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Application of Nano-Additives in Dual Fuel, HCCI, and RCCI Engines: A Comprehensive Review

Vijayakumar Totad[1]
Department of Mechanical Engineering
R R Institute of Technology, Bengaluru ,Karnataka, India

Jagdeeesh Y.J[2],
Department of Mechanical Engineering
BMS Institute of Technology, Bengaluru, Karnataka

Praveen Harari[3]
Department of Mechanical Engineering
CMR University, Bengaluru, 562149, Karnataka, India

Yaliwal V.S[4].
,Department of Mechanical Engineering, SDMCET,
Dharwad, Karnatkaa , India

Abstract* - *Extensive research into enhanced combustion techniques and fuel technologies has been prompted by the growing worldwide concern over the depletion of fossil fuels and strict emission regulations. Internal combustion engine combustion efficiency, brake thermal efficiency (BTE), and emission reduction have all significantly improved because to nanotechnology. The application of nanotechnology, including metal oxide, carbon-based, and hybrid nanoparticles, in three advanced engine technologies—Dual Fuel (DF) engines, Homogeneous Charge Compression Ignition (HCCI) engines, and Reactivity Controlled Compression Ignition (RCCI) engines—is thoroughly examined in this review paper.

Al_2O_3, CeO_2, TiO_2, ZnO, CuO, carbon nanotubes (CNTs), and graphene oxide (GO) are among the important nanoparticle kinds investigated. The study summarizes research on improving thermophysical properties, reducing ignition delay, improving heat release rate, and reducing pollutants such CO, HC, NO_x, and particulate matter (PM). Critical discussion is given to issues such as cost-effectiveness, stability in fuel mixes, agglomeration of nanoparticles, and toxicological concerns. Future research avenues that are highlighted include green synthesis pathways, AI-assisted optimization, and hybrid nano-additives. The conclusion is that nanotechnology has enormous potential for the efficient and clean operation of low-temperature combustion engines of the future.

Keywords - Nano-addtives, Dual fuel, HCCI, RCCI, Performance, Emissions, Combustion

1. INTRODUCTION

Global greenhouse gas emissions and declining air quality are mostly caused by the transportation and energy industries. Over 1.2 billion cars are powered by internal combustion engines (ICEs), which mostly run on petroleum-based fuels and produce large emissions of CO_2, NO_2, CO, and particulate matter (PM). The investigation of alternate fuels, sophisticated combustion techniques, and novel fuel additives has been prompted by the need for cleaner combustion technologies [1-3]. The study and engineering of materials at the 1–100 nm scale, or nanotechnology, has drawn a lot of attention in this regard. High surface area-to-volume ratios, excellent thermal conductivity, and potent catalytic activity are just a few of the distinctive physicochemical characteristics that set nanoparticles (NPs) apart from their bulk counterparts. Nanoparticles work as fuel-borne catalysts, oxygen transporters, and combustion promoters when distributed in conventional or alternative fuels, improving the fuel's characteristics and combustion behavior [4-6]. Concurrently, sophisticated low-temperature combustion (LTC) techniques have been created to get around the drawbacks of traditional SI and CI engines. Among these, Dual Fuel (DF) combustion, Reactivity Controlled Compression Ignition (RCCI), and Homogeneous Charge Compression Ignition (HCCI) have demonstrated remarkable promise in concurrently lowering PM and NO_x emissions while retaining excellent thermal efficiency [7-9].

A cutting-edge field of study is the combination of nanotechnology and highly sophisticated combustion techniques. Nevertheless, there is a dearth of literature that provides a comprehensive and critical analysis of all three engine technologies via the prism of nanotechnology. This essay fills that void by:

- ✓ Going over the principles of DF, HCCI, and RCCI engines.
- ✓ Examining the kinds and characteristics of engine fuel nano-additives.
- ✓ Examining critically how nanoparticles affect each engine type's performance, combustion, and emission characteristics.

2. BACKGROUND: ADVANCED ENGINE TECHNOLOGIES

2.1. Dual Fuel (DF) Engines

A primary gaseous fuel (such as CNG, hydrogen, LPG, or biogas) is introduced through the intake manifold of dual fuel engines, while a liquid pilot fuel (usually diesel or biodiesel) is pumped straight into the cylinder for ignition. The pilot fuel auto-ignites during compression, causing the premixed charge to burn, while the gaseous fuel creates a premixed charge with air. The use of renewable gaseous fuels (biogas, hydrogen), decreased CO_2 emissions (especially when using natural gas), and lower particulate emissions are all benefits of dual fuel operation. Nevertheless, issues include knock susceptibility, increased unburned hydrocarbon (UHC) emissions at partial loads, and incomplete combustion at low loads.

2.2 Homogeneous Charge Compression Ignition (HCCI) Engines

In order to achieve combustion, HCCI engines compress a uniform, highly premixed air-fuel charge until auto-ignition takes place simultaneously throughout the cylinder volume. Diffusion flames are absent from CI engines, whereas spark-assisted ignition is absent from SI engines. A dispersed, low-temperature combustion event is the outcome. The main benefits of HCCI include almost no soot production and incredibly low NO_x emissions (caused by low peak combustion temperatures). HCCI engines emit more CO and HC because of incomplete oxidation at low temperatures, and regulating combustion phasing across different loads and speeds is still a major difficulty.

2.3 Reactivity Controlled Compression Ignition (RCCI) Engines

RCCI is a dual-fuel low-temperature combustion technique that uses two fuels with very different reactivities at the same time. While a high-reactivity fuel (HRF) like diesel or biodiesel is directly injected into the cylinder, a low-reactivity fuel (LRF) like gasoline, ethanol, or methanol is port-injected to create a premixed charge. Engine-out emissions of PM and NO_x can be simultaneously reduced thanks to the reactivity gradient between the two fuels, which also regulates combustion phasing. In comparison to HCCI, RCCI provides better combustion control, increased indicated thermal efficiency, and fuel combination flexibility. RCCI is a great option for next-generation clean combustion engines because of these qualities.

3. NANOTECHNOLOGY AND NANO-ADDITIVES: AN OVERVIEW

3.1 Fundamentals of Nanoparticle Properties

Materials with at least one dimension between 1 and 100 nm are called nanoparticles. Quantum effects and significantly higher surface-to-volume ratios give them their remarkable characteristics. Nanoparticles affect a number of crucial factors when they are applied to engine fuels:

Thermal conductivity: Evaporation is accelerated by improved heat transmission from hot combustion gases to fuel droplets.

Catalytic activity: By acting as oxidation catalysts, metal oxide nanoparticles lower the activation energy of combustion reactions.

Oxygen buffering: During combustion, NPs like CeO_2 store and release oxygen to facilitate more thorough oxidation.

Surface energy: NPs with high surface energy encourage fuel droplet secondary atomization and microexplosions, which enhance spray properties.

Cetane number improvement: Certain NPs reduce ignition delay by improving gasoline mixtures' ignition quality.

3.2 Classification of Nano-additives

Engine fuel nano-additives can be roughly categorized as:

Metal-based NPs: Copper (Cu), Boron (B), Iron (Fe), and Aluminum (Al).

Metal oxide NPs: Al_2O_3, CeO_2, TiO_2, ZnO, CuO, Fe_2O_3, and Co_3O_4.

Carbon based NPs: Carbon nanotubes (CNTs), graphene oxide (GO), graphene nanoplatelets (GNPs), and carbon quantum dots.

Hybrid / Composite NPs: $Al_2O_3 + CeO_2$, $TiO_2 + Al_2O_3$, CNT + GO, CuO + ZnO.

Different physical and chemical interactions with the basic fuel and the combustion process are represented by each category.

3.3 Nanofluid Preparation and Stability

Reliable engine experiments require stable nanofluids and proper preparation. Typical techniques consist of:

Two-step process: Ultrasonic homogenization is used to distribute NPs in base fuel after they have been independently produced.

One-step method: NPs are produced directly in the base fluid, which improves stability but has restricted scalability.

Zeta potential measurements (numbers greater than ±30 mV indicate good stability), sedimentation observation, and UV-Vis spectroscopy are commonly used to evaluate stability. To stop agglomeration, surfactants like oleic acid, Span 80, and cetyltrimethylammonium bromide (CTAB) are frequently utilized.

4. NANOTECHNOLOGY IN DUAL FUEL ENGINES

4.1 Performance Characteristics

Performance measures have consistently improved when nano-additives are added to the pilot fuel in dual fuel engines. The effects of TiO_2, CNT, $Al2O_3$, CuO, and CeO_2 nanoparticles at 100 ppm concentration in combination with hydrogen in a modified dual fuel engine were thoroughly examined by Manigandan et al. (2020). When compared to neat diesel operation, the CNT and TiO_2 blends showed roughly 23% and 22% reductions in brake specific fuel consumption (BSFC), respectively, while CeO_2 and Al_2O_3 enhanced BTE by 4.3% and 2.5% at full engine load. Studies on dual fuel engines that use mixtures of biodiesel and nanoparticles as pilot fuel and natural gas as primary fuel have consistently shown gains in BTE. Because the pilot fuel supply is tiny and must consistently ignite the gaseous charge, the catalytic impact of nanoparticles reduces the activation energy needed for combustion initiation in dual fuel mode. BTE increases of up to 24.7% were found in studies using Al_2O_3 nanoparticles in Jatropha biodiesel at a B20 mix concentration of 50 ppm. By lowering the pilot fuel's surface tension and viscosity, metal oxide nanoparticles enhance fuel atomization and produce a finer spray cone with a smaller Sauter Mean Diameter (SMD). This improves the pilot charge's ignition quality by encouraging faster evaporation and improved air-fuel mixing.

4.2 Combustion Characteristics

Nanoparticle additions mainly impact the heat release and combustion phasing properties of dual fuel engines. By adding more oxygen to the combustion zone, CeO_2 nanoparticles accelerate the beginning of combustion and reduce ignition delay. Peak heat release rate (HRR) advanced with increasing NP concentration in experiments comparing CeO_2 concentrations of 10, 20, and 40 ppm in neat diesel as pilot fuel, indicating increased combustion quality. The inclusion of nanoparticles to the pilot diesel fuel is especially advantageous for hydrogen dual fuel engines. CuO nanoparticles and hydrogen-enriched diesel blends were shown to reduce CO from 3.1 to 1.45 g/kWh (a 53% decrease) and CO_2 from 270 to 225 g/kWh at lower engine speeds. With R-values greater than 0.99, the artificial neural network (ANN) models used in these investigations to forecast engine results demonstrated exceptional accuracy. Because the use of nanoparticles improves combustion rates, peak cylinder pressure values rise. Because of the increased surface area of NPs, fuel molecules oxidize more quickly, producing a steeper pressure rise and greater peak cylinder pressures that enhance work production.

4.3 Emission Characteristics

Dual fuel operation with nanoparticle assistance has shown notable reductions in emissions. The catalytic oxidation function of metal oxide nanoparticles is crucial for CO and HC emissions. NPs' large surface area makes it more likely that unburned fuel molecules will collide with oxygen, which encourages post-flame oxidation. For methyl ester of waste cooking oil (B10) blends with 100 ppm TiO_2, maximum HC reductions of 70.94% and CO reductions of 80% have been documented. The addition of nanoparticles to NO_x emissions in dual fuel engines creates a complicated picture. By acting as oxygen buffers, nanoparticles can somewhat offset the tendency of hydrogen addition to raise NO_x because of higher flame temperatures. Due to lower in-cylinder temperatures made possible by encouraged early combustion, CeO_2 at 40 ppm showed a maximum NO_x reduction of 42.7% when compared to clean diesel. Nano-additives significantly lower PM emissions and smoke opacity. Metal oxide nanoparticles' ability to release oxygen inhibits the production of soot precursors. Combining Al_2O_3 and CeO_2 (30 ppm each) with a Jatropha biodiesel blend resulted in a 32% decrease in smoke emissions along with concurrent reductions of 13% in NO_x and 60% in CO.

5. NANOTECHNOLOGY IN HCCI ENGINES

5.1 Overview of HCCI Combustion with Nano-additives

Since chemical kinetics rather than physical injection events essentially control auto-ignition time, the HCCI combustion mode is sensitive to the physicochemical characteristics of the fuel. Therefore, HCCI combustion is significantly impacted by nanoparticle additions that change ignition latency, cetane number, thermal conductivity, and oxidation kinetics. The addition of Al_2O_3 to the neat fuel increased BTE by 11.27% for conventional DI combustion and by 18.31% for HCCI-DI combined combustion, according to research by Lionus Leo et al. (2024) on an HCCI-DI engine powered by waste cooking oil biodiesel incorporating Al_2O_3 and $FeCl_3$ nano-additives along with gasoline port injection. Additionally, in HCCI mode, emissions of HC, CO, and smoke decreased by 54.17%, 50%, and 22.69%, respectively. In line with HCCI's lower peak temperature combustion feature, HCCI-DI combustion reduced NO_x emissions by 4.3% as compared to conventional DI operation. The diluted, premixed HCCI combustion mode and nanoparticle-enhanced fuel work together to reduce emissions.

5.2 Effect on Premixed Charge Combustion Characteristics

Nanoparticles scattered in the fuel have various effects on the auto-ignition and charge preparation processes in HCCI engines.

Enhancement of thermal conductivity: The fuel's thermal conductivity is increased by nanoparticles scattered throughout it, which speeds up fuel vaporization during the intake and compression strokes. A more uniform charge formation results from this.

Catalytic ignition promotion: By lowering the oxidation reactions' activation energy, metal oxide nanoparticles enable the premixed charge to auto-ignite earlier. Because HCCI engines experience delayed auto-ignition under lean and low-temperature circumstances, this effect is very helpful in increasing the load range of these engines.

Micro-explosions and secondary atomization: Fuel droplets containing nanoparticles experience micro-explosions during the port injection phase (or early direct injection for HCCI-DI) as a result of the base fuel and NPs being heated differently. The charge's homogeneity is enhanced by this secondary atomization.

The high surface-to-volume ratio of multi-walled carbon nanotubes (MWCNTs) enhances thermal conductivity, increasing combustion efficiency and improving the heat release profile during HCCI combustion, according to research on MWCNTs added to Tamanu methyl ester (TME) in a premixed charge compression ignition engine. Significant improvements in engine performance and emission characteristics were observed in HCCI mode using mixes of graphene oxide and dimethyl carbonate.

5.3 Performance and Emission Outcomes in HCCI Mode

Experimental studies using different nano-additives in HCCI engines have revealed:

Improvements in BTE: Generally between 5 and 18%, depending on the kind, concentration, and base fuel of the nanoparticles. Because of its steady catalytic activity and excellent thermal conductivity, Al2O3 usually exhibits the highest BTE improvement.

BSFC reduction: There have been reports of BSFC reductions of 8–15% in tandem with the BTE improvements. Because of the increased combustion efficiency, less fuel is required to generate the same amount of labor.

NO_x emissions: Because of spread, low-temperature combustion, HCCI mode naturally produces extremely little NO_x. The impact of nanoparticle additions on NO_x in HCCI mode is limited; some studies claim minor reductions, while others report slight increases because of increased local combustion temperatures caused by catalytic activity.

HC and CO emissions: The main pollution issues with HCCI engines are CO and HC emissions. In the combustion chamber, nanoparticles function as catalytic converters, more efficiently oxidizing CO and unburned HC. As oxygen donors, Al_2O_3 and CeO_2 are very good at cutting these emissions by 50–60%.

Smoke and PM: Because of the premixed, fuel-lean charge, HCCI combustion already produces almost no soot. In contrast to traditional CI mode, where the PM reduction advantage is more noticeable, the inclusion of nanoparticles in HCCI mode does not considerably change PM.

5.4 HCCI Load Range Extension Using Nano-additives

The limited operational load range of HCCI engines is one of their main drawbacks; they frequently misfire at low loads due to inadequate charge reactivity and knock at high loads due to an excessively quick pressure rise. A partial solution is provided by nano-additives:

Catalytically active NPs (CeO_2, CuO) efficiently extend the lean combustion limit by lowering auto-ignition temperature at low loads, allowing for dependable combustion initiation at leaner conditions.

By controlling the NP concentration at high loads, knock can be avoided by moderating the rate of heat emission.

In comparison to neat citronella oil, studies using cobalt chromium nanoparticles in HCCI engines running on citronella oil revealed better combustion stability and a longer operational range. By facilitating more even heat escape, the nanoparticles decreased the possibility of pressure oscillations linked to HCCI knock.

6. NANOTECHNOLOGY IN RCCI ENGINES

6.1 Role of Nano-additives in RCCI Combustion

To accomplish regulated, phased combustion, RCCI combustion depends on a reactivity gradient between the LRF and HRF. The reactivity, ignition behavior, and spray properties of the HRF (usually diesel or biodiesel) are altered by nano-additives, which have an impact on the in-cylinder reactivity stratification and combustion phasing. Jayabal et al. (2025) conducted a thorough investigation on a dual-fuel RCCI engine that used a mixture of 5% methane and 15% hydrogen as the LRF and 20% spirulina biodiesel combined with diesel as the HRF. Nanoparticles of copper oxide (CuO) and zinc oxide (ZnO) were added to the HRF at concentrations ranging from 25 to 75 parts per million. The best engine performance and emission characteristics were found using a hybrid Deep Neural Network optimized with the Gannet Optimization Algorithm (DNN-GOA), illustrating the collaboration of machine learning and nanotechnology in RCCI research.

6.2 Effects on Reactivity and Combustion Phasing

Reactivity stratification is impacted by the addition of nanoparticles to the HRF in RCCI engines in a number of ways:

Enhanced HRF reactivity: By encouraging low-temperature oxidation processes, metal oxide nanoparticles (NPs) like CeO_2 and CuO raise the cetane number of the HRF, hence raising the reactivity gradient between LRF and HRF. This enhances the control of combustion phasing.

Modified spray characteristics: The viscosity and surface tension of the directly injected HRF are changed by the inclusion of nanoparticles, which has an impact on the spray cone angle, penetration depth, and droplet size distribution. Local fuel-air mixing inside the injected zones is enhanced by finer droplets from NP-assisted atomization.

Heat release rate regulation: Research on RCC by distributing the energy release over a little longer crank angle window, NP addition to the HRF tends to mitigate the main heat release event in I engines. This reduces peak pressure increase rates that might cause ringing intensity, a knock-like occurrence in RCCI.

6.3 Performance Characteristics in RCCI Mode

Positive performance results have been repeatedly demonstrated by research on biofueled RCCI engines with nanoparticle additives. According to a thorough analysis of biofueled RCCI engines, BTE was enhanced by 1.39% by raising the compression ratio from 16.5 to 18.5 and by 0.36% by adding CuO nanoparticles. CuO nanoparticle-enhanced blends showed better combustion efficiency than baseline in RCCI engine studies utilizing n-butanol/gasoline as LRF and biodiesel blends as HRF. Nanoparticles can be selectively introduced in the HRF channel, where their impact on ignition and combustion is maximized, thanks to the fuel flexibility of RCCI. Higher diesel injection pressure increases peak nanoparticle number distribution (NMP) while decreasing accumulation mode particles (AMP), according to research on nanoparticle emissions from RCCI engines (Nanoparticle emissions study, 2019). This knowledge is essential for assessing how employing nano-fuel additives would affect the environment overall.

6.4 Emission Characteristics in RCCI Mode

RCCI engines are renowned for achieving low PM and NO_x at the same time. These emission improvements have been discovered to be further extended by the combination of RCCI combustion technique with nanoparticle additives:

CO emissions: When compared to biodiesel-only operation, CuO nanoparticles decreased CO emissions in biofueled RCCI engines by 11.55%. This is in line with CuO's catalytic oxidation function, which lowers the CO-to-CO_2 conversion barrier.

PM emissions: In RCCI mode, the inclusion of CuO nanoparticles decreased particulate matter emissions by 20.24%. Metal oxide nanoparticles' ability to release oxygen encourages soot oxidation, which opposes the directly injected HRF's propensity to create soot.

NO_x emissions: Although RCCI already reaches sub-Euro 6 NO_x levels, the inclusion of nanoparticles has conflicting results. Due to higher combustion temperatures, highly reactive NPs (H_2 + biodiesel + CuO combinations) have demonstrated NO_x increases from 1.41 to 3.43 g/kWh. This emphasizes how important careful concentration optimization is.

HC and CO_2: At lower engine speeds, hydrogen-nanoparticle-enhanced blends in RCCI mode showed notable CO2 reductions from 270 to 225 g/kWh, indicating better combustion efficiency and partial substitution of hydrogen for carbon-containing fuel.

7. TYPES OF NANOPARTICLES: PROPERTIES AND ENGINE PERFORMANCE IMPACTS

7.1 Metal Oxide Nanoparticles

Aluminum Oxide (Al_2O_3): Because of their high thermal conductivity (~30 W/mK), chemical stability, and reasonable cost, Al_2O_3 NPs are among the most researched. Their main functions in fuel are as carriers of oxygen and improvers of thermal conductivity. Research indicates that at ideal concentrations (50–150 ppm), Al_2O_3 can increase BTE by up to 18–25%. Across load ranges, the addition of Al_2O_3 to biodiesel lowers NO_2 emissions by 9–38%. CO emissions in Al_2O_3-doped diesel typically rise by 4.4–7.5%, indicating partial catalytic activity under certain operating circumstances.

Cerium oxide (CeO_2): Because of its distinct Ce^{3+}/Ce^{2+} redox cycle, which allows it to store and release oxygen in response to local combustion circumstances, cerium oxide (CeO_2) is a very effective catalytic nanoparticle. With 40 ppm CeO_2 in diesel, NO_x reductions of up to 42.7% have been reported, making CeO_2 an efficient oxidation catalyst for CO and soot. The addition of CeO_2 to biodiesel maintains BTE improvements while reducing NO_x by 25.7% and CO considerably. With NO_x reductions of 15.7% and CO reductions of 15.4%, the use of iron-doped CeO_2 ($FeCeO_2$) significantly increases catalytic activity.

Titanium Dioxide (TiO_2): TiO_2 NPs show significant emission reductions: smoke opacity by 32.98%, CO by 30%, and HC by 28.68%. They also increase BSFC by up to 25%. TiO_2 mainly serves as an enhancer of heat conductivity and a photocatalyst. TiO_2 at 100 ppm lowers NO_x in hydrogen dual fuel engines by 7% as compared to plain diesel. TiO_2 nanofluids are stable for long when combined with CTAB surfactant and ultrasonication-enhanced dispersion.

Copper Oxide (CuO): RCCI and dual fuel engine applications have benefited greatly from CuO NPs' potent catalytic activity. CO reductions of 53% were shown in dual fuel setups when CuO was added to biodiesel-diesel blends with hydrogen enrichment. CuO increased BTE in RCCI mode while concurrently lowering CO and PM emissions; nevertheless, because of higher combustion temperatures, NO_x slightly increased.

Strontium-Zinc Oxide (Sr@ZnO) and Zinc Oxide (ZnO): ZnO NPs have moderate thermal conductivity and considerable surface activity. In comparison to baseline biodiesel blends, Sr@ZnO hybrid nanoparticles have been produced and evaluated for CRDI diesel engine applications, exhibiting enhanced BTE and decreased emissions. At 60 ppm, Sr@ZnO demonstrated the best performance balance.

7.2 Carbon-Based Nanoparticles

Carbon Nanotubes (CNTs): Both single-walled (SWCNT) and multi-walled (MWCNT) CNTs have remarkable mechanical strength, electrical conductivity, and thermal conductivity (up to 3000 W/mK). CNTs facilitate faster evaporation and more thorough burning in motor fuels by enhancing heat transmission from combustion gases to fuel droplets. Carbon-based compounds have been shown to increase BTE in CI engines by an average of 0.5–2.5%. When compared to clean diesel, CNTs at 100 ppm in hydrogen dual fuel mixes decreased BSFC by 23% and NO_x by 28%. CNTs' distinctive tubular shape enhances soot oxidation, reducing smoke opacity by up to 44.6%.

Graphene Oxide (GO) and Graphene Nanoplatelets (GNPs): Among carbon materials, graphene-based NPs have the strongest surface activity and the best thermal conductivity. Engine performance and emissions were greatly improved in HCCI-DI mode with graphene oxide. When compared to baseline biodiesel, the graphene-based mix reduced HC by 68%, CO by 4.6%, and NO by 2.5%. The greatest reported results for hybrid nano-additive systems are a 25% reduction in hydrocarbon emissions and an 18% increase in BTE when GO and CNTs are combined.

The combined HCCI + GO + H_2 approach showed synergistic improvement in both performance and emissions in a study on Euglena Sanguinea (ES) biodiesel in HCCI mode with graphite oxide (GO) nanoparticles at different concentrations (20–80 ppm) with hydrogen gas induction, highlighting the potential of multi-technology integration.

7.3 Hybrid and Composite Nanoparticles

To produce synergistic effects, hybrid nanoparticles combine the characteristics of two or more NP kinds. Typical pairings consist of:

Al_2O_3 + CeO_2: Combines the thermal conductivity of Al_2O_3 with the catalytic oxygen buffering of CeO_2. Research has shown that Jatropha biodiesel blends containing 30 ppm of Al_2O_3 and CeO_2 reduce NO by 13%, CO by 60%, UHC by 33%, and smoke by 32%. TiO_2 + Al_2O_3: Combines photocatalytic and thermally conductive properties for more extensive emission control.

$FeCl_3$ + Graphene: These hybrid NPs at 50–75 mg/L significantly enhanced both performance and emission characteristics when used in a ternary fuel mixture investigation.

CuO + ZnO: Shows improved combustion control and emission reduction when used in RCCI engines with biodiesel + methane + hydrogen.

8. MECHANISMS OF ACTION OF NANOPARTICLES IN ADVANCED COMBUSTION ENGINES

8.1 Thermophysical Property Enhancement

Several thermophysical characteristics essential to combustion are altered when nanoparticles are added to liquid fuels:

Calorific value: High-energy NPs (particularly carbon-based NPs and metallic Al, B) raise the fuel blend's volumetric calorific value, allowing for greater energy release per unit volume.

Viscosity: At higher concentrations, NPs typically make fuel more viscous, which could exacerbate atomization. Surface energy effects predominate and viscosity increases are negligible at optimal concentrations.

Flash point and fire point: The use of nanoparticles usually increases the flash and fire points, enhancing storage safety.

Cetane number: By lowering the ignition temperature, catalytically active NPs raise the fuel's cetane equivalent and shorten the ignition delay.

Thermal conductivity: NPs speed up charge homogenization and droplet evaporation by raising the fuel's effective thermal conductivity.

8.2 Spray and Atomization Enhancement

Fuel spray properties are impacted by nanoparticles in a number of ways:
Secondary atomization and micro-explosions: When droplets containing nanoparticles are subjected to high temperatures during injection, internal tensions are created by the difference in thermal expansion between the fuel liquid and the NPs, which leads to explosive secondary fragmentation of the droplets. This enhances the quality of mixing by creating much finer secondary droplets.
Reduction of surface tension: When NPs are present at the liquid-gas interface of fuel droplets, surface tension is reduced, which lowers the Weber number threshold for droplet breakdown and results in finer atomization.
Enhancement of spray cone angle: Changes in surface tension and viscosity modify the spray dynamics, usually causing the spray cone to widen and the penetration depth in the near-nozzle region to shorten, which improves air-fuel mixing.

8.3 Catalytic Combustion Mechanism

The following processes allow metal oxide nanoparticles to function as heterogeneous catalysts during combustion:
Adsorption: On the extremely reactive NP surface, fuel molecules are adsorbed.
Surface reaction: Compared to gas-phase reactions, adsorbed hydrocarbons react with chemisorbed oxygen or lattice oxygen (in CeO_2) at lower temperatures.
Desorption: The NP surface is refilled with oxygen from the surrounding combustion environment after products (CO_2, H2O) desorb off it.
Regeneration: The Ce^{3+}/Ce^{2+} cycle in CeO_2 permits continuous oxygen storage and release, allowing the NP to repeatedly take part in catalytic cycles.
This process efficiently reduces the ignition delay and encourages CO and unburned hydrocarbons to burn more completely.

9. CHALLENGES IN NANOTECHNOLOGY APPLICATION TO ADVANCED ENGINES

9.1 Nanoparticle Stability and Agglomeration

Keeping NP dispersions in fuel stable over time is one of the biggest issues. Van der Waals forces and electrostatic interactions cause nanoparticles to clump together, creating bigger clusters that can:

- ✓ Fuel injector blockages.
- ✓ The non-homogeneous fuel mix causes uneven combustion.
- ✓ Deposit on the injector tips and walls of the combustion chamber.
- ✓ Lower the amount of effective surface area that can be used for catalytic reactions.

Surfactant addition (CTAB, Span 80, oleic acid), ultrasonic dispersion, surface functionalization, and pH correction are examples of stabilization techniques. However, the long-term effects of surfactants on injector materials are not entirely understood, and they may introduce new combustion products.

9.2 Toxicological and Environmental Concerns

Concern over the effects of engine emissions of nanoparticles on human health and the environment is developing. NPs in the 1–100 nm range that are carried by exhaust can enter the bloodstream after penetrating deeply into the respiratory system and reaching the alveolar region. At high concentrations, several metal oxide nanoparticles (CuO, ZnO) are cytotoxic.
The stability, environmental effect, and toxicity of nanoparticles continue to be major obstacles to their widespread use. Future studies should concentrate on multifunctional hybrid nanomaterials that can be safely regenerated or neutralized after combustion, eco-friendly production, and integration with second-generation biodiesel.
Further concerns are raised by the possibility that NPs will biodegrade in biological contexts. Biodegraded nanoparticles may build up inside cells and cause intracellular changes including gene modifications or loss of organelle integrity. Prior to widespread commercial implementation, these issues must be addressed in nanotoxicology research.

9.3 Cost and Scalability

Engineered NPs continue to be substantially more expensive to produce than traditional fuel additives. Precision equipment and energy-intensive procedures are required for the production of Al_2O_3, CeO_2, and particularly CNTs and graphene-based NPs. It is theoretically difficult to increase NP production while preserving consistent size distribution, purity, and surface characteristics.
Because synthesis costs, dispersion costs, and the possibility of injector maintenance must be taken into consideration in economic analyses of nanoparticle-enhanced fuels, the technology is currently only practical for specialized high-value applications. Research on cutting costs through green synthesis methods (using microbial processes and plant extracts) is ongoing.

9.4 Compatibility with Engine Materials

Fuel pumps, injector needles, and combustion chamber surfaces are among the fuel system components that may experience abrasive wear due to high-concentration nanoparticle dispersions. Concerns over long-term engine wear are raised by the hardness of some metal oxide nanoparticles (Al_2O_3, TiO_2) being close to that of steel parts. There are currently few long-term engine durability studies using fuels augmented with nanoparticles in the literature, which constitutes a substantial research gap. For engine components to be commercially viable, coating treatments that prevent abrasion from nanoparticles may be necessary.

9.5 Emission-Trade-off Challenges

While nano-additives lower emissions of CO, HC, and PM, they frequently increase emissions of NO_x, especially at higher concentrations and with more catalytically active NPs. NP-enhanced advanced combustion engines partially duplicate the NO_x-PM trade-off found in conventional diesel engines. Achieving simultaneous NO_x and PM reductions without sacrificing other emission limits requires careful optimization of NP type, concentration, and engine operating parameters.

10. FUTURE RESEARCH DIRECTIONS

10.1 Green and Sustainable Synthesis of Nano-additives

Future studies should focus on environmentally benign synthesis techniques, such as hydrothermal processes devoid of dangerous chemicals, microbial synthesis, and biogenic synthesis employing plant extracts (phytosynthesis). Comparable catalytic activity has been shown by green-synthesized NPs, which also have cheaper synthesis costs and less of an impact on the environment.

10.2 Hybrid and Ternary Nano-additive Systems

A possible direction is the creation of multi-component hybrid NP systems designed for particular engine types. Superior performance-emission trade-offs could be achieved by hybrid NPs that combine the oxygen buffering of Al2O3 with the surface energy increase of GO, or the thermal conductivity of CNTs with the catalytic activity of CeO_2.

10.3 Nano-coatings and Nano-structured Engine Components

Nanotechnology can be used on engine surfaces in addition to fuel additives by applying nano-coatings (TiO_2, AlO_3, and YSZ thermal barrier coatings) to combustion chambers, cylinder liners, and piston crowns. In addition to fuel-borne NP addition, these coatings can catalytically stimulate surface combustion processes, lower heat losses, and improve combustion temperature uniformity.

10.4 Integration with Hydrogen and Ammonia Fuels

HCCI and RCCI engines running on green hydrogen and ammonia will need specific nano-additives to control ignition behavior when the energy transition quickens (hydrogen has a broad flammability range, while ammonia has a high resistance to ignition). NPs that alter these fuels' reactivity—more especially, lowering the ignition delay of ammonia while regulating the knock tendency of hydrogen—represent urgent research demands.

10.5 Long-term Engine Durability Studies

It is imperative to conduct systematic research on the wear, deposit formation, and material compatibility of engine components under extended operation of fuel supplemented with nanoparticles. Short-term experimental investigations predominate in the current literature; long-term endurance data are required for evaluating commercial viability.

10.6 Regulatory and Standardization Framework

Industrial adoption is hampered by the lack of defined procedures for NP fuel additive testing, classification, and safety evaluation. It is necessary to create regulatory frameworks with particular requirements for NP size, composition, concentration limits, and exhaust NP emission norms that are comparable to those for conventional gasoline additives.

11. CONCLUSIONS

The use of nanotechnology in dual fuel, HCCI, and RCCI engines has been thoroughly investigated in this review, which has included nanoparticle kinds, methods of action, performance and emission implications, and practical problems. It is possible to reach the following important conclusions:

- ✓ With highest improvements of 24.7% in dual fuel mode (Al_2O_3 @ 50 ppm) and 18.31% in HCCI-DI mode (Al_2O_3 + $FeCl_3$), nanotechnology continuously increases BTE in all three engine types.
- ✓ Significant emission reduction is achieved by metal oxide nanoparticles (NPs): in different configurations, they reduce CO by up to 80%, HC by up to 71%, and NO_x by up to 42.7% (CeO_2).
- ✓ In the HCCI mode, where charge homogeneity is crucial, carbon-based NPs (CNTs, graphene oxide) show the greatest improvement in thermal conductivity. Al_2O_3 + CeO_2 combinations show simultaneous decreases in NO_x, CO, HC, and smoke. Hybrid NP systems that combine metal oxide and carbon-based NPs yield synergistic effects.
- ✓ Nanoparticle modification of the HRF reactivity is advantageous for RCCI engines because it allows for simultaneous NO_x-PM reduction, which is the main difficulty of this combustion mode, and more precise control over combustion phasing.
- ✓ With ANN, RF, and DNN-GOA models attaining prediction accuracies above 99%, machine learning integration with nanoparticle engine research is speeding up optimization and lowering experimental complexity.
- ✓ NP stability in long-term fuel storage, injector compatibility, toxicological effects, high synthesis costs, and the NO_x-trade-off at high NP concentrations are some of the main obstacles.
- ✓ Green NP production, nano-structured engine coatings, integration with hydrogen/ammonia fuels, and the creation of regulatory frameworks for nanoparticle fuel additives are examples of future directions.

One of the most promising and versatile technologies for attaining clean and efficient combustion in next-generation advanced engines is nanotechnology. To fully realize its promise, interdisciplinary research integrating materials science, combustion engineering, computer modeling, and toxicity must continue.

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