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Review

Performance and Emission Characteristics of Second-Generation Biodiesel with Oxygenated Additives

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Abstract: Biofuels are environmental friendly renewable fuels, that can be directly used in a diesel engine. However, a few shortcomings like a higher density, viscosity, a lower calorific value and increase in NOx emissions, has caused researchers to look for fuel additives to improve the physiochemical properties of these fuels and to enhance their performance and reduce harmful emissions. It is for this reason that modern research is focused on blending oxygenated additives such as alcohols and ethers with different generations of biodiesel. Since most studies have covered the effect of alcohol on biodiesel, there are few studies which have investigated the effect of oxygenated additives such as alcohols and ethers, especially related to second-generation biodiesel. Moreover, the details of their composition and molecular structure are still lacking. Hence, this study focuses on the performance and emission characteristics of biodiesel with the inclusion of oxygenated additives (alcohols and ethers) of non-edible-oil-based second-generation blends. The reviewed results showed that *Neem* biodiesel with methanol or diethyl ether reduced brake-specific fuel consumption by 10%, increased brake thermal efficiency by 25% and reduced CO and HC emissions due to a higher oxygen content. Diethyl ether reduced NOx emissions as well by producing a cooling effect, i.e., a reduced in-cylinder temperature. The addition of heptane, butanol and di ethyl ether to *Jatropha* biodiesel showed an improved brake thermal efficiency and an increment in brake-specific fuel consumption (5–20%), with reduced HC and CO_2 (3–12%) emissions. *Calophyllum inophyllum* biodiesel also showed impressive results in terms of improving efficiency and reducing emissions with addition of butanol, pentanol, decanol and hexanol. Other factors that influenced emissions are the cetane number, viscosity, density and the latent heat of evaporation of tested biodiesel blends. This review would help the research community and the relevant industries to consider an efficient biodiesel blend for future study or its implementation as an alternate fuel in diesel engines.

Keywords: second-generation biodiesel; biodiesel feedstock; engine performance; exhaust emissions; oxygenated additives

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1. Introduction

Non-conventional energy sources have to be adopted because increased energy security is unavoidable [1]. In the worldwide market, diesel engines have been identified as a major means of transportation and are widely employed in power stations [2,3]. Furthermore, rising greenhouse gas emissions, particularly carbon dioxide, has led to a considerable rise in global temperatures [4]. The level of carbon dioxide is expected to

rise by approximately 80% from 2007 to 2030 [5]. Due to diminishing fuel supplies and growing environmental concerns, researchers have shifted their focus to alternative fuels [6]. Several nations have made developments on the use of biodiesel through government-led initiatives that involve both incentives and volumetric demands [7]. Biofuels have seen rapid growth in the global fuel market over the last decade due to their eco-friendliness and nontoxicity, and this trend is expected to continue [8,9]. Biodiesel is a mono alkyl ester produced from fatty acid esters of first-, second-, and third-generation feedstocks, namely edible, non-edible, and waste oils, respectively [10,11]. As first-generation biodiesel comprises edible oils, its utilization to produce biodiesel on a mass scale may lead to severe consequences, like a lack of agricultural land for food crops and a hike in the prices of agricultural and produced goods. It is for these reasons that second-generation biodiesel is preferred [12]. Biodiesel derived from various feedstocks has shown impressive properties such as a high aromatic content, cetane number, lubricity and oxygen concentration, and lower sulfur-emission levels. However, the few disadvantages may include a low calorific value, and a high viscosity, volatility and flash point [13]. While biodiesel can be utilized directly within the CI engine without substantial changes, there is a serious problem with the loss of torque and power because of its lower heating value [14]. The utilization of biodiesel as the only fuel in CI engines is overlooked due to its high viscosity and NOx-emission issues. Diesel can be blended with oxygenated additives like alcohols or ethers to obtain desirable results [15,16]. These additives reduce the viscosity of the biodiesel blend and may also reduce emissions in a diesel engine when blended with biodiesel [17–19]. In most cases, utilizing biodiesel with or without diesel reduces the engine performance by increasing brake-specific fuel consumption and decreasing brake thermal efficiency [20]. Due to this loss in engine performance, researchers are focusing on bringing these performance characteristics to diesel fuel so that utilizing biodiesel can also be beneficial in terms of engine performance, just like it is already, whilst simultaneously showing reductions in emissions, except for NOx. Hence, this research will continue utilizing biodiesel in diesel engine until it becomes beneficial in terms of engine performance and emissions.

This article reviews the previous studies conducted on the performance and emission characteristics of diesel engines for oxygenated second-generation biodiesel, i.e., biodiesel produced from non-edible oil and blended with oxygenated additives. This review will help researchers to analyze and consider the different second-generation feedstocks for biodiesel production and the effect of oxygenated additives on this feedstock in terms of engine performance and emissions.

2. Experimental and Numerical Techniques

2.1. Experimental Techniques for Performance

Fuel performance is measured in terms of brake thermal efficiency (BTE), brake-specific energy consumption (BSEC), brake-specific fuel consumption (BSFC), indicated mean effective pressure (IMEP), in-cylinder pressure measurement, heat-release rate and ignition-delay analysis using a wide range of diesel engines [20]. Among the most used diesel engines for research are Cussons and Kirloskar engines, as shown in Figure 1. Different types of dynamometers are used to measure the power and torque of the engine under various operating conditions. Performance maps can be generated to analyze parameters such as torque, power, fuel consumption and efficiency under varying conditions to obtain the optimum results. Fuel consumption can be determined by measuring the amount of fuel consumed by the engine over a specified period. This can be achieved by using fuel-flow meters or by weighing the fuel before and after the test. The air/fuel ratio is monitored using exhaust gas analysis or oxygen sensors to obtain real-time data. The heat release rate is analyzed by quantifying the rate and timing of heat released during combustion. Heat-release data are obtained from the in-cylinder pressure-curve and crank-angle analysis. Utilizing advanced sensors, data-acquisition systems and control units, various engine parameters, such as temperature, pressure, fuel flowrate, and exhaust-gas composition can be continuously monitored and recorded during the engine operation. These data are

essential for performance evaluation and optimization as it provides valuable information regarding the performance, efficiency, and emission behavior of diesel engines.

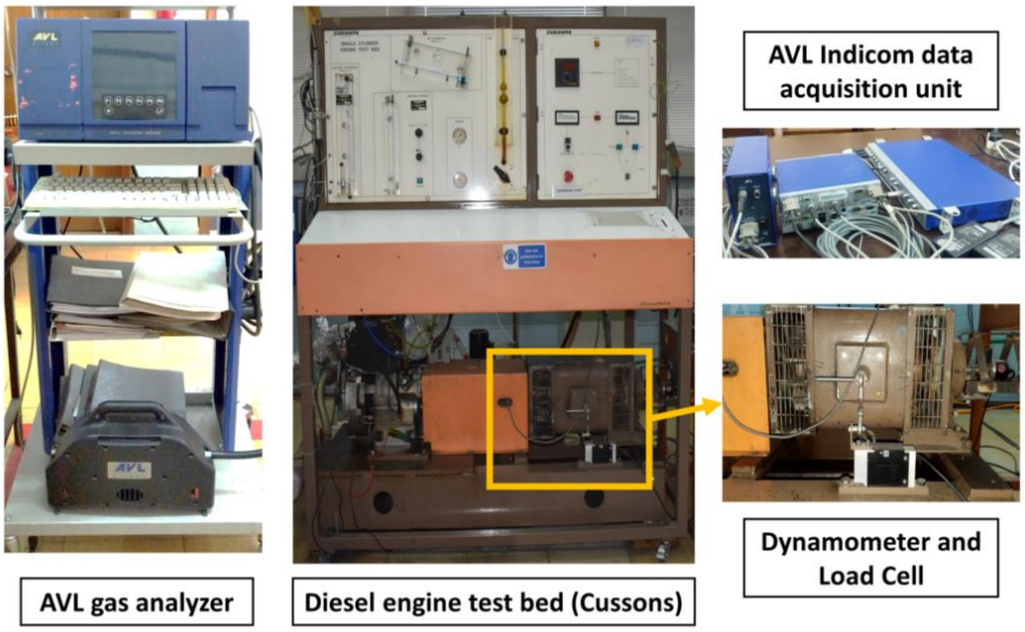

Figure 1. An experimental setup for analyzing combustion, performance, and emissions.

2.2. Experimental Techniques for Emissions

Various types of emission analyzers are used to measure and quantify different pollutants emitted by engines. AVL offers a range of gas analyzers for various applications, including exhaust-gas analysis, emission measurement, and combustion analysis. These analyzers are used by automotive manufacturers, research institutions, and regulatory bodies to assess vehicle emissions, optimize engine performance, and ensure their compliance with environmental regulations. Figure 1 shows an AVL gas analyzer along with an AVL indicom module for data acquisition. Gas analyzers from Testo are also very reliable and have a wide range of applications due to their portability. FTIR spectrometers are advanced tools used to analyze the composition of exhaust gases and to quantify a wide range of gases, including both primary pollutants and trace gases. Smoke intensity from the exhausts is measured by a smoke-opacity meter which measures the amount of light blocked by exhaust smoke. They provide a quick and indirect assessment of particulate emissions. Nitrogen oxide (NO and NO_2) emissions are analyzed using chemiluminescence analyzers. They exploit the phenomenon of light emission during chemical reactions involving NOx, providing accurate and real-time measurements of NOx concentrations [11]. The flame ionization detector is commonly used for measuring hydrocarbon emissions, including unburned hydrocarbons (HC) in the engine exhaust. It operates by ionizing hydrocarbon molecules in a hydrogen flame and measuring the resulting ion current, which is proportional to the hydrocarbon concentration. PM emissions are analyzed using techniques like gravimetric analysis, light scattering, or optical methods to quantify particulate emissions [17].

2.3. Experimental Analysis of Combustion

Combustion analysis involves studying the characteristics, behavior, and interactions of flames in combustion systems. Several experimental methods have been employed to investigate flame dynamics and gain insights into combustion processes [18]. Some commonly used experimental methods include high-speed imaging techniques, such as high-speed cameras or laser-induced fluorescence (LIF), which capture the temporal and spatial evolution of flames. They provide visual information about the flame structure,

flame front propagation, and flame-stabilization mechanisms. Flame chemiluminescence analysis involves optical techniques to capture and analyze the emitted light from excited photons during combustion, providing information about the flame shape, location, and stability. Some commonly used laser diagnostics methods include laser-induced fluorescence (LIF), planar laser-induced fluorescence (PLIF), laser-induced incandescence (LII), and laser Doppler velocimetry (LDV) [16]. These techniques can provide information about species concentration, temperature, lamina flame velocity, and turbulence within the flame. Particle image velocimetry (PIV) is a technique used to measure fluid flow velocities within the flame region. By seeding the flow with particles and illuminating them with a laser sheet [13], PIV captures the motion of the particles, allowing for velocity vector mapping and the analysis of flame flow dynamics. Acoustic techniques, such as microphones or pressure sensors, are used to analyze the sound generated by the combustion process. These measurements help in detecting and studying combustion instabilities, and can be useful for controlling and optimizing combustion systems. These experimental methods, when combined with appropriate data-acquisition systems and analysis techniques, provide valuable insights into flame dynamics, combustion performance, pollutant formation, and overall combustion-system optimization.

Quantifying the ignition-delay time is also crucial for understanding the combustion characteristics of fuels and assessing their performances in internal combustion engines. The ignition-delay time refers to the time interval between the start of fuel injection or the introduction of an ignition source and the onset of visible combustion. A constant-volume chamber alongside a rapid compression machine (RCM) or a shock tube, is typically used for ignition-delay measurements [19]. These chambers provide controlled conditions and allow for the precise measurements of the ignition-delay time.

2.4. CFD Models for Combustion, Performance and Emissions

Several models and experimental methods can be employed to model combustion and emissions. Mathematical models are often used to simulate the behavior of diesel engines and predict their performances and emissions. These models are based on the fundamental principles of thermodynamics, fluid mechanics, and combustion. They take into account factors such as engine geometry, fuel properties, injection timing, and combustion characteristics to estimate engine performance parameters and emission levels. computational fluid dynamics (CFD) tools analyze the fluid flow, combustion, and heat-transfer processes inside the diesel engine [21]. It involves the discretization of the fluid domain, and then solves the governing equations for fluid flow and combustion using computational algorithms. CFD can provide detailed insights into the flow patterns, combustion efficiency, and pollutant formation within the engine.

AVL FIRE is specifically designed for engine simulation and allows the detailed modeling of diesel-engine processes, including combustion, air-fuel mixing, and pollutant formation. CONVERGE is another CFD-based software that offers advanced modeling capabilities for diesel engines, including spray modeling, combustion chemistry, and emission prediction. Diesel RK [22] and Ricardo WAVE is a 1D engine-simulation software used for modeling the gas dynamics and thermodynamics of internal combustion engines. It provides tools for diesel-engine performance analysis, emissions prediction, and system-level optimization. These software packages provide a range of features and functionalities for diesel-engine analysis and simulation.

Combustion analysis involves measuring in-cylinder pressure and temperature using pressure transducers and thermocouples. These data help evaluate the combustion efficiency, peak pressure, ignition delay, and heat-release characteristics. Modelling combustion involves reaction kinetics that consist of rates of chemical reactions occurring during fuel oxidation and combustion [23]. The first step is to understand the fuel composition and the set of reactions involved, which may be obtained from existing databases, such as the GRI-Mech, AramcoMech, or CHEMKIN libraries, or developed through experimental and theoretical studies. For each reaction in the mechanism, the corresponding rate ex-

pression needs to be defined. The rate expressions incorporate temperature, pressure, and species concentrations as variables. Different types of rate expressions can be used, such as Arrhenius, Troe, or Lindemann forms, depending on the reaction kinetics and reaction mechanisms involved [23]. The various reaction parameters involved in reaction kinetics are the rate coefficients, activation energies, and pre-exponential factors. These are obtained through experimental measurements, quantum-chemical calculations, or estimated using correlations and data from similar reactions.

The developed kinetic mechanism of a reaction can be integrated into computational models, such as CFD simulations or detailed chemical kinetic solvers [24]. These models solve the conservation equations for mass, momentum, and energy along with the chemical reactions described by the kinetic mechanism. The models simulate the combustion process, including ignition, flame propagation, and pollutant formation, based on the chemistry described by the mechanism.

3. Feedstock for Biodiesel Production

According to the report of the "European Academies' Science Advisory Council" released in 2012, biodiesels are classified as first-, second-, and third-generation biodiesels based on their origin, with fourth-generation biodiesel already in the early phases of fundamental research using man-made biological instruments [10]. First-generation biodiesels are made from edible feedstocks such as rapeseed oil, palm oil, corn oil, mustard oil, soybean oil, rice oil, etc. [25]. Edible feedstock was frequently employed in the production of biodiesel during the outset of the biodiesel era [26]. The major advantages of first-generation feedstocks are crop accessibility and a reasonably easy processing technique. The risk of food-supply shortages is a key drawback of employing these feedstocks that boost the cost of food items [27]. Flexibility to environmental conditions, high expenses, and restricted growing space are other barriers to biodiesel synthesis from edible sources. These disadvantages have pushed consumers to seek out alternatives to biodiesel production. Thus, researchers have shifted towards second-generation feedstock based upon non-edible oils [28,29]. Third-generation feedstock is based upon waste oils which are exempt from the consideration of being edible or non-edible. The current study focuses on second-generation feedstocks in detail.

3.1. Second-Generation Feedstocks

3.1.1. *Calophyllum inophyllum* (*Alexandrian laurel*)

Calophyllum inophyllum is a non-edible oilseed decorative greenish tree in the Clusiaceae family [30]. It is called Penaga Laut in Malaysia. It grows near the shore and in lowland woods, although it may also be found inland at higher altitudes. Eastern Africa, Southeast Asia, southern coastal India and Australia are its natural habitats [31]. In English, *Calophyllum inophyllum* is also known as "*Alexandrian laurel*". *Calophyllum inophyllum* is an evergreen sub-marine tree that grows to be medium to large in size, i.e., to a height of 8 to 20 m, and has a broad spreading crown of uneven branches. Its leaves are elliptical, tough and glossy. *Calophyllum inophyllum* kernels are the source of non-edible oil, having a high oil content of 75%, with the oil containing around 71% unsaturated fatty acids (mainly linoleic and oleic acids) [32].

3.1.2. *Jatropha* (*Jatropha curcas*)

Jatropha grown in marginal, semi-arid, regions is an oilseed plant. It is a Euphorbiaceae family plant that may reach a height of 5–7 m. Scrub may be gathered twice a year, is rarely visited by cattle, and can be productive for 30 to 50 years [33]. After one year of plantation, seeds may be obtained from the plant, and its output is greatest after five years of plantation. The *Jatropha* plant requires 100 to 150 cm of rain each year [32]. The seeds of the *Jatropha* plant contain around 20% to 60% oil [34]. *Jatropha* contains primarily unsaturated components such as linoleic acid (31.3% to 43.3%) and oleic acid (34.2% to 44.8%), as well as some saturated components such as stearic acid (7.0% to 7.3%) and

palmitic acid (13.3% to 15.2%) [35]. *Jatropha* oil has a density of 916 kg/m^3 (at 15 °C), a heating value of 38.96 MJ/kg and a viscosity of 37.280 mm^2/s (at 40 °C) [36].

3.1.3. *Karanja* (*Pongamia pinnata*)

China, South-east Asia, Australia, and the United States are the primary producers of *Karanja* [37]. The *Karanja* plant may grow to a height of 15 m to 25 m. It is a member of the Leguminosae family [28]. Blooming occurs three to four years after plantation, and it ripens four to seven years afterwards [38]. About 9 kg to 90 kg of seeds can be obtained from a single plant of *Karanja*. The quantity of oil in *Karanja* seed varies greatly 25% to 40% [39]. *Karanja* oil has a density of 933 kg/m^3 (at 15 °C), a heating value of 35.992 MJ/kg, and a viscosity of 39.90 mm^2/s (at 40 °C). *Karanja* oil contains 10.8% to 18.4% linoleic acid, 2.4% to 9.0% stearic acid, and 44.3% to 71.4% oleic acid [40].

3.1.4. *Jojoba* (*Simmondsia chinensis*)

The primary producers of the *Jojoba* plant are Mexico, Arizona, California, and India [41]. The Simmondsiaceae family includes the *Jojoba* plant. The plant may reach a height of 1 m to 2 m. The leaves of the *Jojoba* plant have an oval profile and greyish green color, with a width of 1.5 cm to 3 cm and a length of 2 cm to 4 cm [42]. The liquid wax ester and oil produced from the seeds of the *Jojoba* plant are the main products. *Jojoba* oil has a viscosity of 24.89 mm^2/s (at 40 °C), a density of 868 kg/m^3 (at 15 °C) and a heating value of 46.47 MJ/kg [43]. The seeds of the *Jojoba* plant contain around 43.4% to 66.1% oleic acid and 25.1% to 34.5% linoleic acid with 40% to 50% of oil content [44].

3.1.5. *Mahua* (*Madhuca longifolia*)

It is an evergreen tree of the Sapotaceae family. A warm and humid atmosphere is ideal for the cultivation of the *Mahua* plant. Every year, 20 kg to 200 kg of seeds are generated from a single *Mahua* plant [45]. The *Mahua* plant may grow to a maximum height of 20 m. The average age of a *Mahua* plant is 60 years, and seeds begin to develop after 10 years of cultivation [46]. *Mahua* seeds have 35% to 50% oil content. *Mahua* oil has a density of 942 kg/m^3 (at 15 °C), a heating value of 36.85 MJ/kg, and a viscosity of 32.01 mm^2/s (at 40 °C). It contains 41% to 52% oleic acid, 16.0% to 28.3% palmitic acid, 20% to 25.2% stearic acid, and 8.9% to 18.4% linoleic acid [28,47].

3.1.6. Rubber Seed (*Hevea brasiliensis*)

Rubber seed is mostly produced in Brazil, although it is also produced in Indonesia, Thailand, Malaysia, and India. It is a member of the Euphorbiaceous family [48]. The rubber tree is quite tall, reaching heights of up to 34 m. Rubber-plant growth requires a non-frosty climate and a lot of rain. Copra or its kernel contains 40% to 50% brown oil, while its seed has 50% to 60% oil [49]. Rubber-seed oil has a viscosity of 42.54 mm^2/s (at 40 °C), a density of 917 kg/m^3 (at 15 °C), and a heating value of 38.64 MJ/kg. Rubber-seed oil has a high concentration of unsaturated fatty acids such as 16.3% linolenic acid, 24.6% oleic acid and 39.6% linoleic acid [28].

3.1.7. *Neem* (*Azedarach indica*)

Pakistan, Bangladesh, India, Australia, Sri Lanka, Japan, and Indonesia are the primary producers of *Neem*. *Neem* is a member of the Meliaceae family. It may be grown in all types of sand, including dry, calcareous, saline, rocky soil, shallow soil, and clay soil [50]. This plant may grow to a height of 12 m to 18 m. The lifespan of the *Neem* plant is around 150 to 200 years, with the maximum output after 15 years. The oil content of the *Neem* seed is 20% to 30% [48]. *Neem* oil has a density of 929 kg/m^3 (at 15 °C) and a viscosity of 38.875 mm^2/s (at 40 °C). *Neem* oil has a high proportion of unsaturated fatty acids such as 6% to 16% linoleic acid and 25% to 54% oleic acid, as well as saturated fatty acids such as 9% to 24% stearic acid [51].

3.1.8. *Castor* (*Ricinus communis*)

Castor (also known as *Castor bean* and *Ricinus communis* L.) is a tree or shrub that may grow from approximately 1 m to several meters under perennial culture, depending on the cultivar [51]. *Castor* oil seeds typically contain 40% to 55% oil, indicating a very high potential when compared to other often used oil crops [52]. Furthermore, the cost of plantation might be 50% less than the cost of growing *Jatropha*. Ricinoleic acid content in *Castor* oil is from 80 to 90 percent (12-hydroxy-9-cis-octadecenoic acid) [53–55]. Because of this peculiar composition, its viscosity is approximately seven times greater than that of other vegetable oils, which makes it unsuitable for biodiesel synthesis [54]. In addition to ricinoleic acid, *Castor* oil may include trace amounts of oleic, palmitic, linoleic, linolenic, and stearic acids depending on its origin [56].

4. Biodiesel Production

Biodiesel generation from any feedstock comes from the same renewable origin. It is produced from photosynthesis, or the transformation of solar energy to chemical energy. Hence, the production of biodiesel is dependent upon solar energy, which is the foundation of a sustainable bioeconomy [28]. Despite considerable advances in the conversion of solar energy into electricity via photovoltaic cells, biodiesel continues to serve an important role in modern life, notably in transportation. According to the ASTM, "biodiesel" refers to monoalkyl esters of long-chain fatty acids produced by the transesterification of triglycerides using a catalyst and methanol [57]. After the transesterification process, glycerol is formed as a by-product. Methanol is widely utilized for biodiesel production due to its low cost and ease of availability. Table 1 summarizes the various reaction conditions and reagents, such as the catalyst used for the production of biodiesel from various second-generation feedstocks.

Table 1. Parameters and reaction conditions for biodiesel production from second-generation feedstock, using methanol as the alcohol.

Biodiesel Feedstock	Catalyst	Catalyst Amount	Alcohol:Oil Ratio	Reaction Conditions	Yield (%)	Reference
Jatropha Oil	KOH	2.09 wt%	7.5:1	60 min/60 °C	80.5	[58]
Jatropha Oil	Li-CaO	5 wt%	12:1	120 min/65 °C	>99	[59]
Jatropha Oil	$CaO-Al_2O_3$	n/a	5:1	180 min/100 °C	82.3	[60]
Karanja Oil	Li-CaO	5 wt%	12:1	60 min/65 °C	>99	[59]
Karanja Oil	H_2SO_4	1 mL	6:1	60 min/55 °C	98.6	[61]
Castor Oil	KOH	0.73 wt%	5.4:1	2.5 h/64 °C	97.8	[62]
Castor Oil	KOH	1.25 wt%	12:1	60 min/60 °C	94.9	[63]
Mahua Oil	KOH	1 wt%	8:1	60 min/55 °C	95.71	[61]
Mahua Oil	KOH	0.7 wt%	6:1	30 min/60 °C	98	[64]
Rubber Seed Oil	NaOH	5 g	9:1	30 min/45 °C	98	[65]
Rubber Seed Oil	H_2SO_4	0.5 wt%	6:1	120 min/40–50 °C	99	[65]
Neem Oil	Cu-ZnO	10 wt%	10:1	60 min/55 °C	97.18	[66]

5. Oxygenated Additives

Oxygenated additives are distinguished from fossil fuels by oxygen bonding in their chemical structure. Oxygenated-additive-based blends are a form of synthetic fuel blend in which the fuel is chemically linked by oxygen atoms to supply enough oxygen to accelerate combustion and decrease [17,67]. These additives must have a low volatility, high cetane number and, to avoid separation events, it must generate a homogeneous mixture with biodiesel in order to be utilized in a diesel engine [68]. Alcohols and ethers are the two most common oxygenated additives utilized by researchers in various kinds of biodiesel. This section discusses the oxygenated additives that are currently in use.

5.1. Methanol

The first member of the family of alcohols is methanol which is a single-carbon hydroxyl compound with a 49.93% oxygen content [69,70]. Methanol, being a first member of the alcohol family, has the highest oxygen content compared to other alcohols in the family, making it a viable oxygenated additive to be used with biodiesel and diesel blends in diesel engines. Methanol has been utilized in the racing industry for a long time due to its power-enhancing properties and burning capacity without black smoke [71]. Methanol, when mixed with diesel and biodiesel, shows higher CO and HC levels with less NOx emissions, owing to its lower cetane number. It also shows a longer ignition delay, due to which it cannot be used directly in diesel engines due to its lower ignitability. Apart from that, methanol is cost-effective, and the hydroxyl component in its composition effectively assists in the combustion process [72]. Generally, a short ignition delay is a favorable indicator of reduced emissions and an improved engine efficiency owing to reduced soot and a shorter combustion time [73]. The scientific community has overcome these limitations of methanol by blending or fumigating it with diesel, biodiesel or other additives to improve its cetane number [74].

5.2. Ethanol

Ethanol is among the most studied members of the alcohol family [75]. It has an oxygen content of 34.73%, which is less than methanol but the highest of the other alcohol family members. However, the greater expenses of producing ethanol throughout the nineteenth century significantly reduced the possibilities of its full use, and it was considered primarily in cases of fuel shortages [76]. Another solution proposed was to use it as a fuel additive. Recently, significant advancements in production procedures have resulted in better yields at reduced production costs when compared to conventional processes [77]. With high pollution standards and dwindling fossil-fuel resources, emerging countries have prioritized ethanol as a potential oxygenated fuel additive under a variety of policies. Brazil tops the list owing to its extensive use of ethanol as a blend in fuel because of the high quantity of sugarcane as a feedstock [78]. Ethanol-mixed fuels can offer exceptional absorption qualities, which efficiently clean the fuel-delivery and -distribution systems in automotive vehicles, eliminating dangerous unwanted elements that may have collected over time. Industrial safety measures in material storage must be followed because of its lower flashpoint than diesel [74].

5.3. Propanol

Propanol occurs in nature in two isomers: 1-propanol and 2-propanol, often defined as n-propanol and isopropanol, respectively. Propanol contains an oxygen content of 26.62%, but its higher cost of production has impacted its potential as a replacement fuel since its inception, restricting the amount of studies conducted on this fuel [79]. Propanol outperforms methanol and ethanol in some respects, mainly because of its longer carbon chain, improved solvent properties, reduced corrosive hazards, and higher calorific values and cetane number [74]. Propanol's other beneficial features include a greater flash point and energy density than earlier family members of the alcohols. Propanol also has a higher latent heat of vaporization in contrast to lower-chain alcohols and a lower self-ignition temperature, which decreases the ignition-delay period [80,81].

5.4. Butanol

Butanol is the alcohol that, due to its higher oxygen content of 21.59%, has been researched the most as an oxygenated additive in biodiesel blends. It has a distinct banana odor and is clear and colorless. The –OH group can connect to the four-carbon chain structure in four distinct places, resulting in four isomers [82]. Following their work on ethanol, investigators turned to butanol to overcome the solubility problems of primary alcohols while also providing a higher cetane number when blended [83]. Aside from the virtues listed above, it is less corrosive and toxic than ethanol, and its lower volatility

and higher flash point make it more compatible with contemporary fuel systems [84]. Furthermore, its kinematic viscosity is quite near to that of normal diesel, which is much desired for system lubrication and fuel injection [85]. Butanol offers a significantly superior combustion quality than methanol and ethanol because of its higher heating value and lower heat of vaporization, causing earlier evaporation and reducing cold-start issues [86].

5.5. Pentanol

Pentanol is a five-carbon straight long-chain alcohol with an 18.15% oxygen content that is considered a potential alternative fuel by the scientific community owing to its production methods and benefits over isomers of butanol [87]. Pentanol may be synthesized from glucose using Escherichia coli biosynthesis and from biological processes utilizing designed microbes, similar to the natural fermentation process. Despite its longer chain, these biological production methods use significantly less energy, making pentanol an attractive renewable alternative [88]. Pentanol is distinguished from butanol or other primary alcohols because of its superior blend stability, higher energy content, higher cetane number, and other characteristics including density, viscosity, and latent heat of vaporization that are very close to reference value of diesel [89]. Unlike ethanol and methanol, pentanol also inhibits corrosion, preserving the fuel distribution and supply system. Beside the benefits listed above, pentanol has a low polar interaction parameter thus no incidents of phase separation occur because of its hydrophobic character [74].

5.6. Hexanol

Hexanol, having 15.7% oxygen content, is a colorless alcohol including a six-carbon long chain that is produced via ethanol oligomerization in the industrial sector. Biodegradable agricultural waste and beverage processes provide the bulk of hexanol feedstock [90,91]. Hexanol has a higher energy content, cetane number, blend stability, and density than prior alcohols due to increased carbon chain length. Its density and viscosity are much similar to those of diesel than of primary alcohols, making it a potential alternative fuel. The hexanol's oxygen atom forms a strong hydrogen bond in blends, allowing it to function as an oxygenated additive. It can also be used as an ignition booster [92].

5.7. Octanol

Octanol, having an oxygen content of 12.29%, is an alcohol with an eight-carbon-long chain that is generated industrially by ethylene oligomerization, as opposed to hexanol, which is created using ethanol [93]. Octanol, like other higher alcohols, has received a lot of interest from scientists because of its environmentally favorable production techniques, including oxo-synthesis, bacteria, and fatty-acid reduction [94]. Because of lingo-cellulosic biomass as its source of production, octanol has been recognized as a bio-derived fuel, prompting significant investigation into the fundamental combustion properties of octanol [95]. However, when compared to diesel, its other properties, such as its lower vapor pressure and higher surface tension, compensate for its low boiling point, and give it superior spray characteristics. Due to its lower hygroscopicity, octanol, like other higher alcohols, has non-corrosive qualities [96].

5.8. Decanol

Decanol is a ten-carbon long-chain alcohol with an oxygen content of 10.11%. The liquid is generally colorless to a light yellowish color. It is considerably more useful in the chemical and food industries than as a replacement fuel in diesel engines. However, a new research article has recommended utilizing coconuts as a source for decal synthesis, which contains yeast such as Yarrowia lipolytica or decanoic acid; this method is also cost-effective, giving a high yield [93]. As a result, the promise of using vegetable bio-resources and biomass, such as waste protein and lignocellulosic material, has encouraged researchers to investigate decanol as a potential fuel. The bulk of existing biodiesels and other alcohol family members have a lower calorific value than decanol. It has a

boiling point that is within the spectrum of the diesel's boiling curve, and it includes no aromatic chemicals [97].

5.9. Diethyl Ether

Diethyl ether, having the chemical formula $CH_3CH_2–O–CH_2CH_3$, is the primary ether with an oxygen content of 21.6%. It is composed of two ethyl groups joined by an oxygen atom in the center. Diethyl ether is a potential additive due to its high oxygen content and cetane number. It is a liquid at room temperature, making it ideal for storage. It is a renewable fuel since it is derived from ethanol through a dehydration process [98]. Diethyl ether has a variety of advantageous qualities, including a moderate energy density, a significant cetane number, a high oxygen content, a high volatility and a low auto-ignition temperature. As a result, when used as a pure product or as an additive in diesel fuel, it can help to enhance engine performance while also decreasing cold-starting issues and pollutants [99]. However, it has various drawbacks, such as poor storage stability, low lubricity, and flammability restrictions. Its poor storage stability is due to its proclivity to oxidize and produce peroxides [100].

5.10. Diglycol Methyl Ether

Diglycol methyl ether (2-Methoxyethyl ether) contains an oxygen content of 35.8%. It is often known as diglyme. It is a transparent, colorless liquid with a faint ether smell. Alcohols, hydrocarbon solvents and diethyl ether are all miscible with it. Diglyme is a poisonous substance. The actual cause of its hazardous nature is unknown, although it is most likely linked to diglyme's metabolic process, which produces methoxyacetic acid [68,101]. Diglycol methyl ether, due to its high cetane number of 126 when blended with biodiesel, prepares the blend for self-ignition. Diglyme is generated at high pressures (1 MPa to 1.5 MPa) and temperatures (50 °C to 60 °C) by the catalytic reaction of dimethyl ether with ethylene oxide, with a greater yield of 55–60%. The inclusion of the additive diglycol methyl ether in fuel guarantees a higher oxygen availability, allowing for its complete and efficient combustion in diesel engines [68].

5.11. Methyl-Tertiary Butyl Ether

Methyl-tertiary butyl ether, also referred as methyl tert-butyl ether, was one of the first oxygenated additives. It is produced via a chemical reaction between isobutylene and methanol. It is less sensitive to phase separation in distribution and storage systems, and has a low proclivity to produce peroxides [102]. It is relatively less volatile. Despite its ability to reduce exhaust emissions and improve engine performance, methyl tertiary butyl ether is now almost entirely obsolete. It is neither poisonous nor benign; however, it can produce hazardous breakdown products [103,104].

5.12. Dibutyl Ether

Dibutyl ether ($C_8H_{18}O$) is a colorless liquid that has an ether-like smell and is water insoluble. It is combustible and can produce peroxides when stored. Strong oxidizing agents are contraindicated with it [105]. In terms of human health, dibutyl ether is poisonous and non-lethal yet irritating. Butanol is usually used for its production but ethanol may also be used, making it a high-potential, renewable oxygenated additive. It is also known as a diesel cetane enhancer [106]. The synthesis of dibutyl ether using butanol is typically accomplished by dehydrating n-butanol with H_2SO_4 or catalytically dehydrating it over iron chloride, silica, copper sulphate or silica–alumina at extreme temperatures [68,107].

6. Effect of Oxygenated Second-Generation Biodiesel on Engine Test

When oxygenated additives are used with biodiesel, the engine performance and emissions are affected. The effects of second-generation biodiesel with and without oxygenated additives on brake thermal efficiency (BTE), brake-specific fuel consumption (BSFC), and emissions such as CO, CO_2, HC, and NOx of the diesel engine are summarized here from

the past literature. Tables 2 and 3 show the percent change in engine performance and emissions, respectively, compared to conventional diesel for various oxygenated second-generation biodiesel blends.

Table 2. Effect of oxygenated second-generation biodiesel on engine performance.

Biodiesel	Oxygenated Additive	Engine Testing Condition	Engine Performance		Reference
			BSFC	BTE	
			Percent Change from Diesel		
20% *Calophyllum inophyllum* Biodiesel + 80% Diesel	Without additive	80 N-m constant torque (CT), Variable engine speed (VES) 1000–3000 rpm	+10.7	−7.7	[108]
15% *Calophyllum inophyllum* Biodiesel + 80% Diesel	5% n-Butanol	80 N-m CT, VES 1000–3000 rpm	+6.18	−3.8	
100% *Calophyllum inophyllum* Biodiesel	Without additive	Variable engine load (VEL), Constant Speed (CS)	+27.9	−14	[109]
60% *Calophyllum inophyllum* Biodiesel	40% 1-Butanol	VEL, CS	+66	−31	
60% *Calophyllum inophyllum* Biodiesel	40% 1-Pentanol	VEL, CS	+39.9	−18	
50% *Calophyllum inophyllum* Biodiesel + 50% Diesel	Without additive	VEL, CS	+4.4	−1.5	[110]
40% *Calophyllum inophyllum* Biodiesel + 50% Diesel	10% Diethyl Ether	VEL, CS	+13	−13	
100% *Calophyllum inophyllum* Biodiesel	Without additive	VEL, CS	+38	−12	[111]
20% *Calophyllum inophyllum* Biodiesel + 70% Diesel	10% Iso-Butanol	VEL, CS	+20	−6.4	
50% *Calophyllum inophyllum* Biodiesel + 50% Diesel	Without additive	VEL, CS	+38.29	−14.28	[112]
40% *Calophyllum inophyllum* Biodiesel + 50% Diesel	10% Decanol	VEL, CS	+36	−8.57	
100% *Calophyllum inophyllum* Biodiesel	Without additive	VEL, CS	+33	−5.35	[113]
70% *Calophyllum inophyllum* Biodiesel	30% Octanol	VEL, CS	+8.3	−1.7	
100% Neat *Castor* Oil	Without additive	VEL, CS 1500 rpm	n/a	−30	[114]
40% Neat *Castor* Oil + 30% Diesel	30% Bio-ethanol	VEL, CS 1500 rpm	n/a	−9	
50% *Calophyllum inophyllum* Biodiesel + 50% Diesel	Without additive	VEL, CS 1500 rpm	+13	−10	[115]
10% *Calophyllum inophyllum* Biodiesel + 50% Diesel	40% Hexanol	VEL, CS 1500 rpm	+8.6	−6.8	
50% *Calophyllum inophyllum* Biodiesel + 50% Diesel	Without additive	VEL, CS 1500 rpm	+8	−2.8	[116]
45% *Calophyllum inophyllum* Biodiesel + 50% Diesel	5% Methyl-tertiary butyl ether	VEL, CS 1500 rpm	+15	−14	
45% *Calophyllum inophyllum* Biodiesel + 50% Diesel	5% Diethyl Ether	VEL, CS 1500 rpm	+9	−4	
50% *Calophyllum inophyllum* Biodiesel + 50% Diesel	Without additive	VEL, CS 1500 rpm	+15	−11	[117]
40% *Calophyllum inophyllum* Biodiesel + 50% Diesel	10% Hexanol	VEL, CS 1500 rpm	+20	−23	
10% *Calophyllum inophyllum* Biodiesel + 50% Diesel	40% Hexanol	VEL, CS 1500 rpm	+9	−4	

Table 2. *Cont.*

Biodiesel	Oxygenated Additive	Engine Testing Condition	Engine Performance		Reference
			BSFC	BTE	
			Percent Change from Diesel		
20% *Jatropha* Biodiesel + 80% Diesel	Without additive	80 N-m CT, VES 1000–3000 rpm	+8.8	−10.2	[118]
15% *Jatropha* Biodiesel + 80% Diesel	5% Diethyl Ether	80 N-m CT, VES 1000–3000 rpm	+2.8	−3.6	
100% *Jatropha* Biodiesel	Without additive	VEL, CS	n/a	−19.1	[119]
80% *Jatropha* Biodiesel	20% n-Butanol	VEL, CS	n/a	−8	
20% *Jatropha* Biodiesel + 80% Diesel	Without additive	VES, Constant load (CL)	+25	n/a	[120]
20% *Jatropha* Biodiesel + 70% Diesel	10% Pentanol	VES, CL	+30	n/a	
40% *Jatropha* Biodiesel + 40% Diesel	20% Ethanol	VEL, CS	+16	n/a	[121]
40% *Jatropha* Biodiesel + 40% Diesel	20% Ethanol + 5%$V/V_{BIODIESEL}$ Diethyl Ether	VEL, CS	+20	n/a	
100% *Jatropha* Biodiesel	Without additive	Constant Engine Speed 3600 rpm, Constant Brake Power 4.4 kW	+20	−5	[122]
80% *Jatropha* Biodiesel	20% Butanol	Constant Engine Speed 3600 rpm, Constant Brake Power 4.4 kW	+21	−4	
20% *Jatropha* Biodiesel + 75% Diesel	5% Diethyl Ether	VEL, CS	+7	−13	[123]
100% *Jatropha* Biodiesel	Without additive	VEL, CS 2000 rpm	+4	−5.4	[124]
40% *Jatropha* Biodiesel	40% Decanol + 20% Propanol	VEL, CS 2000 rpm	+2	−3.5	
100% *Jatropha* Oil	Without additive	VEL, CS	+18	−6.25	[125]
90% *Jatropha* Oil	10% Heptane	VEL, CS	+8	+4.2	
20% *Jatropha* Biodiesel + 70% Diesel	10% Diethyl Ether	VEL, CS	+7	+25	[126]
25% *Neem* Biodiesel + 75% Diesel	5% $V/V_{BIODIESEL}$ Methanol	Variable Fuel Injection Pressure 180–240 bar	+25 (cf. DEE)	−2.8 (cf. DEE)	[127]
25% *Neem* Biodiesel + 75% Diesel	5% $V/V_{BIODIESEL}$ Diethyl Ether	Variable Fuel Injection Pressure 180–240 bar	−20 (cf. Methanol)	+3 (cf. Methanol)	
100% *Neem* Biodiesel	Without additive	VEL, CS 1500 rpm	+3	+7.6	[128]
45% *Neem* Biodiesel + 50% Diesel	5% Methanol	VEL, CS 1500 rpm	−10	+25	
20% *Neem* Biodiesel + 80% Diesel	Without additive	VEL, CS	+14	−20	[129]
20% *Neem* Biodiesel + 70% Diesel	10% Diethyl Ether	VEL, CS	−10	+4	
10% *Jojoba* Biodiesel + 80% Diesel	10% Ethanol	VEL, CS 1500 rpm	+200	−36	[130]
5% *Jojoba* Oil + 85% Diesel	10% n-Butanol	VEL, CS 2000 rpm	−8	+10	[131]
100% *Pongamia* Biodiesel	Without additive	VEL, CS 1500 rpm	+20	−10	[132]
100% *Pongamia* Biodiesel	10% $V/V_{BIODIESEL}$ Diethyl Ether	VEL, CS 1500 rpm	+11	−6	
100% *Karanja* Biodiesel	Without additive	VEL, CS 1500 rpm	+50	−10	[133]
90% *Karanja* Biodiesel	10% 1-Pentanol	VEL, CS 1500 rpm	+38	−6.5	

Table 2. *Cont.*

Biodiesel	Oxygenated Additive	Engine Testing Condition	Engine Performance		Reference
			BSFC	BTE	
			Percent Change from Diesel		
10% *Karanja* Biodiesel + 80% Diesel	10% Diethyl Ether	VEL, CS 1500 rpm	+0.5	+3.3	[134]
20% Rubber Seed Oil Biodiesel + 80% Diesel	Without additive	VEL, CS	+2.3	−6.25	[135]
20% Rubber Seed Oil Biodiesel + 80% Diesel	5% $V/V_{BIODIESEL}$ Diglyme	VEL, CS	+2	−5.5	
100% Rubber Seed Oil Biodiesel	Without additive	VEL, CS 1500 rpm	+4	+6.25	[136]
80% Rubber Seed Oil Biodiesel	20% Butanol	VEL, CS 1500 rpm	+40	−15	
30% *Castor* Biodiesel + 70% Diesel	Without additive	VEL, CS 1500 rpm	n/a	−10	[137]
20% *Castor* Biodiesel + 70% Diesel	10% n-Butanol	VEL, CS 1500 rpm	n/a	+6	
20% *Castor* Biodiesel + 75% Diesel	5% Di butyl ether	VEL, CS 3600 rpm	+31	−2.8	[138]
20% *Mahua* Biodiesel + 80% Diesel	Without additive	VEL, CS 1500 rpm	+2.5	−6	[139]
20% *Mahua* Biodiesel + 80% Diesel	10% $V/V_{BIODIESEL}$ Diethyl Ether	VEL, CS 1500 rpm	−4.4	+5	

6.1. Effect on Brake-Specific Fuel Consumption

Brake-specific fuel consumption tells how efficiently fuel is burnt to produce unit power. When biodiesel was used in diesel engines, BSFC increased in general when compared to regular diesel fuel. In previous studies, an improvement i.e., a decrease in BSFC was also reported when oxygenated additives were added with biodiesel for diesel-engine operation. In most of the studies as shown in Figure 2, it was found that BSFC in the case of an oxygenated/biodiesel blend decreased compared to biodiesel alone. Even in those very few studies, it was also found that BSFC decreased compared to diesel fuel as well when biodiesel was blended with oxygenated additives. In the instance of 5% methanol and 10% diethyl ether blends with *Neem* biodiesel blends, the highest drop of 10% was found when compared to diesel fuel [128,129].

The *Neem* biodiesel blend without oxygenated additive also revealed a minor increment in BSFC compared to other second-generation biodiesels. Due to this, *Neem* biodiesel with methanol and diethyl ether showed a significant reduction in BSFC compared to other biodiesels and diesel as well. *Mahua* biodiesel when blended with 10% diethyl ether also showed a 4.4% reduction in BSFC as compared to diesel as it had minor increment in BSFC without the oxygenated additive [139]. Both *Mahua* and *Neem* biodiesel blend with diesel had physiochemical properties comparable to diesel due to which an insignificant increase in BSFC was reported. When ethers, particularly diethyl ether, were mixed with biodiesel, they reduced kinematic viscosity, increased oxygen concentration, and enhanced the blend's cetane number. Reduced kinematic viscosity and a greater oxygen content results in the full combustion of fuel, which produces more power and lowers BSFC [129]. The latent heat of evaporation of the fuel blend is also important for BSFC. The BSFC will be higher if the latent heat of evaporation of the biodiesel blend is higher since the energy emitted will be absorbed. Higher-alcohol-based oxygenated additives like hexanol, octanol and decanol have a less latent heat of evaporation compared to lower-chain alcohols due to the fact that when *Jatropha* biodiesel was blended with higher alcohols such as heptanol and decanol, it showed a reduction in BSFC compared to the biodiesel blend without oxygenated additives [125]. On the other hand, when *Jatropha* biodiesel was blended with lower-chain alcohols such as ethanol, butanol and pentanol, it showed an increase in BSFC

compared to the biodiesel blend (without oxygenated additives) and diesel [120,122]. This increased BSFC might be caused due to the poor atomization quality of *Jatropha* in contrast to diesel [140]. *Calophyllum inophyllum* biodiesel and rubber-seed biodiesel, when blended with lower-chain alcohols, i.e., 40% 1-Pentanol and 20% Butanol, showed the highest BSFC as compared to the biodiesel blend (without oxygenated additive) and diesel [106,133]. However, oxygen content in the lower-chain alcohols is higher as compared to higher-chain alcohols, so the literature suggests blending lower-chain alcohols with biodiesel that already have a less latent heat of evaporation to obtain the efficient oxygenated second-generation biodiesel blend in terms of BSFC.

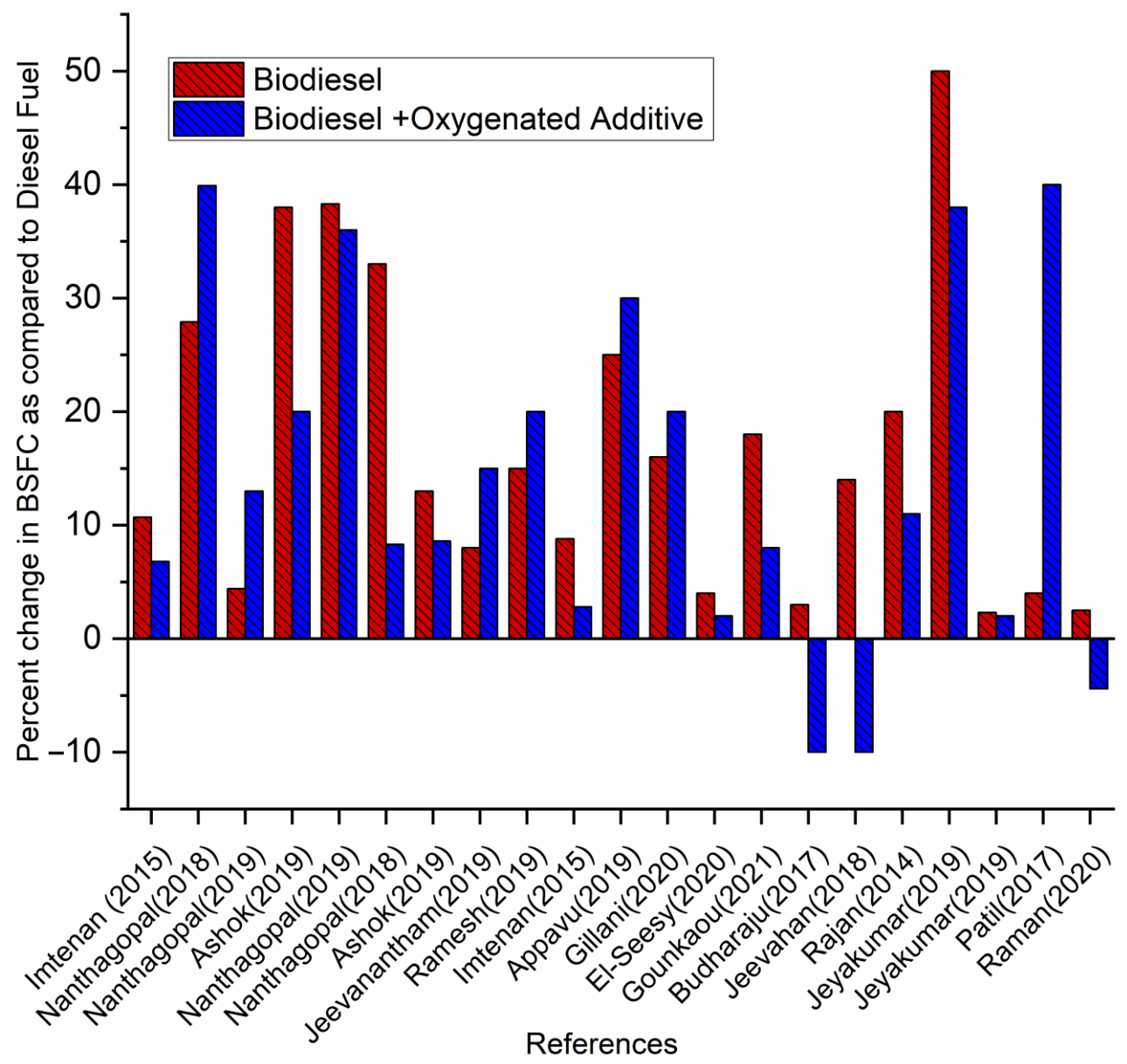

Figure 2. Trends of brake-specific fuel consumption from the literature [108–118,120,122,124,125,128,132,133,135,138,140].

However, the following points can be drawn as a summary to above discussion:

- The addition of oxygenated additives in a biodiesel blend may decrease the kinematic viscosity of the blend, which can result in good fuel atomization and thus a decreased BSFC.

- The addition of oxygenated additives in a biodiesel blend may decrease the density of the blend, which can result in less fuel consumption to produce high power outputs.
- The addition of oxygenated additives in a biodiesel blend increases the oxygen concentration of the blend, which may facilitate complete combustion, resulting in high power outputs with less fuel consumption.
- Blending the biodiesel blend with an oxygenated additive that has a high latent heat of evaporation can increase the BSFC because it absorbs the fuel-emitted energy instantly. Therefore, more fuel has to be consumed in order to achieve high power.

6.2. Effect on Brake Thermal Efficiency

Brake Thermal Efficiency (BTE) refers to brake power of diesel engine depending upon the energy supplied by the fuel. Many factors influence brake thermal efficiency of diesel engine, including compression ratio, air fuel ratio, injection time and most significantly, the calorific value of the fuel blend. In general, when biodiesel was utilized in diesel engine, BTE decreased as compared to conventional diesel fuel. In contrast, an improvement in BTE was also reported in previous studies when oxygenated additives such as ethers and alcohols were used as blends with biodiesel. The effect of biodiesels with oxygenated additives on the BTE of an engine, as reported in the literature, is tabulated in Table 2 and illustrated in Figure 3. In most of the studies, it was found that BTE, in the case of an oxygenated/biodiesel blend, increased compared to biodiesel alone. Even in very few studies, it was also found that when biodiesel was used with oxygenated additives, the BTE increased compared to diesel fuel as well. The highest increment of 25% compared to diesel fuel was reported in the case of 5% methanol with the *Neem* biodiesel blend. Moreover, *Neem* biodiesel without oxygenated additive showed an increment in BTE unlike other second-generation biodiesel blends. Due to this reason, *Neem* biodiesel with methanol showed a significant improvement in BTE compared to other second-generation biodiesels and diesel. When methanol was mixed with *Neem* biodiesel, the oxygen concentration of the blend improved, resulting in a higher combustion quality and therefore, an increased BTE. Furthermore, an improved fuel blend density, calorific value, and viscosity affect the engine's BTE [128]. It was also found that a *Neem* biodiesel blend with 10% diethyl ether showed a 4% increase in BTE compared to diesel fuel. With the addition of diethyl ether, the kinematic viscosity of the blend decreased and thus, the better fuel atomization and the improved combustion led to improved BTE [129]. Similarly, when 10% V/V diethyl ether was blended with *Mahua* biodiesel, a 5% improvement in BTE was found in comparison to diesel fuel. This increment in BTE was due to a higher oxygen content of the *Mahua* biodiesel diethyl ether blend [139].

When *Castor* biodiesel was blended with 10% butanol, a 4% increase in BTE was found in comparison to diesel fuel. It was reported that the addition of butanol to a *Castor* biodiesel blend slightly decreased the cetane number which improved air/fuel mixing and enabled fast energy release, which improved the combustion efficiency and thus the BTE as well [137]. In contrast, when 10% hexanol was blended with *Calophyllum inophyllum*, it showed a significant reduction in BTE compared to the biodiesel blend (without oxygenated additive) and diesel. When *Calophyllum inophyllum* biodiesel was blended with 40% hexanol, it showed an improvement in BTE compared to the biodiesel blend without oxygenated additive. It was reported that when percentage of hexanol was increased, the oxygen content of the blend increased, and the calorific value of the blend was also improved which led to an improved combustion efficiency and hence improved BTE. The literature suggests to blend higher-chain alcohols in a high percentage with biodiesel to obtain benefits in terms of BTE [117]. *Calophyllum inophyllum* biodiesel when blended with 5% methyl-tertiary butyl ether, showed a 14% reduction in BTE compared to diesel and showed a significant reduction compared to biodiesel without oxygenated additives. On the other hand, when it was blended with 5% diethyl ether, it showed an improvement in BTE. It was reported that diethyl ether contained a high amount of oxygen, which aids in the full combustion of the fuel, hence, improving the combustion efficiency. Furthermore,

because of the high volatility of diethyl ether, the air/fuel mixing before combustion was significantly enhanced, thus boosting its BTE. The estimated cetane index of the diethyl ether biodiesel blend was greater than that of the methyl tertiary butyl ether blend, leading to better combustion and as a result, improvement in BTE was observed [113]. Most of the literature suggested diethyl ether as a viable oxygenated additive for second-generation biodiesels to obtain benefits in terms of BTE.

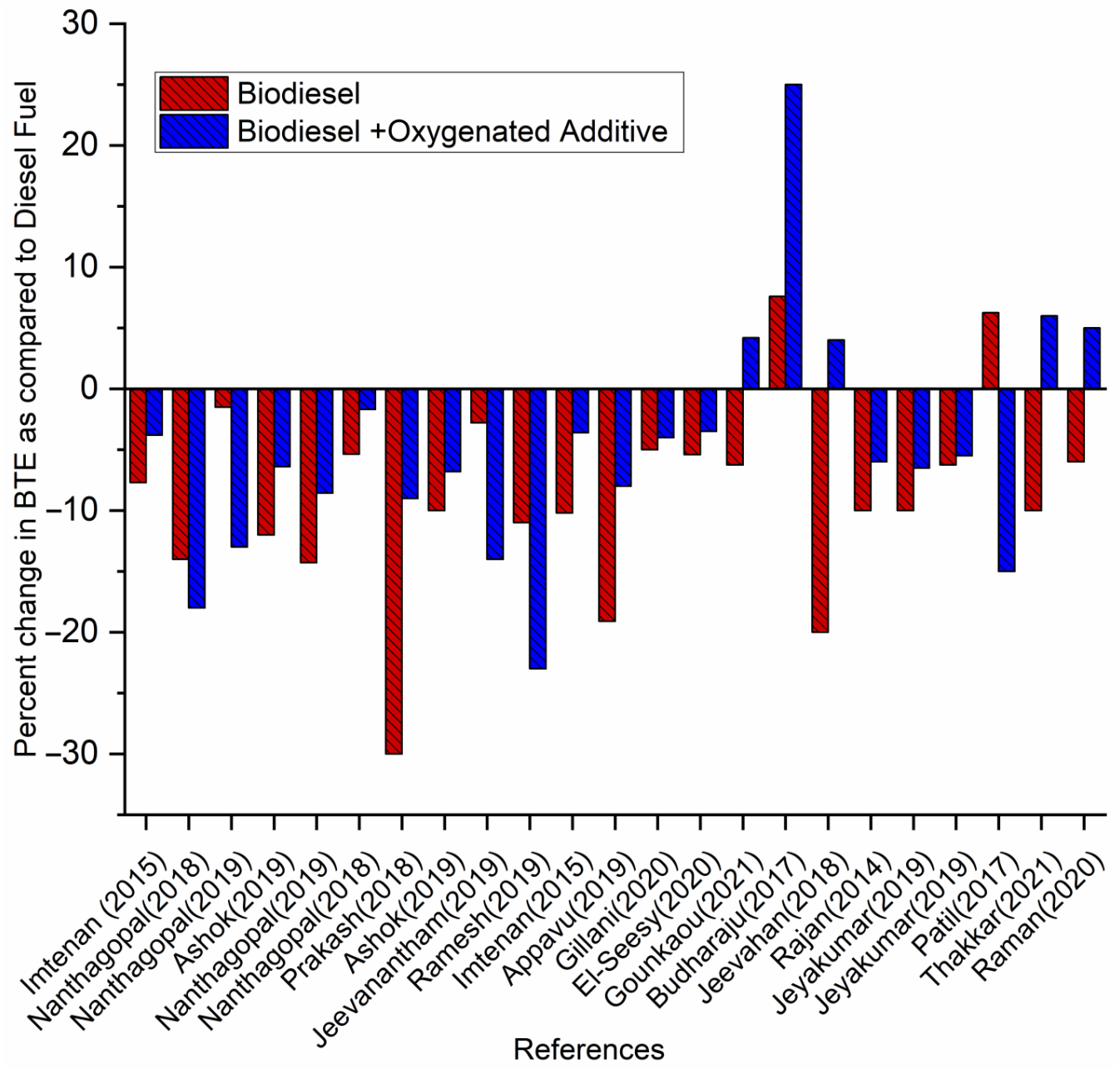

Figure 3. Trends of brake thermal efficiency from the literature [108–119,122,124,125,128,129,134,135,137–140].

However, the following points can be drawn as a summary to above discussion:

- Blending biodiesel with an oxygenated additive that slightly decreases the cetane number of the blend may increase BTE due to a slight increase in ignition delay, causing the improved air/fuel mixing.

- The addition of oxygenated additive in the biodiesel blend increases the oxygen concentration of the blend which may facilitate the improvement of the combustion efficiency and therefore enhance the BTE.
- The addition of oxygenated additive in a biodiesel blend may decrease the kinematic viscosity of the blend, which can result in good fuel atomization and thus an increased BTE.
- Blending biodiesel with an oxygenated additive that has a high volatility enhances air/fuel mixing, which results in an increased BTE.
- The addition of oxygenated additives in a biodiesel blend may decrease the density of the blend, which can result in a high power output with less fuel consumption, causing increased BTE.

Table 3. Effect of oxygenated second-generation biodiesel on emissions.

Biodiesel	Oxygenated Additive	Engine Testing Condition	Emissions				Reference
			CO	CO_2	HC	NOx	
			Percent Change from Diesel				
20% *Calophyllum inophyllum* Biodiesel + 80% Diesel	Without additive	80 N-m Constant torque (CT), VES 1000–3000 rpm	−21	n/a	−20	+13.7	[108]
15% *Calophyllum inophyllum* Biodiesel + 80% Diesel	5% n-Butanol	80 N-m CT, VES 1000–3000 rpm	−36	n/a	+10	+16	
100% *Calophyllum inophyllum* Biodiesel	Without additive	VEL, CS	−39	+11	−64	+52	[109]
60% *Calophyllum inophyllum* Biodiesel	40% 1-Butanol	VEL, CS	−30	−8.5	−7.1	+7	
60% *Calophyllum inophyllum* Biodiesel	40% 1-Pentanol	VEL, CS	−23.9	−7	−40	+5.3	
50% *Calophyllum inophyllum* Biodiesel + 50% Diesel	Without additive	VEL, CS	−4.1	+1	−48	+20	[110]
40% *Calophyllum inophyllum* Biodiesel + 50% Diesel	10% Diethyl Ether	VEL, CS	−2	+0.5	−35	−37.5	
100% *Calophyllum inophyllum* Biodiesel	Without additive	VEL, CS	−70	n/a	−50	+26	[111]
20% *Calophyllum inophyllum* Biodiesel + 70% Diesel	10% Iso-Butanol	VEL, CS	−60	n/a	+15	+12	
50% *Calophyllum inophyllum* Biodiesel + 50% Diesel	Without additive	VEL, CS	−12.5	n/a	−5.5	+16	[112]
40% *Calophyllum inophyllum* Biodiesel + 50% Diesel	10% Decanol	VEL, CS	−28	n/a	−11	+24	
100% *Calophyllum inophyllum* Biodiesel	Without additive	VEL, CS	−35.7	n/a	−58.8	+13	[113]
70% *Calophyllum inophyllum* Biodiesel	30% Octanol	VEL, CS	−17	n/a	−43	+6	
100% Neat *Castor* Oil	Without additive	VEL, CS 1500 rpm	+340	n/a	+266	−41	[114]
40% Neat *Castor* Oil + 30% Diesel	30% Bio-ethanol	VEL, CS 1500 rpm	+100	n/a	+116	−3.5	

Table 3. *Cont.*

Biodiesel	Oxygenated Additive	Engine Testing Condition	Emissions				Reference
			CO	CO_2	HC	NOx	
			Percent Change from Diesel				
50% *Calophyllum inophyllum* Biodiesel + 50% Diesel	Without additive	VEL, CS 1500 rpm	−11	n/a	−4.5	+11	[115]
10% *Calophyllum inophyllum* Biodiesel + 50% Diesel	40% Hexanol	VEL, CS 1500 rpm	−55	n/a	−84	+32	
50% *Calophyllum inophyllum* Biodiesel + 50% Diesel	Without additive	VEL, CS 1500 rpm	−6.8	+2	−55	+18	[116]
45% *Calophyllum inophyllum* Biodiesel + 50% Diesel	5% Methyl-tertiary butyl ether	VEL, CS 1500 rpm	−8	−1	−60	−8	
50% *Calophyllum inophyllum* Biodiesel + 50% Diesel	Without additive	VEL, CS 1500 rpm	−65	+2	−30	+32	[117]
40% *Calophyllum inophyllum* Biodiesel + 50% Diesel	10% Hexanol	VEL, CS 1500 rpm	−46	+1.8	−48	+25	
20% *Jatropha* Biodiesel + 80% Diesel	Without additive	80 N-m CT, VES 1000–3000 rpm	−25	n/a	−40	+7.6	[118]
15% *Jatropha* Biodiesel + 80% Diesel	5% Diethyl Ether	80 N-m CT, VES 1000–3000 rpm	−30	n/a	−18	+10	
100% *Jatropha* Biodiesel	Without additive	VEL, CS	−15	n/a	−25	+12.5	[119]
80% *Jatropha* Biodiesel	20% n-Butanol	VEL, CS	−50	n/a	+20	+3.5	
100% *Jatropha* Biodiesel	Without additive	VEL, CS	−2.7	n/a	−4	+3	[141]
90% *Jatropha* Biodiesel	10% Butanol	VEL, CS	−40	n/a	−30	−4	
20% *Jatropha* Biodiesel + 80% Diesel	Without additive	VES, CL	−5.2	n/a	n/a	+2.56	[120]
20% *Jatropha* Biodiesel + 70% Diesel	10% Pentanol	VES, CL	−6.5	n/a	n/a	−35	
40% *Jatropha* Biodiesel + 40% Diesel	20% Ethanol	VEL, CS	−48	+8	+24	+11	[121]
40% *Jatropha* Biodiesel + 40% Diesel	20% Ethanol + 5%V/$V_{BIODIESEL}$ Diethyl Ether	VEL, CS	+28	+15	+40	−1	
100% *Jatropha* Biodiesel	Without additive	Constant Engine Speed 3600 rpm, Constant Brake Power 4.4 kW	+20	+1	−8	−20	[122]
80% *Jatropha* Biodiesel	20% Butanol	Constant Engine Speed 3600 rpm, Constant Brake Power 4.4 kW	+65	+0.5	+15	−22	
100% *Jatropha* Biodiesel	Without additive	VEL, CS	−12.5	n/a	−10.8	+6	[142]
90% *Jatropha* Biodiesel	10% Decanol	VEL, CS	−15	n/a	−14	+1.5	
20% *Jatropha* Biodiesel + 75% Diesel	5% Diethyl Ether	VEL, CS	−33	n/a	+300	−4.7	[123]

Table 3. *Cont.*

Biodiesel	Oxygenated Additive	Engine Testing Condition	Emissions				Reference
			CO	CO_2	HC	NOx	
			Percent Change from Diesel				
100% *Jatropha* Biodiesel	Without additive	VEL, CS 2000 rpm	−2	n/a	−33	+3	[124]
40% *Jatropha* Biodiesel	40% Decanol + 20% Propanol	VEL, CS 2000 rpm	−8	n/a	−60	+8	
20% *Jatropha* Biodiesel + 70% Diesel	10% Diethyl Ether	VEL, CS	−11	n/a	+100	+66	[126]
25% *Neem* Biodiesel + 75% Diesel	5% $V/V_{BIODIESEL}$ Methanol	Variable Fuel Injection Pressure 180–240 bar	+40 (cf. DEE)	−13 (cf. DEE)	+20 (cf. DEE)	−18 (cf. DEE)	[127]
25% *Neem* Biodiesel + 75% Diesel	5% $V/V_{BIODIESEL}$ Diethyl Ether	Variable Fuel Injection Pressure 180–240 bar	−28 (cf. Methanol)	+15 (cf. Methanol)	−16 (cf. Methanol)	+23 (cf. Methanol)	
100% *Neem* Biodiesel	Without additive	Variable Brake Power, CS 1500 rpm	+25 (cf. DEE)	n/a	+28 (cf. DEE)	+11 (cf. DEE)	[143]
80% *Neem* Biodiesel	20% Diethyl Ether	Variable Brake Power, CS 1500 rpm	−20 (cf. WA)	n/a	−22 (cf. WA)	−10 (cf. WA)	
100% *Neem* Biodiesel	Without additive	VEL, CS 1500 rpm	n/a	+190	+200	+10.7	[128]
45% *Neem* Biodiesel + 50% Diesel	5% Methanol	VEL, CS 1500 rpm	n/a	+180	−20	+55	
20% *Neem* Biodiesel + 80% Diesel	Without additive	VEL, CS	−12	n/a	−10	+5	[129]
20% *Neem* Biodiesel + 70% Diesel	10% Diethyl Ether	VEL, CS	−60	n/a	−75	−15	
100% *Neem* Biodiesel	Without additive	VEL, CS	−30	n/a	−10	+56	[144]
90% *Neem* Biodiesel	10% Butanol	VEL, CS	−36	n/a	−14	+40	
20% *Neem* Biodiesel + 80% Diesel	Without additive	VEL, CS 2600 rpm	+10	+2	+100	+80	[145]
20% *Neem* Biodiesel + 80% Diesel	5% $V/V_{BIODIESEL}$ Butanol	VEL, CS 2600 rpm	−11	+8	+90	+75	
10% *Jojoba* Biodiesel + 80% Diesel	10% Ethanol	VEL, CS 1500 rpm	−15	n/a	+460	−55	[130]
20% *Jojoba* Biodiesel + 70% Diesel	10% n-Butanol	VEL, CS 2000 rpm	−50	n/a	−65	−85	[146]
5% *Jojoba* Oil + 85% Diesel	10% n-Butanol	VEL, CS 2000 rpm	−8.3	n/a	−50	−50	[131]
100% *Pongamia* Biodiesel	Without additive	VEL, CS 1500 rpm	−4	n/a	+22	+21	[132]
100% *Pongamia* Biodiesel	10% $V/V_{BIODIESEL}$ Diethyl Ether	VEL, CS 1500 rpm	−10	n/a	+35	−23	
100% *Karanja* Biodiesel	Without additive	VEL, CS 1500 rpm	+27	−65	+29	+21	[133]
90% *Karanja* Biodiesel	10% 1-Pentanol	VEL, CS 1500 rpm	+10	−48	+20	+12	
10% *Karanja* Biodiesel + 80% Diesel	10% Diethyl Ether	VEL, CS 1500 rpm	n/a	+4.5	−31	−8.4	[134]
20% Rubber Seed Oil Biodiesel + 80% Diesel	Without additive	VEL, CS	−40	n/a	−53	−16	[135]
20% Rubber Seed Oil Biodiesel + 80% Diesel	5% $V/V_{BIODIESEL}$ Diglyme	VEL, CS	−55	n/a	−65	−14	

Table 3. *Cont.*

Biodiesel	Oxygenated Additive	Engine Testing Condition	Emissions				Reference
			CO	CO_2	HC	NOx	
			Percent Change from Diesel				
100% Rubber Seed Oil Biodiesel	Without additive	VEL, CS 1500 rpm	+50	−44	−64	−66	[136]
80% Rubber Seed Oil Biodiesel	20% Butanol	VEL, CS 1500 rpm	+300	+20	+92	−30	
30% *Castor* Biodiesel + 70% Diesel	Without additive	VEL, CS 1500 rpm	−10	n/a	+10	+85	[137]
20% *Castor* Biodiesel + 70% Diesel	10% n-Butanol	VEL, CS 1500 rpm	−50	n/a	+3	−37	
20% *Mahua* Biodiesel + 80% Diesel	Without additive	VEL, CS 1500 rpm	−42	n/a	−25	+36	[139]
20% *Mahua* Biodiesel + 80% Diesel	10% $V/V_{BIODIESEL}$ Diethyl Ether	VEL, CS 1500 rpm	−55	n/a	−30	−2	

6.3. Effect on Carbon Monoxide Emission

Carbon Monoxide (CO) emissions are usually produced due to less oxygen content in the fuel. Less oxygen content leads to incomplete combustion and forms CO emissions instead of CO_2 emissions. In general, when biodiesel was utilized in diesel engines, CO emissions decreased compared to diesel fuel due to the higher oxygen content in biodiesel. The effect of biodiesel blend with oxygenated additives on the CO emissions of a diesel engine, as reported in the literature, is tabulated in Table 3 and illustrated in Figure 4. In most of the literature, it was found that CO emissions further decreased when second-generation biodiesel was used with oxygenated additives. Some unexpected results of increased CO emissions were also reported in the case of *Jatropha*, *Neem*, rubber-seed and *Karanja* biodiesel blends (without oxygenated additives) compared to diesel fuel [133,136,145]. These unexpected increases in CO may be attributed to the poor air/biodiesel mixing or atomization. The highest reduction of 60% was found in case of 10% iso-butanol and 10% di-ethyl ether blends with *Calophyllum inophyllum* and *Neem* biodiesel, respectively [108,126]. It was also found that a *Calophyllum inophyllum* biodiesel blend even without oxygenated additives, due to it containing a higher oxygen content, showed a significant reduction in CO emissions compared to other second-generation biodiesel blends. Furthermore, it was found that when 10% iso-butanol was blended with *Calophyllum inophyllum* biodiesel, it showed a reduction in CO emissions compared to diesel fuel but higher CO emissions compared to a biodiesel blend without iso-butanol. It was reported that a higher latent heat of evaporation and poor ignition properties of iso-butanol led to incomplete combustion and thus increased CO emissions compared to biodiesel blend without iso-butanol [111]. In contrast, when 10% butanol was blended with *Neem*, *Jojoba*, *Castor* and *Jatropha* biodiesel blends, the results showed significant reduction in CO emissions due to overall higher oxygen content of the blend [119,145]. Callophyllum inophyllum biodiesel already had a higher oxygen content so the literature suggests to blend it with higher-chain alcohols which have a lower oxygen content but good ignition properties and a less latent heat of evaporation compared to lower-chain alcohols. It was also found that when 10% hexanol was blended with *Calophyllum inophyllum* biodiesel, it showed a reduction in CO emissions compared to diesel fuel but showed an increase in CO emissions compared to biodiesel blend without hexanol [117]. On the other hand, when 40% hexanol was blended with a *Calophyllum inophyllum* biodiesel blend, it showed a reduction in CO emissions compared to both diesel and the biodiesel blend (without hexanol) [115]. The reason for this reduction in case of the high-percentage blend of higher-chain alcohol was that a larger amount of higher-chain alcohol compensated for less oxygen content in the low-percentage blend and, thus, gave a less latent heat of evaporation and good ignition properties

to the fuel blend to facilitate complete combustion. Hence, it is suggested to consider a high-percentage blend of higher-chain alcohol with *Calophyllum inophyllum* biodiesel to obtain benefits in terms of CO emissions. In most of the studies, ethers such as diethyl ether, diglyme and methyl tertiary butyl ether, when blended with second-generation biodiesels such as *Pongamia* [132], *Jatropha* [108], *Calophyllum inophyllum* [110], *Neem* [129], *Mahua* [139] and rubber-seed biodiesel [136], showed a significant reduction in CO emissions compared to diesel fuel and biodiesel blend (without oxygenated additive) as well. It was reported that higher oxygen contents in these ethers led to decreased CO emissions.

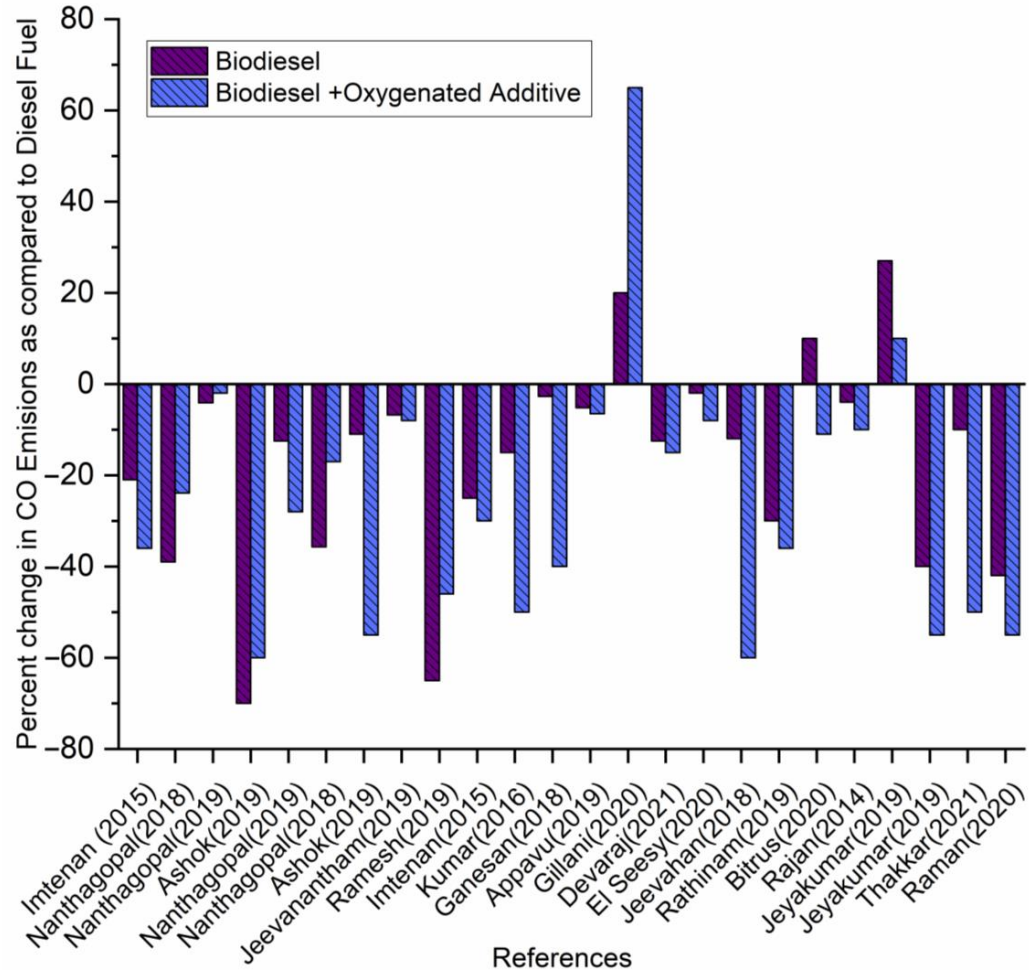

Figure 4. Trends of carbon monoxide emissions from the literature [108–113,115–120,122,124,129,133,135,137,139–142,144,145].

However, the following points can be drawn as a summary to the above discussion:

- Blending biodiesel with oxygenated additives that have a high latent heat of evaporation can lead to a fuel blend with poor ignition properties and, therefore, can become the reason for incomplete combustion and an increase in CO emissions.
- Blending biodiesel with oxygenated additives with a higher oxygen content, such as ethers, can facilitate the reduction of CO, i.e., the conversion of CO to CO_2.
- Higher-chain alcohols have a less latent heat of evaporation but also a lower oxygen content. Therefore, blending them with biodiesel in high concentrations can produce a blend with a high oxygen content and a less latent heat of evaporation, which can be beneficial in complete combustion to reduce CO emissions.

6.4. Effect on Carbon Dioxide Emission

The amount of carbon dioxide released increases when there is enough oxygen for full combustion. The hydroxyl radical OH, which is the oxidizing agent, converts carbon monoxide (CO) into carbon dioxide (CO_2) when there is enough oxygen available. Trends in most of the previous studies have showed that CO_2 emissions generally increase for biodiesel compared to diesel fuel when used in diesel engines, as illustrated in Figure 5. This increase was attributed to the higher availability of oxygen in biodiesel. However, when mixed with oxygenated additives, it was found in numerous studies that CO_2 emissions decreased. The reason reported was that oxygenated additives such as ethers and alcohols had a lower carbon content, making less CO_2, but still had a higher oxygen content that facilitated CO_2 formation, and hence, the trends observed in these studies were dependent upon the type of oxygenated additive blend as well as the second-generation biodiesel. When 5% methyl tertiary butyl ether was blended with *Calophyllum inophyllum* biodiesel, CO_2 emissions reduced by 1% compared to diesel. Methyl tertiary butyl ether had a higher heat of evaporation that caused slower air/fuel mixing prior to combustion. This poor mixing caused incomplete fuel combustion and hence reduced CO_2. Furthermore, its poor ignition quality caused incomplete combustion [116]. In another study, [133] it was also noted that utilizing a biodiesel blend (without oxygenated additive) reduced its CO_2 emissions compared to diesel. This reduction was reported in the case of *Karanja* biodiesel which is a highly viscous second-generation biodiesel. The high viscosity of biodiesel affected fuel conversion efficiency, which is a crucial parameter for fuel combustion for its efficient conversion to CO_2. However, the addition of 10% 1-pentanol led to a small rise in CO_2 compared to *Karanja* biodiesel (without oxygenated additive) due to the improved viscosity of the blend [133].

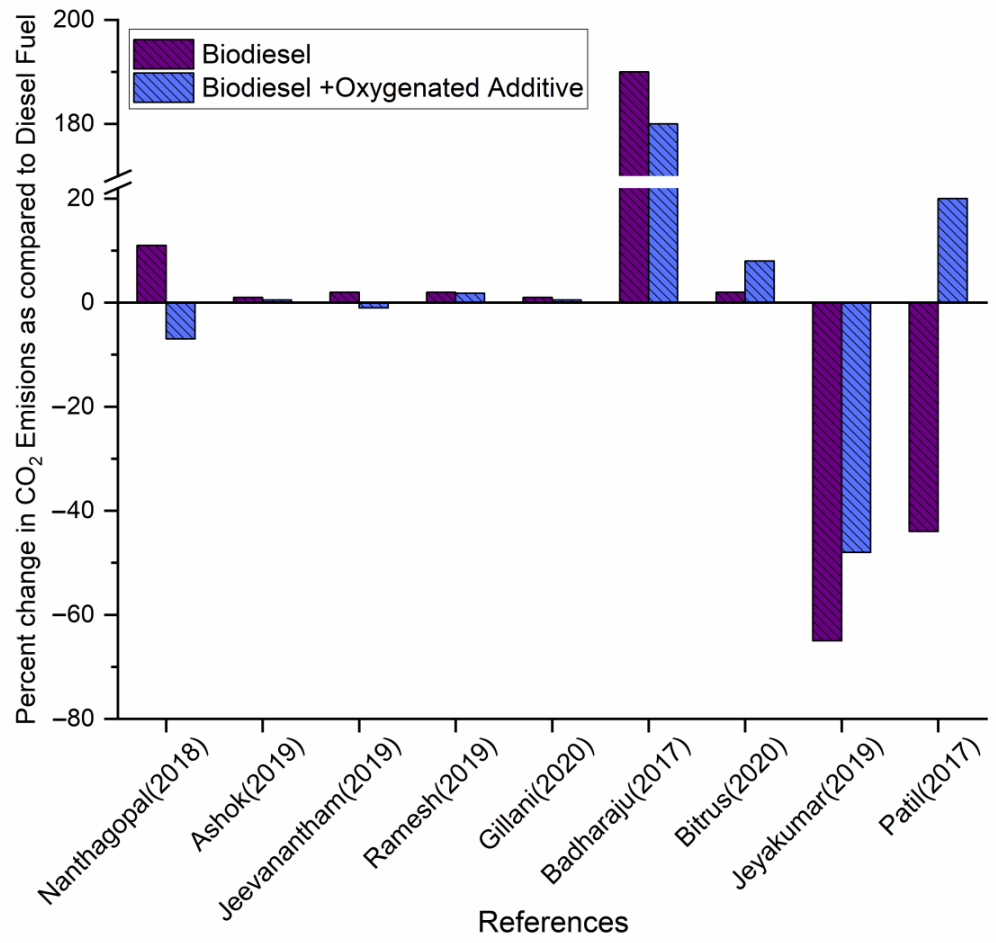

Figure 5. Trends of carbon dioxide emissions from the literature [109,110,116,117,122,128,133,138,145].

However, following points can be drawn as a summary to the above discussion:

- Blending biodiesel with an oxygenated additive that has a high latent heat of evaporation may cause poor air/fuel mixing and thus incomplete combustion, resulting in reduced CO_2 emissions.
- Biodiesel blend with a high viscosity can cause incomplete combustion and thus a reduction in CO_2. Therefore, blending biodiesel blends with oxygenated additives may decrease the viscosity of the blend, which can facilitate complete combustion and the formation of CO_2.
- The availability of oxygen and carbon in the fuel blend influences the formation of CO_2 emissions. Therefore, despite the availability of the high oxygen content, blending biodiesel with an oxygenated additive with has low carbon content may decrease CO_2.

6.5. Effect on HC Emissions

Hydrocarbon (HC) emissions are formed due to a lack of oxidation. In general, biodiesel utilization reduced the amount of HC emissions compared to diesel fuel. This happens because second-generation biodiesel has a higher oxygen content and low carbon content. A similar reduction in HC emissions was found in most of the previous studies in the case of biodiesel, as illustrated in Figure 6. A reduction in HC emissions was also reported compared to diesel and biodiesel when oxygenated additives were blended with second-generation biodiesel. This reduction was attributed to the sufficient oxygen content present in oxygenated additives such as ethers and alcohols. The highest reduction of 84% compared to diesel was reported in the case of the *Calophyllum inophyllum* biodiesel blend when used with 40% hexanol. This reduction was attributed to the higher oxygen content in the blend. In the case of *Neem* biodiesel, it was found that HC emissions increased compared to diesel fuel [128]. Meanwhile, others have reported a reduction in HC emissions in similar studies conducted on *Neem* biodiesel [129]. However, in the studies conducted by M. V. Budharaju et al. [128] and R. Bitrus et al. [145], where higher HC emissions in the case of the *Neem* biodiesel blend were reported, they found a reduction in HC when oxygenated additives such as methanol and butanol were blended with second-generation *Neem* biodiesel. It was also found in the case of *Karanja* biodiesel that HC emissions increased compared to diesel [132]. It was reported that a slower rate of oxidation or incomplete combustion could be the reason for this reduction, as *Karanja* is highly viscous. High viscosity can affect fuel conversion efficiency and thus combustion. Furthermore, it was also found that when diethyl ether was blended with *Karanja* biodiesel, HC emissions were further increased compared to the use of no additives. The low calorific value of diethyl ether and its incomplete combustion facilitated HC formation. In contrast to the other study, it was also found that the addition of diethyl ether to *Karanja* biodiesel reduced HC emissions by 8.4% compared to diesel fuel [134]. This reduction was attributed to the higher oxygen content of diethyl ether, which facilitated complete combustion. Similarly, in a few other studies, the addition of diethyl ether to *Jatropha*, *Mahua*, *Neem* and calophyllum biodiesel blends showed a high percentage of reduction in HC emissions compared to diesel, due to its higher oxygen content [118,129]. It was also found that when 20% butanol was blended with rubber-seed biodiesel, HC emissions increased compared to the diesel and biodiesel blends (without additive). The addition of butanol with rubber-seed biodiesel reduced the cetane number, which resulted in incomplete combustion [136]. The same trend of increased HC upon butanol addition was reported in the case of the *Jatropha* biodiesel blend [122]. In contrast, in another study, when butanol was blended with *Jatropha* biodiesel, reduced HC emissions compared to both the diesel and biodiesel blends were observed [141]. It was reported that the high oxygen content of butanol and the reduced ignition delay in the case of the butanol blend improved combustion. Moreover, butanol blending enhanced the mixing rate of fuel and reduced the viscosity of the blend, which improved combustion and reduced HC emissions.

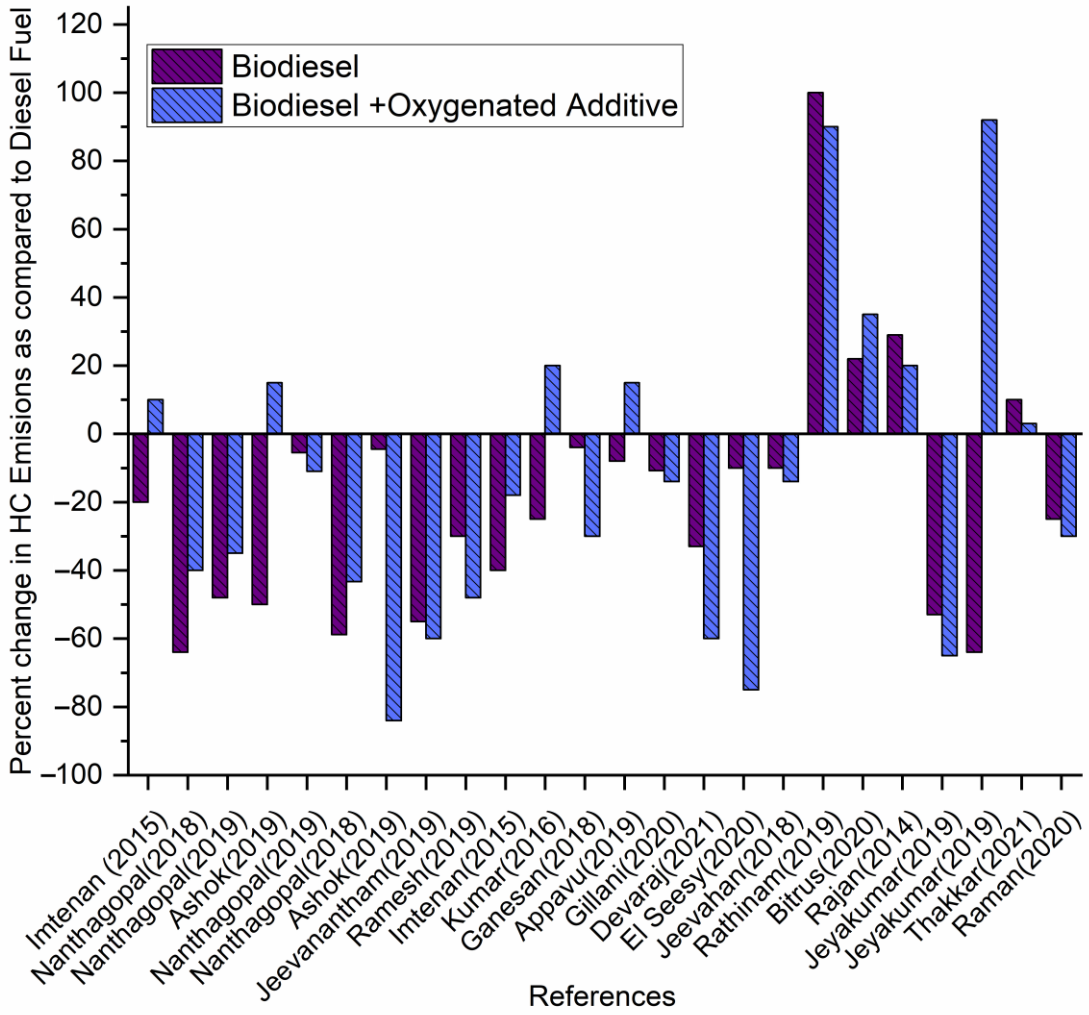

Figure 6. Trends of hydrocarbon emissions from the literature [108–113,115–119,122,124,129,134,135,137–144].

However, the following points can be drawn as a summary to the above discussion:

- The addition of oxygenated additives in the biodiesel blend increases the overall oxygen content of the blend, which can facilitate oxidation and thus a reduction in HC emissions.
- The addition of oxygenated additives in the biodiesel blend decreases the viscosity of the blend and its adverse effects on fuel conversion efficiency, which proves beneficial for a reduction in HC emissions.
- Blending biodiesel with an oxygenated additive that has a lower calorific value may decrease the fuel conversion efficiency and so increase unburnt HC formation.
- Blending biodiesel with an oxygenated additive that has a lower cetane number may increase the ignition delay, which results in incomplete combustion and thus an increase in HC emissions.

6.6. Effect on NOx Emissions

NO and NO_2 are considered together as NOx. However, in the engine cylinder, the most common oxide that is generated is NO. During the combustion reaction, N_2 in the air combines with O_2 to generate NOx emissions at higher gas temperatures (over 1500 °C). A high adiabatic flame temperature, a low radiative heat transfer, a swift burning rate, and accessible inherent surplus oxygen are all factors that contribute to NOx formation. Because diesel and biodiesel both contain only 0–2% nitrogen, the majority of the nitrogen

that causes NOx emissions comes from the air. The presence of O_2 is important in the production of NOx. NOx emissions rise in the lean-mixture region, when O_2 molecules proliferate, and combustion temperatures rise. Generally, in diesel engines, the utilization of biodiesel caused an increase in NOx emissions compared to diesel, as illustrated in Figure 7. In most of the previous studies, it was also found that oxygenated additives, such as ethers and alcohols, as blends with biodiesel reduced NOx emissions compared to biodiesel blends (without oxygenated additives), and sometimes even a reduction was reported compared to diesel. In very few studies, an increase in NOx emissions were also reported compared to the diesel and biodiesel blend when oxygenated additives were used with biodiesel. This effect might be attributed to the higher oxygen content in oxygenated additives that aids in NOx formation. While oxygenated additives also improved the burning rate, which can mitigate the formation of NOx, a suitable biodiesel blend with a specific oxygenated additive is needed to achieve an overall decline in NOx emissions. It was found that NOx emissions reduced compared to diesel in the case of rubber-seed biodiesel, and this reduction was in contrast with a general trend of the increase in NOx in the case of the biodiesel blend [135,136]. The poor combustion of rubber-seed biodiesel led to a reduced in-cylinder temperature that caused a reduction in NOx. Furthermore, the addition of 5% diglyme in rubber-seed biodiesel as the oxygenated additive increased NOx compared to the biodiesel blend (without additive) but still showed a reduction in NOx compared to diesel fuel [135]. Moreover, the addition of diglyme increased NOx compared to biodiesel due to its high oxygen content which facilitated complete combustion. Additionally, double bonds present in this oxygenated additive increased adiabatic flame temperature, which facilitated NOx formation. In another study, the same trend was found when 20% butanol was added to rubber-seed biodiesel, which lead to increased NOx compared to the biodiesel blend but still showed a reduction compared to diesel [136]. It was also found that increasing the butanol percentage in the rubber-seed biodiesel blend decreased NOx, since increasing the butanol percentage increased the oxygen content in the blend. Regarding solely the oxygen concentration, NOx should have increased, however, it was found that increasing the percentage of butanol decreased the cetane number of biodiesel blend that decreased NOx, due to which combustion started late. The late initiation of combustion led to a lesser reaction time for fuel which prompted a move towards incomplete combustion, which produced less NOx. Similarly, the addition of 10% butanol in *Castor* biodiesel blends reduced NOx emissions compared to both the diesel and biodiesel blends. It was reported that the butanol–*Castor* biodiesel blend was exposed to higher temperatures for a shorter time, which caused a lower NOx formation [137]. A similar reduction in NOx was reported in the case of butanol blended with *Jatropha* and *Jojoba* biodiesel [146]. Similarly, the addition of 10% ethanol to *Jojoba* biodiesel reduced NOx by 55% percent compared to diesel fuel [130]. In several studies, a slightly higher NOx level was reported when higher-chain alcohols were blended with second-generation biodiesel, because higher-chain alcohols such as pentanol, hexanol, decanol, etc., have a higher cetane number compared to lower-chain alcohols that started combustion earlier and thus the reaction time for the fuel increased that increased the NOx formation [112,115]. A decline in NOx emissions compared to both biodiesel blend (without additive) and diesel was also found when 10% V/V diethyl ether was blended with *Mahua* biodiesel blend. It was reported that a high latent heat of evaporation of diethyl ether produced a cooling effect i.e., reduced in-cylinder temperature that reduced NOx emissions [141]. Therefore, to gain benefits in terms of NOx, it is suggested to blend oxygenated additive with biodiesel which can have a moderate oxygen content and cetane number to obtain an optimized engine performance in addition to better emission characteristics.

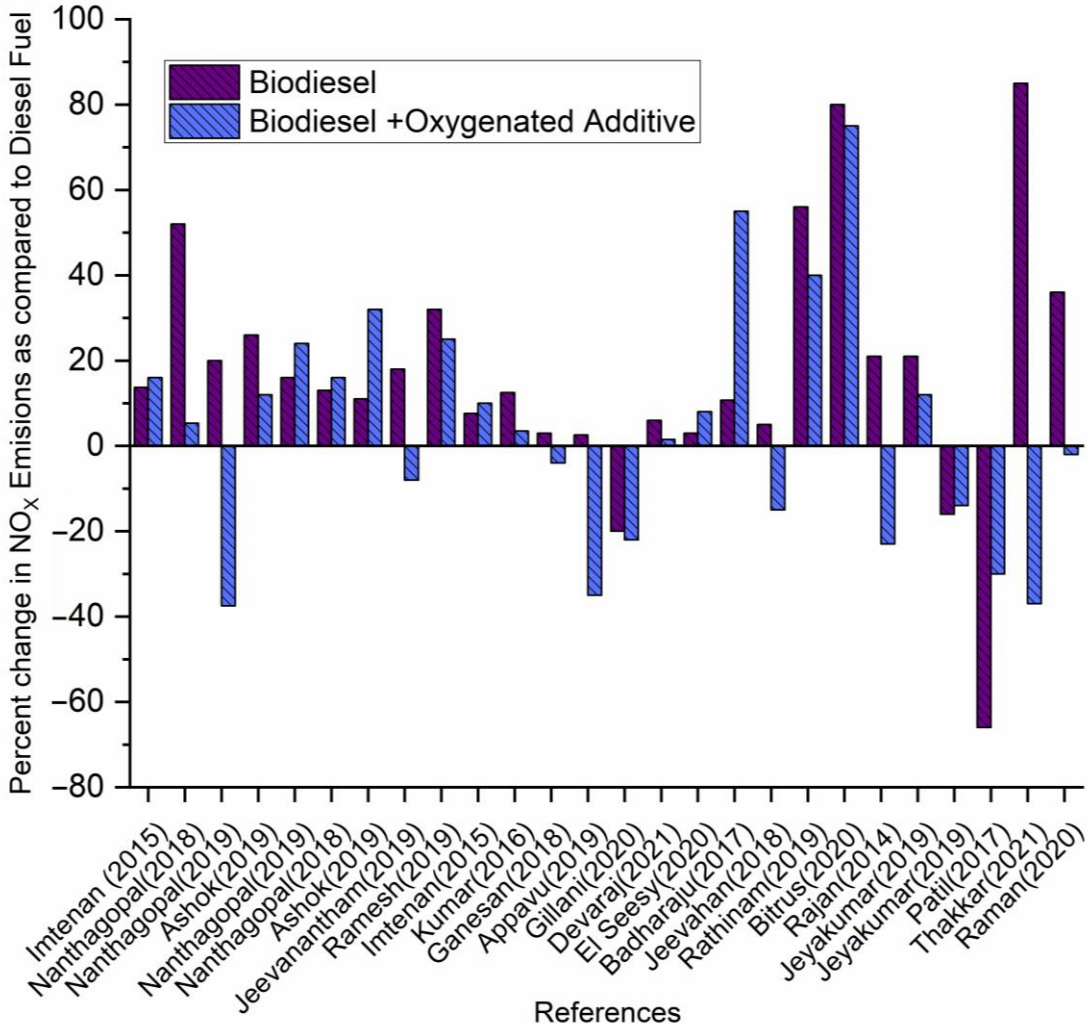

Figure 7. Trends of nitrogen oxide emissions from the literature [108–113,115–120,122,124,128,129,134,135,137–144].

However, the following points can be drawn as a summary to the above discussion:

- The addition of oxygenated additive in a biodiesel blend increases oxygen concentration of blend, which may facilitate NOx formation, but on the other hand, improves the burning rate which can mitigate NOx formation as well.
- Double bonds present in the oxygenated additive increase the adiabatic flame temperature, which can facilitate NOx formation by boosting engine cylinder temperature.
- Blending biodiesel with an oxygenated additive that has a lower cetane number can increase the ignition delay and reduce the reaction time. Therefore, fuel exposure to high temperatures for short intervals reduces NOx formation.
- Blending biodiesel with an oxygenated additive that has a high latent heat of evaporation can cause a cooling effect inside the engine cylinder that reduces NOx emissions.

7. Conclusions and Future Outlook

The impact of several oxygenated additive-based second-generation biodiesel blends on the performance and emissions of a diesel engine was investigated in this review article. In comparison to conventional diesel, changes in brake-specific fuel consumption and brake thermal efficiency, as well as changes in emissions such as carbon monoxide, carbon dioxide, hydrocarbons, and oxides of nitrogen, were examined. The significant findings of the study are mentioned below:

- When oxygenated additives were used with biodiesel blends, a greater BSFC was observed than diesel in most of the investigations. However, for *Neem* biodiesel with 5% methanol and 10% diethyl ether, a substantial drop in BSFC was observed. When compared to diesel fuel, there was a 10% drop in BSFC in both blends. The BSFC is higher if the latent heat of evaporation of the biodiesel blend is higher, since the energy emitted will be absorbed. Lower-chain alcohols have a higher latent heat of evaporation than higher-chain alcohols, but they also have a higher oxygen content. Therefore, blending lower-chain alcohols with second-generation biodiesel that already have a lower latent heat of evaporation is suggested. Furthermore, ethers, especially diethyl ether, lowered the kinematic viscosity and increased the oxygen concentration when combined with second-generation biodiesel blends. This resulted in the better combustion of fuel, resulting in more power and, as a result, a lower BSFC.
- The highest BTE with an increment of 25% compared to diesel fuel was reported in the case of the blend of 5% methanol with *Neem* biodiesel. Moreover, the addition of 10% diethyl ether to the *Neem* biodiesel blend elicited a 4% improvement of BTE compared to diesel fuel. *Neem* biodiesel without any oxygenated additive itself was efficient at improving BTE compared to other second-generation biodiesels. Additionally, diethyl ether, due to its high amount of oxygen, aided in the complete combustion of the fuel. Furthermore, because of the high volatility of diethyl ether, the air/fuel mixing before combustion was significantly enhanced, thus increasing the BTE. For the use of alcohols as oxygenated additives, it was suggested that using higher-chain alcohols in a high percentage in a biodiesel blend can be beneficial in terms of the BTE.
- To reduce CO emissions, the literature suggests blending higher-chain alcohols at a high percentage with biodiesel. Higher-chain alcohols have a lower oxygen content, but good ignition properties and a less latent heat of evaporation compared to lower-chain alcohols. The higher percentage of higher-chain alcohol compensated for a lower oxygen content in a lower-percentage blend, and thus, contributed a less latent heat of evaporation and good ignition properties to the fuel blend to facilitate complete combustion, which led to a reduction in CO. Furthermore, it was also found in the literature that ethers reduced CO emissions when blended with second-generation biodiesels due to the higher oxygen content in ethers.
- The CO_2 emissions decreased compared to the biodiesel blend when oxygenated additives were used with second-generation biodiesels. The reason reported was that oxygenated additives, such as ethers and alcohols, had a lower carbon content that caused less CO_2; however, they had a higher oxygen content that facilitated CO_2 formation, and hence, the trend observed in these studies was dependent upon the type of oxygenated additive and on the second-generation biodiesel. The lowest CO_2 emissions were reported in the case of the *Karanja* biodiesel blend which is highly viscous biodiesel. High viscosity was an obstacle in fuel conversion efficiency that led to decreased CO_2. The addition of 1-pentanol to *Karanja* biodiesel increased CO_2 emissions slightly compared to the *Karanja* biodiesel blend (without additive) because of the improved viscosity of the blend which increased fuel conversion efficiency and led to decreased CO_2.
- Slightly higher NOx emissions were reported when higher-chain alcohols were used with biodiesel because higher-chain alcohols have higher cetane number compared to lower-chain alcohols, due to which combustion started earlier, and thus, the reaction time for fuel increased and the exposure to higher temperatures increased, leading to higher NOx levels. Diethyl ether, in most of the cases when used with the biodiesel blend, reduced NOx emissions due to producing a cooling effect i.e., a reduced in-cylinder temperature.

For future work, we recommend investigating the effect of various ethers and alcohols on *Castor* biodiesel. *Castor* oil feedstock is usually ignored due to its high viscosity. However, the blending of *Castor* biodiesel with diesel and oxygenated additives may provide new insights for its analysis regarding engine performance and emissions.

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Nomenclature

BTE	Brake thermal efficiency
BSEC	Brake-specific energy consumption
BSFC	Brake-specific fuel consumption
IMEP	Indicated mean effective pressure
CF	Computational fluid dynamics
CT	Constant torque
CS	Constant speed
VEL	Variable engine load
CL	Constant load
VES	Variable engine speed

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