

# Performance, Combustion and Emission Characteristics of Oxygenated Diesel in DI Engines: A Critical Review

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## Abstract

The transition from non-renewable to renewable energy sources is a significant challenge of our time. In the fuel industry, oxygenated additives such as butanol are transforming conventional fuels into renewable biofuels. This technology has been utilized in reciprocating engines for decades. This paper reviews the viability of using an n-butanol blend as a short-term replacement for diesel by analyzing its physical and chemical properties, combustion, performance, and emission characteristics in compression ignition (CI) engines under various conditions, including variable load, speed, acceleration, and both stationary and transient cycles. N-Butanol exhibits higher viscosity, better lubricity, higher heating value, improved blend stability, enhanced cold-flow properties, and higher density. These factors influence spray formation, injection timing, atomization, and combustion characteristics. Its higher oxygen content improves the diffusion combustion stage and efficiency. Adding 5% and 10% n-butanol to diesel increases pressure and apparent heat release rate, slightly reduces temperature, and improves thermal efficiency, with mixed effects on CO and THC emissions and a notable decrease in particulate matter emissions. Fuel consumption increases, while the impact on NO<sub>x</sub> emissions varies. A 10% butanol blend is considered optimal for enhancing performance and reducing particulate emissions without significantly affecting NO<sub>x</sub> emissions. Blending up to 40% butanol with diesel does not require engine modifications or ECU recalibrations in engines calibrated for pure diesel. Due to its advantageous properties and performance, n-butanol is recommended as a superior alcohol-diesel blend than ethanol for short-term diesel replacement.

## Keywords

Diesel Engine, Alcohol Additives, N-Butanol, Combustion and Properties

## 1. Introduction

Internal combustion engines using liquid fuels will continue to be the main power sources for road and air transportation for decades, likely throughout most of this century. The global demand for liquid transportation fuels from petroleum and other fossil resources has grown immensely. This will render the economy unsustainable, becoming infeasible only in the distant future [1]. The use of petroleum oil in transportation significantly contributes to environmental deterioration through emissions such as nitrogen oxides (NO<sub>x</sub>), unburned hydrocarbons (UHC), carbon monoxide (CO), particulate matter (PM), and carbon dioxide (CO<sub>2</sub>). These pollutants accumulate in the atmosphere, contributing to the greenhouse effect, global warming, and climate change. Oxygenates, including alcohols, have emerged as alternatives for improving the octane number and oxygen content in conventional fuels (gasoline, diesel) [2].

Studies, such as one by (Dogan 2011) on compression ignition engines, investigated engine performance and exhaust emissions where alcohol fuels, namely methanol and ethanol, were added to diesel fuels [2]. Lower alcohols, such as methanol and ethanol, are commonly used. Their production can be cheaper and more environmentally friendly than that of petroleum fuels and biodiesel [3] [4]. Methanol can be produced from coal or petrol-based fuels at a low cost, though it has limited solubility in diesel fuel. Conversely, ethanol, a renewable fuel, is produced through the alcoholic fermentation of sugars from vegetable materials like corn, sugar cane, sugar beets, barley, sweet sorghum, cassava, and molasses, among others. Additionally, agricultural residues such as straw, feedstock, and waste wood can also be used, utilizing existing and proven technologies [5]. The use of alcohol as additives in diesel fuel presents several challenges. The primary issue is their solubility with diesel, leading to phase separation. This instability, influenced by the diesel and alcohol composition and temperature, has been extensively researched. For instance, ethanol blends with diesel show two phases below 10°C. Furthermore, the alcohol percentage and its water content significantly affect solubility. To mitigate this, additives are introduced to improve solubility. However, incorporating alcohol alters the fuel's properties, including cetane number, viscosity, lubricity, heating value, and ignitability. These changes are also affected by the alcohol's chain length and structure [6]. Generally, n-butanol has several advantages over methanol and ethanol, including a higher tolerance to water contamination (n-butanol is more hydrophobic than ethanol) and compatibility with the existing fuel distribution infrastructure, allowing the use of current distribution pipelines (Bryan, Kumar *et al.* 2011), less corrosion to aluminum or polymer components in fuel system, ability to blend in gasoline or diesel at high fraction without modifying vehicles, and better fuel economy due to high energy density. The primary goal of this review paper is to examine the physical and chemical properties, combustion, performance, and emission characteristics in CI engines across different operating conditions. It has been noted that there remains a considerable gap in research concerning the

effect of oxygenated fuels, such as n-butanol, on diesel when using specific proven mix ratios. This gap exists largely because n-butanol is primarily utilized as a chemical compound in the food industry, leading to its undeveloped production from non-petroleum sources and higher cost. Consequently, this review aims to analyze various combustion phases and determine n-butanol-diesel ratios that could enhance emission characteristics without adversely affecting engine performance parameters.

## 2. Historical Overview of N-Butanol


Butanol production, one of the oldest fermentation processes known as acetone-butanol-ethanol (ABE), AB, or solvents, is employed for the commercial production of a chemical benefiting mankind. Butanol can be produced through fermentation using various microorganisms, including *Clostridium acetobutylicum* and *Clostridium beijerinckii* [7].

The acetone-butanol-ethanol (ABE) fermentation process was discovered by French microbiologist Louis Pasteur in 1861. Research into butanol was revived during World War I due to the high demand for acetone, [8] leading to a patent for the process being filed and tested in the United Kingdom. However, there was a need for an organism to increase acetone production. Strange and Chaim Weizmann succeeded in isolating *Clostridium acetobutylicum* from garden soil for ABE fermentation, which could produce large amounts of acetone. During World War I, Britain needed to produce large quantities of acetone as it was a crucial chemical for making cordite, an alternative to gunpowder. Following the war, the demand for butanol increased, leading to the establishment of the first large-scale industrial plants in Canada and the USA. After 1936, ABE production industries were set up in the Soviet Union, Japan, China, South Africa, and Egypt. By 1945, at the beginning of the Second World War, Japan started producing butanol from sugar plants, primarily as airplane fuel [9]. In the 1950s, a petrochemical route for n-butanol production emerged, primarily involving the aldol condensation of acetaldehydes, followed by dehydration and hydrogenation of crotonaldehyde. This rapid industrial advancement, known as the Oxo synthesis, led to the abandonment of fermentation processes [10]. By the 1960s, most industrial ABE fermentation facilities had closed due to the lower cost of oil, which favored chemical production methods. The last such factory closed in 1986 in South Africa. However, this chemical production method was short-lived, as a rise in crude oil prices led to a resurgence of industrial ABE fermentation facilities, particularly in China and Brazil. Today, numerous plants have been established worldwide, including in the USA, Slovakia, France, and the UK, to produce bio-butanol as fuel [11].

### Physical and Chemical Properties of N-Butanol

**Table 1** displays the physical and chemical characteristics of n-butanol, including its structures and nomenclature.

**Table 1.** Physical and chemical properties of n-butanol [12].

Parameter	n-Butanol
Structure	
Empirical Formula	C <sub>4</sub> H <sub>10</sub> O
CAS#	71-36-3
Common Names	1-Butyl alcohol; Propyl carbinol; Butanol; Butyl alcohol; Butyric Alcohol; n-Butanol (NH 2004)
Physical state	Refractive liquid (U.S. EPA 1994)
Molecular Weight	74.12 (U.S. EPA 1994)
Melting Point	-90°C (U.S. EPA 1994)
Boiling Point	117°C - 118°C (U.S. EPA 1994)
Water Solubility	9.1 mL/100 mL H <sub>2</sub> O @ 25°C (U.S. EPA 1994)
Vapor Pressure	7.00 mm Hg @ 25°C [930 Pa] (U.S. EPA 1994)
Log Kow	0.88 (U.S. EPA 1994)
Henry's Law Constant	8.81 × 10 <sup>-6</sup> atm·m <sup>3</sup> /mole @ 25°C (U.S. EPA 1994)
Relative Density (Water = 1)	0.8 (NIOSH 1995)

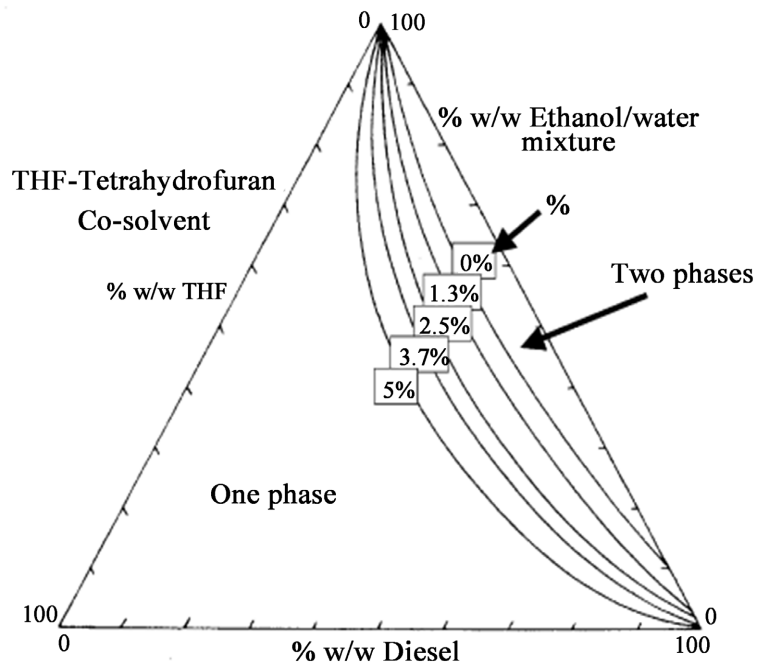
### 3. Ethanol and Its Properties

Ethanol, a colorless alcohol with a distinctive aroma, evaporates at a relatively low temperature and is highly hydrophilic, meaning it can dissolve indefinitely in water and many other organic and inorganic substances. Its high latent heat results in a cooling effect on intake air, allowing more fuel-air mixture to be filled into the cylinder when used in engines. This, combined with ethanol's high octane number, enhances its anti-knocking properties, enabling a higher compression ratio and improved engine efficiency. Recently, ethanol has been increasingly used as a blending fuel in internal combustion engines, especially in countries like Brazil with abundant ethanol sources. However, its lower flash point compared to conventional diesel fuel and its corrosive nature require careful handling and storage. Ethanol, like methanol, is part of the lower alcohols group and shares the same chemical formula as di-methyl-ether (C<sub>2</sub>H<sub>6</sub>O), though it exhibits different thermodynamic behavior [3] [13]. The use of ethanol in engines has been extensively researched due to its potential as an alternative to petroleum-derived fuels. It is a renewable resource that can be produced through the fermentation of sugar- or starch-rich vegetable materials such as corn, barley, molasses, sugarcane, sugar beets, sorghum, etc. [14] [15]. Additionally, other agricultural or municipal residues, such as straw, wood waste, and byproducts from food and paper processing, are utilized to produce ethanol using demonstrated processes [16] [17]. The high polarity of these lower alcohols results in poor miscibility with diesel when directly mixed. To achieve high substitution ratios, techniques such as dual fuel injection and alcohol-diesel emul-

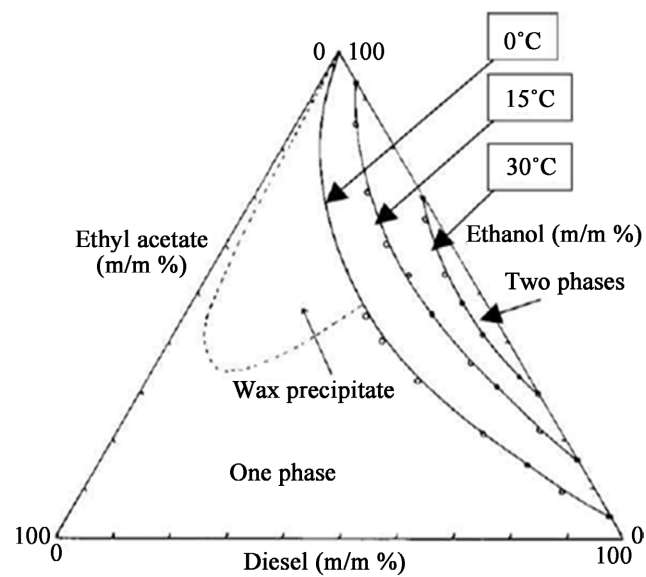
sions are necessary, which increases the cost and complexity of the diesel engine system [18]. Meanwhile, properties such as low cetane number, low energy density, and high latent heat of vaporization make these lower alcohols less suitable for diesel engines [19].

Ethanol solubility in ordinary diesel is mainly influenced by temperature and the water content of the blend. At ambient temperatures, dry ethanol readily mixes with diesel fuel. However, below about 10°C, the two fuels separate—a common occurrence in many parts of the world for much of the year. To prevent this separation, two methods can be employed: i) adding an emulsifier to suspend small ethanol droplets within the diesel fuel, or ii) using a co-solvent that acts as a bridging agent to ensure molecular compatibility and bonding, resulting in a homogeneous blend [20] [21]. Emulsification typically involves heating and blending to produce the final mixture, while co-solvents enable “splash-blending,” simplifying the process. Both emulsifiers and co-solvents have been tested with ethanol and diesel fuel. Moses *et al.* (1980) studied micro-emulsions of aqueous ethanol (5% water) and diesel fuel using a commercial surfactant [21]. They reported that the blends formed spontaneously, requiring only minor stirring and appeared transparent, indicating that the dispersion sizes were smaller than a quarter of a wavelength of light, making them “infinitely” stable, *i.e.*, thermodynamically stable with no separation even after several months. Approximately 2% surfactant was needed for every 5% aqueous ethanol added to diesel fuel. Boruff *et al.*, 1982, developed formulations for two micro-emulsion surfactants, one ionic and the other non-detergent. Blends of these surfactants with aqueous ethanol and diesel were transparent and stable at temperatures as low as 15.5°C. Researchers in Sweden tested a blend of 15% aqueous ethanol (5% water) with diesel, containing DALCO, an emulsifying agent developed in Australia [22]. Early studies by Letcher (1980), Meiring *et al.* (1981), and Letcher (1983) identified tetrahydrofuran, sourced affordably from agricultural waste, and ethyl acetate, inexpensively produced from ethanol, as effective co-solvents. Ternary liquid-liquid phase diagrams in **Figure 1** and **Figure 2** illustrate how moisture content and temperature impact blend stability, showing the need for increasing amounts of co-solvent with higher moisture and temperature to maintain a single-phase liquid. Letcher (1983) determined that a consistent ratio of ethyl acetate to ethanol of 1:2 is required for complete miscibility down to 0°C. Gerdes and Suppes (2001) found that the solubility of ethanol in diesel, and thus the effectiveness of emulsifiers and co-solvents, is also influenced by the diesel’s aromatic content. The polar nature of ethanol allows it to interact strongly with aromatic molecules, which remain compatible with other hydrocarbons in diesel, acting as bridging agents and co-solvents. Reducing the aromatic content in diesel fuels impacts the miscibility of ethanol in diesel and affects the required amount of additive for a stable blend [20] [21].

The physicochemical and combustion properties of ethanol are indicated in **Table 2** below.



**Figure 1.** Liquid-liquid ternary phase diagram for diesel fuel, tetrahydrofuran, and ethanol or ethanol water mixtures with the temperature controlled at 0°C. Source [20] [21].



**Figure 2.** Liquid-liquid ternary phase diagram for diesel fuel, ethyl acetate, and dry ethanol mixtures. Source [20] [21].

**Table 2.** Physicochemical and combustion properties of ethanol [23] [24].

Parameter	Ethanol
Molecular formula	C <sub>2</sub> H <sub>5</sub> OH
Density (kg/m <sup>3</sup> )	792
Viscosity (cSt)	1.04
Latent heat (kJ/kg)	840

**Continued**

Boiling point (°C)	78
Cetane number	7
Oxygen content (%)	34
Lower heating value (MJ/kg)	27
Auto-ignition temperature (°C)	434

#### 4. Significance of N-Butanol

Butanol has garnered significant research interest as a second-generation biofuel in recent years, being considered as a potential alternative to ethanol for replacing gasoline and diesel [25]. Until recently, it was less studied than ethanol or methanol, mainly due to its use in the food industry, undeveloped production from non-petroleum sources, and higher costs. However, interest in butanol has surged [6].

Butanol (C<sub>4</sub>H<sub>9</sub>OH) is a higher-chain alcohol with a four-carbon structure and exists in different isomers, which vary in physical properties based on the location of the hydroxyl (OH) group and the carbon chain structure [26]. These are 1-Butanol (also known as n-butanol), 2-butanol (also known as sec-butanol), isobutanol, and tert-butanol. 1-Butanol has a straight-chain structure with the alcohol (OH) group at the terminal carbon. 2-Butanol has the hydroxyl group at an internal carbon. Isobutanol is a branched isomer with the OH group at the terminal carbon, and tert-butanol is a branched isomer with the OH group at an internal carbon. The different structures of butanol isomers directly impact their physical properties [26]. Laminar velocities decrease in the following order: 1-butanol, sec-butanol, iso-butanol, and tert-butanol. Gu, Huang *et al.* (2010) state that the laminar flame speed, or fuel burning velocity, is a crucial parameter of a combustible mixture. This physicochemical property influences combustion duration and performance in spark ignition engines, affecting the fuel burning rate in internal combustion engines, thus impacting efficiency and emissions. The molecular structure of combustible mixtures, particularly the isomers of butanol, affects their laminar flame stability. 1-butanol exhibits the highest flame burning velocity. Functional groups significantly influence laminar burning velocity; branching (-CH<sub>3</sub>) decreases it, while the hydroxyl functional group (-OH) attached to terminal carbon atoms increases laminar velocity. Terminal C-H bonds possess higher bond energies than those of inner C-H bonds. High bond energies hinder the H-abstraction reaction, leading to a lower reaction rate. Consequently, n-butanol, which mostly contains inner C-H bonds, has the highest laminar flame velocity, while tert-butanol has the lowest [2].

Higher alcohols, such as butanol and pentanol, have properties closer to diesel fuel than lower alcohols [27]. Compared to commonly used alcohols like ethanol and methanol, butanol offers a higher heating value, meaning it contains more energy and can reduce fuel consumption. It also has a higher cetane number,

making it a more suitable diesel additive than ethanol and methanol. Additionally, its lower vapor pressure decreases the likelihood of cavitation issues. Butanol's lower autoignition temperature improves cold start ignition problems. Being less hydrophilic, it is less corrosive and less prone to separation in diesel blends when contaminated with water [13] [27] [28]. Despite possessing properties similar to diesel fuel, the use of butanol alone is incompatible with certain components of diesel engines, and its heating value remains lower than that of conventional diesel fuel [28].

Research on butanol as an alternative fuel is continually growing. Generally, adding butanol to diesel slightly increases brake specific fuel consumption and brake thermal efficiency. Exhaust gas temperatures, nitrogen oxides, and carbon monoxide decrease with lower butanol blending ratios, while unburned hydrocarbons and nitric oxide levels increase. Notably, the reduction of smoke opacity in exhaust emissions is significant [2] [27].

## 5. Properties that Make N-Butanol More Attractive than Ethanol as a Blend

### 5.1. Higher Density

Density influences spray formation, injection timing, atomization, and combustion characteristics, among others [29]. The density of n-butanol is lower than that of diesel fuel, resulting in a smaller volume of alcohol being pressurized and injected by the fuel pump, as the dosage is volumetric [30]. However, n-butanol has a higher density than ethanol. The excess volume of liquid blends indicates the presence of molecular interactions, which significantly affects fuel consumption and fuel tank sizing. Thus, understanding the density of blends is crucial. Currently, there is limited research on butanol-diesel systems. The excess volume of butanol-diesel blends is observed to be higher than that of ethanol-diesel blends [31]. This is due to the fact that butanol has a larger carbon chain than ethanol, making its non-polar (aliphatic chain) part more dominant and reducing its polar character [32]. Consequently, in butanol-diesel blends, the interaction between the hydroxyl group of the alcohol molecule and the aromatic hydrocarbons is weaker due to dispersive forces. Aissa *et al.* and Dubey *et al.* reported a positive excess volume for blends of n-butanol and n-hexadecane, a common diesel surrogate, at temperatures of 298.15, 303.15, 308.15, and 313.15 K. In contrast, Mehra *et al.* found a negative excess volume in the range from 303.15 to 318.15 K. For alcohol-biodiesel blends, stronger interactions form between the hydroxyl groups of alcohols and the ester groups of biodiesels through hydrogen bonds, resulting in a lower excess volume than for alcohol-diesel blends. This reduction in excess volume is even more pronounced in ethanol-biodiesel blends [33] [34].

### 5.2. Higher Viscosity

Fuel atomization is typically influenced by viscosity, affecting the size of fuel

droplets, the formation of engine deposits, and the fuel's lubricity when injected into the combustion chamber [35] [36]. High-viscosity fuels necessitate more energy in the fuel pump and lead to increased wear in the injection system [37]. On the contrary, fuels with excessively low viscosity may not provide enough lubrication for the injection system, leading to increased pump and injector leakage. This increases fuel return and, consequently, fuel consumption due to higher pumping power. Viscosity values decrease with higher alcohol contents in alcohol-diesel blends. Results also indicate that viscosity is not proportional to the volumetric, mass, or molar alcohol content [34]. According to the EN 590 standard for diesel fuels, which mandates that viscosity values must be higher than 2 cSt [34], only ethanol-diesel blends with an ethanol content of up to 36% (v/v) meet this requirement [38]. Given that the viscosity of alcohol increases with a longer carbon chain, n-butanol blends ranging from 0% to 100% in diesel fuel would face no restrictions [38]. However, the study by Kuszewski *et al.* (2018) showed that when the viscosity of diesel fuel at 40°C is near the lower limit of EN 590, only butanol-diesel blends of up to 7% (v/v) meet this standard. The decrease in viscosity from mixing alcohols (ethanol or n-butanol) with diesel can be offset by adding biodiesel [34] [39]. Although alcohols are extensively used in chemical and petroleum industries, precise and reliable viscosity data are essential for designing transport equipment or pipelines [34]. Generalized correlations are necessary for predicting the viscosity of liquid mixtures. Cano-Gómez *et al.* [40] studied various butanol-biodiesel blends and found that the Grunberg-Nissan equation provided a better fit to experimental data compared to other modeling methods like the Kendall-Monroe or Bingham equations. The Grunberg-Nissan equation has also been applied in different studies [34] [38] to model the viscosity of different alcohols (methanol, ethanol, propanol, n-butanol, and n-pentanol) with diesel and biodiesel fuels [34].

### 5.3. Better Lubricity

Controlling fuel lubricity is crucial for protecting engine components like injectors, fuel pumps, and fuel rails from wear. Pure n-butanol offers better lubricity than pure ethanol [34]. Vinod Babu *et al.* [41] reported that the lubricity of pure alcohols generally improves, resulting in a smaller wear scar, with increasing molecular weight. However, diesel blends with long-chain alcohols (n-butanol and n-pentanol) exhibit worse lubricity (larger wear scar) than those with short-chain alcohols (ethanol and propanol). Surprisingly, the lubricity of ethanol-diesel blends with an intermediate ethanol content was better than expected, likely due to alcohol evaporation from the lubricating layer [20] [42].

### 5.4. Higher Heating Value

Alcohols have lower heating values than conventional diesel fuels, necessitating a higher volume of alcohol to achieve the same power output in engines. However, the heating value increases with the number of carbon atoms. For instance,

n-butanol has a 25% higher energy density by volume than ethanol, thereby reducing the fuel consumption required to maintain a specific load in diesel engines [43] [44]. The study by Kuszewski *et al.* tested butanol-diesel blends with 5%, 10%, 15%, 20%, and 25% (v/v) butanol content and found that a 25% butanol content reduced the lower heating value by 6% compared to diesel fuel. Given that the lower heating value of diesel typically ranges from 41 to 44 MJ/kg, butanol-diesel blends up to 17% (v/v) and ethanol-diesel blends up to 10% fall within this range [34] [45].

### 5.5. Better Blend Stability

Alcohol-diesel blends can be separated into different phases under specific conditions. This stability depends on temperature, humidity, and fuel composition. In fact, as temperature decreases, the unstable region expands. Additionally, moisture presence adversely affects miscibility. Alcohols with longer carbon chains exhibit better blending stability than those with shorter chains [34]. The polarity of alcohols is induced by the hydroxyl group (R-OH), one of the most polar chemical groups. Since butanol has a longer carbon chain than ethanol, its overall polarity is lower. Therefore, butanol exhibits better blending stability with the primarily non-polar structures of diesel fuels [32]. Low blend stability was reported for ethanol-diesel blends, specifically at intermediate ethanol contents (from 15% to 75% ethanol content) [46]. In fact, Kwanchareon *et al.* [47] reported that ethanol-diesel blends with 20% to 80% ethanol by volume form two liquid phases at temperatures below 10°C. However, butanol blends exhibited superior blending behavior, with butanol-diesel blends remaining stable across the entire butanol range at temperatures above 0°C. Unlike ethanol blends, butanol-diesel blends do not require emulsifying agents as they do not separate even after several days [34].

### 5.6. Better Cold-Flow Properties

Bio alcohols, known for their low freezing temperatures, have been identified as a sustainable solution to enhance the cold flow properties of diesel fuels, particularly biodiesel [48]. Issues with biodiesel filter plugging have been observed in countries experiencing mild to cold weather. These problems are primarily due to the crystallization of monoacylglycerols from saturated fatty acids, sterol glycosides, and other impurities [49]. Additional requirements have been proposed in both European and non-European countries to address operability issues in diesel engines. In Europe, standard EN 590 sets limits for the cold filter plugging point (CFPP) and cloud point (CP), but there are no established limits for pour point (PP). Only British and Australian standards specify limits for filterability (FBT). The benefits of blending light alcohols like methanol and ethanol with diesel fuels are constrained by their poor miscibility. The solubility of ethanol-diesel blends decreases at lower temperatures, affecting the cold flow properties (CFPP, CP, and PP) due to the formation of a gelatinous phase or phase

separation [34]. Due to its enhanced blend stability across a broad temperature spectrum for all concentration levels, n-butanol improves the cold flow properties of diesel fuels, particularly at high alcohol content. Regarding alcohol-biodiesel blends, Makareviciene *et al.* [48] reported that adding n-butanol to biodiesel gradually decreased the cloud point and the cold filter plugging point. Bouaid *et al.* [50] justified the significant improvement n-butanol brings to the cold-flow properties of diesel and biodiesel fuels compared to ethanol, due to its less polar character [34].

### 5.7. Higher Cetane Number

Among the properties affecting the combustion process, the cetane number is a limiting factor. Generally, alcohols have low cetane numbers, limiting their concentrations in unmodified diesel engines due to the significant impact on engine efficiency. The higher cetane number of n-butanol compared to ethanol suggests that its maximum concentration in diesel blends could be increased relative to that recommended for ethanol [13] [51]. Based on the cetane number, literature indicates that diesel engines can use butanol-diesel blends with n-butanol content up to 40% (v/v) without any engine modifications [41]. However, blends with higher butanol content lead to excessively high ignition delays [52], resulting in large, premixed phases that cause excessive heat release rates and peaks in cylinder pressure [34]. However, considering the EN 590 standard limits, only butanol blends with diesel fuel up to 3% meet this requirement [52]. This limitation can be compensated by using cetane improvers. The increase in ignition delay for butanol blends is similar whether it is blended with diesel or biodiesel fuels. However, when ethanol is blended with diesel or biodiesel fuels, larger delay times are observed in the former case [34] [52].

### 5.8. Lower Enthalpy of Vaporization.

Since ethanol and butanol have a higher enthalpy of vaporization than diesel fuel, more heat is required to evaporate the alcohol, leading to a smaller increase in gas temperature and potentially causing starting difficulties [13]. Among alcohols, n-butanol's lower enthalpy of vaporization (620 kJ/kg) compared to ethanol (944 kJ/kg) suggests that a diesel engine may start more easily with butanol than with ethanol in cold conditions [34] [44].

### 5.9. Better Distribution and Storage

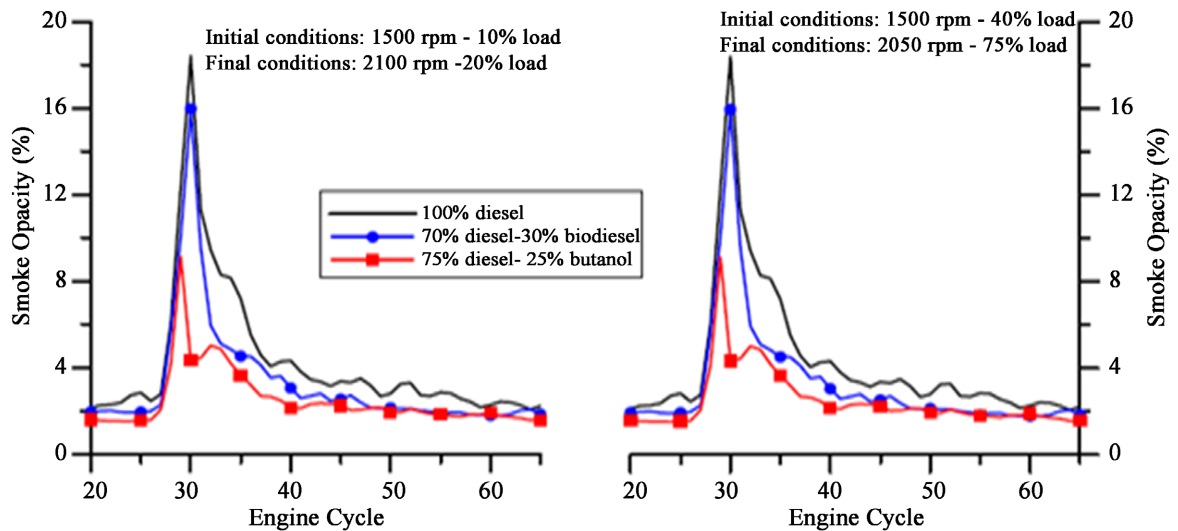
N-butanol has a higher flash point and lower volatility compared to ethanol, making butanol blends safer for transportation, fuel handling, and storage [16] [43]. Pipeline corrosion is largely due to the polarity and hygroscopic nature of alcohol molecules. Metals like magnesium, lead, and aluminum are vulnerable to chemical attack by alcohol. Additionally, wet corrosion, primarily resulting from alcohol's moisture absorption ability, oxidizes most metals. Non-metallic components, especially those made of elastomeric materials, are also impacted by al-

cohols [20]. Corrosion affects materials in fuel delivery and injection systems, among others. High polarity and water content in alcohols increase corrosion. Since ethanol is more polar and soluble in water than butanol, butanol is less prone to water contamination and more suitable for distribution through existing pipelines. Additionally, n-butanol's lower corrosiveness compared to ethanol contributes to better storage stability over extended periods. Yanai *et al.* 2015 [53] noted that butanol could corrode plastic parts and swell rubber components. However, this issue can be addressed by replacing rubber seals with materials more resistant to alcohol [34] [53].

## 6. Effects of N-Butanol on Performance, Combustion, Particle and Gaseous Emissions

The properties of n-butanol significantly influence combustion parameters. Its presence impacts the fuel-air mixing process and the development of the injection spray. N-butanol's lower density and kinematic viscosity compared to diesel fuel result in improved atomization quality for butanol-diesel blends. Moreover, n-butanol's higher volatility facilitates a quicker evaporation process. Both enhanced atomization and accelerated evaporation help in forming more homogeneous fuel-air mixtures, thereby reducing soot formation [41]. The cetane number is a crucial parameter for combustion quality as it aids in optimizing combustion timing. For n-butanol blends, the peak pressure in the combustion chamber during combustion decreases with higher butanol content due to three main effects: the energy effect, which is the reduction in heating value; the chemical effect, related to the decrease in the equivalence ratio; and the dilution effect, caused by over-dilution and large delay times. Both the chemical and dilution effects reduce flame velocity, thereby increasing heat transfer to the chamber walls during combustion and diminishing combustion quality [52].

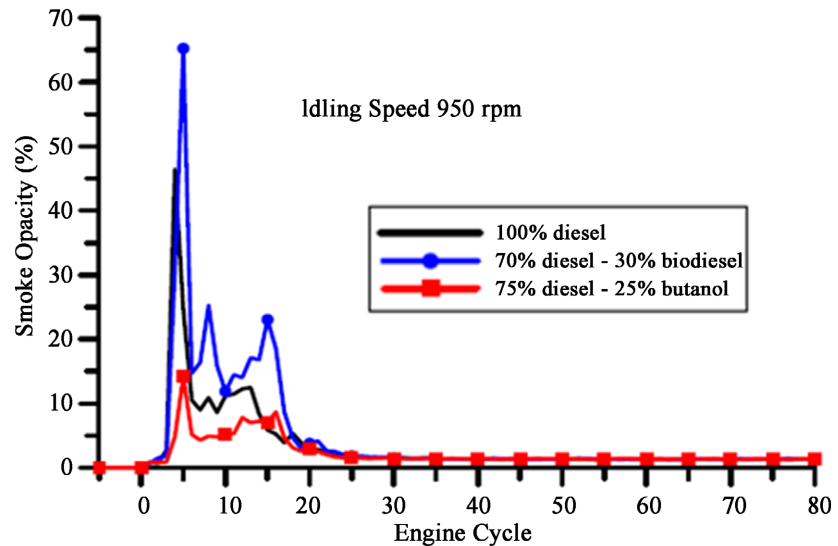
Rakopoulos *et al.* conducted a comprehensive study on the impact of n-butanol on diesel engine emissions during discrete transient schedules, focusing on n-butanol/diesel blends during acceleration [54] and hot starts of a turbocharged diesel engine. The research found that in all acceleration tests, the n-butanol/diesel blend produced less smoke than pure diesel, albeit with higher NO emissions (in ppm). The study also compared a biodiesel/diesel blend, offering a unique comparison of the effects of two biofuels. **Figure 3** exemplifies the findings reported in Ref. [54]. The illustration shows how a six-cylinder, medium-duty, turbocharged, direct injection (DI) diesel engine responds during medium to high-speed acceleration while running on neat diesel fuel, a blend of 25% n-butanol and 75% diesel fuel (Bu25), and a blend of 30% (sunflower-cottonseed) biodiesel with 70% diesel (B30). Both biofuel blends, as shown in **Figure 3**, were found to reduce engine smoke emissions during demanding acceleration, with further improvements observed at the final steady-state conditions. The reduction in smoke emissions was significantly more pronounced for the n-butanol blend than for the biodiesel blend, which also had a higher oxygen content. Although fuel injection and spray development slightly differed from



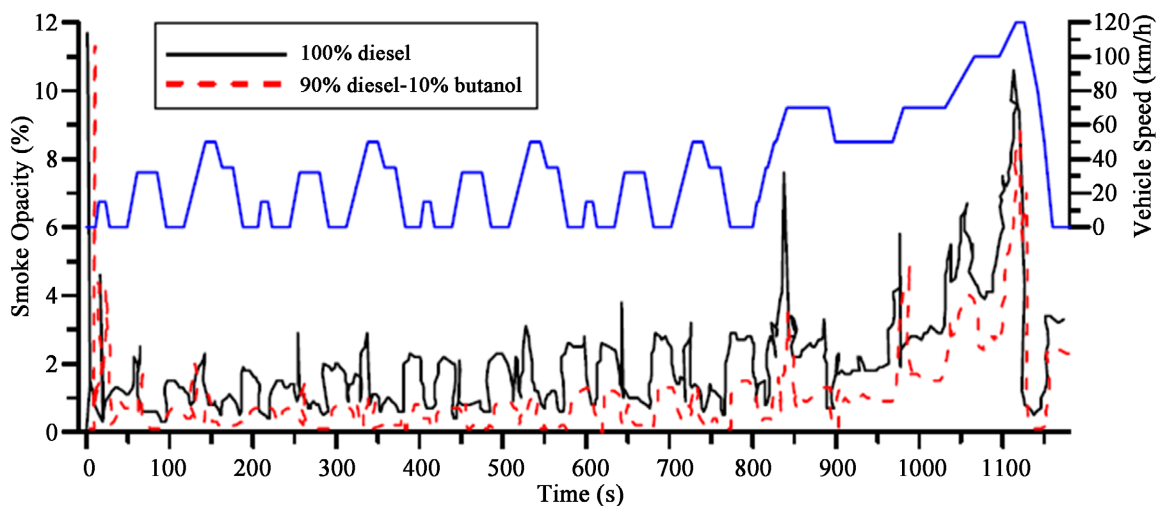
**Figure 3.** Development of smoke opacity response during two accelerations of a medium duty turbocharged diesel engine for neat diesel, Bu25 and B30 fuel blends [54].

the neat diesel fuel case, it was suggested that this behavior was due to the engine running 'leaner' compared to when it used neat diesel fuel. This holds true because the trapped relative air-fuel ratio remained essentially the same, with the combustion being assisted by the fuel-bound oxygen in the biodiesel or n-butanol in locally rich zones, which had the dominant influence. In fact, the higher oxygen mass percentage of the n-butanol blend compared to the biodiesel blend led to its superior smoke behavior. As a result, while the peak opacity value was reduced by 13% for the biodiesel blend, the n-butanol blend (with higher oxygen content) saw a significant decrease of 50% compared to neat diesel fuel operation. Further, results are documented in **Figure 4** for hot starting this time. Here, the effect of each biofuel on smoke emissions was found to be contradictory. Specifically, the biodiesel blend increased both the peak soot value and the duration of unacceptable smoke emissions, whereas its n-butanol counterpart (confirmed also by the results of Armas *et al.* [55] substantially decreased both of them, compared to the neat diesel fuel case; the relative differences were +40% and -69%, respectively, in the maximum opacity value. Furthermore, opacity exceeded 10% for 10, 14, and just 3 engine cycles (or 1.9, 2.5, and 0.5 seconds), respectively, for neat diesel fuel, biodiesel, and normal butanol blends. For the diesel/n-butanol blend, the improvement in smoke emissions was attributed to the engine running leaner. This was due to combustion being aided by the higher fuel-bound oxygen content of n-butanol in the locally rich zones, which appeared to have a dominant influence. During turbocharged diesel engine transients, the extra oxygen available inside the cylinder compensates for the significant air deficiency from the compressor during turbocharger lag, proving crucial for the emission development shown in **Figure 4**. Similarly, n-butanol's lower viscosity and higher volatility compared to biodiesel (and diesel fuel) are expected to reduce soot production. Not surprisingly, the cleaner operation of the engine with added n-butanol, as reported in [54] during warm/hot starting, also

resulted in an increase in emitted nanoparticles [55]. The arguments for discrete transient schedules are strengthened by comparing smoke emissions from neat diesel fuel and a Bu10 blend, as shown in **Figure 5**. This figure displays the instantaneous smoke emissions during the 1180-second European passenger car New European Driving Cycle (NEDC). The n-butanol blend consistently maintained lower levels of smoke emissions, including during the cold start phase. This was particularly notable at the beginning of each acceleration event, where the effects of turbocharger lag—caused by a sudden shortage of air from the turbocharger compressor—are more significant [13].



**Figure 4.** Development of smoke opacity during hot starting of a medium-duty turbocharged diesel engine for neat diesel, Bu25 and B30 fuel blends [56].



**Figure 5.** Development of smoke opacity during the NEDC for neat diesel and a Bu10 blend of a passenger car diesel engine (experimental results adapted from Kozak [57]).

Gvidonas, L. *et al.* (2021) performed experiments and investigated the effects of biodiesel-n-butanol fuel blends on performance and emissions in a diesel en-

gine. The combustion of neat biodiesel produced the highest total NO<sub>x</sub> emissions at 2290 ppm. However, the addition of n-butanol to biodiesel did not significantly reduce NO<sub>x</sub> emissions as expected. At full engine load with a BBU20 blend, nitrogen oxides emissions decreased by 23.5%. At low engine load, the highest carbon monoxide emissions were recorded with neat biodiesel (302 ppm), while the lowest was with the BBU20 blend (241 ppm). The n-butanol oxygenated biodiesel blends BBU10 and BBU20 significantly reduced carbon monoxide emissions at full load. Furthermore, at full load, smoke opacity decreased by 28.5% and 35% with BBU10 and BBU20 blends, respectively, compared to neat biodiesel. Renewable binary biodiesel-n-butanol blends are suitable for powering diesel engines, replacing fossil-origin diesel fuels, reducing climate change, and preserving untouched nature for future generations. Due to the absence of polycyclic aromatic hydrocarbons in these renewable biofuel blends, lower maximum NO<sub>x</sub> emissions, drastically reduced CO emissions, and decreased smoke opacity (PM) can be expected. This is attributed to the potentially improved homogeneity of the combustible mixture and the benefits to particulate matter (PM) emissions, suggested by the higher n-butanol-oxygen mass content (21.62 wt%) and a much lower carbon-to-hydrogen ratio (4.8) [58].

### 6.1. Engine Performance

In the last decade, n-butanol derived from lignocellulosic residual feedstocks has emerged as a promising and sustainable green energy source for diesel engines [59], due to its superior fuel properties compared to low carbon alcohols (methanol, ethanol, etc.) [60]. The low heating value (LHV) of n-butanol is 33.1 MJ/kg compared to 26.8 MJ/kg for ethanol and 19.9 MJ/kg for methanol [61], which is favorable for engine performance characteristics. Additionally, n-butanol has a higher flash point, improved miscibility with fossil-based diesel at low temperatures, and is less toxic and volatile [62]; this property makes n-butanol a much safer and more suitable fuel component for transport on existing fuel infrastructure. Due to its lower autoignition temperature, higher cetane number (CN), and lower heat of vaporization compared to other alcohols, n-butanol is a superior choice for cold start ignition in compression ignition (CI) engines [63]. Its higher lubricity and viscosity protect engine components such as fuel rails, fuel pumps, and injectors from wear. Additionally, the oxygen molecule in n-butanol enhances the diffusion combustion stage, and its higher laminar flame speed (45 cm/s) compared to diesel (33 cm/s) increases combustion efficiency [64]. The physical properties of fuel, including density, viscosity, and bulk modulus of compressibility, influence the delivery rate and injection characteristics. These properties directly affect the quality of the air-fuel mixture, which in turn impacts the combustion process, brake thermal efficiency, and the ecological parameters of the diesel engine. Alternative and renewable biofuels differ from conventional diesel fuel in specific properties such as density, viscosity, calorific value, cetane number, freezing point, etc. Staying updated with the latest trends in using lighter and more environmentally friendly biofuels is crucial for pow-

ering diesel engines [60] [65].

## 6.2. Combustion Characteristics

To better understand the effect of n-butanol blending on engine performance, Luis Tipanluisa *et al.* [60] did an extensive study on a World Harmonized Steady-State Cycle (WHSC) under varying operating conditions. The findings were categorized into three groups based on combustion characteristics: a low load (25% engine load) at three speeds (25%, 35%, and 45% of engine speed, respectively), a full load (100% engine load) at three speeds (35%, 55%, and 75% of engine speed, respectively), and a medium speed (55% of engine speed) at three loads (25%, 50%, and 70% of engine load, respectively). The study focused on three specific scenarios: constant low load with varying speed, constant high load with varying speed, and constant medium speed with varying load. The fuels tested included reference diesel and n-butanol blends (DBu5, DBu10, and DBu20) [60].

### 6.2.1. In-Cylinder Pressure

A slight increase in maximum pressure of up to 1% was observed for the DBu5 and DBu10 blends, mainly at low load. This is attributed to the high oxygen content in n-butanol and a greater amount of fuel burned under premixed combustion. Oxygen in fuel can lower the local equivalence ratio (the ratio between the averaged fuel/air mass ratio entered into the engine cylinder and the stoichiometric fuel/air ratio for each operating condition), enhancing combustion efficiency [66]. Additionally, the increased volatility of the blended fuel improves air-fuel mixing, resulting in a more uniform gas mixture and a higher proportion of premixed combustion, thereby increasing in-cylinder pressure [67]. The DBu20 blend shows no significant changes compared to diesel at engine speeds up to 35% under a 25% load. However, at the same load and a higher engine speed of 45%, there was a noticeable reduction in in-cylinder pressure by up to 1.4%. Moreover, a greater reduction in maximum pressure (about 2.6%) was observed for the DBu20 blend at a constant medium speed with varying loads, attributed to the lower cetane number (CN) and calorific value of the n-butanol blended fuel. The blend's low CN increased the ignition delay period, leading to more fuel accumulation and, consequently, a lower peak in-cylinder pressure [68]. Furthermore, the higher latent heat of vaporization of the blend results in a combustion cooling effect, leading to lower in-cylinder pressure [20]. On the other hand, at a constant low load with varying speed, the peak in-cylinder pressure is achieved at a crankshaft angle between 4 and 7 degrees for all fuels. Additionally, a higher engine speed slightly reduces the peak in-cylinder pressure. However, under constant high load with varying speed, the peak in-cylinder pressure increases with engine speed, reaching its maximum at a crankshaft angle between 11 and 13 degrees for all fuels. The DBu20 blend exhibited a significantly greater reduction in in-cylinder pressure compared to diesel, with an increase in speed up to 45% under low load (25%) conditions.

Meanwhile, at full load (100%) conditions, the variation in peak in-cylinder pressure was considerably higher at lower engine speeds (35%) than at higher engine speeds (75%), with values of 2.5% and 0.5%, respectively. This can be understood because as the engine speed increases, a greater amount of air enters with higher turbulence intensity, leading to a faster air-fuel mixture and a greater amount of injected fuel reacting rapidly during the premixed combustion phase. At a constant medium speed with varying load, the peak in-cylinder pressure was attained at a crankshaft angle between 8 and 12 degrees for all fuels. Moreover, a higher engine load significantly increases the peak in-cylinder pressure [60].

### 6.2.2. Apparent Heat Release Rate

At a constant low load with varying speed, the apparent heat release rate (AHRR) peak becomes sharper, and the use of DBu5 and DBu10 mixtures slightly raises its maximum value by around 3% - 4%, respectively. This increase results from the higher volatility of the blended fuel, which enhances air-fuel mixing, leading to a more homogeneous gas mixture and a higher proportion of premixed combustion, thus elevating the maximum AHRR value [69]. This can also be attributed to the higher oxygen content in n-butanol blends. However, using the DBu20 blend results in a 7% reduction in the maximum value of AHRR due to the lower LHV of n-butanol. Additionally, a shift in the crankshaft position ( $-1^{\circ}$  to  $3^{\circ}$  CA) of the peak AHRR is observed with increasing engine speed, leading to a decrease in the maximum AHRR value. Conversely, at a constant high load with varying speed, AHRR peaks are more spread out, reaching their maximum values at a crankshaft angle between  $6^{\circ}$  and  $7^{\circ}$  CA. A reduction in AHRRmax value was observed with increasing engine speed. The use of DBu5 and DBu10 blends showed no significant variations in AHRRmax values compared to diesel. However, for the DBu20 blend, reductions between 3.6% and 6.5% were observed. Generally, except for mode 12, using n-butanol did not significantly affect the position of the AHRR peak compared to diesel under all tested operating conditions. This is related to the fuel injection timing and the effect of pilot injection on the main AHRR; it has been reported that the heat released by the pilot injection shortens the ignition delay period of the main injection [30] [60] [70]. It was also observed that at a constant medium speed with varying load, AHRR values increase with an increasing load [60] [65].

### 6.2.3. In-Cylinder Temperature

The use of n-butanol blends slightly reduces the maximum in-cylinder temperature by up to 1.5% for the DBu20 blend, while the temperature at the end of combustion (measured at 80 CA) decreases by up to 3.5%. This reduction in temperature at the end of combustion may be attributed to the lower heating value (LHV) and latent heat of vaporization of n-butanol blended fuel [71]. The reduction in temperature at the end of combustion leads to a slower start of the next combustion cycle, resulting in a longer ignition delay. However, the DBu5 and DBu10 blends do not show considerable variations in maximum in-cylinder

temperature compared to diesel. This is attributed to the additional oxygen supply from the n-butanol in the blended fuel. Additionally, improved and accelerated vaporization of the fuel and an enhanced air-fuel mixture intensify the combustion, thereby leading to a higher temperature [65]. Meanwhile, at the end-temperature (at 80 CA), reductions of up to 2% and 3.1% are observed for the DBu5 and DBu10 blends compared to diesel, respectively [60].

**Table 3** provides a detailed summary of studies from 2008 to 2023 on the performance and regulated emissions of butanol-diesel blends in diesel engines [34]. Consistent with existing literature, numerous researchers have found that using n-butanol in mixtures up to 20% (by volume) does not require recalibrations of the electronic control unit (ECU) or modifications to the engine [60].

David Fernández *et al.* (2021) and Luis Tipanluisa *et al.* (2022) conducted extensive research on the combustion, performance, and emissions of diesel/n-butanol blends in DI diesel engines [34] [60]. Diesel fuels can be blended with bio-alcohols, especially n-butanol, to introduce a renewable component and to provide a certain oxygen content [34].

**Table 3.** Summary of butanol-diesel blends tested in diesel engines.

Research Group	Publication Year	Type of engine	Butanol blend (%v/v)	Operating conditions	CO	THC	NO <sub>x</sub>	Particles	Fuel Consumption (%)	References
Miers <i>et al.</i>	2008	Mercedes Benz C220 diesel passenger car, four-cylinder, common rail, direct injection diesel engine equipped with single turbocharger and intercooler	20, 40	Transient cycle. Cold start UDDS (transient)	↑↑	↑↑	↑	↓↓	↑	[72]
Rakopoulos <i>et al.</i>	2010	Mercedes-Benz OM 366 LA, six-cylinder, four-stroke, turbocharger and air-to-air after cooler, direct injection	25	Accelerations	-	-	↑	↓↓	-	[54]
Rakopoulos <i>et al.</i>	2010	Single-cylinder, four-stroke, compression-ignition, direct injection, naturally aspirated	8, 16, 24	Stationary conditions. Three loads	↓	↑	↓	↓↓	-	[27]
Rakopoulos <i>et al.</i>	2010	6-cylinder, 5.958 L, turbocharger, and air-to-air aftercooler	8, 16	Variable speed: 1200 rpm - 1500 rpm, variable load: 20% - 60%	↓	↑	↓	↓	↑	[73]
Yao <i>et al.</i>	2010	Six-cylinder, four valves, turbocharged intercooler, heavy-duty direct injection, common rail system	5, 10, 15	Stationary conditions. Different injection strategies	↓↓	-	-	↓↓	-	[30]

Continued

Rakopoulos <i>et al.</i>	2011	Mercedes-Benz OM 366 LA, six-cylinder, four-stroke, turbocharger and air-to-air aftercooler, direct injection	8, 16	Stationary conditions. Three loads	-	-	↓	↓↓	↑	[74]
Dogan	2011	Single-cylinder, four-stroke, direct injection, naturally aspirated, air-cooled	5, 10, 15, 20	Stationary conditions. Different engine loads	↓	↑	↓	↓↓	↑	[75]
Kozak	2011	Passenger car, four-cylinder, direct injection, common rail turbocharged intercooled	10	NEDC	↑	↑	-	↓↓	-	[57]
Yamamoto <i>et al.</i>	2012	1 cylinder, 0.875 L, NA, water cooled	30, 40, 50	1200 rpm, variable load: 0.13 MPa - 0.51 MPa	-	↑	↑	↓	-	[76]
Zhang <i>et al.</i>	2012	1 cylinder, 1.081 L, common rail, water-cooled, air compressor	20, 40	1400 rpm at different EGR rates	↓	↓	-	↓	-	[77]
Siwale <i>et al.</i>	2013	Volkswagen 1.9 L four-cylinder, turbo-direct injection	5, 10, 20	Stationary conditions. Different loads	↓	↑	-	↓↓	-	[2]
Chen <i>et al.</i>	2013	Four-cylinder, 16 valves, turbocharger inter-cooled, common rail injection system	20, 30, 40	Stationary conditions. Different engine loads	↓	↑	↑	↓↓	↑	[78]
Liu <i>et al.</i>	2013	1 cylinder, 1.081 L, common rail, water-cooled, air compressor	20	1400 rpm, variable EGR: 0% - 62%. Injection pressure 1300 bar	-	-	-	↓	-	[79]
Iannuzzi <i>et al.</i>	2014	Four-cylinders, four valve per cylinder equipped with a common rail injection system, direct injection, turbocharger	20	Stationary conditions. Different injection strategies	-	↓	-	↓↓	-	[80]
Chen <i>et al.</i>	2014	Single-cylinder, heavy-duty, four-stroke, common rail injection	40	Stationary conditions. EGR study	↑	↑	↑	↓↓	-	[81]
Choi <i>et al.</i>	2014	Hyundai D4CB, four-cylinder, turbocharger and intercooler, common rail injection system	10, 20	European Stationary Cycle	↑	↑	↑	↓↓	-	[82]
Armas <i>et al.</i>	2014	Nissan 2.0 M1D, four-cylinder, four-stroke, turbocharged, intercooled with common rail	16	NEDC	↓	↑	↑	↓↓	-	[83]

## Continued

Rakopoulos <i>et al.</i>	2014	1 cylinder, 0.5 L, NA, water-cooled	8, 16, 24	2000 rpm, variable load: 1.40 bar 5.37 bar	↓	↑	↓	↓↓	↑	[71]
Balamurugan <i>et al.</i>	2014	1 cylinder, 0.661 L, NA, water cooled	4, 8	1500 rpm, variable load: 20% - 100%	↑	↑	↓	↑	↓	[68]
Zheng, <i>et al.</i>	2015	1 cylinder, 1.081 L, common rail, water-cooled, air compressor	30	1500 rpm, EGR of 46%. Different injection strategies	↑	↑	↑	↓	-	[84]
Zheng, <i>et al.</i>	2015	1 cylinder, 1.081 L, common rail, water-cooled, air compressor	20, 40	1500 rpm, variable EGR: 0% - 65%. Injection pressure 1300 bar	↑	↑	↓	↓	-	[85]
Sahin <i>et al.</i>	2015	4-cylinder, 1.461 L, common rail, turbocharger, water-cooled	2, 4, 6	2000 rpm, variable load: 145 Nm - 132 Nm. 4000 rpm, variable load: 110 Nm - 96 Nm	-	↑	↕	↓	↕	[86]
Kumar <i>et al.</i>	2015	One-cylinder, four-stroke, naturally aspirated, air cooled, direct injection	10, 20, 30	Stationary conditions. Different engine loads	↓	↑	↓	↓	↑	[87]
Rakopoulos <i>et al.</i>	2015	Mercedes-Benz OM 366 LA, six-cylinder, four-stroke, turbocharger and air-to-air aftercooler, direct injection	8, 16	Accelerations	-	-	↓	↓	-	[88]
Choi <i>et al.</i>	2015	Hyundai D4CB, four-cylinder, turbocharger and intercooler, common rail injection system	5, 10, 20	European Stationary Cycle	↑	↑	↑	↓↓	↑	[89]
Huang <i>et al.</i>	2016	4-cylinder, 1.99 L, common rail, turbocharger, water-cooled	30	1600 rpm, 0.6 MPa. Different EGR ratios	↑	↑	↕	↓	↑	[90]
Huang <i>et al.</i>	2017	4-cylinder, 1.99 L, common rail, turbocharger, intercooler	20	1600 rpm, 0.8 MPa load. Different fuel injection pressures	↑	↑	↓	↓	↑	[91]
Nabi <i>et al.</i>	2017	Six-cylinder, high pressure common rail, turbocharged	2, 4, 6	13-Mode European Stationary Cycle	-	↓	↓	↓	↑	[92]
Fayad <i>et al.</i>	2017	Single-cylinder, four-stroke, naturally aspirated, common-rail	20	Stationary conditions. Different injection strategies	↑	↓	↑	↓	↑	[93]
Emiroğlu <i>et al.</i>	2018	1 cylinder, 0.349 L, NA, air-cooled	10	1500 rpm, variable load: 2.5 Nm - 10 Nm	↓	-	↕	↓	↓	[94]

Continued

He <i>et al.</i>	2018	1 cylinder, 1.081 L, common rail, water-cooled, air compressor	15, 40	1400 rpm, 1.4 MPa load. Different EGR rates	↑	-	↓	↓	-	[63]
Saxena <i>et al.</i>	2018	1 cylinder, 0.661 L, NA, water cooled	10, 20, 30	1500 rpm, variable load: 25% - 100%	↓	↑	↓	↓	↑	[67]
Huang <i>et al.</i>	2018	4-cylinder, 1.99 L, common rail, turbocharger	20	1600 rpm, variable load: 0.4 MPa - 1.6 MPa	↑	↓	↑	↓	↑	[69]
Wakale <i>et al.</i>	2018	1 cylinder, 0.693 L, common rail, NA, water-cooled	5, 10, 20	1050 rpm, 80% load. Different fuel injection Pressures	-	-	↓	-	-	[95]
Atmanli <i>et al.</i>	2018	Four-cylinder, direct injection, naturally aspirated, air-cooled	5, 25, 35	Stationary conditions. Different engine loads	↑	↑	↓	-	↑	[96]
Lapuerta <i>et al.</i>	2018	Euro 6 Nissan 1.5 dCi, four-cylinder, four-stroke, turbocharged intercooled, common-rail	10, 13, 16, 20	NEDC	↑	↑	-	↓	↑	[97]
Lapuerta <i>et al.</i>	2018	Euro 6 Nissan Qashqai 1.5 dCi light-duty vehicle, four-cylinder, four-stroke, turbocharged, intercooled, common-rail	10, 13, 16, 20	NEDC	↑	↑	-	↓	↑	[62]
Wu <i>et al.</i>	2019	4-cylinder, 1.996 L, common rail, turbocharger	5	Variable speed: 2000 rpm-2800 rpm	↑	↑	-	↓	↑	[98]
Huang <i>et al.</i>	2019	4-cylinder, 1.99 L, common rail, turbocharger	20	1600 rpm, 0.8 MPa load. Different pilot injection rates	↑	↑	↑	↓	-	[99]
Rakopoulos <i>et al.</i>	2019	6-cylinder, 5.958 L, turbocharger, and air-to-air aftercooler	8, 16	Variable speed:1200 rpm-1500 rpm, variable load: 20% - 60%	↓	↑	-	↓	-	[100]
Li <i>et al.</i>	2019	4-cylinder, 4.334 L, NA, water cooled	20	1800 rpm, variable load: 20% - 80%	↑	↑	-	↓	↑	[101]
Huang <i>et al.</i>	2019	4-cylinder, 1.99 L, common rail, turbocharger	30	1600 rpm, 0.6 MPa load. Different pre injection ratios	↑	↑	↑	↓	↑	[102]
Emiroğlu	2019	1 cylinder, 0.349 L, NA, air-cooled	10	Variable speed: 1600 rpm - 3600 rpm, 80% load. Different injection pressures	-	-	↑	↓	↑	[103]
Huang <i>et al.</i>	2019	Four-cylinder, 16 valves, turbocharger, common-rail injection system	20	Stationary conditions. Study of EGR effect	↑	↑	↑	↓	↑	[70]

## Continued

Yusri <i>et al.</i>	2019	Isuzu, four-cylinder, four-stroke, turbocharged, common-rail	5, 10, 15	Stationary conditions. Low load	↓	↓	↓	-	↑	[104]
Nour <i>et al.</i>	2019	Single-cylinder, direct injection, naturally aspirated, air cooled	10, 20	Stationary conditions.	↑	↑	↓	↓	↑	[65]
Joy <i>et al.</i>	2019	Kirloskar TV1, single-cylinder, four-stroke	10, 20	Stationary conditions.	↓	↓	↓	↓	↓	[105]
Zhou <i>et al.</i>	2020	4-cylinder, 2.169 L, common rail, turbocharger	10, 20, 30	1400 rpm, 0.8 MPa load. Different EGR rates and post injection	↓	↑	↑	↓	↑	[106]
Ganesan <i>et al.</i>	2020	1 cylinder, 0.661 L, NA, water cooled	40	1500, 4 bar load. Different EGR rates and start of injection	-	-	↑	↓	↑	[107]
Fayad	2020	1 cylinder, 0.499 L, common rail, NA, water-cooled	20	1800 rpm, 4 bar load. Different EGR rates	↓	↓	↓	↑	↑	[108]
Pan <i>et al.</i>	2020	YC-4Y22, 4-cylinder, 4-valve, 4-stroke, common rail, variable-geometry turbocharger	50	Stationary conditions. Different injection pressures	↑	↑	↑	↓	↑	[109]
Jamrozik <i>et al.</i>	2021	1 cylinder, 0.573 L, NA, air-cooled	10, 20, 30, 40, 50, 60	1500 rpm, 100% load	↓	↑	↑	↓	-	[110]
Pan <i>et al.</i>	2021	4-cylinder, 2.169 L, common rail, turbocharger	10, 20	1400 rpm, 0.6 MPa load. Different post injection rates	↓	↑	↓	↓	↓	[111]
Yan <i>et al.</i>	2021	1 cylinder, 0.51 L, common rail, water-cooled	20, 40	1200 rpm, variable load: 0.45 MPa - 0.65 MPa. Different intake pressures	↓	↕	↑	↓	↑	[66]
Pinzi <i>et al.</i>		4-cylinder, 2.298 L, common rail, turbocharger, intercooler	10, 20	WLTP and five steady state operating modes	-	↑	↕	↓	-	[112]
Siva Prasad <i>et al.</i>	2021	Single-cylinder, 4-stroke, direct injection	20, 40	Stationary conditions. Different engine loads	↓	↑	↓	↓	-	[113]
Li <i>et al.</i>	2021	Yanmar, single-cylinder, four-stroke, common rail	50	Stationary conditions. Different injection pressures and strategies	-	↑	↓	↓	↑	[114]

## Continued

Luis Tipanluisa <i>et al.</i>	2022	four-cylinder heavy-duty diesel engine (HDDE).	5, 10, 20	Different speed and load conditions	↓	↑	↑	-	↓	[60]
Zhu, Qiren <i>et al.</i>	2023	common-rail diesel engine	20, 50	under two distinct loads (~30%, ~60%) and two injection pressures (40 MPa, 60 MPa)	-	↑	↓	↓	-	[115]

## 7. Potential of N-Butanol Diesel Blends

Diesel engines are recognized for their high efficiency, high compression ratio, and excellent stability, but have traditionally been associated with significant emissions of particulate matter (PM) and nitrogen oxides (NO<sub>x</sub>). In recent decades, manufacturers have substantially reduced these harmful emissions by introducing new technologies [116]. B. Mahr *et al.* [117] investigated the future and potential of diesel injection systems, suggesting that new product engineering, such as new nozzle designs (k-factor, vario nozzle) or newly developed actuators, are key factors for the development of fuel injection systems. With a flexible diesel injection system, it is possible to achieve the optimum rate shaping, injection timing, and multiple injections at each point of the engine map, allowing for the best compromise between emission reduction and fuel consumption. Besides the injection system, other important measures to improve combustion and achieve low exhaust gas raw emissions in heavy-duty engines include the exhaust gas recirculation (EGR) rate, turbocharging, intercooling, four-valve technology, the shape of the combustion chamber, compression ratio, air motion, and the air-fuel ratio. A significant reduction in soot emission can be achieved with higher boost pressure. Suitable engine modifications include higher maximum combustion peak pressure, increased EGR rate, and higher charge air pressures through variable turbine geometry (VTG) or, even more effectively, with two-stage turbocharger systems. X. Zhou *et al.* [106] investigated the potential of n-butanol/diesel blends for CI engines under post-injection strategy and varying EGR rates. A turbocharged diesel engine was utilized to examine the effects of n-butanol and EGR rates on engine emissions and combustion performance. The results indicate that post-injection has a minimal impact on ignition delay time and brake thermal efficiency (BTE), and it reduces the emissions of CO, HC, NO, and soot. Under certain post-injection strategies, the addition of n-butanol (10%, 20%, and 30%) significantly reduced CO and soot emissions. Among these after-treatment systems, a selective catalytic reduction (SCR) system is used to convert NO<sub>x</sub> emissions to nitrogen (N<sub>2</sub>). The NH<sub>3</sub>-SCR technology is preferred by manufacturers due to its higher efficiency in NO<sub>x</sub> conversion, nearly 95% within a temperature range between 200°C and 350°C [118] [119]. Rakopoulos *et al.* conducted a study on exhaust emissions with ethanol or n-butanol diesel fuel blends during transient operation. They identified

and discussed the main mechanisms of transient emissions for all exhaust pollutants, noting many of these mechanisms are interrelated with the inherent discrepancies observed during transients, most notably turbocharger lag [13].

Manufacturers continue to experiment with diesel engines, adding significant extra costs to vehicles and breaking the trend of ever-increasing engine efficiency [116]. The global trend towards stricter vehicle emissions standards requires a deeper understanding of advanced biofuels like butanol. This knowledge is essential for developing strategies to decrease the reliance on non-renewable fossil fuels and minimize the environmental impact of road transport vehicles with diesel engines. Research indicates a promising potential for n-butanol as an advanced biofuel for partially replacing fossil diesel in diesel engines. Further studies have explored the use of n-butanol and conventional diesel fuel blends under the World Harmonized Steady-State Cycle (WHSC) in commercial heavy-duty diesel engines. The combination of modern De-NO<sub>x</sub> post-treatment devices and the anticipated increase in advanced biofuels within commercial diesel fuels presents a new challenge for engine manufacturers and the biofuel industry. Additionally, there is a significant lack of information on the effects of n-butanol blends with commercial diesel, which will be necessary for future European Union (EU) regulations to ensure the reliability of diesel engines and post-treatment systems under more realistic operating conditions [119].

## 8. Conclusions

The paper reviewed the use of butanol as a biofuel in diesel engines for road freight transportation, tractors, harvesters, and cogeneration. It specifically explored the sustainability of lignocellulosic butanol, the physical and chemical properties of butanol-diesel blends, and their impact on combustion, performance, and emission characteristics in CI engines under various operating conditions. N-butanol, primarily produced through biological processes like acetone butanol ethanol (ABE) fermentation, has significant potential to reduce greenhouse and exhaust gas emissions compared to fossil diesel fuel. Higher alcohols such as butanol have properties closer to diesel fuel than lower alcohols like ethanol. Despite ethanol being the most commonly used alcohol in the transport sector, n-Butanol demonstrates advantages such as higher viscosity, better lubricity, higher heating value, improved blend stability, better cold-flow properties, and higher density. Therefore, N-butanol is a superior renewable component compared to ethanol for diesel blends due to its higher flash point, lower volatility, and less corrosive nature, making butanol blends safer for transportation, fuel handling, and storage. Its properties significantly impact the combustion characteristics of the alcohol blend, affecting temperature, pressure, and apparent heat release rate. Literature shows that 5% and 10% blends increase pressure and apparent heat release rate but may slightly lower temperature, enhancing thermal efficiency, whereas 20% blends reduce pressure, apparent heat release rate, and temperature under all operating conditions.

Studies have shown that adding n-butanol, in blends of 5% to 10%, to conventional fuels can either decrease or increase CO and THC emissions, while sharply reducing particulate matter emissions. However, for NO<sub>x</sub> emissions, the effect of blending alcohol into diesel fuel is uncertain, with both increases and decreases reported. This variability depends on the specific alcohol percentage, engine calibration, and characteristics of the transient schedule. It has been observed that a 10% butanol blend is suitable for n-butanol-diesel due to its favorable performance and reduction in particulate emissions, without significant changes in NO<sub>x</sub> gaseous emissions. Furthermore, blending up to 40% butanol with diesel does not require additional engine modifications or ECU recalibrations in diesel engines calibrated for 100% diesel fuel.

### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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