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Multifunctional Additives for Sludge Mitigation and Fuel System Reliability in Biodiesel Blends: A Systematic Review

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ABSTRACT

This systematic review examines the mechanisms of sludge formation in biodiesel blends and evaluates the role of multifunctional additives in improving fuel system reliability. Biodiesel, particularly fatty acid methyl ester (FAME)-based blends, is susceptible to oxidation, water absorption, microbial growth, and deposit formation, which may lead to filter plugging, injector fouling, corrosion, and unstable combustion. A systematic literature review was conducted using the PRISMA framework, focusing on studies related to biodiesel degradation, sludge or deposit formation, and fuel additives. The review identifies sludge formation as a multi-stage process involving FAME oxidation, hydroperoxide decomposition, polymerization, acid formation, emulsion instability, and microbiologically influenced degradation. The findings indicate that single-function additives are insufficient to manage these interconnected pathways. Dispersant–demulsifier additives can reduce water-related sludge and particle agglomeration, antioxidant–corrosion inhibitor systems can suppress oxidative degradation and material damage, while cetane improvers can reduce combustion-related deposits. This review highlights the need for integrated multifunctional additive formulations capable of simultaneously controlling chemical degradation, water–fuel interactions, corrosion, and combustion residues. Future research should prioritize system-level additive design, long-term validation, and adaptive fuel treatment strategies for biodiesel applications.

INTRODUCTION

The use of biodiesel as an alternative fuel continues to rise in line with global demands for clean energy and reduced exhaust emissions, although challenges related to chemical stability and mechanical reliability still dominate technical debates. Biodiesel is known to be susceptible to oxidation due to its high content of unsaturated fatty acids, which triggers the formation of gum, sediment, insoluble matter, and increased viscosity that disrupts fuel system performance (Longanesi et al., 2022). This oxidation process produces oxygenated components that accelerate deposit formation on filters and injectors, thereby disrupting the continuity of fuel flow (Masudi et al., 2022). On the other hand, microbial growth in biodiesel stored for extended periods leads to the formation of biofilms and sludge, which accelerate fuel quality degradation while causing blockages in mechanical components (Hazrat et al., 2021). This degradation process is also influenced by environmental parameters such as light exposure, the presence of transition metals, and storage temperature, which accelerate peroxidation (M. Kumar & Sharma, 2015). Thus, the complexity of biodiesel's chemical properties and its sensitivity to degradation underscore the urgency of understanding the relationship between fuel stability and fuel system reliability.

In the context of biodiesel blends, particularly at medium to high ratios (e.g., B20–B50), various studies indicate a significant increase in the risk of sludge and deposit formation, which directly impacts fuel system performance. The use of biodiesel is reported to increase the tendency for sludge formation due to microbial activity and to heighten the potential for fuel filter clogging (Baihaqi et al., 2025; Lobato et al., 2023). Compounds such as monoacylglycerols and other lipophilic components that are initially soluble can precipitate as solid residues, becoming the primary cause of filter fouling (Seniorita et al., 2021). The thermal and oxidative stability of biodiesel also influences the formation of asphaltene-like materials, which can accumulate in high-temperature fuel lines and accelerate clogging (Kivevele & Huan, 2015; Rashed et al., 2015). These conditions are exacerbated by temperature fluctuations, complex injection patterns, and metal surface interactions that accelerate further oxidation reactions (Gopalan et al., 2019). Several studies (Kim et al., 2019; Y. Zhang et al., 2024; Zhao et al., 2025) indicate that deposits resulting from oxidative polymerization reduce atomization efficiency and increase differential pressure in the injection system. These findings confirm that sludge formation is a multidimensional phenomenon involving interactions between chemical degradation, biological contamination, and the mechanical response of the fuel system.

Although various studies have examined biodiesel degradation, including oxidation processes, thermal degradation, and instability during storage (David & Kopac, 2023), most of these studies still focus on chemical aspects without fully linking them to mechanical reliability or engine component performance (Chandran, 2020; Fazal et al., 2019). Conversely, studies at the system level have primarily highlighted engine performance and deposit formation without linking them to fuel degradation pathways (Alves-Fortunato et al., 2020; Burke et al., 2020; Hoang & Le, 2019b, 2019a). This fragmented approach has limited our ability to explain how chemical changes at the molecular level evolve into operational issues such as filter plugging and injector fouling. Consequently, there is currently no conceptual framework capable of comprehensively explaining the transition pathway from fuel degradation to system failure.

Methodologically, most studies remain partial and case-specific and thus have not yet produced a standardized and generalizable synthesis. Conceptually, the integration of chemical degradation pathways, sludge formation, and fuel system response remains limited, making it difficult to predict sludge behavior under real-world operating conditions. On the other hand, existing mitigation strategies are still dominated by the use of single-function additives, such as antioxidants, dispersants, or cetane improvers. This approach has not yet considered interactions between additives that can be either synergistic or antagonistic. Consequently, additive performance in real systems is often inconsistent and difficult to predict, making the single-function additive approach no longer sufficient to explain the complexity of modern biodiesel systems.

Meanwhile, recent studies by Chen et al. (2023), Lei et al. (2024), Sun et al. (2023), X. Zhang et al. (2024) have developed multifunctional polymer-based additives and nanocomposites capable of simultaneously improving oxidative stability and low-temperature flow properties of biodiesel blends. However, their effectiveness is highly dependent on the interactions between the chemical structure of the additives, fuel composition, and system operating conditions. This variability indicates that the relationship between the molecular design of additives and the response of the fuel system has not yet been comprehensively understood, so the generalizability of study results remains limited.

Based on these gaps, this study aims to: (1) integrate biodiesel chemical degradation pathways with sludge formation and its impact on the fuel system; (2) develop a conceptual framework linking fuel characteristics to system operational responses; and (3) evaluate the role of multifunctional additives by considering inter-mechanism interactions in controlling sludge formation. Thus, this study not only fills existing gaps in the literature but also provides a conceptual foundation for the development of more effective additive strategies to enhance fuel stability and the reliability of biodiesel-based fuel systems.

RESEARCH DESIGN

This study employs a systematic review approach following the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) framework to ensure transparency and reproducibility in the identification, screening, eligibility assessment, and selection of relevant studies. The review integrates evidence from chemical, microbiological, and fuel-system studies to explain the relationships among biodiesel degradation, sludge formation, additive intervention, and fuel system reliability. Rather than merely summarizing previous findings, the review applies structured literature selection, systematic data extraction, thematic classification, and comparative analysis to develop an integrated understanding of sludge formation and mitigation in biodiesel blends (Page et al., 2021).

Systematic Search and Literature Retrieval

This study applied a systematic search protocol to obtain relevant and representative literature. The search strategy included the development of structured keywords, the selection of the database, and the application of predefined inclusion and exclusion criteria (Hazrat et al., 2021). The search was conducted in the Scopus database due to its broad coverage and relevance to the fields of fuels, chemical engineering, and engine systems. The search strategy focused on three main domains: biodiesel, sludge or deposit formation, and fuel additives. This approach ensures that the selected literature covers all aspects relevant to the research objectives.

The search string used was: (“B35” OR “biodiesel blend” OR “fatty acid methyl ester” OR “FAME”) AND (“sludge formation” OR “filter plugging” OR “fuel degradation” OR “deposit formation”) AND (“additive” OR “dispersant” OR “demulsifier” OR “antioxidant” OR “corrosion inhibitor” OR “cetane improver”). The term “B35” was retained as part of the search strategy, but the scope of the analysis was not limited to a single blend ratio. This study covers biodiesel blends in general to produce a comprehensive and generalizable synthesis (M. Kumar & Sharma, 2015).

The search process yielded 6,425 initial records. Applying the publication-year restriction of 2021–2026 removed 2,221 records, leaving 4,204 records. Further restrictions based on document type (journal articles), language (English), and open-access availability removed 3,523 records, leaving 681 records for title, abstract, and keyword screening. During this screening stage, 324 records were excluded because they did not sufficiently address the scope of biodiesel degradation, sludge or deposit formation, or fuel additives. Consequently, 357 reports were retained for full-text eligibility assessment. No reports were unavailable for retrieval. Following the full-text assessment, 199 reports were excluded because they were not relevant to multifunctional additives (n = 112), provided insufficient discussion of sludge formation (n = 53), or presented methodological limitations that prevented meaningful synthesis (n = 34). Accordingly, 158 studies were included in the final systematic review.

The 2021–2026 publication-year restriction was applied to studies included in the systematic evidence synthesis. Earlier publications were used only as supporting references to explain established mechanisms or provide historical context and were not counted among the 158 studies included in the PRISMA-based synthesis.

The overall literature selection process is shown in Figure 1, which was developed based on the PRISMA framework (Page et al., 2021). The diagram illustrates the stages of identification, screening, eligibility assessment, and inclusion of studies used in this research.

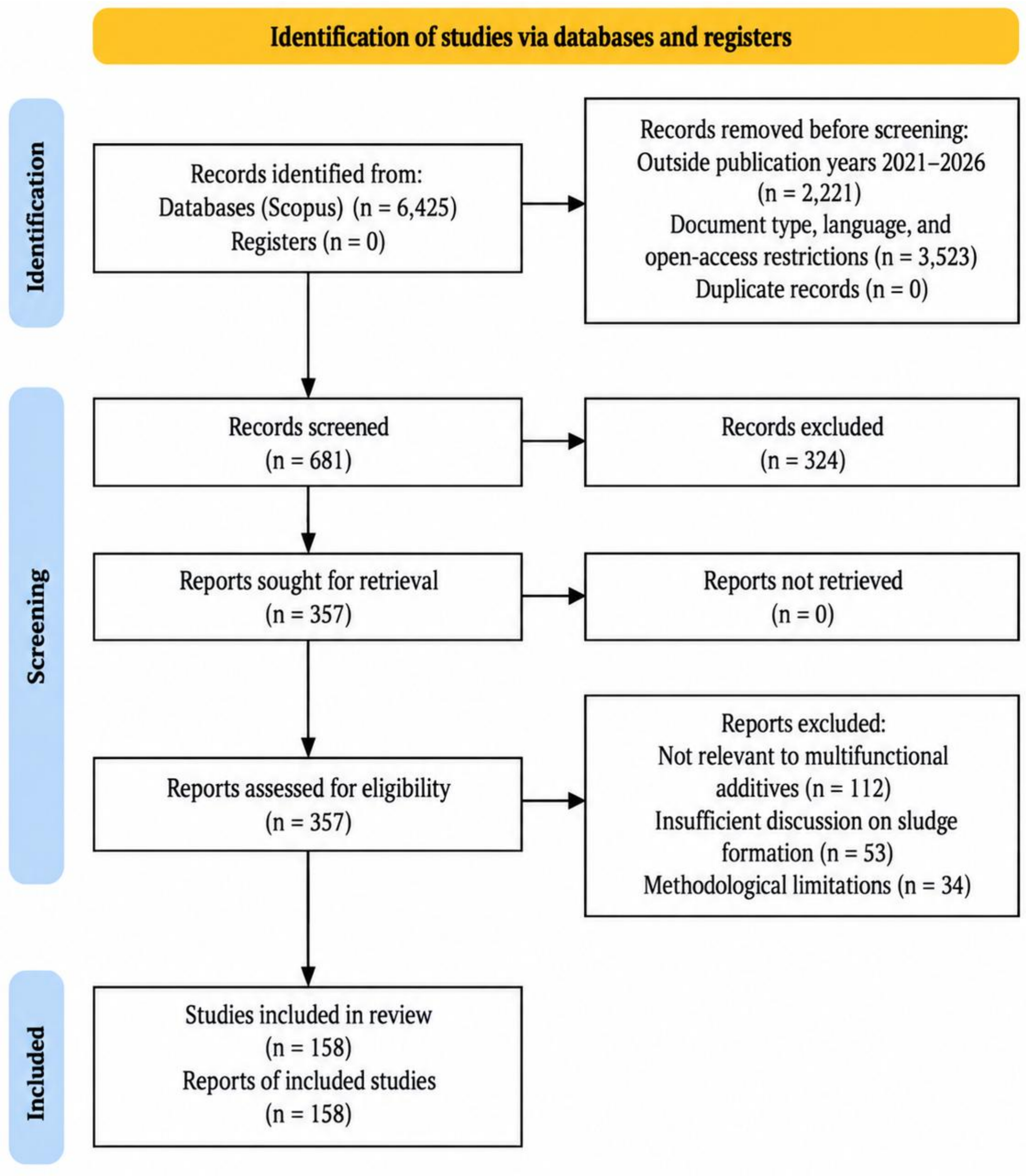

Figure 1. PRISMA flow diagram for study selection.

Data Extraction and Thematic Analysis

All studies meeting the eligibility criteria were analyzed using a structured data extraction matrix. The extracted information included bibliographic information, biodiesel or feedstock type, biodiesel blend ratio, additive class and function, experimental or operating conditions, fuel degradation indicators such as oxidation stability and acid value, sludge or deposit characteristics, and fuel-system impacts including filter clogging, injector fouling, corrosion, and combustion-related deposits.

The extracted evidence was subsequently organized into three analytical domains. The first domain covered sludge formation mechanisms associated with chemical degradation, water–fuel interactions, and microbiological activity. The second domain addressed additive intervention mechanisms, including dispersant–demulsifier systems, antioxidants, corrosion inhibitors, cetane improvers, nanoparticle-based additives, and integrated multifunctional formulations. The third domain covered the consequences of fuel degradation and additive intervention for fuel-system performance and operational reliability. Thematic analysis was then used to identify recurring mechanisms, relationships among variables, inconsistencies between studies, potential trade-offs, and research gaps. In addition, a critical comparative analysis was conducted to identify potential interactions among additive functions and to evaluate their implications for integrated sludge mitigation. The results of this analysis formed the basis for the subsequent discussion of sludge formation mechanisms, additive performance, comparative assessment, and future research directions.

MECHANISMS OF SLUDGE FORMATION IN BIODIESEL

Chemical Instability of FAME

The chemical instability of fatty acid methyl esters (FAME) is an inherent property of biodiesel determined by its molecular structure, particularly by the presence of carbon-carbon double bonds (C=C) in unsaturated fatty acids. This structure increases FAME's reactivity toward oxygen, heat, transition metals, and water. Consequently, FAME is more prone to degradation during storage and during fuel system operation. Generally, FAME degradation proceeds through a series of sequential reactions involving oxidation, the formation and decomposition of hydroperoxides, polymerization, and the formation of acidic compounds. This series of reactions constitutes the primary pathway for sludge formation, which ultimately reduces fuel quality and fuel system reliability (Longanesi et al., 2022). This degradation process not only explains the chemical changes in the fuel but also represents the initial stage of a multi-step process that ultimately determines sludge formation and its impact on the fuel system.

The initial stage of FAME chemical degradation occurs through a free radical oxidation mechanism. This reaction begins with hydrogen abstraction at the allylic position of an unsaturated FAME molecule, resulting in the formation of a highly reactive carbon-centered radical, as shown in Equation (1).

$$RH \rightarrow R^{\cdot} + H^{\cdot} \quad (1)$$

The alkyl radicals formed then react rapidly with oxygen to produce peroxy radicals, as shown in Equation (2).

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot} \quad (2)$$

The peroxy radicals then abstract hydrogen atoms from other molecules, forming hydroperoxides as the primary oxidation products, as shown in Equation (3).

$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \quad (3)$$

The oxidative stability of biodiesel is greatly influenced by the degree of unsaturation of its constituent fatty acids. Winfield et al. (2025) demonstrated that biodiesel containing high levels of unsaturated fatty acids has a shorter induction period. This indicates that such biodiesel is more prone to oxidation. Additionally, Laemthong et al. (2025) reported that the presence of water accelerates oxidation reactions even when antioxidants have been added. This finding suggests that water contamination can worsen the oxidative stability of biodiesel.

Hydroperoxides formed during the propagation stage are unstable. These compounds readily undergo thermal decomposition and generate more reactive secondary radicals, such as alkoxy radicals and hydroxy radicals, as shown in Equation (4).

$$\mathrm{ROOH} \rightarrow \mathrm{RO^{\cdot}} + \cdot\mathrm{OH} \tag{4}$$

These secondary radicals subsequently undergo fragmentation and form secondary oxidation products, such as aldehydes, ketones, and organic acids. These products possess high reactivity and act as precursors for deposit formation. Vergara-Juarez et al. (2025) demonstrate that unsaturated FAME has a higher thermal degradation rate compared to saturated compounds. In fuel systems, these conditions are further exacerbated by repeated heating cycles in high-pressure injectors, which can accelerate the formation of internal diesel injector deposits (IDIDs) (Hruby et al., 2025).

In addition to producing secondary oxidation products, FAME degradation products can also undergo polymerization and condensation reactions. These reactions occur via free-radical mechanisms and produce insoluble high-molecular-weight molecules. Simply put, polymerization can be represented by the recombination of two free radicals, as shown in Equation (5).

$$\mathrm{R^{\cdot}} + \mathrm{R^{\cdot}} \rightarrow \mathrm{R} - \mathrm{R} \tag{5}$$

Furthermore, carbonyl compounds, such as aldehydes, can undergo condensation reactions and form polymeric compounds, as illustrated in Equation (6).

$$\mathrm{R} - \mathrm{CHO} + \mathrm{R'} - \mathrm{CHO} \rightarrow \text{Polymeric Compound} \tag{6}$$

These polymerization and condensation processes produce complex structures in the form of resins, gums, and gels, which serve as the primary precursors of sludge. Bai et al. (2026) demonstrated that the aggregation of FAME molecules can form crystalline structures that subsequently develop into solid precipitates. Hidayat (2024) also reported a significant increase in sediment mass during biodiesel storage. These results indicate that polymerization and agglomeration processes play a significant role in sludge formation.

The final stage of chemical degradation is marked by the formation of acidic compounds that increase the acid value of biodiesel. Acids can form through two main pathways. The first pathway is the hydrolysis of FAME esters by water, as shown in Equation (7).

$$\mathrm{RCOOCH_3} + \mathrm{H_2O} \rightarrow \mathrm{RCOOH} + \mathrm{CH_3OH} \tag{7}$$

The second pathway is the further oxidation of aldehydes to carboxylic acids, as shown in Equation (8).

$$R - CHO + [O] \rightarrow R - COOH \quad (8)$$

The formation of these acidic compounds causes the biodiesel to become increasingly corrosive. Laemthong et al. (2025) show that the acid value of biodiesel increases during storage under conditions containing water contamination. Aslan et al. (2024) also show that an increase in total acid number is directly correlated with the rate of metal corrosion. Thus, acid formation not only indicates the chemical degradation of the fuel but also links this degradation to material damage in the fuel system.

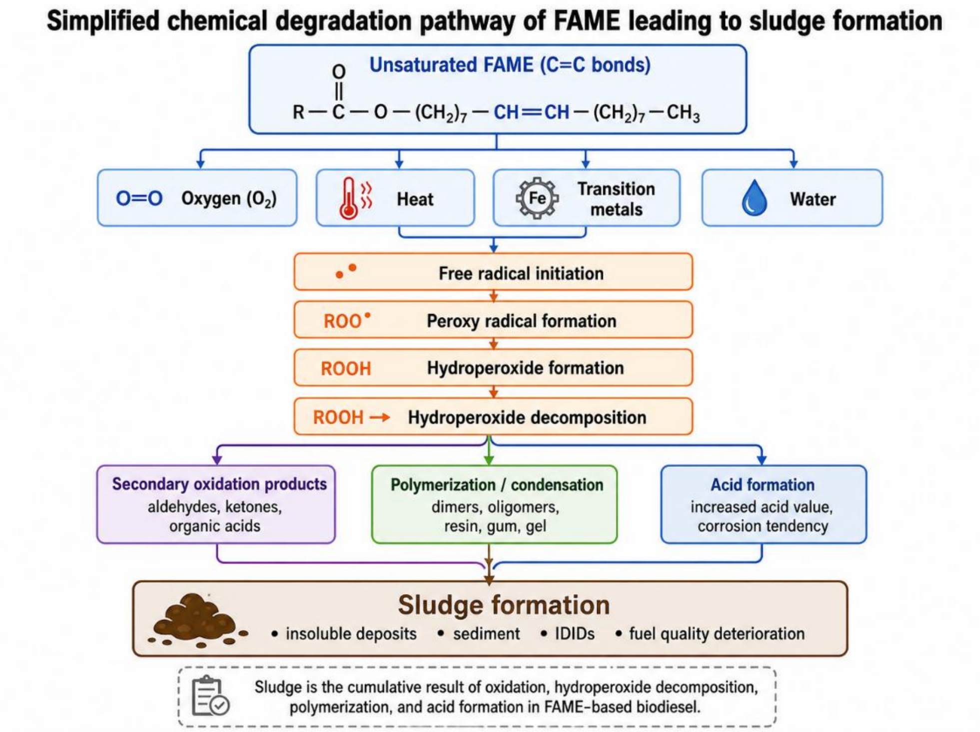

Figure 2. Schematic overview of FAME chemical degradation and sludge formation.

Overall, the chemical degradation pathways of FAME, which include oxidation, hydroperoxide formation, hydroperoxide decomposition, polymerization, and acid compound formation, are presented schematically in Figure 2. The figure shows that unsaturated FAME, under the influence of oxygen, heat, transition metals, and water, undergoes a chain reaction that begins with free-radical initiation, followed by the formation of peroxy radicals and hydroperoxides, and then branches into the formation of secondary oxidation products, polymeric compounds, and acidic compounds. These three pathways ultimately lead to sludge formation, characterized by the formation of insoluble deposits, sediments, internal diesel injector deposits (IDIDs), and a decline in fuel quality. Thus, Figure 2 confirms that sludge formation is the cumulative result of progressive and interrelated chemical degradation reactions of FAME.

However, these chemical degradation mechanisms do not occur in isolation within real-world systems. This series of reactions interacts with environmental factors, particularly the presence of water and interfacial phenomena, which not only accelerate oxidation reactions but also modify the degradation pathways toward a more complex system.

Water Absorption and Microbiological Effects

FAME has hygroscopic properties that increase its tendency to absorb water during storage and distribution. Water enters through condensation, tank contamination, and higher partial solubility compared to petrodiesel. The presence of water leads to the formation of a two-phase system that reduces fuel stability. Laemthong et al. (2025) demonstrate that increased water content can significantly accelerate biodiesel degradation. Thus, the presence of water acts as an initial trigger linking physical changes in the fuel to further chemical degradation.

The interaction between water, FAME, and polar compounds produces a metastable emulsion that accelerates fuel degradation. Compounds such as monoacylglycerols and free fatty acids act as natural emulsifying agents that maintain the colloidal system. Hidayat (2024) shows that increased sedimentation occurs even though the water content remains relatively constant, indicating the formation of a complex emulsion system. This emulsion increases the surface area of interaction between water and fuel, thereby accelerating oxidation reactions and sludge formation.

In addition to affecting the physical and chemical stability of the fuel, water also creates an environment that supports the growth of microorganisms, particularly at the water–biodiesel interface. Microorganisms can utilize FAME as a carbon source and produce biofilms, acidic compounds, and extracellular polymers. Aslan et al. (2024) show that microbial growth in fuel systems can increase the rate of corrosion and the formation of biological sludge. This microbiological activity produces biomass and extracellular polymeric substances (EPS) that reinforce the sludge structure and increase the tendency for particle agglomeration. Hruby et al. (2025) show that the interaction between water and contaminants produces complex deposits in fuel systems.

Microbiological sludge forms from the accumulation of biomass, EPS, corrosion products, and chemical degradation products of biodiesel. The resulting sludge structure is generally sticky, unstable, and prone to accumulating at the bottom of tanks or within filtration systems. Hidayat (2024) reported substantial sediment accumulation during biodiesel storage, indicating the progressive formation and agglomeration of suspended degradation products.

The mechanisms of water absorption, emulsion formation, microbiological activity, and bio-sludge formation are schematically presented in Figure 3. The figure shows that increased water content in biodiesel can initiate two main degradation pathways. The first pathway is associated with physicochemical degradation, including the formation of a two-phase system, metastable emulsion formation, an increased water–fuel interfacial area, oxidation, hydrolysis, and the formation of sediment or sludge. The emulsion may be stabilized by polar compounds such as monoacylglycerols and free fatty acids, which act as natural emulsifiers.

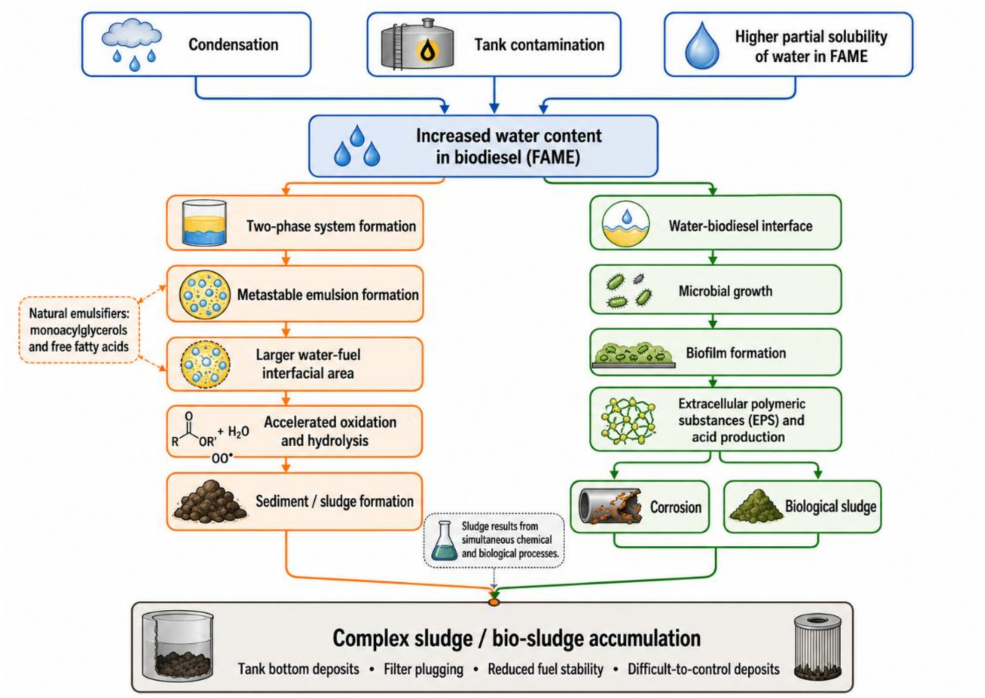

Figure 3. Water absorption, emulsion formation, microbiological activity, and sludge formation in biodiesel (FAME) systems.

Figure 3 illustrates the integrated mechanism of water absorption, emulsion formation, microbiological activity, and sludge accumulation in biodiesel systems. Water may enter biodiesel through condensation, tank contamination, and the relatively higher partial solubility of water in FAME. The increased water content then promotes the formation of a two-phase system and metastable emulsions, particularly in the presence of polar compounds such as monoacylglycerols and free fatty acids, which act as natural emulsifiers. The formation of emulsified water droplets increases the water–fuel interfacial area, thereby accelerating oxidation and hydrolysis reactions that contribute to sediment and sludge formation.

Concurrently, the water–biodiesel interface provides an environment conducive to microbial growth. Microorganisms can utilize FAME as a carbon source and form biofilms on this interface. Their metabolic activity produces extracellular polymeric substances (EPS) and acidic compounds that reinforce the sludge structure and increase the risk of corrosion. These biological processes, along with physicochemical degradation pathways, lead to the accumulation of complex sludge or bio-sludge. The resulting deposits can accumulate at the bottom of the tank, clog fuel filters, reduce fuel stability, and form hard-to-control deposits within the fuel system.

The simultaneous interaction between chemical degradation, emulsion formation, and microbiological activity ultimately results in sludge accumulation in the fuel. However, this accumulation does not directly represent system failure. Critical impacts only emerge when the sludge and degradation products interact with the fuel system and translate into operational disruptions in engine components. Thus, the interaction between chemical degradation, interfacial dynamics, and microbiological activity forms a transitional stage that links fuel instability to tangible fuel system responses.

Interaction with the Diesel Fuel System

The interaction between FAME-based biodiesel and the diesel fuel system represents a critical transition in which chemical, physical, and biological fuel degradation is translated into measurable operational problems. Degradation products may affect filtration, injection, atomization, and combustion processes, thereby linking fuel instability directly to overall fuel-system reliability.

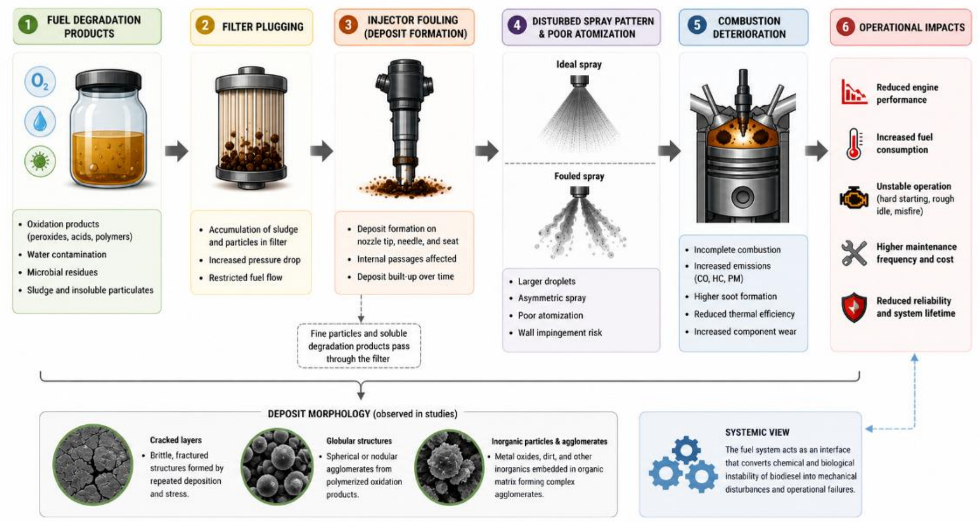

Figure 4. Schematic pathway linking biodiesel degradation to operational impacts in diesel fuel systems.

As shown in Figure 4, the initial stages of this process begin with the formation of fuel degradation products, which include oxidation products, sludge, insoluble particles, water contamination, and microbiological residues. These components then accumulate in the filtration system and cause filter plugging. This phenomenon is progressive, characterized by an increase in filter pressure drop, a decrease in fuel flow capacity, and the potential for disruption of fuel supply to the engine. Hidayat (2024) demonstrates that during B30 storage, sediment buildup can increase progressively after a certain induction period, helping explain why filter clogging may emerge after a seemingly stable storage period. Bai et al. (2026) also confirm that FAME degradation products tend to form solid, aggregated structures, which increase the risk of clogging, particularly under low-temperature conditions. Therefore, filter plugging can be viewed as an early indicator of failure in fuel degradation control within real-world systems.

When fine particles and degradation compounds bypass the filter or form downstream of the filtration system, subsequent impacts occur in the injection system through the phenomenon of injector fouling. As shown in Figure 4, deposits formed at the nozzle tip and within the injector's internal channels disrupt the fuel spray pattern and reduce atomization quality. Hruby et al. (2025) reported that internal diesel injector deposits (IDIDs) form due to complex interactions between FAME degradation products, fuel additives, and contaminants, resulting in gel-like or metal soap-like deposit structures. Additionally, Vergara-Juarez et al. (2025) demonstrate that unsaturated FAME produces degradation products that are more reactive toward metal surfaces, thereby accelerating deposit layer formation. These injector disruptions subsequently cause the spray pattern to become asymmetrical, droplet size to increase, and the atomization process to become inefficient.

These atomization disturbances have direct implications for the combustion process within the combustion chamber. As shown in Figure 4, these conditions lead to incomplete combustion, increased emissions, soot formation, and reduced thermal efficiency (Warju et al., 2025). In the long term, this phenomenon not only increases fuel consumption but also accelerates engine component wear due to deposit formation and combustion residues.

The morphological characteristics of deposits formed in the fuel system reflect their formation mechanisms and help determine the severity of operational impacts. These deposits are not homogeneous but consist of various structures such as cracked layers, globular clusters, and inorganic particles. Hruby et al. (2025) identified the presence of cracked layers rich in metal carboxylates, as well as globular structures formed from polymerized oxidation products. Meanwhile, Hidayat (2024) demonstrated that biodiesel sediments are dominated by agglomerates of heavy compounds that form dense structures and are difficult to redisperse. This morphological variation indicates that deposit formation results from the simultaneous interaction of oxidation, water contamination, microbiological activity, and thermal conditions within the fuel system.

Overall, Figure 4 illustrates the hierarchical relationship between fuel degradation and the operational impacts on diesel fuel systems. Fuel instability first manifests as filter plugging, then progresses to injector fouling, followed by atomization and combustion disturbances, ultimately leading to reduced engine performance, unstable operation, increased maintenance requirements, and decreased system reliability. Thus, operational disruptions cannot be viewed as isolated phenomena but rather as the cumulative result of fuel degradation processes that occur from the early stages of storage through to use.

Overall, sludge formation in biodiesel is a multi-stage process involving the chemical degradation of FAME, physical interactions due to the presence of water, and biological activity, which ultimately manifests as operational disruptions in the fuel system. This sequence indicates that sludge forms through interconnected multi-stage interactions and cannot be explained by a single mechanism. Consequently, mitigation strategies cannot focus on a single point of intervention but must be capable of simultaneously controlling these various stages, ranging from fuel chemical stability and interfacial dynamics to the fuel system's response during operation. Therefore, a multifunctional additive-based approach is crucial as an integrated strategy to comprehensively intervene in the sludge formation pathway, as discussed in the following section.

MULTIFUNCTIONAL ADDITIVES FOR SLUDGE MITIGATION IN BIODIESEL BLENDS

The sludge formation described in the previous section indicates that biodiesel degradation occurs through several interrelated pathways, namely the water–fuel interface pathway, the chemical oxidation pathway, fuel–material interactions, and the combustion stage. Therefore, an effective additive strategy cannot be viewed as a single intervention but rather as a stepwise control system operating at different points in the sludge formation chain. This section discusses three main additive groups based on their intervention points: dispersants–demulsifiers in the interface and dispersion phases, antioxidants–corrosion inhibitors in the chemical degradation and material protection phases, and cetane improvers in the combustion phase. Within this framework, each class of additive is evaluated not only based on its individual function but also on its contribution to integrated sludge control.

Dispersant–Demulsifier Additives

As an early intervention in the liquid fuel phase, dispersant–demulsifier additives play a role in controlling sludge formation triggered by FAME polarity, the presence of water, emulsion formation, and the accumulation of deposit precursors in biodiesel blends. In biodiesel blends, ester groups and oxygenated compounds increase the fuel's affinity for water and facilitate the formation of water-in-fuel emulsions. These conditions accelerate chemical degradation, support microbial growth, and increase deposit formation that can potentially clog the fuel system (Sekhar & Gupta, 2025; Yang et al., 2025). In this context, dispersant–demulsifier additives do not stop primary degradation but control the evolution of degradation products so they do not develop into solid sludge that interferes with filtration and injection processes.

As shown in Figure 5, the mechanism of action of this additive consists of two main pathways occurring in parallel: the water pathway controlled by the demulsifier and the solid pathway controlled by the dispersant. In the water pathway, the primary function of the demulsifier lies in its ability to disrupt emulsion stability by modifying the interfacial balance between the water phase, fuel, and natural polar compounds in biodiesel. Compounds such as monoglycerides, free fatty acids, and early oxidation products of FAME act as natural emulsifiers that keep water droplets small and stable. Demulsifiers displace these species at the interface, reducing emulsion stability and accelerating the coalescence of water droplets into larger phases that can be easily separated via drainage or filtration (Yao et al., 2021). By reducing the residence time of water in the system, the potential for microbial sludge formation, acid formation, and corrosion in storage and distribution systems can be mitigated (Sudarshan et al., 2025).

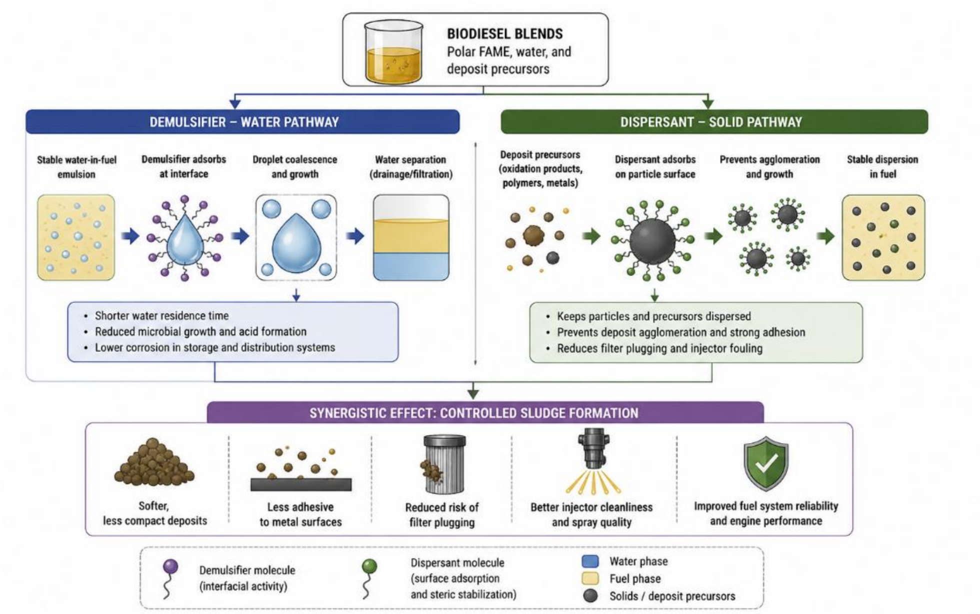

Figure 5. Mechanism of dispersant–demulsifier additives in controlling sludge formation in biodiesel blends.

At the same time, the dispersant component acts on the solid and semi-solid fractions formed as a result of oxidation, polymerization, and the interaction of FAME with metals or contaminants. As shown in Figure 5, the dispersant adsorbs onto the surface of deposit precursors and forms a protective layer that prevents agglomeration. Polyisobutylene succinimide (PIBSI)-based dispersants are widely used because they possess an amphiphilic structure that enables strong interactions with both polar and nonpolar particles (Özdemir et al., 2025). Corral-Casas et al. (2025) demonstrated that the adsorption strength of the succinimide head groups is a key factor in preventing the growth and coalescence of deposit particles. Thus, dispersion stability is highly dependent on the compatibility between the chemical structure of the dispersant and the chemical properties of the deposit precursors.

The need for dispersants increases as the biodiesel fraction in the fuel blend rises. An increase in FAME content leads to higher polarity and a greater number of oxygenated compounds in the system. Jikol et al. (2024) demonstrate that increasing the biodiesel ratio from B20 to B50 results in deposits with greater mass, broader distribution, and stickier properties. This indicates the dominance of non-volatile and polymerized compounds in deposit formation. Under these conditions, dispersants do not remove deposits that have already formed, but rather keep the particles dispersed in the fuel stream so they do not develop into large agglomerates that can clog filters or adhere strongly to metal surfaces (Sudarshan et al., 2025).

Overall, the effectiveness of dispersant–demulsifier additives is determined by the complementary action of the two mechanisms in controlling the two main pathways of sludge formation: the water–microbiological pathway and the deposit precursor aggregation pathway. As summarized in Figure 5, demulsifiers reduce the presence of the aqueous phase, which serves as a growth medium for microorganisms, while dispersants stabilize solid particles to prevent them from forming compact deposits. The combination of these two functions results in deposits that are softer, less adherent, and more easily carried away by the fuel flow.

Thus, dispersant–demulsifier additives serve as a bridge between controlling fuel interface properties and protecting the fuel system against sludge formation. However, this function has a critical limitation because controlling emulsion and particle dispersion is insufficient to halt the formation of sludge precursors derived from FAME oxidation. Oxidation products can still develop into gum, acidic compounds, and reactive deposits if the chemical degradation pathway is not controlled. Therefore, control at the interface phase must be complemented by interventions regarding fuel oxidative stability and system material protection.

Antioxidant–Corrosion Inhibitor Additives

After controlling the interfacial phase and particle dispersion, the next critical step is to inhibit the chemical degradation of FAME and prevent material damage caused by oxidation products. This step is crucial because sludge forms not only from particle agglomeration but also from the evolution of oxidation compounds into gums, organic acids, and reactive deposits. In this context, antioxidant–corrosion inhibitor additives serve to control the two main consequences of biodiesel degradation: the formation of reactive oxidation products and metal material damage caused by an increasingly acidic and corrosive environment. In biodiesel blends, the oxidation of FAME produces hydroperoxides, aldehydes, ketones, and organic acids that reduce fuel stability and trigger the formation of gum and deposits (Bello et al., 2025; David & Kopac, 2023). In this context, antioxidants act as controllers of the chemical degradation pathway, while corrosion inhibitors protect system materials from the subsequent effects of such degradation. The combination of both makes this additive a link between fuel stability and fuel system integrity during storage and use.

As shown in Figure 6, the mechanism of action of these additives proceeds through two complementary main pathways: the chemical pathway controlled by antioxidants and the material pathway controlled by corrosion inhibitors. In the chemical pathway, synthetic phenolic antioxidants such as TBHQ, BHT, and BHA function by donating hydrogen atoms to peroxyl radicals (ROO•), thereby halting the propagation of oxidation reactions. Conceptually, this mechanism can be described as a radical scavenging reaction, in which the antioxidant (AH) reacts with the peroxyl radical to form a hydroperoxide (ROOH) and a more stable antioxidant radical, thereby breaking the oxidation reaction chain. Through this mechanism, the formation of further oxidation products can be suppressed, and fuel stability can be maintained.

The effectiveness of this mechanism is evident in its ability to extend the induction period and reduce the rate of hydroperoxide formation during the early stages of degradation (Bello et al., 2025). However, the effectiveness of antioxidants is not solely determined by their radical scavenging ability but also by their thermal stability and the characteristics of their degradation products. Dai et al. (2024) show that BHT has fairly good thermal stability, but its oxidation products, such as BHTOOH, have a lower decomposition activation energy. This indicates that antioxidants can act as sources of secondary radicals if formulation and storage conditions are not properly controlled.

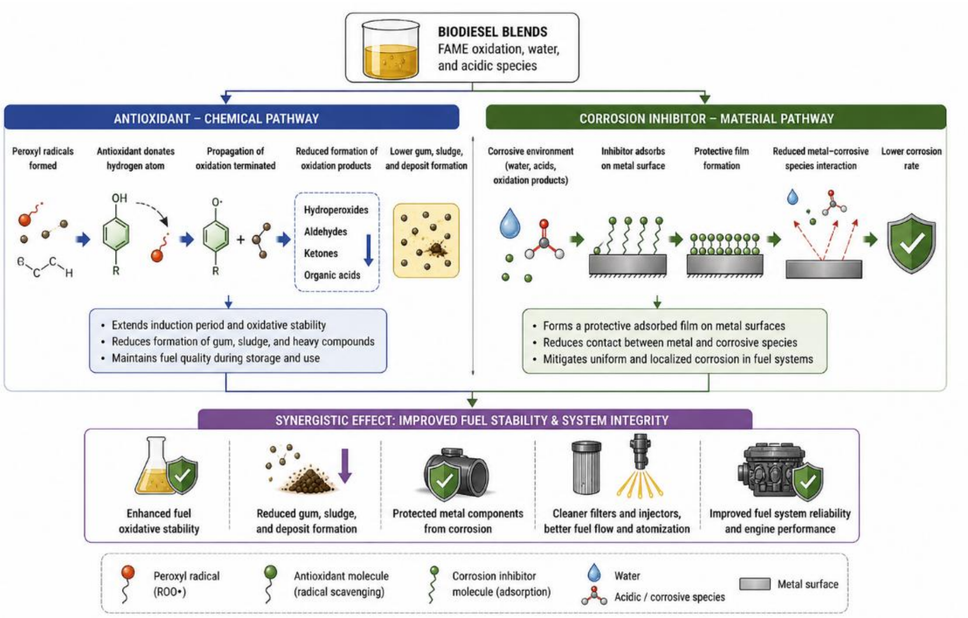

Figure 6. Mechanism of antioxidant–corrosion inhibitor additives in biodiesel blends.

In addition to synthetic antioxidants, natural antioxidants also play a crucial role in enhancing the oxidative stability of biodiesel. Compounds such as tocopherols, β-carotene, and phenol-rich plant extracts can slow the rate of oxidation, although their effectiveness is generally lower than that of synthetic antioxidants at the same concentration (Bello et al., 2025; David & Kopac, 2023). Grabowski & Szwarczyńska (2024) demonstrated that FAME still containing natural antioxidants exhibited lower anisidine values during thermal aging. These findings indicate that natural antioxidants remain relevant, particularly in additive formulations that consider sustainability and environmental compatibility.

Controlling oxidation through antioxidants can reduce the progression of secondary oxidation reactions associated with viscosity increase, gum formation, and the accumulation of deposit precursors during storage. Therefore, antioxidant effectiveness should be evaluated not only by its ability to extend the oxidation induction period but also by its capacity to limit the formation of secondary oxidation products under prolonged storage conditions (Bello et al., 2025; David & Kopac, 2023; Laemthong et al., 2025).

On the other hand, the material pathway shown in Figure 6 illustrates the role of corrosion inhibitors in protecting fuel system components. The accumulation of acidic compounds and the presence of water create an aggressive environment at the fuel–metal interface, particularly in carbon steel tanks and lines. Aslan et al. (2024) demonstrate that biodiesel systems with high water content and microbial activity experience increased corrosion, both uniformly and locally. Amines and phosphate ester-based corrosion inhibitors work by adsorbing onto the metal surface and forming a protective layer that inhibits direct interaction between the metal and corrosive species. This layer acts as a physical and chemical barrier that reduces the corrosion rate without directly affecting the fuel's oxidative stability.

Overall, the combination of antioxidants and corrosion inhibitors provides dual control over biodiesel degradation, both at the fuel level and at the system material level. As summarized in Figure 6, antioxidants suppress the formation of oxidation products that trigger gum and sludge, while corrosion inhibitors maintain metal resistance against acidic and aqueous environments. The synergy of these two mechanisms enhances fuel stability while protecting system components from damage. Thus, the success of antioxidant–corrosion inhibitor additives depends on the formulation's ability to maintain fuel quality and preserve the integrity of the fuel system simultaneously.

Nevertheless, oxidation control and material protection do not entirely eliminate the potential for deposit formation during the combustion process. Incomplete combustion residues can still form downstream in the system, particularly when ignition delay increases, atomization is disrupted, and combustion becomes unstable. Thus, sludge mitigation strategies cannot stop at the fuel storage and distribution phase but must be extended to the energy utilization stage within the engine. This role is fulfilled by cetane improvers as a downstream control against the formation of combustion residues and subsequent deposits.

Cetane Improvers

Unlike additives that work during the fuel storage and distribution phases, cetane improvers function as downstream controls that operate during the combustion stage. This role is critical because some deposits within the engine system originate not only from fuel degradation during storage but also from incomplete combustion residues. These additives are used to address ignition delay in biodiesel blends influenced by the physicochemical characteristics of FAME, particularly lower volatility and different combustion properties compared to conventional diesel fuel. In diesel engine systems, ignition delay increases the fraction of uncontrolled premixed combustion, thereby increasing the likelihood of incomplete combustion and residue formation. These residues can serve as precursors to deposits on injectors, in the combustion chamber, and within the lubrication system. Therefore, cetane improvers play a role in controlling the downstream aspect of deposit formation by improving combustion quality.

As shown in Figure 7, the primary difference between conditions with and without a cetane improver lies in ignition delay duration and combustion stability. Without additives, fuel containing FAME tends to exhibit a longer ignition delay, leading to fuel accumulation before combustion occurs. This condition results in rapid and unstable premixed combustion, followed by a sudden increase in cylinder pressure and the formation of incomplete combustion products. Conversely, with the addition of a cetane improver, the ignition process occurs earlier and is more controlled, allowing combustion to proceed gradually and more efficiently, with lower residue formation.

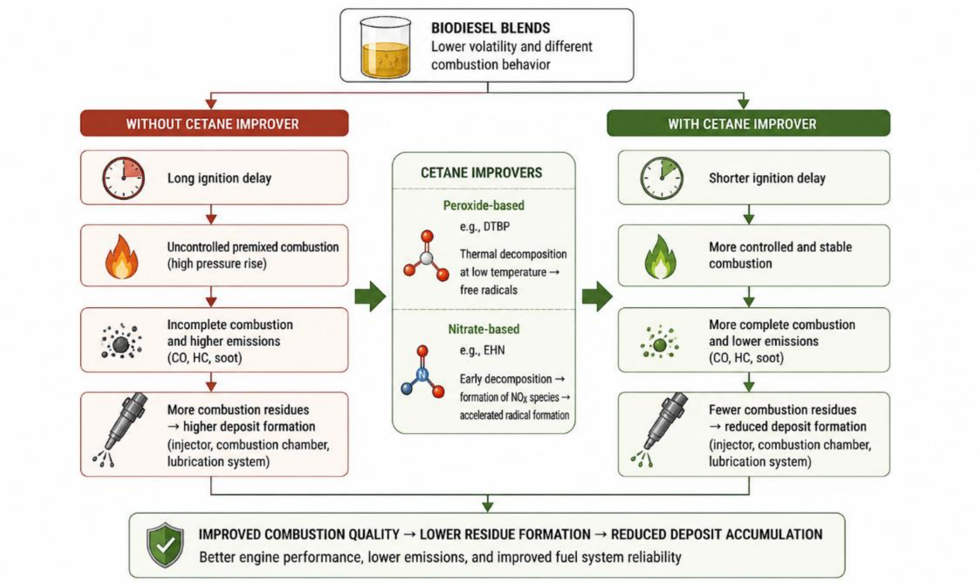

Figure 7. Mechanism of cetane improvers in reducing ignition delay and mitigating deposit formation in biodiesel blends.

Cetane improvers generally include peroxide- and nitrate-based compounds that promote the formation of reactive species during the pre-ignition and early combustion stages. Their principal function is to accelerate low-temperature oxidation reactions, shorten ignition delay, and improve combustion stability. In biodiesel-fueled diesel engines, these effects can influence heat-release characteristics, combustion efficiency, and exhaust emissions. However, their effectiveness depends on additive chemistry, dosage, biodiesel composition, blend ratio, and engine operating conditions (Nayak & Devarajan, 2024). Thus, cetane improvers should be interpreted primarily as combustion-stage interventions rather than direct inhibitors of fuel degradation during storage.

Among nitrate-based cetane improvers, 2-ethylhexyl nitrate (2-EHN) is one of the most widely investigated compounds because of its strong ability to enhance fuel autoignition. Unlike antioxidants or demulsifiers that act primarily in the liquid-fuel phase before combustion, 2-EHN becomes particularly active during the pre-ignition stage. Its decomposition is initiated mainly through cleavage of the O–N bond, producing reactive intermediates such as 2-ethylhexoxy radicals and nitrogen dioxide (NO_2). These intermediates contribute to the radical pool involved in low-temperature fuel oxidation and accelerate subsequent chain reactions, thereby promoting earlier autoignition and reducing ignition delay. Recent kinetic investigations have confirmed that the decomposition chemistry of 2-EHN strongly influences the early-stage ignition process and explains its effectiveness as a cetane-enhancing additive (Xie et al., 2026).

Experimental studies on biodiesel-containing fuels further demonstrate the influence of 2-EHN on combustion behavior. Chacko et al. (2021) reported that the addition of EHN to a B20 karanja biodiesel–diesel blend shortened ignition delay and modified the premixed combustion phase, demonstrating its ability to alter early-stage combustion characteristics. Kumar & Pal (2022) similarly reported improvements in performance and emission-related parameters when 2-EHN was applied to an algal biodiesel–diesel system. More recent studies have shown comparable tendencies in other biodiesel blends. Ahmed et al. (2025), for example, reported that the addition of 2-EHN to a biodiesel–2-methylfuran blend improved cetane characteristics, promoted earlier combustion initiation, and affected brake-specific fuel consumption and exhaust emissions. Gugulothu et al. (2025) also demonstrated that 2-EHN addition to mahua biodiesel blends influenced brake thermal efficiency, brake-specific fuel consumption, and emission characteristics. Collectively, these findings indicate that the effects of 2-EHN are not uniform but are strongly dependent on fuel composition, additive concentration, and engine operating conditions.

The relevance of cetane improvers to sludge and deposit mitigation is therefore indirect but important within a system-level framework. By shortening ignition delay and promoting more stable combustion, cetane improvers can reduce operating conditions associated with incomplete combustion and the formation of soot, unburned hydrocarbons, and other combustion-derived residues. These products may contribute to deposit accumulation on injector tips, combustion-chamber surfaces, and other downstream engine components. Accordingly, cetane improvers can help reduce the downstream contribution of combustion-related residues to overall deposit formation. However, this mechanism should be clearly distinguished from the direct control of sludge generated during fuel storage and distribution.

Cetane improvers do not directly inhibit FAME oxidation, prevent hydroperoxide formation, separate accumulated water, suppress microbiological growth, protect metal surfaces from corrosion, or stabilize suspended particles against agglomeration. These functions are instead associated with antioxidants, demulsifiers, corrosion inhibitors, and dispersants. Therefore, within the multifunctional additive framework proposed in this review, cetane improvers should be considered complementary downstream controls that operate after upstream degradation mechanisms have already influenced the fuel. Their main contribution lies in improving ignition and combustion quality rather than directly preventing storage-derived sludge formation.

This distinction is particularly important because most available studies on cetane improvers evaluate ignition delay, combustion characteristics, engine performance, and emissions rather than directly measuring long-term sludge or deposit suppression. Consequently, the available evidence supports a plausible relationship between improved combustion and reduced formation of combustion-related residues, but direct experimental evidence demonstrating that 2-EHN or other cetane improvers independently suppress long-term sludge accumulation remains limited. Further studies linking fuel storage degradation, injector deposit formation, and combustion-stage additive effects are therefore required to establish this relationship more conclusively.

Overall, the role of cetane improvers complements the functions of additives acting at earlier stages of the sludge-formation pathway. Dispersants–demulsifiers primarily control water–fuel interactions and particle agglomeration, while antioxidants and corrosion inhibitors suppress chemical degradation and protect fuel-system materials. Cetane improvers subsequently act at the combustion stage by shortening ignition delay and reducing conditions that favor incomplete-combustion residues. Thus, multifunctional sludge mitigation should be understood as a multi-stage intervention strategy in which each additive class addresses a different degradation or deposit-formation mechanism rather than as a single additive acting across all stages.

COMPARATIVE ASSESSMENT & CRITICAL ANALYSIS

Sludge mitigation in biodiesel blends cannot be understood as the function of a single additive, but rather as the result of interventions in several interrelated sludge formation pathways, namely FAME oxidation, water–fuel interactions, microbiological activity, material corrosion, and residue formation during combustion. Experimental evidence indicates that each of these pathways is controlled by different classes of additives, so the system's effectiveness depends heavily on cross-functional integration, not the individual performance of additives.

In the early stages, the presence of water and emulsions is the primary trigger for bio-sludge formation and microbiological corrosion. Studies on the B35 system show that water–biodiesel interactions facilitate microbial growth and biofilm formation, which accelerate corrosion and deposit accumulation (Aslan et al., 2024). In this context, dispersants–demulsifiers play a crucial role in reducing water hold-up and preventing particle agglomeration. Molecular design-based approaches even indicate that the adsorption strength of surfactants toward deposit precursors is a key factor in inhibiting deposit growth (Corral-Casas et al., 2025). However, these additives do not halt FAME oxidation, so sludge precursor formation continues unless combined with oxidation inhibitors.

Controlling the oxidation pathway is crucial because the degradation of FAME directly produces hydroperoxides, aldehydes, and organic acids that act as precursors for gum and deposits. Experimental studies show that copolymer-based antioxidants can significantly improve oxidative stability through radical scavenging and metal chelation mechanisms (Bai et al., 2026). Additionally, increased temperature and the presence of water have been shown to accelerate oxidative degradation, which can be slowed by the addition of antioxidants such as TBHQ (Laemthong et al., 2025). However, thermal studies indicate that antioxidant oxidation products (e.g., BHTOOH) have lower stability and the potential to generate secondary radicals (Dai et al., 2024). This underscores that the effectiveness of antioxidants depends on formulation and operational conditions.

On the other hand, chemical degradation also has direct implications for material corrosion. Acidic environments and the presence of water increase the corrosion rate of metals, particularly in biodiesel storage systems (Vergara-Juarez et al., 2025). The use of corrosion inhibitors has been shown to reduce biofilm formation and corrosion, although in some cases there is a trade-off regarding fuel quality, such as an increase in acid value (Aslan et al., 2025). Therefore, a combination of antioxidants and corrosion inhibitors is essential to maintain both fuel stability and system integrity.

Unlike the two previous classes of additives, cetane improvers act during the combustion stage as downstream controls. The addition of additives such as di-tert-butyl peroxide (DTBP) has been shown to improve combustion quality and reduce CO emissions as well as unburned hydrocarbons (Nayak & Devarajan, 2024). Similar effects have also been observed with the use of nanoparticles, which improve thermal efficiency and reduce particulate emissions (Kayed et al., 2024). Although they do not control sludge formation during storage, improvements in combustion quality contribute to a reduction in carbon residues and deposits in the injection system.

A broader comparison among the principal additive intervention classes and emerging multifunctional formulation approaches is presented in Table 1.

Table 1. Comparative assessment of additive functions for sludge mitigation in biodiesel blends

Additive class	Intervention stage	Primary mechanism	Main contribution	Limitations	Ref
Dispersant–Demulsifier	Interface & dispersion	Emulsion breaking, particle stabilization	Reduces water content, biofilm formation, and particle agglomeration	Does not inhibit oxidation	(Aslan et al., 2024; Corral-Casas et al., 2025)
Antioxidant	Chemical oxidation	Radical scavenging, metal chelation	Suppresses the formation of gum and sludge precursors	Oxidation by-products may remain reactive	(Bai et al., 2026; Dai et al., 2024; Laemthong et al., 2025)
Corrosion inhibitor	Fuel–material interaction	Surface adsorption and protective film formation	Reduces corrosion and deposit formation associated with metal surfaces	Does not directly control sludge formation	(Aslan et al., 2025; Vergara-Juarez et al., 2025)
Cetane Improver	Combustion stage	Reduces ignition delay	Improves combustion efficiency and reduces residual deposits	Ineffective during the storage phase	(Nayak & Devarajan, 2024)
Nanoparticle additives	Combustion stage	Enhanced reactivity and soot oxidation	Reduces particulate emissions and	Potential cost and secondary	(Kayed et al., 2024)

Additive class	Intervention stage	Primary mechanism	Main contribution	Limitations	Ref
			combustion-related deposits	residue issues	
Multifunctional additives	Multi-stage	Integrated multifunctional mechanisms	Simultaneous control across multiple degradation pathways	Formulation complexity and compatibility issues	(Bai et al., 2026)

Table 1 shows that no single class of additives is capable of controlling all sludge formation pathways. Dispersants–demulsifiers are effective at the interface phase, antioxidants–corrosion inhibitors control chemical degradation and material interactions, while cetane improvers act during the combustion stage. Thus, sludge mitigation must be understood as a multi-stage intervention system. Consequently, additive formulations for biodiesel blends, particularly at medium to high ratios such as B30–B35, must be designed in an integrated manner. A multifunctional approach enables simultaneous control of oxidation, the aqueous phase, particle dispersion, corrosion, and combustion residues. However, the complexity of this formulation also demands optimization based on operational conditions, as interactions between additives can produce both synergistic and antagonistic effects.

Overall, this analysis confirms that the effectiveness of sludge mitigation is not determined by the strength of a single additive, but by the suitability of the combination of functions within the fuel system. Therefore, future additive development needs to be directed toward integrated formulation designs capable of linking fuel chemical stability with the overall system response.

RESEARCH GAPS AND FUTURE PERSPECTIVES

Although various approaches have been developed to improve biodiesel stability and reduce sludge formation, the analysis in the previous section shows that most studies still focus on additive mechanisms or functions in isolation. This approach has not yet fully captured the complexity of real-world systems, where biodiesel degradation occurs through simultaneous interactions between chemical oxidation, water–fuel interface dynamics, microbiological activity, and combustion processes. Therefore, there are several key research gaps that need to be addressed to develop more effective and practical sludge mitigation strategies.

Lack of system-level integration in additive design

Most studies still develop additives with a single dominant function, such as antioxidants, demulsifiers, or cetane improvers, without considering the interactions between functions within a single fuel system. However, as discussed in the previous sections, sludge formation results from interconnected multi-stage interactions. Recent studies on multifunctional copolymer-based additives demonstrate the potential for integrating oxidative, interfacial, and material protection functions within a single formulation; however, these remain limited to the laboratory scale and have not been evaluated under long-term operational conditions (Bai et al., 2026).

Moving forward, a system-level engineering-based additive design approach is needed, where antioxidant, emulsion control, and dispersion stabilization functions are developed simultaneously within a single molecular platform. This also involves optimizing inter-component interactions to avoid functional conflicts, such as increased polarity due to oxidation products that could destabilize the emulsion.

Limited understanding of additive interactions and trade-offs
Comparative analysis reveals trade-offs between additive functions, for example, between oxidative stability and emulsion stability, or between improved combustion performance and residue formation. Studies on antioxidants such as BHT show that its oxidation products (e.g., BHTOOH) have lower thermal stability and can serve as a source of secondary radicals (Dai et al., 2024). On the other hand, the use of biological inhibitors or essential oils can reduce corrosion but increase the fuel's acid value (Aslan et al., 2025).

However, such interactions between additives are still rarely studied systematically. Most studies only evaluate the performance of each additive individually. Therefore, future research should focus on multi-additive interaction modeling, through both experimental and molecular simulation approaches. This approach is crucial for understanding the synergies and antagonisms among components in multifunctional additive formulations.

Insufficient linkage between storage degradation and combustion-stage deposits
Most studies separate degradation during storage from deposit formation during combustion, even though these two phenomena are interconnected. Studies on sediment formation in B30 show that deposit accumulation increases significantly after a certain induction period during storage (Hidayat, 2024), while other studies indicate that combustion quality strongly determines the formation of residues and deposits within the engine (Nayak & Devarajan, 2024).

However, the direct relationship between sludge precursors during storage and deposits during combustion has not yet been extensively explored. Future research needs to develop an integrated approach linking these two stages, for example through full-cycle testing (storage–injection–combustion) and cross-stage deposit characterization.

Limited real-world validation under long-term operational conditions
Most research findings are still based on short-term laboratory tests, such as oxidative stability testing, engine emission testing, or controlled corrosion analysis. Meanwhile, real-world conditions involve far more complex variables, including temperature fluctuations, water contamination, operating cycles, and variations in fuel composition. FMEA studies on biodiesel indicate that the primary risks actually arise during long-term storage and operation, not under ideal laboratory conditions (Ceylan et al., 2026).

Additionally, studies on microbiologically influenced corrosion (MIC) in B35 indicate that interactions between water, microorganisms, and system materials can cause significant localized corrosion under real-world conditions (Aslan et al., 2024). Therefore, long-term field validation is crucial to ensure the effectiveness of additive formulations.

Emerging opportunities: advanced materials and data-driven approaches

Recent developments highlight the potential of advanced materials and data-driven approaches to enhance biodiesel performance. The use of nanoparticles, such as TiO_2 and Al_2O_3, has been shown to improve combustion efficiency and reduce particulate emissions (Anish et al., 2025; Kayed et al., 2024), although challenges related to stability and cost remain.

Data-driven approaches also provide emerging opportunities for biodiesel-related optimization. Machine-learning techniques have been explored for optimizing biofuel production and performance-related parameters (Ramalingam et al., 2025). Although real-time adaptive additive dosing has not yet been widely established for biodiesel systems, data-driven monitoring and optimization may provide a foundation for future adaptive fuel-treatment strategies.

Future Perspectives

Based on the identified gaps, future research directions can be summarized into three main focuses:

1. **Integrated multifunctional additive design**
   Developing additives capable of simultaneously controlling oxidation pathways, water interfaces, and combustion.
2. **System-level evaluation framework**
   Linking degradation during storage to deposit formation during engine operation through an integrated experimental approach.
3. **Smart and adaptive fuel systems**
   Integrating advanced materials and data-driven approaches to optimize fuel performance in real time.

By adopting this approach, future research is expected to move from descriptive studies toward **sludge mitigation strategies that are truly systemic, adaptive, and applicable on an industrial scale**.

CONCLUSION

This systematic review demonstrates that sludge formation in biodiesel blends is a multi-stage phenomenon involving FAME oxidation, water–fuel interactions, microbiological activity, particle agglomeration, and fuel–material interactions. These degradation pathways can progressively affect the fuel system through filter plugging, injector fouling, corrosion, atomization disturbances, and combustion-related deposits. The findings therefore indicate that fuel-system reliability cannot be separated from the chemical and physical stability of biodiesel during storage, distribution, and engine operation.

The reviewed evidence further shows that different additive classes act at different stages of the degradation–deposit pathway. Dispersant–demulsifier systems primarily control water separation and particle agglomeration, antioxidants suppress oxidative degradation, corrosion inhibitors protect fuel-system materials, and cetane improvers provide downstream control of combustion-related residue formation. Consequently, no single additive function is sufficient to address all sludge-formation pathways.

These findings support the development of integrated multifunctional additive strategies in which complementary functions are combined according to the dominant degradation mechanisms and operating conditions. However, direct evidence regarding the long-term compatibility, synergy, and potential trade-offs among multiple additive functions remains limited. Future research should therefore prioritize integrated formulation testing, full-cycle evaluation from storage to combustion, and long-term validation under realistic biodiesel operating conditions.

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