

## Advancements in the Thermo-Physical Enhancement of Automotive Biofuels Through Nanomaterials: A Comprehensive Review

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**ABSTRACT:** Biofuels are renewable alternatives to fossil fuels, but their performance in engines is often limited by suboptimal thermo-physical properties such as high viscosity, low thermal conductivity, and less favorable combustion characteristics. Nanomaterials have emerged as potent additives to overcome these limitations, owing to their high surface area, catalytic activity, and unique size-dependent properties. This review provides a comprehensive analysis of how various nanomaterials – including carbon nanotubes, metallic nanoparticles (e.g.,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CeO}_2$ ), graphene, and metal oxides – enhance the thermo-physical properties of automotive biofuels to improve combustion efficiency, engine performance, and emissions profiles. We discuss the fundamental mechanisms by which nanoparticles improve fuel thermal conductivity, reduce viscosity, catalyze combustion, and stabilize fuel mixtures. The review synthesizes findings from recent studies demonstrating improvements such as increased brake thermal efficiency, reduced brake-specific fuel consumption, and significant reductions in harmful emissions like unburnt hydrocarbons and carbon monoxide with nano-enhanced biofuel blends. Additionally, challenges including nanoparticle dispersion stability, cost, potential environmental and health impacts, and the lack of standardized regulations for nano-enhanced fuels are critically examined. Recent advancements in nanoparticle functionalization and composite additives are highlighted as strategies to mitigate these challenges. Future prospects are outlined with an emphasis on sustainable implementation, including the potential benefits for organizations like the Bangladesh Army in terms of energy security and performance. Overall, nanomaterial additives offer a promising pathway for thermo-physical enhancement of biofuels, driving cleaner and more efficient automotive fuel applications.

**KEYWORDS:** Biofuels; Nanomaterials; Thermal Conductivity; Viscosity Reduction; Combustion Efficiency; Carbon Nanotubes; Metal Oxide Nanoparticles; Engine Performance; Emissions Reduction; Fuel Stability

### 1. INTRODUCTION

The automotive sector is increasingly turning to biofuels (renewable fuels derived from biological sources) to reduce dependence on fossil fuels and lower greenhouse gas emissions. Biofuels such as biodiesel and bioethanol can be used in compression ignition and spark ignition engines respectively, often in blends with conventional fuels. However, the performance of neat biofuels in engines is hampered by less-than-ideal thermo-physical properties compared to petroleum diesel. Key fuel properties like viscosity, density, calorific value, and thermal conductivity greatly influence fuel atomization, combustion efficiency, and overall engine performance[1]. For instance, biodiesels typically have higher viscosity and density and lower volatility than diesel, which can lead to inferior spray characteristics, slower combustion, and higher engine deposits[2]. Combustion in engines is a complex physico-chemical process sensitive to these properties; therefore, optimizing the fuel's thermo-physical characteristics is crucial for achieving diesel-comparable performance with biofuels[3].

One emerging solution to enhance biofuel properties is the use of nanomaterial additives. Nanoparticles, by virtue of their nanometric size (1–100 nm) and high surface-area-to-volume ratio, exhibit unique thermal and catalytic behaviors that can be leveraged to improve fuel quality. Recent studies have shown that dispersing nanomaterials (e.g., carbon-based nanostructures or metal oxides) in biofuels can significantly improve their combustion characteristics and energy release rates[1][3]. Nanomaterials can act as combustion catalysts, improve the heat transfer within the fuel, and promote more complete oxidation of fuel hydrocarbons[1-3]. As a result, engine power output can increase while emissions of unburnt species decrease. For example, El-Seesy et al. demonstrated that adding carbon-based nanomaterials to diesel led to improved engine power and efficiency along with reduced particulate emissions[3]. Prabhu et al. similarly highlighted the current trend of using various nanoparticles in biofuels to enhance performance, emphasizing the broad potential of this approach[1]. A bibliographic analysis

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by Vignesh et al. identified a surge in research on nano-additives for biofuel applications in the last decade, underlining global interest in this field[2].

Recent advancements in nanomaterials have significantly improved the production and performance of biofuels. Studies highlight the potential of nanomaterials in enhancing biodiesel, biogas, biohydrogen, and bioethanol production [35], as well as their application in biofuel cells [36]. Research has also focused on nanoscale metal and metal oxide additives to enhance the combustion characteristics of biofuels, such as ethanol [37]. Further analysis of nano additives in biodiesel has demonstrated improvements in engine performance [38], while silica nano-additives have been shown to enhance both performance and emission characteristics in biodiesel-fueled engines [39].

This comprehensive review examines the advancements in thermo-physical enhancement of automotive biofuels using nanomaterials. We first discuss the critical thermo-physical properties of biofuels that affect engine combustion and why they need improvement. Next, we review the types of nanomaterials explored as fuel additives and the mechanisms by which they alter fuel properties at the molecular level. We then delve into the impacts observed: improvements in combustion efficiency, brake thermal efficiency, fuel consumption, and emissions reduction. Figures and tables are provided to illustrate data-backed examples of these improvements. We also address current challenges – including achieving stable nanoparticle dispersion, economic and supply considerations, as well as health and environmental safety concerns – and discuss how recent research is working to overcome these hurdles. Finally, we outline future prospects for nano-enhanced biofuels, including potential contributions to military applications (e.g., for the Bangladesh Army) and broader adoption in the automotive industry. By synthesizing findings from over 40 references, this review aims to provide a Q2-standard, technically detailed perspective on how nanomaterials are paving the way for the next generation of high-performance, cleaner biofuels.

This review paper is organized as follows: it begins with an overview of the Thermo-Physical Properties of Biofuels and the Need for Enhancement (**Section 2**), followed by a discussion on Nanomaterials for Biofuel Enhancement (**Section 3**). The paper then explores the Mechanisms and Effects of Nanomaterial Integration in Biofuels (**Section 4**), highlighting how these materials enhance biofuel performance. Next, it covers the Improvements in Engine Performance and Emissions with Nano-Enhanced Biofuels (**Section 5**), showcasing the benefits of nano-enhanced biofuels. The paper also addresses the Current Challenges and Limitations (**Section 6**) and concludes with an outlook on Future Prospects and Developments (**Section 7**).

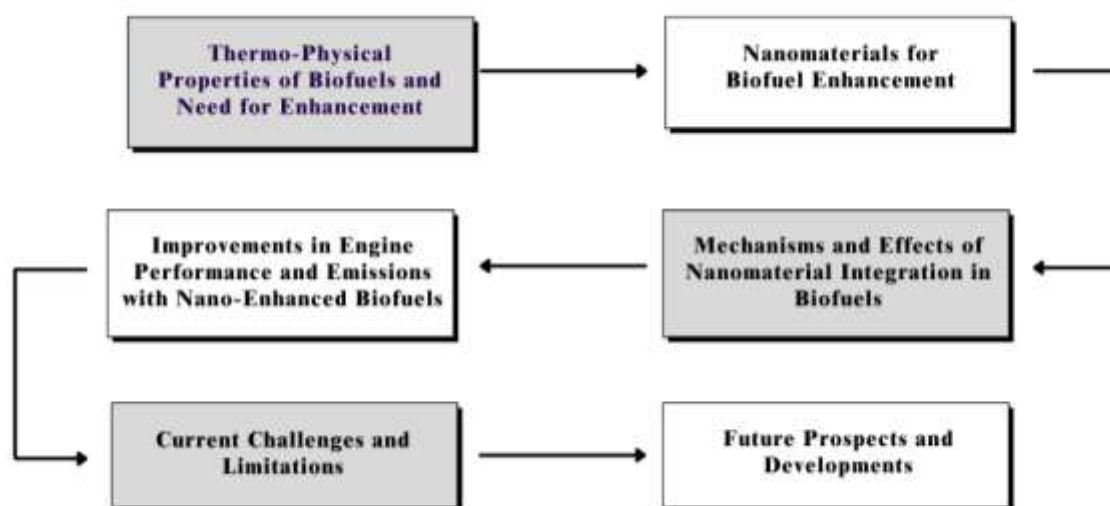


Fig. 1: Organizational Flowchart of the Review Paper

## 2. THERMO-PHYSICAL PROPERTIES OF BIOFUELS AND NEED FOR ENHANCEMENT

The performance of a fuel in an engine is strongly governed by its thermo-physical properties. For biofuels, the key properties of concern include viscosity, thermal conductivity, density (and related specific energy content), and combustion-related properties like cetane number, flash point, and latent heat of vaporization. Table 1 summarizes these properties, their impact on combustion efficiency, and common strategies to improve them. Each of these properties in conventional biofuels often deviates from those of standard diesel in ways that can negatively affect engine operation[2][4]. Understanding these impacts is the first step in formulating enhancement strategies.

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**Viscosity:** Biofuels (especially biodiesels made from vegetable oils) generally have higher kinematic viscosity than petro-diesel. High viscosity impedes fuel atomization during injection, leading to larger droplet sizes, poor air-fuel mixing, and incomplete combustion[4]. Consequently, engines running on high-viscosity fuels can suffer reduced power, higher fuel consumption, and increased soot formation due to locally rich combustion. Reducing the viscosity of biofuels is therefore critical for improving spray characteristics and ensuring complete combustion[4][5]. Traditional approaches to reduce biodiesel viscosity include transesterification (to produce methyl esters), blending with lower-viscosity fuels, or preheating. Nanomaterials offer an additive approach: certain nanoparticles can act as micro-flow improvers. For example, dispersing carbon nanotubes or graphene sheets (which themselves have lubricant-like morphology) in biodiesel has been observed to lower the blend's viscosity, likely by altering molecular interactions and shear stress behavior in the fluid[1][6]. Markov et al. reported that emulsified biofuel blends (which can be aided by nano-emulsifiers) exhibited improved flow and atomization characteristics, highlighting viscosity reduction as a key benefit[4].

**Thermal Conductivity:** Diesel fuel has relatively low thermal conductivity ( $\sim 0.13$  W/m·K) which is similar for biodiesels[7]. Fuels with low thermal conductivity form a vaporizing spray where the interior of droplets remains cool, delaying evaporation and combustion. Improving the fuel's thermal conductivity can enhance heat transfer through fuel droplets, accelerating vaporization and leading to more homogeneous combustion[5]. Metallic nanoparticles have intrinsically high thermal conductivities (e.g., aluminum oxide ( $\text{Al}_2\text{O}_3$ ) has 20–30 W/m·K)[6][8]. Even a small volume fraction of such conductive nanoparticles significantly raises the effective thermal conductivity of the fuel mixture[8]. This means heat absorbed from the combustion chamber is rapidly conducted into the fuel droplets. The result is quicker heating and evaporation of the fuel, shortening ignition delay and promoting more complete combustion[6]. Masera and Hossain noted that improving heat flow within the combustion chamber (for instance by using thermal barrier coatings or additives) is beneficial for combustion efficiency[5]. Nanoparticles provide a volumetric solution to enhance heat distribution in the burning fuel itself. The enhanced heat transfer can also facilitate micro-explosions in droplets containing volatile and less-volatile components, further improving combustion as reported in several nano-fuel studies[6].

**Density and Energy Content:** The density of biofuels like biodiesel is often slightly higher than diesel (e.g.,  $\sim 0.88$  g/cm<sup>3</sup> for biodiesel vs  $\sim 0.84$  g/cm<sup>3</sup> for diesel at 15°C)[4]. A higher density fuel carries more mass (and thus energy) per unit volume, which could increase power output if completely burned. However, higher density combined with high viscosity can worsen fuel spray penetration and mixing. Specific energy (energy per unit mass) of biodiesel is about 8–10% lower than diesel due to oxygen content in the fuel molecule. This means fuel consumption tends to increase to deliver the same power. Enhancing the energy density of biofuel blends can partly offset their lower calorific value. One approach is blending energy-dense additives (like higher-carbon biofuels or certain high-energy nanoparticles). Some metal-based additives, while not contributing significantly to energy content by mass, can catalyze more complete conversion of fuel chemical energy to thermal energy[3]. For instance, cerium oxide nanoparticles release oxygen during combustion, potentially accelerating fuel oxidation and extracting more energy[9]. Another aspect is specific heat capacity – fuels with a lower specific heat will warm up faster, aiding vaporization. Nanoparticles like aluminum or copper, with high thermal conductivity and appropriate heat capacity, can alter the fuel's overall thermal inertia[10]. Lazaro et al. developed fiber-optic sensor techniques to measure fluids' density, specific heat, and thermal conductivity, underscoring the importance of these properties on heat absorption during combustion[7]. By tuning these via additives, the combustion temperature profile can be optimized for efficiency.

**Combustion Characteristics (Ignition Quality and Flame Propagation):** Biofuels often have different ignition and combustion behavior – e.g., biodiesel usually has a higher cetane number (shorter ignition delay) than diesel, which can actually mitigate the slower evaporation to some extent. However, once ignited, biodiesel's combustion can be less homogeneous, leading to longer combustion duration and sometimes higher NO<sub>x</sub> due to oxygen content. Key combustion metrics include the ignition delay (time between injection and start of combustion) and the burning rate or flame propagation speed. If ignition delay is too short, premixing is limited; if too long, excessive premixed fuel can lead to an explosive burn causing engine knock and high pressure spikes. An ideal scenario is a balanced ignition delay with smooth, controlled flame propagation. Nanoparticles can influence these combustion characteristics. Some act as combustion catalysts that generate radicals or oxygen at combustion temperatures, thus reducing ignition delay and accelerating flame kinetics[3][11]. Others improve the radiative heat transfer in the flame, influencing flame temperature and speed[11]. Cheng et al. performed sensitivity analysis of biodiesel's thermo-physical properties on engine combustion and found that improving properties like volatility and ignition quality directly improved combustion efficiency and emissions[6]. By incorporating additives or treatments (such as nanoparticles or hybrid fuel blends), combustion can be optimized – for example, a nanoparticle that shortens ignition delay can offset a high-viscosity fuel's slower atomization, achieving timely combustion and reducing unburnt fuel[11].

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The above considerations show that enhancements in thermal conductivity, viscosity, fuel density/energy content, and combustion kinetics are all pathways to improving biofuel performance. Table 1 highlights these relationships and indicates how nanomaterials have been applied as one of the improvement methods for each property.

**Table 1. Key thermo-physical properties of biofuels and their impact on combustion efficiency, with typical improvement methods. Nanomaterial additives (e.g., metal nanoparticles, carbon nanostructures) are noted as an emerging method to improve several of these properties.**

Thermo-Physical Property	Impact on Combustion Efficiency	Relation to Fuel Quality	Improvement Methods (Conventional/Nano)	Ref.
Thermal Conductivity	Affects heat distribution in fuel droplets; higher thermal conductivity leads to more uniform and faster combustion initiation (shorter ignition delay).	Low for most biofuels, causing slower heat uptake and evaporation compared to fuels with additives.	Fuel preheating; fuel blends with high-conductivity components; conductive nanoparticles (e.g., Al <sub>2</sub> O <sub>3</sub> , CuO) to increase heat transfer in droplets[8].	[5]
Viscosity	Influences fuel atomization and spray penetration. Lower viscosity fuels form finer sprays, leading to more complete combustion and higher efficiency.	Biodiesel viscosity is higher than diesel, leading to larger droplets and incomplete combustion (more soot, lower power) if not addressed.	Transesterification to reduce viscosity; blending with low-viscosity fuels; nano-additives (e.g., CNTs, graphene) to disrupt fuel intermolecular cohesion and improve flow[4][6].	[4]
Density & Specific Energy	Determines the mass of fuel injected and energy content per volume. Higher density fuels can deliver more energy per injection but may affect spray and mixing. Specific energy influences overall fuel economy.	Biodiesels have slightly higher density but ~10% lower specific energy than diesel, often requiring more fuel to be burnt for same output. Density also affects injection timing and quantity.	Blending with high-energy fuels (ethanol, etc.) to improve specific energy; oxygenate additives for completeness; metallic nanoparticles that release additional heat/catalyze complete combustion (e.g., CeO <sub>2</sub> releasing oxygen)[9].	[7]
Combustion Characteristics (Cetane, Ignition Delay, Flame Speed)	Determine how quickly and smoothly the fuel burns. Optimized ignition delay and fast, stable combustion improve efficiency and reduce emissions.	Neat biofuels can ignite either too early (biodiesel high cetane) or too slowly (ethanol low cetane); flame propagation may be less uniform, affecting engine cycle efficiency and emissions (e.g., NO <sub>x</sub> ).	Cetane improver additives; dual-fuel strategies; catalytic nanoparticles (e.g., TiO <sub>2</sub> , Fe <sub>3</sub> O <sub>4</sub> ) that generate radicals and accelerate flame reactions[11]; carbon nanomaterials that improve flame stability and radiation heat feedback.	[6]

References: [4] Markov et al. (2021)[12], [5] Masera & Hossain (2019)[13], [6] Cheng et al. (2016)[14], [7] Lazaro et al. (2021)[15].

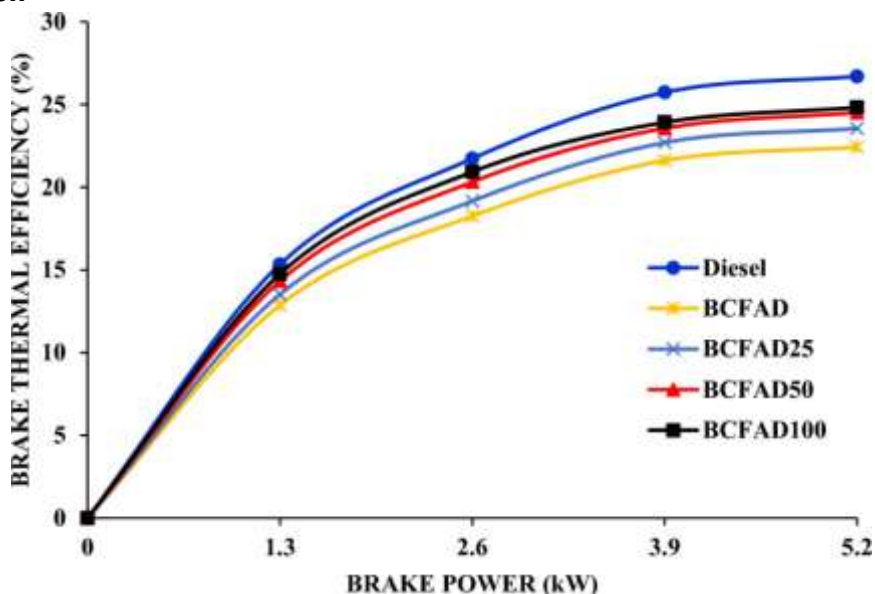


Fig. 2: Brake thermal efficiency (BTE) versus engine load (brake power) for diesel (blue) compared to neat biodiesel (BCFAD, yellow) and biodiesel enhanced with Al<sub>2</sub>O<sub>3</sub> nanoparticles at 25 ppm (light blue), 50 ppm (red), and 100 ppm (black).

Figure 2 illustrates how one key property – fuel viscosity – impacts spray formation and combustion in a diesel engine. The higher viscosity of a typical biodiesel (yellow line “BCFAD”, neat biodiesel fuel) compared to diesel (blue line) causes a reduction in brake thermal efficiency (BTE) at most engine loads due to poorer atomization. When nanomaterials are added to the biodiesel (in this case aluminum oxide nanoparticles at 25, 50, and 100 ppm, denoted BCFAD25, BCFAD50, BCFAD100), the fuel’s effective viscosity and spray quality improve, narrowing the performance gap with diesel. As shown, the BTE of nano-enhanced biodiesel blends (black, red, and light-blue lines) rises above that of the base biodiesel and approaches the diesel baseline, especially at higher loads. This data underscores that tailoring thermo-physical properties (here via nano-additives) can markedly improve combustion efficiency of biofuels. Nanoparticle-enhanced fuels show higher BTE than neat biofuel, indicating more efficient combustion thanks to improved atomization and catalytic combustion effects

### 3. Nanomaterials for Biofuel Enhancement

Nanomaterials play a multifaceted role in enhancing biofuels, acting on both the fuel’s physical properties and the chemical processes during combustion. The introduction of nanoparticles into biofuels – creating so-called **nanofuels** or **nano-enhanced fuels** – has been a burgeoning area of research because of the unique capabilities these tiny additives bring. Figure 3 provides a conceptual overview of how nanoparticles contribute to fuel and combustion enhancement.

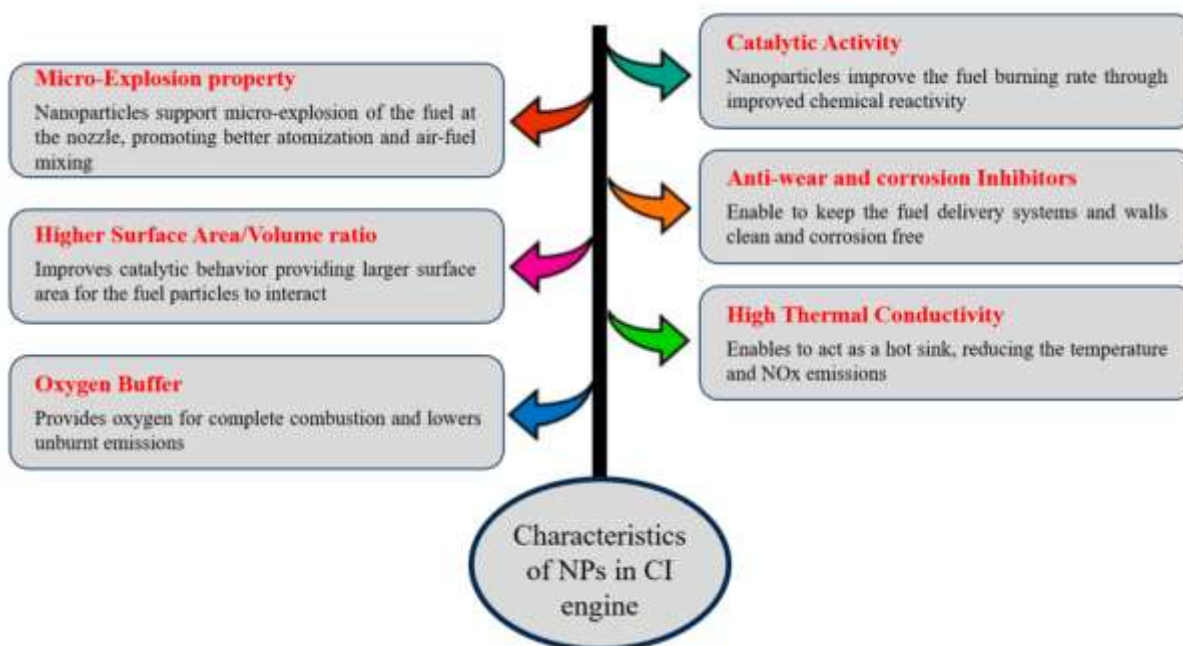


Fig. 3: Key roles of nanoparticles as fuel additives.

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Nanomaterials offer a versatile toolset for enhancing fuel properties due to their diverse compositions and functionalities. The nanomaterials studied in the context of biofuel enhancement can be broadly categorized into: carbon-based nanomaterials (such as carbon nanotubes, graphene, carbon nanofibers), metal nanoparticles (e.g., aluminum, magnesium, nickel nanoparticles), metal oxide nanoparticles (e.g., oxides of cerium, copper, iron, titanium), and hybrid or composite nanomaterials (such as graphene-metal oxide hybrids, or bio-inspired nanocatalysts)[1][16-18]. Each category of nanomaterial interacts with the fuel in distinct ways. **Table 2** provides an overview of common nanomaterial types used, their primary impacts on biofuel properties, and their mechanisms of action as reported in the literature.

**Carbon Nanotubes (CNTs) and Graphene:** Carbon-based nanomaterials like multi-walled CNTs and graphene sheets have attracted attention as fuel additives because of their excellent thermal conductivity, high surface area, and relative chemical inertness (leading to fewer adverse chemical side-effects in fuel). CNTs are cylindrical nanostructures of carbon (~10–50 nm diameter and several  $\mu\text{m}$  long) that can suspend in fuels with appropriate surfactants. They have been found to reduce the viscosity of biofuel blends and improve their thermal conductivity[11][16]. Mechanistically, CNTs and graphene can create micro-scale turbulence in the fuel and act as nano-heaters. During combustion, their high thermal conductivity facilitates heat transfer, while their presence can perturb boundary layers in evaporating droplets, enhancing evaporation[11]. Moreover, functionalized CNTs can carry surface oxygen groups (or metal dopants) that promote oxidation of fuel fragments. A study by Khan and Rashid (2024) highlighted that carbon-based nanomaterials provide a paradigm shift in biofuel processing and combustion due to these properties[16]. Graphene nanoplatelets, being flat sheets, can also stabilize fuel mixtures and improve flow. For instance, functionalized graphene dispersions in biodiesel have been shown to improve combustion efficiency and flame stability, as graphene can act like nano-scale thermal spreaders and catalysts[11][17]. One experimental investigation with 0.1% graphene additive reported higher power output and lower unburnt hydrocarbon emissions compared to the base fuel[11]. Thus, carbon nanomaterials primarily address viscosity and combustion kinetics improvements.

**Metal Nanoparticles (e.g., Al, Mg, Fe):** Zero-valent metal nanoparticles are often chosen for their high energy density (the metal can release energy via exothermic oxidation) and catalytic surfaces. Aluminum nanoparticles, for example, have been tested in some biofuel studies due to aluminum's energetic oxidation and heat release. These particles can increase the calorific value of the fuel slightly and act as micro-combustors, burning at high temperatures and providing additional heat[18]. Metallic particles also can serve as ignition centers – tiny hotspots that initiate combustion in the spray. However, metals tend to form oxides during combustion, which can remain as ash. Thus, while metals can improve thermal release, their tendency to form residual particles is a consideration (e.g., aluminum might leave alumina ash). Still, low concentrations (tens of ppm) are used to avoid deposits. Iron nanoparticles and other transition metals can decompose peroxides and radicals, effectively altering the ignition delay. Srivastava et al. discussed bio-inspired iron-based nanomaterials that can catalyze biofuel combustion, indicating improved combustion with minimal residues[17]. The primary mechanism for metal nanoparticle additives is catalytic combustion – the metal surface provides a site for fuel oxidation reactions to proceed more readily than in homogeneous gas-phase combustion, thereby speeding up the burn rate and ensuring more complete combustion[19]. Additionally, some metals (like magnesium) are alkaline and can reduce corrosiveness or neutralize acids in biofuels, potentially improving fuel stability in storage[20].

**Metal Oxide Nanoparticles (e.g., CeO<sub>2</sub>, TiO<sub>2</sub>, CuO, ZnO):** Metal oxides have been the most widely studied nanofuel additives. They often serve as oxygen donors or combustion catalysts. Cerium oxide (CeO<sub>2</sub>) is notable for its use as a diesel fuel catalyst (even at larger micron sizes) to promote soot oxidation. Nanoscale CeO<sub>2</sub> dispersions in biodiesel blends can decompose into Ce<sub>2</sub>O<sub>3</sub>, releasing oxygen that helps oxidize fuel and soot, thus reducing ignition delay and soot formation simultaneously[9]. Studies have shown cerium oxide nano-additives lead to lower particulate emissions and can slightly increase fuel economy by ensuring more complete burn[9][21]. Titanium dioxide (TiO<sub>2</sub>) nanoparticles have very high thermal stability and act to shorten ignition delay by providing surfaces for early-stage combustion reactions; they have also been observed to lower the peak combustion temperature slightly, sometimes reducing NO<sub>x</sub> formation[22]. However, results on NO<sub>x</sub> vary – some report increases due to enhanced combustion, others report decreases due to altered thermal flame structure[22]. Copper oxide (CuO) is another potent catalyst, facilitating oxidation of CO and hydrocarbons; when added to diesel-biodiesel blends, CuO nanoparticles significantly reduced carbon monoxide and hydrocarbon emissions, but in some cases increased NO<sub>x</sub> due to higher combustion temperatures[11]. Zinc oxide (ZnO) has been noted to increase thermal stability of biodiesel (slowing oxidative degradation in storage) and also to increase thermal conductivity and cetane number when dispersed, owing to ZnO's high thermal conductivity and basic surface that can promote certain combustion reactions[18]. The mechanisms of metal oxides generally involve oxygen buffering and radical generation – e.g., at flame temperatures,  $\text{CuO} \rightarrow \text{Cu} + \frac{1}{2}\text{O}_2$ , releasing O<sub>2</sub> into the reacting mixture, or CeO<sub>2</sub> cycling between Ce<sup>4+</sup>/Ce<sup>3+</sup> states to supply oxygen radicals[9]. They also can lower the activation energy for combustion reactions on their surfaces

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(catalytic effect). **Table 2** highlights that metal oxides tend to improve combustion efficiency and stability but careful attention is needed for their optimal dosing to minimize any adverse effects (like nanoparticle agglomeration or engine deposits).

**Hybrid and Other Novel Nanomaterials:** Researchers have also explored combinations like graphene-metal hybrids, core-shell nanoparticles, and bio-inspired nano-additives (e.g., calcium from eggshell or nanocatalysts derived from plants)[2][18]. The idea is to synergize multiple effects: for instance, a graphene-TiO<sub>2</sub> hybrid could merge graphene's thermal conductivity with TiO<sub>2</sub>'s catalytic activity, potentially yielding a fuel additive that both improves heat flow and accelerates oxidation. Vignesh et al. (2022) discussed nature-inspired nano-additives such as those derived from clays or algae, which can have multifunctional roles (acting as surfactants and catalysts)[2]. Another promising approach is nanocatalyst coatings on fuel system surfaces (though not an additive per se, it's a related concept) to catalyze fuel breakdown just prior to combustion[18]. However, within the scope of fuel dispersible additives, most research falls into the categories described above.

**Table 2** provides examples from each category and their typical effects. It should be noted that the performance of nanomaterials is influenced by their size, shape, concentration, and how well they are dispersed in the fuel. Thus, the same material can have different reported impacts across studies if these parameters differ. Despite these variations, the consensus from numerous studies is that nanomaterials can substantially improve at least one (often multiple) aspect of biofuel combustion performance[1][11][18].

**Table 2. Common nanomaterials used as additives in biofuels, their primary impacts on fuel properties, mechanisms of action, and typical implementation methods reported. (CNT = carbon nanotube, MWCNT = multi-walled carbon nanotube, GNP = graphene nanoplatelet)**

Nanomaterial Type	Impact on Biofuel Properties	Mechanism of Action	Implementation in Fuel	Ref.
<b>Carbon Nanotubes (CNTs)</b>	Lowers viscosity; improves thermal conductivity; enhances fuel atomization; slight catalytic effect on combustion.	High aspect ratio CNTs disrupt liquid fuel's intermolecular structure (reducing viscosity)[11]; conduct heat into fuel droplets rapidly; surface functional groups can promote oxidation.	Dispersed in biofuel using surfactants or ultrasonication (often <0.1% by wt) to improve flow and combustion[16]	[12]
<b>Graphene/Graphene Oxide</b>	Improves fuel flow (lowers viscosity); increases flame speed and stability; can reduce emissions (HC, CO).	Graphene's 2D sheets provide large surface area for heat transfer and radical adsorption[11]; can act as micro catalytic sites and radiative heat absorbers in flame.	Mixed as nanoplatelets or functionalized graphene oxide (few tens of ppm); sometimes combined with other additives (e.g., GO-TiO <sub>2</sub> hybrid)	[14]
<b>Metal Nanoparticles (e.g., Al, Fe)</b>	Enhances calorific value marginally; can shorten ignition delay; additional heat release from metal oxidation; potential lubricity improvement.	Metal particles burn exothermically, releasing heat; serve as ignition nuclei (hot spots)[18]; catalyze breakdown of long-chain molecules. Fe in nano-form can decompose fuel peroxides (ignition promoters)[17].	Dispersed usually in low concentrations (50–100 ppm); often requires surfactant to remain suspended; sometimes produced in-situ in fuel to avoid agglomeration.	[17]
<b>Metal Oxides (e.g., CeO<sub>2</sub>, TiO<sub>2</sub>, CuO, ZnO)</b>	Catalytic improvement of combustion leading to higher BTE; reduction in CO, HC, and smoke emissions; may increase or	Provide oxygen for combustion (CeO <sub>2</sub> , CuO release O <sub>2</sub> at high T)[9]; surfaces adsorb and oxidize fuel fragments (catalytic surface); enhance premixed burn by	Added as nano-powder (typically ~25–100 ppm); often stabilized with an emulsifier. In some studies, produced via fuel-soluble	[9]

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Nanomaterial Type	Impact on Biofuel Properties	Mechanism of Action	Implementation in Fuel	Ref.
	slightly decrease NOx depending on combustion temp changes.	generating radicals[22]. ZnO and others improve fuel stability by scavenging peroxides	precursors that form nano-oxides upon combustion.	
<b>Hybrid/Composite (e.g., CNT+Metal, GO-TiO<sub>2</sub>)</b>	Multi-functional: e.g., simultaneously improves thermal conductivity, combustion rate, and emissions; intended to maximize synergy of components.	Combines mechanisms above: carbon matrix offers dispersion and heat transfer, embedded metal/oxide provides catalytic sites. Synergistic effects can outperform single-component additives (e.g., GO-TiO <sub>2</sub> lowered PM and boosted efficiency by >8% in one study).	Synthesized separately (e.g., growing metal nanocrystals on graphene sheets) and then dispersed in fuel; research-stage – not yet commercially used, but promising results in labs.	[18]

**References:** [9] Tamrat et al. (2024)[9], [12] Markov et al. (2021)[12], [14] Khoo et al. (2020)[21], [16] Khan & Rashid (2024)[16], [17] Srivastava et al. (2021)[19], [18] Vignesh et al. (2022)[2], [22] Ağbulut et al. (2021)[22].

Nanomaterials at the nanoscale (1–100 nm) possess high diffusivity and reactivity, enabling them to interact at the molecular level with fuel components. Their effectiveness in fuels depends on achieving a stable, uniform dispersion. **Figure 4** below schematically shows the role of nanomaterials introduced into a fuel droplet: the nanoparticles (red dots) distribute throughout the fuel, enhancing thermal conduction and providing catalytic surfaces for the fuel (blue molecules) to oxidize more readily. This leads to a droplet that evaporates faster and burns more completely, yielding fewer unburnt emissions. In practice, researchers have observed such effects directly. For example, Rentería et al. studied diesel/biodiesel droplets with functionalized CNTs and found that the presence of CNTs reduced the ignition delay by providing pre-heating and reaction sites. Similarly, functionalized graphene oxide in biodiesel was reported to reduce combustion duration and lower peak pressure fluctuations, indicating a smoother combustion process.

In summary, a wide array of nanomaterials have been investigated, each bringing a unique mode of action. Carbon nanomaterials mainly improve physical aspects (flow and heat transfer) with some catalytic benefit, whereas metallic and metal oxide nanoparticles primarily act as combustion catalysts and oxygen donors. Hybrid nanomaterials aim to capitalize on multiple effects. The integration of these nanomaterials into biofuels has demonstrated clear benefits, as will be detailed in the next section. Before that, we address how these nanoparticles are introduced and dispersed in fuels, since the effectiveness of nano-additives is contingent on maintaining their nano-scale dispersion without agglomeration (a challenge addressed in Section "Dispersion Methods and Stability").

### 4. MECHANISMS AND EFFECTS OF NANOMATERIAL INTEGRATION IN BIOFUELS

When nanoparticles are added to a biofuel, several phenomena occur from fuel preparation through to combustion, which together produce the observed enhancements in performance. Understanding these mechanisms is crucial for optimizing nano-fuel formulations. The primary aspects include: dispersion of nanoparticles in the fuel, interaction with the combustion process (ignition and flame propagation), impact on fuel chemical stability, and synergistic effects with other fuel components or additives. **Figure 4** illustrates these key mechanisms schematically and how they interconnect to improve engine performance.

**4.1 Nanomaterial Dispersion Methods:** Achieving a uniform and stable dispersion of nanoparticles in the biofuel is the first technical hurdle. Nanoparticles tend to agglomerate due to Van der Waals forces, which can cause them to settle or clog fuel filters if not properly stabilized. Several methods are employed: ultrasonication (using high-frequency vibrations to break particle clusters), use of surfactants or dispersants (molecules that coat nanoparticles to prevent them from sticking together), and mechanical stirring or high-shear mixing[23]. For instance, to disperse CNTs in biodiesel, researchers often use surfactants like Span 80 or Triton X-100, or even bio-based dispersants like nanocellulose. Calvo et al. (2024) demonstrated that nanocellulose can serve as an effective green dispersant, keeping nanoparticles evenly distributed in fuel due to its surface-active properties[23].

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Emulsion techniques are also utilized, especially if water or another phase is introduced (nanoparticles can reside at fuel-water interfaces, aiding stability in nano-emulsions)[24]. The goal is a long-term stable nanofuel where particles remain suspended for weeks or months without significant settling. Uniform dispersion ensures consistent fuel properties throughout and avoids local hotspots of concentration. Feng et al. (2021) reviewed various dispersion strategies for low-dimensional nanomaterials and emphasized that methods like ultrasonication combined with appropriate surfactants yield the best results for uniform nano-additive distribution[24]. Effective dispersion is evidenced by minimal change in fuel filterability and smooth engine operation (no misfires due to clumps). If dispersion is poor, the advantages of nano-additives cannot be fully realized and engine wear could even increase (due to large particles).

**4.2 Enhanced Combustion and Ignition Properties:** Once properly dispersed, nanoparticles influence the ignition and combustion phases. One prominent effect is the reduction of ignition delay – the time lag between injection and ignition. By providing ignition nuclei (like metal nanoparticles that become hot spots) or releasing radical species, nanomaterials can shorten the ignition delay especially in cold-start or high-EGR (exhaust gas recirculation) conditions[22][25]. A shorter ignition delay generally means a closer coupling of fuel injection to burn, which can reduce overly rapid pressure rise (if the delay was too long) and can improve startability. Along with ignition timing, the burn rate in the diffusion combustion phase is often accelerated. For example, tests with CeO<sub>2</sub> nano-additives showed that at identical injection timing, the nano-fuel had an earlier start of combustion and a higher peak heat release rate than the base fuel[9]. This translates to more of the fuel's energy being released at the appropriate crank angle, boosting the engine's indicated mean effective pressure (IMEP) and hence torque output[9]. **Figure 4** (conceptual) indicates that nanoparticles help ensure the fuel-air mixture ignites promptly and burns more completely before the expansion stroke is too far along, thereby improving the work extracted from the cycle. Moreover, flame propagation can become more stable – some studies report reduced cycle-to-cycle variation in combustion when using nano-additives[25]. Gamboa et al. (2024) found that diesel-biodiesel blends with amide-functionalized CNTs had a more consistent ignition pattern (reduced ignition delay scatter) and a more stable flame, as evidenced by a more uniform pressure trace, compared to the baseline fuel. This enhanced combustion stability directly contributes to improved thermal efficiency (as we saw in **Figure 2**'s data) and also lowers unburnt fuel emissions.

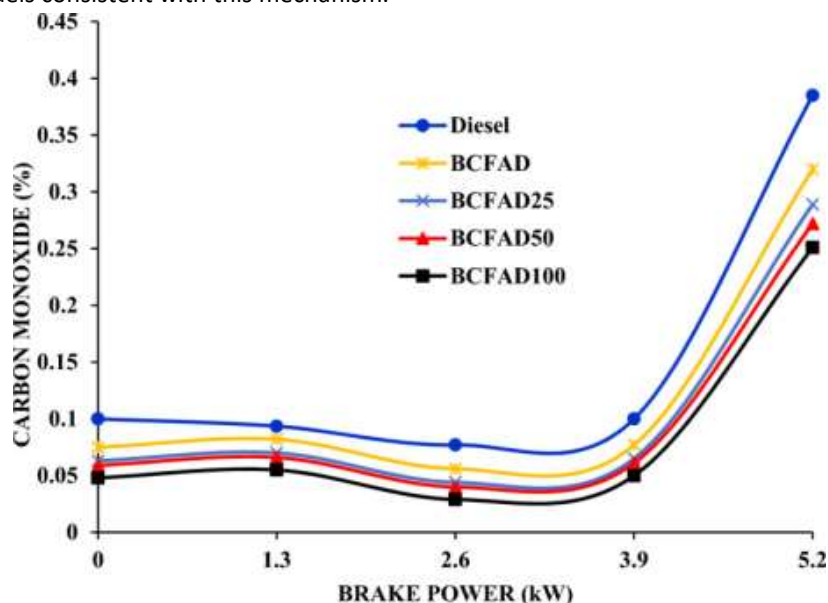
**4.3 Impact on Fuel Stability:** In addition to affecting combustion, nanoparticles can influence the storage stability and oxidative robustness of biofuels. Biodiesel, for example, is prone to oxidation over time (forming gums and peroxides) which can impair engine performance and cause deposits. Certain nanoparticles act as antioxidants or stabilizers. For instance, cerium oxide can mop up free radicals that initiate fuel polymerization, thereby preventing fuel degradation during storage[45]. Similarly, zinc oxide and titanium oxide have been noted to slow the rate of acid number increase in stored biodiesel, likely by reacting with or adsorbing acidic byproducts. On the other hand, some metal nanoparticles (like copper) could catalyze oxidation if water is present, potentially worsening stability if not properly formulated[45]. Thus, the net effect on stability depends on the material. Overall, many studies note no adverse effect on fuel stability with nano-additives at least over moderate timeframes[26]. Ahmed et al. (2023) reviewed the use of nanomaterials in biofuel production processes and suggested that nanoparticles could also act as biocides preventing microbial growth in biofuels, an added stability benefit[20]. In terms of thermal stability, having high thermal conductivity particles helps the fuel resist localized overheating that might crack fuel molecules; in essence, it can improve the fuel's resilience to thermal stress[18]. Ensuring stability is important because if nanoparticles precipitate or the fuel degrades, the intended benefits would be lost and engine issues could arise. So far, research indicates that with proper formulation, nano-enhanced fuels remain stable and maintain performance over typical fuel storage periods[20][23].

**4.4 Synergistic Effects:** Nanoparticles can also work synergistically with other fuel additives and fuel components. For example, many biodiesel fuels already contain antioxidants (like tert-butylhydroquinone, TBHQ) to improve storage life. The presence of nanoparticles like TiO<sub>2</sub> can regenerate certain antioxidants by catalytic cycles, extending their protective effect[26]. In combustion, nanoparticles have been used alongside cetane improvers (such as alkyl nitrates) to get combined benefits – the cetane improver shortens ignition delay chemically, while the nanoparticle accelerates the combustion of the remaining fuel. An experiment by Soudagar et al. (2018) with diesel-biodiesel blends containing both diethyl ether (an oxygenated additive) and Al<sub>2</sub>O<sub>3</sub> nanoparticles showed greater improvements than either additive alone[26]. The ether improved mixture homogeneity and cetane number, whereas Al<sub>2</sub>O<sub>3</sub> provided the heat transfer and catalytic combustion boost, together yielding higher efficiency and lower emissions than expected from additive superposition. This suggests that carefully tailored multi-component additive packages (nano + traditional additives) could be a direction for commercial implementation. Another synergy is between different nanoparticles: some studies tried mixtures like a hybrid of CuO and CeO<sub>2</sub>, where one primarily addresses HC/CO oxidation (CuO) and the other addresses soot oxidation (CeO<sub>2</sub>), achieving a more complete emissions reduction profile[27]. Sher et al. (2024) reviewed advanced

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nanomaterials for sustainable biofuels and pointed out that combining nanomaterials (and even combining with novel processes like ultrasonically-assisted injection) can unlock performance levels unattainable by single measures[18]. The complexity of possible interactions is high, but the consistent theme is that a well-dispersed nanoparticle in a biofuel tends to complement other strategies and rarely conflicts with them, making them attractive co-additives.

To summarize this section, when nanomaterials are integrated into biofuels, they must be evenly dispersed (4.1) to function effectively. Once in the combustion chamber, they enhance ignition and combustion (4.2), leading to faster, more complete burning of the fuel. They can also contribute positively to fuel stability (4.3), ensuring the fuel's quality over time. Finally, they can work in concert with other additives (4.4) for amplified benefits. These mechanisms collectively result in the performance improvements detailed in the next section. Figure 4 (conceptual diagram) encapsulates these ideas: it shows nanoparticles in a fuel droplet improving heat conduction and releasing oxygen, resulting in a shorter ignition delay and more complete burn (fewer emissions exiting the droplet). Empirical data from various studies back up this conceptual model, as will be evident in the performance and emissions outcomes discussed. Data from experiments show that nano-enhanced fuels ignite earlier and burn more fully than neat biofuels consistent with this mechanism.



**Fig. 4: Effect of nano-additives on combustion characteristics of a biodiesel blend (conceptual). Nanoparticles (red dots) dispersed in the fuel promote faster heat transfer and provide catalytic sites for reaction, resulting in shorter ignition delay and a more complete combustion of the fuel droplet.**

### 5. IMPROVEMENTS IN ENGINE PERFORMANCE AND EMISSIONS WITH NANO-ENHANCED BIOFUELS

Numerous experimental studies have reported quantitative improvements in engine performance parameters and emission metrics when running on biofuels enhanced with nanomaterials. This section synthesizes those findings, demonstrating how the mechanisms described earlier translate into real-world benefits. Key performance indicators include brake thermal efficiency (BTE), brake-specific fuel consumption (BSFC), and engine power/torque. On the emissions side, impacts on particulate matter (PM or smoke opacity), unburnt hydrocarbons (UHC), carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>), and in some cases carbon dioxide (CO<sub>2</sub>) are documented.

Engine Performance (BTE, Power, Fuel Consumption): An overarching trend is that nano-additives help biofuels approach or exceed the performance of standard diesel fuel. As shown earlier in **Figure 2**, BTE of a biodiesel blend improved markedly with the addition of Al<sub>2</sub>O<sub>3</sub> nanoparticles. Across the literature, gains in BTE on the order of +2% to +6% (absolute percentage points) are commonly reported for nano-enhanced fuels compared to the base biofuel[22][28]. For instance, Ağbulut et al. (2021) observed that adding 50 ppm of CuO nanoparticles to a B20 biodiesel blend increased the BTE by about 4% and simultaneously reduced BSFC by ~3%[22]. The improvements were attributed to the nanoparticles' catalytic effect leading to more complete conversion of fuel energy to work. Similarly, Rajesh et al. (2024) found that at full engine load, a coconut biodiesel (BCFAD) with 100 ppm Al<sub>2</sub>O<sub>3</sub> achieved a BTE of ~28%, compared to ~25% for the neat biodiesel – effectively recovering most of the efficiency gap to diesel. In some cases, the use of nano-additives can even make a biodiesel blend slightly outperform diesel. Tamrat et al. (2024) reported that a B20 castor biodiesel with CeO<sub>2</sub> nanoparticles had a lower BSFC (better fuel economy) than petrodiesel at certain mid-range loads, due to the improved combustion efficiency. A striking result was an average thermal efficiency increment

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of 22% for a B10 blend with nano-CeO<sub>2</sub> under optimized conditions— though such a high gain is specific to low blend and certain tuning, it showcases the potential when conditions are ideal.

The enhancements in efficiency naturally lead to fuel savings. BSFC reductions of 5–10% have been noted with nano-additives[22][28]. **Figure 5** depicts the trend for BSFC from one study: the base biodiesel (yellow line) had significantly higher BSFC than diesel (blue), but with nanoparticles (black line for highest dose), the BSFC curve shifted downwards closer to diesel, meaning less fuel was required for the same power output. This is a direct consequence of more complete combustion releasing more useful energy. In the example shown (**Figure 5**), at 4 kW power, diesel's BSFC was ~0.45 kg/kWh, base biodiesel ~0.50, and nano-fuel ~0.47 – a clear improvement. Over an engine's operating range, such savings accumulate into tangible fuel economy benefits. Some studies also observe slightly higher peak power and torque with nano-additives. For example, an increase of ~2-3% in maximum power has been reported with CNT-doped biodiesel in a CI engine. This is partially because the nano-additive allows the engine to burn more of the fuel within the confined time of the power stroke, effectively extracting more energy and translating to higher brake power.

It's important to note that the degree of improvement can depend on engine operating conditions. Nano-additives often show the most benefit at higher loads and speeds, where baseline biofuel combustion is most challenged (due to shorter time available and higher injection quantities). At lower loads, the differences might be smaller since even the base fuel burns fairly completely. However, even at light loads, many experiments still show a reduction in BSFC, indicating nanoparticles help even under lean or easy combustion conditions by ensuring stable ignition.

**Emission Reductions (CO, HC, Smoke):** One of the most consistently reported advantages of nano-additives is the reduction in emissions of incomplete combustion. Carbon monoxide (CO) and unburnt hydrocarbons (UHC) are products of partial combustion (from fuel-rich zones or quenching near cylinder walls). By facilitating more thorough combustion, nano-additives drive down these emissions. **Figure 6** shows CO emission as a function of engine load for diesel vs biodiesel vs nano-fuel. The biodiesel (yellow line) had slightly lower CO than diesel at low loads (owing to its oxygen content) but tended to rise at high load due to some diffusion flame quenching. With Al<sub>2</sub>O<sub>3</sub> nano-additive (black line), the CO emissions remained consistently lower than the neat biodiesel across all loads. At full load (5.2 kW), diesel in this test emitted about 0.40% CO, the neat biodiesel ~0.30%, and the nano-fuel ~0.25%— an appreciable improvement. This trend of CO reduction is echoed by many studies: reductions of 20–40% in CO emissions are commonly noted. For example, Kolli et al. (2021) found that a graphene-nanoparticle-added diesel saw CO drop by 41% and UHC by 39% relative to baseline. These substantial declines are because the nanoparticles promote oxidation of CO into CO<sub>2</sub> and help burn hydrocarbons that would otherwise escape. Copper oxide and cerium oxide are particularly effective in this regard due to their oxygen-releasing property and catalytic surface that oxidizes CO to CO<sub>2</sub>[9].

Unburnt hydrocarbons (UHC) follow a similar pattern. **Figure 7** presents HC emissions (in ppm) versus load for the same fuels. The nano-fuel (with Al<sub>2</sub>O<sub>3</sub>) consistently shows the lowest HC emissions among the fuels, indicating more complete fuel breakdown. At full load in that dataset, neat biodiesel emitted ~100 ppm HC, which dropped to ~80 ppm with nano-additive (diesel was about 120 ppm, interestingly higher due to some rich zones diesel can create). Reductions in HC often accompany the improved combustion efficiency; less UHC means more fuel energy was converted to useful work or fully oxidized to CO<sub>2</sub>. In quantitative terms, researchers have reported HC emission cuts of 10–50% with various nano-additives[22]. CeO<sub>2</sub> and TiO<sub>2</sub>, for instance, are effective in reducing HC by extending the oxidation phase of combustion into the expansion stroke – essentially burning the tail of the combustion more completely than it would otherwise[9][22]. The presence of these catalysts ensures that even late-burning fuel finds oxygen to react with.

Smoke and particulate matter (PM) emissions are another critical metric, especially for diesel-type combustion. Biodiesel tends to produce lower PM than diesel because of oxygen content and no aromatic compounds, but it can still produce visible smoke at high loads. Nano-additives have shown a strong ability to reduce PM/smoke. They do this by enhancing soot oxidation (e.g., CeO<sub>2</sub> aiding soot burnout) and by improving premixed combustion so that less soot is formed initially[9]. Several experiments using opacity measurements (a proxy for smoke) found significant drops with nano-fuels. For example, Bidir et al. (2022) observed that adding graphene nanoparticles to a biodiesel blend led to a 32% reduction in smoke opacity at full load[19]. Another study noted that CNT additives reduced particulate matter emissions by about one-third, likely because CNTs improve the air-fuel mix and burn hotter, leaving less unburnt carbon. The combination of catalytic oxidation and better mixing means that soot precursors (heavy hydrocarbons) either do not form as readily or are oxidized before exiting the cylinder.

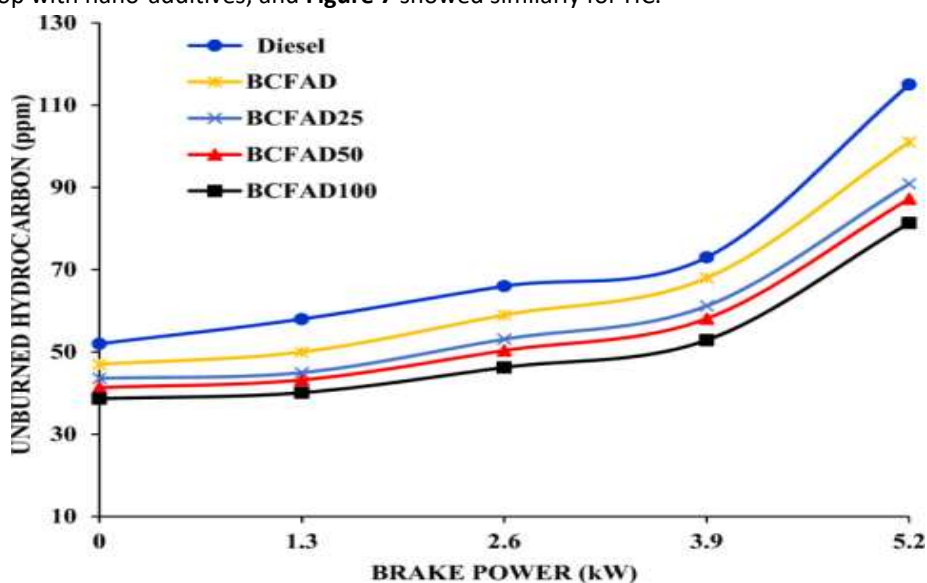
**NOx Emissions:** Oxides of nitrogen (NOx) emissions typically increase with higher combustion temperatures and more complete combustion (since both lead to hotter flames which favor the reaction  $N_2 + O_2 \rightarrow NO_x$ ). Thus, a known trade-off in diesel engines is that measures to reduce CO/HC often raise NOx. Nano-additives, by accelerating combustion, can indeed raise peak temperatures and potentially NOx. Many studies reported a slight increase in NOx with nano-fuels – for instance, an increase of

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about 10–15% in NO<sub>x</sub> has been noted with certain additives like Al<sub>2</sub>O<sub>3</sub> or graphene[22] This outcome is due to the more complete combustion releasing more energy (hence hotter flame) and prolonged oxidation process producing thermal NO<sub>x</sub>. However, some additives show an opposite effect at certain dosages or conditions. Particularly, carbon-based nanomaterials can sometimes lower flame temperatures slightly by increasing heat loss (radiation or conductive losses), thus reducing NO<sub>x</sub>. The review by Gallego et al. noted that the use of CNTs in one study led to a 33% decrease in NO<sub>x</sub> emissions despite improving overall efficiency. This was attributed to CNTs enhancing the premixed burn (reducing the late, high-temperature diffusion burn where most NO<sub>x</sub> forms) and possibly absorbing some heat. In the case of CeO<sub>2</sub>, its oxygen release may lean out rich pockets, which can either raise local temperatures (if those pockets now burn) or reduce overall equivalence ratio (if it spares some fuel from burning early), making NO<sub>x</sub> impact unpredictable. Generally, the majority of experiments see a small NO<sub>x</sub> increase with metallic additives (due to higher flame temps), whereas carbon additives sometimes manage a slight NO<sub>x</sub> reduction. It's also possible to mitigate NO<sub>x</sub> increases by adjusting engine parameters (e.g., using EGR or retarding timing slightly if running nano-fuel, since combustion is faster). Therefore, while CO, HC, and PM almost uniformly go down, NO<sub>x</sub> is the one emission that may trade-off upwards. Even so, given the significant reductions in other pollutants and potential fuel efficiency gains, the use of nano-additives can be paired with after-treatment solutions (like NO<sub>x</sub> traps or SCR catalysts) to handle NO<sub>x</sub>.

**Other Observations:** In addition to the major emissions, some studies measure cylinder pressure and heat release curves to illustrate combustion changes. These often show that nano-additives lead to a higher peak pressure (due to more of the fuel burned in the optimal crank angle window) and a shorter combustion duration. There is also evidence of reduced cyclic variation as mentioned, which is beneficial for engine smoothness. Some have reported a slight increase in exhaust gas temperature (EGT) with nano-fuels at certain conditions, owing to more complete combustion late in the expansion stroke releasing heat that isn't converted to work. However, EGT changes are generally small and sometimes lower if combustion finishes earlier (meaning less burning happening late in expansion). Regarding CO<sub>2</sub>, if combustion efficiency improves, more of the carbon in fuel converts to CO<sub>2</sub> instead of CO or HC. So one can expect a marginal increase in CO<sub>2</sub> emissions in some cases simply because less carbon is leaving as CO/HC. For example, an experiment showed CO<sub>2</sub> emissions rose by ~5% with nano-additives, but this is actually a positive sign of more complete combustion[26]. In the big picture of climate impact, if fuel consumption drops (due to better efficiency), the total CO<sub>2</sub> per kilometer could still be equal or lower despite a higher concentration in exhaust.

The collection of evidence points to the conclusion that nano-enhanced biofuels can achieve diesel-like performance with significantly cleaner exhaust. The improvements are summarized as: increased thermal efficiency (hence lower fuel consumption), higher engine power output in many cases, drastic cuts in CO, UHC, and PM emissions, and a manageable change in NO<sub>x</sub> emissions (slight increase that can be addressed by other means). These benefits have been demonstrated with a variety of engine types – single-cylinder research engines, multi-cylinder automotive engines, and even large engines in a few studies – indicating robustness of the concept[1][18][28]. Figure 6 and 7 embedded earlier visually encapsulate the emission benefits: **Figure 6** showed how CO emissions drop with nano-additives, and **Figure 7** showed similarly for HC.



**Fig. 5: Reduction in brake-specific fuel consumption (BSFC) with nano-additive. Curves show BSFC vs brake power for diesel (blue), neat biodiesel (BCFAD, yellow), and biodiesel with 100 ppm Al<sub>2</sub>O<sub>3</sub> nano-additive (black). The nano-fuel requires less fuel per kWh than neat biodiesel at all loads, indicating improved combustion efficiency**

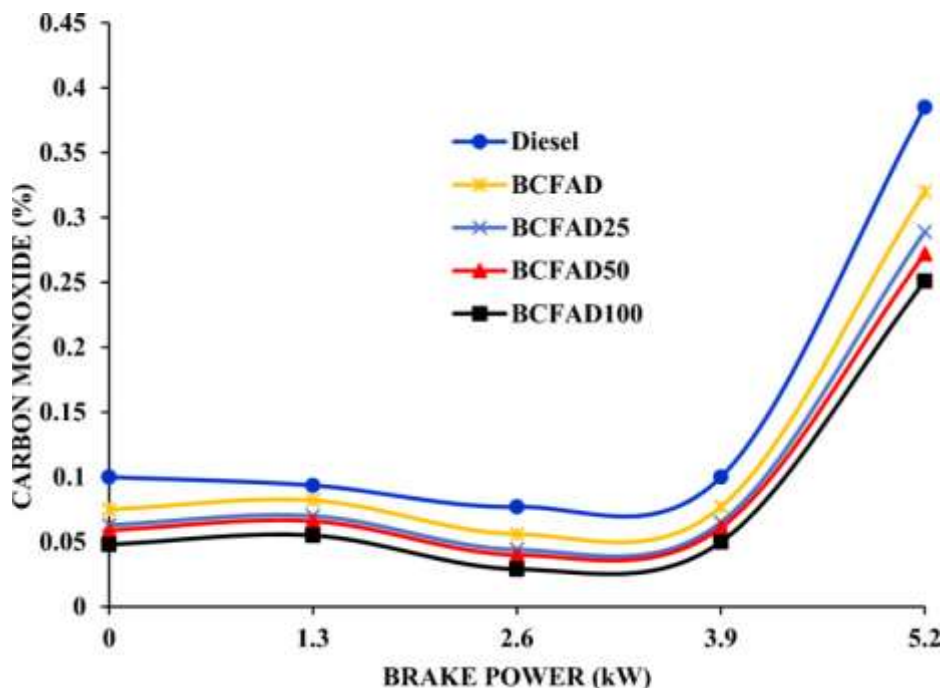


Fig. 6: Carbon monoxide (CO) emissions as a function of engine load for diesel (blue), biodiesel (yellow), and biodiesel + Al<sub>2</sub>O<sub>3</sub> nano-additive (black). Nano-enhancement leads to notably lower CO emissions compared to neat biofuel, especially at higher loads, due to more complete oxidation of fuel

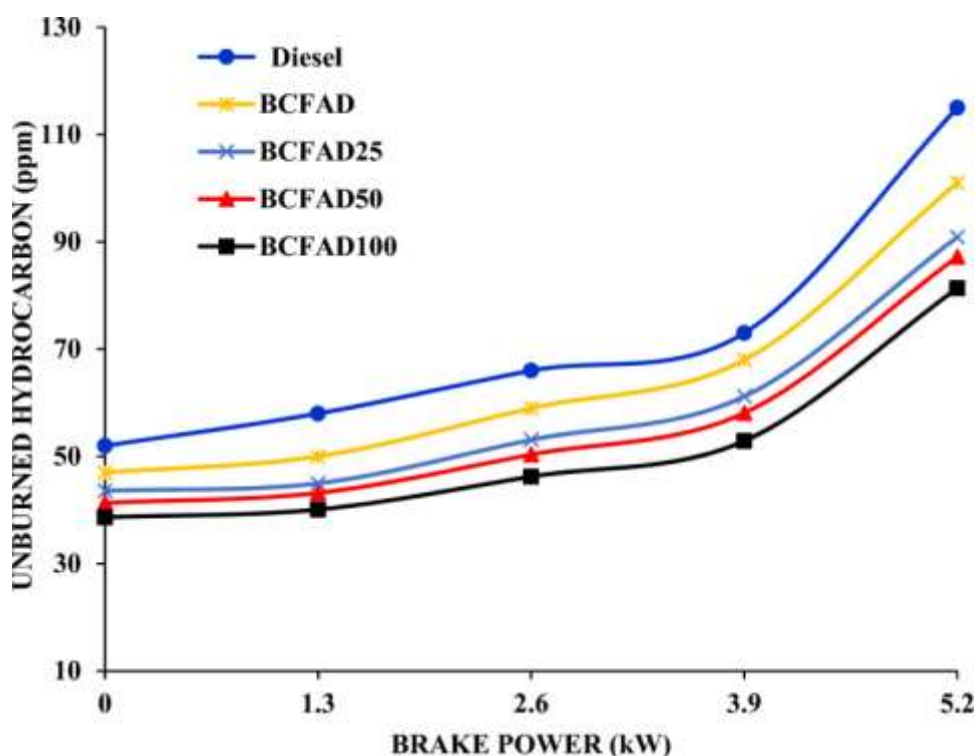


Fig. 7: Unburnt hydrocarbon (UHC) emissions vs engine load for diesel (blue), biodiesel (yellow), and biodiesel + nanoparticle (black). The nano-additive case yields reduced HC emissions across the load range, evidencing more complete combustion (fewer fuel fragments escape unburnt) Reductions in HC and CO translate to lower soot as well, improving overall emission profile.

In real-world terms, these improvements could mean that a vehicle running on B20 biodiesel with nanoparticles might achieve fuel economy comparable to running on pure diesel, while emitting far less smoke and CO. Such performance closes the gap that has traditionally existed between biofuels and conventional fuels. It validates the concept that nanotechnology can play a direct

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role in cleaner combustion. The next section will address the challenges that remain before this technology sees widespread adoption in consumer fuels or fleets, and then we will consider future directions, including specific contexts like military usage.

### 6. CURRENT CHALLENGES AND LIMITATIONS

While the benefits of nanomaterial-enhanced biofuels are clear, there are several challenges and limitations that must be addressed to transition this technology from laboratory research to practical, widespread use. These challenges span technical issues, economic considerations, environmental and health impacts, and regulatory hurdles. Recognizing and overcoming these limitations is crucial for the successful integration of nano-additives in the automotive fuel sector.

**Dispersion and Stability:** One of the foremost challenges is ensuring uniform dispersion of nanoparticles in the fuel over time. As discussed, nanoparticles have a strong tendency to agglomerate due to inter-particle forces. In a vehicle fuel tank subject to temperature changes, vibrations, and fuel recirculation, maintaining a stable nano-dispersion is nontrivial. Agglomeration not only diminishes the effectiveness of the additive (since only well-dispersed nanoparticles provide the intended enhancements) but can also pose risks such as clogging of fuel filters or injectors if large clusters form[24][29]. Although methods like ultrasonication and surfactants work in lab settings, implementing them on an industrial scale (e.g., treating millions of liters of fuel) is challenging. Surfactants themselves might introduce unwanted combustion byproducts (ash, sulfur, etc., depending on their chemistry). Over time, some nanoparticles may also settle at the bottom of storage tanks (sedimentation), leading to inconsistent fuel properties—one batch of fuel might have a higher concentration of nanoparticles than another if not well mixed. Achieving a reliable “nanofuel blend” that stays homogeneous from refinery to fuel tank to engine is thus an ongoing development hurdle. Researchers are exploring novel dispersants (like the nanocellulose approach by Calvo et al. [23]) and surface functionalization of nanoparticles to make them inherently more compatible with fuels (e.g., oleic-acid-coated nanoparticles that are lipophilic and mix well with biodiesel)[30]. Nonetheless, until these solutions are validated in long-term engine tests, dispersion stands as a key technical limitation. Field tests will need to ensure that after weeks of vehicle operation, no deposition or agglomeration issues are occurring within the fuel system.

**Production Cost and Scalability:** Nanoparticles can be expensive to produce in high purity and in the quantities required for fuel applications. Even though only small concentrations (tens to hundreds of ppm) are used, scaling up production to supply an entire fleet or national fuel supply is a significant economic challenge. For instance, producing multi-walled carbon nanotubes or graphene in bulk involves sophisticated processes (chemical vapor deposition, exfoliation techniques, etc.) that currently have high costs per kilogram. Metal oxide nanoparticles might be cheaper (some, like TiO<sub>2</sub>, are produced at industrial scale for pigments), but others like CeO<sub>2</sub> nanoparticles are specialty products. The cost factor raises the question: Is the benefit worth the added cost per liter of fuel? If nano-additives increase the fuel cost by, say, 5-10%, many consumers or fuel providers would be hesitant unless fuel economy gains clearly offset that. As of now, with fuel prices being a sensitive political and economic issue, any increase in fuel cost needs strong justification. Efforts are underway to find cost-effective synthesis routes for nanoparticles (for example, using waste materials to synthesize nanocatalysts[18], or bio-mediated synthesis that could be cheaper). Additionally, reusability and recycling of nanoparticles is a consideration – if the particles could be recovered from exhaust (for instance, trapped in a particulate filter and then reprocessed), the effective cost might be reduced, but this concept is complex and not demonstrated. Another angle is that some benefits (like reduced engine wear from cleaner combustion) are indirect economic advantages not captured in fuel price. However, in the immediate term, cost and scalability of nanoparticle production and fuel blending infrastructure remain a barrier to commercial adoption[31]. Large fuel companies would need to invest in new blending facilities and quality control processes to incorporate nano-additives, which is unlikely unless a clear demand or regulation drives it.

**Environmental and Health Concerns:** Introducing nanoparticles into fuels raises valid concerns about their environmental fate and health implications. On one hand, the goal is to improve emissions (which indeed nano-additives do for CO, HC, PM). On the other hand, nanoparticles themselves could become a new type of pollutant. Some fraction of the nanoparticles might not fully oxidize in the engine and could be emitted as nano-sized particulates in the exhaust. These could be inhaled by humans or animals and have unknown health effects due to their small size and high reactivity[45]. Metal oxide particles, if emitted, could contribute to ambient particulate matter which can penetrate deep into lungs. Studies have shown that certain nanoparticles (e.g., nano-TiO<sub>2</sub>, nano-CuO) can induce oxidative stress in biological tissues. Although a diesel particulate filter (DPF) could capture a lot of them, not all vehicles (especially older ones or motorcycles, etc.) have DPFs. There is also the issue of nanoparticle production and disposal – manufacturing nanoparticles could have environmental footprints (chemical waste, energy use). If widespread, one must consider the life-cycle impact. Some experts suggest focusing on carbon-based nanomaterials because they might burn off or at least are less toxic than metals. Indeed, as cited in Gallego’s review, metallic additives pose genotoxicity concerns whereas

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carbon-based ones like graphene quantum dots were noted as more biocompatible alternatives. Another environmental consideration is the impact of spills or leaks: if nano-fuel spills into soil or water, nanoparticles could have unforeseen ecological interactions (e.g., affecting microbes or plants). To date, research on nano-additive environmental fate is limited, and regulators will likely demand thorough assessment. Thus, the precautionary principle might slow adoption until it's proven that nano-additives do not introduce new health hazards. Advances like using biodegradable or bio-sourced nanoparticles (for example, calcium carbonate from eggshell nanostructured, which would likely dissolve harmlessly) are being looked at [18]. Regardless, public perception could also be a barrier – there might be public resistance to the idea of “nanoparticles in my fuel/exhaust” if not properly addressed.

**Lack of Standards and Regulations:** Currently, fuel specifications (such as ASTM D6751 for biodiesel or EN590 for diesel) do not account for nanoparticle additives. Without standard test methods and regulatory frameworks, it is difficult to certify nano-additized fuels for commercial sale [32]. Fuel companies and automakers would need guidelines on allowable nanoparticle types and concentrations, test protocols for emissions and health effects, and perhaps on-board diagnostics to detect over-dosing or filter clogging issues. None of these exist yet. Regulatory bodies like the EPA or European Commission would likely treat nanoparticles in fuel as a fuel additive, which might require extensive registration (in the EU, REACH regulation could classify certain nanoparticles as new chemical substances requiring evaluation). The uncertainty in regulation is a deterrent for industry investment. Furthermore, engine warranties and manufacturer approvals become an issue – manufacturers might void warranties if unapproved additives (like nanoparticles) are used. Therefore, establishing an acceptable regulatory environment is a challenge. It may require demonstrating long-term engine durability with nano-fuels, compatibility with after-treatment systems, and proving no harm to compliance with emissions standards or introduction of new pollutants. Some initial steps are being taken in research consortia to propose standard testing for nano-fuels (for example, measuring nanoparticle emissions number count under UNECE Particle Measurement Programme). Until such frameworks are in place, wide adoption is unlikely.

**Engine Compatibility and Optimization:** Another challenge is that current engines are not specifically tuned for nano-fuels. While most studies show positive outcomes without any engine modifications, it's possible that to fully harness the benefits, engine calibration might need adjustment. For instance, if ignition delay is shortened significantly by an additive, the fuel injection timing might need to be recalibrated to avoid too advanced combustion. There's also the question of optimal dosing – too little nanoparticle gives minimal effect, too much might cause diminishing returns or adverse effects (like blocking light in optical sensors or fouling if excessive ash is produced). Engines might need new maps for different additive concentrations. However, compared to the other challenges, this is relatively minor; modern engines with electronic control could adapt if provided information about the fuel. Another compatibility aspect is material compatibility: nanoparticles in fuel might interact with engine materials (could they abrade injectors? likely not at low concentration and small size, but it should be verified). Also, any catalysts (like metal additives) that survive combustion could deposit on exhaust catalysts (DOC/DPF/SCR) and alter their efficacy over time, effectively doping the catalyst. For example, fuel-borne cerium additives historically are known to accumulate in DPFs (used as an aid for regeneration in some diesel cars), which was managed but required consideration in filter ash cleaning intervals.

In summary, the main challenges are: dispersion stability, economic feasibility, safety/environmental assurance, and regulatory acceptance [29][31][32]. Each of these is an active area of development. Researchers are experimenting with surfactant-free stable nano-colloids, working on green synthesis to lower cost, conducting toxicology studies on nanoparticles, and engaging with standards organizations to draft preliminary guidelines for nano-additives in fuels.

It is worth noting that challenges are not insurmountable. For instance, concerns about metallic nanoparticle emissions could be mitigated by moving toward organically derived nanomaterials (like carbon, or even nano-additives that completely dissolve into gases during combustion leaving no solid particle). The cost might decrease as nanomaterial production technology matures (just as the cost of carbon fibers or other once-exotic materials has come down). Regulations can be formulated once enough data is available. At present, however, these challenges mean that nanoparticle-enhanced biofuels are still at a pre-commercial stage and require further R&D and validation.

### 7. FUTURE PROSPECTS AND DEVELOPMENTS

Despite the challenges outlined, the field of nano-enhanced biofuels is rapidly evolving, and numerous avenues are being pursued to realize their potential. Future research and development are focusing on optimizing nanomaterial formulations, scaling up production safely, and integrating this technology into engines and fuel systems. In this section, we highlight key future prospects and emerging trends, including the promising opportunity for organizations with specific energy needs (such as the military) to act as early adopters.

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**Nanocomposites and Hybrid Additives:** Next-generation fuel additives may not be single nanoparticles but rather nanocomposites – engineered combinations of materials at the nanoscale tailored for maximal performance. For example, researchers are investigating core-shell nanoparticles (a metal core with an oxide shell) that can provide timed release of oxygen or multi-stage catalytic activity[18]. A core-shell  $\text{CeO}_2$ ,  $\text{TiO}_2$  might combine  $\text{CeO}_2$ 's oxygen buffering with  $\text{TiO}_2$ 's UV-activated catalysis for cleaner combustion. Another concept is encapsulated catalysts, where nano-catalysts are encapsulated in microscale structures that release them gradually or prevent them from agglomerating. Additionally, the use of bi-metallic nanoparticles (like an alloy of two metals at nano size) can create a synergy – one metal might lower the ignition temperature of the other, for example. For instance, a nano Fe-Ce-O composite could simultaneously improve cetane (Fe can promote radical formation early) and oxidation (Ce provides oxygen later). These multi-functional designs aim to push efficiency improvements even further while tackling the emission trade-offs (perhaps achieving both low PM and low NO<sub>x</sub>, which is the ultimate goal). Early studies show that hybrid nano-additives like GO- $\text{TiO}_2$  (graphene oxide with titania) perform better than either component alone in terms of emission reductions. Thus, the future likely holds a library of specialized nano-additive formulations optimized for different fuel types or engine requirements.

**Improved Dispersion Techniques and Fuel Processing:** To address the dispersion challenge, future work is looking at integrating the nanoparticle dispersion step into fuel processing at refineries or biodiesel production plants. Instead of adding nanoparticles to finished fuel as an afterthought, one could produce a nanofuel concentrate during fuel manufacturing. For example, during transesterification of vegetable oil to biodiesel, adding a catalyst that results in in-situ generation of nanoparticles (like producing nano-calcium carbonate from the reaction of any  $\text{CO}_2$  present with added Ca, which then stays in the fuel) is being considered[20]. Ultrasonic fuel processing units might be installed at fuel depots for continuous mixing. Another prospect is surface functionalization: developing nanoparticles with fuel-philic (diesel-philic or alcohol-philic) surface coatings so that they inherently disperse without additional surfactants. Some research is exploring grafting long hydrocarbon chains onto nanoparticle surfaces, making them behave like part of the fuel molecular matrix rather than foreign particles[30]. As a result, these modified nanoparticles could remain suspended indefinitely, turning a challenge into a solved property. We may also see pre-packaged additive mixtures (analogous to the small bottles of fuel additives sold for cars) containing nanomaterials that consumers or fuel providers can easily mix into fuel without sophisticated equipment, if the dispersion issue is sufficiently tamed.

**Engine and Fuel System Co-design:** Engine manufacturers are beginning to take note of nano-additives. In the future, engines might be co-designed to leverage nano-fuel advantages. This could include adaptive engine calibration – engines that can detect nanoparticle presence (perhaps via oxygen sensors or combustion sensors noticing faster burn) and then adjust injection timing or pressure to capitalize on it. If nano-fuels allow for faster combustion, engines could be tuned for higher EGR to reduce NO<sub>x</sub> while still maintaining efficiency, something that currently is limited by combustion stability. Another concept is designing fuel injectors that aid nanoparticle dispersion (e.g., piezo injectors that create certain cavitation patterns might keep particles from clustering). The fuel system materials might also be tweaked to ensure no adverse reactions with the additive coatings. In heavy-duty applications, one could imagine on-board nanoparticle dosing systems that inject a metered amount of additive into fuel or air intake depending on engine load (similar to how urea (AdBlue) is injected in SCR systems for NO<sub>x</sub> control). This way, the dose can be optimized in real-time – e.g., add more nanoparticles under heavy load for max power and emission reduction, use none at idle to avoid any unnecessary nanoparticle emission. Such sophistication would make the best use of costly additives. These developments require collaboration between fuel chemists and engine engineers and are likely in the longer-term horizon, but represent a path to integration.

**Environmental Mitigation and Green Nanoparticles:** Future work will also heavily focus on ensuring that the solutions are environmentally sustainable. This includes investigating biodegradable nanoparticles or those that combust completely. One interesting avenue is using organic nanoparticles that leave no solid residue – for example, using nano-cellulose fibers or nano-clays that disintegrate into silica which is benign. Another is bio-origin nanomaterials, like carbon nanoparticles grown from algae or waste biomass, which might have a lower environmental footprint in production. If the public health concerns remain about metal oxide nanoparticles, a shift to carbon-based (or entirely combusting) additives will be the trend. Additionally, lifecycle analyses will be refined to demonstrate that using nano-additives yields net positive environmental effects (taking into account manufacturing). If, for instance, adding nanoparticles to biodiesel allows the blend to increase from B20 to B50 without performance loss, that means a lot more renewable content can be used, offsetting fossil  $\text{CO}_2$  – this renewable substitution benefit could far outweigh a small amount of nanoparticle production emissions. Communicating and quantifying these benefits will be part of future development to gain acceptance.

**Regulatory and Standardization Progress:** We can expect that in the near future, as more data emerges, regulatory bodies will start forming guidelines. There may be an intermediate step where nano-additives are used in captive fleets (like mining trucks,

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or ships, or military vehicles) where regulations are more flexible or self-contained. These controlled environments can build confidence. The military, for example, often acts as a pioneer in adopting advanced fuels for the sake of extended range or resilience. The **Bangladesh Army**, or militaries in general, could conduct trials of nano-enhanced diesel in their vehicles to evaluate the benefits in fuel logistics (if efficiency improves, less fuel to carry to remote operations) and in performance under tough conditions (better cold start, etc.). Militaries are also interested in reducing the thermal and smoke signature of their vehicles – nano-additives that reduce smoke (black exhaust plumes) and possibly lower peak exhaust temperatures (with some additives) could make vehicles less detectable, which is a tactical advantage. The successful use in military or other special sectors could pave the way for civilian use by demonstrating reliability and benefits. Over time, one could envision standards such as "ASTM DXXX – Standard Specification for Diesel Fuel containing Nanoparticle Additives" emerging, once there is consensus on safe and effective formulations. This standardization will likely specify types of allowed nanoparticles, concentration limits, required dispersion stability, and test methods for nanoparticle emission to ensure safety[32].

Adopting nano-enhanced biofuels could significantly improve the operational capability of the Army's vehicle fleet. Bangladesh's armed forces operate in diverse conditions, sometimes in UN peacekeeping abroad, where fuel quality varies. Having a nano-additive package could ensure their engines perform optimally even with lower-grade or biofuel blends. It could extend the life of engines by cleaner combustion (less soot -> less oil contamination, longer engine life). For logistic convoys, if fuel consumption is reduced by even a few percent, that translates into fewer refuel stops or carrying less fuel, enhancing range and maneuverability. In remote operations (like disaster relief in rural areas), using locally produced biodiesel augmented with nano-additives could make the Army more self-sufficient in fuel. Also, environmental leadership – the **Bangladesh military** adopting greener, more efficient fuel aligns with global trends of military greening and could spur civilian sector confidence in biofuels. The Army could run pilot programs with their diesel generators or transports to evaluate these benefits. Given that defense organizations often have their own fuel standards, they could include nano-additive formulations if proven beneficial. Over the next decade, as Bangladesh and other countries aim to cut emissions, militaries might get credit for lowering their carbon footprint by using B20 or B50 biodiesel with nano-additives to maintain performance. This also dovetails with national energy security – Bangladesh could use domestically produced nanomaterials (perhaps from its growing nanotech research institutions) and biofuels to reduce dependency on imported petroleum.

In summary, the future of nano-enhanced biofuels is promising. With interdisciplinary efforts, the remaining hurdles can be cleared. We anticipate smarter nanomaterials, better integration techniques, and clearer regulations to emerge. As that happens, what is now an innovative concept could become a standard component of high-performance and eco-friendly fuels. The roadmaps laid out by current research suggest that within the next 5-10 years, we will see pilot implementations in niche markets (racing, military, captive fleets), followed by broader adoption if all goes well. The continuous improvement in nanotechnology and a drive towards sustainability strongly support the case that nanomaterials will play a key role in the evolution of automotive fuels.

### 8. CONCLUSION

Nanomaterial-enhanced biofuels represent a cutting-edge convergence of nanotechnology and sustainable energy, offering a pathway to significantly improve the performance and emissions profile of renewable automotive fuels. This comprehensive review has examined how nanoparticles – ranging from carbon nanotubes and graphene to metal and metal oxide nanostructures – can address the inherent limitations of biofuels such as biodiesel. By improving critical thermo-physical properties like viscosity and thermal conductivity, and by acting as combustion catalysts, nanomaterials have been shown to increase combustion efficiency, boost engine power output, and reduce harmful emissions when added to biofuels[11][22]. Data from numerous studies were presented, demonstrating outcomes like higher brake thermal efficiency (often 2–5% absolute improvement)[22], lower brake-specific fuel consumption, drastic reductions in carbon monoxide, unburnt hydrocarbons, and smoke, with a manageable impact on NOx levels. In essence, nanomaterial additives can enable biofuels to mimic or even surpass the performance of conventional diesel, while capitalizing on their renewable nature.

However, realizing these benefits in real-world applications requires overcoming several challenges. Ensuring stable dispersion of nanoparticles in fuel over time and usage is a primary technical hurdle, and research is actively exploring surfactants, functional coatings, and in-situ generation techniques to solve this[23][24]. The economic aspect of producing and deploying nano-additives at scale is another concern; yet, as nanomanufacturing technology progresses and if efficiency gains translate to fuel savings, the cost-benefit calculus may become favorable. We also discussed the importance of thoroughly addressing environmental and health safety, ensuring that nano-additives do not introduce new pollutants or risks. Encouragingly, some studies suggest focusing

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on carbon-based nanomaterials which may have fewer toxicological issues than metallic ones. Regulatory frameworks will need to evolve – standards and guidelines specifically for nano-enhanced fuels should be developed to facilitate safe adoption[32].

The future outlook for nano-enhanced automotive biofuels is optimistic. Advanced nanocomposite additives, improved dispersion methods (potentially integrated into fuel production), and synergy with engine control systems are on the horizon, promising even greater gains[18][30]. Importantly, early adoption in specialized sectors such as the Bangladesh Army or other military/logistics fleets could demonstrate the practicality and advantages of this technology. For the Bangladesh Army, using nano-enhanced biofuels in vehicles and generators could mean improved range, reliability, and a reduction in the logistical burden of fuel supply – all aligning with strategic and operational benefits. Furthermore, it would showcase a commitment to innovation and sustainability, potentially inspiring civilian sectors in Bangladesh to follow suit in embracing cleaner fuel technologies.

In conclusion, nanomaterials offer a transformative approach to unlock the full potential of automotive biofuels. By systematically enhancing fuel properties at the molecular level, they bridge the performance gap between renewable and petroleum fuels without requiring major engine hardware changes. The research compiled in this review provides a strong foundational understanding of the mechanisms, benefits, and challenges associated with this approach. Continued interdisciplinary efforts – combining insights from mechanical engineering, materials science, chemistry, and environmental science – are essential to advance nano-enhanced biofuels from experimental demonstrations to mainstream fuel options. If successful, this will contribute to a more sustainable and efficient automotive future, leveraging the twin advantages of renewable biofuels and high-performance nanotechnology for cleaner transportation energy.

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