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Catalytic Nanoparticle Modifiers for Biodiesel-Diesel Blends: Performance Recovery, Emission Suppression, and Stability Constraints

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ABSTRACT

Sustainable liquid fuels are vital for decarbonizing compression-ignition engines in transport, agriculture, marine power, and decentralized energy systems. Biodiesel is renewable and oxygenated, but its lower heating value, higher viscosity, increased fuel consumption, and variable NOx emissions limit wider use. This review examines nanoparticle-enhanced biodiesel blends as sustainable fuel systems for improving combustion and emissions. A Scopus-based corpus from 2017–2026 was screened, yielding 74 studies, each classified by nanoparticle type, feedstock, engine platform, co-additive strategy, response domain, and optimal dosage. Al_2O_3, TiO_2, and CeO_2 are the most studied additives, while graphene, carbon nanostructures, CuO, ZnO, and iron-based particles are emerging.

Keywords: biodiesel blend; nanoparticles; compression-ignition engine; nano-additives; combustion; renewable energy

1. Introduction

Decarbonizing the existing diesel fleet remains an engineering problem of transition rather than replacement. Heavy-duty transport, agricultural machinery, decentralized power generation, marine auxiliaries, and industrial compression-ignition systems still depend on liquid fuels with high volumetric energy density, rapid refueling, and established supply chains. Biodiesel has therefore retained strategic importance because it is renewable, sulfur-free, oxygenated, and compatible with existing diesel infrastructure at low-to-moderate blending ratios. The literature frames biodiesel as an available substitute rather than a speculative future fuel, particularly when produced from waste cooking oil, non-edible oils, microalgae, or mixed low-value lipids, thereby avoiding direct competition with food systems [1]. At the same time, the corpus also shows why biodiesel has not displaced petroleum diesel more aggressively. Compared with diesel, biodiesel blends usually exhibit higher viscosity and density, lower heating value, altered volatility, and oxygen-driven combustion behavior that can lower CO and HC but still impose fuel-consumption penalties or stimulate NOx formation under certain load and injection conditions [2]. The question is no longer whether biodiesel can run a diesel engine; that question was resolved years ago. The unresolved question is how to restore diesel-like efficiency and combustion controllability while preserving the environmental advantages of oxygenated renewable fuel.

Nanoparticle addition has emerged in this context as a targeted combustion-engineering intervention rather than a purely materials-science novelty. The reviewed studies repeatedly invoke four coupled mechanisms. First, nanoparticles modify effective thermophysical properties, especially thermal conductivity and, sometimes, apparent cetane behavior, thereby altering ignition delay and the rate of premixed heat release [3]. Second, catalytic oxides such as CeO_2, TiO_2, CuO, and ZnO supply active oxygen or promote oxidation pathways that accelerate the burnout of CO, unburned hydrocarbons, and soot precursors [4]. Third, nanoscale additives can indirectly improve atomization and secondary breakup by moderating viscosity or locally intensifying heat transfer, thereby reducing incomplete-combustion zones within the spray plume [5]. Fourth, carbon nanostructures and graphene-derived materials introduce high-surface-area reaction sites that intensify combustion kinetics but also raise new questions regarding dispersion stability, deposit formation, and downstream particulate chemistry [6]. These mechanistic hypotheses explain why the field has converged on small additive loadings, typically in the tens of ppm, rather than bulk reformulation.

The corpus further shows that nanoparticle-assisted biodiesel research evolved through distinct phases. Early studies focused on proof-of-concept demonstrations, asking whether a specific oxide such as alumina or nanoceria could compensate for biodiesel's efficiency penalty in a standard single-cylinder diesel engine [7]. By 2020-2022, the field broadened into comparative materials studies that tested multiple oxides, multiple blend ratios, and, in some cases, competing additive classes such as alcohols and antioxidants [8]. The most recent period shifts from simple additive screening toward optimization-rich frameworks that integrate response surface methodology, machine learning, multi-criteria decision methods, exergoeconomic analysis, and hybrid operating strategies such as EGR, hydrogen enrichment, low-heat-rejection combustion, electrostatic particulate capture, and dual-fuel assistance [9]. This methodological transition is important because it indicates a maturing field that increasingly treats nanoparticle selection as a multi-objective optimization problem rather than a one-variable additive experiment.

Despite that maturation, the literature remains structurally uneven. Figure 1 of the present review shows a sharp increase in publications after 2022, but Figure 10 also shows that most studies still rely on single-cylinder, steady-state test platforms. CRDI engines, which are more relevant to modern road diesels, appear only rarely in the supplied corpus, as do HCCI-DI hybrids, marine engines, low-heat-rejection systems, and gaseous-fuel-enriched dual-fuel configurations [10]. Likewise, much of the evidence is still anchored in full-load or quasi-steady load sweeps at fixed speeds, whereas transient operation, cold start, aftertreatment compatibility, and long-term injector or ring-pack durability remain weakly documented. This imbalance matters because nanoparticle benefits are strongly condition-dependent. Improvements that are clear at one compression ratio, injection pressure, or air-fuel dilution level do not automatically transfer to other engine architectures or duty cycles [11]

A second source of inconsistency lies in the diversity of base fuels and co-additives. The present corpus includes waste-derived biodiesel, non-edible oils, edible oils, algal lipids, hybrid biodiesel systems, and ternary or quaternary blends containing ethanol, butanol, diethyl ether, dimethyl carbonate, antioxidants, essential oils, hydrogen, biogas, dispersants, or exhaust-gas recirculation. Each of these modifiers changes oxygen availability, latent heat, evaporation rate, viscosity, and ignition chemistry. As a result, nanoparticle performance cannot be interpreted independently of the surrounding blend architecture. TiO_2 combined with high-rate EGR produces one type of NOx-particulate trade-off; CeO_2 combined with biodiesel ratio variation in a CRDI engine produces another; Al_2O_3 used together with hydrogen, cetane improver, or low-heat-rejection hardware produces yet another [12]). The literature therefore requires comparative synthesis at the level of mechanisms, operating windows, and contradictions, not at the level of isolated paper summaries.

This review is designed to provide that synthesis. this evaluates the supplied corpus as a systematic evidence base and reorganizes it along material, methodological, operational, and application dimensions. The central thesis emerging from the literature is that nanoparticles do not "solve" biodiesel in a universal sense; rather, they shift the combustion-emissions balance in a controllable way when three constraints are respected: stable dispersion, low-to-moderate dosage below the agglomeration threshold, and calibration matched to the oxidation intensity of the base fuel. Under those constraints, most studies report higher brake thermal efficiency, lower specific fuel consumption, lower CO and HC, and lower smoke or particle output, but they also reveal persistent uncertainty in NOx response, insufficient knowledge of long-term material compatibility, and almost no consensus on economic or toxicological viability at scale [13]. The following sections therefore move from a systematic methodology to classification, comparative analysis, critical interpretation, and a research agenda aimed at advancing the field from laboratory-scale efficacy to deployable engine-fuel systems. One additional reason a comparative review is necessary is the lack of methodological standardization in nano-fuel preparation and reporting. The supplied studies use different ultrasonication times, surfactants (with or without), mass- versus volume-based dosing, particle sizes, storage durations, and stability criteria. At the same time, several abstracts do not report zeta potential, sedimentation time, or post-test fuel-property drift at all. The result is a literature in which apparently similar fuels are not necessarily comparable at the colloidal level, even before they enter the engine. That weakness becomes especially important for carbon-based additives, graphene derivatives, and higher-load oxide systems, whose benefits are often dose-dependent and whose penalties can emerge abruptly once agglomeration or injector-wall deposition begins [14].A rigorous review must therefore evaluate not only whether a nanoparticle improved engine response, but also whether the study design enables that improvement to be transferred.

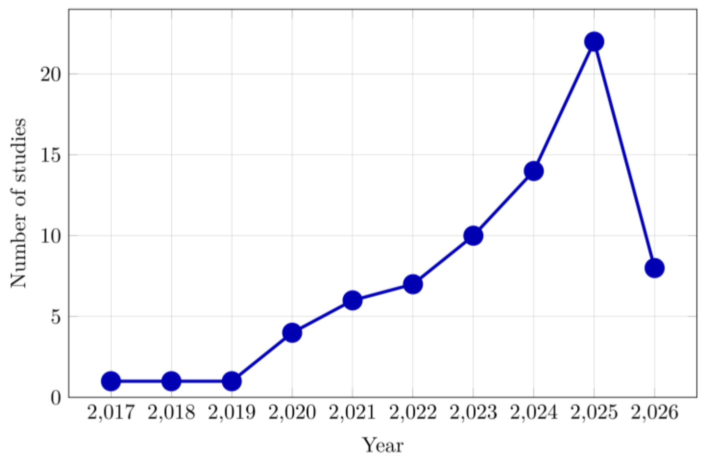

Figure 1. Annual publication trend in the included corpus.

Publication output was almost flat until 2020, then accelerated sharply after 2022, indicating that nanoparticle-assisted biodiesel blending shifted from scattered exploratory work to a rapidly expanding research stream (Figure 1).

2. Methodology

The evidence base for this review was a Scopus export supplied by the user as a comma-separated bibliographic dataset containing titles, abstracts, author names, publication years, source titles, keywords, citation counts, volume and issue data, page spans, and digital object identifiers. The initial dataset contained 75 records published between 2017 and 2026. Because the objective was to synthesize the literature already collected by the user rather than to replicate a database-wide search from scratch, the review treated this export as the primary study universe. A semantic duplicate screen was then performed by comparing normalized titles and abstracts. One near-duplicate record describing the same CeO_2-CRDI study was removed, leaving 74 unique evidence units for analysis. Figure 2 summarizes this workflow. The resulting corpus is therefore systematic within the boundaries of the supplied dataset, but should be interpreted as a structured review of a topic-specific Scopus export rather than a universal census of all global publications on nanoparticle-assisted biodiesel blends.

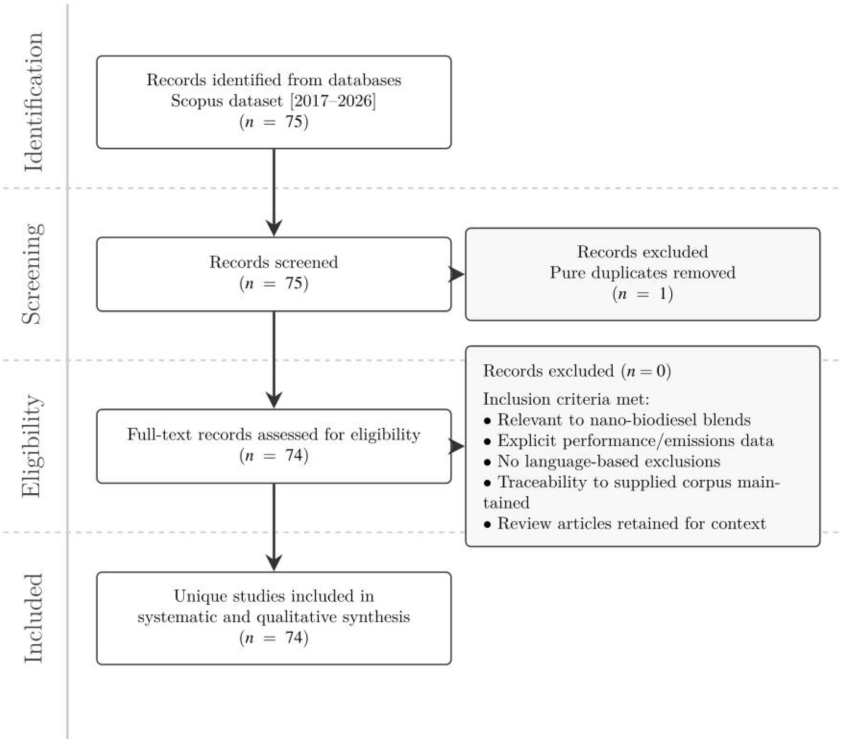

Figure 2. Study selection and synthesis workflow used in the present review.

The review used74 unique evidence units from 75 supplied Scopus records, showing a narrowly defined but internally coherent evidence base suitable for structured comparison rather than statistical meta-analysis (Figure 2).

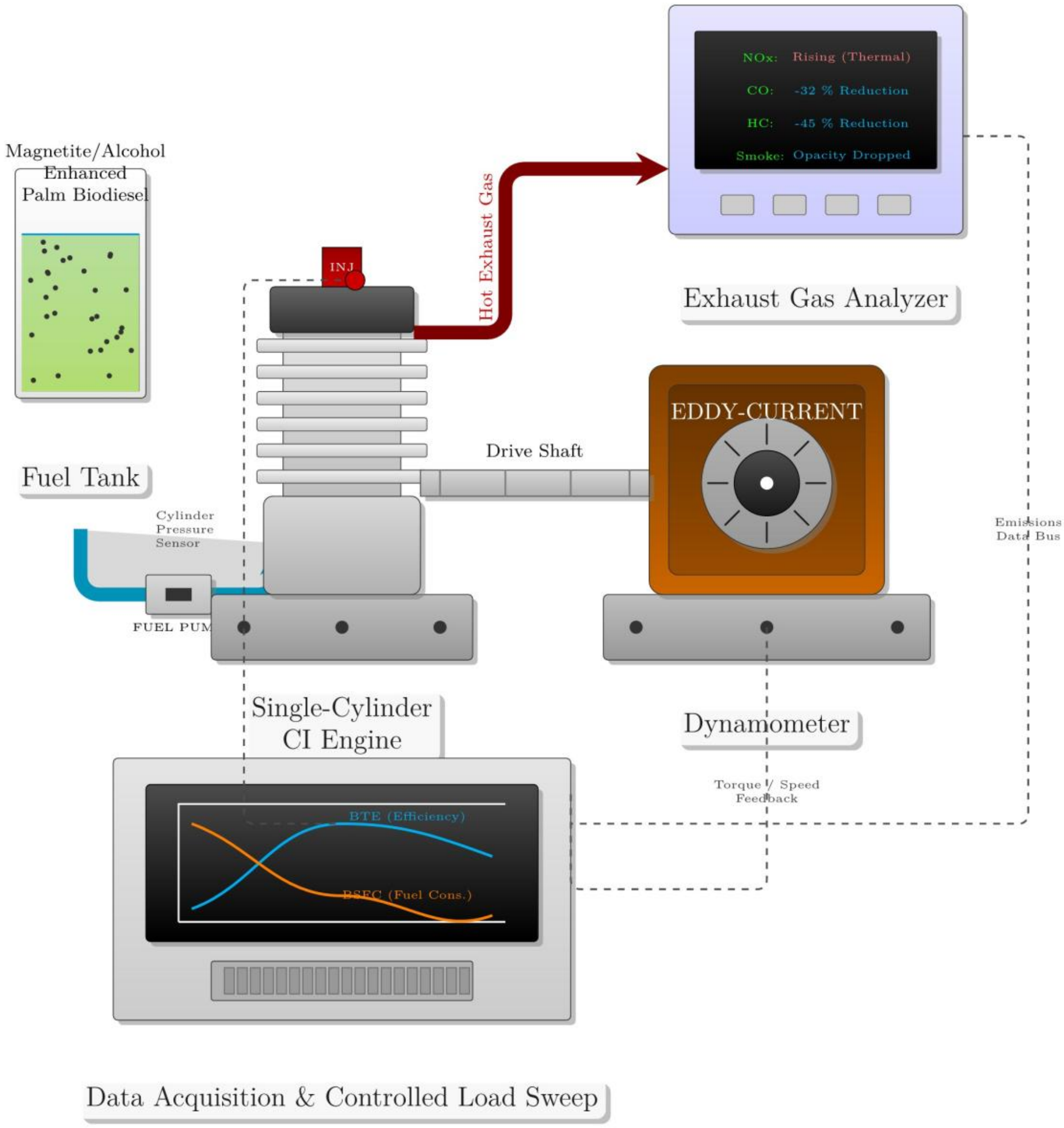

Figure 3. Ultrasonic dispersion and speed-measurement hardware used during preparation and testing of CuO-doped sunflower biodiesel blends.

The hardware image documents a common preparation-and-testing practice in the literature: ultrasonication for short-term dispersion stability followed by bench-scale speed monitoring during engine operation. Its relevance to the review lies in highlighting that additive performance claims depend strongly on how the suspension is prepared immediately before testing (Figure 3).

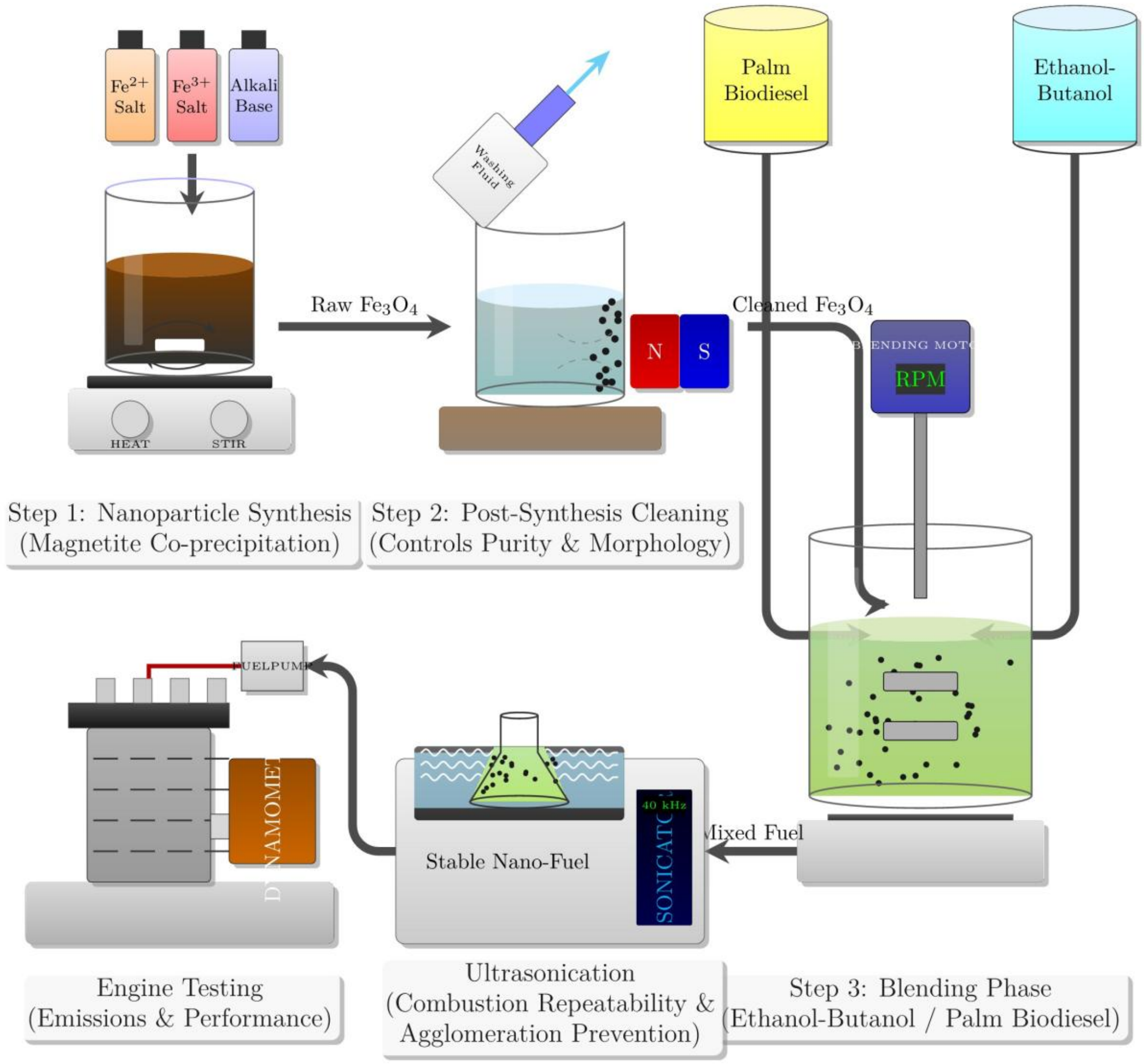

Figure 4. Two-step process flow used to synthesize and clean magnetite nanoparticles before blending with ethanol-butanol/palm biodiesel fuel [15]

The synthesis flowchart shows that several recent studies treat nanoparticle preparation as part of the fuel-design problem rather than as a purchased black-box additive. This matters because particle morphology, purity, and post-synthesis cleaning can alter agglomeration behavior and, in turn, combustion repeatability (Figure 4).

Figure 5. Engine-dynamometer-emissions test rig used for single-cylinder evaluation of hybrid magnetite/alcohol additives in palm biodiesel operation [15].

The representative test bed confirms the strong experimental standardization across the corpus: a single-cylinder engine, an eddy-current dynamometer, a gas analyzer, and a controlled load sweep. The figure 5 supports the review's conclusion that methodological comparability is high within laboratory studies but low relative to modern on-road diesel hardware.

Study selection was intentionally conservative. Records were retained when the title and abstract indicated direct relevance to biodiesel-diesel or biodiesel-centered blends containing nanoparticles and when engine performance, combustion, emissions, fuel properties, sustainability metrics, or optimization outcomes were explicitly discussed. No language-based exclusions were applied within the supplied dataset. Review articles were retained because they contributed field-level interpretation and helped contextualize the more recent experimental papers, but they were treated differently from primary experimental evidence during synthesis. Purely duplicate records were excluded. No additional records were inserted from external databases because the user request explicitly anchored the review to the collected papers, and the uploaded export already contained complete abstracts and DOI metadata for every entry. This decision preserved traceability between the review and the supplied corpus.

Each record was coded along five axes. The first axis was material classification, including Al_2O_3, CeO_2, TiO_2, ZnO, CuO, graphene-derived materials, carbon nanomaterials, iron-based or magnetite systems, and niche additives such as Ni2O3, MgO, and boron-based compounds. The second axis was methodological architecture: experimental only, experimental plus optimization or machine learning, experimental plus thermodynamic or sustainability analysis, review, and fuel synthesis or characterization. The third axis captured fuel-system context, including feedstock class, nominal biodiesel fraction when identifiable, and the presence of co-additives such as ethanol, butanol, diethyl ether, dimethyl carbonate, antioxidants, essential oils, EGR, hydrogen, biogas, dispersants, or electrostatic particulate control. The fourth axis captured engine application: single-cylinder CI, CRDI, multi-cylinder DI, low-heat-rejection engine, HCCI-DI hybrid, marine diesel, or dual-fuel/enriched combustion. The fifth axis captured response domains: performance, combustion, gaseous emissions, particulate or soot emissions, noise or vibration, fuel properties, and exergy or sustainability metrics. This coding framework allowed the literature to be reorganized by engineering logic rather than by publication chronology.

Quantitative findings reported changes in brake thermal efficiency, brake-specific fuel consumption, carbon monoxide, hydrocarbons, nitrogen oxides, smoke opacity, particulate matter, particle number, heat release rate, exergy efficiency, sustainability index, and related variables. Where a paper reported a best-performing blend or optimum dosage in the abstract, that value was retained for comparative tabulation. Where no explicit number was given, the study provided only directional evidence. This distinction is important because the present review is based on abstract-complete metadata rather than full texts. It therefore privileges robust comparison over false precision. The review does not fabricate missing operating conditions, particle-size distributions, or preparation procedures when those parameters were absent from the abstract. Instead, trends were inferred only when supported by repeated evidence and established combustion principles, and these interpretive steps are explicitly stated in the discussion.

Publication-year trends, material frequencies, methodology distributions, engine-platform distributions, response-domain coverage, co-additive architectures, and reported optimum-dosage windows were generated directly from the structured evidence map produced during coding. The qualitative trade-off matrix was constructed as an interpretive synthesis using the dominant direction of reported outcomes for each major nanoparticle family.

The review also incorporated a proportional weighting logic during interpretation, although not in the form of a formal meta-analysis. Three considerations shaped the weight assigned to a study in the narrative. First, papers with explicit quantitative outcomes received more comparative emphasis than papers reporting only generic improvement statements. Second, studies on modern or less common platforms such as CRDI, dual-fuel, EGR-integrated, low-heat-rejection, or marine engines were emphasized because they expand external validity relative to the overwhelmingly single-cylinder literature. Third, studies addressing particulate chemistry, exergy, exergoeconomics, sustainability, optimization, or machine learning were treated as strategically important because they broaden the field beyond basic emissions and efficiency testing [16]. Citation count was examined only as a descriptive indicator of visibility, not as a surrogate for experimental quality.

The principal limitation of this methodology is also its strength. Because every included record contained an abstract and DOI, the corpus supported broad, internally consistent comparative analysis; however, full-text-only variables such as exact sonication duration, surfactant chemistry, storage stability, uncertainty analysis, injector geometry, or post-test deposit inspection were not always accessible from the uploaded file. Consequently, the review is strongest in identifying robust directional trends, recurring operating windows, and structural gaps in the field. It is weaker when the literature is inconsistent or when essential methodological details are absent from abstracts. This limitation is acknowledged throughout the critical discussion and directly informs the research-gap and future-scope sections. Within those boundaries, the methodology provides a transparent and reproducible framework for converting a heterogeneous bibliographic corpus into a journal-ready systematic comparative review.

Table 1. Structural profile of the reviewed corpus.

Dimension	Observed structure in the corpus	Technical implication
Records included	74 unique studies (2017-2026)	Rapid publication acceleration after 2022 indicates a fast-moving but still consolidating field.
Methodology	50 experimental; 17 experimental+optimization/ML; 3 experimental+thermodynamic; 3 reviews; 1 fuel synthesis/characterization	Most evidence still comes from bench experiments; predictive and systems-level work is emerging but not yet dominant.
Engine platform	62 single-cylinder/standard CI; 2 CRDI; 5 dual-fuel/enriched; 2 LHR; 1 HCCI-DI; 1 marine; 1 multi-cylinder	The dominance of simplified single-cylinder rigs limits external validity.
Feedstock class	17 waste-derived; 17 non-edible/underutilized; 14 edible/agro-seed; 3 algal; 2 mixed; 21 unspecified biodiesel	Waste and non-edible pathways dominate, aligning the corpus with second-generation biodiesel logic.
Most studied nanoparticles	Al_2O_3 (22 mentions), TiO_2 (15), CeO_2 (12), graphene-based (8), carbon nanomaterials (8)	The field is concentrated around a small set of well-known catalytic or high-surface-area additives.
Response domains	63 gaseous-emission studies; 51 performance; 46 combustion; 30 particulate/soot; 20 fuel properties; 19 optimization/modeling; 6 exergy/sustainability; 4 noise/vibration	Gas-phase emissions and BTE/BSFC dominate, while durability and toxicity remain under-measured.

3. Classification of Literature

The first and clearest organizing principle in the literature is material type. Figure 6 shows that Al_2O_3, TiO_2, and CeO_2 dominate the field, with carbon nanomaterials and graphene-derived additives forming a strong second tier and CuO, ZnO, and iron-based systems representing smaller but still technically important clusters. Alumina holds the largest share because it is comparatively accessible, chemically stable, and consistently associated with higherombustion intensity and lower incomplete-combustion emissions in biodiesel blends [17]. TiO_2 appears nearly as frequently because it has been evaluated not only as a direct nano-additive but also in conjunction with alcohols, EGR, response-surface optimization, and recent machine-learning workflows [18]. CeO_2 is strongly represented because of its oxygen-buffering and catalytic oxidation role, especially in studies targeting soot and NOx trade-offs, particle-size effects, or CRDI particulate chemistry [19]. Carbonaceous additives can be divided into two distinct streams: graphenic materials, which are increasingly assessed for exergy, sustainability, and high-intensity combustion promotion, and CNT/MWCNT/quantum-dot systems, which are often framed as high-reactivity combustion enhancers but raise Harper concerns regarding dispersion stability, ash behavior, and materials handling [20]. CuO and ZnO studies are fewer in number but are distributed across green synthesis, response-surface optimization, and conventional engine testing, makinghem disproportionately informative for cost-sensitive application scenarios [21].

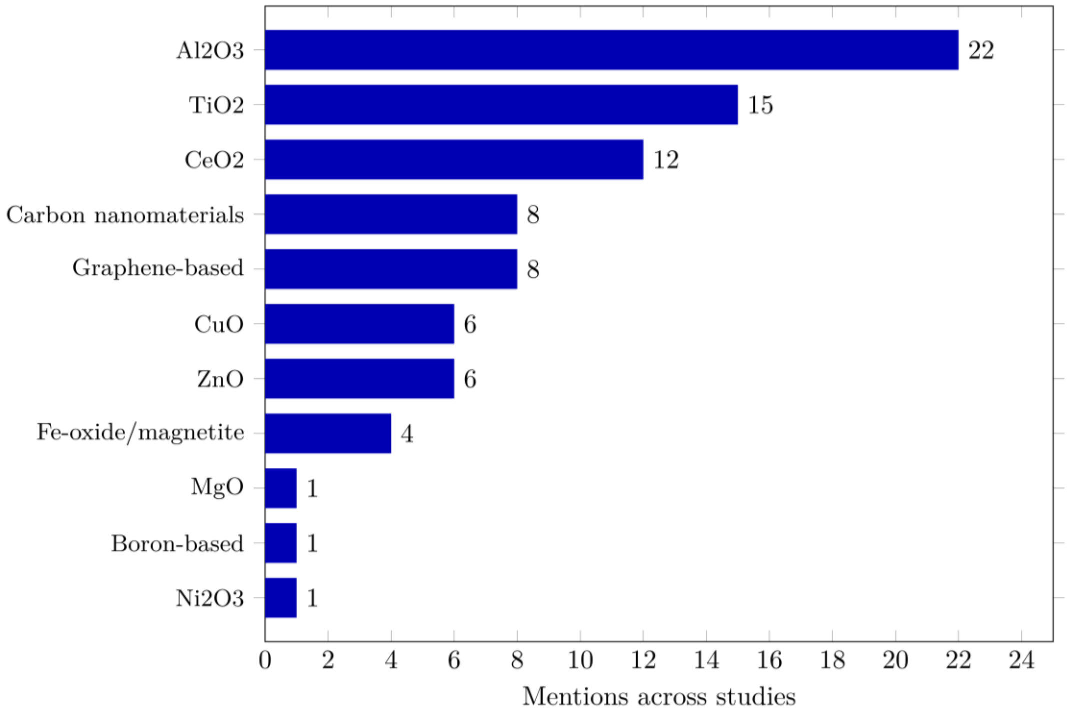

Figure 6. Frequency of nanoparticle families investigated.

Al_2O_3, TiO_2, and CeO_2 dominate the literature, whereas CuO, ZnO, iron-based systems, and carbonaceous additives form smaller but technically important clusters. The distribution confirms that the field favors low-cost metal oxides with established catalytic or oxygen-buffering behavior (Figure 6).

Material classification alone does not explain the field's structure, because the same nanoparticle family is deployed under very different methodological logics. Figure 10 shows that direct experiments still dominate the corpus, but a substantial secondary cluster combines experiments with optimization, machine learning, or multi-criteria decision analysis. This difference matters. The experimental-only papers typically test a fixed engine platform across load or speed sweeps and ask whether a given nano-fuel outperforms neat diesel or an additive-free biodiesel blend. Such studies are indispensable for identifying first-order effects, but they often search only a narrow portion of the parameter space [22]. Optimization-rich studies, in contrast, treat nano-fuel design as a response surface in which nanoparticle dosage, engine speed, compression ratio, injection pressure, or blend composition interact nonlinearly; consequently, they are better suited for locating operating windows and exposing performance-emissions trade-off[23]. A smaller but strategically significant subset couples engine data with exergy, exergoeconomic, or sustainability analysis, thereby shifting the evaluation criterion from local combustion improvement to system-level rationality [24]. Review papers, though few in number, confirm the same pattern: the field has already produced enough heterogeneous evidence that synthesis, rather than simple accumulation, is now the limiting step.

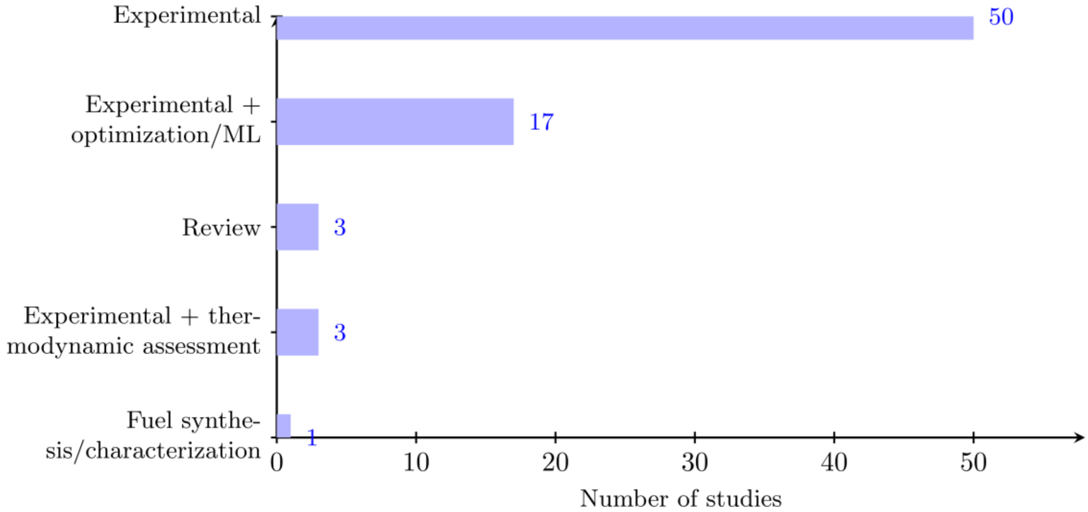

Figure 7. Methodological composition of the corpus.

Direct engine experiments remain the dominant approach, while optimization-assisted, review, and thermo-economic studies occupy a smaller share. The figure 7 confirms that empirical screening still outweighs statistically designed operating-window exploration.

The feedstock dimension introduces another important category. Figure 11 shows that waste-derived and non-edible feedstocks together comprise a large share of the corpus, reflecting the field's movement away from first-generation edible oils. Waste cooking oil is particularly common because it offers both environmental motivation and a practical route to lower-cost biodiesel, and it has been paired with CeO_2, TiO_2, MWCNT, graphene derivatives, Fe-doped oxides, and mixed-additive systems [25]. Non-edible or underutilized feedstocks such as jatropha, neem, mahua, Bombax ceiba, Prosopis juliflora, Ceiba pentandra, calophyllum, Bauhinia malabarica, water hyacinth, litchi, croton, and parsley are similarly well represented, largely because they align with the sustainability logic of biodiesel without direct food-fuel conflict [26]. Edible or agro-seed systems such as soybean, palm, sesame, cottonseed, pumpkin seed, jute, and canola remain visible, often because they provide baseline fuels with known transesterification behavior or regionally available test materials [27]. Algal pathways and mixed-feedstock biodiesels remain a minority, but their presence is scientifically important because they extend the nano-additive question beyond conventional methyl ester families into fuels with distinct molecular distributions and potentially different combustion kinetics [28].

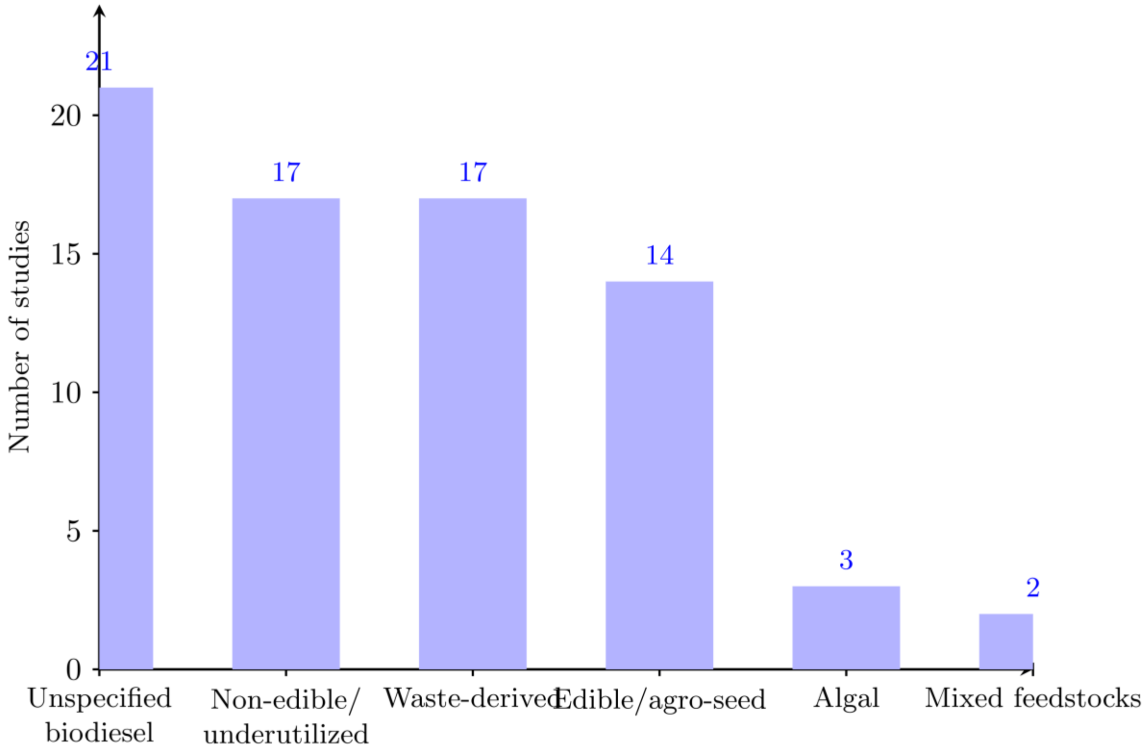

Figure 8. Biodiesel feedstock classes represented in the corpus.

Waste cooking oil and non-edible feedstocks account for most studies, indicating that the field is driven more by sustainability and waste valorization logic than by edible-oil benchmarking (Figure 8). The emphasis on parameters can also classify the literature. Figure 9 shows clear that gaseous emissions and gross performance indices remain the dominant response domains, followed by combustion metrics. This hierarchy reveals a field still anchored in classic diesel test-bench observables: BTE, BSFC, CO, HC, NOx, smoke opacity, cylinder pressure, and heat release rate. The dominance of these metrics is rational because they provide a quick first-order picture of whether the additive recovers the efficiency penalty of biodiesel and whether the combustion process becomes cleaner or dirtier [29]. Yet the distribution also reveals what is underdeveloped. Particulate and particle-number studies remain comparatively rare despite the direct relevance of nanoparticle addition to soot oxidation, ash chemistry, and health risk. Only a few studies moved beyond opacity to particle-size distributions, PM2.5 composition, or soot nanostructure. These papers often changed the interpretation of additive effectiveness by showing that apparently “cleaner” combustion at the gas-analyzer level can still shift the particulate spectrum in complex ways [30] Noise, vibration, and knock received even less attention. However, the small number of available papers suggests that altered premixed combustion can modify both the pressure-rise rate and the acoustic response [31]. Fuel-property and stability studies also remain secondary, even though they govern whether any combustion benefit is practically deployable.

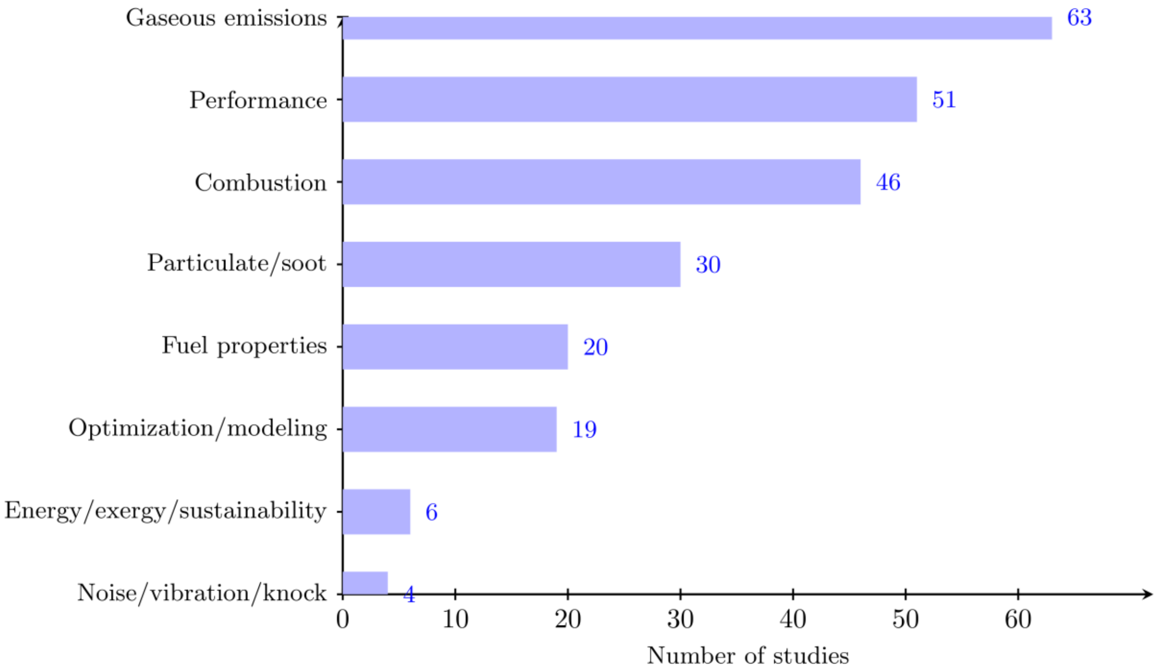

Figure 9. Outcome domains evaluated across the corpus.

Performance and gaseous-emission metrics dominate the evidence base, whereas particulate chemistry, durability, and stability measurements remain comparatively sparse. This imbalance explains why apparent combustion benefits often exceed the practical certainty of deployment. Application category is another decisive organizational line. Figure 10 shows an overwhelming reliance on standard single-cylinder CI platforms, making the corpus internally comparable but externally narrow. These engines are useful for isolating combustion behavior, yet they do not fully represent modern common-rail injection, closed-loop emissions control, multiple injection events, or commercial durability constraints. The relatively small CRDI subset is therefore disproportionately important. The CeO_2 and TiO_2 CRDI studies in the corpus connect nanoparticle use to particle number, PM2.5 species, and EGR-mediated soot-NOx trade-offs, moving the field closer to contemporary diesel-relevant questions [32]). Dual-fuel and enrichment studies constitute another specialized category. Here, the additive not only corrects biodiesel properties but also interacts with hydrogen or biogas to reshape ignition, diffusion, and burn rate, as well asmission chemistry [33]. Low-heat-rejection and HCCI-DI studies occupy a further niche in which nanoparticle effects are inseparable from altered wall temperature, premixed charge fraction, and combustion phasing [34] Marine and multi-cylinder engines appear only sporadically, yet they are essential because they test whether the nano-fuel concept survives beyond academic single-cylinder benches [35]

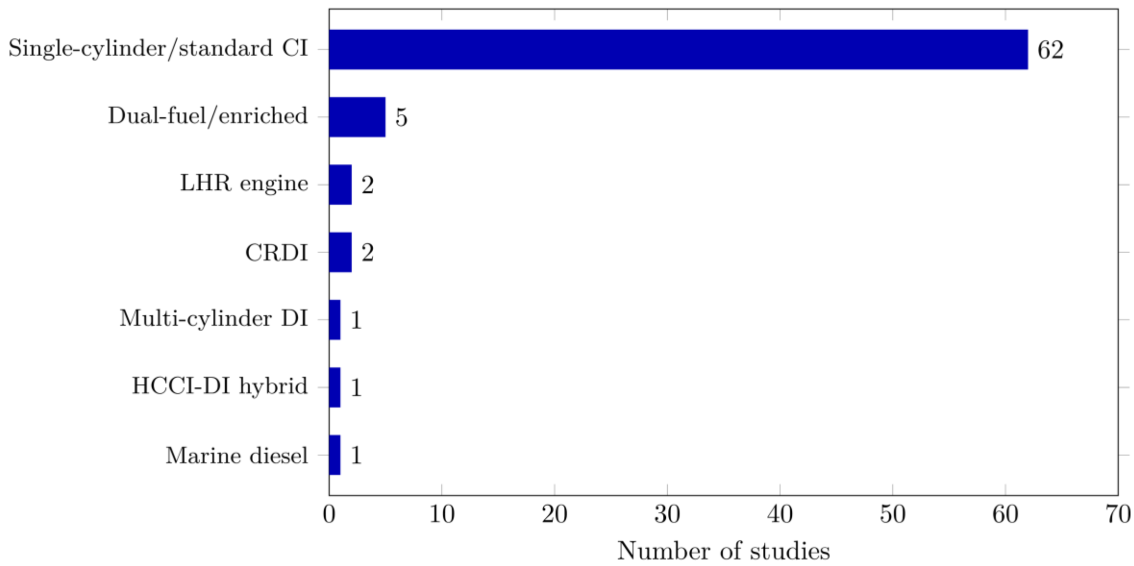

Figure 10. Engine configurations and application platforms.

Single-cylinder naturally aspirated CI engines overwhelmingly dominate the literature. The platform concentration improves internal comparability but limits transferability to CRDI, multi-cylinder, marine, and dual-fuel systems. Finally, a meaningful classification emerges around blend architecture itself. Figure 11 shows that although many studies evaluate “nanoparticle only” systems, a large secondary stream uses oxygenated or control-oriented co-additives. Alcohols such as ethanol, butanol, dimethyl carbonate, and diethyl ether are widely used because they modify viscosity, oxygen content, and volatility in ways that can complement or conflict with nanoparticle effects [36] Antioxidants and essential oils form a smaller cluster aimed primarily at NOx moderation or stability enhancement [37].EGR, hydrogen, biogas, cetane improvers, dispersants, and electrostatic precipitators define a third class in which nanoparticles are embedded within a larger combustion-control or aftertreatment strategy rather than treated as the sole intervention [38].This classification is important because it reveals that the field is no longer merely additive-centric. It is increasingly system-centric, which is precisely why comparative analysis must attend to interaction effects rather than to isolated material identities. In that sense, the literature now spans from single-variable material screening to coupled fuel-engine-system design, even though the latter remains the minority approach.

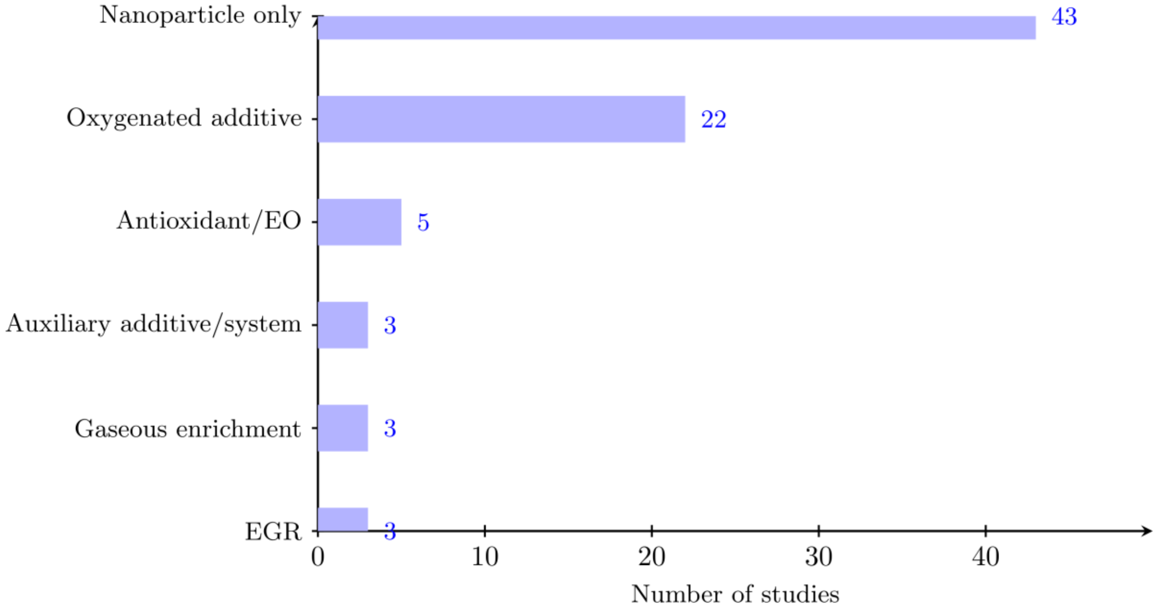

Figure 11. Co-additive and auxiliary strategies used with nanoparticles.

Most studies still test nanoparticles as stand-alone additives, but a substantial minority combines them with oxygenated fuels, antioxidants, EGR, or gaseous enrichment. Figure 11 shows a transition from single-variable additive screening to coupled fuel-system design.

4. Comparative Analysis

The aggregate comparison across the corpus shows a clear asymmetry between performance and emissions responses. Table 1 summarizes the database structure and shows that most studies evaluated performance, combustion, and gaseous emissions simultaneously, whereas particulate chemistry, exergy, and noise were assessed in only limited subsets. That asymmetry influences the strength of conclusions. The evidence supporting gains in brake thermal efficiency and decreases in specific fuel consumption is broad and consistent, particularly for low-dose oxide nanoparticles dispersed in B20-B30 base fuels. Multiple studies on Al_2O_3, CeO_2, TiO_2, ZnO, CuO, GO, and CNT-class additives reported that these additives partially or fully recovered the efficiency losses introduced by biodiesel blending, usually through increased oxidation intensity, higher cylinder pressure, or shorter combustion duration relative to the additive-free biodiesel blend [39].

Table 2. Representative comparative evidence from studies reporting explicit quantitative outcomes (part I).

Nanoparticle family	Representative fuel-platform context	Best-reported dosage	Key gains	Qualification or penalty	Reference
CeO_2	WCO B20, single-cylinder CI	80 ppm, 30 nm	BSFC -2.5%; NOx -15.7%;	Particle size, not just chemistry,	[40]

			smoke -34.7% vs additive-free B20	controlled the benefit	
CeO_2	B15 in CRDI engine	20 ppm	CO -32.16%; HC -45.59%; NOx +5.97%; particle size shifted to ~10-37 nm	Gas-phase gains coexisted with a NOx penalty and changed particle spectrum	[41]
TiO_2	Bombax ceiba biodiesel + n-butanol blend	60 ppm	CO -22.91%; UHC -12%; optimum performance at 60 ppm	A narrow optimum window was reported	[42]
TiO_2 + EGR	Castor biodiesel C20D in CRDI context	25-40 ppm TiO_2 + 30% EGR	BTE +2.8%; BSFC -6.5%; NOx -17.34 to -21.83% with EGR	NOx reduction required EGR; EGR increased PM relative to TiO_2 case without EGR	[43]
Al_2O_3	Bauhinia malabarica biodiesel-diesel blend	~100 ppm class	BTE +5.2%; BSFC -4.2%; HC -13.7%; CO -14.9%; NOx -5.8%; smoke -15.5%	PM increased 47.2% without electrostatic capture	[44]
ZnO	Waste-cooking-oil biodiesel blends	50 ppm	Torque +4.9% and BSFC -6.44% for B20ZnO at 2300 rpm	Combustion improved, but full emissions set was not equally resolved	[45]

Table 2 compares representative studies with explicit quantitative outcomes and illustrates that the strongest consensus concerns incomplete-combustion products rather than NOx. Nanoceria provides a useful example. In a waste-cooking-oil B20 system, Dinesha et al. (2021) showed that 30 nm CeO_2 at 80 ppm reduced BSFC by 2.5%, NOx by 15.7%, and smoke opacity by 34.7% relative to additive-free B20, demonstrating the importance of particle size as well as additive chemistry. In a CRDI engine, Yusuf et al. (2022) reported that 20 ppm CeO_2 in a B15 blend reduced CO by 32.16% and HC by 45.59%, while simultaneously shifting particle diameters to approximately 10-37 nm; however, NOx still increased by 5.97%. Recent CeO_2-based optimization studies reinforce the same pattern. Kumar and Choudhary (2023) showed that a B30 blend containing diphenylamine and 50 ppm CeO_2 improved performance and emission ranking under multi-criteria optimization, while Shaisundaram et al. (2025) identified an optimum CeO_2 window near 48.55 ppm for pumpkin-seed biodiesel blends. Taken together, CeO_2 appears particularly effective for CO, HC, smoke, and particle control, but it does not guarantee NOx suppression unless paired with additional calibration or co-additive strategies.

TiO_2 studies exhibit a similar, but more calibration-sensitive, behavior. Sandhi et al. (2021) reported that a Bombax ceiba biodiesel-diesel-n-butanol blend containing 60 ppm TiO_2 reduced CO by 22.91% and UHC by 12%, identifying 60 ppm as the best-performing dosage in that dataset. Razzaq et al. (2023) later showed that in waste-cooking-oil B30 systems, increasing TiO_2 concentration to 120 ppm and engine speed to 2150 rpm lowered BSFC and increased BTE, but NOx increased slightly as both speed and concentration increased. Fayad et al. (2023) added a crucial comparative dimension by integrating TiO_2 with 30% EGR in a CRDI context. Without EGR, TiO_2 increased BTE by 2.8% and reduced BSFC by 6.5% relative to neat C20D, while maintaining NOx near diesel levels. With high EGR, NOx fell by 17.34-21.83%, but PM concentrations rose relative to the non-EGR TiO_2 case, even though soot nanoparticles became smaller at the higher 40 ppm TiO_2 level. These results establish that TiO_2 is highly effective in tuning the NOx-particulate compromise, but only within a wider combustion-control strategy rather than as a universal standalone solution.

Table 2 (continued). Comparative evidence from studies reporting explicit quantitative outcomes (part II).

Nanoparticle family	Representative fuel-platform context	Best-reported dosage	Key gains	Qualification or penalty	Reference
CuO	Parsley B20 blend	50 ppm	BTE increased from 32.5% to 33.0%; BSFC -3.28%; CO -5.7%; HC -1.6%; NOx -4.7%	Green-synthesized CuO remained effective at low dosage	[46]
Graphene oxide	D85B15 blend	100 ppm	Exergy efficiency 25.82% to 27.05%; sustainability index 1.348 to 1.371	Higher GO loading worsened exergy and cost metrics	[47]
RGO	WCOME B20 blend	80 ppm	BTE +11.67%; smoke -14.63%;	NOx increased by 2.5%	[48]

			HC -21.42%; CO -16.67%		
MWCNT	WCO biodiesel + ethanol ternary blend	30 ppm	NOx -35%; CO -37%; HC -39%	Benefits were strong but depend critically on dispersion quality	[49]
Fe-doped ceria	WCO B30 blend	Low-dose $FeCeO_2$	Lower BSFC; higher BTE at low-medium load; NOx -15.7%; CO -24.6%	Benefits were load-dependent	[50]

Al_2O_3 remains the most heavily studied material family and also one of the most versatile. Ghanbari et al. (2021) showed in a six-cylinder engine that alumina-enhanced diesel-biodiesel blends could be optimized with response surface methodology, indicating that nanoparticle effectiveness persists beyond single-cylinder laboratory rigs [51]. Kaushik et al. (2022) reported that alumina improved both performance and emissions in neem-biodiesel blends, with stronger benefits at higher compression ratios [52]. Vellaiyan (2025) quantified the effect more explicitly: Al_2O_3 increased BTE by 5.2% and reduced BSFC, HC, CO, NOx, and smoke by 4.2%, 13.7%, 14.9%, 5.8%, and 15.5%, respectively, in Bauhinia malabarica biodiesel-diesel blends. Yet the same study also identified a major trade-off, showing a 47.2% increase in PM when the nanoparticle-enriched blend was used without electrostatic particulate capture; the electrostatic precipitator then reduced PM by 54.2%. That single result is methodologically important because it reminds the field that a gas-analyzer improvement does not automatically imply a benign particulate outcome. Recent Al_2O_3 studies in water-hyacinth, cottonseed, Ceiba pentandra, and low-heat-rejection contexts generally confirm the family's usefulness, but they also indicate that the strongest gains often occur when alumina is paired with another intervention such as antioxidants, hydrogen, cetane improvers, or altered wall-temperature conditions [53].

The comparative performance of ZnO and CuO is less extensive in the literature, but it remains technically persuasive. El-Adawy (2023) showed that 50 ppm ZnO improved torque by 4.9% and reduced BSFC by 6.44% in a B20 blend at 2300 rpm while simultaneously increasing heat-release rate and in-cylinder pressure. Kavalli et al. (2022) identified a green-synthesized ZnO dosage of 30 mg as optimal for a discarded cooking oil blend and demonstrated that the green route did not compromise the additive's effectiveness. In a recent calophyllum biodiesel/diesel/propanol system, Srinivasarao et al. (2025) [54] extended ZnO research into machine-learning-supported modeling. CuO shows comparable promise. Bitire and Jen (2022) found that a 50 ppm parsley-biodiesel CuO blend raised BTE from 32.5% to 33.0%, lowered BSFC by 3.28%, and reduced CO, HC, and NOx by 5.7%, 1.6%, and 4.7%, respectively [55]. Rastogi et al. (2023) used response surface methodology to optimize a jojoba-biodiesel/CuO system and reported target outputs of 27.18% BTE, 0.1981 vol% CO, 24.572 ppm HC, and 710.947 ppm Nox [56]. Raj et al. (2025) and Akroot et al. (2024) further showed that

CuO remains effective in ternary and concentration-varying systems. Table 3 therefore places CuO and ZnO in the “high-potential but under-sampled” class: they repeatedly improve performance and lower incomplete-combustion emissions [57], but the evidence base is still too small to rank them above the larger Al_2O_3-TiO_2-CeO_2 triad.

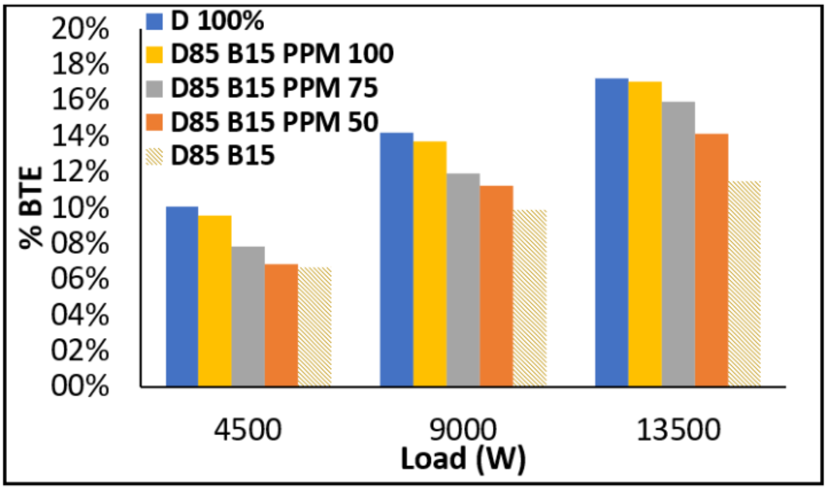

Figure 12. Brake thermal efficiency response of a D85B15 sunflower biodiesel blend as CuO dosage increases at 1600 rpm [57].

The CuO-series figure illustrates a recurring comparative pattern: biodiesel alone depresses BTE, but controlled nanoparticle dosing partially restores it. The monotonic rise toward diesel-like efficiency at higher CuO concentration supports the broader corpus-level conclusion that CuO is effective mainly within a narrow low-ppm dosage window (Figure 12).

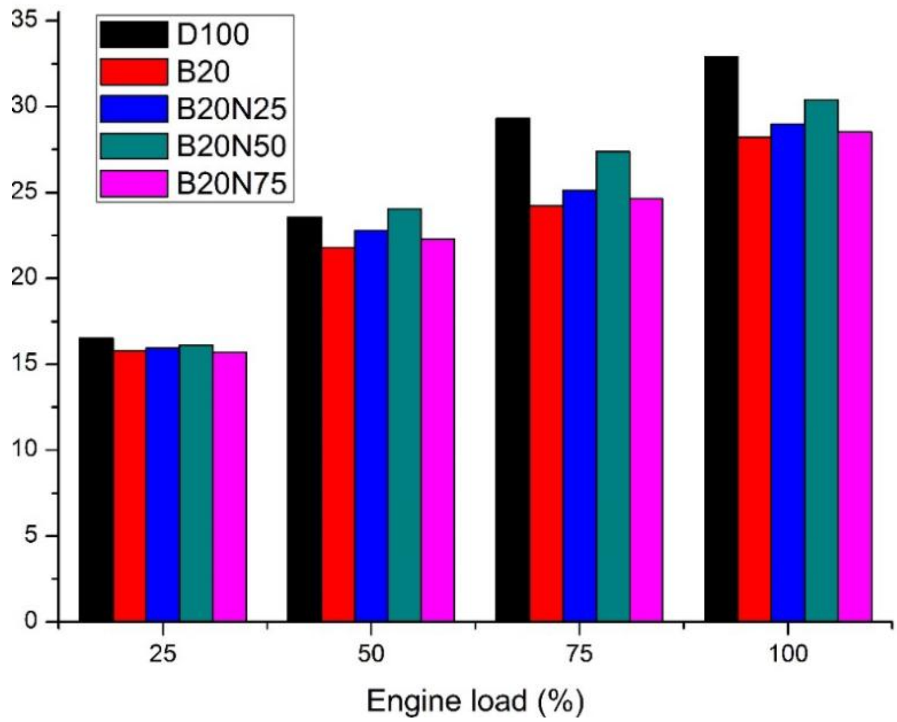

Figure 13. Brake thermal efficiency variation with engine load for diesel, B20, and CuO-doped B20 blends in a single-cylinder diesel engine [32] This load-sweep plot shows that BTE gains from CuO addition become more visible as engine load rises, which is consistent with catalytic enhancement becoming more relevant when in-cylinder temperature and oxidation demand increase. It reinforces the review's argument that reported benefits are highly condition-dependent rather than universal.

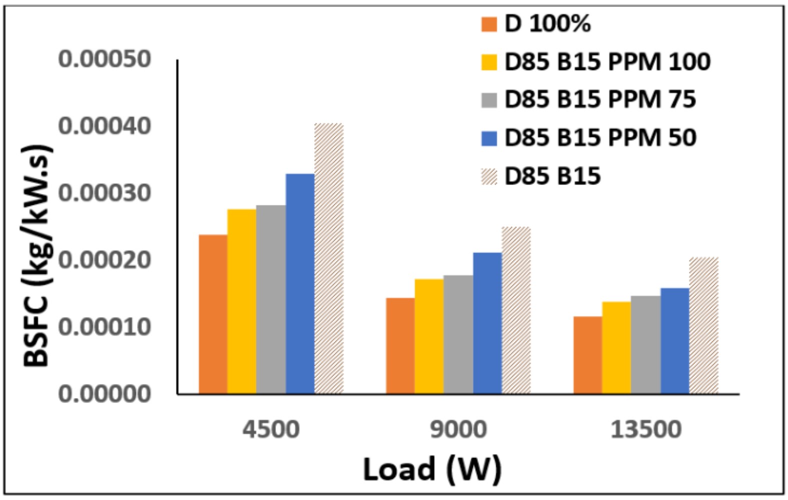

Figure 14. Brake-specific fuel consumption response of CuO-dosed D85B15 sunflower biodiesel blend at 1600 rpm [56].

The BSFC trend complements Figure 12 by showing that efficiency recovery is accompanied by lower fuel demand at equivalent output, especially at the upper dosage range examined. The figure therefore captures the central performance mechanism reported for CuO systems: better atomization and oxidation offset the lower heating value of biodiesel blends.

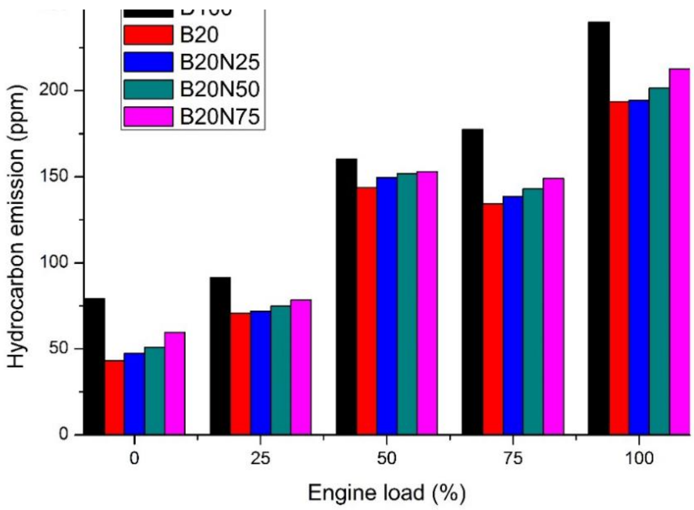

Figure 15. Hydrocarbon emission response versus engine load for diesel, B20, and CuO-doped B20 palm biodiesel blends [31].

The HC plot (Figure 15)shows the most reproducible emissions benefit reported across the nanoparticle literature: incomplete combustion products decrease as catalytic oxygen transfer and improved spray breakup promote more complete oxidation. The separation between B20 and CuO-doped B20 increases with increasing load, again emphasizing operating-point sensitivity.

Table 3. Material-family comparison of recurring strengths, operating windows, and uncertainties.

Family	Recurring strengths	Typical optimum window	Main uncertainty	References
Al_2O_3	Broadest evidence base; robust BTE/BSFC recovery; compatible with antioxidants, hydrogen, LHR, and ESP-integrated systems	Mostly 50-100 ppm	Particulate behavior and deposit risk insufficiently resolved	Kandasamy and Jabaraj (2017); Ghanbari et al. (2021); Vellaiyan (2025); Gift et al. (2026)
CeO_2	Strong soot/CO/HC control; oxygen-buffering and catalytic oxidation advantages; clear particle-size sensitivity	Mostly 20-80 ppm	NOx remains context-dependent, especially in hotter CRDI operation	Hawi et al. (2019); Dinesha et al. (2021); Yusuf et al. (2022); Shaisundaram et al. (2025)
TiO_2	Effective combustion promoter; strong synergy with oxygenates, RSM optimization, and EGR-based NOx control	Mostly 40-60 ppm, extending to 120 ppm	Performance gains can be accompanied by NOx rise unless calibration is adjusted	Sandhi et al. (2021); Razzaq et al. (2023); Fayad et al. (2023); Janaki et al. (2026)
ZnO/CuO	Low-dose, cost-sensitive alternatives with repeatable performance and emission gains	Mostly 30-80 ppm	Evidence base smaller; ranking against major oxides remains uncertain	Kavalli et al. (2022); Bitire and Jen (2022); El-Adawy (2023); Rastogi et al. (2023)
Graphene-based	High upside for exergy and combustion intensity; good PM/HC/CO control in several studies	Mostly 80-100 ppm	Higher doses can degrade sustainability or raise NOx; dispersion demands are stricter	Uysal et al. (2022); Belludi et al. (2024); Megiso et al. (2025)

CNT/MWCNT/CQD	Large reductions in incomplete-combustion emissions are possible at very low dose	Mostly 20-30 ppm	Particle-number behavior, storage stability, and hardware interactions remain weakly characterized	Wu et al. (2018); Sonachalam et al. (2024); Özgören et al. (2025)

Graphene-derived and other carbonaceous additives form the most interesting comparative contrast to metal oxides. Unlike conventional oxides, these materials are frequently discussed not only in terms of BTE and emissions but also in terms of exergy, sustainability, and advanced surface chemistry. Uysal et al. (2022) reported that adding 100 ppm graphene oxide to D85B15 increased exergy efficiency from 25.82% to 27.05% and improved the sustainability index from 1.348 to 1.371, whereas higher GO loadings degraded both performance and cost metrics. Belludi et al. (2024) found that RGO80 raised BTE by 11.67% and reduced smoke opacity, HC, and CO by 14.63%, 21.42%, and 16.67%, respectively, but NOx rose by 2.5%. Megiso et al. (2025) reported even broader gains in marine microalgae biodiesel systems, with GO reducing CO by 12-18%, HC by 14%, PM by 15-18%, and NOx by 6-8%, all statistically significant. The carbon-nanomaterial branch shows equally strong but less predictable behavior. Sonachalam et al. (2024) identified a B20+E10+30 ppm MWCNT blend as optimal and reported reductions of 35% in NOx, 37% in CO, and 39% in HC, whereas Wu et al. (2018) had earlier shown that carbon-coated aluminum nanoparticles could increase particle number even when some performance and gaseous-emission responses improved. The comparison suggests that carbonaceous materials can be exceptionally effective but are more sensitive to dispersion protocol and particulate interpretation than the best-studied oxides.

Fe-based and hybrid additive systems sit at the boundary between conventional nano-fuel studies and broader combustion-system engineering. Hawi et al. (2019) showed that Fe-doped ceria improved BTE and lowered BSFC in waste-cooking-oil B30 blends while reducing NOx by up to 15.7% and CO by up to 24.6%. Sule et al. (2023) found that magnetite combined with n-butanol reduced CO, HC, and smoke emissions, but NOx remained problematic. Almanzalawy et al. (2024) reported that ferric oxide and alcohols improved thermal efficiency, peak pressure, and heat release while decreasing CO and smoke, yet NOx increased. These data make Fe-based systems a useful diagnostic category. They show particularly clearly that performance benefits and lower incomplete-combustion emissions do not necessarily align with lower NOx, because higher oxidation intensity can shift the engine toward a hotter, cleaner burn.

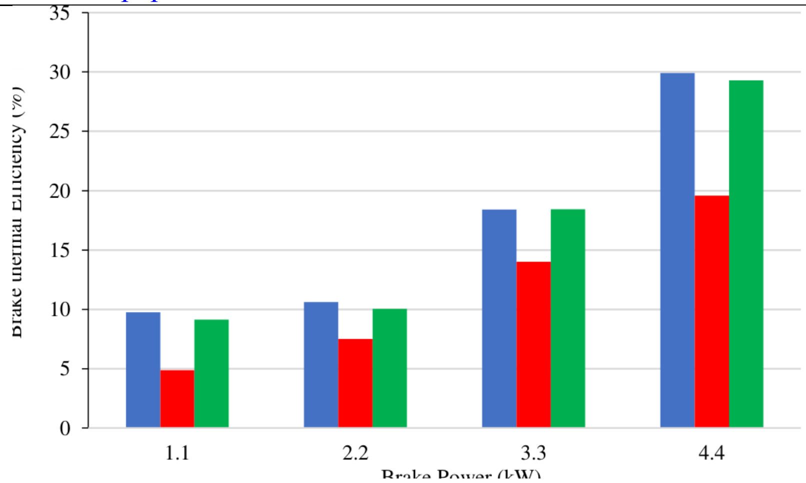

Figure 16. Brake thermal efficiency as a function of brake power for palm biodiesel with magnetite-ethanol-butanol hybrid additive relative to diesel and neat B100 [15].

The hybrid-additive case shows that nanoparticles do not operate independently of co-additives. Here, the combination of ethanol and butanol brings BTE closer to diesel while outperforming neat B100, illustrating why several recent studies have shifted from single-additive screening to a synergistic blend architecture (Figure 16).

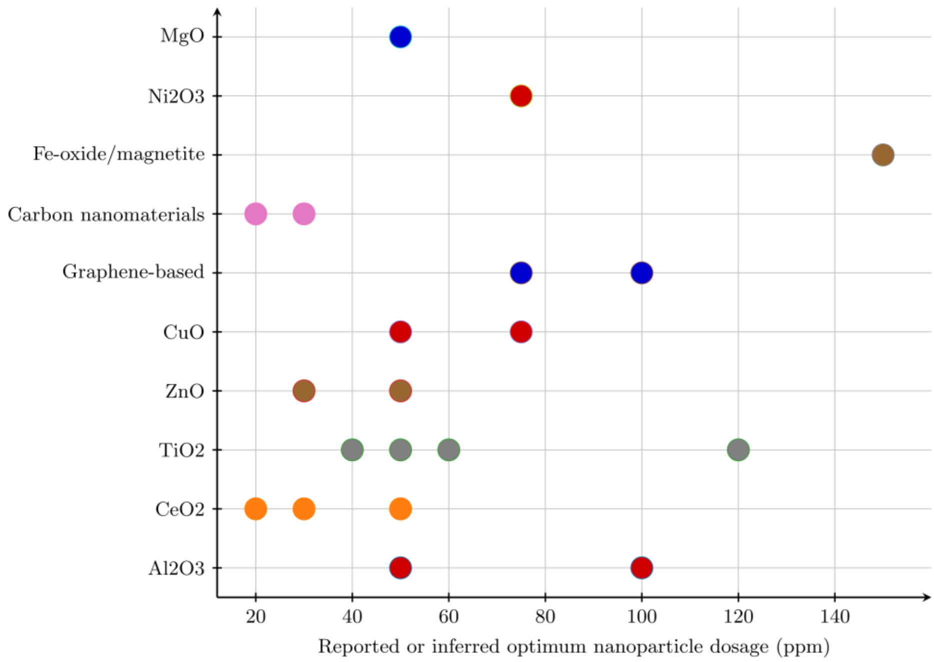

Figure 17. Reported optimum dosage windows across nanoparticle families.

Across all material classes, dosage behaves as a unifying comparative variable. Figure 17 shows that reported optimum values cluster strongly between 20 and 100 ppm for most oxide and carbon additives, although exceptions exist. CeO_2 often performs best between 20 and 80 ppm depending on particle size and engine platform; TiO_2 commonly clusters around 40-60 ppm but can extend to 120 ppm in high-speed optimization studies; ZnO and CuO often sit around 30-80 ppm; graphene-based systems show optimum values around 80-100 ppm; and MWCNT/CNT systems often favor about 20-30 ppm . Table 4 summarizes these operational windows together with the principal penalties reported beyond the optimum region. The comparative message is direct: nanoparticles behave as catalytic triggers, not as bulk replacement components. Once dosage rises beyond the stable colloidal and combustion-optimum window, agglomeration, altered spray behavior, deposit risk, or adverse NOx shifts can erode the very benefits that motivated their use.

The best-performing dosage window clusters mainly between 20 and 100 ppm for most nanoparticle families. This concentration range supports the interpretation that nanoparticles act as catalytic triggers or dispersion modifiers rather than bulk energy contributors (Figure 17).

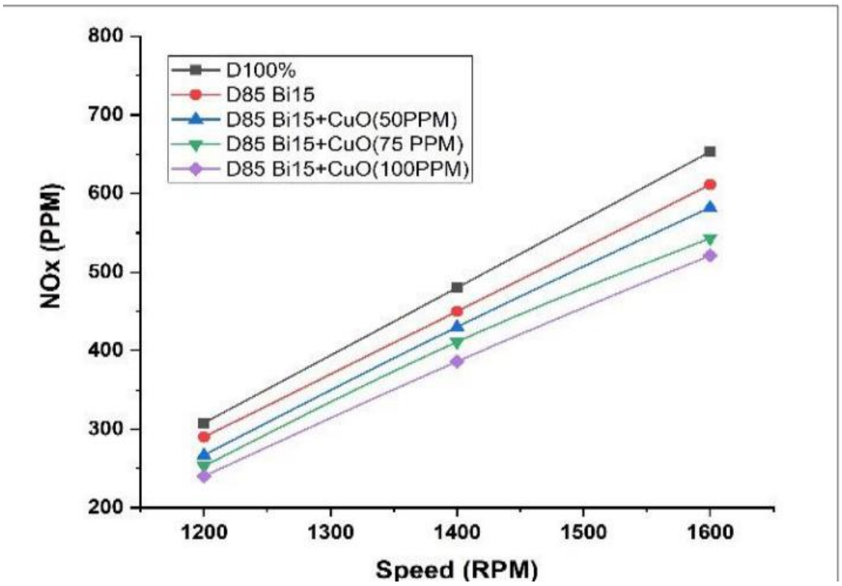

Figure 18. Nitrogen oxide emission trend versus engine speed at fixed 13.5 kW load for CuO-treated sunflower biodiesel blend and diesel reference fuels [57].

The NOx plot illustrates why the literature remains contradictory on oxides: even when CuO improves efficiency and lowers CO/HC, NOx still rises with engine speed because thermal pathways intensify. The figure supports the review's position that nanoparticle success should be judged by multi-objective balance rather than by single-metric improvement (Figure 18).

5. Critical Discussion

The comparative results indicate that the field's strongest mechanistic claim is not simply that nanoparticles "improve combustion," but that they redistribute combustion in ways that can either help or hurt depending on where the base biodiesel already sits on the reactivity-oxygen-temperature landscape. Biodiesel itself is not an inert background fluid; it already contains built-in oxygen, different unsaturation chemistry, and altered spray properties relative to petro-diesel. Adding a redox-active oxide, such as CeO2 or CuO, to a biodiesel-rich blend therefore does more than simply raise thermal conductivity. It changes oxidation timing, local radical availability, and the balance between premixed and diffusion burning [58]. This explains why many studies report simultaneous reductions in CO, HC, and smoke together with higher cylinder pressure or heat release rate, because the additive is accelerating oxidation in zones that otherwise remain partially burned [59]). It also explains why the best additives are generally effective at low dosage. The objective is catalytic leverage, not brute-force energy substitution.

The same mechanistic framework clarifies the persistent NOx contradiction. When nanoparticles improve atomization, shorten ignition delay, or intensify premixed burning, they often raise local flame temperature and oxygen availability at precisely the time scale that favors thermal NOx formation. This is why a study can report lower CO, HC, and smoke levels alongside higher NOx, especially when the engine calibration remainsnchanged [60].NOx falls only when a compensating mechanism becomes dominant, such as lower overall fuel consumption, oxygen buffering by ceria, dilution from EGR, moderated pressure rise, or altered combustion phasing through a co-additive or hardware intervention [61]. The field should therefore stop presenting NOx reduction as a general property of nanoparticles. It is a conditional outcome. A more precise formulation is that nanoparticles expand the available calibration space for managing the NOx-soot-efficiency compromise, but they do not eliminate the compromise itself.

Particle size and dosage reinforce that conclusion. Dinesha et al. (2021) clearly showed that 30 nm CeO2 outperformed both smaller and larger particles, indicating that a competition between reactivity gain and transport penalty governs nanoparticle behavior. Particles that are too small can intensify reactivity but also destabilize the dispersion or interact differently with the liquid fuel matrix; particles that are too large sacrifice surface-area-driven benefits. The same logic appears in dosage studies, where most families converge toward optima below about 100 ppm. Graphene oxide illustrates the point particularly well: Uysal et al. (2022) found that 100 ppm improved exergy efficiency, while higher concentrations degraded exergy and sustainability performance. Similar non-monotonic behavior appears in TiO_2, CuO, and magnetite systems, where the best condition is rarely the highest concentration tested [62]). This means that nanoparticle-enhanced biodiesel is fundamentally an optimization problem with sharp local maxima, not a linear materials-addition problem. Studies that test only one dosage therefore contribute weakly to engineering design.

Dispersion stability is the least standardized and perhaps most underappreciated variable in the entire field. Many abstracts state that ultrasonication was used, but few report zeta potential, sedimentation time, re-agglomeration after storage, injector-line residence effects, or whether the tested fuel was re-sonicated immediately before each engine run. Yet these details determine whether the nominal nanoparticle concentration is the actual concentration entering the injector. The risk is highest for graphene derivatives, CNT-class materials, and higher-load oxide systems, where surface chemistry, aspect ratio, and van der Waals attraction can quickly destroy colloidal uniformity [63] A literature that claims ppm-level optimization but does not consistently characterize stability is vulnerable to false precision. Two fuels labeled “50 ppm TiO_2” are not equivalent if one remains dispersed for hours and the other sediments during the test sequence. This is a methodological weakness, not a minor reporting omission.

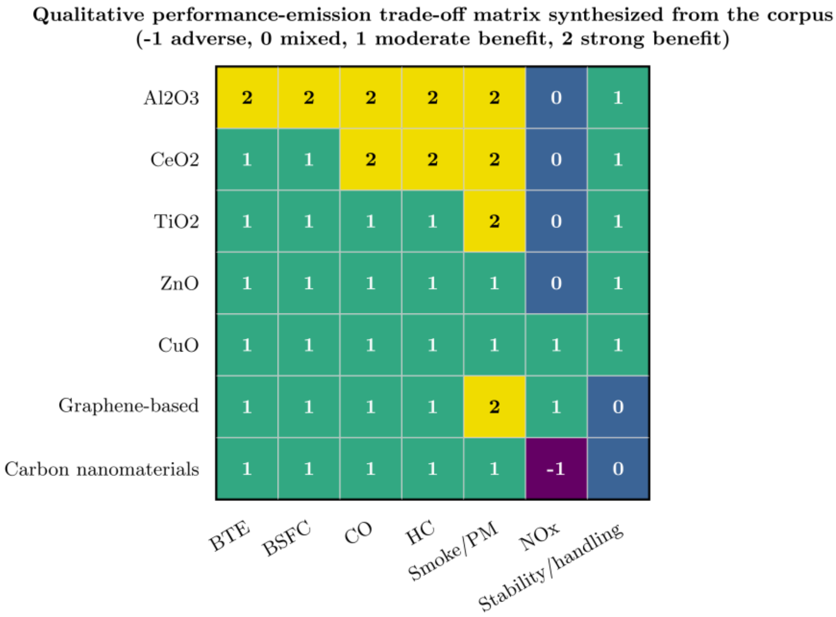

Figure 19. Qualitative performance-emission trade-off matrix synthesized from the corpus. Score definition: -1 adverse, 0 mixed, 1 moderate benefit, 2 strong benefit.

The matrix shows that most additives improve CO, HC, and smoke more consistently than NOx. CeO_2, TiO_2, and selected CuO systems offer the most balanced profiles, whereas carbonaceous additives exhibit stronger sensitivity to dispersion quality and dosage control (Figure 19).

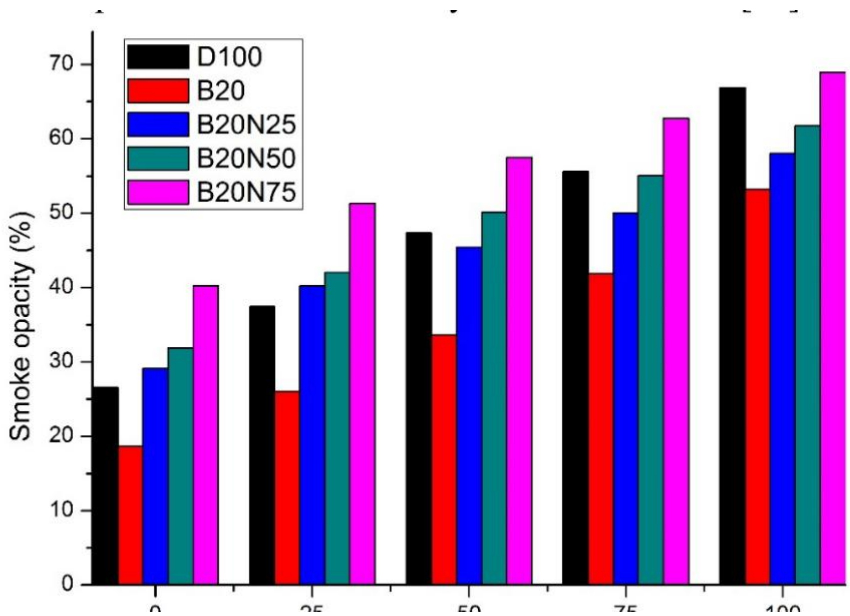

Figure 20. Smoke-opacity response versus engine load for diesel, B20, and CuO-doped B20 palm biodiesel blends [32].

The smoke-opacity plot confirms a frequent benefit of nanoparticle-assisted biodiesel operation: soot-related opacity declines relative to untreated biodiesel blends, especially at moderate-to-high load. Compared with other additives, smoke reduction is one of the most robust advantages of metal-oxide additives, although full particulate-number and ash-composition evidence remains limited (Figure 20).

The discrepancy between gas-phase and particulate conclusions is another issue requiring sharper Several studies report reduced smoke opacity or lower particulate mass, which is encouraging, but the few papers that measured particle number, PM2.5 composition, soot size, or downstream particulate capture showed a more complex picture. Yusuf et al. (2022) observed a shift toward smaller particles in biodiesel/CeO_2 CRDI operation. Fayad et al. (2023) showed that TiO_2 plus EGR could reduce NOx while altering PM behavior and soot particle size. Vellaiyan (2025) found that Al_2O_3 improved most conventional emissions but increased PM substantially until an electrostatic precipitator was added. These studies collectively imply that nanoparticles can change not only how much particulate matter forms but also what kind of particulate matter is produced and how it interacts with aftertreatment or human exposure pathways. For a field that explicitly introduces solid nanoscale matter into the fuel, the continued reliance on smoke opacity as the dominant particulate proxy is not defensible.

A related concern is hardware durability. Very few abstracts discuss injector coking, pump wear, lubrication oil contamination, filter plugging, ash accumulation, or metal deposition on combustion-chamber surfaces. That silence does not indicate absence of risk; it indicates absence of measurement. The problem is especially serious for metal oxides and carbonaceous additives because any real deployment would require thousands of hours of operation, not a short-duration bench test. Higher in-cylinder pressure and heat release rate often accompany improved combustion, but these same benefits can intensify wall loading, nozzle thermal stress, and deposit adherence if the additive is not fully oxidized or evacuated [64] The current literature is strong on short-term functional performance and weak on tribology, corrosion, deposit chemistry, and maintenance economics. As long as that imbalance persists, claims of commercial readiness remain premature.

Table 4. Comparative assessment of what is established versus what remains weak across key application themes.

Comparative theme	What the literature establishes	What remains weak	Engineering implication
Standard single-cylinder CI tests	Basic BTE/BSFC/CO/HC/NOx trends are well documented	Transient response, cold start, and durability are largely absent	Current evidence is strong for screening but weak for deployment decisions
CRDI and EGR-integrated operation	Nanoparticles can reshape the NOx-soot trade-off and particle-size spectrum	Only a few studies exist; aftertreatment compatibility is largely untested	Modern diesel relevance is high, so this category deserves priority expansion
Dual-fuel, hydrogen, and biogas enrichment	Nanoparticles can compensate part of the combustion instability of enriched fuels	Evidence is sparse and strongly platform-specific	Useful for stationary and decentralized energy applications
LHR and HCCI-DI systems	Nano-additives can interact strongly with wall temperature and combustion phasing	Data remain too limited for general rules	Mechanism-rich niche with high research value

Particulate chemistry and toxicology	A few studies measured particle number, PM2.5 species, or soot size	Most of the field still relies on smoke opacity alone	Future studies need size-resolved and composition-resolved exhaust characterization
Optimization and machine learning	Nonlinear dosage-speed-blend interactions are now recognized	Models are mostly small-data and single-lab	Physics-constrained and externally validated models are the next step
Durability and economics	Short-term performance benefits are established	Injector wear, ash deposition, storage logistics, and life-cycle cost remain unresolved	Commercial viability cannot be inferred from short bench tests

The emerging use of machine learning and multi-criteria optimization deserves a similarly critical reading. The newest papers report high coefficients of determination and successful ranking of blend options using ANN, GRNN, XGBoost, MCDM, and response-surface frameworks [15] These tools are valuable because nanoparticle dosage, blend composition, and operating conditions interact nonlinearly. However, most models are trained on small, single-laboratory datasets collected from a single engine family over limited operating points. High in-sample fit therefore should not be confused with generalizable predictive power. In the present field, data scarcity and procedural heterogeneity are more limiting than model selection. Physics-constrained or transfer-learning approaches would offer far more value than additional high-R2 single-bench regressions trained on narrow design spaces.

The thermodynamic and sustainability studies also require careful Exergy and exergoeconomic analyses, which shift attention from simple output gain to energy quality, work potential, and the cost of useful output. Karagoz et al. (2021), Uysal et al. (2022), and Rao et al. (2025) show that some nanoparticle-doped fuels outperform neat biodiesel or diesel-biodiesel blends from this broader perspective. Yet even these studies rarely account for nanoparticle production costs, synthesis energy, recovery, occupational exposure controls, or end-of-life environmental burdens. A nano-fuel that raises exergy efficiency by one or two percentage points but requires energy-intensive synthesis, unstable storage, and special handling might still fail at the system level. The sustainability narrative in this literature is therefore directionally credible but not yet complete.

The critical synthesis from the corpus is thus more demanding than the standard “nanoparticles improve biodiesel” conclusion found in many introductory paragraphs. The evidence supports a more precise position. Nanoparticles are effective micro-scale combustion modifiers that can recover a substantial fraction of biodiesel’s efficiency penalty and suppress incomplete-combustion emissions when matched carefully to fuel chemistry, dosage, and engine calibration. Their benefits are strongest in low-dose, well-dispersed systems and can become especially valuable when combined with EGR, oxygenated co-additives, antioxidants, or advanced optimization. Their limitations are equally clear: NOx remains conditional, particulate interpretation is incomplete, stability reporting is weak, durability evidence is scarce, and the economic and toxicological boundaries for real deployment remainnresolved [66]. That is not a failure of the field. It is a sign that the field has advanced past simple proof-of-concept and now faces the more difficult requirements of engineering validation.

6. Research Gaps

The most immediate research gap is external validity. The literature is saturated with steady-state experiments on single-cylinder engines, yet the technologies most likely to use biodiesel blends at scale—modern road diesels, agricultural fleets, industrial gensets, and marine auxiliaries—operate under transient load, start-stop duty, multiple injection events, exhaust aftertreatment, and long maintenance intervals. Only a small fraction of the corpus addresses CRDI behavior, dual-fuel operation, low-heat-rejection engines, or marine systems, and almost none of it tests standardized transient cycles or durability intervals long enough to reveal injector fouling, deposit growth, lubricant contamination, or aftertreatment interactions [67] Until those gaps are addressed, the field cannot claim transferability from bench-scale success to fleet-scale implementation.

A second gap is the absence of standardized nano-fuel preparation and reporting. The corpus widely uses ultrasonication, but it does not report a consistent set of stability descriptors, such as sonication energy density, storage duration before testing, zeta potential, particle-size distribution after mixing, sedimentation rate, or re-agglomeration under thermal cycling. Several studies also omit dispersant chemistry or avoid stabilizers entirely in the interest of practical simplicity, which is useful experimentally but makes cross-study comparison difficult [68]. The field therefore lacks a minimum reporting standard comparable to ASTM fuel-property reporting. Without that standard, ppm-level optimization results remain partially laboratory-specific.

The third gap concerns particulate toxicology and nanoparticle fate. Conventional diesel-emission studies typically stop at CO, HC, NOx, smoke opacity, or total PM. That is inadequate for nano-doped fuels. The few studies measuring particle number, PM2.5 composition, or soot size already show that beneficial changes in one particulate metric can coexist with adverse shifts in another [69] What remains largely unknown is whether the additive survives combustion as ash, transforms into new oxide phases, embeds into soot agglomerates, or alters toxicological potency after exhaust release. This is a central gap because any sustainability claim for nano-biodiesel blends depends not only on tailpipe mass reduction but also on chemical form and exposure risk.

A fourth gap is economic and systems-level realism. Exergy, exergoeconomic, and sustainability analyses are increasing, but most still treat nanoparticle use as if the additive were costless and operationally benign once blended [70] Few studies quantify nanoparticle synthesis energy, blending cost, storage logistics, occupational safety requirements, or recovery and disposal pathways. Fewer still compare nano-additives against competing decarbonization options such as renewable diesel, calibration changes, advanced EGR, or aftertreatment upgrades. The field therefore lacks the techno-economic benchmark needed to justify the deployment of nanoparticles outside research settings.

The final gap is epistemic rather than experimental: the literature still lacks a common mechanism-based framework for comparing materials across feedstocks and engines. Many papers conclude that one nanoparticle is "best" within one dataset, but those rankings often emerge from different base fuels, different operating points, and different response priorities. What is needed is a cross-platform design logic that links particle chemistry, surface area, oxygen buffering, thermal conductivity, blend polarity, and spray-combustion regime to predicted performance windows. Until that framework exists, additive selection will remain largely empirical, and the accumulation of studies will continue to outpace the accumulation of transferable engineering rules.A related and underdeveloped gap concerns statistical reproducibility. Although several recent papers incorporate ANN, GRNN, XGBoost, RSM, or MCDM, most experimental datasets remain small, single-lab, and weakly standardized, which limits cross-study validation and makes apparently precise rankings fragile outside their local design space [71] The field needs shared benchmark datasets and inter-laboratory round-robin testing so that optimization claims can be evaluated on reproducibility rather than on fit statistics alone.

7. Future **Scope**

The next phase of this field should move from additive screening to engineered nano-fuel platforms with standardized preparation, mechanistic diagnostics, and application-specific validation. The first priority is protocol standardization. Future studies should report a minimum common dataset that includes nanoparticle synthesis route, crystallite size, hydrodynamic size after blending, zeta potential, sonication energy input, storage duration, re-dispersion procedure, and post-test stability. A fuel blend cannot be treated as a reproducible engineering material unless these variables are controlled. Standardized reporting would immediately improve the value of machine-learning models, meta-analyses, and inter-study comparison because the present variability in preparation methods is masking true material effects.

The second priority is to connect macro-scale engine outcomes with micro-scale diagnostics. The literature already infers improved atomization, higher heat-release rates, and catalytic oxidation, but direct mechanistic evidence remains sparse. Future work should therefore couple engine tests with droplet-evaporation imaging, in-cylinder optical diagnostics, particle-size-resolved exhaust analysis, ash and deposit characterization, and post-combustion phase identification. This is particularly important for CeO_2, graphene derivatives, CNT/MWCNT systems, and mixed metal oxides, where the same additive can reduce smoke yet alter particle-number distribution or exhaust chemistry in ways not captured by conventional analyzers [72] The objective should be mechanistic closure: a demonstrable link between nanoparticle state in the liquid fuel, its transformation during combustion, and its fate in the exhaust stream.

The third priority is platform expansion. Modern CRDI engines, hybrid low-temperature combustion systems, marine engines, dual-fuel architectures, and real-duty-cycle generator applications need far greater representation. Nanoparticles should be evaluated under transient cycles, cold starts, high-altitude conditions, and long-duration endurance tests rather than under brief steady-state load sweeps alone. Future work should also explicitly integrate aftertreatment. The literature has already shown that electrostatic capture and EGR can fundamentally reshape the apparent success of a nano-fuel strategy [73] Diesel particulate filters, oxidation catalysts, and SCR systems should therefore be treated as part of the experimental boundary conditions, not as absent background hardware.

A fourth priority is multi-objective optimization anchored in physics rather than in curve fitting alone. Response-surface and machine-learning approaches should evolve toward hybrid models that combine interpretable combustion descriptors with data-driven surrogate optimization. Such models would be more useful for design because they could generalize across fuel families and engines rather than being bound to a single experimental matrix. Shared benchmark datasets, uncertainty-aware training, and external validation across laboratories would convert the current wave of high-R2 local models into a cumulative predictive framework. This is the stage at which additive ranking could become genuinely transferable.

Finally, the field needs full systems assessment before commercial recommendations are made. Future studies should integrate techno-economics, life-cycle assessment, occupational exposure, and end-of-life management of nanoparticles together with combustion data. The decisive question is not whether a nano-additive can raise BTE by a few percentage points on a bench engine; rather, it is whether the net system benefit remains positive after accounting for additive production, storage, safety, durability, and emissions control. If that question is answered rigorously, the most promising outcome is unlikely to be universal use of one "best" nanoparticle. A more realistic future is application-specific formulation: low-dose ceria or titania for particulate-sensitive CRDI operation, alumina or CuO in cost-sensitive stationary engines, graphene-derived materials where exergy gain justifies higher additive value, and hybrid strategies that combine nanoparticles with oxygenates, antioxidants, or advanced control to meet a defined duty cycle.This application-specific direction also opens an important frontier in materials development. Future nano-additives should be designed for controlled redox activity, low ash residue, high storage stability in polar biodiesel matrices, and compatibility with commercial injection equipment. Green synthesis routes are attractive only if they also produce repeatable particle morphology and stable dispersion behavior at the industrial scale [74]. The best future studies will therefore treat nanoparticle design, fuel formulation, combustion calibration, and exhaust control as a coupled optimization problem rather than separate research themes.

8. Conclusion

This review synthesized nanoparticle-assisted biodiesel blending as a combustion-modification pathway for compression-ignition engines, using a structured Scopus export, semantic duplicate screening, material coding, platform classification, and comparative mapping of performance, combustion, emissions, particulate, and optimization domains. The initial dataset contained 75 records, and removal of one near-duplicate record produced the evidence base used for qualitative synthesis. Direct engine experiments accounted for 50 records, while 17 coupled experiments with optimization or machine learning, showing that empirical screening still dominated but predictive design frameworks were gaining visibility. The corpus was strongly concentrated in 62 single-cylinder or standard CI studies, with only 2 CRDI studies, 5 dual-fuel or enriched studies, 2 low-heat-rejection studies, and single HCCI-DI, marine, and multi-cylinder cases, indicating limited transferability beyond laboratory rigs. Material mapping showed 22 Al2O3 mentions, 15 TiO2 mentions, 12 CeO2 mentions, and 8 mentions each for graphene-based and carbon nanomaterial systems, confirming that low-cost oxides shaped the main evidence base. Response-domain coding also showed 63 gaseous-emission studies, 51 performance studies, 46 combustion studies, 30 particulate or soot studies, 20 fuel-property studies, 19 optimization or modeling studies, 6 energy-exergy-sustainability studies, and 4 noise or vibration studies. These outcomes demonstrate that nano-additives provide practical leverage for fuel-engine calibration, yet deployment requires stronger evidence on stability, ash fate, hardware durability, aftertreatment compatibility, toxicity, and life-cycle cost. Future investigations will need long-duration CRDI and marine trials, transient duty cycles, standardized colloidal reporting, size-resolved exhaust chemistry, externally validated optimization datasets, and inter-laboratory reproducibility benchmarks for consistent cross-platform interpretation and regulatory screening.

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