitoleic acid (C16:1)	0.6	—	0.7	—	—
Margaric (17:0)	—	—	0.1	—	—
Stearic acid (C18:0)	2.6	1.2	7	18.1	4.3
Oleic acid (C18:1)	18.6	3.6	44.7	44.5	4.4
Linoleic acid (C18:2)	54.7	5.5	32.8	18.3	1.3
Linolenic acid (C18:3)	0.7	0.5	0.2	0.2	2.1
Ricinoleic acid (18:1-OH)	—	86.0	—	—	—
Arachidic acid (C20:0)	0.3	—	0.2	0.8	0.2
Behenic acid (C22:0)	0.2	—	—	—	—
N-tetracosanoic (C24:0)	—	—	—	—	0.7
N-hexacosanoic (C26:0)	—	—	—	—	0.3
N-octacosanoic (C28:0)	—	—	—	—	25.6
N-nonacosanoic (C29:0)	—	—	—	—	1.2
N-triacontanoic (C30:0)	—	—	—	—	15.0
N-dotriacontanoic (C32:0)	—	—	—	—	8.3
N-tetratriacontanoic (C34:0)	—	—	—	—	11.1
Saturated	25.4	2.5	21.6	37	87.6
Monounsaturated	19.2	89.6	45.4	44.5	4.4
Polyunsaturated	55.4	6.0	33	18.5	3.4

extended fatty acid chains and polar groups that make them appropriate for use in boundary and hydrodynamic lubrication applications in the automotive industry [84].

The sustainable vegetable and animal sources used to produce the bio-additive enable it to function magnificently as a diesel engine fuel [85]. The fact that it doesn't require any modifications to the engine's design makes it practically applicable to all varieties of diesel engines, which is a considerable benefit [86]. Vegetable oil is used to make biolubricant, which is a clean, nonpolluting, and sustainable process. Biolubricants are also nontoxic and biodegradable, making them easier to dispose of in the environment than petroleum-based lubricants [87].

The physicochemical characteristics of vegetable oil are determined by the fatty acid makeup [18]. The amount of double bonds and the length of the carbon chain are used to identify fatty acids. Unsaturated fatty acid chains include double bonds, whereas saturated fatty acid chains do not. The fatty acids palmitic, stearic, oleic, linoleic, and linolenic are frequently found in vegetable oils. The typical fatty acids present in vegetable oil are listed in Table 2.

Due to their close interactions with lubricated surfaces, vegetable oils can function as additives that minimize friction and prevent wear. Due to their lengthy fatty acid chains and polar groups, vegetable oil molecules are amphiphilic and have an excellent film/force connection [83]. The source and ester type both have an impact on the quality of biodiesel [93]. Ester group bio-additives are the main type of bio-additives analyzed in lubricity improvers [37].

Depending on the choice of the feedstock oil or fat, the final biodiesel's position in the tradeoff between cetane number, oxidation stability, and cold flow ability will vary. Higher cetane levels and improved oxidation stability are found in biodiesel made from more saturated feedstock, which has lower cold flow characteristics. Biodiesel made from feedstock oil or fat with low saturated content has better cold flow properties but a lower cetane number and worse oxidation stability [94].

Biodiesel is employed by the majority of the business because it has intrinsic fuel qualities that other additives often lack when compared to standard petroleum-based diesel fuels [95]. As a result, they are also used as a diesel fuel substitute. The majority of biodiesel (98%) is composed of long-chain fatty acid methyl ester (FAME), with the remainder composed of free mono- and di-glycerides and triglycerides, phospholipids, water, sterols, and antioxidants. Biodiesel, in addition to having the potential to be a renewable alternative fuel, has a higher cetane number, improved lubricity, a lower sulfur content, and a higher flash point [96].

Biodiesel made from rapeseed oil and soybean oil has proven itself to be among the alternative fuels that are the most promising and credited to other studies that have shown better lubricity than mustard oil [97, 98]. Biodiesel has been regarded as a bio-additive with effective lubricating characteristics. Even at low levels, blending biodiesel into diesel fuel can increase ULSD fuel lubricity without the need for conventional lubricity additives. The exact blending percentage required to create appropriate lubricity of a maximum 520 μm HFRR wear

scar depends on the qualities of the diesel fuel, although 2% biodiesel nearly invariably imparts adequate lubricity to biodiesel blends [99]. Tall oil fatty acid (TOFA) was one of the bio-additives investigated by HFRR. When the additive concentration was raised from 0 to 500 g/g, the WSD of nonadditive diesel fuel was lowered by 60.3%, from 630 to 250 μm , and the COF was lowered by 95.7%, from 0.47 to 0.02 [100]. Liu et al. [101] created the fatty acid methyl ester based on tung oil and maleate chemical as a lubricating addition for ultralow-sulfur content diesel fuel. Using a HFRR, low addition levels of 500 and 1,000 ppm lowered the wear scar and friction of ultralow-sulfur content diesel fuel by 40% and 46%–47%, respectively [101].

5.1. Types of Diesel Fuel Additive. Chemical compounds known as fuel additives can improve fuel performance and remedy deficiencies. If added at the refineries in concentrations below 1%, they are known as refinery (functional) additives, whereas high concentrations above 1% are known as blending components [102]. Diesel fuel additives serve numerous functions. The following are all applicable areas: pollutant management, fuel handling, fuel stability, and engine and fuel delivery system performance [103].

Another way to categorize diesel fuel additives is based on their design use. Flame additives, such as emulsifiers, pour point depressants, and dispersants, are made to solve pre-combustion problems. They serve as agents for cleaning. Improve the combustion chamber's efficiency, raise the cetane number, lessen sludge formation, stop fuel oxidation and rusty filter clogging, and prevent possible explosions due to changes in static electricity. On the other hand, afterburning additives are supposed to minimize carbon deposits, smoke, and engine emissions [104, 105].

5.2. The Role of Diesel Fuel Bio-Additives. To regain lubricity, Low sulfur petrol diesel needs to be blended with another lubricant-rich fuel or bio or chemical additions. Biodiesel and its mixes significantly reduced unburned hydrocarbon and carbon monoxide emissions while slightly increasing nitrous oxide emissions [106]. The effect of adding soybean biodiesel to ULSD fuel by the use of the HFRR test on the tribological properties. As per ASTM D6079-11, measurements were taken for the COF, film %, and WSD. The results demonstrated that increasing the amount of biodiesel enhances film formation and reduces the friction coefficient [107].

When compared to traditional petroleum diesel, biodiesel has some technical advantages.

- (i) Its engine output is comparable to that of a traditional diesel.
- (ii) Suitable for standalone usage or mixed with diesel [108].
- (iii) Biodiesel is nontoxic, nonflammable, nonexplosive, and biodegradable. In addition, its application has resulted in the decrease of several hazardous exhaust emissions.

- (iv) Inherently greater lubricity [109–111].
- (v) Sulfur oxides (SO_x), particulates, and soot emissions are nearly nonexistent, and emissions of polycyclic aromatic hydrocarbons can be decreased.
- (vi) Increased cetane number and flash point [112, 113].

However, using biodiesel will present some technical challenges. The primary concerns are as follows:

- (i) Filter plugging and injector coking [114, 115].
- (ii) Chains of unsaturated hydrocarbons are reactive (unsaturated fatty acid ester is unstable to light, catalytic system, and atmospheric oxygen) [116, 117], etc.
- (iii) Increased nitrogen oxide (NO_x) emissions in the exhaust gas, which is subject to stringent environmental standards and fluid properties [118]. Compared with diesel, the coldness is relatively poor. A further concern is the biodiesel's oxidation stability.

The stability of Biodiesel throughout storage and usage is a critical factor to take into account when using vegetable oil-based fuels.

6. Conclusion

The expanding environmental catastrophe and the energy crisis, which are the two most significant driving causes behind bio-additives worth and research, have generated a lot of interest in the fuel. Over the past few years, various countries have imposed laws on the production, emission, and alertness of ULSD and bio-additives.

It is critical to add additional additives to ensure adequate lubricity since ULSD reduces SO_x and particle emissions while retaining a low level of lubricity, which will cause friction and wear. Since the majority of the additives are hazardous to the environment, the problem becomes more complicated. To address this dilemma, some of the fuel used in internal combustion engines has been replaced with biodiesel.

According to the literature, adding bio-additives to diesel fuel boosts its lubricity. Biodiesel has long been considered a bio-additive with excellent lubricant properties. Even at low levels, blending biodiesel into diesel fuel can increase ULSD fuel lubricity without the need for conventional lubricity additives. The exact blending percentage required to create appropriate lubricity of a maximum 520 μm HFRR wear scar depends on the qualities of the diesel fuel, although 2% biodiesel nearly invariably imparts adequate lubricity to biodiesel blends.

TOFA was one of the bio-additives investigated by HFRR. When the additive concentration was raised from 0 to 500 g/g, the WSD of nonadditive diesel fuel was lowered by 60.3%, from 630 to 250 μm , and the COF was lowered by 95.7%, from 0.47 to 0.02. As a lubricant additive for ULSD fuel, Liu et al. [101] developed a fatty acid methyl ester based on tung oil and maleation chemical. When evaluated utilizing a HFRR, modest addition levels of 500 and 1,000 ppm reduced the wear scar and friction of ultralow-sulfur content diesel fuel by 40 and 46%–47%, respectively.

Because of its renewability, reduced emissions, and excellent lubricity, biodiesel is an excellent candidate. However, several disadvantages to biodiesel need to be addressed, including an increase in nitrogen oxide (NO_x) emissions in exhaust gas, oxidation stability, a problem with cold flow, etc. Biodiesel's oxidation sensitivity can differ and is mostly influenced by the feedstock and the presence of natural antioxidants. The type of fatty acid content, which requires careful consideration, determines the feedstock oil or fat to use.

Advanced research is needed to lower the cost of producing biodiesel and raise its yield by concentrating on nonedible oil, genetically modified plants, and microalgae feedstock to ensure the sustainability of bio-additives over the long period. Another issue that needs more attention in future research is developing low-cost emission reduction methods. To find out how fuel chemistry and combustion impact wear in engines that are subjected to a range of mechanical and thermal loads, future studies will include long-term endurance testing.

Nomenclature

ASTM:	American Society for Testing and Materials
AW:	Antiwear additive
BOCLE:	Ball-on-cylinder lubricity evaluator
EGR:	Exhaust gas recirculation
EHL:	elastohydrodynamic lubrication
EN:	European standard
EP:	Extreme pressure
EPA:	Environmental Protection Agency
FM:	Friction modifiers
HFRR:	High-frequency reciprocating wear rig
HRC:	Rockwell hardness
HiTOM:	High-temperature oscillating machine
LNT:	Lean NO_x trap
NO_x :	Nitrogen oxides
ppm:	Parts per million
SCR:	Selective catalytic reduction
SO_x :	Sulfur oxides
ULSD:	Ultralow-sulfur diesel
WSD:	Wear scar diameter.

Data Availability

The data is available within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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