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Retardation of oxidation and material degradation in biodiesel: a review

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In the automobile sector, biodiesel has received considerable attention as a promising diesel substitute because of its enhanced lubricity and reduced emissions. Biodiesel is composed of both saturated and unsaturated fatty acid methyl esters. The unsaturated components of biodiesel make it susceptible to corrosion for automotive components. The corrosiveness of biodiesel and its blend can be attributed to its oxygen moieties, auto-oxidation, high polarity, and hygroscopic nature. These properties may also cause tribological degradation. The present study reviews different aspects of corrosion and tribological degradation of automotive materials in biodiesel. This review will help in understanding the major characteristics and the possible degradation mechanisms of corrosion for both ferrous and nonferrous metals in biodiesel. This article extends an overview of tribological degradation of automotive materials. Remedial measures and related mechanism for both corrosion and tribological degradation have also been emphasized which made this study unique from other reviews.

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1. Introduction

The hike in petroleum diesel consumption in the automobile sector has led to a rapid depletion of fossil fuels.^{1,2} This alarming growing demand for fuel has led to the consideration of alternative energy sources. Exhaust emissions after burning of gasoline and diesel also pose a significant threat to the environment.³ Stringent regulations such as EN-590 and ASTM D 975 have been legislated to reduce diesel emissions.^{3,4} Hydro-treatment of diesel reduces emission, but its poor contents of sulfur and polar nitrogen compounds cannot provide adequate lubricity. The European Union (EU) has improved the lubricity of diesel by allowing the 5.75% blend of biodiesel into petrodiesel, which also provides minimum emissions. It can provide some technical advantages over petroleum diesel including higher cetane number and flash point, improved lubricity *etc.*⁵ Thus, biodiesel received widespread acceptance as an anti-wear additive and emission inhibitor for diesel engines.^{6,7} The increasing demand for biodiesel established it as a potential alternative fuel.^{8–10} However, biodiesel as a substitute must be technically feasible and should exhibit properties similar to those of diesel fuel.^{11–14} Pure biodiesel (B100) significantly minimizes polycyclic aromatic hydrocarbon emissions by 19.4%.¹⁵ B100 inherently offers enhanced lubricity because of the high affinity of esters to metals. The polar group of esters forms a protective layer on the tribo-contact surface, which is advantageous in reducing engine

wear and friction.^{16–20} Conversely, the susceptibility of biodiesel to oxidation is a major drawback because of its unsaturated hydrocarbons, such as oleic acid, linoleic acid, and linolenic acid.^{21–24} The presence of double-bonded carbon atoms in mono- ($C_nH_{2n-1}-COOH$), di- ($C_nH_{2n-3}-COOH$), tri- ($C_nH_{2n-5}-COOH$), and poly-unsaturated fatty acids is also responsible for the easy formation of a peroxide (ROO^*) or hydro-peroxide ($ROOH$) compound. This oxidative nature of biodiesel may lead to oxidative wear in automotive materials.²⁵ The hygroscopic nature of biodiesel leads to the hydrolysis of ester bonds and the formation of free fatty acid molecules.^{26,27} These unstable fuel properties of biodiesel and its blends appear more aggravated when fuel comes in contact with automotive materials. At present, automobile companies do not offer a warranty for diesel with >5% blends of biodiesel.²⁸ According to Kousoulidou *et al.*,^{29,30} the maximum blending ratio of saturated biodiesel can reach 30%, which reduces emissions without significantly affecting the vehicle parts. B20 (20% biodiesel and 80% diesel) significantly minimizes polycyclic aromatic hydrocarbons emissions by 13.1%.¹⁵ Low yields of blended biodiesel reduced the knock of residual oxygen in the combustion chamber, particularly for B20. However, B20 slightly influences the power and torque, and this effect is unnoticeable to the user.³¹ Moreover, B20 is the possible reason for the increased corrosion and oxidative wear, which challenges the compatibility of material–fuel interface.³² Several studies on tribology^{33–36} and corrosion^{37–44} of automotive materials exposed to various biodiesel and their blends have been conducted to quantify the compatibility. These studies are mostly focused on the low percentage of biodiesel blend.⁴⁵

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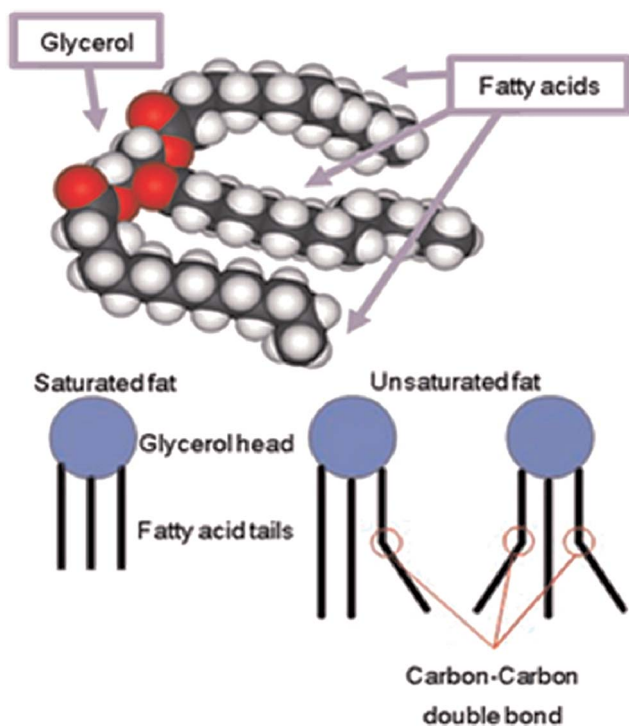


Fig. 3 Diagram represents a triglyceride, a saturated fat, and an unsaturated fat.⁵¹ Reproduced from Ref. A. Gopinath, K. Sairam, R. Velraj and G. Kumaresan, Effects of the properties and the structural configurations of fatty acid methyl esters on the properties of biodiesel fuel: a review, *Proc. Inst. Mech. Eng., Part D*, 2015, **229**, 357–390 with permission from SAGE PUBLICATIONS LTD, copyright [2016].

its potential commercial applications;⁶¹ these issues will be described later. These limitations can be solved by either material modification or chemical alteration of biodiesel.

3. Nature of biodiesel

Although biodiesel exhibit properties very similar to those of petroleum diesel, the major concerns of using biodiesel in diesel engines persist. These concerns include corrosiveness, hygroscopic nature, and auto-oxidation.⁵⁸ When the oxidation rate increases, the total acid number increases and can cause corrosion in metal parts.²² Oxidation can indirectly increase wear and reduce the lubricity of engine parts.³⁴ During long-term storage, the compositions can be changed because of the presence of air, sunlight, temperature, or material of storage container. Storage instability can degrade fuel properties such as induction period, acid value, and viscosity. If the storage duration is extended, the acid value, peroxide value, density, and viscosity will increase.⁵⁸

3.1 Oxidation

Biodiesel is chemically degraded by oxidation, which occurs because of aerobic contact during storage. The degradation of biodiesel also occurs by hydrolysis and thermal decomposition. Auto-oxidation is responsible for the formation of hydroperoxides (ROOH).⁶² The situation becomes more complicated

in case of metal-assisted secondary oxidation reaction, which finally results in products such as organic acids, aldehydes, dimers, and polymers.⁶³ The oxidation of biodiesel also depends on the solubility of water in it. During storage, transportation, and application, water can be condensed and interpose a thin layer of water–biodiesel mixture between the biodiesel and the metal surface.⁶⁴ This water reconverts esters into fatty acids *via* hydrolysis, thereby increasing the degree of unsaturation and causing auto-oxidation.⁶⁵ The oxidation rate of biodiesel can be determined by the number of allylic and bis-allylic methylene moieties adjacent to C=C bonds of oleic acid, linoleic acid, and linolenic acid (Fig. 3).⁶⁶ Relative oxidation susceptibility among the common unsaturated esters are ordered as linolenates > linoleates > oleates.⁶⁷ The OX index determines a clear picture of relative oxidation rate.⁶⁸ This index depends on the coefficients of oleic (O), linoleic (L), and linolenic (Ln) acid methyl ester, which can be determined by the formula of oxidizability ($OX = (0.02\%O + \%L + 2\%Ln)$) (Fig. 4).⁶⁹

Bis-allylic methylene moieties induce greater effects on oxidation than allylic methylene moieties. The presence of polyunsaturated methyl esters in biodiesel is more vulnerable than monounsaturated methyl esters to oxidation. Oxidation is a three-part process of radical chain reaction, consisting of initiation, propagation, and termination, as shown in Fig. 5. This process initiates with the removal of hydrogen from

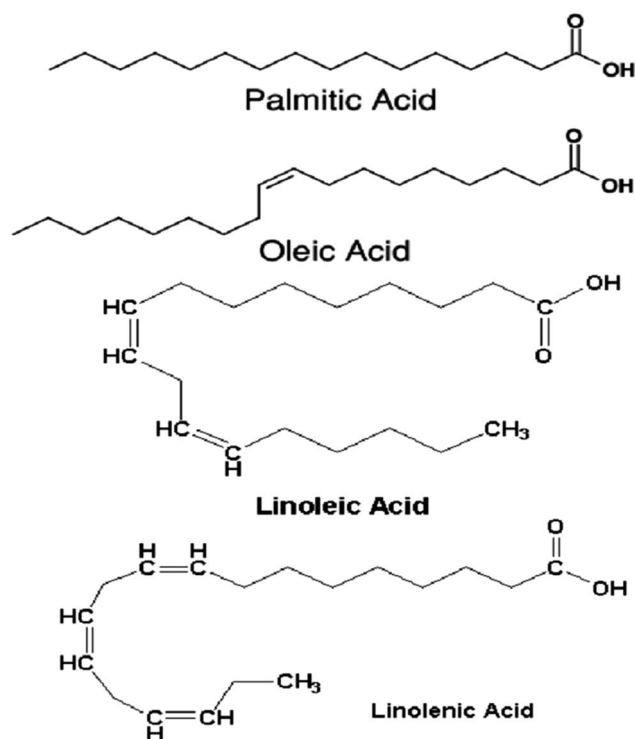


Fig. 4 Common fatty acid methyl ester biodiesel molecules with increasing C=C bonds.²⁵ Reproduced from Ref. Z. Yaakob, B. N. Narayanan and S. Padikkaparambil, A review on the oxidation stability of biodiesel, *Renewable Sustainable Energy Rev.*, 2014, **35**, 136–153 with permission from Elsevier, copyright [2016].

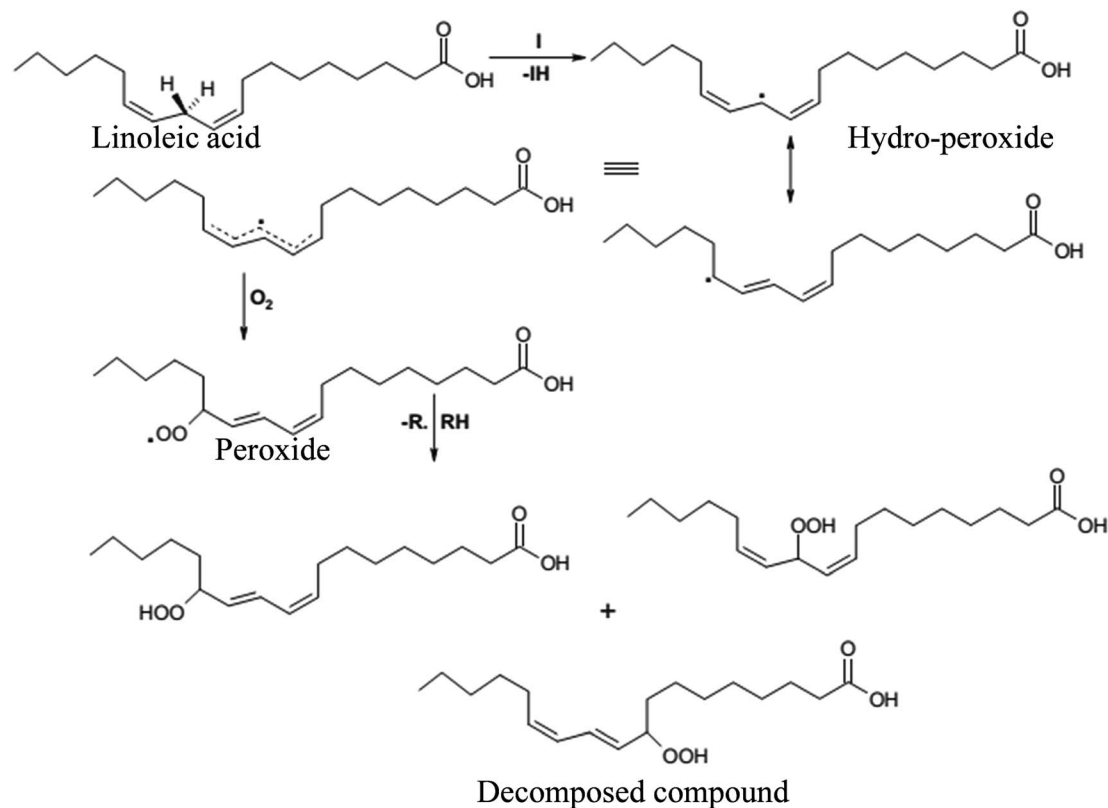


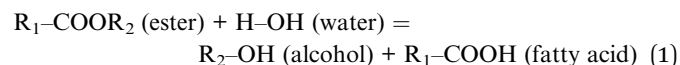
Fig. 5 Oxidation mechanism of poly-unsaturated linoleic acid methyl ester.²⁵ Reproduced from Ref. Z. Yaakob, B. N. Narayanan and S. Padikkaparambil, A review on the oxidation stability of biodiesel, *Renewable Sustainable Energy Rev.*, 2014, **35**, 136–153 with permission from Elsevier, copyright [2016].

polyunsaturated fatty acid (bis-allylic acid) to form carbon-based free radicals. These radicals react with dissolved O_2 and forms peroxide (ROO^{\cdot}) and hydro-peroxide ($ROOH$) radicals; this reaction is known as the propagation reaction. Compared with hydro-peroxides, peroxide radicals demonstrate higher affinity with O_2 ; this affinity results in auto-oxidation and increases the percentage of hydro-peroxides. Consequently, this auto-oxidation results in the formation of decomposed compounds, such as acids, aldehydes, esters, ketones, peroxides, and alcohols.⁴⁶ These decomposed compounds are responsible for the high total acid number (TAN) and the formation of insoluble gums and sediments, which reduce the quality of fuel and engine performance.^{70,71}

3.2 Hydrolysis

The degradation of biodiesel occurs through hydrolysis and thermal decomposition. The hydrolysis of biodiesel occurs with the presence of moisture, whereas thermal decomposition is caused by elevated temperature.^{25,48,72} Hydrolysis is a reaction in which the molecular bonding of esters is broken by the reaction with water. According to ASTM D6751, the maximum allowable amount of water in biodiesel is 0.05%. The hygroscopic and polar nature of biodiesel makes the water molecules attracted to the esters; thus, the water content in biodiesel may become reactive with time. This attraction initiates the hydrolysis of esters, as shown in eqn (1).⁷³ The hydrolysis of esters alters the

properties and composition of fuels. Fazal *et al.*¹¹ indicated that the water content in biodiesel increased significantly after the immersion test; they found that the tendency of biodiesel to absorb water is roughly 30 times higher than that of petroleum diesel. Water found in biodiesel may exist in either dissolved or dispersed form. Phase separation remains often imperfect, and water tends to stay in the final biodiesel product in a finely dispersed form.⁷⁴ The presence of water accelerates its corrosive interactions with the metal surface.



The existence of water in biodiesel also enhances the microbial growth, which in turn may accelerate fuel degradation.⁷⁵ Microbial growth rate is comparatively faster than hydrolysis.⁷⁶ The moisture absorption of biodiesel can reach up to 150 ppm,⁷⁷ which sufficiently decreases the heat of combustion.⁷⁸ This moisture also affects the engine respiratory system *via* microbe colonization and gel formation, which in turn may lead to fuel system plugging and injector coking. Biodiesel with high amounts of secondary products (mono- and di-glycerides) is more prone to moisture absorption,⁷⁹ whereas water-contaminated biodiesel exhibits enhanced corrosiveness.^{43,80} During the distillation and purification of biodiesel, natural antioxidants are destroyed, making biodiesel susceptible to degradation.⁷⁵

3.3 Thermal decomposition

High temperature significantly affects the accelerated oxidation of biodiesel by yielding polymerized compounds and increasing the weight of biodiesel.^{72,81} At elevated temperatures, the oxidation temperature decreases along with increasing amounts of bis-allylic hydrogens in biodiesel.⁸² At thermal instability, the poly-unsaturated linoleic acid methyl ester initially forms a cyclohexene ring *via* isomerization and then forms a dimer *via* thermal dimerization; this process is known as the Diels–Alder reaction, which is illustrated in Fig. 6.²⁵ In such manner, the elevated temperature and degree of unsaturation lead to thermal oxidation, which may produce aldehydes, ketones, and carboxylic acids, as well as limit the commercial use of biodiesel in automotive applications.⁸³

Elevated temperatures considerably influence the alteration of biodiesel properties, including oxidation, lubricity, corrosiveness, composition, induction period, viscosity, and density. According to Horel,⁸⁴ the formation of CO₂ in the presence of O₂ (*i.e.*, respiration) increases along with temperature. Severe corrosion is attributed to the presence of a higher acid number owing to oxidation. Photo-oxidation occurs as a result of exposed duration with intense light. In addition, various impurities, such as chloride ions in water, facilitate the anodic reaction and then degrade themselves and the metal surface in contact.

3.4 Co-metabolic biodegradation

Co-metabolic biodegradation⁸⁵ refers to the alteration of biodiesel and petroleum diesel by microorganisms, such as bacteria (*Pseudomonas fluorescens*, *Bacillus* sp., *Bacillus subtilis*, *Alcaligenes* sp., *P. aeruginosa*, *Acinetobacter lwoffii*, *Flavobacterium* sp., *Micrococcus roseus*, and *Corynebacterium* sp.), fungi (*Amorphoteca*, *Neosartorya*, *Talaromyces*, and *Graphium*), and yeast (*Candida*, *Yarrowia*, and *Pichia*).^{86,87} Biodiesel is more active than petroleum diesel because of its fatty acid with a hydrocarbon chain and two oxygen atoms. Moreover, fatty acids present great affinity to the abovementioned microorganisms.⁸⁸ The acid is oxidized at the position of β -carbon attached to the functional group and degraded to acetic acid. Afterward, the newly formed fatty acid with two fewer carbons breaks down to CO₂ and H₂O in the presence of microorganisms by a series of reactions.⁸⁹ Biodiesel is more prone to degradation than petroleum diesel because the latter contains aliphatic cyclic hydrocarbon, benzene, and other complex hydrocarbons with strong chemical stability and requiring more energy for microorganisms to penetrate the structure.⁸⁹ By contrast, biodiesel contains oxygenated moieties that can be easily attacked by microorganisms and promotes further degradation.⁹⁰

These factors induce significant effects on the chemical stability of biodiesel and the long-term durability of the automotive component, thereby limiting the commercialization of

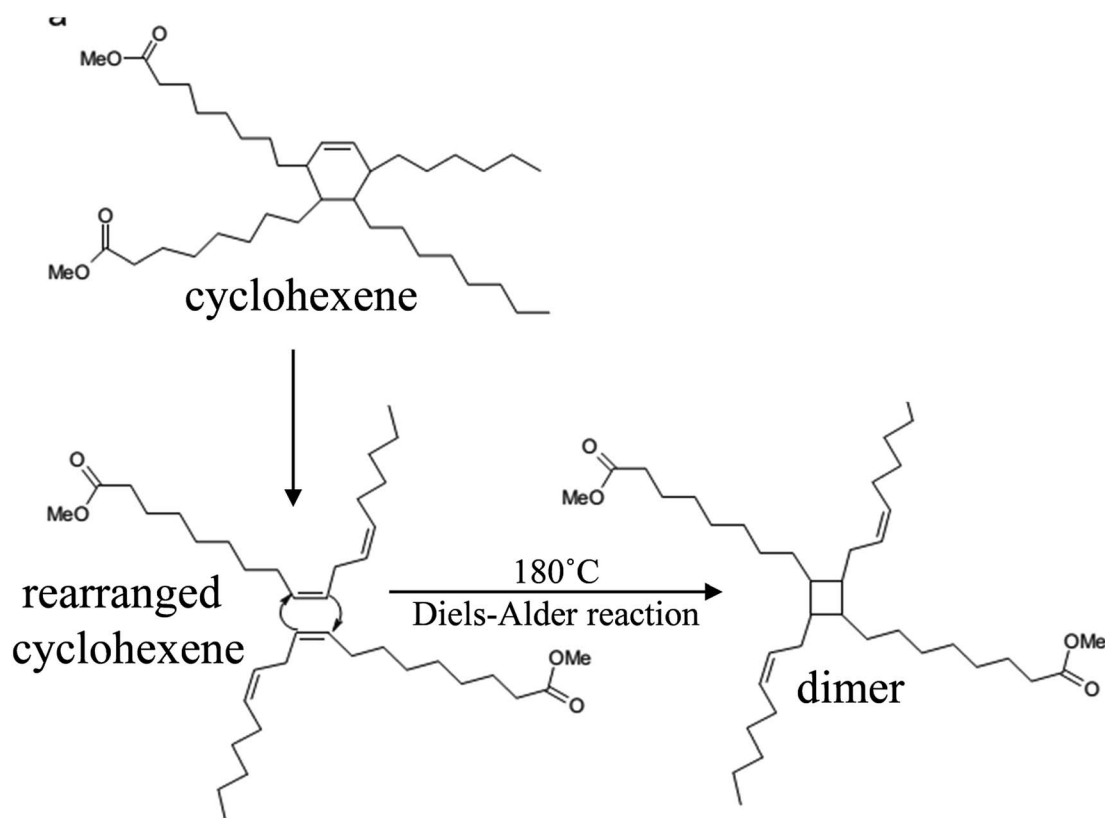


Fig. 6 Formation of dimer *via* Diels–Alder reaction.²⁵ Reproduced from Ref. Z. Yaakob, B. N. Narayanan and S. Padikkaparambil, A review on the oxidation stability of biodiesel, *Renewable Sustainable Energy Rev.*, 2014, 35, 136–153 with permission from Elsevier, copyright [2016].

biodiesel as a transportation fuel. The chemical stability of biodiesel can be improved by applying some preventive measures or alterations, such as modifying or curing with additives.³³

3.5 Remedies

The auto-oxidative stability of biodiesel can be improved by reducing the degree of poly-unsaturation and blending the biodiesel with diesel fuel.²⁵ Auto-oxidation forms hydroperoxides that decompose and cause secondary oxidation known as polymers.^{91,92} Kamalesh *et al.*⁴⁶ reported that the oxidation stability of biodiesel was inversely proportional to the percentage of linoleic and linolenic acids. Such limitations can be addressed by reducing the affinity of oxygenated moieties to the metal surface.

The deoxygenation of biodiesel is another concurrent remedial measure that poses a high atomic ratio of hydrocarbon with a remarkable reduction in O/C ratio and ensures a higher energy density. Biodiesel without deoxygenation contains oxygenated compounds, such as carboxylic acids (C₇–C₁₀) and esters that threaten the engine components.⁹³ Among the various deoxygenation methods, the application of semi-batch intermediate liquid fraction by using CaO and treated hydrocalcite (MG70) as catalysts at 400 °C achieved 85% to 88% of hydrocarbons.⁹⁴ Bio-oil was deoxygenated by promoting the reactions of decarboxylation and decarbonylation to remove oxygen atoms *via* the formation of CO₂ and CO byproducts. The successfully deoxygenation-converted biofuel mainly comprised hydrocarbons with a high atomic ratio H/C and a low atomic ratio O/C. With less oxygen content, biodiesel is considered a suitable candidate as a transportation fuel. Moreover, a remarkable reduction in oxygen ensures the high chemical stability of biodiesel, thereby inhibiting its corrosiveness and improves its tribological compatibility against automotive materials. Fuel modification with additives is another popular method for minimizing the auto-oxidation of biodiesels.⁹¹ Among the most commonly used corrosion inhibitors are

imidazolines, primary amines, diamines, amino-amines, oxy-alkylated amines, naphtheneic acid, phosphate esters, and dodecyl benzene sulfonic.⁴² The use of additives or inhibitors, such as *tert*-butyl hydroxyl quinone (TBHQ), butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), propyl gallate (PrG), pyrogallol (PY), *tert*-butylamine (TBA), ethylenediamine (EDA), *n*-butylamine (nBA), and benzotriazole (BTA), achieves chemical stability by procrastinating auto-oxidation. These feasible remedial measures against the auto-oxidation of biodiesel motivate researchers to rethink biodiesel as an alternative fuel in automotive applications.

4. Materials used in automotive engine and fuel system

The automobile application of biodiesel was first tested by Rudolf Diesel in the 18th century.⁹⁵ Numerous endeavors have followed to make biodiesel as a suitable alternative fuel because of its favorable tribological and environmental benefits.¹⁶ The engine and fuel systems in automobiles comprise various static and dynamic components, such as piston, piston ring, cylinder liner, exhaust valve, injector needle, filter plunger, fuel tank, feed pump, fuel filter, and fuel line (Fig. 7). Table 1 describes these components, the materials, and the types of material degradation. All these components are made of either ferrous or nonferrous materials, and their alloys are exposed to biodiesel under different operating conditions.^{28,96} When the chemical properties are changed, the biodiesel becomes susceptible to those metals. Therefore, a suitable blend of biodiesel and metal must be selected for both the static and dynamic parts of automobiles.

Although biodiesel has attracted a very high acceptance in automobile applications because of its environmental and tribological benefits, the corrosiveness of this material remains controversial. In,¹⁰⁷ the automotive components made of ferrous and nonferrous metals were damaged because of the accelerated oxidation or moisture absorption of



Fig. 7 Automotive components in engine and fuel systems: (a) fuel tank, (b) fuel pump, (c) fuel line, (d) fuel filter, (e) fuel injector, (f) piston, (g) piston ring, (h) cylinder liner, (i) valve, and (j) fuel filter plunger. Adopted from: <http://www.certifiedmastertech.com/wordpress/2011/08/08/automotive-fuel-tank-problems/>, <http://www.ebay.com/itm/Metal-Fuel-Line-09-10-VW-Jetta-Golf-MK5-TDI-CBEA-Diesel-03L-201-360-F-/351165118882>, http://www.agcoauto.com/content/news/p2_articleid/219, <http://dieseliq.com/common-reasons-diesel-fuel-injectors-fail>, <http://www.hotrod.com/how-to/engine/hrdp-9808-piston-ring-science/>, <http://www.hotrod.com/how-to/engine/hrdp-9808-piston-ring-science/>, <http://rajkot.all.biz/cylinder-liner-sleeves-g264983#.V06yPmh97b0>, <http://www.dealernews.com/dealernews/article/honda%E2%80%99s-crf450r-gets-engine-makeover-pro-circuit>, <http://boschnozzle.blog.163.com/blog/static/18481836020113222451735/>.

Table 1 Typical diesel engine and fuel system components, materials, and type of material degradation

Ref.	Component	Types of alloy used	Major type of degradation
37, 46 and 97	Fuel tank	Iron, nickel, manganese, cobalt, copper, leaded bronze	Corrosion
46 and 98	Fuel pump	Aluminum alloy, iron-based alloy, copper-based alloy	Corrosion
28, 83 and 99	Fuel lines	Steel, copper	Corrosion
99 and 100	Fuel filter housing	Aluminum	Corrosion
99 and 101–103	Fuel injector plunger and barrel	18CrNi8 steel: (Cr: 16% to 18%, Ni: 10% to 14%, C: 0.03%, Mn: 2%, Si: 0.75%, P: 0.045%, S: 0.03%, N: 0.10%, and Mo: 2% to 3%)	Tribology
104	Piston	Aluminum alloy: (Si: 11% to 13% Cu: 3% to 5%, Mg: 0.5% to 1.2%, Ni: 1% to 3%, Fe: 0.3%, Mn: 0.3%, Ti: 0.2%, Zn: 0.3%, Zr: 0.2%, V: 0.18%, Cr: 0.05%, and Al: remaining)	Tribology
8	Piston ring	CrMoV18 steel: (C: 0.85% to 0.95%, Si: 1%, Mn: 1%, P: 0.04%, S: 0.015%, Cr: 17% to 19%, Mo: 0.9% to 1.30%, V: 0.07% to 0.12%, and Fe: remaining)	Tribology
8 and 105	Cylinder liner	Gray cast iron: (C: 3.40% to 3.70%, Si: 2.30% to 2.80%, Mn: 0.50% to 0.80%, S: 0.15%, P: 0.25%, and Fe: remaining)	Tribology and corrosion
106	Valve	Austenitic stainless steel: (C: 0.03% to 0.10%, Si: 0.50%, Mn: 0.50%, P: 0.015%, S: 0.015%, Cr: 14.0% to 17.0%, Mo: 0.50%, and Fe: remaining)	Tribology

biodiesel, as shown in Fig. 8. The hygroscopic nature of biodiesel leads to microorganism contamination and enhances the corrosion process.^{108,109} Therefore, the corrosive nature of biodiesel poses a serious concern for the long-term

durability of automotive components and requires a rigorous investigation. The following sections discuss the degradation of automotive materials exposed to a biodiesel environment.

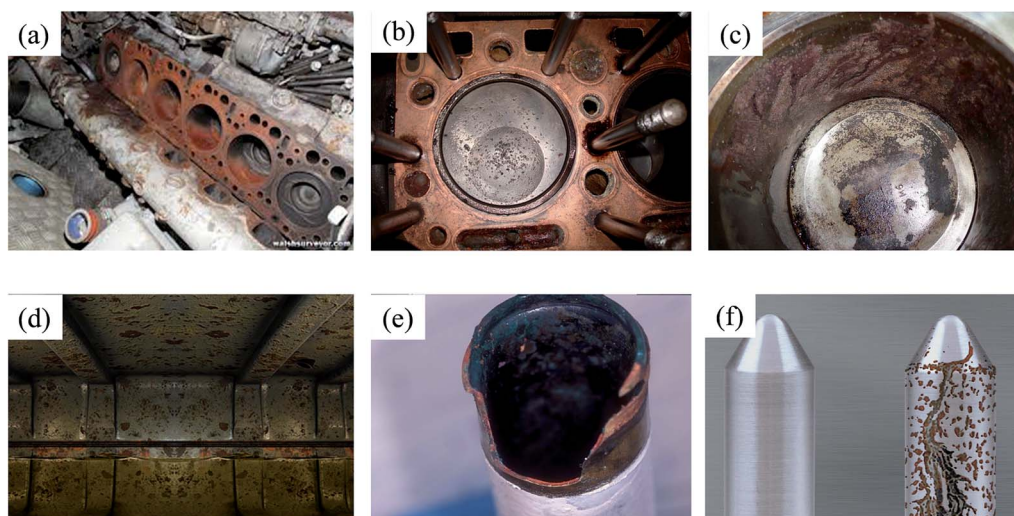


Fig. 8 Corroded automotive components in engine and fuel systems: (a) engine block, (b) piston head, (c) cylinder liner, (d) fuel tank, (e) fuel line, and (f) fuel injector. Adopted from: <http://www.walshsurveyor.com/yachts/articles/engines/index.htm>, <http://sharpmagazine.com/2016/04/28/shell-sharp-heres-how-to-protect-your-dream-car-inside-and-out/>, <http://www.goldeagle.com/STA-BIL360-Performance-Campaign>, <http://stevedmarine-consulting.com/author/katie/page/2/>, <http://landroverforums.com/forum/discovery-ii-18/water-corrosion-pistons-sleeves-63360/>, <http://www.redpowermagazine.com/forums/topic/66527-what-pistons-fit-a-wd-9-take-a-look-at-mine/>.

5. Corrosion behavior of automotive materials

Automotive materials mostly comprise ferrous and non-ferrous metals, such as iron, iron-based alloys, steel, copper, copper-based alloys, aluminum, and aluminum-based alloys, which are more or less corrosive in biodiesel. The corrosion compatibility of these materials exposed to biodiesel presents a key research issue. According to Sakae *et al.*,¹¹⁰ the corrosion of automotive materials can be classified into perforation corrosion, cosmetic corrosion, and edge corrosion, of which perforation corrosion is the most common problem.¹¹⁰ Agarwal *et al.*¹¹¹ introduced general corrosion, dry corrosion, and wet corrosion when the automotive materials were exposed to ethanol. Ionic impurities (chloride ions and acetic acid) and polar molecules are responsible for general and dry corrosion, respectively, whereas oxidized compounds and azeotropic water are responsible for wet corrosion. Prieto *et al.*¹¹² introduced galvanic corrosion, which was attributed to the very low conductivity of biodiesel as an electrolyte (4.06×10^{-9} milli-Siemens per cm) and the polarized covalent bond compound in between hydrogen–oxygen and carbon–oxygen bonds. Biodiesel is slightly more polar than diesel fuel because of the electron negativity of oxygen with enhanced corrosion.^{113,114} The O₂, H₂O, CO₂, and RCOO[−] radicals in biodiesel act as leading factors in enhancing the corrosiveness of biodiesel. During storage, the generation of aerobic and anaerobic microorganisms promotes bacterial activities and increases acidity (pH = 3.5).¹¹⁵ Chemical- or microbiological-influenced corrosion may occur in automotive materials, as discussed in the following sections.²⁷

5.1 Corrosion of ferrous metal

Corrosion generally occurs on the sample surface in a uniform or localized manner. For corrosion, Kaul *et al.* performed a 300-day static immersion test of piston and cylinder liner metal in biodiesel for various feedstocks.¹¹⁶ They found that *Salvadora* and *Jatropha* feedstocks were more corrosive than the biodiesel from other feedstocks (Table 2). The biodiesels from Karanja and Mohua feedstocks showed similar corrosion behavior as diesel. Table 2 shows that stainless steel demonstrates the best corrosion resistance among all ferrous metals, which may be attributed to its low carbon content.¹¹⁷ However, the effect of elevated temperature on the corrosion of metal and the degradation of biodiesel remains unknown.

Tsuchiya *et al.*¹²¹ studied the corrosion of steel immersed in diesel and 5% FAME blended diesel at 80 °C for 500 h. The pitting corrosion even for 2% FAME biodiesel confirmed that the extremely corrosive free fatty acids, such as formic acid, acetic acid, propionic acid, and caproic acid after oxidation, are responsible for such pitting corrosion. Fazal *et al.*²³ later investigated the corrosion behavior of cast iron and mild steel at different elevated temperatures in 50% palm biodiesel for 1200 h. Jin *et al.*¹²⁰ recently investigated ASTM 1045 mild steel at different temperatures and exposure times in palm biodiesel and diesel. Fig. 9 shows the corrosion behavior model of mild steel in diesel and palm biodiesel with the functions of time and temperature. In both kinds of fuels, the corrosion rate increases along with temperature and duration.

The corrosion of metal and the degradation of fuel both increase along with temperature. An increasing temperature is also accompanied by an increasing presence of oxygen in the

Table 2 Corrosion of ferrous metals under different operating conditions^a

Ref.	Ferrous metal	Biodiesel	Duration h	Temperature °C	Corrosion rate mpy
116	Cast iron	B0	7200	RT	0.006
118		B100	1200	RT	0.077
38		B100	2880	RT	0.112
116		Jatropha	7200	40	0.078
		Karanja, Mahua	7200	40	0.006
		Salvadora	7200	40	0.132
119		FB-80	7200	38	0.192
23	Mild steel	B0	1200	27	0.046
		B100			0.052
23		B0	1200	80	0.05
		B100			0.059
120		B0	720	27	0.0015
	B100			0.004	
120		B0	1440	50	0.0014
		B100			0.055
120		B0	2880	80	0.027
		B100			0.08
39	Carbon steel	Rapeseed oil and methanol	1440	43	0.018
44		Sunflower	3000	RT	0.170
		Sunflower	3000	60	0.336
39	Stainless steel	Rapeseed oil and methanol	1440	43	0.001
43		B100	1200	80	0.015

^a Note: B100: palm biodiesel, PB50: 50% biodiesel in diesel, FB80: 80% fat-based bio-fuel blend, and RT: room temperature.

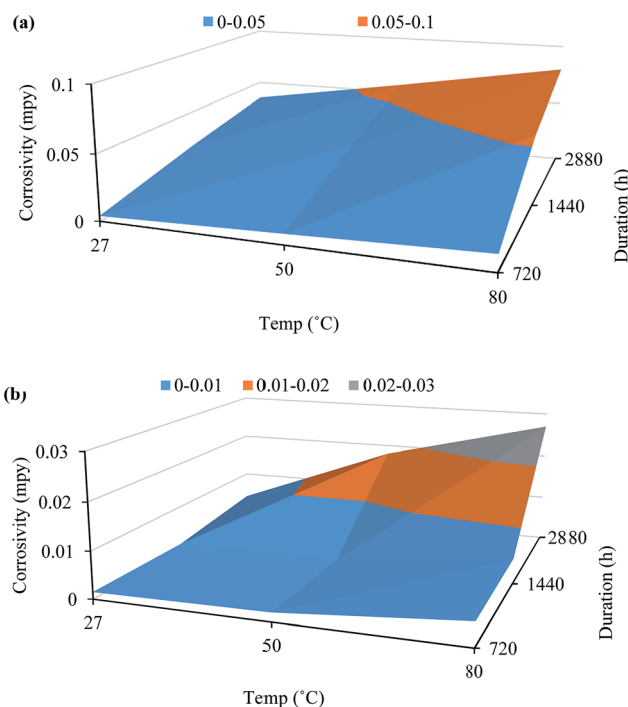


Fig. 9 Corrosion behavior of ASTM 1045 mild steel exposed to (a) B100 and (b) B0 with different temperatures and exposure times.¹²⁰

form of compounds, such as iron carbide or iron oxides. The subsequent dissolution of these compounds degrades the metal surfaces. Cast iron is highly vulnerable to corrosion mostly in palm biodiesel, followed by mild steel and carbon steel. The higher temperature and relatively higher duration in the metal-fuel interface may also contribute to the increasing corrosion.⁴³ Guthrie *et al.*¹²² clarified the corrosion mechanism of these ferrous metals, as discussed in the following section.

5.2 Corrosion mechanism of ferrous metal

According to Guthrie *et al.*,¹²² oxidation generates iron ions that form hydrated oxide with hydroxide ions in the presence of moisture and oxygen. The further reaction of iron hydroxide initiates the corrosion of iron or iron alloy. Cast iron forms a small concentration of Fe_2O_3 and $\text{Fe}(\text{OH})_2$ in diesel, whereas relatively higher amounts of FeCO_3 , Fe_2O_3 , $\text{Fe}(\text{OH})_2$, and $\text{Fe}_2(\text{OH})_2\text{CO}_3$ are formed in biodiesel. Fazal *et al.*^{23,38} investigated the cast iron and mild steel surface degradation when exposed to biodiesel (Fig. 9), and their XRD report ensured the formation of iron compounds (*e.g.*, FeCO_3 , Fe_2O_3 , and $\text{Fe}(\text{OH})_2$) at higher concentrations. Recently, D. Jin *et al.*¹²⁰ examined the corrosion behavior of ASTM 1045 mild steel in palm biodiesel and reported that on the basis of the relative area ratio, the quantity of Fe^{+3} in the corrosion product was higher than that of Fe^{+2} . Such finding is attributed to the presence of higher oxygen in biodiesel, thereby improving the interaction of biodiesel with metal to form metal compounds. For ferrous metals, the compound results from the following chemical reactions (2) (Fig. 10):

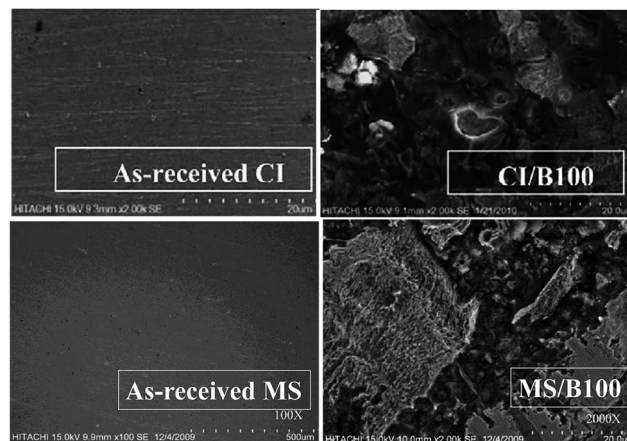
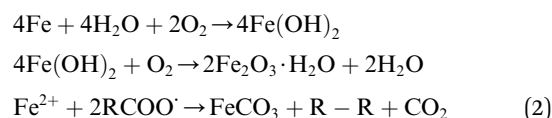


Fig. 10 SEM micrographs of cast iron (CI) and mild steel (MS) surface before and after exposure in biodiesel (B100).^{23,38} Reproduced from Ref. M. A. Fazal, A. S. M. A. Haseeb and H. H. Masjuki, Effect of temperature on the corrosion behavior of mild steel upon exposure to palm biodiesel, *Energy*, 2011, **36**, 3328–3334 and M. A. Fazal, A. S. M. A. Haseeb and H. H. Masjuki, Degradation of automotive materials in palm biodiesel, *Energy*, 2012, **40**, 76–83 with permission from Elsevier, copyright [2016].



5.3 Corrosion of non-ferrous metal

After a 10-month immersion test at 38 °C, Geller *et al.*^{119,123} observed that copper and brass demonstrated the highest and second highest weight loss because of pitting corrosion.¹²⁴ Fazal *et al.* performed a similar study on palm biodiesel^{23,38} and reported that copper was not corroded in biodiesel but also acted as a catalyst to degrade fuel properties. Table 3 shows that copper is very much aggressive in rapeseed methyl ester (0.915 mpy corrosion rate) compared with palm and sunflower. Palm and sunflower show almost similar corrosion behavior for copper and aluminum. Chew *et al.*⁴⁰ conducted a similar experiment on magnesium, which was 35% lighter than aluminum yet exhibited almost similar strength. Magnesium yielded a significantly higher corrosion rate than aluminum and copper. Magnesium, copper, and copper-based alloys are the most vulnerable to corrosion among all non-ferrous metals, whereas leaded bronze shows the best corrosion resistance capability among all copper-based alloys. Aluminum and its alloys demonstrate higher corrosion resistance than all non-ferrous materials in all kinds of biodiesel tests and can be used as benchmarks for the corrosion of other materials.¹¹⁶ The compatibility of different ferrous and non-ferrous materials has been reported, and the following section will discuss the corrosion mechanism for non-ferrous materials as clarified by Amin *et al.*¹²⁵ and Fazal *et al.*³⁸

5.4 Corrosion mechanism of non-ferrous metal

The surface of the material exposed to biodiesel was characterized *via* SEM to illustrate clearly the corrosion attack

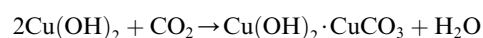
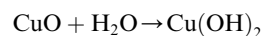
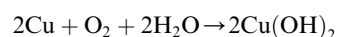
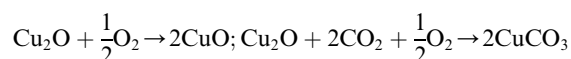
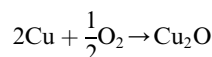
Table 3 Corrosion of non-ferrous metals under different operating conditions^a

Non-ferrous metal	Ref.	Biodiesel	Duration sec	Temperature °C	Corrosion rate mpy
Copper	39	Rapeseed oil and methanol	1440	43	0.023
	37	B100	2640	RT	0.042
	38	B100	2880	RT	0.392
	43	B100	1200	80	0.586
	37	B100 (oxidized)	840	60	0.053
	123	FB80	7200	38	0.557
	126	RME 100	600	80	0.915
	44	Sunflower	3000	RT	0.323
				60	0.640
Leaded bronze	37	B100	2640	RT	0.018
		B100 (oxidized)	840	60	0.023
Aluminum	40	B100	720	RT	0.123
			1440		0.052
	38	B100	2880	RT	0.173
	39	Rapeseed oil and methanol	1440	43	0.003
	43	B100	600 to 1200	80	0.202
	126	RME 100	600	80	0.35
	44	Sunflower	3000	RT	0.162
			60	0.316	
Aluminum alloy	116	Jatropha	7200	40	0.011
		Kanarja, Salvadora	7200	40	0.005
		Mahua	7200	40	0.012
Magnesium	40	B100	720	RT	3.091
			1440		2.656
Brass	38	B100	2880	RT	0.209

^a Note: B100: palm biodiesel, PB50: 50% biodiesel in diesel, FB80: 80% fat-based biofuel blend, RME 100: 100% rapeseed methyl ester.

(Fig. 11). Fazal *et al.*^{38,41} investigated the corrosion mechanisms for copper, brass, and aluminum. Their rigorous study on the corrosion mechanism of Cu clearly illustrated the

corrosion phenomenon, whereas their XRD pattern on the copper surface indicated the presence of comparatively higher concentrations of CuCO₃ along with other copper compounds, such as CuO, Cu₂O, Cu(OH)₂, and CuCO₃·Cu(OH)₂. These results suggest that for copper and copper-based alloys, copper carbonate (CuCO₃) and cuprite oxide (Cu₂O) are the dominant compounds formed in biodiesel and diesel, respectively. According to eqn (3), the O₂ and CO₂ dissolved from the atmosphere¹²⁷ or the RCOO[·] radical generated from esters play important roles in the formation of copper compounds. Fazal *et al.*⁴¹ concluded that the ion concentration in biodiesel and the Cu acted as catalysts for enhanced corrosion. Amin *et al.*¹²⁵ investigated the degradation of aluminum exposed to biodiesel and found that a tri-hydroxide film was formed when the aluminum was exposed to OH⁻ ion. They added that an increase in pH would accelerate the corrosion by damaging the film.



(3)

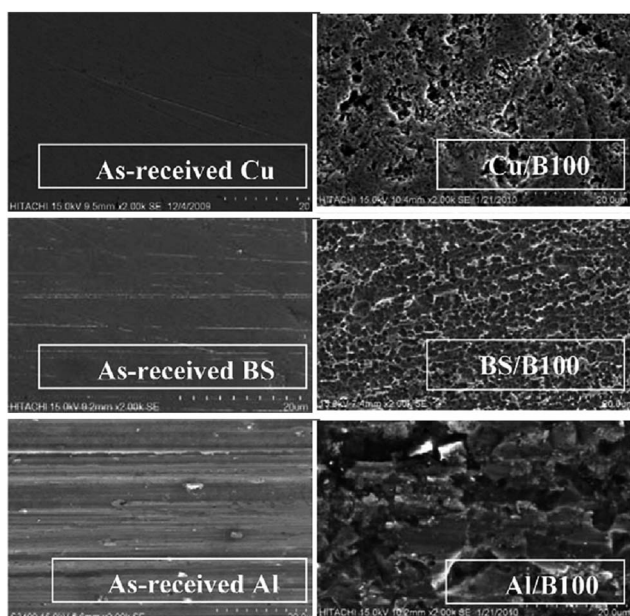


Fig. 11 SEM images of Cu, BS, and Al surfaces before and after exposure to biodiesel (B100).³⁸ Reproduced from Ref. M. A. Fazal, A. S. M. A. Haseeb and H. H. Masjuki, Degradation of automotive materials in palm biodiesel, *Energy*, 2012, **40**, 76–83 with permission from Elsevier, copyright [2016].

5.5 Remedial measures for corrosion of automotive materials

Most studies show that metals are more corrosive in biodiesel than in diesel. Material susceptibility always follows an order of corrosion rate, where magnesium > copper > brass > cast iron > mild carbon steel > aluminum > stainless steel.³⁹ Hu *et al.* argued that copper, cast iron, and mild carbon steel were significantly more susceptible than aluminum and stainless steel because of their higher presence of carbon. Although stainless steel is the best corrosion-resistant automotive material in biodiesel, this material remains corrosive in biodiesel and is not economically viable to use for automotive components.

Some characteristics of biodiesel, such as oxygen-containing functional groups (moieties), free fatty acids, unsaturation degree, and hygroscopic nature, challenge the compatibility of the material–fuel interface. Therefore, the retardation of engine material part degradation and biodiesel corrosiveness is a main topic of concern that can be mitigated by corrosion inhibitors.¹²⁸ The inhibitor is not used to prevent corrosion but to extend the time of corrosion.¹¹⁴ According to Yildirim *et al.*,¹²⁹ the effectiveness of corrosion inhibitors depends on their adsorption capabilities on reactive sample surfaces. As shown in Fig. 12a–c, the adsorption on the metal surface inhibitor successively forms a protective layer over the metal surface and prevents the direct contact between the reactive metal and corrosive biodiesel.

Yildirim *et al.* also added that among all corrosion inhibitors (*i.e.*, bearing nitrogen (N), oxygen (O), or sulfur (S) heteroatoms), amine-based inhibitors showed the best corrosion inhibition because the adsorption of molecules on the metal surface *via* heterocyclic moiety increased the interaction of N atoms (protonated amine) much higher than that of other heteroatoms that prevented the direct contact between the active metal and fuel. Amine-based corrosion inhibitors, such as TBA, EDA, nBA, and BTA, demonstrate excellent corrosion prevention performance through adsorption on the metal surface. Such

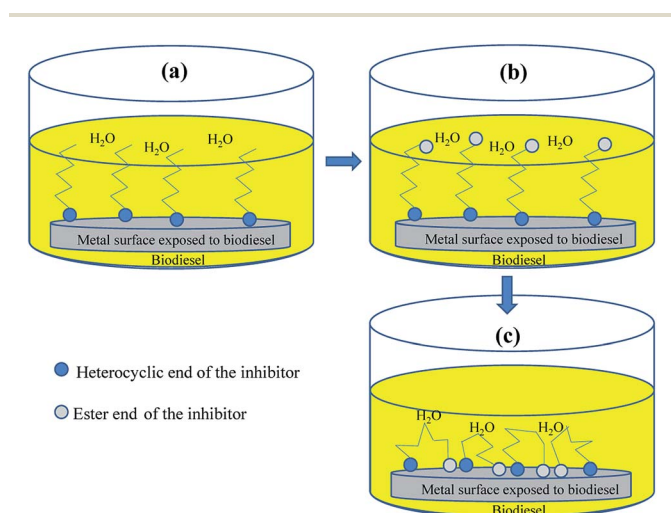


Fig. 12 Possible orientation of the inhibitor on the metal stripe surface exposed to biodiesel.

adsorption may be classified into two major types, namely, (1) electrostatic attraction between the charged molecules and charged metal (spontaneous physical adsorption) and (2) interaction of unshared electron pairs in the molecule, the π -electrons of the nitrogen atom, or the metal (chemisorption).¹³⁰ Fazal *et al.*¹¹⁸ investigated the effects of EDA, TBA, and nBA on the corrosion of copper, brass, aluminum, and cast iron and found that 100 ppm TBA-doped biodiesel was an effective corrosion inhibitor with 49.41% inhibition efficiency. The existence of a new phase ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) on the metal surface that may be formed *via* TBA contributes to corrosion retardation. Nevertheless, further studies with different additive concentrations and elevated temperatures must be conducted to identify the inhibition action and adsorption type of additives on different automotive materials. Deyab^{131,132} investigated the adsorption of ascorbyl palmitate (AP) and butylated hydroxytoluene (BHT) on exposed carbon steel, ethanol-blended gasoline, and blended biodiesel by using the weight-loss method and electrochemical impedance spectroscopy (EIS). They confirmed that the concentration inhibition efficiency increases at a specific temperature, whereas the temperature inhibition efficiency decreases at a specific concentration. M. A. Deyab^{131,132} also justified the adsorption isotherm model of inhibitors with the help of thermodynamic functions, such as activation energy (E_a), free Gibbs energy (ΔG_{addi}), and standard enthalpy (ΔH_{addi}). The following section discusses the inhibition mechanism in detail (Table 4).

5.6 Corrosion inhibition mechanism

The inhibition mechanism of additives through adsorption can be investigated by the weight loss of degraded materials. The measured weight loss can be converted into corrosion rate and inhibition efficiency as follows:^{41,131}

$$\text{Corrosion rate } (C_R) = \frac{8.76 \times 10^9 W}{DtA} \quad (4)$$

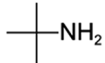
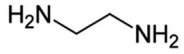

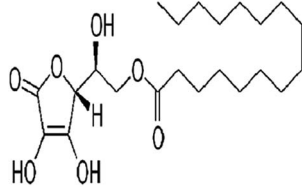
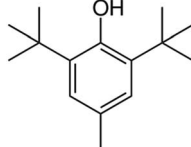
and

$$\text{Inhibition efficiency } (\eta) = \left[\frac{C_R - C_{Ri}}{C_R} \right] \times 100\%, \quad (5)$$

where corrosion rate (C_R) is expressed in micrometer per year ($\mu\text{m year}^{-1}$); W , D , t , and A denote weight loss (kg), density of material (kg m^{-3}), immersion time (h), and exposed area (m^2), respectively. In eqn (3), C_R and C_{Ri} represent the corrosion rates in biodiesel and additive-doped biodiesel, correspondingly.

5.6.1. Adsorption isotherms for the inhibition system. The performance of the additive was investigated using the recently proposed adsorption isotherms.^{131–135} Previous research provides basic information on the interaction between the additive and metal surface. The best-fitted experimental data for the isotherm model are determined and can be used to develop a suitable model of adsorption. The Langmuir model is the easiest and widely used isotherm.¹³⁶ Langmuir hypothesized that a surface contains a certain number of sites where species can adhere through physisorption or chemisorption. Surface coverage (θ) is needed to determine the characteristic curve of

Table 4 Corrosion inhibition in diesel and biodiesel

Corrosion inhibitors	Structural formula	Medium	Concentration	Material	Corrosion rate	Inhibition efficiency	Ref.
<i>Tert</i> -butylamine (TBA)		B100	100 ppm	Cast iron	0.039 mpy	49.41%	118
Ethylenediamine (EDA)		B100	100 ppm	Cast iron	0.053 mpy	31.38%	118
<i>n</i> -Butylamine (nBA)		B100	100 ppm	Cast iron	0.068 mpy	12.06%	118
Ascorbyl palmitate (AP)		Ethanol-blended gasoline	120 mg l ⁻¹	Carbon steel	1.6 × 10 ⁻⁵ mg cm ⁻² h ⁻¹	98.8%	131
Butylated hydroxytoluene (BHT)		20% wost cooking-oil-blended diesel	150 mg l ⁻¹	Carbon steel	1.38 × 10 ⁻⁵ mg cm ⁻² h ⁻¹	94.4%	132

the adsorption isotherm. For different concentrations of the additive, θ can be calculated using the inhibition efficiency equation ($\theta = \eta/100$). The calculated values help in plotting a graph and finding a suitable adsorption isotherm. The Langmuir mathematical relationship is used to fit the θ values¹³⁷ as follows:

$$C_{\text{addi}}/\theta = 1/K_{\text{eqi}} + C_{\text{addi}}, \quad (6)$$

where C_{addi} is the concentration of the additive, and K_{eqi} is the equilibrium constant of the adsorption and denotes the strength between the adsorbate (biodiesel) and adsorbent (material surface). The reciprocal of the intercept of the isotherm line represents the equilibrium constant of the adsorption. High values of K_{eqi} indicate the stronger adsorption of the inhibitor.¹³⁴ The K_{eqi} value is employed to determine the separation factor (K_L) and energy of the adsorption as follows:¹³⁸

$$K_L = [1 + K_{\text{eqi}}C_{\text{addi}}]^{-1} \quad (7)$$

The above equation identifies the type of isotherm under the following conditions: (i) favorable adsorption if $0 < K_L < 1$ and (ii) unfavorable adsorption if $K_L > 1$.¹³⁸ The standard free energy of adsorption (ΔG_{addi}) must be determined to identify whether the adsorption process is spontaneous. The ΔG_{addi} of the inhibitor on the material surface can be calculated as follows:¹³⁹

$$\Delta G_{\text{addi}} = -RT \ln(55.5 \times 10^6 K_{\text{eqi}}) \quad (8)$$

where ΔG_{addi} , R , T , and K_{eqi} denote the adsorption energy of the inhibitor (kJ mol⁻¹), the universal gas constant (8.314472 J mol⁻¹ K⁻¹), the operating temperature (K), and the equilibrium

constant of the adsorption process, respectively. Depending on the value of ΔG_{addi} , the adsorption process can be classified as (i) chemical adsorption (if $\Delta G_{\text{addi}} < -40$ kJ mol⁻¹), (ii) physicochemical adsorption (if $-40 \leq \Delta G_{\text{addi}} \leq -20$ kJ mol⁻¹), or (iii) physical adsorption (if $\Delta G_{\text{addi}} > -20$ kJ mol⁻¹).¹³⁴

5.6.2. Thermodynamic functions of the corrosion inhibition mechanism. The effect of elevated temperature on corrosion inhibition can be identified by several thermodynamic functions, such as activation energy (E_a) and standard enthalpy (ΔH_{addi}), for adsorption processes. These functions help define the adsorption nature of different concentrations of additives on the metal surface that is exposed to biodiesel at elevated temperatures as well as the nature of adsorption reaction. The following equation computes the activation energy (E_a) of the corrosion process in different additive concentrations:¹⁴⁰

$$E_a = \frac{2.303R \times \log \frac{C_{\text{R@RT}}}{C_{\text{R@ET}}}}{\left(\frac{1}{T_{\text{ET}}} - \frac{1}{T_{\text{RT}}}\right)} \quad (9)$$

where $C_{\text{R@RT}}$ and $C_{\text{R@ET}}$ denote the inhibited corrosion rates at room temperature (T_{RT}) and elevated temperature (T_{ET}) (K), respectively. The endothermic or exothermic process in adsorption can be distinguished by considering another thermodynamic parameter, namely, the standard enthalpy of adsorption (ΔH_{addi}), which can be calculated by the linear regression between $\Delta G_{\text{addi}}/T$ and $1/T$ of the following Gibbs-Helmholtz equation:¹⁴¹

$$\frac{\Delta G_{\text{addi}}}{T} = \frac{\Delta H_{\text{addi}}}{T} + C \quad (10)$$

In the exothermic process, the absolute value of ΔH_{addi} is lower than 40 kJ mol^{-1} . However, in the endothermic process, the absolute value of ΔH_{addi} approaches 100 kJ mol^{-1} or above.¹⁴² This process for biodiesel requires further study.

6. Tribological degradation

In automobiles, 48% of the total energy that is developed by an engine is lost because of friction.¹⁴³ The United States Department of Energy reported that reducing the friction and wear in the tribological components of engine can save US\$ 120 billion per year.¹⁴⁴ Therefore, the importance of reducing tribological degradation has been increasingly acknowledged. Several studies have also been conducted to understand the lubricity of biodiesel for automotive materials.^{33–36}

6.1 Wear and friction

Friction and wear play important roles in defining the durability of mating components against tribological degradation where the sliding contact takes place. Diesel engine and its fuel systems comprise numerous dynamic tribo-pairs, such as piston and piston ring to cylinder liner, valve to valve guide, injector needle to injector inner chamber, and filter plunger to plunger guide. Most of these tribo-pairs are directly exposed to fuel, which solely provides the lubricity of these mating components.⁹⁶ Biodiesel shows excellent lubricity by reducing friction and wear through its unsaturated hydrocarbon content.^{23,46,145} Several experiments using reciprocating motion, rotating motion with four-ball, pin-on-disk, and ball-on-plate arrangements were performed to evaluate the wear behavior in the metal and biodiesel interface. For example, Xu *et al.*¹⁴⁶ investigated the effect of different biodiesels on automotive materials in relative motion. They found a better lubricity yet a rough surface texture in surface morphology because of the oxidation of biodiesel. The main wear mechanism was identified as oxidative wear. In,¹²¹ a black corrosive organic product was observed adjacent to the worn surface because of the oxidation of biodiesel, thereby creating corrosive acid at a higher temperature.^{147,148} However, this oxidation creates an inorganic oxide layer or lubrication film and provides less abrasive wear,¹⁴⁹ which can be attributed to the higher oxidation rate of fresh biodiesel, which in turn forms relatively higher molecular weight compounds and increases viscosity or lubricity.¹⁵⁰ In their analysis of the tribological performance of biodiesel (Jatropha), Kumar *et al.*¹⁴⁸ found high coefficients of friction and wear at a high temperature and load because of the accelerated oxidation of biodiesel at high temperature as shown in Fig. 13. These findings indicated that temperature and load individually and collectively affected the tribological performance of biodiesel. Blends with lower concentrations of biodiesel showed a higher frictional coefficient because of the non-uniformity of heteroatom.³⁴ Abrasive wear, which is observed for pure diesel fuel and lower concentrations of biodiesel, can be identified by the particle sizes of extruded debris of less than $20 \mu\text{m}$.¹⁵¹ These third body abrasions may exist if the debris size ranges from $1 \mu\text{m}$ to $4 \mu\text{m}$ with less than $20 \mu\text{m}$ clearance. In

actual practice, the debris rolls within the clearance and grooves, thereby resulting in less friction and no further abrasive wear.

The lubricity of diesel or biodiesel protects a tribo-pair from friction and wear. The reduction of friction and wear reduces fuel consumption with increased torque, improves durability, increases reliability with a low maintenance cost, and extends the life service interval.¹⁵² Given the poor lubricity of conventional diesel, the pure biodiesel or its blends may present promising alternatives that can address the challenges in lubricity. To improve lubricity, ASTM-D7467 has mandated biodiesel blends, such as B10 (10% biodiesel and 90% diesel) and B20 (20% biodiesel and 80% diesel).²⁹ The standard mixture of biodiesel (B20) can reduce particulate emissions by 15% to 20%.¹⁵³ The presence of sulfur in diesel provides a favorable lubricity, but the high sulfur content of diesel negatively affects the thermal and thermo-oxidative stability as well as the SO_2/SO_3 emission.¹⁵⁴ Conversely, biodiesel offers better lubricity than diesel fuel with extremely low sulfur content.¹⁵⁵ Such better lubricity can be attributed to the elements in biodiesel (*i.e.*, unsaturated components, free fatty acids, oxygenated molecules, and long chain molecules), the polarity, moderate viscosity, and oxidative nature of ester molecules, and the contaminants (*i.e.*, glyceride and triglycerides).^{33,34} The lubricity of biodiesel mainly depends on methyl esters and mono-glycerides, whereas free fatty acids, diglycerides, and triglycerides almost have no effects on lubricity. Drown *et al.*¹⁵⁶ argued that long chain fatty acids and the

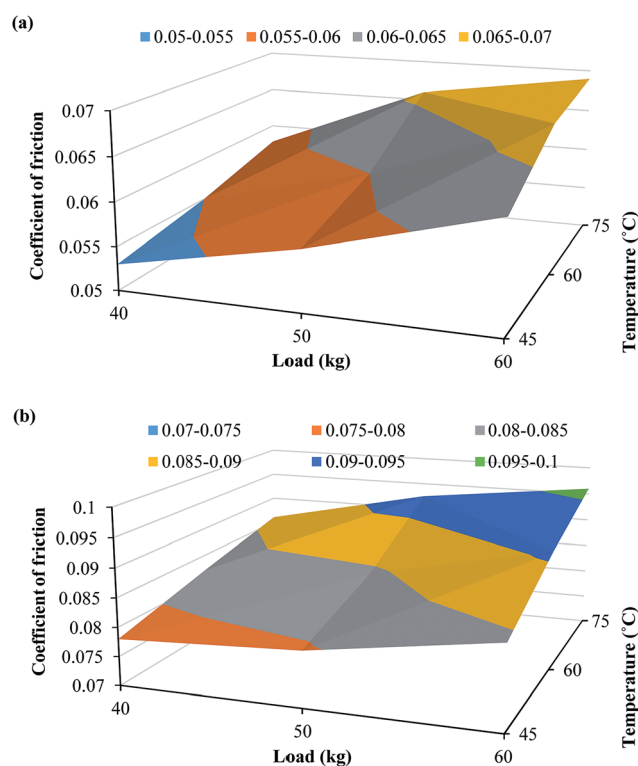


Fig. 13 Tribological behavior of steel exposed to (a) Jatropha and (b) B0 with different temperatures and load.¹⁴⁸

residual glycerin rate of oleic acid in biodiesel can behave favorably with better lubricity. Sharma *et al.*¹⁵⁷ explained that each molecule of the aliphatic fatty acid ($C_nH_{2n+1}COOH$) contained a polar long covalently bonded hydrocarbon chain. The long chain ends have high affinity to partially positive-charged metal surfaces and align themselves normally to the surface to create a monolayer film for the sliding surface. This sliding layer provides a favorable lubricity because of the absence of direct metal-to-metal contact and the reduced thermal energy.⁵⁷ Minami and Mitsumune¹⁵⁸ reported that the anti-wear properties of biodiesel depended on the amount of peroxide, which can decompose the anti-wear additives and introduce higher wear. The presence of oleic acid rate in biodiesel also has a vital role on the lubricity property.¹⁵⁹

6.2 Metal surface degradation

The fuel properties of biodiesel are affected during auto-oxidation. Fig. 14 shows that the changes in fuel properties can lead to degradation or damage the automotive components, thereby affecting the lubricity of biodiesel. Some products, such as hydro-peroxides and organic acids, are formed during oxidation, create an insoluble residue, and decrease lubricity. Table 5 presents the results of the biodiesel lubricity tests on HFRR (ASTM D6079) and four ball wear machine (ASTM D4172) under different biodiesel blends. These tests reveal that temperature friction and wear both increase along with decreasing lubricity,^{26,34,148} which may be attributed to the reduced thickness of the film created at the contact surface as a result of the increased temperature. This phenomenon may also be explained as the fragmentation of film through polymerization, cross linking, and decomposition at elevated

temperatures.^{57,160,161} Generally, the tables indicate that all blends of different feedstocks behave better than diesel fuel with better lubricity, less friction, and less wear without engine modifications. From the tribological perspective, coconut oil achieves the best results in the rigorous test followed by sunflower and palm biodiesel because a higher percentage of saturated fatty acid can ensure better lubricity by preventing the reconversion of unsaturated fatty acid. These results may also be attributed to the fact that the carbon chains of fatty acids in coconut oil are longer than those of fatty acids in sunflower and palm oil.

Although additive-free biodiesel lubrication film is superior to additive-free diesel, the former has a higher wear rate than commercial lubricants.¹⁶² The hydrodynamic and/or boundary lubrication film thickness can be reduced by the high temperature, load, and frequency, as well as the low viscosity and concentration.^{161,164} Oxidation instability, as a consequence of temperature, moisture absorption, and reactivity of the unsaturated hydrocarbon chain, has negative effects on the lubricity and wear for different blended fuels.^{19,22} Moreover, oxidation increases viscosity and demonstrates better lubricity in the short-term test, but the degradation of fuel reduces lubricity in the long-term study.¹²¹ The degradation of fuel enhances corrosion and subsequently leads to the rapid tribological degradation of automotive materials. Therefore, the remedial measures with inhibitors must be investigated to improve the lubricity of biodiesel and its blends.

6.3 Remedial measures for wear reduction

Antioxidants are naturally present in triglyceride yet is neutralized through transesterification, thereby deteriorating

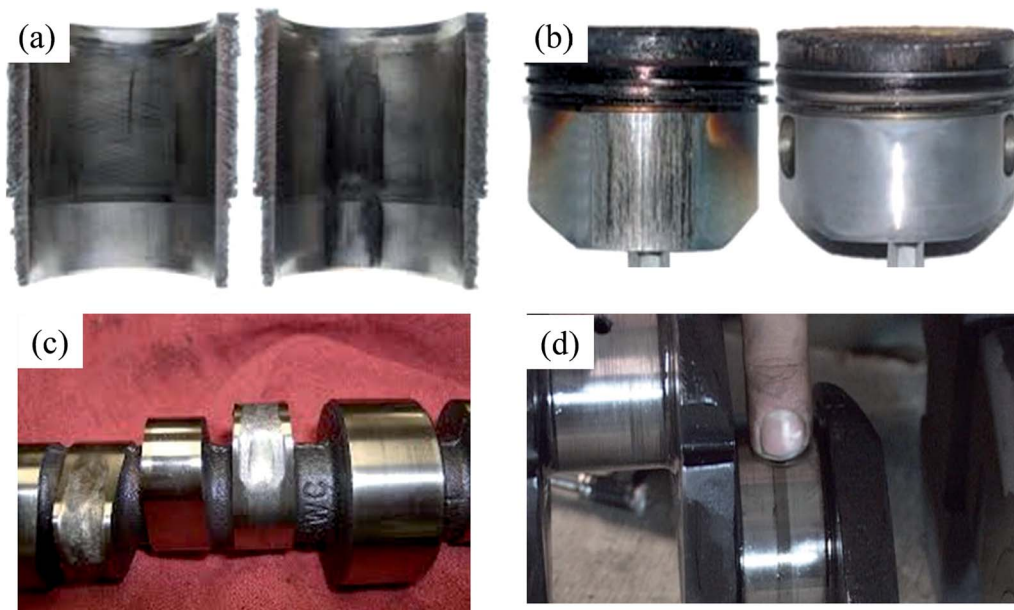


Fig. 14 Tribological degradation of automotive components: (a) cylinder liner, (b) piston, (c) cam, and (d) crank shaft. Adopted from: <http://dev.pceo.com/ViscosityModifierPart2.html>, http://www.zmax.com/about_zmax/testing/, <http://garage.grumpysperformance.com/index.php?threads/cast-roller-cams-and-high-spring-pressures-don-t-work-well.1489/>, <http://vintagetractorengineer.com/2012/12/mf35-perkins-3a-152-strip-down/>.

Table 5 Wear scar diameter and friction coefficient at various operation parameters

Ref.	Biodiesel	Blends	Tribo-pair	Load (N)	Speed/frequency/rotation	Temp (°C)	WSD (mm)	COF	Duration h
162	Coconut	B100	CI	1226	50 km h ⁻¹	—	0.54	0.07	2
34	Palm	B0	Cr-alloy steel	392	1500 rpm	75	0.95	0.09	1
		B10					0.927	0.0892	
		B20					0.848	0.08775	
		B50					0.82	0.086	
		B100					0.76	0.0857	
148	Jatropha	B0	Steel	588	1500 rpm	45–75	1	0.08–0.1	1
		B20/B40/B100					0.5–0.7	0.055–0.075	
163	Soybean	B0	Low C-steel	100	—	60	0.4	0.11	1
		B20					0.27	0.10	
158	Sunflower	B100	Steel	392	1200 rpm	75	0.3	—	1
154	Rapeseed	B100	Steel	2	50 Hz	60	0.217	0.125	1.5

oxygen stability.²⁵ In tribology, the oxidative deterioration of biodiesel introduces oxidative wear.¹⁴⁶ Some other factors, such as moisture absorption, deposit formation, corrosiveness, contaminants, elevated temperature, and reduced viscosity, have negative effects on biodiesel lubricity.^{26,34} Biodiesel oxidation cannot be fully eradicated yet can be significantly minimized by using antioxidants that can retardate the reconversion of free fatty acids to triglycerides. Therefore, antioxidants are needed to improve the oxidation stability of biodiesel and reduce oxidative wear. Small percentages of hydroxylated and unsaturated components can be used to improve the lubricity of low-sulfur diesel fuels.¹⁶⁵ However, a higher percentage of biodiesel is currently used as an alternative to petro diesel to reduce emission. Such percentage must be free from hydroxylated and unsaturated components to prevent oxidation, which can lead to poor atomization, sticking, and coking. Therefore, researchers must search for a suitable antioxidant to improve lubricity. Antioxidants are generally divided into hydro-peroxide decomposers and chain breakers. Phenolic types are most commonly used as chain-breaking antioxidants. The active hydroxyl group in phenolic antioxidant provides protons that intercept the peroxide radical (RCOO[•]) to prevent the creation of another radical as illustrated in Fig. 15. Therefore, the chain reaction of auto-oxidation is hampered as follows:



Radical termination stage: $\text{A}^{\bullet} + \text{A}^{\bullet} = \text{A-A}$ or non-radical material

The inhibition efficiency of phenolic antioxidants can be determined by the number of hydroxyl/phenolic groups that are found in the molecular structure. The inhibition efficiency of several additives can be explained based on the number of hydroxyls and OH groups that are attached to the aromatic ring. TBHQ, PG, and PY contain two OH groups, whereas BHT and BHA only contain one OH group that is attached to the aromatic ring. Based on theory of electro-negativity, TBHQ, PG, and PY provide more locations to react with the free radical, thereby terminating the auto-oxidation chain reaction without forming any acidic products.⁵⁸ Moreover, decomposer antioxidants (*i.e.*, sulfides and phosphides) convert hydroperoxides into alcohols and become stable after transforming into an oxidized form.

Table 6 shows the commonly used synthetic antioxidants, with each antioxidant behaving differently for various feedstocks and fatty acid ester compositions.¹⁶⁸ TBHQ, AP, PrG, and PY have more than one hydroxyl groups that is attached to the aromatic ring; therefore, these antioxidants are more effective than BHT and BHA. TBHQ is considered a more active antioxidant for palm biodiesel, soybean, and sunflower because this antioxidant can rapidly form a complex bond with the free radicals of these feedstocks than those of other feedstocks. By contrast, PY and PrG have also been reported as the best antioxidants because of their molecular structures, which have a larger number of hydroxyl groups attached to their rings.¹⁶⁹ Table shows that PY is the most effective antioxidant for biodiesel, whereas TBHQ is the best antioxidant for palm biodiesel. Several studies have attempted to quantify the inhibition effectiveness of specific biodiesels as shown in Table 6. However, the inhibition mechanism of additives on the tribological degradation of different automotive materials has attracted limited research. The following section discusses the materials and methods for identifying the retardation mechanism of degradation because of wear and friction.

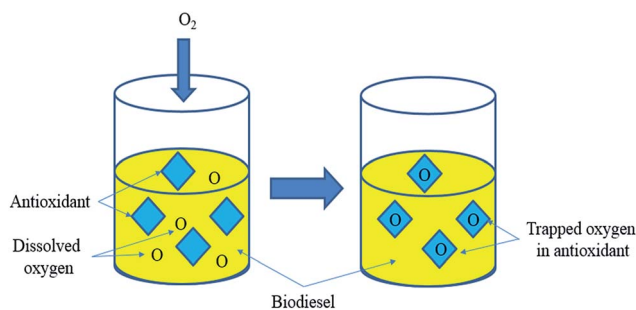
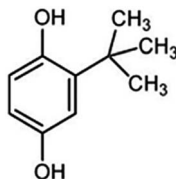
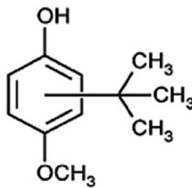
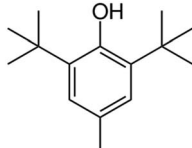
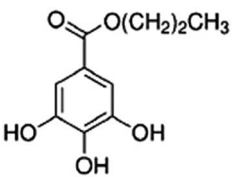
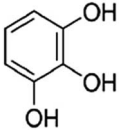


Fig. 15 Retardation mechanism of the chain reaction of auto-oxidation.

Table 6 Antioxidants used for wear reduction

Ref.	Name	Structural formula	Suitable medium
166	<i>Tert</i> -butyl hydroxyl quinone (TBHQ)		Palm biodiesel, soybean, sunflower
58	Butylated hydroxyanisole (BHA)		Castor oil, methyl soyate
72	Butylated hydroxytoluene (BHT)		Soyabean oil ethyl este, Tallow
167	Propyl gallate <i>i.e.</i> 3,4,5-trihydroxybenzoate (PrG)		Soyabean
46	Pyrogallol <i>i.e.</i> 1,2,3-trihydroxybenzene (PY)		Rapeseed oil, cooking oil, tallow, Karanja oil, Jatropha oil, croton oil

6.4 Retardation mechanism of tribological degradation

The lubrication regime must be determined to characterize the retardation mechanism, whereas the minimum film thickness to surface ratio must be identified to determine the lubrication regime or specific lubrication film thickness.

6.4.1. Film thickness. The specific lubrication film thickness can be determined as follows:¹⁷⁰

$$\lambda = \frac{h_{\min}}{\sqrt{R_{a,1}^2 + R_{a,2}^2}} \quad (11)$$

where λ is a specific lubrication film thickness, h_{\min} is the minimum film thickness (m), and $R_{a,1}$ and $R_{a,2}$ denote the average roughness for the interface materials. The corresponding minimum film thickness for isoviscous lubricant can be predicted by using the well-known Hamrock and Dowson formula as shown in eqn 3.^{171,172} This equation is widely applied in many tribo-pairs with varying contact geometries, including the point contact of hemisphere (ball) on a flat surface (plate).^{173,174} The minimum film thickness equation is expressed as follows:

$$h_{\min} = R_C \left[2.8 \left(\frac{V \eta_0}{E R_C} \right)^{0.6} \left(\frac{L}{E R_C^2} \right)^{-0.21} \right] \quad (12)$$

where R_C , V , η_0 , L , and E denote the radius of curvature,¹⁷⁵ surface velocity (m s^{-1}), dynamic viscosity at atmospheric pressure of the lubricant (Pa s)—which can be obtained by multiplying the measured kinematic viscosity ($\text{m}^2 \text{s}^{-1}$) by density (kg m^{-3})—normal load (N), and modulus of elasticity (Pa), respectively. Therefore, we obtain the following:

$$\frac{1}{E} = \frac{1}{2} \left(\frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right) \quad (13)$$

where ν and E denote the Poisson's ratio and young modulus of the interfaced materials, respectively.

6.4.2. Adsorption of lubricant on the metal surface. The adsorption isotherm can be derived from the coefficient of friction. This isotherm shows the relationship between the concentration of additives in biodiesel and its coverage on the tribo-interface surfaces. The friction-derived adsorption isotherm can be obtained from the fractional surface coverage at a specific concentration as follows:^{176,177}

$$\theta = \frac{\mu_{\text{blend}} - \mu_{\text{ac}}}{\mu_{\text{blend}} - \mu_{\text{bc}}} \quad (14)$$

where μ_{blend} is the coefficient of friction (COF) of biodiesel blend, μ_{ac} is the COF at a specific additive concentration, and

μ_{bc} is the COF at the concentration above which the COF no longer increases or decreases. The Langmuir isotherm is the simplest adsorption model that provides useful insights into the concentration dependence surface adsorption.¹⁷⁸ K_{eqi} is the equilibrium constant of the adsorption and is required to yield the ΔG_{ads} values of the additives on the rubbing surfaces. The equilibrium constant can be defined as follows in terms of surface coverage (θ) and additive concentration (C):¹⁷⁸

$$K_{eqi} = \frac{\theta}{(1 - \theta)C} \quad (15)$$

$$\frac{1}{\theta} = \left[\frac{1}{K_{eqi}} \times \frac{1}{C} \right] + 1 \quad (16)$$

The slope of the θ^{-1} versus C^{-1} isotherm line represents the equilibrium constant of the adsorption (K_{eqi}).¹⁷⁸ K_{eqi} is related to the Gibbs free energy for the adsorption process. The negative value of ΔG_{addi} indicates the spontaneous adsorption of the inhibitor on the sample surface.¹³⁴ The numerical value of ΔG_{addi} determines the type of adsorption as physical, chemical, or physicochemical.^{134,179} The ΔG_{addi} of the inhibitor on the material surface can be calculated as follows:¹³⁹

$$\Delta G_{addi} = -RT \ln(55.5 \times 10^6 K_{eqi}) \quad (17)$$

where ΔG_{addi} , R , T , and K_{eqi} denote the adsorption energy of the inhibitor (kJ mol⁻¹), the universal gas constant (8.314472 J mol⁻¹ K⁻¹), the operating temperature (K), and the equilibrium constant of the adsorption process, respectively.

7. Conclusions

This study reveals that the oxidation stability of pure biodiesel depends on the degree of saturated fatty acids, which varies across different feedstocks. The changes in the physical properties and chemical instability of biodiesel initiate the corrosion and tribological degradation of automotive materials, such as iron, iron-based alloy, steel, copper, copper-based alloy, aluminum, and aluminum-based alloy. Even when blended with diesel, biodiesel remains highly prone to corrosion and tribological degradation. Therefore, the degradation of the material and stability of biodiesel must be hampered by altering or modifying the fuel or metal surface. The use of antioxidants or corrosion inhibitors for fuel alteration is more feasible than material surface modification. Antioxidants delay auto-oxidation and retain the oxidation stability of biodiesel, whereas corrosion inhibitors form a protective oxide layer through the physical, chemical, or physicochemical adsorption processes. Such processes can be justified through different adsorption models and thermodynamic functions to quantify the effectiveness of corrosion inhibitors. Although many studies have investigated the corrosion inhibition of the fuel-metal interface by using different inhibitors, few studies have investigated the inhibition mechanism. Moreover, considering that palm biodiesel with different additive concentrations and elevated temperatures has never been investigated, the

inhibition action and adsorption types of additives remain unknown. Therefore, future studies must investigate the inhibition mechanism of palm biodiesel against corrosion and the tribological degradation of its material. Improving the inhibition mechanism in any operating condition may allow the large-scale replacement of petrodiesel and the commercialization of biodiesel.

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