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Review Article

Performance, Emissions, Optimization of Ammonia and Biodiesel Utilization in Compression Ignition Diesel Engines: A Review

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Abstract

The global energy crisis and decarbonization demands emphasize the need for low-carbon fuels that remain compatible with conventional diesel engines. Ammonia and biodiesel have emerged as complementary candidates for compression ignition engine applications. This article summarizes 56 publications discussing engine performance, emission characteristics, and optimization strategies for their use, both separately and in dual-fuel configurations. The study results show that a blend of 40% ammonia and 60% biodiesel can increase thermal efficiency by up to 21.3%, decrease specific fuel consumption by 4.06%, and reduce CO_2 emissions by 6.6% compared to pure diesel. A dual injection strategy with a timing of 25° BTDC proved effective in shortening the ignition delay and increasing heat release. Predictive approaches based on Artificial Neural Network (ANN) and Response Surface Method (RSM) also demonstrated high accuracy ($R^2 > 0.99$). However, significant technical challenges remain, particularly increased NOx emissions, ammonia slip, and N_2O formation. This study confirms the potential of ammonia–biodiesel as a transition fuel towards a low-carbon energy system, requiring the implementation of emission control technologies, precision injection engineering, and adaptive combustion strategies. Open research areas include long-term durability testing, performance in multi-cylinder engines under transient conditions, and the development of a multi-objective optimization algorithm based on the integration of ANN, RSM, and evolutionary methods.

Keywords: *Biodiesel; ammonia; compression ignition engines; exhaust emissions; dual-fuel combustion.*

1. Introduction

The global environmental crisis is increasingly fueled by reliance on fossil fuels, which are a major contributor to CO_2 emissions and accelerated global warming [1]. Diesel engines, despite their high thermal efficiency, remain a significant source of CO_2, NO_x, and harmful particulate emissions [2]. This phenomenon is not only an ecological threat but also a multidimensional pressure trigger for the modern energy and transportation system to undergo comprehensive reforms. This situation emphasizes the urgency of a transition to low-carbon fuels that can be integrated without requiring major changes to existing engine technology.

Ammonia (NH_3) is currently gaining attention as a potential carbon-free fuel candidate for internal combustion engines [3]. Its advantages include relatively high volumetric energy density, the availability of large-scale production lines based on renewable energy, and compatibility with existing distribution infrastructure [4]. In practical applications, ammonia is often configured with hydrocarbon fuels such as diesel or biodiesel in dual-fuel systems to overcome its limitations in ignition and flame stability [5], [6]. This naturally presents limitations in the form of high autoignition temperatures, low flame stability, and potential NO_x and ammonia slip emissions, making it a major implementation challenge [7].

Biodiesel, derived from biomass sources such as vegetable oils and animal fats, offers chemical characteristics that make it an attractive alternative energy source. Biodiesel, derived from vegetable oils and animal fats, offers complementary characteristics to ammonia. Its internal oxygen content supports more complete combustion, while its high cetane number accelerates reaction initiation [8]. However, biodiesel has drawbacks such as high viscosity, the potential for increased NO_x emissions, and corrosive effects on fuel injection systems.

Experimental and simulation studies have shown that ammonia-biodiesel blends have the potential to reduce carbon emissions without compromising engine performance [9]. Adjusting the injection strategy and blend ratio are key factors in optimizing combustion efficiency. Innovations such as multi-stage injection, in-situ hydrogen reforming, and artificial intelligence (ANN) and response surface method (RSM)-based approaches have proven promising in extending the operational range of dual-fuel systems [10]. Previous research also reported that the addition of 10% to 30% biodiesel increases ignition delay, peak cylinder pressure, and heat release rate, thus affecting the thermal dynamics of the combustion chamber [11].

Considering the urgency of the energy transition and the need for low-carbon fuel solutions that are compatible with existing engine technology, this article aims to present a comprehensive scientific review of the use of ammonia and biodiesel in Compression Ignition (CI) diesel engines. The study focuses on fuel characteristics, their effects on engine performance and emissions, and the effectiveness of ANN and RSM-based optimization strategies. The study's main contributions are identifying research gaps, mapping emerging technological approaches, and offering technical policy directions to encourage the development of feasible and sustainable low-carbon dual-fuel systems.

2. Materials and Methods

This article is structured as a systematic literature review focusing on the utilization of ammonia and biodiesel in compression ignition diesel engines. The method used not only maps and classifies scientific sources but also conducts a thematic synthesis to identify trends, challenges, and development directions for dual-fuel systems. A schematic of the study methodology is shown in Figure 1.

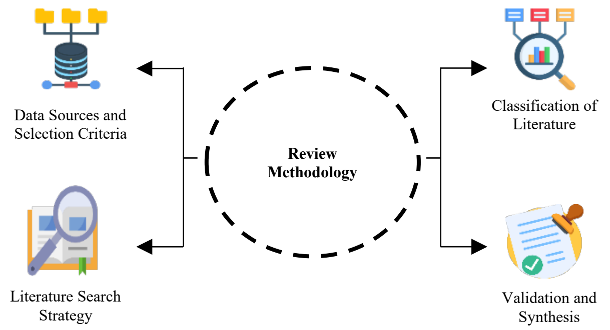

Figure 1. Review methodology scheme.

The study is structured progressively. The initial section describes the basic characteristics of ammonia and biodiesel, followed by a discussion of dual-fuel strategies and their effects on engine performance. The analysis is then expanded to include key exhaust emissions, predictive modeling-based optimization strategies, and a critical evaluation of research gaps and technology development prospects. Literature sources were obtained from the ScienceDirect, IEEE Xplore, SpringerLink, and MDPI databases using the following keyword combinations: "ammonia fuel" OR "NH_3 combustion," "biodiesel," "diesel engine" OR "compression ignition engine," "emissions" OR "performance," and "dual fuel" OR "co-combustion." The search process yielded over 300 articles. After screening based on title and abstract, 103 articles were selected, and 56 articles were retained as the primary sources for the analysis in Figure 2.

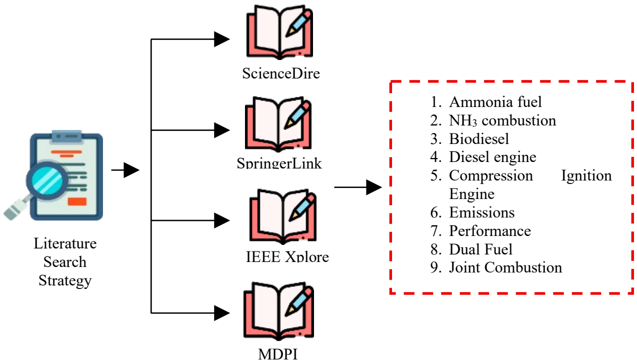

Figure 2. Literature search scheme.

Inclusion criteria included: (1) publication between 2015–2025, (2) focus on the utilization of ammonia, biodiesel, or their combination in CI diesel engines, and (3) use of experimental, numerical, or review approaches with data on performance, thermal efficiency, emissions, and fuel injection strategies. Conversely, articles that discussed ammonia outside the context of CI engines, were available only as abstracts, or did not present empirical data were excluded from the analysis. This selection approach ensured that the studies remained relevant to current technological developments and representative of research needs. The selected articles were classified into four main categories: (1) fuel physicochemical characteristics, (2) engine performance, (3) exhaust emission profiles, and (4) optimization strategies and predictive modeling (Figure 3). This classification allowed for a structured and comprehensive discussion of the technical and environmental implications of the ammonia–biodiesel dual-fuel system.

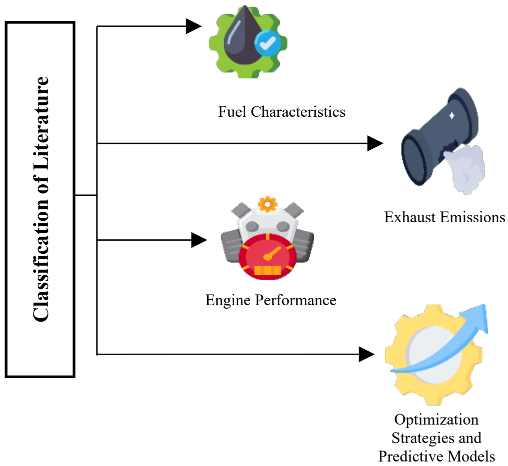

Figure 3. Main categories of research focus.

Data analysis was performed by examining operational parameters such as injection pressure, ignition timing, fuel mixture ratio, and combustion chamber temperature. Results from various studies were compared to identify consistent patterns, such as the relationship between ammonia–biodiesel mixture ratio and specific fuel consumption (BSFC), thermal efficiency, and emission characteristics. A synthesis of the results is presented within a thematic discussion framework visualized in Figure 4, allowing for objective generalizations and identifying future research directions.

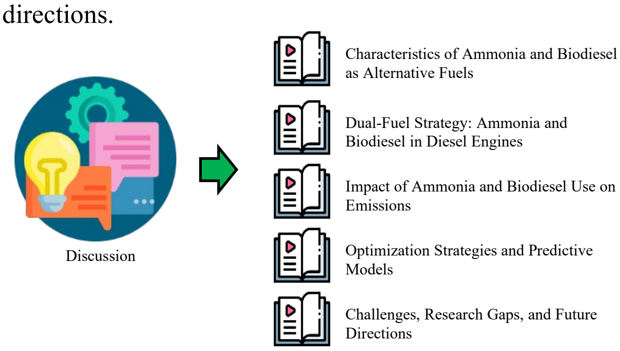

Figure 4. Discussion of journal article review results.

3. Results And Discussion

This section presents a thematic synthesis of key findings related to the utilization of ammonia and biodiesel in dual-fuel systems for compression ignition diesel engines. An analysis of 56 experimental and numerical studies categorizes the results into four main aspects: (1) physicochemical characteristics of the fuel, (2) effects on combustion and engine performance, (3) impact on exhaust emissions, and (4) predictive model-based optimization strategies. Each aspect is comparatively evaluated based on operational variables, including mixture ratio, injection pressure, ignition timing, and injection pattern. This synthesis not only summarizes experimental trends but also assesses the effectiveness of the technologies and highlights research gaps that require further study.

3.1 Characteristics of Ammonia and Biodiesel as Alternative Fuels

The physicochemical properties of ammonia and biodiesel determine their suitability as alternative fuels, particularly in dual-fuel compression ignition systems that rely on flame stability, combustion rate, energy density, and emission profiles [12]. Ammonia offers the advantage of being a carbon-free fuel with a high octane rating and infrastructure compatibility, but is limited by its low energy density (18.6 MJ/kg) and high autoignition temperature (~650 °C), which prolongs ignition delay and increases the risk of NO_x and residual NH_3 emissions [13], [14], [15], [16], [17].

In contrast, biodiesel (FAME) offers a high cetane number (50–60) and an oxygen content of 10–12%, accelerating initial ignition and reducing CO, HC, and particulate emissions [18, 19], although it has the potential to increase NO_x due to its high combustion temperature [20]. The synergy of both fuels has been shown to be thermally and environmentally effective: biodiesel accelerates the formation of reactive radicals (OH, CH_3O) that favor ammonia decomposition, improving flame stability and combustion efficiency while reducing carbon emissions [21]. Dimitriou and Javaid [22], reported that configurations with ammonia energy fractions up to 95% maintained efficiency, as long as injection parameters and ignition timing were optimized.

3.2 Dual Fuel Strategy between Ammonia and Biodiesel in Diesel Engine

A dual-fuel strategy in diesel engines offers an efficient decarbonization solution, utilizing ammonia as a carbon-free fuel and biodiesel as a high-cetane pilot fuel [23]. This configuration can reduce fossil fuel consumption and GHG emissions without major engine modifications. In pilot injection mode, ammonia is supplied through the intake manifold, while biodiesel is injected directly into the combustion chamber to trigger ignition. Biodiesel shortens the ammonia ignition delay (~650°C, cetane number <10) by forming reactive radicals that accelerate thermal decomposition [24], [25], [26].

Alternatively, direct dual injection schemes using staged or differential injection techniques allow precise control of the mixture ratio, ignition timing, heat distribution, and cylinder pressure, resulting in increased efficiency and reduced emissions [25], [26], [27], [28]. The integration of in-situ reforming has also been shown to thermally generate hydrogen, accelerating combustion kinetics and reducing NH_3 and N_2O emissions [29]. The effectiveness of this configuration is measured through the Ammonia Energy Share (AES). Studies show that AES of 40–70% is suitable for partial loads [30], [31]; while AES of 60–80% is optimal for medium to high loads with significant CO_2 reduction. AES >80% is only stable if supported by multi-stage injection, peak temperature cooling (e.g., via EGR), or in-situ reforming. For example, the A40 configuration (40% ammonia, 60% citronella biodiesel) successfully reduced CO_2 emissions [32], and energy replacement of up to 69.4% with ammonia has been achieved without compromising engine stability [30]. On the other hand, low AES configurations such as D/B/N7.5 (7.5% ammonia) were reported to improve thermal efficiency (BTE) and reduce specific fuel consumption (BSFC) [33]. Schematic diagram of dual injection and ammonia–diesel/biodiesel fuel flow in a diesel engine in Figure 5.

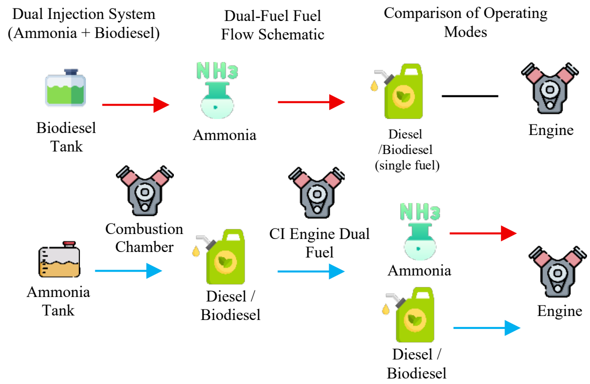

Figure 5. Schematic diagram of dual injection and ammonia–diesel/biodiesel fuel flow.

3.2.1 Combustion and Engine Performance

The ammonia and biodiesel dual-fuel configuration exhibits complex combustion dynamics but offers significant potential for improving diesel engine efficiency. As shown in Figure 6, ammonia serves as the primary fuel, while biodiesel acts as a pilot fuel, promoting early ignition due to its high cetane number and combustion stability. This combination is designed to overcome ignition delays caused by ammonia's high autoignition temperature (~650°C) and low cetane number. The classification of the impact of using a dual fuel configuration of ammonia and biodiesel can be seen in Figure 6.

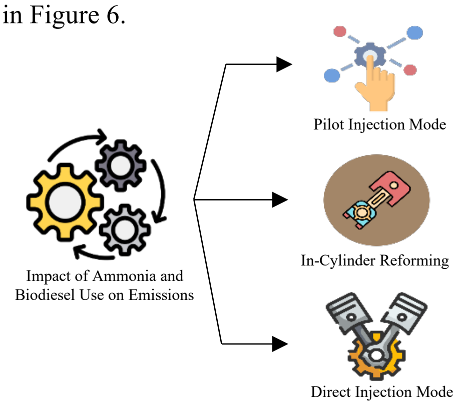

Figure 6. Dual-fuel configuration of ammonia and biodiesel.

Two approaches are commonly used: (1) intake fumigation and DI biodiesel, where ammonia is routed through the manifold and biodiesel is injected directly; and (2) dual direct injection (DDI) with staged or differential modes, which allows precise control of ignition delay, heat release rate (HRR), SOI, and injection pressure. The DDI configuration has been shown to regulate heat distribution, maintain flame stability at high AES, and reduce NO_x emissions [30], [34]. Nadimi et al. [30], showed that substitution of up to 69.4% biodiesel with ammonia maintained BTE. Similar results were reported by Elkelawy et al. [34], who noted an increase in BTE from 20.5% to 23.5% and a decrease in BSFC from 455.56 g/kWh to 391.08 g/kWh using a blend of ammonia hydroxide and diesel. This correlation supports the importance of precise injection timing to optimize premixed combustion and prevent excessive heat release early in the cycle.

The ammonia-biodiesel ratio significantly affects HRR. A high biodiesel fraction accelerates ignition, while ammonia dominance without an adequate injection strategy risks causing a cylinder pressure spike [35]. Cheng et al. [36] emphasized that the stability of a dual-fuel system is highly dependent on the duration of the pilot fuel chemical delay. A study by Uyumaz et al. [37] also highlighted the potential of biodiesel from poppy seed oil as a non-food alternative with competitive thermal performance and reduced particulate emissions.

The addition of ammonia–water (25%) to diesel fuel has also been reported to affect combustion kinetics: ignition delay increases and combustion duration is prolonged, but HRR remains high and flame stability remains within operational limits [38]. Temizer and Cihan [39] showed that the addition of 3–6% hydrogen to canola biodiesel blends (B10, B20) increases peak pressure and combustion homogeneity, with the best performance achieved with B20 and 6% H_2. AVL-FIRE simulations support these findings. A study by İnce et al. [40] showed that B10 in a single-cylinder diesel engine increases power and torque and reduces BSFC by up to 17.54% compared to pure diesel (D100). However, the high oxygen content of B10 and B20 also increases NO_x and CO_2, highlighting a trade-off between efficiency and emissions, necessitating further optimization strategies.

Summary of Experimental Findings:

- B10 and B20 blends increase in-cylinder pressure compared to D100.
- Ignition delay in ammonia–biodiesel blends is shortened by higher biodiesel fractions, especially at low loads.
- Thermal efficiency tends to decrease with higher biodiesel fractions due to the lower calorific value.

3.2.2 Dual Fuel Experimental Study

A series of experimental studies confirmed the effectiveness of an ammonia–biodiesel dual-fuel system in improving diesel engine performance and efficiency. Ramalingam et al. [38] reported that a blend of 40% ammonia with 60% biodiesel not only increased thermal efficiency by 5.4%, but also reduced NO_x emissions by 17%, CO_2 by 6.6%, and smoke by 9.8%. These findings highlight the synergy between the two fuels in reducing emissions without compromising engine performance. Similar results were reported by Elkelawy et al. [33], who demonstrated a 21.26% increase in thermal efficiency across five blends, accompanied by a 4.06% decrease in specific fuel consumption (BSFC), and significant reductions in NO_x and CO emissions compared to conventional diesel. Nadimi et al. [41] explored higher ammonia ratios, up to 84% of total energy, and found that engine stability was maintained. However, a spike in NO_x emissions was recorded when inadequate emission controls were not in place. These findings align with Cheng et al. [36] , who emphasized that pilot injection timing is crucial to prevent pressure surges and excessive heat release, especially in premixed combustion modes. An additional study by Ramalingam et al., [38] showed that the use of a 25% ammonia–water blend in diesel fuel prolonged the ignition delay and combustion duration, although the HRR remained high and efficiency was not significantly degraded. This suggests that combustion dynamics can remain manageable as long as the blend characteristics are properly controlled. Temizer and Cihan [39] evaluated the addition of hydrogen (3–6%) to canola biodiesel blends (B10 and B20), and found increased peak pressure, more homogeneous mixture distribution, and the highest combustion stability in B20 + 6% H_2. These findings were confirmed by CFD simulations using AVL-FIRE. Meanwhile, İnce et al., [40] reported that the use of B10 in a single-cylinder diesel engine resulted in increased torque and power, as well as a 17.54% reduction in BSFC compared to D100. The use of B10 and B20 also reduced smoke opacity, although this resulted in increased NO_x and CO_2 emissions due to the high oxygen content in biodiesel. These findings highlight the trade-off between thermal efficiency and emissions, which requires further optimization of combustion strategies. Summary of the results of the experimental study of biodiesel and its mixtures in diesel engines can be seen in Table 1.

Table 1. Summary of experimental study results of biodiesel and its blends in diesel engines.

Engine Type and Operating Conditions	Fuel Type / Mixture Ratio	Focus and Parameters	Results	Ref.
Diesel engine, dual fuel mode	40% ammonia and 60% biodiesel	Efficiency and emissions	Efficiency up 5.4%; NOx emissions down 17%; CO_2 down 6.6%; smoke down 9.8%.	[38]
Diesel engine with five mixture variations	Ammonia-biodiesel vs. pure diesel	Efficiency, fuel consumption, emissions	Efficiency increased by 21.26%; fuel consumption decreased by 4.06%; NO_x and CO were lower than pure diesel.	[33]
Diesel engine, stability test	84% NH_3 and 16% biodiesel	Stability and emissions	Stable operation maintained; NO_x increased without aftertreatment	[41]
Diesel engine, pilot injection strategy	Ammonia and biodiesel	Combustion process	Injection timing critical to avoid excessive heat release and peak pressure	[36]
Diesel engine with ammonia–water–diesel blend	25% ammonia, air and diesel fuel	Combustion characteristics	Longer ignition delay; extended combustion duration; high HRR maintained	[38]
Direct-injection diesel + AVL-FIRE simulation	B10 and B20 biodiesel canola as well as 3%–6% hydrogen	Performance and combustion	Peak pressure and heat release rate increase; fuel distribution is more even; B20 and 6% H_2 provide the most stable flame and highest efficiency.	[39]
Single-cylinder, 4-stroke, air-cooled diesel	D100, B10, B20	Power, torque, fuel consumption, emissions	B10 increases power, torque, and reduces fuel consumption by 17.54%; B10 and B20 reduce smoke, but increase NO_x and CO_2.	[40]

3.3 Impact of Ammonia and Biodiesel Use on Emissions

Exhaust emission analysis is a fundamental component in assessing the technical, environmental, and sustainable feasibility of using alternative fuels in compression ignition engines. Conventional diesel engines generally produce emissions consisting of CO_2, NO_x, hydrocarbons (HC), carbon monoxide (CO), and significant amounts of particulate matter. Partial or complete substitution of diesel with ammonia or biodiesel results in changes in combustion characteristics that directly impact these emission patterns.

Ammonia is known as a carbon-free fuel; however, its complex combustion kinetics often result in ammonia slip (incompletely burned NH_3) and the formation of nitrous oxide (N_2O), both reactive pollutants that contribute to air quality degradation and increased global warming potential [31]. On the other hand, biodiesel through its natural oxygen content can reduce CO_2 and particulate matter emissions when used in diesel engines. However, various studies consistently show that both ammonia and biodiesel have a tendency to increase NO_x formation through thermal and NO-prompt mechanisms.

These findings indicate that the assumption regarding the potential of these two fuels to balance each other's environmental impacts has not been fully proven. In fact, their simultaneous use has the potential to increase the production of reactive nitrogen compounds, necessitating a more comprehensive emissions control strategy. Therefore, the implementation of a decarbonization pathway based on an ammonia-biodiesel blend must be accompanied by the implementation of NO_x mitigation technologies, such as selective catalytic reduction (SCR), exhaust gas recirculation (EGR), or intelligent control-based combustion parameter optimization.

To provide a more systematic analytical overview, the emissions evaluation in this study is classified into several main groups: CO_2, CO and HC, NO_x, NH_3 slip, N_2O, and particulates/soot. The reduction magnitude of each parameter is calculated using Equation (1), while the interaction between the variables is visualized in Figure 7. This relationship pattern demonstrates a clear trade-off between reducing carbon emissions and increasing nitrogen oxide components, particularly under oxygen-rich combustion conditions and high peak temperatures.

$$\text{Reduction (\%)} = \frac{X_{diesel} - X_{blend}}{X_{diesel}} \, x \, 100\% \tag{1}$$

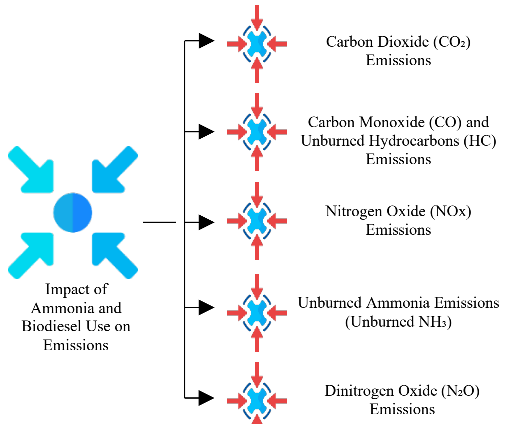

Figure 7. Impact of ammonia and biodiesel use on emissions.

3.3.1 Carbon Dioxide (CO_2) Emissions

As a carbon-free compound, ammonia does not produce CO_2 during combustion, unlike conventional fossil fuels such as diesel. This characteristic makes ammonia one of the most promising candidates for decarbonization strategies for the transportation sector, maritime industry, and internal combustion engine-based power plants [42]. In dual-fuel configurations, the use of ammonia has consistently been reported to reduce CO_2 emissions without decreasing thermal efficiency; some studies even indicate increased efficiency due to the more stable reactivity of the mixture.

Ramalingam et al. [32] found that the magnitude of CO_2 reduction is influenced by the ammonia energy share (AES), injection strategy, and engine operating conditions. For example, an A40 blend consisting of 40% ammonia and 60% citronella biodiesel in a low-temperature combustion engine configuration based on RCCI can reduce CO_2 emissions by up to 6.6% compared to pure diesel. Meanwhile, in large-scale maritime engine applications, the application of in-cylinder reforming gas recirculation (IRGR) techniques has been reported to reduce CO_2 emissions by up to 97% [29]. In theoretical scenarios, the use of pure ammonia has the potential to completely eliminate CO_2 emissions, although strict control of NO_x emissions is required [43], [44]. A comparison of research results related to CO_2 reduction is shown in Table 2.

Table 2. Results of comparison of carbon dioxide emissions.

Method	Operation Condition	CO_2 Reduction (%)	Insight	Ref
A40 (40% ammonia + 60% biodiesel citronella)	Low-Temperature Combustion Engine – Reactivity Controlled Compression Ignition (LTC–RCCI)	6.6%	Good flame stability, suitable for partial loads	[32]
Ammonia-Diesel Dual Fuel (AES ≥ 35.9%)	Marine diesel engines	97%	Reformed hydrogen enhances combustion; CO_2 reduction is very significant	[29]
IRGR (In-cylinder Reforming Gas Recirculation)	CI engine/ generator	100%	Does not produce CO_2; the main constraints are combustion stability and Nitrogen Oxides (NO_x) emissions.	[43], [44]

3.3.2 Carbon Monoxide (CO) and Unburned Hydrocarbons (HC) Emissions

The use of ammonia as a primary fuel tends to increase CO and HC emissions, mainly due to incomplete combustion due to ammonia's low reactivity. Conversely, the use of biodiesel as a pilot fuel can help reduce these emissions by improving initial flame stability. A study by Elkelawy et al. [33], showed that the D20B80N7.5 blend, containing a higher portion of biodiesel, produced lower CO and HC emissions than a diesel-dominated blend. In addition, injection strategies such as split injection and ignition timing adjustment have been shown to reduce CO emissions by up to 25% compared to conventional combustion. The results of the study on CO and HC emissions from the use of ammonia as a fuel can be seen in Table 3.

Table 3. Carbon monoxide and unburned hydrocarbons emissions.

CO Emission Results	HC Emission Results	Description	Ref.
Down 21.4%	Reduced 15.68%	Optimal split injection	[38]
Decrease	Increased (33 ppm vs 14 ppm on diesel)	Incomplete combustion due to low temperature	[33]
Decrease	Not reported quantitatively	NH_3/CH_4 produces lower CO	[45]
Decrease	Decrease	A40 (40% NH_3 + citronella) showed high combustion efficiency.	[32]
Down 3.8%	Down 10.4%	The addition of NH_3 increases evaporation and mixing.	[46]

3.3.3 Nitrogen Oxide (NO_x) Emissions

Various fuel injection parameters significantly influence the combustion and emission characteristics of ammonia-fueled engines. Increasing Total Start of Injection (TSOI) has been shown to shorten ignition delay, accelerate combustion, and suppress NO_x and N_2O emissions, although this is accompanied by an increase in ammonia slip. Setting the Start of Ammonia Injection (SOAI) at 8° CA ATDC has been reported to reduce NO_x emissions by more than 50%, while higher Ammonia Injection Pressure (AIP) improves combustion quality but tends to increase N_2O [47]. The impact of these parameters depends on the type of emissions observed. At high Ammonia Energy Share (AES), N_2O emissions can increase up to >1000 times compared to n-heptane, but remain low under optimal conditions (high temperature and low equivalence ratio). NO_x emissions are formed through three main pathways fuel-NO, prompt-NO, and thermal-NO with thermal-NO dominant above 2600 K. Meanwhile, the potential for soot formation decreases with lower carbon content. The soot formation equivalence ratio limit was recorded at $\varphi = 2.20$ for n-heptane, $\varphi = 2.65$ (AES 20%), $\varphi = 5.05$ (AES 50%), and was not reached at AES ≥ 80%, confirming that the ammonia-based mixture has a very low tendency towards soot formation [48]. The summary of NO_x emission results is shown in Table 4.

Table 4. Nitrogen oxide emissions.

NO_x Emission Results	Description	Ref.
Increase	Because of the nitrogen in the fuel NH_3	[22]
Decreased (to 91.2% N_2O)	With IRGR (in-cylinder reforming circulating gas)	[29]
Decrease	Because the exhaust temperature is lower	[34]
Decreasing (in rich condition)	The use of H_2/CH_4 on NH_3 limits NO_x	[45]
Down 17%	The result of A40 mixture in RCCI engine	[32]

3.3.4 Unburned Ammonia Emissions

One critical aspect of the ammonia combustion process is the formation of unburned ammonia due to slow reaction kinetics and combustion characteristics that tend to be difficult to trigger. The presence of NH_3 in the exhaust gas not only reflects the imperfection of the oxidation process, but also has significant toxicological and environmental implications. This compound has an acute irritating effect on the respiratory system, and contributes to the formation of secondary particulates through atmospheric reactions with acidic compounds. Therefore, controlling ammonia slip is a major technical challenge in the development of ammonia-fueled engines and dual-fuel configurations. Zhou et al. [29], showed that, under operating conditions without an integrated emission control strategy, the concentration of unburned NH_3 can reach 250 ppm–350 ppm. This value is far above the exposure limits recommended by occupational safety standards and international ambient air quality guidelines, so it cannot be ignored in practical implementation. These findings underscore the urgency of implementing appropriate mitigation technologies, such as catalytic oxidation, equivalence ratio optimization, in-cylinder reforming, or temperature-based control strategies, to ensure that ammonia utilization does not pose secondary environmental risks. A summary of ammonia slip measurement results from various experimental and simulation studies is presented in Table 5, which shows variations in NH_3 emission concentrations based on fuel configuration, injection strategy, engine operating conditions, and the presence of additional emission control technologies.

Table 5. Summary of unburned ammonia emission results under various conditions.

NH_3 Emission Results	Operating Condition / Method	Description	Ref
High	General observation	Indicates the need for after-treatment technology	[22]
Down 89.3%	Implementation of IRGR (Internal EGR)	Significant reduction achieved with IRGR method	[29]
High (14,800 ppm)	Diesel–ammonia dual-fuel combustion	Substantial unburned NH_3 observed in dual-fuel mode	[41]

3.3.5 Dinitrogen Oxide (N_2O) Emissions

Nitrous oxide (N_2O) is a greenhouse gas with a global warming potential approximately 298 times greater than CO_2. This gas is formed in significant quantities when ammonia combustion occurs at moderate temperatures, especially when incomplete combustion occurs. A study by Jang et al. [49] noted that N_2O emissions can reach 0.3–0.5 g/kWh at high ammonia ratios. Controlling these emissions remains a major challenge, requiring high-precision combustion technology and effective post-combustion systems. Overall, the combination of ammonia and biodiesel in a dual-fuel system has great potential to reduce carbon emissions, but still carries the risk of reactive nitrogen emissions. The success of its implementation is largely determined by the combustion strategy, adaptive injection system design, and the integration of appropriate post-emission technologies.

3.3.6 Soot Emissions

Soot formation in diesel engines generally results from the incomplete combustion of carbon-rich fossil fuel mixtures. Ammonia, as a carbon-free fuel, does not form particle nuclei through the hydrocarbon pyrolysis pathway, thus theoretically eliminating the potential for soot formation. A study by Pedersen et al. [48] showed that increasing the Ammonia Energy Share (AES) significantly reduced the propensity for soot formation. At AES ≥ 80%, the equivalence ratio for soot initiation was not reached, resulting in near-zero particulate emissions. Even at AES of 20–50%, the equivalence ratio limit for soot formation increased (φ = 2.65–5.05), significantly higher than that of n-heptane (φ = 2.20), indicating a significant reduction. Biodiesel as a pilot fuel also contributes to reduced soot emissions. Its internal oxygen content accelerates carbon oxidation during the diffusion phase of combustion [19]. However, a high biodiesel fraction can increase peak temperatures and promote NO_x formation. Therefore, blend ratio optimization strategies need to consider the balance between soot reduction and reactive nitrogen emission control. A summary of factors affecting performance and emissions in the ammonia–biodiesel system can be seen in Table 6.

Ammonia–Biodiesel System Emission Summary:

- Biodiesel reduces CO, HC, and particulate matter, but tends to increase NO_x.
- Ammonia substitution of up to 80% can reduce CO_2 emissions by >90%, but has the potential to increase CO, HC, and NH_3 slip.
- Soot formation is virtually eliminated in blends with a high ammonia fraction.

Table 6. Summary of factors affecting performance and emissions in ammonia–biodiesel systems.

Parameters	Increasing Factors	Decreasing Factors	Determining Factors
NOx	• High ammonia fraction without control [41], [48] • Long ignition delay [47] • Small pilot or late injection [31]	• Retard timing or split injection [47], [50] • Dual injection staged [28] • Lean burn, EGR, SCR [29], [34]	• Peak temperature, • Combustion phasing, • N content
CO & HC	• Low load with high AES [33], [41] • Low combustion chamber temperature [33] • Pilot too small/retarded [31]	• High cetane biodiesel pilot [32], [33] • Split injection [48] • High injection pressure [47]	• Flame stability, • Oxidation, internal oxygen
N_2O	• High AES, medium temperature [48] • Long ignition delay [41] • High EGR [29]	• High temperature lean burn [48] • In-situ hydrogen reforming [29] • Fast injection [47]	• Temperature 900–1100 K, • Fuel-N_2O pathway
Soot	• Poor atomization [37] • Low injection pressure [31]	• AES ≥80% (nearly zero soot) [44], [48] • Oxidative pilot biodiesel [18], [41] • Precise injection staging [29], [48]	• Fuel carbon, • Internal oxygen, • Mixture homogeneity
BTE	• Moderate AES (40–60%) [32], [33] • Optimal CA50 [47] • In-cylinder hydrogen reforming [29]	• High AES without optimization [41], [48] • Low load (quenching) [36]	• Combustion phasing, • Injection strategy,
BSFC	• Low calorific value high AES [41], [48] • Low efficiency, high CO/HC [33]	• Injection optimization (ANN, RSM, GA) [32], [33], [50] • In-cylinder reforming [29] • Moderate AES with biodiesel pilot [32], [33]	• Mixture calorific value, • Thermal efficiency, • Injection optimization

3.4 Optimization Strategies and Predictive Models

Nitrous oxide (N_2O) is a greenhouse gas with a global warming potential approximately 298 times greater than CO_2. In diesel engine regulations, the N_2O emission threshold is typically set at 0.3g/kWh. However, a study by Elbaz et al. [51] showed that in an ammonia–biodiesel dual-fuel system, N_2O emissions can reach 0.3–0.5g/kWh, well within or even exceeding the recommended limit. This increase generally occurs during combustion at intermediate temperatures, particularly if the ignition delay is long or the flame is unstable. Therefore, combustion strategies need to be optimized so that the decarbonization benefits of ammonia are not offset by spikes in reactive nitrogen emissions. Mitigation measures include: (i) adjusting the ammonia–biodiesel energy ratio to maintain flame stability; (ii) adjusting the biodiesel injection timing to shorten the ignition delay and control the rate of heat release; and (iii) the application of staged or differential injection that effectively reduces local temperature peaks and N_2O emissions without sacrificing efficiency [47], [50]. Integrating these strategies into an adaptive combustion model allows for real-time parameter adjustment, maintaining engine performance while minimizing N_2O emissions.

3.4.1 Dual Fuel Injection Strategy

Injection timing and pattern play a key role in ammonia–biodiesel dual-fuel systems because they directly affect the ignition process, combustion stability, and emission characteristics. Three main strategies commonly applied in the literature include.

(1) Pilot Injection

This strategy injects a small portion of biodiesel early to trigger ammonia ignition through the formation of active radicals (OH·, CH_3O·). Elumalai et al. [50] reported that injection at 25° BTDC increased Brake Thermal Efficiency (BTE) by 7.5% and reduced CO and HC emissions. The increase in BTE can be explained by Eq. (2):

$$\eta_{bth} = \frac{P_b}{\dot{m}_f x LHV} \text{x } 100\% \tag{2}$$

(2) Multi-Stage Injection

Injection is divided into two or more stages to regulate heat distribution and reduce the rate of peak pressure rise. Chiong et al. [52] showed that this strategy effectively suppresses NO_x at high ammonia energy fractions. The total energy can be calculated using Eq. (3).

$$Q_{total} = \sum_{k=1}^{n} \dot{m}f, k \text{ x LHV} \tag{3}$$

(3) Injection Pressure and Equivalence Ratio (ϕ) Settings

High pressure improves fuel atomization, resulting in a more homogeneous mixture. The equivalence ratio is calculated using Eq. (4).

$$\phi = \frac{(F/A)_{actual}}{(F/A)_{stoich}} \quad (4)$$

Operating under lean conditions ($\phi < 1$) has been shown to reduce combustion temperature and NO_x emissions. Overall, the application of pilot injection, staged injection, and pressure and ϕ regulation are strategic foundations for achieving high thermal efficiency while controlling reactive carbon and nitrogen emissions in an ammonia–biodiesel dual-fuel system.

3.4.2 Application of Artificial Neural Network (ANN)

The complexity of ammonia-biodiesel dual-fuel systems is often difficult to address using conventional experimental approaches or deterministic models, primarily due to the non-linear relationships between parameters. In this context, Artificial Neural Networks (ANNs) have proven effective in predicting engine performance and optimizing operational parameters. Elkelawy et al. [52], developed an ANN model based on experimental data to map the effects of fuel ratio (diesel/biodiesel/ammonia) and injection angle on outputs such as thermal efficiency (BTE), specific fuel consumption (BSFC), and NO_x and CO emissions. The model demonstrated high accuracy with an $R^2 > 0.99$, confirming the reliability of ANNs in engine performance modeling. The advantages of ANNs include their ability to handle complex parameters, time efficiency compared to direct testing, and the potential to identify optimal configurations without trial and error. ANNs can also be used to design fuel injection maps, accelerate engine calibration, and support artificial intelligence-based control systems. Furthermore, the combination of ANN with optimization methods such as RSM or Genetic Algorithm (GA) improves design process efficiency and overall system performance. This approach opens up opportunities for developing smarter and more adaptive combustion engines, supporting the transition to low-carbon energy technologies.

3.4.3 Response Surface Method (RSM)

Response Surface Method (RSM) is a statistical technique used to design experiments, analyze interactions between variables, and build quadratic equation-based predictive models for multi-objective optimization. In a study by Krishnamoorthy et al. [32], RSM was applied to evaluate the effect of ammonia substitution ratio, injection pressure, and ignition angle on thermal efficiency (BTE) and NO_x emissions. The results showed that the optimal configuration was achieved at 60% ammonia substitution, 700 bar injection pressure, and 27° BTDC injection angle, resulting in the highest BTE and the lowest NO_x emissions. The advantages of RSM lie in its efficiency in reducing the number of experiments, visually identifying parameter relationships, and providing reliable statistical model-based optimization solutions for engine operation settings.

3.4.4 Integration of ANN–RSM and Evolutionary Algorithms

The integration of Artificial Neural Networks (ANNs) and Response Surface Method (RSM) with evolutionary algorithms such as Genetic Algorithm (GA) and Particle Swarm Optimization (PSO) has proven effective in identifying optimal configurations for ammonia–biodiesel dual-fuel systems. This approach allows for the search for operating parameters that simultaneously maximize thermal efficiency (BTE) and minimize specific fuel consumption (BSFC). Experimental results show that in-cylinder reforming with 70%–80% ammonia energy substitution results in a consistent increase in BTE and decrease in BSFC [29]. Variation in composition from D80B20N7.5 to D20B80N7.5 shows a BTE increase of up to 21.26% and a BSFC decrease of 4.06% [33]. Ammonia energy substitution of 84% can maintain BTE up to 70%, but BSFC increases at higher ratios [41]. Meanwhile, RSM simulations identified an optimal point at 60% ammonia with an injection pressure of 700 bar [32]. The A40 formulation (40% ammonia) also showed a 5.4% increase in BTE compared to diesel [53], and the use of 20%–60% ammonia with a biodiesel pilot resulted in a 6–8% increase in BTE, despite an increase in BSFC [54]. In general, optimization success is determined not only by the ammonia energy ratio, but also by the injection strategy and the application of predictive algorithms capable of adaptively adjusting operating parameters. A comprehensive overview of performance and emission metrics from various experimental studies can be observed in Table 7. Combustion Strategy and Optimization:

- Dual pilot injection and injection timing are effective in reducing ignition delay and controlling NO_x emissions.
- The optimal blend is at a B10–B20 ratio with 40%–60% ammonia substitution, which provides the best balance between efficiency, performance, and emissions.

Table 7. A Comprehensive overview of performance and emission metrics from diverse experimental studies.

Fuel Configuration	Method	Ammonia Energy Substitution	Effect on BTE	Effect on BSFC	Ref.
In-cylinder NH_3 Reforming	Experiment (multi-cylinder)	NH_3 as 70% to 80% of the energy	Steady increase	Decrease	[29]
D80B20N7.5 to D20B80N7.5	ANN and Experiment	7.5% NH_3 in all mixtures	Increase up to 21.26%	Decrease 4.06%	[33]
Ammonia and Biodiesel dual-fuel	Experiment CI engine	84%	Stable up to 70%; decreases above that	Increase when substitution >70%	[41]
RSM – D/B/N Variation	Simulation and Optimization	30% to 70% NH_3	Optimum at 60%	Minimum at 700 bar pressure	[32]
Ammonia 40% and Biodiesel 60%	Experiment	40%	Increase 5.4% over diesel	Significant decrease	[53]
NH_3 with Biodiesel pilot	Experiment	20% to 60%	Increase 6% to 8%	Increase	[54]

3.5 Challenges, Research Gaps, and Future Directions

Although ammonia–biodiesel blends hold promise as low-carbon diesel fuels, their industrial-scale implementation is hampered by the difficult-to-control nature of ammonia. High ignition temperatures (~650°C) and low cetane number (<10) cause ignition delays, misfires, and NH_3 slip at low loads [16], [22], [55]. Furthermore, NO_x emissions increase through thermal and fuel-NO_2 pathways, which still rely on control systems such as EGR, SCR, or lean combustion most of which have not yet progressed beyond the laboratory stage [8], [48], [56]. Most studies have been conducted on single-cylinder engines [28], [30], so the system response to variable loads and transient conditions in multi-cylinder engines is not yet fully understood. Practical experience shows that real-world implementation requires high-precision injection systems, multi-stage strategies, controlled air cooling, and adaptive thermal management. Additional challenges include metal corrosion (especially copper), elastomer damage, lubricant degradation, and component wear all of which have generally not been tested in long-term durability scenarios [35], [51], [56]. Future research directions include: (i) full testing on multi-cylinder engines with varying loads; (ii) integration of ANN–RSM models with multi-objective optimization (NSGA-II, MOPSO); (iii) development of sensor-based injection and closed-loop control; and (iv) long-term field testing to assess performance, material durability, and emissions. Life-cycle cost evaluation and economic analysis are also essential to assess its commercial viability. If technical challenges can be overcome, this system has the potential to be a low-carbon energy transition solution compatible with internal combustion engines.

4. Conclusions

The use of ammonia and biodiesel as alternative fuels in compression ignition diesel engines offers strategic opportunities in the transition to a low-carbon energy system. Ammonia effectively reduces CO_2 and particulate emissions, while biodiesel thanks to its cetane number and oxygen content improves combustion stability. The combination of the two in a dual-fuel system has been shown to improve thermal efficiency, optimize flame characteristics, and reduce fossil fuel consumption. A review of 56 studies shows that ammonia substitution of up to 60% can increase efficiency by up to 20%, accompanied by reductions in BSFC and carbon emissions. However, technical challenges such as increased emissions of NO_x, NH_3 slip, and N_2O remain a concern. Controlling these emissions requires strategies such as injection timing, equivalence ratio optimization, and the implementation of post-combustion systems. Artificial intelligence-based predictive technologies (ANN, RSM) have proven effective in modeling performance and designing optimal operating parameters. The integration of optimization algorithms opens up opportunities for data-driven adaptive combustion systems. Despite its significant potential, issues such as flame stability, the readiness of multi-cylinder injection systems, and the impact of material wear still require further validation, particularly on an industrial scale and in long-term durability testing. By addressing these challenges, ammonia-biodiesel has the potential to become a solution for decarbonizing the transportation sector. Realizing this technology requires cross-sector support from academia, industry, and progressive public policy.

Conflict of Interest

The authors affirm that, to the best of their knowledge and judgment, they have no conflicts of interest whatsoever, whether financial or non-financial. Furthermore, the authors have no affiliations or common interests with any party, including institutions, organizations, or individuals, that could compromise the integrity, objectivity, or independence of the review or preparation of this article.

Credit Author Statement

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Nomenclature

ANN	Artificial Neural Network [-]
AIP	Ammonia Injection Pressure [bar]
AES	Ammonia Energy Share [%]
BTE	Brake Thermal Efficiency [%]
BSFC	Brake Specific Fuel Consumption [g/kWh]
CA	Crank Angle [°]
CI	Compression Ignition [-]
CO	Carbon Monoxide [ppm]
CO_2	Carbon Dioxide [ppm or %]
EGR	Exhaust Gas Recirculation [-]
HC	Hydrocarbon Emissions [ppm]
HRR	Heat Release Rate [J/°CA or kW]
NH_3	Ammonia [-]
NO_x	Nitrogen Oxides [ppm or g/kWh]
N_2O	Dinitrogen Oxide (Nitrous Oxide) [ppm or g/kWh]
RSM	Response Surface Method [-]
SOAI	Start of Ammonia Injection [°CA ATDC]
TSOI	Total Start of Injection [°CA BTDC]
φ	Equivalence Ratio [-]

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