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Review

A Review of Isobutanol as a Fuel for Internal Combustion Engines

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Abstract: Isobutanol, one of the four isomers of butanol (C_4H_9OH), possesses some favorable properties that make it an attractive fuel for internal combustion engines. For instance, when compared to ethanol, isobutanol features a higher heating value and lower hygroscopicity (which prevents corrosion and enables it to be transported via pipelines). Moreover, its addition to gasoline does not distort the fuel blend's vapor pressure to the same extent as ethanol does. All of this while having a high octane rating. Those advantages over ethanol suggest that isobutanol has the potential to be used as a gasoline oxygenate or even as a neat fuel. Furthermore, the advances made in biotechnology have enabled isobutanol to be produced from biomass more efficiently, allowing it to be used in compliance with existing renewable energy mandates. This article reviews some of the relevant literature dedicated to isobutanol as a motor fuel, covering its merits and drawbacks. Several studies on its combustion characteristics are also discussed. Most of the included literature refers to the use of isobutanol in spark-ignition (SI) engines, as its properties naturally lend themselves to such applications. However, isobutanol's utilization in diesel engines is also addressed, along with a couple of low-temperature combustion examples.

Keywords: internal combustion engine; butanol; isobutanol; combustion; emissions; renewable; fuel blends; oxygenate; biofuel

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1. Introduction

Owing to growing concerns regarding the environmental risks associated with climate change, fossil fuel depletion, and energy security, the use of alternative renewable sources of energy has been increasing. Of particular interest, is the utilization of carbon-neutral renewable fuels in internal combustion engines.

For instance, in the European Union, the 2009 Renewable Energy Directive ("RED"), was created to increase the share of renewable energy use from 8.5% in 2005 to 20% by 2020. In December 2018, revised legislation was adopted, the so-called "RED II" [1], which is to be fully implemented by 2030. It states that the share of renewable energy consumption should be increased to at least 32% overall and 14% in the transportation sector alone. Similarly, in the United States, the Renewable Fuel Standard (RFS) [2], the world's largest existing biofuel program, was created in 2005 and greatly expanded in 2007. It requires that transportation fuels contain minimum annual amounts of renewables, to be increased each year, with volumetric targets existing for several advanced biofuel types, including biomass-based diesel and those made from cellulosic feedstocks [3].

Ethanol has long been the foremost example of a fuel obtained from renewable sources that has achieved widespread adoption, almost exclusively for SI (spark-ignition) engines. The worldwide production of ethanol increased from 18 billion liters in 2000 to 110 billion liters in 2019, falling to 98.6 billion liters in 2020 owing to the COVID-19 pandemic [4]. The world's largest ethanol producers are, by far, the United States and Brazil (where it is produced from corn and sugar cane, respectively), for which the combined outputs account for around 84% of the global production [5]. Besides sugar cane and corn, ethanol can be produced from sugar beets and a variety of starchy feedstocks, such as wheat, barley, rye, sorghum, cassava, rice, and triticale [6]. In the U.S., ethanol is typically available as E10 and E85, which are gasoline blends containing 10 and 85 vol.% of anhydrous ethanol, respectively. The vehicles that are designed to use such high-concentration blends of ethanol are known as flexible fuel vehicles (FFVs). FFVs have historically been designed for operation on E0/E10 and E85 and are certified for emission compliance by testing with either fuel. For decades, neat hydrous ethanol (E100) has been available as a fuel in Brazil, a country where FFVs (in this case, able to run on any proportions of ethanol and gasoline) have been sold since 2003 and the market share has been around 90% [7] every year since 2007.

However, despite its huge popularity, ethanol exhibits some well-known drawbacks. For instance, the addition of ethanol to gasoline typically increases the blend's vapor pressure [8] and affects its distillation properties [9]. In addition, ethanol is highly hygroscopic and corrosive, which precludes it from being transported in existing fuel-supply pipelines. Also, ethanol's heating value is about one-third lower than the heating value of gasoline on a volumetric basis, though ethanol's lower stoichiometric air/fuel ratio (AFR) and latent heat of vaporization can make up for its lower energy content.

Isobutanol, on the other hand, is less corrosive than ethanol and is much less hygroscopic, which enables it to be transported using the existing fuel infrastructure [10]. Additionally, when compared to ethanol, isobutanol has a heating value that is much closer to the heating value of gasoline, and a higher stoichiometric AFR, making it more compatible with gasoline and with existing lambda control strategies, simplifying the adoption of isobutanol as a drop-in oxygenate for the existing vehicle fleet. These characteristics enable the addition of higher concentrations of alcohol to gasoline, using the existing fuel distribution networks [10]. Finally, isobutanol exhibits a lower latent heat of vaporization and a lower volatility than ethanol, which could potentially reduce the number of cold-start issues and the tendencies toward cavitation and vapor lock [11]. In summary, owing to its physical properties, isobutanol is a fuel that is more compatible with gasoline than ethanol is.

Owing to its favorable physicochemical properties, isobutanol was among the ten most promising biomass-based gasoline blendstocks with the potential to increase the efficiency of advanced light-duty engines, according to a recently published report by the Co-Optima (Co-Optimization of Fuels & Engines) initiative [12], a multi-agency research project sponsored by the United States Department of Energy. The project participants evaluated more than 400 blendstocks, including single components, simple mixtures, and complex mixtures. Besides being among the top performers, isobutanol was also one of the six blendstocks assessed to have the fewest significant practical barriers to adoption and use. In addition, depending on how it was produced, renewable isobutanol was considered as having the potential to reduce life-cycle greenhouse gas emissions by at least sixty percent and as being able to be produced at a competitive cost.

When it comes to diesel-engine applications, ethanol has only been used very rarely as a fuel, primarily owing to its resistance to autoignition (i.e., its low cetane rating). Ethanol has been used in diesel engines [13], with the help of ignition improvers [14,15] or through other approaches, albeit at a much smaller scale [16]. Moreover, because ethanol is poorly miscible with diesel fuel, the use of ethanol–diesel blends has been very limited [17,18]. Isobutanol, which is a larger molecule, has slightly better autoignition properties and better affinity with diesel than ethanol. Accordingly, there have been more than just a few studies on isobutanol as a CI (compression-ignition) engine fuel, though most articles deal with isobutanol as a fuel for SI engines.

There has been a scarcity of Review articles encompassing a broad overview of isobutanol utilization in internal combustion engines. The present work attempts to fill this gap by providing a concise but adequate summary of the relevant literature and gives several examples of isobutanol as a fuel, ranging from engine tests to investigations using complete vehicles, including its use as a fuel blend component, as an alternative to ethanol, or as a neat fuel. Comparisons between isobutanol and the other butanol isomers are also included, along with studies on isobutanol's combustion and its effect on the characteristics of fuel blends. Although isobutanol usage in diesel engines is less common, a few examples of that application are also included and discussed.

In the following paragraphs, a brief description of isobutanol and its properties is presented, followed by a general overview of its production methods, from both fossil and renewable sources.

2. Isobutanol Characteristics

Isobutanol (also known as isobutyl alcohol or 2-methyl-1-propanol) is a primary alcohol and one of the four butanol structural isomers, for which structures are shown in Figure 1. Isobutanol is a clear, colorless liquid at room temperature with a characteristic odor. Isobutanol is primarily used in the field of surface coating, where it is used either directly as a solvent for varnishes, or it is converted into derivatives, such as esters, which then serve as solvents or monomer components. Isobutanol can also be used as a diluent and additive for nitrocellulose and synthetic resins, as a wetting agent, cleaner additive, and component of printing inks and related products [19]. Some important properties of the four butanol isomers are shown in Table 1. Isobutanol, having a high octane rating, has the potential to produce higher engine thermal efficiencies, due to the improved knock resistance. Moreover, because of the presence of fuel-bound oxygen (approximately 21.6 wt.%), the engine-out particulate matter (PM) emissions are expected to be lower with isobutanol, compared to using a non-oxygenated fuel. Throughout this article, for the sake of consistency, *n*-butanol and *sec*-butanol are referred to as "1-butanol" and "2-butanol", respectively (unless the former designations appear in the title of a reference).

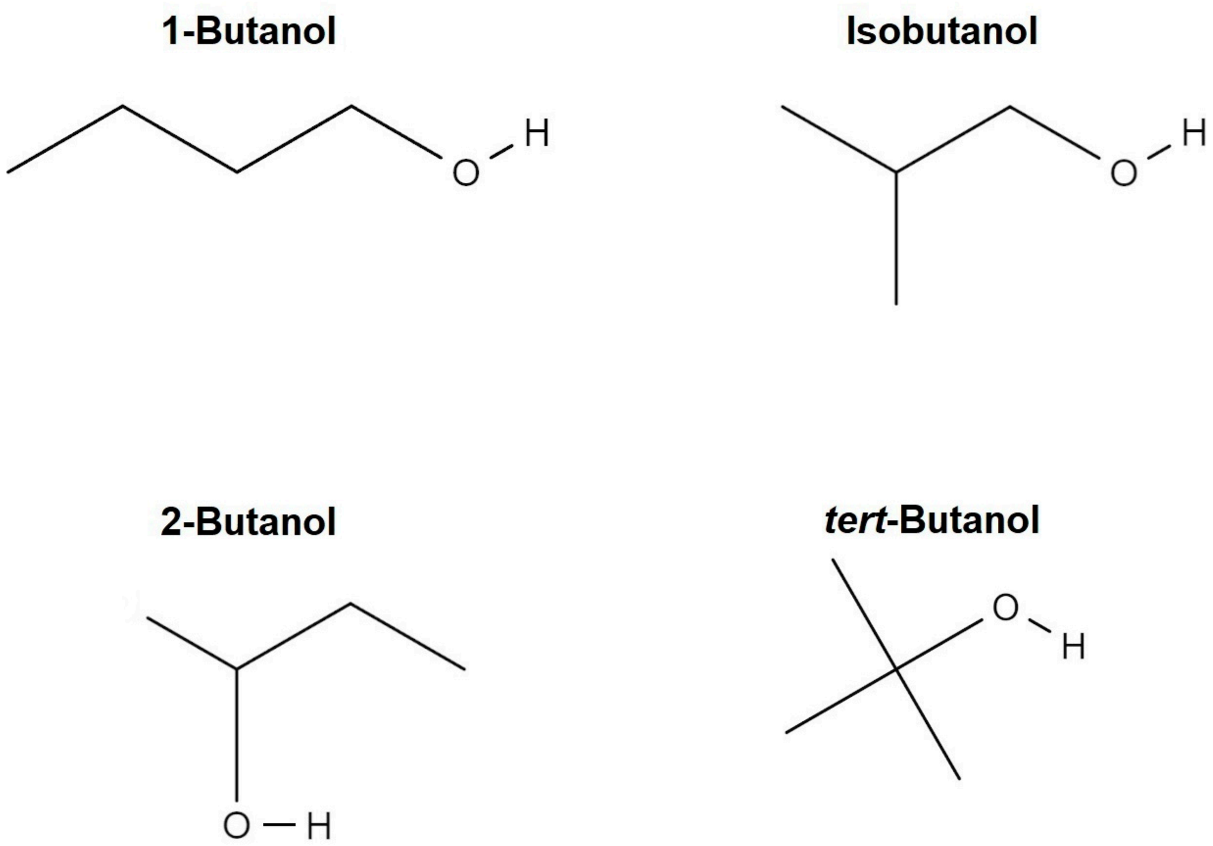

Figure 1. Molecular structures of the four butanol isomers.

Table 1. Some selected fuel properties [8,20–22].

	1-Butanol	2-Butanol	Isobutanol	*tert*-Butanol	Ethanol	Gasoline
Density (kg/m^3) (20 °C)	810	808	802	789	794	715–765
Lower heating value (MJ/kg)	33.2	33.0	33.2	32.6	27.0	42.7
Research octane number (RON)	98	105	105	107	109	88–98
Motor octane number (MON)	85	93	90	94	90	80–88
Autoignition temperature (°C)	343	406	427	478	423	~300
Boiling point (°C)	118	99	108	83	78	25–215
Heat of vaporization (kJ/kg)	708	671	686	630	920	380–500
Reid vapor pressure (RVP) (kPa)	2.2	5.3	3.3	12.2	16	60–62

3. Isobutanol Production

3.1. Isobutanol Production from Fossil Sources

The most important process for the manufacture of isobutanol from fossil sources is the hydroformylation (also known as oxo synthesis) of propylene, followed by the catalytic hydrogenation of the formed aldehydes into the corresponding alcohols, a method that produces both isobutanol and 1-butanol simultaneously [19]. A related process is the carbonylation of propylene, also known as the Reppe process, in which the olefin, carbon monoxide, and water are reacted under pressure in the presence of a catalyst, a method that can produce isobutanol and 1-butanol directly from propylene [19].

3.2. Isobutanol Production from Renewable Sources

Isobutanol can be biosynthesized by a number of microorganisms, utilizing various biomass feedstocks [23]. When glucose (from starch, for instance) is used as a substrate, microorganisms, like *Escherichia coli* and *Saccharomyces cerevisiae*, produce isobutanol through the pathway for the biosynthesis of valine, using enzymes to convert pyruvate to 2-ketoisovaleric acid, then to isobutyraldehyde, and finally to isobutanol [24]. It should be noted that most microorganisms do not produce isobutanol on their own, so they need to be genetically manipulated to enhance the expression of the key enzymes, to inhibit byproduct formation, and to strengthen their resistance against the cytotoxicity of the alcohol. *E. coli* and *S. cerevisiae* are also able to synthesize isobutanol from lignocellulosic biomass, along with bacteria, such as *Clostridium cellulolyticum* and *Clostridium thermocellum*, for instance [23]. However, when cellulose is used as a substrate, usually much lower product concentrations are achieved in comparison with isobutanol obtained from starch, owing to the challenges associated with the degradation of cellulose to simple sugars (like glucose) [25]. An overview of isobutanol produced from biomass can be found in a recent article by Dedov et al. [26].

Isobutanol can also be obtained from a mixture of methanol and another alcohol (such as ethanol), using the Guerbet reaction [27]. If renewable methanol is used, the final product could be partly considered as an e-fuel [28].

The cost of producing isobutanol from biomass depends heavily on the fermentation titer because it is closely related to the energy necessary for product purification [29]. A 2019 study by Roussos et al. [30] investigated the production cost of cellulosic isobutanol, using simulations. Utilizing an improved technique for product removal, the authors found that the isobutanol titer increased from 22 g/L to 50 g/L, corresponding to a reduction in production costs from USD 2.24/L to USD 1.42/L. As a rough comparison, the cost of cellulosic ethanol has been estimated at USD 2.76 per gallon, which corresponds to USD 0.73 per liter, according to a 2017 study by Lynd et al. [31].

4. Isobutanol Combustion

The literature contains a great number of studies dedicated to the combustion of butanol isomers, regarding the flame structure and chemical composition, flame temperature and velocity, pollutant formation, and chemical kinetics, among other topics. Therefore, only a handful of combustion studies is described in this Review.

Arguably most articles found in the combustion literature concern experimental and/or modeling studies on butanol flame characterization, and many of those are comparative investigations of the four isomers of butanol. For instance, in 2005, McEnally and Pfefferle [32] investigated the flames of the four butanol isomers by measuring the temperature and chemical composition in co-flowing methane/air flames doped with each of the four isomers of butanol and the two isomers of butane. Among other conclusions, the authors found that all four butanol isomers produced much higher concentrations of aldehydes and ketones, as intermediate species, than the butanes, a fact that is relevant regarding pollutant formation when butanol is used as a fuel. Another study on intermediate identification was conducted by Yang et al. and described in their 2007 article [33], in which the concentration profiles of the reactants, intermediates, and products were measured by gas chromatography and infrared spectrometry. In another study by Grana et al. [34], the authors investigated the pyrolysis and oxidation mechanisms of the four butanol isomers and found that those are similar to the mechanisms involved in the pyrolysis and oxidation of hydrocarbon fuels. Two related studies, one published in 2011 by Oßwald et al. [35] and the other published in 2012 by Frassoldati et al. [36], identified the compositions of 57 intermediate compounds present in the flames of the four butanol isomers. The authors found that the isomers' flames exhibited strikingly similar temperature and major species profiles. However, there were also significant variations in the intermediate species pool among the butanol isomers, suggesting that different pollutant emissions are expected, regarding both their chemical properties and their concentrations. A comprehensive chemical kinetic combustion model for the four butanol isomers was presented by Sarathy et al. in their 2012 article [37]. Their model predicted the general combustion features and the dominant reaction pathways for the four butanol isomers, taking into account the structural features of the individual isomers that can influence the combustion process.

The autoignition of the four butanol isomers was investigated and their ignition delay times were measured in shock tubes in a 2008 study by Moss et al. [38]. Based on their results, a kinetic model was also developed. Among their results, the authors found that isobutanol was the second most reactive isomer (i.e., it had the second shortest ignition delay), behind 1-butanol, whereas *tert*-butanol and 2-butanol were the least reactive ones. Among other chemical kinetic-related topics, the ignition delay of the butanol isomers was also investigated by Yasunaga et al. [39] and Stranic et al. [40], with both studies featuring experimental work and the development of kinetic models.

The flame velocity of the four butanol isomers was the subject of a 2010 article by Gu et al. [41], in which the authors found that although the adiabatic flame temperatures of the butanol isomers were roughly the same, there were marked differences in their laminar burning velocities, a result that was attributed to the isomers' molecular structures. It was found that isobutanol had the second lowest burning velocity, ahead of *tert*-butanol, while 1-butanol exhibited the fastest flame, followed by 2-butanol. The same results were observed in the 2011 study by Veloo and Egolfopoulos [42], in which experiments and simulations were used to study the propagation of the flames of all four butanol isomers. Finally, Wu and Law [43], in their 2013 article, also concluded that the fastest burning butanol isomer is 1-butanol, followed by 2-butanol, isobutanol, and *tert*-butanol. The authors attributed the lower flame velocities of the branched butanol isomers (isobutanol, 2-butanol, and *tert*-butanol) to the formation of more branched and chemically stable intermediates during their combustion, such as isobutylene, isopropanol, and acetone. Based on the results from the studies referenced above, the flame velocities of isobutanol combustion in air are roughly equivalent to the corresponding flame velocities of gasoline–air mixtures, as described in an article by Sileghem et al. [44]. The peak velocities achieved under stoichiometric conditions are typically in the range 45–50 cm/s at atmospheric pressure and temperatures around 340–360 K.

Soot formation with butanol fuels has been the topic of many articles found in the literature, including the 2013 study by Camacho et al. [45], where the influence of fuel-bound oxygen on the sooting behaviors of isobutanol and 1-butanol was experimentally investigated. The authors also carried out similar experiments on isobutane and 1-butane flames to better understand the effects of the molecular structure and the presence of the hydroxyl group on the processes of soot nucleation and growth. According to the authors, the onset of soot nucleation was faster in the branched fuels, compared to their straight-chain counterparts. In addition, a reaction model for isobutanol and 1-butanol was used to study the soot precursor chemistry. As in the measured soot onset, benzene was computed to nucleate earlier in the flames of the branched compounds, when compared to the ones with straight-chain molecules. Another comparison of the soot formation processes for the isomers of butanol and butane was conducted by Singh et al. [46]. Not surprisingly, the authors found that the butane isomers formed more soot than the butanol isomers, owing to the presence of the hydroxyl group in the latter. Moreover, according to their study, the sooting tendency of isobutanol was the second lowest of all the compounds that were investigated. The formation of polycyclic aromatic hydrocarbons (PAHs) and soot from the pyrolysis of the four butanol isomers was investigated in a 2017 study by Viteri et al. [47]. According to their results, isobutanol had the lowest tendency to produce both PAHs and soot, whereas *tert*-butanol had the highest one, followed by 2-butanol and 1-butanol.

In their 2017 study, Chen et al. [48] investigated the PAH and soot formation characteristics of the four butanol isomers in premixed flames by mixing each isomer in different proportions with a diesel fuel surrogate made up of n-heptane and toluene. The distributions and concentrations of PAHs and soot volume fractions were determined using laser techniques. In addition, a kinetic model for the combustion of the n-heptane–toluene–butanol blends was constructed. According to their results, the branched-chain butanols (isobutanol and *tert*-butanol) tended to produce more PAHs, owing to the enhanced formation of propargyl radicals. Moreover, the soot volume fractions obtained with isobutanol and *tert*-butanol were even higher than those obtained without the butanol addition to the base fuel. The authors concluded that the PAH and soot formation tendency of the butanol isomers, in decreasing order was as follows: *tert*-butanol > isobutanol > 2-butanol > 1-butanol. It is worth noting that the soot formation tendency does not exactly match the one described in the study mentioned above, by Viteri et al. [47].

As is usually the case with alcohols, the combustion of isobutanol may lead to an increase in aldehyde emissions [49]. As an example, in a 2002 study by Zervas et al. [50], conducted on a CFR engine, a thorough overview is provided for the impacts of the fuel composition and λ on the exhaust emissions of alcohols and aldehydes/ketones.

5. Use of Isobutanol in SI Engines

Primarily owing to its high octane rating (RON of around 113), the highest among the four butanol isomers, isobutanol has good potential to be used as an SI fuel. Indeed, as already explained, its higher heating value, much lower affinity to water, and more compatible vapor pressure characteristics make isobutanol an attractive alternative to ethanol as an oxygenate for gasoline. Those favorable properties also mean that isobutanol can even be used in neat form as an SI fuel (though its lower vapor pressure can pose a problem regarding engine cold starts, see Section 5.2.1). However, most of the research has, so far, been dedicated to the use of isobutanol as a gasoline blendstock.

In the next sections, the physicochemical properties of blends of isobutanol with gasoline are introduced, followed by a more extensive discussion of the performance of such blends. Comparisons between blends of gasoline with the different butanol isomers and with different alcohols (mostly ethanol) are then presented through several examples from the literature.

5.1. Properties of Gasoline–Isobutanol Blends

In their 2010 article [9], Andersen et al. presented a comprehensive set of distillation data for several gasoline–alcohol mixtures that are potentially important as biofuel blends. The investigated blends contained 10, 20, 50, and 85 vol.% of each of the following alcohols: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, isobutanol, and *tert*-butanol. According to their results, most gasoline–alcohol blends form near-azeotropic mixtures that significantly affect the shape of the distillation curve. Their study also showed that unlike the lower alcohols (methanol, ethanol, and 2-propanol), the initial part of the distillation curves of low-concentration gasoline–isobutanol blends are very similar to that of the base gasoline. However, in the distillation regions corresponding to T30 and beyond, the distillation temperatures of such low-concentration blends are lower than the gasoline distillation temperatures; yet, when compared to mixtures of gasoline and the lower alcohols, the differences are small, roughly half the temperature difference observed with such alcohols. The authors also point out that the molecular structure of isobutanol (along with the other butanol isomers) is closer to those of gasoline hydrocarbons than, for instance, methanol. As a result, butanol mixes with gasoline with less impact when compared to methanol; that is, butanol–gasoline mixtures are closer to ideal solutions than methanol–gasoline blends.

In a study similar to the previous one [8], the same authors measured the Reid vapor pressures (RVPs) of several gasoline–alcohol blends containing between 5 and 85 vol.% of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, isobutanol, and *tert*-butanol. In line with the results of their previous investigation, the authors found that most alcohols form near-azeotropic blends with gasoline that exhibit non-ideal volatility behaviors. Moreover, the addition of isobutanol to gasoline, in increasing concentrations, resulted in lower RVP values, when compared to those of the blends of gasoline with the C1-C3 alcohols. This decrease in volatility is consistent with the lower vapor pressure of isobutanol.

The effect of adding different oxygenates, including isobutanol, to gasoline and assessing their impact on the final fuel blends was the topic of a study by Christensen et al. [51]. In that article, several types of oxygenated compounds were mixed with three different blendstocks for oxygenate blending (BOBs), in amounts up to 3.7 wt.% oxygen (the oxygen content of E10) in the final blends. The chemical and physical properties of the final blends were then compared to the requirements of the ASTM D 4814 standard (“Specification for Automotive Spark-Ignition Engine Fuel”) [52]. The vapor pressure, vapor lock properties, distillation temperatures, density, octane rating, viscosity, and potential for extraction in water were measured. Their results showed that regarding isobutanol, its addition to the BOBs caused a reduction in vapor pressure of up to 10 kPa when compared to the vapor pressure of the base blendstock. In addition, isobutanol also improved the blends’ vapor lock protection and caused their distillation parameters to be within the specification limits. It was also determined that although isobutanol can increase the octane rating of a base BOB, the anti-knock index (AKI) of the final blend may only be within the specifications (AKI = 87) if the isobutanol is mixed with a BOB having a sufficiently high octane rating. Finally, the authors concluded that among the other compounds, isobutanol has good potential to be used as a gasoline oxygenate, owing to its favorable properties.

Similarly, a 2016 study by Rodriguez-Anton et al. [53] investigated the impact of adding isobutanol, ethanol, or ethyl *tert*-butyl ether (ETBE) to gasoline on the blend’s RVP, distillation curves, and density, among other properties. It was concluded that isobutanol has advantages over ethanol regarding the energy density, air/fuel ratio, vapor pressure, and renewable content.

In a 2014 article by Li et al. [54], the compatibility of isobutanol with gasoline was investigated. In their study, blends consisting of isobutanol mixed with neat gasoline in ratios of 10–90 vol.% were prepared. No phase separation was observed at each blending ratio. The physical and chemical properties of the gasoline–isobutanol blends were either determined using test methods from fuel standards or they were calculated. The properties included the density, LHV, distillation temperatures, viscosity, stoichiometric AFR, octane number, copper corrosiveness, and oxygen content. The results showed that isobutanol and gasoline have similar densities and the density of their blends is suitable to be used in existing engines because the density determines the amount of fuel that is volumetrically injected. With increasing isobutanol content in the blend, the initial boiling point and the T10 distillation temperature increased gradually, whereas the T50 and T90 temperatures exhibited a gradual decrease. Because the measured kinematic viscosities of isobutanol were found to be nine times higher than those of gasoline, the authors did not advise the use of gasoline–isobutanol blends at low ambient temperatures. It was also found that adding isobutanol to gasoline can improve its anti-knock properties. Moreover, gasoline–isobutanol blends did not exhibit signs of copper corrosion, which rules out the need to change fuel storage facilities when using such blends.

The question of how much the addition of isobutanol affects the octane rating of gasoline–isobutanol blends was addressed in a recent study by Alleman et al. [55]. Their article describes the creation and validation of volumetric and molar linear blending models that can be used to predict the RON and MON of gasoline–isobutanol blends, based on the properties and composition of both substances. To validate the models, 34 gasoline BOBs were mixed with isobutanol in concentrations of 12.5 and 16 vol.% (which has the same oxygen content as E10). The behavior of the octane number of the finished gasoline–oxygenate blends can be complex and difficult to predict. In line with this fact, the authors found that the nonlinear volumetric model was the one that gave the best prediction of the finished blend ON. Finally, the authors found that paraffinic gasoline blendstocks have a synergistic effect with butanol and olefins, whereas aromatic gasolines have an antagonistic effect.

Isobutanol was one of the fuels with the potential to enable the development of advanced SI engines, according to a comprehensive study by McCormick et al. [56], published in 2017. In that article, the authors developed a list of potential renewable blendstocks for which properties and characteristics were determined and stored in an online database. Screening criteria were then developed to determine whether a potential bio-blendstock could meet the requirements to be used in advanced SI engines. Moreover, many of these compounds were blended into gasoline blendstocks to experimentally study their blending properties. It has been shown that for modern spark-ignition engines, fuels with increased octane sensitivity (the difference between the RON and MON) exhibit greater resistance to auto-ignition [57]. From the results, the authors concluded that isobutanol, as well as other biofuels, exhibit the minimum acceptable properties for making high-octane advanced SI engine fuels, that is, a RON of at least 98 and an octane sensitivity of at least 8.

5.2. Performance of Gasoline–Isobutanol Blends

This section summarizes the literature on the topic of blends of gasoline with isobutanol, showing numerous examples of how isobutanol behaves as a fuel extender when it is mixed with gasoline, which is an important topic because the physicochemical properties of any fuel blend have a direct impact on the engine performance.

Table 2 presents an overview of the studies discussed in this article.

Table 2. An overview of the studies included in this article.

Use of Gasoline–Isobutanol Blends in SI Engines				
Reference	**Author(s)**	**Year Published**	**Main Topic**	**Engine/Test Type**
[10]	Regalbuto et al.	2012	Performance and emissions	PFI engine
[58]	Alasfour	1998	NOx emissions	PFI engine
[59]	Alasfour	1999	HC emissions	PFI engine
[60]	Baustian and Wolf	2012	Cold-start performance	Vehicle, PFI, and DI engines

Table 2. *Cont.*

Use of Gasoline–Isobutanol Blends in SI Engines				
Reference	**Author(s)**	**Year Published**	**Main Topic**	**Engine/Test Type**
[61]	Irimescu	2011	Engine efficiency	Vehicle, PFI engine
[62]	Sayin and Balki	2015	Engine efficiency	PFI engine
[63]	Vojtisek-Lom et al.	2015	PM emissions	Vehicle, DI engine
[64]	Li et al.	2017	Combustion and emissions	DI engine
[65]	Yusoff et al.	2017	Performance and emissions	PFI engine
[66]	Rice et al.	1991	Gaseous emissions	Carbureted engine
[67]	Popuri and Bata	1993	Performance and knock	CFR engine
[68]	Wallner and Frazee	2010	Regulated and unregulated emissions	DI engine
[69]	He et al.	2010	PM emissions	DI engine
[70]	Wasil et al.	2012	Performance and emissions	DI two-stroke and PFI four-stroke
[71]	Wasil and Wallner	2014	Performance and emissions	DI two-stroke and PFI four-stroke
[72]	Wallner et al.	2014	Performance and emissions	PFI engine
[73]	Storey et al.	2014	Regulated and unregulated emissions	DI engine
[74]	Poitras et al.	2015	Unregulated emissions	PFI engine
[75]	Irimescu	2009	Engine performance	Vehicle, PFI engine
[76]	Stansfield et al.	2012	Emissions	Vehicle, DI engine
[77]	Ratcliff et al.	2013	Unregulated emissions	Vehicle, PFI engine
[78]	Karavalakis et al.	2013	Emissions	Vehicle, PFI engine
[79]	Karavalakis et al.	2014	Regulated and unregulated emissions, PM emissions	Vehicle, PFI, and DI engines
[80]	Karavalakis et al.	2014	Gaseous and PM emissions	Vehicle, DI engine
[81]	Karavalakis et al.	2014	Gaseous emissions	Vehicle, PFI engine
[82]	Karavalakis et al.	2015	Gaseous and PM emissions	Vehicle, DI engine
[83]	Chan	2015	PM emissions	Vehicle, PFI, and DI engines
[84]	Storey et al.	2019	PM emissions	Vehicle, DI engine
Use of Neat Isobutanol in SI Engines				
[85]	Irimescu	2009	Engine efficiency	Vehicle, PFI engine
[86]	Pechout et al.	2014	Engine performance	Vehicle, PFI engine
[87]	Sileghem et al.	2015	Performance and emissions	Vehicle, DI engine
[88]	Pechout et al.	2017	Combustion	PFI engine

Table 2. *Cont.*

Use of Gasoline–Isobutanol Blends in SI Engines				
Reference	**Author(s)**	**Year Published**	**Main Topic**	**Engine/Test Type**
Use of Isobutanol Blends in CI Engines				
[89]	Al-Hasan and Al-Momany	2008	Engine performance	Single-cylinder engine
[90]	Karabektas and Hosoz	2009	Performance and emissions	Single-cylinder engine
[91]	Ozsezen et al.	2011	Performance and emissions	Heavy-duty DI engine
[92]	Pal et al.	2013	Performance and emissions	Single-cylinder engine
[93]	Gu et al.	2013	Performance and emissions	DI engine
[94]	Rajesh Kumar et al.	2016	Performance and emissions	Single-cylinder engine
[95]	Krishnan and Rajkumar	2022	Performance and emissions	Dual-fuel engine
[96]	Yang et al.	2016	Emissions	Ternary fuel blends
[97]	Altinkurt et al.	2022	Performance and emissions	Ternary fuel blends
[98]	DelVescovo et al.	2015	Performance and emissions	LTC
[99]	Mack et al.	2016	Performance and emissions	LTC
[100]	Rajesh Kumar and Saravanan	2016	Performance and emissions	LTC
[101]	Shahsavan and Mack	2018	Performance and emissions	LTC

5.2.1. Performance of Gasoline–Isobutanol Blends in General

The effect of adding isobutanol to gasoline on engine-out NOx emissions was described in an article by Alasfour, published in 1998 [58]. In that study, isobutanol was mixed with fossil gasoline at a fixed ratio of 30 vol.%. The engine tests were conducted on a port-fuel-injected (PFI) single-cylinder engine operating under wide-open throttle (WOT) conditions, at maximum brake torque (MBT) spark timings, and at a constant velocity. The author found that a maximum reduction of 9% in NOx emissions was achieved with the gasoline–isobutanol blend, when compared to pure gasoline. The decrease in NOx was more evident under isobutanol-rich operating conditions, and it was attributed to the higher latent heat of vaporization of the isobutanol, which leads to lower peak cycle temperatures, as the thermal mechanism is the dominant source of NOx at the peak combustion temperatures achieved in engines [102]. Another interesting result was that the presence of isobutanol in the gasoline caused the MBT spark setting to be more retarded when compared to running the engine on pure gasoline, which suggested that the gasoline–isobutanol blend burned faster than pure gasoline.

Using the same engine and the same gasoline–isobutanol blend as in the study described above, the author performed a subsequent investigation on the impact of the gasoline–isobutanol blend on the emissions of unburned hydrocarbons (HC) [59]. That study assessed the influence of the fuel/air equivalence ratio, spark timing, and engine velocity on the engine-out emissions of HC, as measured with a flame ionization detector (FID). Also, the effect of the coolant temperature on HC emissions was investigated at three different ϕ levels, corresponding to lean, stoichiometric, and rich conditions. The results showed that by optimizing the operating variables, such as retarding the ignition timing, increasing cooling water temperature, and increasing engine velocity, the HC emissions could decrease by up to 30% when a gasoline–isobutanol blend of 30 vol.% was used as fuel.

The cold-start performance of gasoline–isobutanol blends was the subject of a 2012 article by Baustian and Wolf [60], in which the authors evaluated the efficacy of the ASTM Drivability Index through chassis dynamometer tests with a number of vehicles equipped with PFI and direct-injection spark-ignition (DISI) engines. The fuel matrix in the study comprised blends containing 0, 16, and 24 vol.% isobutanol in fossil gasoline. The cold-start and warm-up drivability tests were performed at 4 °C (40 °F). The authors concluded that the current drivability relationship is inadequate for predicting the drivability performance of gasoline–isobutanol blends, and a new drivability performance metric was developed.

An investigation on fuel conversion efficiency, based on the first law of thermodynamics, was performed by Irimescu [61] on a vehicle equipped with a PFI SI engine fueled by gasoline blends containing 10, 30, and 50 vol.% isobutanol. The efficiency in question refers to the fraction of fuel energy delivered to the wheels of the vehicle, as measured on a chassis dynamometer over the vehicle's entire engine velocity and load ranges. The tests were conducted on a chassis dynamometer and covered. The results showed a drop in fuel conversion efficiency, from 6 to 12%, at part loads with the gasoline–isobutanol blends. At full load, the fuel conversion efficiencies were very consistent for all the fuel blends, and the performance levels were within narrow limits, with variations under ±5% in the mid-rpm ranges. The author concluded that isobutanol is better suited as a gasoline oxygenate compared to ethanol because it can be blended with gasoline in higher concentrations and be used in unmodified engines.

The effect of varying the compression ratio on the performance and emissions of a small PFI SI engine, running on different gasoline–isobutanol blends, was investigated by Sayin and Balki [62]. Using neat gasoline as a baseline, gasoline–isobutanol blends containing 10, 30, and 50 vol.% isobutanol were prepared and tested under WOT conditions at a constant engine velocity. According to the results, the brake-specific fuel consumption (BSFC), the brake thermal efficiency (BTE), and CO_2 emissions increased with increasing isobutanol content for all the compression ratios, whereas the hydrocarbon and carbon monoxide emissions decreased. The increase in BTE was attributed to the higher heat of vaporization of isobutanol compared to neat gasoline. Increasing the compression also reduced the CO and HC emissions. In addition, the authors reported that in general, increasing the isobutanol content in the blends caused the peak cylinder pressure to increase and caused the heat release curve to shift toward earlier crank angle degrees, suggesting faster combustion due to the presence of isobutanol in the fuel (which agrees with the study by Alasfour [58], as mentioned above).

5.2.2. Comparison with other Butanol Isomers

The studies included in this Section show how isobutanol performs when compared to the other butanol isomers: 1-butanol, 2-butanol, and *tert*-butanol.

The effects of three of the four butanol isomers on the engine performance and emissions were investigated by Regalbuto et al. in their 2012 study [10]. The evaluated butanol isomers were 1-butanol, 2-butanol, and isobutanol. Blends of those isomers with gasoline were prepared at the fixed concentration of 30 wt.%. The engine experiments were conducted on a PFI single-cylinder SI engine at a constant velocity of 1200 rpm, at three load levels, while keeping constant the air/fuel ratios and spark timing. The test results showed that although the three isomers performed similarly regarding the brake torque and in-cylinder pressure, their behavior was very distinct regarding emissions. In other words, pollutant formation is strongly dependent on the fuel's chemical structure, which determines the reaction pathways and, consequently, the type and number of intermediates produced during combustion. Isobutanol produced the highest average CO emissions, 1-

butanol produced the highest average NOx emissions, and 2-butanol produced the highest average hydrocarbon emissions.

The impacts of using 1-butanol and isobutanol as gasoline oxygenates on the PM emissions from a passenger car were evaluated by Vojtisek-Lom et al. [63]. The vehicle was equipped with a turbocharged DISI engine, and it was tested on a chassis dynamometer in the World-harmonized Light-duty Test Procedure (WLTP), the Artemis driving cycles, and on the road along a 55 km route, including urban, suburban, and highway driving. The tested fuels were a blend of 1-butanol in gasoline (nBu25) and another of isobutanol in gasoline (iBu25). Both alcohols were mixed at a fixed 25 vol.% ratio. As reference fuels, in addition to neat gasoline (E0), a blend of 15 vol.% ethanol in gasoline (E15) was used. According to their results, the vehicle performed well when running on the alcohol blends regarding general performance, cold-start performance, drivability, and off-cycle particulate emissions. Although both butanol blends decreased the solid particulate number (PN) emissions (>23 nm particle size) by about one-half, the effect on the other pollutants was less consistent or not significant. The results also showed that only roughly half of the particles were larger than 23 nm and among those, only about half comprised solid particles. Overall, the authors found that compared to neat gasoline, both 1-butanol and isobutanol produced significant reductions in PN concentrations, mostly during high-power operation, whereas E15 had a small impact on those emissions.

The effects of the four butanol isomers, when blended with gasoline, on the combustion and emissions from a turbocharged DISI engine were investigated by Li et al. [64]. Each butanol isomer was mixed with neat gasoline at blending ratios ranging from 10 to 50 vol.%. The engine was stoichiometrically operated at a constant velocity and at varying loads. Moreover, the fuel injection and spark timings were set to either MBT or knock-limited advance. The results showed that at low blending ratios, isobutanol, along with 1-butanol and 2-butanol, increased the peak in-cylinder gas temperatures, when compared to gasoline. However, at higher blending ratios, they caused a decrease in the peak temperatures, owing to the charge-cooling effect. Regarding the particulate emissions, the gasoline–isobutanol blends had the second highest PN concentrations behind the *tert*-butanol blends and followed by the 1-butanol and the 2-butanol blends. The authors also found that the difference in the particle mean diameter of the four isomers was not significant.

In their study [65], Yusoff et al. tested the impacts of all four butanol isomers on the performance and emissions of a light-duty PFI SI engine. The gasoline–butanol blends were prepared by mixing each isomer with the base gasoline fuel (having a RON of 95) at a fraction of 20 vol.%. The base gasoline and the four butanol blends were tested on the engine under steady-state WOT conditions and at constant velocities ranging from 1000 to 5000 rpm. Their results showed that among all the fuels, the isobutanol blend produced the highest engine torque, brake power, and BTE. Together with the 1-butanol blend, it also produced the lowest CO and HC emissions. However, the isobutanol blend gave the highest concentrations of NO, when compared to neat gasoline, especially at higher engine velocities.

5.2.3. Comparison with other Gasoline–Alcohol Blends

Many of the fuel studies published about isobutanol are the ones comparing it to other alcohols that have been used in blends with gasoline, with ethanol being the foremost example. This section shows several examples of how gasoline–isobutanol blends compare to blends of gasoline with other alcohols, regarding engine performance and emissions. Studies performed on engines and on vehicles are considered separately.

Engine Tests

As an example of an earlier article [66] dealing with isobutanol blends, Rice et al. investigated the effects of blending alcohols with gasoline on exhaust emissions. The alcohols were methanol, ethanol, and isobutanol, all blended with gasoline at the same ratio of 20 vol.%. The experiments were performed on a four-cylinder carbureted passenger-car engine, running under different steady-state conditions with varying relative fuel–air ratios for each fuel blend. According to the results, the emissions of carbon monoxide and nitrogen oxides were lower for the alcohol blends, in comparison with neat gasoline. The primary reason was attributed to the leaning effect caused by the lower stoichiometric air/fuel ratio of the alcohols. In addition, the lower peak combustion temperatures exhibited by the alcohols contributed to the lower NOx levels produced by the gasoline–alcohol blends. More specifically, about isobutanol, the authors concluded that its blend showed emission characteristics that were comparable to the ones from the methanol and ethanol blends. In summary, the authors found that isobutanol had the potential to be further explored owing to its advantages, such as low affinity for water and a vapor pressure and latent heat of vaporization that are more compatible with those of gasoline. Isobutanol blends resulted in more power, higher thermal efficiency, and lower BSFCs than the corresponding methanol and ethanol blends.

In another earlier study, Popuri and Bata [67] evaluated the use of gasoline–isobutanol blends as fuels for SI engines by comparing them with the more common gasoline–methanol and gasoline–ethanol blends. The gasoline–alcohol blends were prepared by mixing each of the three alcohols with the baseline gasoline at 5, 10, and 20 vol.%. The engine tests were carried out on a Waukesha CFR (Cooperative for Fuel Research) engine at a range of compression ratios from 7:1 to 15:1 at a constant velocity of 800 rpm. Furthermore, three different fuel/air equivalence ratios were used, and the spark timings were varied from 5 to 25 CAD BTDC in 5 CAD increments. Their results showed that increasing the blend alcohol content improved the anti-knock quality of the blends, with all three alcohols exhibiting nearly the same anti-knock effect. The brake power decreased, and the BSFC increased, owing to the inherently lower heating value of the gasoline–alcohol blends. When compared to methanol and ethanol, the isobutanol blends resulted in overall increased performance. In general, the gasoline–isobutanol blends resulted in increased power, better fuel economy, and higher thermal efficiency, due to isobutanol having a higher heating value in comparison with methanol and ethanol. The authors attributed this to the higher in-cylinder peak pressures observed with the gasoline–isobutanol blend during combustion. It was then concluded that isobutanol seemed like a promising alternative to methanol and ethanol as a gasoline oxygenate.

The impacts of isobutanol as a gasoline oxygenate on both regulated and unregulated gaseous emissions were investigated in a 2010 study by Wallner and Frazee [68], in which a naturally aspirated DISI engine was used. Besides the baseline gasoline, the following six alcohol blends were investigated: ethanol at 10 and 50 vol.% fractions plus both 1-butanol and isobutanol at 16 and 83 vol.% concentrations each. The concentrations of the butanol isomers were determined as having the same oxygen content as the ethanol blends. The engine was run at six different test points, and the emissions were measured using a conventional emissions bench as well as an FTIR (Fourier-transform infrared) analyzer. Their results showed that the use of isobutanol resulted in an increase in the emissions of benzene precursors, such as propene, 1,3-butadiene, and acetylene, meaning that the PM emissions are expected to be significantly higher with the isobutanol blends, as opposed to the ethanol blends. The isobutanol blends also increased the formation of both formaldehyde and acetaldehyde. The authors concluded that even though isobutanol has clear advantages over ethanol as a gasoline oxygenate, its use in higher blend fractions may increase the emissions of unregulated species, such as aldehydes.

The PM emissions were the focus of an investigation by He et al. [69] in which gasoline–isobutanol and gasoline–ethanol blends were compared through engine tests. The particulate emissions, expressed both as size distributions and total concentrations, were measured under engine-out and tailpipe (post three-way catalyst) conditions. The experiments were performed on a turbocharged, wall-guided DISI engine. The test matrix comprised 10 steady-state engine operating conditions. In addition to neat gasoline (E0), three gasoline–alcohol blends were tested, containing 10 and 20 vol.% ethanol (E10 and E20, respectively) and 12 vol.% isobutanol (Bu12). The total particle number concentrations and size distributions were measured by a TSI Model 3091 Fast Mobility Particle Sizer (FMPS) spectrometer, operating in the size range from 5.6 to 560 nm. According to the results, under most operating conditions, the blend consisting of 12 vol.% isobutanol (Bu12) achieved a 30% reduction in the nucleation-mode (mostly volatile) particles, whereas this blend caused an even higher percentage reduction in the emissions of accumulation-mode (solid) particles.

Wasil et al. [70], in their 2012 study, investigated the performance of gasoline–isobutanol blends as a fuel for recreational boats. In their investigation, field emission experiments were performed on two recreational boats fueled by a gasoline blend containing 16 vol.% isobutanol and a gasoline blend containing 10 vol.% ethanol in addition to the baseline indolene certification gasoline. One boat was equipped with a supercharged four-stroke engine, whereas the other one was powered by a spray-guided direct-injection (DI) two-stroke engine. Their tests lasted for six months and represented well over 50 h of operation. Throughout the tests, the authors reported that no engine runability, startability, or other issues took place when the engines operated on the gasoline–isobutanol blend. Hydrocarbon and NOx emissions were unchanged for the four-stroke engine, whereas the two-stroke engine had a slight increase in NOx emissions. The emissions of CO decreased for both engines. It was concluded that gasoline–isobutanol blends have the potential to be used in recreational marine engine applications.

Another study comparing gasoline–isobutanol and gasoline–ethanol blends, performed on recreational boats, was conducted by Wasil and Wallner and published in 2014 [71]. The outboard engines used in the experiments were a PFI four-stroke SI engine and a DI two-stroke SI engine (not the same engines from the study mentioned above). Both engines featured an open-loop control strategy, meaning that there were no combustion feedback sensors to compensate for the different air/fuel ratios required by the test fuels. Three fuels were used: indolene certification gasoline, a blend of 10 vol.% ethanol in gasoline (E10), and a blend of 16 vol.% isobutanol in gasoline (iB16), with both alcohol blends containing the same amount of oxygen. Those blends were prepared by mixing the respective alcohols with a BOB and not the indolene fuel. The engines were tested in a five-mode steady-state marine test cycle, and the gaseous and particulate emissions were measured. Both gasoline–alcohol blends reduced the PM mass by up to 30%, compared to the baseline indolene fuel, together with a significant reduction in organic carbon (OC) emissions. However, the emissions of the elemental carbon (EC) showed a moderate increase with the alcohol blends. The authors concluded that based on the gaseous and PM emissions results, iB16 seemed to be a promising blend, relative to E10, and could be used to increase the use of renewable fuels in recreational boats.

The same PFI four-stroke engine used in the previous study was used in another recreational boat investigation carried out by Wallner et al. [72], where gasoline–isobutanol and gasoline–ethanol blends were compared by focusing on performance and emissions. Just like in the previous study, the investigated fuels were indolene certification gasoline, a blend of 10 vol.% ethanol (E10), and a blend of 16 vol.% isobutanol (iB16), both alcohol blends made with a BOB. The engine was tested on a full-load curve and in a five-mode steady-state marine engine test cycle. The results showed that both gasoline–alcohol blends exhibited the same full-load performance as the indolene fuel, together with a slight improvement in BTE. This was attributed to changes in the air/fuel ratio with the different fuels because the engine's open-loop control system did not keep the ratio constant. The authors believed that the open-loop control strategy also affected the lower CO and the higher combined HC + NOx emissions observed with the gasoline–alcohol blends. Finally, the alcohol blends produced higher concentrations of both formaldehyde and acetaldehyde.

Storey et al. investigated the performances of gasoline–isobutanol and gasoline–ethanol blends under rich conditions ($\lambda = 0.91$) to simulate a vehicle acceleration event at typical loads [73]. Their tests were conducted on a DISI engine, and a gasoline having an AKI of 87 (E0) was chosen as the reference fuel. In addition, a blend of gasoline with 30 vol.% ethanol (E30) and another with 48 vol.% isobutanol (iBu48) were tested. PN, OC, EC, soot hydrocarbon speciation, plus aldehydes and ketones were measured during the tests. The results showed that the isobutanol blend produced the lowest level of OC, whereas the levels of EC remained roughly unchanged. The PM analysis showed that PAHs were the most prevalent hydrocarbon species, and the presence of fuel-bound oxygen appeared to suppress their formation. Finally, the emissions of aldehydes were prevalent with both alcohol blends.

Unregulated gaseous emissions were the highlight of a 2015 study by Poitras et al. [74]. In that study, the authors tested gasoline–ethanol blends containing 10 and 15 vol.% ethanol (E10 and E15, respectively) and a gasoline–isobutanol blend with 16 vol.% isobutanol (iB16). In addition, a dual-alcohol blend containing 8 vol.% isobutanol and 10 vol.% ethanol (iB8-E10) was tested. The experiments were performed on a small two-cylinder PFI SI engine, running in a six-mode steady-state test cycle. According to the results, when compared to E0 (neat gasoline), the iB16 blend decreased the cycle-weighted CO emissions by 11.4%, whereas the ethanol blends decreased them by 12%. Also, the isobutanol blend decreased the HC emissions by 8.2% (10.9% with the ethanol blends). The iB16 blend also appeared to decrease the NOx emissions, but the results were not statistically significant. The carbon dioxide emissions decreased with the iB16 blend by 4.2% (3.2% with the ethanol blends). Finally, the isobutanol blend increased the emissions of butyraldehyde, propionaldehyde, and methacrolein, whereas the ethanol blends significantly increased the emissions of acetaldehyde, compared to neat gasoline.

As the examples above have shown, the effects of adding isobutanol to gasoline on the performance and emissions can be largely dependent on engine technology, that is, on the engine hardware configuration and calibration strategy, and on the operating conditions. This means that sometimes, it can be difficult to ascribe the impact on the performance and emissions to isobutanol alone. That being said, some tendencies can be observed. For an unmodified engine, the presence of isobutanol in the fuel will probably result in lower power output, given the lower heating value of the alcohol. Knock resistance is expected to increase with increasing isobutanol content, owing to the alcohol's high octane rating. Regarding emissions, isobutanol, being an oxygenated fuel, has the potential to decrease engine-out PM emissions, particularly in DISI engines, where the less homogeneous fuel–air mixture can produce particles in larger amounts. The emissions of hydrocarbons and carbon monoxide can be decreased with isobutanol, which is also due to its oxygen content. Owing to the lower peak combustion temperatures exhibited by alcohols, lower NOx emissions can be achieved with isobutanol. Finally, as is typically the case with alcohol fuels, the addition of isobutanol to the fuel increases the emissions of aldehydes.

Vehicle Tests

In addition to studies of gasoline–isobutanol blends performed on engines installed in test cells, the literature contains multiple examples of studies carried out on vehicles fueled by such blends, running on chassis dynamometers. A description of a few selected studies, based on their relative recency and perceived relevance, follows.

In a 2009 study, Irimescu [75] investigated the impact of gasoline–isobutanol blends on the engine performance under WOT conditions. Pure gasoline; 10, 30, 50, and 70 vol.% isobutanol blends; together with neat isobutanol (See Section 5.3) were used as fuels. The experiment was carried out on a passenger car on a chassis dynamometer. The vehicle was equipped with an unmodified PFI, naturally aspirated SI engine. The results showed that under WOT conditions, the engine brake power dropped significantly with gasoline–isobutanol blends higher than 30 vol.%. when compared to operation with pure gasoline. For the 50 vol.% blend, the loss in brake power was about 10%, and the engine operation started to become erratic. At the isobutanol blend fraction of 70 vol.%, the engine power dropped by about 25%. The author concluded that with blends with up to 30 vol.% isobutanol in gasoline, the engine performance under WOT conditions remained within acceptable limits and that increasing the isobutanol content above that value was not recommended.

Stansfield et al. tested and compared gasoline–isobutanol blends and gasoline–ethanol blends through vehicle tests on a chassis dynamometer [76]. The vehicle was equipped with a DI engine. Their investigation included two gasolines (with 95 RON and 102 RON), three gasoline–ethanol blends (containing 10, 22, and 85 vol.% mixed with the 95 RON gasoline), and two gasoline–isobutanol blends (containing 16 and 68 vol.% mixed with the 95 RON gasoline). The vehicle was tested in the New European Driving Cycle (NEDC) and on a full-load curve, i.e., under WOT conditions. For the mid-level alcohol blends, the authors found that the emissions of CO and NOx were mostly unaffected, while for the high-level alcohol blends, CO decreased and NOx increased significantly. However, HC emissions were mostly unaffected with the alcohol blends. The results also showed that the WOT performance improved with all the alcohol blends.

The unregulated emissions from the gasoline blended with ethanol, 1-butanol, and isobutanol are described in a 2013 article by Ratcliff et al. [77]. Their study investigated blends of gasoline containing the following alcohols: ethanol (blended at 16 vol.%), 1-butanol (blended at 17 vol.%), and isobutanol (blended at 21 vol.%). In addition, a dual-alcohol blend containing 12 vol.% isobutanol and 7 vol.% ethanol was prepared. All the blends were tested on a passenger car equipped with a PFI engine, and the vehicle was tested in triplicate LA92 driving cycles on a chassis dynamometer. A major goal of the investigation was to identify the effects of butanol on potentially toxic carbonyl and hydrocarbon emissions. According to the results, both butanol blends, in comparison to the ethanol blend, exhibited much lower levels of unburned alcohol emissions. However, they produced much higher carbonyl emissions, with the isobutanol blend exhibiting a 60% increase in formaldehyde concentrations compared to the base gasoline. Besides formaldehyde, the isobutanol blend also produced significant amounts of acetone and 2-methylpropanal.

A 2013 study by Karavalakis et al. [78] investigated the influence of gasoline–isobutanol and gasoline–ethanol blends on the emissions from three passenger cars tested in the Federal Test Procedure (FTP) and Unified Cycle (UC) driving cycles on a chassis dynamometer. All three vehicles had PFI engines. In addition to E10, three blends were investigated: E15, E20, and Bu16, containing 15 vol. % and 20 vol.% ethanol and 16 vol.% isobutanol, respectively. In one of the vehicles, a dual-alcohol blend containing 10 vol.% ethanol and 8 vol.% isobutanol (E10/B8) was also tested. According to the results, the three vehicles showed different emission results for the alcohol blends but no consistent fuel trend was observed. However, formaldehyde and acetaldehyde were the dominant carbonyl emissions for the gasoline–alcohol blends. The particulate emissions exhibited a more consistent pattern, with the gasoline–isobutanol blend, in general, producing higher particle number and higher black carbon emissions than the ethanol blends.

In a subsequent study [79], similar to the previous one, the authors investigated the influences of seven different gasoline–alcohol blends, prepared with either ethanol or isobutanol, on both regulated and unregulated gaseous emissions, as well as on the particulate emissions from three passenger cars with PFI engines and two having wall-guided DI engines. The isobutanol blends were prepared by mixing isobutanol with gasoline at the concentrations of 16, 24, and 32 vol.%. The vehicles were tested on a chassis dynamometer in triplicate FTP and UC. Regulated emissions included CO, HC, and CO_2, while unregulated species included carbonyl compounds. Additionally, the particle mass, total particle number, and black carbon (BC) concentrations were measured. The results showed that the higher-concentration butanol blends exhibited some decreases in HC, CO, NOx, and CO_2 emissions, but these trends were not observed in the vehicle fleet as whole. As expected, the DI vehicles exhibited higher particle mass, particle number, and black carbon emissions. Formaldehyde and acetaldehyde were the most common aldehydes in the exhaust gases, with butyraldehyde also being significant for the isobutanol blends.

Another work by Karavalakis et al. [80] investigated the impacts of gasoline–ethanol and gasoline–isobutanol blends on the gaseous and particulate emissions from two passenger cars equipped with wall-guided DI engines. In addition to NOx, CO, HC, non-methane hydrocarbons (NMHC), methane (CH_4), and CO_2, the gaseous emissions included carbonyl compounds, such as aldehydes, 1,3-butadiene, and benzene. The total particle number emissions, black carbon (BC) emissions, as well as the particle size distributions were also determined. The vehicles were tested on a chassis dynamometer in the FTP driving cycle. The gasoline–ethanol blends E10, E15, and E20 plus the gasoline–isobutanol blends Bu16, Bu24, and Bu32 (containing 16, 24, and 32 vol.% isobutanol, respectively) were tested, along with a dual-alcohol blend containing 10 vol.% ethanol and 8 vol.% isobutanol. The authors found that the high-level isobutanol blends produced lower levels of total hydrocarbons (THC), NMHC, as well as some reductions in CO_2, when compared to the Bu16 blend. No clear trends were observed among the fuel blends regarding CO and NOx emissions. The emissions of formaldehyde and acetaldehyde exhibited both increases and decreases with the higher-butanol blends, in comparison to Bu16. In addition, the isobutanol blends increased the emissions of butyraldehyde. The particle mass emissions decreased as the fuel oxygen content increased. The total particle number concentrations decreased with high isobutanol contents, compared to the Bu16 blend. Finally, the BC emissions decreased significantly with Bu16 (relative to E10) for one of the vehicles, whereas for the other, the differences were negligible, suggesting that the results were engine-specific and technology-dependent.

Karavalakis et al. conducted an investigation in which gasoline–ethanol and gasoline–isobutanol blends were tested on two FFV pickup trucks on a chassis dynamometer in the FTP and UC driving cycles [81]. Both vehicles were equipped with PFI engines. The following four fuels were used throughout the experiments: the baseline E10, plus two gasoline–ethanol blends at higher concentrations, E51 and E83, and, finally, a gasoline blend containing 55 vol.% isobutanol (Bu55). According to the results, the emissions of butyraldehyde increased with the isobutanol blend. Further, the emissions of NMHC and carbon monoxide decreased with increasing alcohol content, whereas neither THC nor NOx exhibited strong fuel influences. The PM mass, number, and soot mass emissions were strongly reduced with increasing alcohol content in the gasoline. The particle size distributions showed that the number concentration of accumulation mode particles tended to decrease with increasing alcohol content and, in most cases, the increased alcohol content shifted the size of the particles toward smaller sizes.

A 2015 article by Karavalakis et al. [82] describes experiments performed on two passenger cars equipped with DI engines, one with a wall-guided and the other with a spray-guided configuration, running on different gasoline–ethanol and gasoline–isobutanol blends. Both vehicles were tested on a chassis dynamometer in the FTP and UC driving cycles. The test fuels included E10 as a reference, plus E15 and E20. In addition, the gasoline–isobutanol blends Bu16, Bu24, and Bu32 (containing 16, 24, and 32 vol.% isobutanol, respectively) were investigated. Besides the measurement of regulated and unregulated gaseous emissions, PM measurements were made, including particle mass, PN, and the real-time measurements of particle size distributions and soot mass emissions. The results showed that formaldehyde and acetaldehyde were the main carbonyls, with butyraldehyde being significant with the isobutanol blends, compared to ethanol. Both the ethanol and isobutanol blends gave reductions in PM mass, PN, and soot emissions. Finally, the blends with higher alcohol contents exhibited smaller accumulation mode particles than the baseline E10 fuel.

An investigation of the PM emissions from vehicles fueled by gasoline–isobutanol and gasoline–ethanol blends was carried out by Chan and published in 2015 [83]. One of the vehicles in that study was equipped with a PFI engine, whereas the other one had a wall-guided DI engine. Both vehicles were tested on a chassis dynamometer in the FTP-75 and US06 driving cycles, and their exhaust gases were sampled using a constant-volume sampling (CVS) dilution tunnel. The diluted gases were then analyzed using a number of instruments to measure particle size distributions, solid particle number concentrations, and black carbon (BC) emissions. Besides neat gasoline (E0), a blend containing 10 vol.% ethanol (E10) and another containing 16 vol.% isobutanol (iB16) were prepared and tested.

The results showed that the iB16 blend consistently produced increased solid PN and BC mass during phase 1 of the FTP-75 cycle. However, for the DI vehicle, that blend appeared to be more effective in reducing those emissions, compared to the E10 blend. In contrast, for the PFI vehicle, during the FTP-75 cycle, the iB16 blend caused an increase in BC emissions. On the other hand, during the US06 cycle, the BC emissions seemed to have decreased with the isobutanol blend, but the results were not statistically significant.

The impact of gasoline–isobutanol and gasoline–ethanol blends on the particulate emissions during vehicle start–stop operation was investigated by Storey et al. [84]. Their goal was to compare the emissions of the PM mass, transient PN, and size distributions, along with the soot mass during engine operation with and without the start–stop functionality. The tests were conducted on a passenger car equipped with a naturally aspirated DI engine on a chassis dynamometer. The vehicle was run in different phases of the FTP driving cycle, including both cold- and hot-starts. In addition to the baseline E0 gasoline, with an AKI of 87, a blend of 21 vol.% ethanol in gasoline (E21) and a blend containing 12 vol.% isobutanol (iBu12) were tested. The results showed that both E0 and iBu12 produced increased PM mass emissions with start–stop, whereas the E21 blend showed no difference. In particular, the iBu12 blend produced higher levels of PM mass, soot mass, and PN emissions with the start–stop mode, compared to the case without it.

As in the case of engine tests, the influences of isobutanol fuel on the engine performance and emissions, evaluated through vehicle tests, can hard to predict as they can be strongly dependent on the engine and vehicle technology, emission standards, and driving cycle. Nevertheless, as in the case of the engine tests described above, the presence of isobutanol in the fuel can potentially decrease engine-out emissions, though it will probably increase aldehyde formation.

5.3. The Use of Neat Isobutanol in SI Engines

As previously mentioned, isobutanol exhibits properties that enable it to be used even in neat form, although there are comparatively much fewer examples of such applications in the literature, as most studies have been dedicated to its use as a gasoline blendstock. However, a few studies are described below.

In a 2009 study by Irimescu [85], an analysis based on the first law of thermodynamics was conducted on a passenger car equipped with a PFI SI engine running on a chassis dynamometer, a similar setup as in a previous study [75]. The following three different fuels were used: neat fossil gasoline, neat isobutanol, plus a blend of 50 vol.% isobutanol mixed with gasoline. The vehicle engine's ECU was modified to increase the fuel injection times to compensate for the lower heating value of the isobutanol. According to the results, the engine's full-load performance was maintained with isobutanol and with the 50 vol.% isobutanol blend. Moreover, at full-load, the fuel conversion efficiency increased by up to 6% with the 50 vol.% blend but decreased by 9% with the neat isobutanol. At part-loads, the fuel conversion efficiency decreased by up to 3%, with the 50 vol.% blend and by up to 11% with the neat isobutanol. The author attributed the drop in the efficiencies to incomplete fuel evaporation caused by the presence of the isobutanol. Because of that, the author recommended that an engine running on neat isobutanol should have its air–fuel mixture heating redesigned to ensure complete evaporation of the fuel.

In their 2014 study, Pechout et al. [86] described an experiment in which an unmodified PFI SI engine, fitted with a three-way catalyst, was operated on neat isobutanol, 1-butanol, and their blends in gasoline under a number of steady-state engine conditions. The engine was controlled by an ECU featuring a closed-loop feedback to adjust the injected fuel amount to keep the air/fuel ratio constant. In addition to the neat fuels, gasoline–alcohol blends were prepared with either isobutanol or 1-butanol in concentrations of 30, 50, and 85 vol.% mixed with a gasoline having a RON of 95. The test matrix comprised 13 steady-state engine operating conditions. The emissions of the regulated pollutants were measured both upstream (i.e., engine-out) and downstream (i.e., tailpipe) of the three-way catalyst. The results showed that the neat alcohol and its blends could be used without significant adverse effects on the maximum engine torque, air/fuel ratio, exhaust-gas temperature, heat release rates, as well as the emissions of regulated gaseous pollutants, both upstream and downstream of the three-way catalyst. However, the alcohol blends exceeding 30 vol.%, together with the neat alcohols, resulted in worse cold-engine startability. Moreover, the differences in heat release rates were largely negligible, except in the case of the 85% butanol blends, where a small retardation in the combustion phasing was detected.

A 2015 article by Sileghem et al. [87] describes experiments conducted on a DISI passenger car engine running on neat isobutanol, as well as on neat methanol and ethanol, with the goal of evaluating the effects of the alcohol fuels on the engine performance and engine-out emissions (NOx, CO, HC, and PM). The engine was run under a number of steady-state engine operating conditions, and pure gasoline was used as the reference fuel. Their results showed that the engine's BTE was significantly improved with the alcohol fuels, when compared to gasoline. Moreover, all the alcohols, including isobutanol, produced lower gaseous and soot emissions when compared to the neat gasoline.

The use of isobutanol and 1-butanol in neat form, as well as in 30 and 60 vol.% blends with gasoline, was investigated by Pechout et al. [88] on a small PFI spark ignition engine with fully adjustable fuel injection and spark timing. Their goal was to evaluate the influence of the spark timing and fuel injection strategy on the combustion behavior with the different butanol fuels. According to the authors, the engine was able to operate on all the tested fuels without any problems. They recommended that compared to operation on pure gasoline, the spark timing should be retarded when running the engine on the neat butanol isomers at low loads. At mid to high loads, however, adjusting the spark timing was found to be unnecessary. The exhaust gas temperatures decreased with the higher-butanol blends and with the neat isomers. The authors found that this effect was more pronounced with 1-butanol than with isobutanol. Additionally, the three-way catalyst exhibited high efficiency throughout the tests. Overall, their study confirmed the feasibility of the operation of a spark ignition engine with neat isobutanol and 1-butanol and with their blends with gasoline.

As the examples above show, the extent to which an engine will satisfactorily perform with neat isobutanol depends primarily on how its ECU can adapt to the alcohol, because isobutanol's stoichiometric AFR and heating value are markedly different from those of gasoline. One important characteristic to consider is the potential for cold-start problems when using neat isobutanol, owing to its lower volatility. However, with proper engine optimization, this problem can be overcome, and an engine should be able to perform well running on neat isobutanol.

6. Use of Isobutanol in CI Engines

Because isobutanol exhibits properties (such as a high octane rating) that make it a good fuel for SI engines, most studies found in the literature are devoted to its use in SI applications. Nevertheless, isobutanol can also be used in diesel engines, typically in blends with diesel fuel, and numerous studies devoted to the topic have been published, a few of which, based on the relevance of their contents, are presented and discussed in the following sections. In addition, the utilization of isobutanol in low-temperature combustion (LTC) applications is exemplified.

6.1. Performance of Diesel–Isobutanol Blends

The subject of the performance of diesel–isobutanol blends has been widely investigated. For example, a study by Al-Hasan and Al-Momany [89], published in 2008, described experiments with diesel–isobutanol blends on a single-cylinder, naturally aspirated, 1.4 L diesel engine. The tested blends contained 10, 20, 30, and 40 vol.% isobutanol. The engine was equipped with an in-line fuel injection pump and was operated at the same rack position (i.e., at constant injection durations) regardless of the fuel type. The authors' goal was to investigate the effects of the isobutanol blends on the air/fuel ratio, exhaust-gas temperature, brake power, BSFC, and BTE. According to the results, the air/fuel ratio, the exhaust-gas temperature, the brake power, and the BTE decreased, whereas the BSFC increased with the isobutanol blends, when compared to the neat diesel fuel.

A small naturally aspirated, single-cylinder diesel engine was also used by Karabektas and Hosoz [90], in their 2009 study, in which they investigated the effects of diesel–isobutanol blends on the engine's performance and emissions under full-load conditions (for the same maximum fuel-injection durations) in the velocity range 1200–2800 rpm, at 200 rpm intervals. The fuel tested blends included diesel–isobutanol blends containing 5, 10, 15, and 20 vol.% alcohol. According to their results, with increasing isobutanol content, the brake power decreased, whereas the BSFC increased, as expected. Moreover, the blend containing 10 vol.% isobutanol gave a slightly higher BTE at higher engine velocities. The authors attributed this result to the higher in-cylinder temperatures observed at high velocities, which improved the fuel vaporization and mixing with air, resulting in shorter ignition delay times. In addition, the emissions of carbon monoxide and nitrogen oxides decreased with the isobutanol blends, whereas the hydrocarbon emissions increased considerably.

Significant reductions in the emissions of CO and NOx, along with a slight increase in HC concentrations and a decrease in the exhaust-smoke opacity, were also reported in a 2011 study by Ozsezen et al. [91]. In this study, the authors tested diesel–isobutanol blends in a turbocharged, 6 L, six-cylinder, DI diesel engine running at a constant velocity of 1400 rpm and at load levels of 150, 300, and 450 N·m (corresponding to 3.17, 6.34, and 9.51 bar brake mean effective pressure [BMEP], respectively). The tested fuel blends contained 5, 10, and 15 vol.% isobutanol mixed with neat diesel. The results also showed that the BTE decreased, whereas the BSFC increased proportionally to the isobutanol content in the fuel blend. In addition, the rate of heat release and the peak in-cylinder pressure slightly increased with the isobutanol blends. The authors concluded that the tested diesel–isobutanol blends could still be used in unmodified engines.

A study by Pal et al. [92], published in 2013, describes experiments in which a blend of 10 vol.% isobutanol in diesel fuel was used on a single-cylinder DI diesel engine. The results showed that the diesel–isobutanol blend, when compared to neat diesel, achieved a higher BTE, which the authors attributed to enhanced combustion caused by the higher oxygen content of the fuel blend. In line with the results from the articles discussed above, the emissions of nitrogen oxides and carbon monoxide and the smoke opacity decreased with the diesel–isobutanol blend, whereas the emissions of unburned hydrocarbons were higher than those with the neat diesel fuel.

A comparison of 1-butanol and isobutanol blending agents with diesel was carried out by Gu et al. [93]. In their study, the authors evaluated the effects of using either butanol isomer blended with diesel on the performance and emissions of a light-duty diesel engine. The fuel blends contained 15 and 30 vol.% of either isomer mixed with fossil diesel fuel. The tests were conducted at light and medium loads at a fixed engine velocity. The authors used different EGR (exhaust-gas recirculation) levels and fuel-injection timings to study the effect of the isomers' different molecular structures on the soot emissions from the engine. According to the results, the diesel–isobutanol blend exhibited a longer ignition delay than the diesel–1-butanol blend. That explains why the diesel–isobutanol blend produced higher peak cylinder pressures and higher premixed heat release rates, when compared to the diesel–1-butanol blend. It was also found that the addition of either butanol isomer to the base diesel fuel substantially decreased the soot emissions, with varying changes in the NOx emissions. The use of low EGR levels and later fuel injection timings were effective in reducing the emissions of NOx. Finally, the results also showed that the soot emissions with the 1-butanol blend were lower than with the isobutanol blend.

For CI engines, isobutanol, being an oxygenated compound, can significantly decrease engine-out soot (smoke) emissions, when mixed with diesel fuel, with the extent of the reduction being roughly proportional to the amount of alcohol in the blend. However, if the isobutanol concentration is large enough, the ignition delay can become excessive, leading to high rates of cylinder pressure rise, which can cause unacceptable harshness.

The detrimental effect on the autoignition properties of the fuel can also increase engine-out hydrocarbon emissions.

6.2. Comparison with Other Alcohols

A number of articles have been published comparing the performances of diesel–isobutanol blends and diesel fuel blends with other alcohols. As an example, the aforementioned Review article by Kumar et al. [17] describes the utilization of several diesel–alcohol blends as fuels for diesel engines. The alcohols included in that Review are methanol, ethanol, 1-butanol, and isobutanol. The authors concluded that when compared to the shorter-chain alcohols methanol and ethanol, butanol is a better alternative to make diesel–alcohol blends, owing to its higher cetane rating, higher energy content, lower corrosiveness, and better miscibility with diesel fuel.

Several different longer-chain alcohols, including isobutanol, were blended with diesel fuel and were tested on a small naturally aspirated, DI, single-cylinder diesel engine, as described in a study by Rajesh Kumar et al. [94], published in 2016. In their investigation, isobutanol, 1-pentanol, 1-hexanol, and 1-octanol were each blended with fossil diesel fuel at a fixed fraction of 30 vol.% and during the tests, the engine was operated at a constant velocity of 1500 rpm, at different loads. According to the results, the diesel–isobutanol blend (ISB30), in particular, exhibited the longest ignition delay and, consequently, it also had the highest peak of in-cylinder pressure and heat release rate, when compared to the other diesel–alcohol blends. The burning rate of the ISB30 blend was also the highest among all the blends, owing to its high premixed heat release, which, in turn, was caused by ISB30 having the longest ignition delay. Similarly, the overall combustion duration of ISB30 was the shortest when compared to the other alcohol blends, which is also a consequence of its high premixed burning rate. Regarding the exhaust emissions, the diesel–isobutanol blend produced the lowest smoke opacity, the lowest CO emissions, but the highest HC emissions among all the diesel–alcohol blends. Interestingly, despite its longer ignition delay, the diesel–isobutanol blend produced the lowest NOx emissions. The authors ascribed this behavior to a leaner engine operation, combined with isobutanol's lower heating value and higher latent heat of vaporization, which caused a cooling effect that resulted in lower NOx formation.

In a recent study by Konjević et al. [103], the properties of blends of diesel with several alcohols were investigated. In the study, the blending alcohols were 1-propanol, 1-butanol, isobutanol, 1-pentanol, 1-hexanol, 1-octanol, and 1-dodecanol. These alcohols were mixed with fossil diesel fuel in ratios of 5, 10, 20, and 30 vol.%. All the blends were evaluated against the EN 590 standard [95] for diesel fuels regarding their density, viscosity, flash point, distillation properties, cold filter plugging point (CFPP), pour point (PP), and lubricity. Except for the 10 vol.% blend of 1-propanol, all the 5 and 10 vol.% blends met the requirements of the EN 590 standard for density, viscosity, distillation properties, CFPP, PP, and lubricity. Among the results, the diesel–isobutanol blends did not exhibit any phase separation. In addition, the isobutanol blends with diesel only caused a small effect on the fuel lubricity, even at the 30 vol.% blending ratio. Furthermore, no blends, including the diesel–isobutanol blend, had a significant effect on the cold-flow properties (CFPP and PP).

The use of isobutanol in dual-fuel engines was described in a recent article by Krishnan and Rajkumar [96]. In their work, isobutanol was introduced to the intake manifold in amounts corresponding to 10, 20, and 30% premixed energy ratios, while directly injecting fossil diesel, B20, or B100 (neat biodiesel). Their results showed that, in general, the use of isobutanol in the dual fuel mode resulted in reductions in CO, NOx, and smoke emissions, while the brake thermal efficiency increased by up to 5.27% under some operating conditions. The authors concluded that the dual fuel combustion of isobutanol using B20 gave the best results in terms of performance, NOx and smoke emissions, and exergy efficiency.

6.3. Ternary Fuel Blends

Blends of diesel fuel with isobutanol and a third component have also been investigated. In a 2016 article, Yang et al. [97] described an investigation in which ternary blends of fossil diesel, isobutanol, and biodiesel derived from waste cooking oil were used as fuels and tested in an unmodified small, single-cylinder, DI genset. The five tested blends were a binary blend of 10 vol.% isobutanol in 90 vol.% diesel and four ternary blends with biodiesel contents of 10, 20, 30, and 40 vol.% mixed with a constant amount (10 vol.%) of isobutanol and fossil diesel in concentrations of 80, 70, 60, and 50 vol.%, respectively. Their results showed that the diesel–isobutanol–biodiesel ternary blends significantly decreased the PM and nitrogen oxide emissions. When compared to neat fossil diesel, the ternary blends caused a decrease in PM emissions of up to 53.1% and decreased NOx emissions by an average of 32.5%. Formaldehyde, acetaldehyde, and acrolein represented up to 83.2% of the carbonyl emissions when burning the ternary blends. With increasing fractions of biodiesel, the ternary blends decreased the emissions of formaldehyde and acetaldehyde, on average, by 14.4 and 54.5%, respectively. The authors concluded that ternary blends comprising fossil diesel, isobutanol, and biodiesel have the potential to be used as an alternative fuel in diesel engines, resulting in decreased exhaust emissions.

The use of diesel–biodiesel–isobutanol ternary blends was also investigated by Altinkurt et al., as reported in a 2022 article [104]. In their study, three ternary blends, containing 20 wt.% biodiesel and increasing isobutanol contents (15, 25, and 35 wt.%) mixed in diesel, were evaluated in a four-cylinder, light-duty, turbocharged, DI diesel engine. In addition, two binary fuel blends, one consisting of 20 wt.% biodiesel (fatty-acid methyl ester—FAME) in diesel and the other containing 15 wt.% isobutanol in diesel, were tested. All the blends were tested at two engine velocities and four different engine loads. The results showed that increasing the isobutanol content in the blends caused an increasingly longer ignition delay and a decreased combustion duration. Increasing the isobutanol fraction also increased BSFC, decreased the hydrocarbon and carbon-monoxide emissions, but increased the NOx emissions.

6.4. LTC Studies

Low-temperature combustion (LTC) is a term representing advanced combustion concepts for internal combustion engines that have been investigated extensively over the years [98]. LTC technologies have the potential to achieve simultaneous reductions in both NOx and PM emissions, while maintaining high engine thermal efficiencies. Currently, the so-called "Homogeneous Charge Compression Ignition" (HCCI) and "Reactivity-Controlled Compression Ignition" (RCCI) are the most common LTC concepts. Isobutanol has been investigated as a fuel for both, and a few studies on its use in LTC applications are described below.

In their 2015 study, DelVescovo et al. [99] investigated the use of isobutanol on an engine running in the RCCI combustion mode, a dual-fuel mode in which a low-reactivity fuel is port-injected, while multiple direct injections of a high reactivity fuel provide the required equivalence ratio and reactivity stratification in the cylinder, controlling the combustion phasing and achieving very low NOx and PM emissions. In the experiments, the following three fuel combinations were used: EEE gasoline (a U.S. EPA-certified gasoline)–diesel, isobutanol/diesel, and isobutanol–isobutanol + di-*tert* butyl peroxide (DTBP—a high-reactivity compound). The engine was operated under typical LTC conditions, at a range of boost pressures, equivalence ratios, and combustion phasings. It was found that owing to isobutanol's high octane rating and higher heat of vaporization (i.e., low reactivity), a high percentage of directly-injected DTBP was needed to increase the reactivity of the charge. Even with a DTBP fraction of 20 vol.%, the iBuOH/iBuOH + DTBP cases still required high amounts of directly injected fuel, about 60–70%, compared to 25–40% for iBuOH/Diesel and only 5–20% for EEE/Diesel. As a consequence, the NOx emissions increased, while the gross thermal efficiency decreased.

Mack et al. [100] investigated both isobutanol and 1-butanol as fuels for HCCI engines, over a wide range of intake pressures and equivalence ratios. Isobutanol and 1-butanol were compared to ethanol and gasoline as reference fuels. According to the results, both isomers required lower intake temperatures for a fixed combustion phasing, indicating high HCCI reactivity. 1-Butanol exhibited a slightly more stable engine operation and a higher rate of heat release, whereas isobutanol demonstrated higher knock resistance. The exhaust emissions were in the same range for all the fuels. Their results indicated that the butanols were suitable for use in HCCI engines, either in neat form or in blends with gasoline.

In a study by Rajesh Kumar and Saravanan [101], the authors operated a single-cylinder, naturally aspirated, DI diesel engine in LTC mode, using a combination of EGR, late fuel injection timings, and diesel fuel reformulation using blends with isobutanol and 1-pentanol, both mixed at 40 vol.%. Three EGR rates (10, 20, and 30%) and two fuel-injection timings (23 and 21 CAD BTDC) were used throughout the tests, which were conducted at a constant velocity of 1500 rpm and at a constant load of 5.3 bar BMEP. The results showed that when compared to the 1-pentanol blend, the isobutanol blend exhibited a longer ignition delay, lower NOx emissions, and higher smoke-suppression capabilities. The diesel–isobutanol blend also showed an improved effect on the smoke-NOx tradeoff and achieved higher reductions in both pollutants. Moreover, it demonstrated a higher EGR tolerance than the 1-pentanol blend. Finally, the isobutanol blend provided an overall improved performance and a better BSFC than the 1-pentanol blend.

Isobutanol and 1-butanol were the subjects of a numerical investigation of HCCI combustion carried out by Shahsavan and Mack [105], using four different chemical kinetic mechanisms in a single-zone engine model and comparing the results to experimental data. (Two of which, by Grana [34] and Sarathy [37], were discussed above.) A wide range of intake pressures and equivalence ratios were covered by both the simulations and the experiments. The numerical model was able to qualitatively distinguish the ignition behavior between the two butanol isomers. However, the overall results indicated that the existing kinetic mechanisms for 1-butanol and isobutanol do not accurately capture the low-temperature combustion behavior of HCCI engines.

7. Conclusions

This Review provides an overview of recent relevant studies on the use of isobutanol as a transportation fuel. As a result of worldwide increases in the production of renewable fuels, the use of ethanol, as the foremost biofuel, is expected to rise. However, other types of fuels have also been extensively investigated as potential alternatives to ethanol, and isobutanol is among them. Isobutanol possesses some valuable advantages over ethanol, such as being less hygroscopic and having a higher heating value, that make isobutanol more similar to and compatible with gasoline. Accordingly, numerous investigations have been devoted to isobutanol's use as an SI fuel, either through engine tests or through vehicle tests on chassis dynamometers, using engines equipped with either port fuel injection or direct injection. The present work provides relevant examples from the literature of such studies.

Even though the impact of adding isobutanol to gasoline, as an oxygenate, can be largely dependent on the engine technology and test conditions, some generalizations can be made. Regarding the engine performance, the lower heating value of isobutanol can decrease the power output of an engine and increase its fuel consumption, particularly if the engine has not been optimized for operation with gasoline–isobutanol blends. When it comes to emissions, the fuel-bound oxygen of isobutanol can help to reduce the engine-out emissions of CO and PM, especially in the case of DI engines. In addition, the presence of an alcohol in the fuel can decrease peak combustion temperatures, lowering the NOx emissions. Finally, as discussed above, isobutanol, being an alcohol, may lead to an increase in aldehyde emissions.

Although the literature contains a considerable number of isobutanol-related articles, most of them are clearly dedicated to isobutanol's use in fuel blends, whether mixed with gasoline or diesel fuel. There do not seem to be many studies on the use of neat isobutanol as a fuel for SI engines, despite its advantageous characteristics, which suggests the existence of a knowledge gap in the literature. Even though the use of isobutanol in fuel blends would probably be the more realistic scenario, investigations using isobutanol in neat form could complement the already existing studies dedicated to its combustion, which, for instance, could help understand in more detail the pollutant formation mechanisms with that fuel, as well as with other higher alcohols.

Although the number of studies dedicated to the application of isobutanol in CI engines is comparatively much smaller, owing to isobutanol's unfavorable properties, such as its low cetane number, this Review also includes a few of them, illustrating the performance of diesel–isobutanol blends as fuels for diesel engines. Because of the predominantly diffusion-controlled diesel combustion process, the fuel-bound oxygen of isobutanol has the potential to sharply decrease engine-out soot emissions. Lastly, when isobutanol is produced from renewable sources, it can displace fossil fuel usage, even when used in low-concentration fuel blends. And because it has a lower oxygen content than ethanol (21.6 vs. 34.8 wt.%), a larger amount of biomass-based isobutanol must be used to achieve the same oxygen amount in the fuel blend, therefore displacing even larger quantities of fossil fuels. (As discussed above, a blend containing 16 vol.% isobutanol has roughly the same oxygen amount as E10).

In summary, isobutanol has the potential to be used as a fuel for SI engines, primarily in SI engines, in blends with gasoline or in neat form, but also in diesel engines. As the technologies for its production from renewable sources become more established and affordable, isobutanol can, with little doubt, have a place among future carbon-neutral fuels for transportation.

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