Biobutanol Blends in Diesel Engines

Fossil fuels have often been partially replaced by renewable fuels to reduce both the environmental impact and the dependence on conventional fuels in internal combustion engines. When butanol is blended with diesel fuels, PM emissions sharply decrease, THC emissions increase and there is no consensus regarding CO and NOx emissions. No startability problems up to 40% butanol content are concluded for tests at warm ambient temperature

1. Introduction

In 2009, European Directive 2009/28/EC [1] proposed a scenario where transport fuels will include up to 10% of biofuels in 2020. A few years ago, European Directive (EU) 2018/2001 [2] promoted the use of biofuels, increasing the mandatory renewable energy in the transport sector up to 14%, including electrification, and the minimum content of advanced biofuels and biogas up to 3.5%, for 2030. The contribution of heavy-duty vehicles in the transport sector, tractors in the agricultural sector and cogeneration sector to greenhouse gas emissions are nowadays increasing but electrification is not yet a viable option for the usual distances and the current infrastructure. Consequently, researchers are focused on the replacement of fossil fuels with renewable fuels, which have lower emissions than greenhouse gases and other pollutants, and are compatible with modern diesel engine technologies [3][4].

Among the renewable options for substituting partially or totally diesel fuels in the mentioned sectors, biodiesel fuel, generally obtained from conventional feedstocks such as vegetable oils or animal fats through a transesterification process with methanol obtaining a mixture of fatty acid methyl esters (FAME), has been widely used for a couple of decades. Several studies concluded that the power output from biodiesel was similar to that of diesel fuel [5][6]. However, the conventional production of biodiesel fuel together with filter plugging problems, caused by some biodiesel components (sterol glycosides and saturated monoacylglycerols), and storage difficulties derived from fast oxidation, has encouraged researchers to focus on the development and the implementation of advanced biofuels to be blended with diesel fuels or even with biodiesel-diesel blends [7][8][9].

Alcohols produced from waste or lignocellulosic materials through advanced production techniques constitute a sustainable alternative. Among alcohols, ethanol and butanol have been proven to reduce the life-cycle greenhouse gas emissions when produced from biomass and waste feedstocks [10]. Although biobutanol can be produced from both biological and chemical routes [11], the ABE (acetone-butanol-ethanol) fermentation route in which sugar, glycerol or lignocellulose feedstocks are fermented by microorganisms to produce n-butanol, ethanol and acetone, is the most widely used [12]. The low final butanol concentration, the limitations in the butanol recovery during the fermentation process, the presence of unwanted products such as butyrate and acetate (apart from acetone and ethanol) and high feedstock costs hinder the economic competition of biobutanol with respect to petrochemical synthesis [13].

Bioalcohols are not only used to replace gasoline in spark-ignition engines but also to replace diesel fuels in diesel engines [14][15]. Although ethanol was traditionally used as a blending component in the transport sector, ethanol shows some problems related to its cold start (high vapor pressure) and its distribution since it cannot be transferred through the existing pipeline infrastructures without corrosion and damage to the rubber seals [16]. Nowadays, the scientific community shows an emerging interest in studying n-butanol as a blending component. The safer character of biobutanol with respect to ethanol for transportation, fuel handling and storage [17], together with its higher cetane number [18], higher heating value [19], lower volatility [17], higher flash point [20], better lubricity [21] and better miscibility with diesel fuels (especially at a low temperature) [22] of n-butanol have contributed to such interest.

Regarding the use of butanol as a blending component for diesel engines and vehicles, most of the tests found in the literature were carried out under steady conditions [15][23], and only a few of them were conducted following driving cycles [24][25]. The authors of these papers generally concluded that the introduction of n-butanol in diesel fuel sharply decreases

particulate matter (PM) emissions due to the oxygen content of the butanol molecule [26][27], and there is an increase in total hydrocarbons (THC) when n-butanol is used [24][28]. The fuel consumption has been reported to increase for increasing butanol contents due to its lower heating value [29] but without significant penalty in terms of energy consumption for butanol blends with respect to diesel fuel [30]. In terms of startability, cold startability problems have been reported for butanol blends, especially at cold ambient conditions [31].

Since butanol has a significant potential to reduce the life-cycle greenhouse gas emissions with respect to diesel fuel and to introduce a renewable blending component for diesel engines, the aim of this study is to review the properties of butanol, to study their effect on combustion and to compare them with those of ethanol and reference diesel fuel. Additionally, in this review, the different butanol-diesel mixing techniques and their limitations to introduce n-butanol without engine modifications are mentioned. N-butanol benefits in terms of combustion and emissions in diesel engines and vehicles under stationary or transient conditions in the engine test bench or in the chassis dynamometer have been discussed.

The novelty of this review with respect to those previously published regarding biobutanol is mainly focused on: (i) a review of the GHG emissions of biobutanol and bioethanol from different feedstocks compared to those of fossil diesel fuel; (ii) unlike previous studies, this one is focused just on biobutanol as a blending component for diesel engines [32] but has explored this topic in much more detail than was previously carried out, considering a range of different butanol concentrations and the implications on fuel distribution, storage and combustion compared with ethanol blends in diesel engines; (iii) differently to previous reviews about regulated and unregulated emissions from diesel and gasoline engines [33][34], this study focuses on regulated emissions using biobutanol as a blending component, with emphasis on the effect of recent after-treatment technologies.

2. Sustainability of N-Butanol

Prior to the development of petrochemical production routes to n-butanol in the 1950s, the majority of n-butanol worldwide was produced through the ABE fermentation of sugars [35]. Today it is understood that the cultivation of food and feed crops for fuel production can cause environmental impacts due to crop cultivation and land-use change [36]. Therefore, the ABE fermentation process is being developed to use waste or lignocellulosic feedstocks.

The life-cycle GHG emissions of a fuel are calculated by taking into account emissions from the extraction or cultivation of raw materials, annualized emissions from carbon stock changes caused by land-use change and emissions from processing, transport, distribution and the use of the fuel. Under the methodology laid out in EU Directive (EU) 2018/2001 , the emissions from fuel use are taken to be zero for biofuels.

Several greenhouse gas assessments of n-butanol produced from sugars can be found in the literature, including [37][38][39], of which the results of Wu et al. [39] provide the most useful comparison with calculations made using the RED II method due to their use of energy allocation. The production of n-butanol from waste and lignocellulosic sugars has only been demonstrated at a pilot scale, but German et al. Whilst there is a wide range of results due to the uncertainty in the scale-up and development of the process, they estimate that the GHG emissions of lignocellulosic biobutanol could be as low as 38 gCO2eq./MJ.

The GHG emissions from sugar-based butanol [39] and from lignocellulosic butanol [40] are compared in Figure 2. The carbon intensity of butanol is compared with diesel, corn ethanol and lignocellulosic ethanol based on typical values for these fuels provided in Directive (EU) 2018/2001 [2].

Figure 2 supports the conclusions made across many studies (including [37][41][42]) and reflected in the default values of the RED II [2] that advanced processes to produce lignocellulosic bioethanol and biobutanol can achieve lower GHG emissions than the production of the same fuel from crops. Concretely, lignocellulosic butanol can reduce GHG emissions by 60% with respect to diesel fuel, whereas the reduction for butanol from corn reaches 35%. The higher GHG emissions of lignocellulosic butanol compared to lignocellulosic ethanol are likely due to the earlier stage of development of this technology and the lower yield of butanol compared to ethanol [11].

3. Studies on N-Butanol Properties

Ethanol or n-butanol can be used together with diesel fuel through different mixing techniques. The most common methods are blending and fumigation [32]. In the blending method, alcohol and diesel fuels are premixed before being injected through the diesel fuel injector into the cylinder. In the fumigation method, the alcohol is introduced into the intake air upstream of the manifold either by carbureting, vaporizing or injecting [43].

With the fumigation method, higher alcohol content (up to 50% in energy [44]) can be introduced in the mid-load range without being limited by alcohol miscibility problems or affecting the base diesel fuel properties since it is not directly blended. However, at low loads and high loads, the alcohol content introduced should be reduced. High alcohol content at low loads could lead to misfiring. At high loads, introducing high alcohol content could result in preignition and engine knock. Potential mechanical problems have been reported in turbocharged diesel engines using the fumigation technique due to the impact of the liquid spray on the turbocharger. The alcohol evaporation is not complete when the alcohol is introduced downstream of the compressor. Furthermore, the fumigation technique requires the addition of a vaporizer or injector and an additional fuel injection system and fuel tank adaption, which increases the engine weight [45][46]. On the contrary, blending alcohols with diesel fuels allows introducing a renewable component in the diesel engine without any engine modification.

Although the alcohol most commonly used as a blending component in the transport sector is ethanol, the higher cetane number of n-butanol, together with its higher heating value, better viscosity, better lubricity, higher flash point and better miscibility with diesel, particularly at a low temperature, suggest that n-butanol is a better renewable component than ethanol in diesel blends [21][47][48].

The main properties of ethanol and n-butanol are listed in Table 1.

Although the physicochemical properties of n-butanol are more similar to those of diesel than ethanol, it still cannot replace diesel fuel at 100% [20]. The literature reports that butanol-diesel blends can be tested up to 40% butanol content (volume basis) without engine modifications [30][49].

The following points summarize the properties of n-butanol that make it more attractive from a technical point of view than ethanol as a blend component in diesel engines.

- Higher density. The density of n-butanol is lower than that of diesel fuel. Therefore, a smaller amount of alcohol is pressurized and injected by the fuel pump since the dosage is volumetric [50]. However, n-butanol density is higher than that of ethanol.
- Higher viscosity. Viscosity values decrease for increasing alcohol contents in alcohol-diesel blends [48]. According to the EN 590 standard of diesel fuels, which establishes that viscosity values should be higher than 2 cSt [51], only ethanol-diesel blends with ethanol content up to 26% (v/v) fulfill this requirement [52]. Since the viscosity of alcohol increases with a longer carbon chain, n-butanol blends from 0% to 100% in diesel fuel would have no restriction [52].
- Better lubricity. Pure n-butanol shows better lubricity than pure ethanol [48]. For intermediate alcohol concentrations, diesel blends with long carbon chain alcohols (n-butanol and n-pentanol) showed worse lubricity (larger wear scar) than those with a short carbon chain (ethanol and propanol). A detailed study about the lubricity of blends of different alcohols (ethanol, propanol, n-butanol and n-pentanol) with diesel fuel [48] reported that, following EN 590 standard [51], which requires a wear scar lower than 460 μm at 60 °C, only those ethanol-diesel blends with an ethanol content higher than 92% or butanol-diesel blends with butanol content above 35%, both volume basis, would not fulfill this standard.
- Higher heating value. Alcohols show lower heating value than diesel fuels. Comparing ethanol and n-butanol, the latter has 25% more energy density in volume than ethanol, reducing the fuel consumption needed to keep a specific load in diesel engines [33][53]. Since the lower heating value of diesel fuel often ranges from 41 to 44 MJ/kg, butanol-diesel blends up to 17% (v/v) and ethanol-diesel blends up to 10% can be considered within this range [52].
- Better blend stability. Alcohols with long carbon chain show better blending stability than those with low carbon chain [48]. In particular, low blend stability was reported for ethanol-diesel blends, specifically at intermediate ethanol contents (from 15% to 75% ethanol content) [54][55]. Butanol blends showed better blend behavior. In fact, butanol-diesel blends did not show blend stability problems along the whole butanol range for temperatures above 0 °C [22].
- Better cold-flow properties. Bioalcohols, with a low freezing temperature, have proven to be a sustainable alternative to improve the cold flow properties of diesel fuels (especially biodiesel) [56]. Among alcohols, the benefits of blending light alcohols such as methanol and ethanol with diesel fuels are limited by their aforementioned weak miscibility. As a consequence of its better blend stability over a wide range of temperatures for the whole concentration range, n-butanol improves the cold flow properties of diesel fuels (especially for high alcohol content).
- Higher cetane number. In general, alcohols exhibit low cetane numbers, and therefore, only limited concentrations of these alcohols in the blends are recommended for use in unmodified diesel engines because the cetane number significantly affects the engine efficiency [57]. Based on the cetane number, the literature reports that butanol-diesel blends with n-butanol content up to 40% (v/v) can be used in diesel engines without any engine alteration [49]. However, taking into account limits proposed by the EN 590 standard, only butanol blends with diesel fuel up to 3% fulfill this limit [18].

- Lower enthalpy of vaporization. Ethanol and butanol have higher enthalpy of vaporization than diesel fuel [58]. Among alcohols, the lower enthalpy of vaporization of n-butanol (620 kJ/kg) with respect to ethanol (944 kJ/kg), suggests that a diesel engine can start more easily operating with butanol than with ethanol at cold ambient conditions [53].
- Better distribution and storage. As n-butanol has a higher flash point and lower volatility than ethanol, butanol blends are safer for transportation, fuel handling and storage than those of ethanol [59]. The less corrosive character of n-butanol with respect to ethanol also contributes to improve storage over longer time periods [16].

The n-butanol properties previously mentioned have a strong influence on combustion parameters. The lower density and the lower kinematic viscosity of n-butanol with respect to diesel fuel lead to a better atomization quality for butanol-diesel blends. In addition, the higher volatility of n-butanol leads to a faster evaporation process. Both better atomization and faster evaporation contribute to form more homogeneous fuel-air mixtures, thus decreasing soot formation [60][49].

4. Studies on N-Butanol Use in Diesel Engines and Vehicles

This section reviews the use of n-butanol as a blending component in diesel engines and vehicles and reports its effects on combustion, performance and gaseous and particle emissions. Most of the butanol-diesel emission results found in the literature were tested under steady conditions in a Euro 5 (or inferior) engine test bench under warm ambient conditions [15][61][62].

In general, under steady conditions, the authors observed a sharp decrease in PM emissions for butanol blends (due to the role played by the oxygen content to inhibit soot formation and to enhance soot oxidation) [29][63] with respect to 100% diesel fuel. In terms of gaseous emissions, the literature reports and increase in total hydrocarbons (THC) emissions for butanol blends [64][65]. However, there is no consensus regarding CO and NOx emissions [27][66]. Most of the studies observed an increase in fuel consumption for butanol blends associated with its lower heating value [63][66][67][68]. The differences in fuel consumption, described above when butanol is introduced, almost disappear in terms of energy consumption [30]. In studies following transient conditions, trends previously described for steady conditions were confirmed. Literature reported that in both engine and vehicle tests, the particle number and particle mass emissions were reduced as the blend of butanol increased to 16% (v/v), leading to fewer and finer particles. Therefore, particle emissions were found to be minimized for this blend (16% butanol 84% diesel, volume basis). [69].

For those regulated emissions with no clear trend (CO and NOX emissions), a schematic diagram is shown in Figure 3 summarizing trends described by authors about the use of butanol-diesel blends in diesel engines. In terms of CO emissions, 52% of studies reviewed concluded an increase, whereas 43% of the authors reported a reduction in CO emissions when butanol blends are introduced. Regarding NOX emissions, 46% of the studies concluded that introducing butanol-diesel blends is beneficial, and only 36% of them observed an increasing trend. A total of 18% of the publications reviewed reported that NOX emissions remained constant when butanol blends are introduced.

Regarding the cold startability of butanol-diesel blends, Miers et al. [64] studied butanol-diesel blends with 20% and 40% butanol content (v/v) in a light-duty vehicle under transient conditions at a warm ambient temperature, concluding that butanol blends with butanol contents lower than 40% (v/v) could be successfully used in a diesel engine calibrated for 100% diesel fuel without startability problems. That study concluded that butanol-diesel blends up to 20% butanol content (%v/v) could be introduced without startability and driveability problems at 24 °C, whereas only butanol-diesel blends up to 13% (v/v) could be introduced without startability problems at −7 °C. At −7 °C, some driveability difficulties were also reported for this n-butanol blend (13% n-butanol 87% diesel fuel, volume basis).

Table 2 shows a detailed summary of the different studies found in the literature focused on the performance and regulated emissions of butanol-diesel blends in diesel engines and vehicles under stationary or transient conditions. Since in most of the studies, the reviewed engines were water-cooled, the cooling system is specified only when it is not water-cooled.

Since the butanol content in the blend is mainly limited by the cetane number, the flashpoint and the heating value, only low alcohol contents are interesting because for higher alcohol contents, the heating value and the cetane are decreased. Following the target established in the last directives promoting biofuels, the optimal range selected could range up to 20% (v/v) butanol content. Table 2 shows that most authors tested butanol-diesel blends up to 16–20% (v/v), reporting no negative effect on energy consumption for these blends with respect to reference diesel fuels. Although particle emissions find the minimum at 16% (v/v) butanol content, the workable range is reduced up to 13% (v/v) diesel substitution by butanol when startability is studied [31].

Although few studies were found in the literature regarding unregulated emissions from butanol blends, it was concluded that, in general, alcohol blends with diesel fuels lead to higher carbonyl compound emissions than diesel fuel [34][70]. [71] reported that carbonyl emissions are slightly higher for butanol-diesel blends than for ethanol ones. In general, BTX emissions decrease when alcohols are blended with diesel fuels, especially at a high engine load, and consequently, high exhaust temperature [72].

In terms of the soot reactivity, the literature [73][74] concludes that butanol-diesel blends reduce the soot primary particle diameter and the soot mass density with respect to that of diesel fuel. Therefore, the particle reduction, together with the better soot reactivity when butanol blends are used [75][76], contributes to a decrease in the DPF regeneration frequency, and therefore, lower oil dilution [77], lower fuel consumption and a longer after-treatment lifetime [78] can be achieved.

After describing and discussing trends derived from the introduction of butanol as a blending component for diesel fuel in diesel engines, reasons used by the authors to explain these trends in terms of regulated gaseous (CO, THC and NOx) and particle emissions, are discussed in the following points.

- CO and THC emissions. Although there is no consensus regarding CO emissions, most of the authors justified the increases in CO and THC emissions for butanol blends with respect to diesel fuel is because of the high enthalpy of vaporization of n-butanol [79]. The fuel evaporation contributes to reducing the in-cylinder temperature, in particular during a cold start. [64] reported that n-butanol enhances the diesel oxidation catalyst (DOC) activity.
- Regarding NOx emissions from butanol-diesel blends, the literature reports no clear trend because there is compensation between several factors when the engine is tested. The higher enthalpy of the vaporization of butanol with respect to diesel fuel [28] and the low adiabatic flame temperature of n-butanol is derived from its lower C/H ratio [80] contribute to reduce NOx emissions. On the contrary, an engine calibrated for diesel fuel operating with butanol-diesel blends requires higher fueling to achieve the demanded power. Since acceleration position is one of the inputs of the engine calibration maps, a decrease in the exhaust gas recirculation (EGR) rate is established in order to increase the air mass flow. Consequently, the NO formation increases.
- N-butanol contributes to significant benefits in particulate matter emissions. The higher oxygen content and the higher reactivity of the butanol molecule contributes to improve the soot oxidation process [81]. Since the soot formation mainly takes place in the fuel-rich zone at high temperature and pressure conditions, the oxygenated character of n-butanol leads to a local reduction in fuel-rich regions and thus limiting soot formation [58]. Blending diesel fuel with n-butanol reduces the aromatic and sulfur content (the latter does not have a significant influence because of the low sulfur content in current diesel fuels [72]) in the blend leading to a reduction in particulate matter emissions since these compounds are generally considered as soot precursors.

5. Conclusions

This section summarizes the main conclusions derived from the use of butanol as a biofuel for diesel engines used in road freight transportation, tractors, harvesters and cogeneration.

N-butanol, produced from biological processes such as ABE fermentation from lignocellulosic biobutanol can achieve 60% lower GHG emissions than diesel fuels.

Although the alcohol most commonly used as a fuel component in the transport sector is ethanol, the higher cetane number of n-butanol, together with its higher heating value, better viscosity, better lubricity, better cold-flow properties and better miscibility with diesel, particularly at low temperature, suggest that n-butanol is better renewable component than ethanol in diesel blends.

When butanol is introduced directly by blending with diesel fuel in the fuel tank, additional engine modifications or ECU recalibrations are not needed in a diesel engine calibrated for 100% diesel fuel up to 40% (v/v) butanol content. In general, the authors concluded that the presence of n-butanol contributes to a sharp decrease in PM emissions up to 16% butanol content (%v/v) and to an increase in THC emissions for increasing butanol content. However, there was no consensus regarding CO and NOx emissions. Most of the studies observed an increase in fuel consumption for butanol blends. Startability problems are reported for butanol-diesel blends from 13% butanol onwards at cold ambient temperature, whereas no startability problems up to 40% butanol content are concluded for test at a warm ambient temperature.

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