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Review

Review on the Use of Diesel–Biodiesel–Alcohol Blends in Compression Ignition Engines

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Abstract: The use of alternative fuels contributes to the lowering of the carbon footprint of the internal combustion engine. Biofuels are the most important kinds of alternative fuels. Currently, thanks to the new manufacturing processes of biofuels, there is potential to decrease greenhouse gas (GHG) emissions, compared to fossil fuels, on a well-to-wheel basis. Amongst the most prominent alternative fuels to be used in mixtures/blends with fossil fuels in internal combustion (IC) engines are biodiesel, bioethanol, and biomethanol. With this perspective, considerable attention has been given to biodiesel and petroleum diesel fuel blends in compression ignition (CI) engines. Many studies have been conducted to assess the impacts of biodiesel use on engine operation. The addition of alcohols such as methanol and ethanol is also practised in biodiesel–diesel blends, due to their miscibility with the pure biodiesel. Alcohols improve the physico-chemical properties of biodiesel–diesel blends, which lead to improved CI engine operation. This review paper discusses some results of recent studies on biodiesel, bioethanol, and biomethanol production, their physicochemical properties, and also, on the influence of the use of diesel–biodiesel–alcohols blends in CI engines: combustion characteristics, performance, and emissions.

Keywords: compression ignition engine; diesel; biodiesel; ethanol; methanol

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1. Introduction

As argued in [1,2], from the road mobility point of view, today, there are three major problems facing humanity: (1) greenhouse gas (GHG) emissions and global warming; (2) renewable or sustainable sources of energy; and (3) energy security. Consequently, in October 2014, "the European Council endorsed a binding European Union (EU) target of at least 40% domestic reduction in GHG emissions by 2030 compared to 1990". Moreover, "an EU binding target of at least 27% is set for the share of renewable energy consumed in the EU in 2030; and an indicative target at the EU level of at least 27% is set for improving energy efficiency in 2030, compared to projections of future energy consumption based on the current criteria" [3]. Actually, as expressed in March 2018 by the European Commission (EC), the EU ambitious objective is "to achieve climate neutrality by 2050, through a fair transition encompassing all sectors of the economy" [4,5]. These problems generated intense discussions at the international level on the impact of the road mobility at global scale. Transport is responsible for around a quarter of GHG emissions in the EU, according to [5]. About 75% of this CO_2 is produced by road transportation, which is a significantly growing sector worldwide [2,6]. Therefore, decarbonization of transport is a must. Consequently, as it is very well known, today, the automotive industry heavily invests in zero- and ultra-low-emission vehicles (ZEV, ULEV) such as electric vehicles (EV) or plug-in hybrid electric vehicles (PHEV). However, the electrification of road transport will not be the single silver bullet. If this is relatively easy to do in the sector of passenger cars or light-duty vehicles (PC and LDV), it will not be as easy to do this in the sector of heavy-duty vehicles (HDV) such as long-haul trucks and coaches. Until electrification reaches a better cost and performance level and even a better well-to-wheel efficiency, it is our opinion, as well, that the alternative fuels will continue to be important in the future of road transport. In fact, the global demand for transportation fuels will certainly grow continuously at between 1.2% and 1.7% per year, thus, debates on the current state and the future of transportation fuels are still very important [5]. According to the BP Statistical Review of World Energy report from 2018 [7], the average increase in global oil consumption in the year 2017 was 1.8% or 1.7 million barrels per day, which exceeds for the third consecutive year the last 10-year average of 1.2%. At the same time, the global oil production increased by 0.6 million barrels per day, which is below the average growth for the second consecutive year. This is an indication of the fact that fossil fuels resources are depleting; therefore, the researchers are looking for environment friendly renewable fuel sources.

Biofuels are the most important kinds of alternative fuels. Currently, thanks to the new manufacturing processes (described in Section 2) of biofuels, there is an important potential to decrease GHG emissions compared to fossil fuels on a well-to-wheel basis. An early discussion on future options for alternative fuels already took place during the 1980s [1]. The idea was that the most prominent alternative fuels for replacing fossil fuels in internal combustion engines would be biofuels (biodiesel, bioethanol, bio-methanol, etc.). Biofuels that are obtained from vegetable oil resources seem to be a very good substitute for fossil fuels; their production is rather simple; they are cleaner, biodegradable, nontoxic, recyclable, and benzene-free [1,6,8–14].

CO_2 emissions result from the combustion of biofuel in an internal combustion engine (ICE) are compensated by the photosynthesis phenomenon of biomass from which it is obtained. However, in biomass production and biofuel production processes, GHG emissions may be relatively high, due to the use of fossil fuels used for agricultural machinery and transportation. On the other hand, the pollution of the soil with fertilizers, herbicides, and insecticides has to be considered as well. Thus, a life cycle analysis (LCA) of different types of bio-fuels is a necessary tool for choosing strategies in this area (raw materials, land-change techniques, biofuel manufacturing technologies, etc.). Figure 1 shows a simplified LCA scheme.

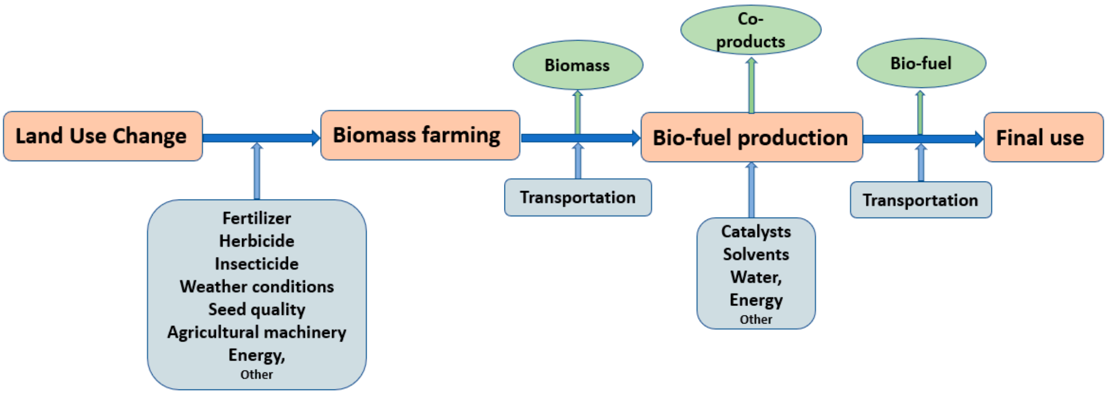


Figure 1. Simplified life cycle analysis (LCA) scheme.

On this particular aspect, in their review article, Caldeira-Pires et al. [15] discuss the developments in the assessment of the environmental and economic impacts of the production of biodiesel and bioethanol from different biomass sources; they present some results of LCA: cost assessment and structural path analysis. Their conclusion was the following: using biofuels in transport is a way to mitigate the GHG emissions. Nonetheless, they claim that a more important effort to improve agricultural management practices is needed, in order to lower the consumption of fuel, fertilizers, and herbicides.

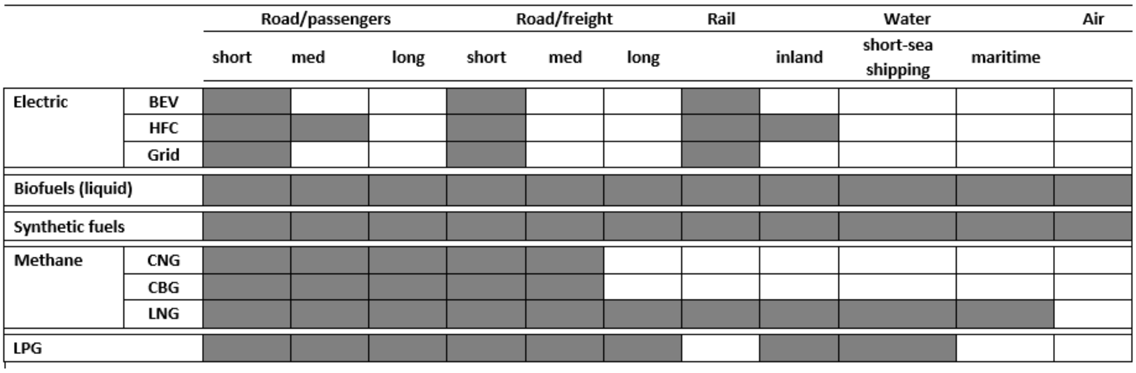
Moreover, O'Connor et al. [16] conducted a study on the production of biodiesels from different raw materials (soy, canola, and tallow), addressing the interaction between LCA and induced land-use change (ILUC). For comparison, fossil diesel was used as a reference. The results for biodiesel obtained from soybeans show the following: (i) GHG emissions: 76% reduction—not taking ILUC into account; 66–72% reduction when different cases of ILUC were considered; (ii) the consumption of fossil fuels in the process of obtaining and distributing soybean biodiesel was 80% lower than in the case of fossil diesel. The authors conclude that ILUC and energy consumption are very important elements when it comes to the production and use of biodiesel.

Paredes-Sánchez et al. [17] present a study on Spain's resources, technology, and bioenergy management. The authors state that the proper use of biomass, especially from forest and agricultural wastes, to obtain energy, can have positive effects, such as: the reduction of fossil fuel consumption; improvement of the quality of the environment, biomass that is CO_2 neutral; its ability to reduce foreign energy dependency; the promotion of socio-economic development and adequate forest management. Also, citing the APPA—2012 (Asociacion de Empresas de Energias Renovables) report, Paredes-Sánchez et al. state that the use of liquid biofuels reduced CO_2 emissions by 4.5 Mt in 2011; the calculations were made according to GHG savings calculation rules associated with the lifecycle of biofuels by Directive 2009/28/EC.

Mohd Alsaleh et al. [18] have analyzed the costs, prices, and technical efficiency in the EU bioenergy industry, taking into account the effects of the internal factors, as well as the external factors of each country. The authors present a comparison between developed and developing countries. Thus, the results show the mean values as follows: the costs or economic efficiency are equal in both cases; the price efficiency is higher in developing countries; the technical efficiency is higher in developed countries. The capital cost was the most significant internal variable, and the most significant macroeconomic variable was gross domestic product (GDP). The results of the study provide the authorities and those involved in the field of bioenergy with the opportunity to develop coherent energy development strategies for EU countries.

Therefore, through a balanced allocation of labor costs and unexpected macroeconomic changes, real interest rates, and inflation rates, the cost effectiveness of the bioenergy industry can be significantly increased. So, Alsaleh et al. [18] have concluded that technology developments and economic efficiency are important ways of developing the bioenergy sector in Europe.

From a technical standpoint, the challenge resulting from the will to replace fossil fuels with biofuels in all transport modes, while still using the current powertrain technologies and fueling infrastructures, is manageable. Regarding this aspect, the European Expert Group from the European Commission, in their Report on Future Transport Fuels (2011), summarized the coverage of different transport modes by different alternative fuels, as in Figure 2.



		Road/passengers			Road/freight			Rail	Water			Air
		short	med	long	short	med	long		inland	short-sea shipping	maritime	
Electric	BEV	▨			▨			▨				
	HFC	▨	▨		▨			▨	▨			
	Grid	▨			▨			▨				
Biofuels (liquid)		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Synthetic fuels		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Methane	CNG	▨	▨	▨	▨	▨						
	CBG	▨	▨	▨	▨	▨						
	LNG	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
LPG		▨	▨	▨	▨	▨	▨		▨	▨		

Figure 2. Coverage of different transport modes by different alternative fuels [19]. BEV—battery electric vehicle; HFC—hydrogen fuel cell; CNG—compressed natural gas; CBG—compressed biogas; LNG—liquefied natural gas; LPG—liquefied petroleum gas.

As it is well-known, the term "biodiesel" designates a variety of ester-based oxygenated fuels obtained from renewable biological sources. It is used in compression ignition (CI) engines. Biodiesel has better properties than petroleum diesel fuel: it is non-flammable (see the flash point values provided in Table 3), virtually non-toxic, it has an excellent lubricity (this characteristic is not regulated for biodiesel but, for example, Yaşar et al. [20], using the ASTM D 6079 standard method for evaluating the lubricity of diesel fuels, determined for petroleum diesel fuel a lubricity of 380 µm, while for biodiesel obtained from sunflower, the lubricity was 193.5 µm), it is renewable, biodegradable (for example, Demirbas in his work [21] determined that after 30 days, biodiesel degrades to a proportion of 80.4–91.2%, compared to fossil diesel fuel, which degraded at only a level of 24.5%), and it is free of sulfur and aromatics; it also has a better combustion efficiency due to its high oxygen fraction, and it can produce lower emissions and less visible smoke if compared to petroleum diesel. Because of its miscibility with petroleum diesel fuel, it can be used either as a pure fuel, or in mixtures or blends. Its use does not require considerable modifications in the engine, when small amounts are used. Most probably, as discussed in [9,13,22,23], biodiesel blends will consist of no more than 20 per cent of the biofuel in petroleum diesel fuel, because higher ratios of biodiesel require technical modifications in the fueling system of the engine (see Section 4).

Because biodiesel is almost completely free of sulfur and aromatics, and since O_2 (oxygen) is in a higher concentration than in petroleum diesel fuel, the resulting SO_2 (sulfur dioxide), soot, CO (carbon monoxide), and UHC (unburned hydrocarbons) are lower [9].

Besides the superiority of biodiesel, there are obviously disadvantages, as compared to diesel: it suffers from cold weather starting problems [22,24], it is corrosive if exposed to brass and copper, it produces deposits in injector, on the piston head, it causes excessive engine wear, and it has higher production costs [23].

Alcohols are characterized by the existence of a hydroxyl group (–OH) that attached to one of the carbon atoms (R–OH). The Use of alcohol for fueling the internal combustion engine (ICE) is not new at all. Ethanol, for instance, was first commercially used as a fuel in 1908, with Henry Ford's Model T, which used corn alcohol (i.e., ethanol, CH_3CH_2OH). These fuels have been used intermittently in ICE since its birth. Ethanol became accepted as an alternative fuel in the 1970s, due to the oil crisis [25]. Bioethanol is amongst the most important bio-fuels produced from biomass. It is seen as a renewable and "green" fuel alternative, due to its physico-chemical properties such as: a high octane number, a high heat of vaporization, and a low vapor pressure [1]. Ethanol as well as methanol has a higher oxygen content compared to fossil fuels; this helps the ICE to achieve a degree of combustion that is closer to being complete; equally, alcohol-fuelled ICE produces less particulate emissions, as shown in [26]. Storch et al. [27] also declared that thanks to the high oxygen-to-carbon ratio, ethanol is an alternative fuel that is worthy of consideration for the reduction of soot emissions.

Studying the effect of the physicochemical properties of ethanol–gasoline blends on a spark ignition (SI) engine's tailpipe emissions, Piotr Bielaczyc et al. [28] said that ethanol is the most common bio-fuel worldwide, having the potential to lower the GHG with up to 87% over conventional fossil fuels; thus, bioethanol has important potential for making energy consumption in the road mobility sector sustainable.

Nakata et al. [29] have shown the improved effect of using bio-ethanol upon the thermal efficiency of an SI engine, thanks to the its higher Research Octane Number (RON); consequently, they have considered that using alcohols in a lean boosted engine (i.e., a turbocharged engine operating with lean mixture) could be one of the future technologies for road mobility.

Because of its higher RON, ethanol is not only a good SI engine fuel, but it was also experimented in CI engines, as it was reported by Rakopoulos [8].

While anhydrous ethanol is soluble in gasoline, when it is used as an additive in diesel fuel, special care is needed to ensure the solubility of ethanol (which is hygroscopic) in diesel fuel [8,12,26]. Lapuerta et al., in [26] claim that ethanol is unable to be used directly in CI engines. The stability of ethanol–diesel blends is mainly affected by the following three factors: low temperatures, water content, and ethanol content, which favors phase separation. Consequently, the presence of additives is very important. However, as Lapuerta [26] shows, water-free ethanol has good miscibility with petroleum diesel fuel at ambient temperatures.

Other studies [30] claim that methanol would/should be the preferred liquid fuel, as it is 100% renewable. Methanol has the lowest carbon and the highest hydrogen content of any liquid fuel.

Contrary to most of the authors who have defined the sustainability of biofuels in terms of their efficiency of use from biomass, de Castro et al. [31] have concluded that “there are reasonable doubts concerning the use of bio-fuels on a regional and global scale, so that they should not, in principle, be promoted as a renewable energy source, nor is it desirable on such a scale”. Their arguments relate to the following aspects: (i) the real productivity of energy crops (in particular, for ethanol), would be a lot lower than what most of the literature on this subject point out; (ii) the high total territorial impact (the so-called “ecological footprint”) associated with this type of energy production; (iii) the modest nature of the energy balance of bio-fuels (the so-called EROEI—“energy return and other energy related issues”) and their real power density, considering the productivity of the crops used.

In our opinion, the efforts of specialists are already focused on the improvement of the issues addressed by de Castro et al. [31] and this review is an attempt to present some of these concerns, mainly considering the transport issues.

Bentivoglio et al. [32] examined the price transmission patterns between ethanol and related agricultural and energy markets in Brazil and showed linkages between fuel and food prices. The results have shown that sugar and gasoline prices influence ethanol prices. Nevertheless, according to the authors, so far, “studies evaluating the impact of bio-fuel production on food and commodity prices do not provide a clear consensus”.

In opinion of Elnashaie et al. [33], sustainable development is paramount for the development of human society, and it is “cross-disciplinary by its very nature”. Consequently, they have proposed an integrated system approach to sustainability for biofuels and bio-refineries, based on system theory. They defined the energy ratio of a fuel as (Energy of Fuel)/(Energy Consumed to Produce the Fuel), and for bio-ethanol, they found the maximum value compared to other transportation fuels (gasoline, diesel, electricity, natural gas (NG), liquified petroleum gas (LPG)).

In their study [34], Zhang et al. have provided a new approach to studying bioethanol productivity and its environmental impacts from marginal lands, creating a land surface process model (“Environmental Policy Integrated Climate Geographic Information System model”) coupled with a an LCA. They have simulated spatial distribution to produce switchgrass-based bioethanol; equally, they provided results on energy efficiency, and on the environmental impact in its life cycle. In this study, the authors performed a review regarding some results of recent studies on biodiesel, bio-ethanol, and bio-methanol production, and their physico-chemical properties, and also on the influence of diesel–biodiesel–alcohols blends on CI engines: the combustion characteristics, performance, and emissions.

After this first section, which aims to briefly frame the study within the current fuel context, the remainder of the paper comprises three main sections. Section 2 is about biofuel production, with explicit references to biodiesel, bio-ethanol, and bio-methanol. This is followed in Section 3 by a description of the physico-chemical properties of fuels, providing once again explicit figures for the three types of fuels that are taken into discussion in this paper. Then, Section 4 presents a collection of data regarding the effects of the use of diesel–biodiesel–alcohol blends in CI engines. Finally, the conclusions drawn from our review are summarized.

2. Bio-Fuel Production

The raw materials for bio-fuels are divided into three categories, first, second, and third generation. The feedstock used for first-generation bio-fuel production is restricted, because of the need to avoid conflicts with feed crops. Second-generation biofuel production eliminates the shortcomings of the first generation, since it employs non-edible feedstock sourced from agriculture and forestry wastes.

Also, for second-generation bio-fuels, there are more efficient and environmentally friendly new production technologies. Nevertheless, Eggert et al. [35] has said that "it is by no means certain that second-generation bio-fuels will play a central role in the decarbonizing of the transport market". The third generation of bio-fuel feedstocks are usually considered to be algal biomass [36]. However, some authors consider algae as part of the "second-generation" feedstock biofuels [37]. On this particular subject, the scientific community does not seem to have reached an agreement.

Under the Bio-fuels Obligation Scheme in Ireland, Murphy et al. [38] performed a review on the characteristics of algae for biofuel production based on oil yields, cultivation, harvesting, and processing, in terms of the European Union (EU) biofuels sustainability criteria, and concluded that algae is the ideal feedstock for obtaining biofuels. The reasons are related to the high biomass productivity of micro- and macro-algae, along with a favorable biomass composition.

The European Commission developed Directive (EU) 2015/1513, with the aim of limiting the contribution of first-generation bio-fuels in favor of second- and third-generation bio-fuels [32,39].

2.1. Biodiesel Production

The problems that arise when talking about replacing petroleum diesel fuels with biodiesel are those related to high viscosity, low volatility, and the polyunsaturated character of vegetable oils. These can be improved by the use of pyrolysis, microemulsion, dilution, and transesterification techniques.

Pyrolysis is a method that is used to convert one substance into another by heat, with the aid of a catalyst, and without oxygen. The process features no waste, and is pollution free. Compared with other cracking processes, pyrolysis is not a complicated process, and according to [40], it seems to be effective. However, other researchers have criticized this method because of its high energy consumption and low conversion rate [41].

A microemulsion is defined as a "colloidal equilibrium dispersion of optically isotropic fluid microstructures, which form spontaneously from two normally immiscible liquids, and one or more ionic or non-ionic amphiphiles" [40]. According to the same study, it can improve the spray characteristics by explosive vaporization of the low-boiling constituents in micelles. Furthermore, as discussed in [41], on the one hand, it reduces the biodiesel's viscosity, and on the other hand, it has a negative impact on the CI engine operating for a long time, with fuel being obtained through this method (incomplete combustion generating carbon deposits inside the cylinder).

Dilution is defined by Singh in his review [40] as a blend of vegetable oil and petroleum diesel fuel. In this way, the viscosity of the blend is lower than the vegetable oil, and it becomes suitable for running in the engine.

Transesterification is the reaction of a fat or oil with an alcohol, forming esters and glycerol. A catalyst is usually used to improve the reaction rate and yield. Depending on the type of catalyst used in the transesterification reaction, three types of processes are practiced: (i) alkali-catalyzed transesterification using an alkaline catalyst; (ii) acid catalyst transesterification using an acid catalyst; (iii) lipase catalyst transesterification using lipase catalyst [40,41].

From the processes listed above, transesterification is the most commonly used process at an industrial level, due to the following: high conversion rate, relatively low production costs, mild reaction conditions, and the properties of the obtained product being very close to those of fossil diesel [42].

"First generation" biodiesel is produced via the transesterification of triglycerides from vegetable oils derived from rapeseed, soybean, palm, sunflower, coconut, linseed, cottonseed sesame, corn, etc., and animal fats.

These feedstocks have the advantage of having a high level of energy, but have the disadvantage of being in competition with the supply of food for humans and animals.

"Second generation" feedstocks include lignocellulose and non-edible triglycerides (e.g., different vegetable and animal wastes, Jatropha), which are processed via the catalytic hydro-processing of triglycerides, and the thermal conversion (gasification and pyrolysis) of lignocelluloses [37].

These have the advantage of being relatively cheap, and they are found in significant quantities. Their disadvantages are related to their small amounts of fatty acids (FA) content, and the fact that their structure requires more expensive processing technology.

The objectives to be targeted in the biodiesel production process are the low costs and high production capacities. Nowadays, biodiesel research is focused on increasing the conversion and production yields. In this sense, great importance is given, both to the use of new raw materials, and to the development of new technologies. When talking about improving the production technologies, we have in mind the progress of reactors that are used for biodiesel production, and the factors that affect the biodiesel production yield, such as reaction time, agitator rotation speed, temperature, catalyst types, catalyst concentration, the types of solvent, and molar ratio between oil and alcohol. At the beginning of biodiesel production, a batch reactor was generally used. This technology has some disadvantages, such as a large reactor volume and a complicated separation process, which results in high costs. Subsequently, continuous reactors have been used, and also new types of solvents and catalysts. A simplification of the recovery steps is also being done by the use of integrated and in situ separation techniques. As presented by Zahan et al. [42], in comparison with the batch reactor, the continuous reactor offers better performance in improving heat and mass transfer, and reduces the production cost. Thus, a final product of superior quality is obtained.

With regard to the catalysts used in the transesterification process, there are several types: homogeneous catalysts (NaOH, KOH), which have the disadvantages of generating a large amount of wastewater and corroding equipment; heterogenous catalysts (solid acid/base, polymer, zeolites, etc.), which reduce waste generation, but the reaction time is long, and their high viscosity prevents mass transfer; other types of catalysts such as enzymes and ionic liquids are environmental friendly, but expensive and have low stability. Moreover, as indicated by Zahan et al. [42] there are also non-catalytic conditions, i.e., supercritical conditions, meaning that they require high oil/alcohol molar ratio, temperatures, and pressures values; this leads to a low reaction time, but the costs are high.

Xuan et al. [43] have analyzed the catalytically ultrasound-assisted transesterification of non-edible vegetable oils using homogeneous and heterogeneous catalysts for the synthesis of biodiesel. They claimed that in the biodiesel production process, the replacement of mechanical or magnetic mixing by the application of the ultrasonic mixing method can lead to a mass transfer efficiency improvement, and eliminates the need for separate heating and agitation. At the same time, they demonstrated a reduction of the following: alcohol–oil ratio by (16.67–25)%, quantity of catalyst by (20–25)%, reaction time by (25–95.8)%, energy consumption by (33–50)%; equally, an improved conversion and biodiesel yield by (4–27.9)% were reported.

Al-Muhtaseb et al. [44] dealt with the oil extracted from the powder of date palms pits (i.e., the hard seeds growing inside date palms), which was used to synthesize a renewable heterogeneous catalyst named “the green carbon catalyst”, which was subsequently modified by an alkaline earth-metal (CaO) oxide. Consequently, the biodiesel process has been optimized featuring a maximum yield of 98.2%. Thus, it can be concluded that “the green carbon catalyst” synthesized from this waste has a high potential for biodiesel production.

Sulaiman et al. [45] studied the parameters of the biodiesel production process, in which the heterogeneous catalyst was synthesized from fish bones. The maximum yield of biodiesel production was found to be 80.4%, with 10% by weight of the catalyst; therefore, it has been shown that fish waste has a high potential for being used as a catalyst.

Solvents are types of alcohols (ethanol and methanol) that are cheap, but which can cause miscibility problems during the production process. These problems could be mitigated by using other types of solvents (e.g., deep eutectic solvents) but they have higher costs [42].

Kurniati et al. [46] propose an advanced electromagnetic induction technology that provides a fast and easy way to produce biodiesel. This method has the following advantages: it increases the reaction speed, it improves the separation process, it increases production, and it reduces production time and costs compared to conventional or microwave induction methods.

Thus, in conclusion, to improve the biodiesel production process, researchers have considered the following factors: the reactors, the type and concentration of catalyst and solvent, the agitator rotation speed, the reaction time, and the oil/alcohol ratio.

2.2. Bio-Ethanol Production

Alcohol has always been present in the history of human civilization. It began to be viewed as an automotive fuel at the end of the 19th century. Ethanol has two main industrial production pathways: (i) the reaction of ethane with steam, and (ii) alcoholic fermentation and distillation from renewable bio-organic materials; additionally, for second generation bio-ethanol, new production methodologies; namely, pre-treatment and hydrolysis [2,37].

An extensive study on the production of bio-ethanol is presented in a review [36], which also proposes the following improvement solutions through possible interventions: "(i) an integrated energy-pinch of condensers and reboilers in the bio-ethanol distillation train; (ii) the use of Very High Gravity (VHG) fermentation; (iii) the current development of hybrid processes by using pervaporation membranes (or pervaporative separation, a processing method for the separation of mixtures of liquids by partial vaporization through a non-porous or porous membrane) [47]; (iv) the substitution of current ethanol dewatering processes to >99.5 wt % pure ethanol by membrane technology; and (v) additional developments to improve plant operation, such as the use of microfiltration of the fermenter broth to protect heat exchangers, and distillation columns against fouling, or novel distillation concepts".

Thangavelu et al. in their review [48] on bioethanol as alternative fuel, classified the main categories of raw materials used to produce bioethanol: Agriculture residues: wheat straw, rice straw, sweet sorghum bagasse, sugar cane bagasse, rice hulls, rape straw, barley straw, *Miscanthus* (grass), corn stove, hazelnut shell, sugar cane tops, and horticulture waste. Woody biomass: industrial hemp, yellow poplar, and construction and demolition (C&D) wood waste. The authors said that "yellow poplar and C&D wood waste are more suitable for high-yield commercial ethanol production worldwide". Algae biomass: Chlamydomonas reinhardtii, microalgae, red seaweed gracilaria sp., and macroalgae (Eucheuma cottonii) recently began to be recently used for bioethanol production. In summary, the authors state that "Chlamydomonas reinhardtii, microalgae, and red seaweed gracilaria sp. are having high ethanol yields (greater than 20% yield) that are capable for commercial scale bioethanol production; Herbaceous, Industrial and Municipal Solid Waste (MSW): wastes from food and starch processing industries, soft drinks and brewery industries, fruit peel waste, food waste, and waste from herbaceous crops". The same authors also claim that "the energy requirement of the pre-treatment and hydrolysis of MSW is much lower compared to agriculture residues".

Nevertheless, Caldeira-Pires concluded in [15] that the use of straw in cogeneration should also be considered, because it could be used to obtain electricity; however, if doing so, the consequence would be to release large amounts of pollution from the boiler. Moreover, the straw cannot be used any more as an organic fertilizer, which may increase the costs that are associated with fertilizer use. Also, according to the same author, the allocation of bagasse (a fibrous residue resulting from the sugar extraction from cane) for cogeneration, in contrast with its use in the production of second-generation ethanol, must be analyzed, in order to strike a balance between environmental and economic costs.

The feedstock used for first-generation bioethanol production are corn, sugar cane, sorghum, cassava, etc., which are edible crops.

Donke et al. [49] evaluated the environmental and social effects of the integrated production of ethanol from sugar cane, corn, and grain sorghum. They have indicated the great influence of agricultural activities of sugarcane cultivation in Brazil at the social and economic scales; the impacts on climate, human toxicity have also been highlighted.

Bioethanol production from sugarcane represents a good opportunity for urban agricultural development in small communities in Ecuador, as reported by Velazquez-Marti et al. in [50], and in order to decrease costs and to improve ethanol production processes from sugarcane, they have proposed a mathematical model for the evaluation of the dissolved sugar content (using the Brix grade to measure sugar content), in order to estimate the quantity of the alcohol that is produced, as well as its quality

In their study [51], Capecchi et al. investigated the crop factors (soil moisture and harvests time) that influence ethanol production from two representative genotypes of biomass sorghum: sorghum juice (sweet) vs bagasse (fiber sorghum).

Waste biomass, which are generated in sugar factories from the processing of sugar beets, can be used, as raw materials in an Integrated Bioethanol Fermentation/Anaerobic Digestion process, as proposed by Berlowska et al. in [52].

Ferreira et al. [53] showed the potential of five food-grade filamentous fungi, including a Zygomycete and four Ascomycetes strains, for bioethanol production. It may be concluded that the use of these food-grade filamentous fungi results in an increase in the efficiency of the wheat bioethanol production process, by obtaining higher amounts of protein-rich biomass that can be used for animal feed, especially fish, glycerol, and lactic acid (lactic acid and glycerol).

Nuanpeng et al. in [54] conducted a study with regard to ethanol production from sweet sorghum juice (SSJ) at high temperatures, concluding that the thermotolerant yeast strain Saccharomyces cerevisiae DBKKU Y-53 exhibited great potential for this process.

The results of Yu et al. [55] clearly demonstrated the potential for combining a simultaneous saccharification and fermentation process with the thermotolerant yeast Kluyveromyces marxianus for bioethanol production, using carrot pomace as a feedstock, which seems to be a major form of agricultural waste from the juice industry. This production process can be simplified, as the pre-treatment step is eliminated.

In order to produce ethanol from sweet sorghum juice, sweet sorghum stalks were used as a low-cost carrier for immobilization of Saccharomyces cerevisiae NP 01 and the results presented by Ariyajaroenwong et al. [56] show the optimum size of sorghum stalks for the production of repeated-batch ethanol. The use of the immobilization systems can minimize production costs because this system offers more advantages over free cell fermentation operation, i.e., a higher concentration of yeast cells, a higher fermentation rate, easier cell recycling, and a lower product inhibition. Yeast cells immobilized on the $6 \times 6 \times 6$ mm^3 sorghum strain can be reused for at least eight successive lots without reducing the ethanol production efficiency.

Concerning the reduction of the GHG emissions, ethanol has a significant potential: according to Juan P. Hernández et al. [57], "from 21% (in the case of using wheat as feedstock) to 75% (in case of sugar cane ethanol) or even to 87% (in case of wheat straw)".

At the European and global levels, over time, there has been talk about the rising prices of agricultural products, primarily for human and animal feed, with this being this on account of the development of the production and consumption of biofuels produced from the same agricultural materials.

The rapidly growing world population generates an increase in the demand for both food and biofuels which draw attention to food and fuel shortages. Using food crops of any kind in order to produce ethanol raises nutritional and ethical concerns. The objective of Pimentel et al. [58] was to analyze the reliance of food and biofuels on the same land, water, and fossil energy resources in food versus biofuel production; equally, the characteristics of the environmental impact caused by food and bio-fuel production was analyzed. They draw attention to the fact that "many problems associated with bio-fuels have been ignored by scientists and policy makers". They state that the biofuels that are created in order to reduce the dependence on fossil fuels, ironically, depend on fossil fuels; in most cases, more fossil energy would be required to produce a unit of bio-fuel, compared with the energy that is produced. Also, the environmental problems (water pollution, global warming, soil erosion, and air pollution) associated with bio-fuel production seem to be more important. They assert that "there is simply not enough land, water, and energy to produce bio-fuels".

Zhang et al. [59] have conducted a study about "Ethanol, Corn, and Soybean Price Relations in a Volatile Vehicle-Fuels Market". The results obtained are consistent with economic theory, and indicate "that in recent years there are no long-run relations among fuel (ethanol, oil and gasoline) prices and agricultural commodity (corn and soybean) prices". Thus, in the short-run, agricultural commodity prices would increase. An analysis on the effects of ethanol on corn and soybean prices show that, "while ethanol does not appear to influence the long-run equilibrium levels of corn and soybean prices, fuel prices may cause transitory short-run agricultural commodity price inflation".

For second-generation bioethanol production, the feedstocks used are sourced from agriculture and forestry wastes (non-edible). Lignocellulosic and starchy materials are converted to fermentable sugars to be further processed into the end-product, resulting in anhydrous bioethanol. Nevertheless, the cost of the enzymes that are capable of hydrolyzing cellulose is a limiting factor [36]. The existing variants of second-generation bioethanol production methods are: pre-treatment, hydrolysis, fermentation, and distillation [26,36,37].

A very simple schema which describes the process for obtaining bioethanol from lignocellulosic materials is presented in Figure 3.

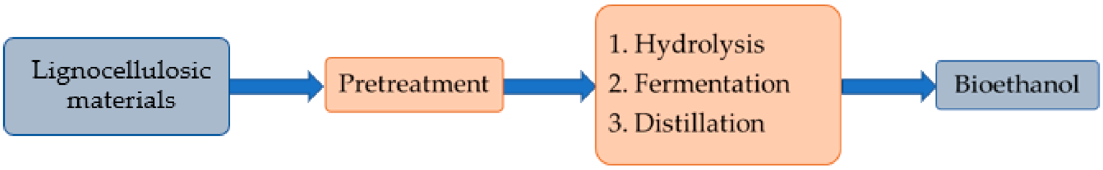


Figure 3. A bioethanol production process based on lignocellulosic materials.

A study of second-generation bioethanol production was presented in the review [2]. A techno-economic analysis of bio-ethanol production from lignocellulosic biomass in China was performed in [10]. The results have led the authors to propose a set of policies to encourage cellulosic ethanol production. The proposed policies are the promotion of research and development in the field of technologies that are involved in the production of liquefied petroleum ethanol, the elimination of consumption tax, and the value added tax (VAT) reimbursements at the time of collection, with surplus electricity that is produced by the ethanol plant to be bought by the network under a certain tariff plan, direct subsidizing for the production of bioethanol.

Utilizing peer-reviewed literature, Zhang et al. [60] have concluded that ethanol production from renewable woody biomass, has seen an increased degree of interest. Based on data that is specific to the U.S., it was shown that using a woody biomass feedstock supply for ethanol production is more environmentally friendly ("about 62% less GHG") compared with the production of petroleum fossil fuels.

In order to sustain bio-ethanol production from lignocellulosic biomasses, alkaline–acid pretreated brewers' spent grain (BSG) after enzymatic hydrolysis with commercial enzymes was evaluated. For fermentation, the strain Saccharomyces cerevisiae NRRL YB 2293 was selected, which was the best producer among five ethanologenic microorganisms [61]. Furfural is recognized as one of the most inhibitory substances in the hydrolysate, and Ylitervo et al. [62] has investigated its effects on the fermentation process.

Due to their higher operating temperatures and broad substrate range, there is an obvious interest in using thermophilic bacteria for bioethanol production from complex lignocellulosic biomass. Scully et al. performed a review focused upon the main genera of thermophilic anaerobes known to produce ethanol; also, recent developments in the techniques used for the production of ethanol were discussed [63].

Taherzadeh et al. have dedicated their work [64] to reviewing the methods for the pretreatment of lignocellulosic wastes for their conversion to ethanol or biogas, starting from the well-known fact that lignocellulosic polymers are resistant to biological degradation. They have presented "milling, irradiation, microwaving, steam explosion, ammonia fiber explosion, supercritical CO_2 and its explosion, alkaline hydrolysis, liquid hot-water pretreatment, organosolv processes, wet oxidation, ozonolysis, dilute- and concentrated-acid hydrolyses, and biological pretreatments".

Cavalaglio et al. [65] have conducted a research project to recover stranded driftwood residues. They developed a process of transformation for these lignocellulosic residues into bio-ethanol.

Kandasamy et al., in [66], have performed an investigation of the potential to produce ethanol from lignocellulosic material, but without enzymatic hydrolysis using the ultrasound technique which shows a higher ethanol production than that usually reported in the literature.

A study which treats "Value Chain Structures that Define European Cellulosic Ethanol Production" is presented in [67]. The authors found that most cellulosic ethanol production plants in the EU are only at the pilot or demonstration scale.

Cotana et al. [68] claim that in the context of a greater level of attention on the production of second-generation bioethanols, the use of lignocellulosic feedstock, Phragmites australis (common reed, which is a perennial grass growing in wetlands or near inland waterways) is particularly a very good choice. In the cited paper, the optimization of the bioethanol production process from Phragmites australis was carried out using steam explosion. The entire process achieved an efficiency of 16.56 g ethanol/100 g raw material.

Eggert et al. [35] have performed a study, in order to promote second-generation bio-fuels, particularly, cellulose-based biochemical ethanol; equally, the authors discusses about policies, which could facilitate the competitiveness of these fuels. They claim that first-generation bio-fuels "have been and are still substantially subsidized, and this has contributed to the increasing production and use of such fuels". The question they are asking is: "does the first generation pave the road for second-generation bio-fuels?" and they have concluded that "even if a favorable environment for innovations and scale economies is created, necessary cost reductions may not be achieved. The GHG emissions from land use change, connected to the large-scale growth of cellulosic feedstock, may turn out to offset the gains from changing fuel".

Switchgrass (a warm-season grass) seems to show very good potential for serving as a non-food bioenergy feedstock for bioethanol production in China; this is due to its high potential yield on marginal lands [34].

Hansdah et al. [69] have discussed the opportunities for obtaining bioethanol from the Madhuca indica flower, which is a forest tree growing abundantly in the tropical regions of Asia and Australia. On the other hand, Madhuca indica seeds are also a potential feedstock for biodiesel production in India.

Chen et al. [70] discusses Landoltia punctata (a widely distributed duckweed strain with the ability to accumulate starch) and its use as a new feedstock for the production of bioethanol. To improve ethanol production, pectinase pretreatment was used to release more glucose and consequently, the highest ethanol concentration reported to date using duckweed as the feedstock was obtained.

Also, the discovery of new raw materials (filamentous fungi), and the improvement of the process of obtaining bio-ethanol by integrating first- and second-generation ethanol production processes is described in [71] which reports a reduction of energy consumption by 2.5%, and an increase of ethanol production by 4%. Connolly et al. [30] have detailed different methods for producing transport fuels, including ethanol and methanol, in terms of the resources, the conversion processes used, and the transport demands met. According to the results of this study, the optimal solution at present consists of liquid fuels; for example, methanol or dimethyl ether. Biomass gasification and electrolysis are technologies that need to be improved.

As introduced before, the third-generation of bio-ethanol feedstocks are algae, which contain lipids, proteins, carbohydrates/polysaccharides, and have thin cellulosic walls. According to [36], while "algal lipids are mostly extracted and transformed into biodiesel, the left-over cake of starch (the storage component) and cellulose (the thin wall component) can be converted into bio-ethanol". Moreover, the resulting combined biodiesel/bio-ethanol process also offers the advantage of producing CO_2 fermentation, which can be captured and used.

Improving on the process of ethanol production is a continuing concern of experts in the field. Lopez et al. [72] have proposed use of a Rh/MCM-41 catalyst for the synthesis of ethanol from syngas.

They studied the effect of water on product selectivity, which was higher in this case, compared to typical Rh/SIO_2 catalyst.

Clostridium ljungdahlii is an anaerobic homoacetogen, which was isolated for its ability to produce ethanol from synthesis gas, mostly a mixture of carbon monoxide and hydrogen [73–75]. Although there are many studies showing that synthetic gas (syngas) fermentation rates can rapidly become limited due to the supply of gaseous substrates, Richter et al. [76] have proposed a continuous syngas fermentation system that is optimized for ethanol productivity, which consists of two stages, both functioning at ambient pressure: (1) an optimal growth stage of Clostridium ljungdahlii while producing mainly acetic acid, and (2) a production stage to achieve the conversion of syngas and of acetic acid (from stage one) into ethanol. Compared to typical average ethanol production rates, syngas fermentation has the potential to succeed them, and the authors are optimistic that further improvements to performance can be made. Also, advanced strategies for distillation to keep the energy balance of the entire process positive are required. Continuous ethanol production from syngas by Clostridium ragsdalei in a trickle-bed reactor was studied by Devarapalli et al. [77]. Their results showed that CO and H_2 conversion efficiencies reached over 90%.

According to [78], integrating fermentation and anaerobic digestion in a biorefinery would allow for the production of ethanol and biogas, which can be used to produce heat and electricity, thus improving the overall energy balance. A. Cesaro et al. in their review [78] present the main studies on the combination of both bioethanol and biogas production processes, aiming to underline the strengths and weaknesses of integrated treatments for industrial applications. The concept of integrated bio-refineries is defined by Elnashaie in [33] as “a complex facility that integrates biomass conversion processes and equipment to produce fuel, power, and chemicals/biochemicals from biomass”.

By resuming, in this section, details on the production of ethanol, both in terms of raw materials and production technologies were given. Particular attention is paid to lignocellulosic biomass, as well as to various food industry residues. Algae, considered to be renewable third-generation resources, seem to be a viable solution for the future of road mobility. Research on the use of different types of fungi in the production process also aim at increasing productivity and lowering the price of the final product.

2.3. Bio-Methanol Production

Methanol is usually obtained from natural gas (NG), coal, coke-oven gas, hydrogen, and biomass. Nevertheless, as indicated by Bae et al. [79], most methanol is produced from syngas, which is composed of CO and H_2.

Wang et al. [80] claimed that methanol is one of the most favorable alternative and renewable fuels for ICE. Its production is derived from the gasification of waste biomass, followed by catalytic synthesis at high pressures. This provides high yields (45–55% in weight), as well as energy efficiency (70–75%). However, as pointed out by the authors, because of its physico-chemical properties (e.g., lower cetane number (CN), higher latent heat of vaporization), it is more difficult to use it as a fuel for the CI engine. The same authors state that through the dual fueling of the CI engine with methanol and diesel, the combustion process has characteristics from both the CI and the SI engines. These combustion characteristics, as well as the resulting emissions, are presented in Section 4.2.

Bioenergy hydrogenation is an important pathway for creating methanol fuel from bioenergy. Thus, the energy potential of the bioenergy resource is maximized by using hydrogen from steam electrolysis. A variety of biomass feedstocks may be used in this process: energy crops, straw, and wood [30]. Below, an example of a chemical reaction for the production of methanol from cellulous biomass, hydrogen and water is shown:

$$\underbrace{C_6(H_2O)_5}_{\text{Biomass (cellulous)}} + \underbrace{6H_2}_{\text{Hydrogen}} + \underbrace{H_2O}_{\text{Water}} \rightarrow \underbrace{6CH_3OH}_{\text{Methanol}}$$

Another pathway for obtaining methanol is CO_2 hydrogenation, using carbon dioxide capture (this would make possible to use carbon-based liquid fuels in cars or aeroplanes without negative impacts on the climate [81]), and recycling or carbon trees [30]. The chemical reactions associated with this pathway are presented as follows:

$$\underbrace{CO_2}_{\text{Carbon dioxide}} + \underbrace{3H_2}_{\text{Hydrogen}} \rightarrow \underbrace{CH_3OH}_{\text{Methanol}} + \underbrace{H_2O}_{\text{Water}}$$

Co-electrolysis is another pathway for obtaining methanol [30]:

$$4\underbrace{H_2O}_{\text{Water}} + 2\underbrace{CO_2}_{\text{Carbon dioxide}} \rightarrow \underbrace{4H_2}_{\text{Hydrogen}} + \underbrace{2CO}_{\substack{\text{Carbon}\\ \text{monoxide}}} + 3\underbrace{O_2}_{\text{Oxygen}} \rightarrow \underbrace{2CH_3OH}_{\text{Methanol}} + \underbrace{3O_2}_{\text{Oxygen}}$$

In conclusion, the hydrogenation of biomass is a good solution for the moment, but in the future, co-electrolysis using captured carbon will be a better option [30].

To conclude on the production of biofuels, as argued in [13], their production is limited by the economy. Nowadays, it is generally accepted that biofuels cannot be obtained at competitive prices, relative to fossil fuels. This could be changed by a favorable taxation system for biofuels, and equally, by subsidizing raw material production. Consequently, it would be important to develop research on the raw materials and production processes, bearing in mind the legislation on pollution, as well as the resulting social implications.

3. Physico-Chemical Properties of CI Engine Fuels

When calibrating an ICE, different ambient conditions are taken into consideration. Consequently, the way in which these influence the fuels is analyzed through their physico-chemical properties. Equally, in order to determine whether blending different combustible substances may be appropriate for their use in ICE, an analysis of the physico-chemical properties of the resulted fuel is needed. As such, below, the main properties of the fuels are introduced in a brief manner.

Viscosity affects the behavior of fuel injection. Since the fuel viscosity increases as the ambient temperature decreases, countermeasures have to be taken into consideration, so to avoid the deterioration of the engine's operation. Thus, when performing a cold start at low ambient temperatures, the resulting higher viscosity of the fuel causes poorer fuel atomization and vaporization, larger droplets, and greater in-cylinder penetration of the fuel spray. As shown in [22], a high viscosity may also reduce fuel flow rates, resulting in inadequate fueling; another aspect reported in the same paper is that a very high viscosity may also result in pump distortion. The final effects may be evident as a bad combustion, higher emissions, and increased oil dilution.

Fuel density is also affected by the temperature: it increases as the temperature decreases; as before, when performing a cold starting at low ambient temperatures, the resulting higher density means that the same injected fuel volume generates a higher mass of the fuel injected, which will affect the air–fuel ratio and the energy content inside the cylinder, as explained in [22].

The cetane number (CN), as is well known, is the main indication of the auto-ignition and combustion quality characteristics of the fuels used in a CI engine. It influences the cold startability of an engine, i.e., as presented by Clenci et al. [22]; in order to decrease the engine's cranking time (the time before the engine reaches "starter off"), a higher CN is needed.

Evaporation characteristics directly influence the spray structure, and have consequences on the air–fuel mixture preparation. The volatility characteristics are described by using the vapor pressure and distillation curves, which are affected by intermolecular interactions [37]. The volatility of the fuel, in other words, the distillation properties, significantly affect fuel spray penetration and mixture formation [82].

Flash point (FP) temperature is the minimum temperature (at 101.3 kPa pressure) at which the fuel ignites (generating a flash) while applying an ignition source. The more volatile a fuel, is the lower the FP [37]. Low FP values are required for proper safety and handling of the fuel.

The operation of CI engines at low ambient temperatures is usually affected by three fuel properties, defined when cooling the liquid fuel:

- The Cloud Point (CP) is the temperature at which solid particles appear in the fuel (microcrystals of ice and crystals of alkanes); consequently, as the name suggests, a clear liquid product becomes cloudy;
- The Cold Filter Plugging Point (CFPP) is the lowest temperature at which a given fuel volume still goes through a standardized filtration device in a specified time;
- Pour Point (PP) is the lowest temperature at which the fuel ceases to flow.

As discussed in [37], in USA and Canada, the Low Temperature Flow Test (LTFT) was developed to predict how fuels will perform at low temperatures.

In conclusion, for a given CI engine, the fuel type must be recommended in concordance with the seasonal and climatic features in the region where the engine is to be operated.

The heating value of a fuel (the lower and higher ones, LHV and HHV) describes its energetic content. Recently, as discussed in [37,83,84], as well, a significant increase in the use of dual-fuel and blended fuels in CI engine and SI engine was recorded. Consequently, it is of paramount importance to develop models and techniques to estimate/measure the LHV & HHV of the used mixtures.

The water content is also important for a given fuel. Obviously, the fuel should be free of water, as water can plug fuel filters at negative ambient temperatures, leading to the blockage of fuel flow towards the engine. Water also increases corrosivity, accelerates oxidation, and promotes microbial growth.

3.1. Biodiesel Physico-Chemical Properties

Biodiesel fuel that is produced through transesterification of triglycerides contains many individual fatty acid methyl ester (FAME) species. So far, the most commonly used alcohol to esterify FA (fatty acids) is the methanol; the resulting product is called FAME. A good knowledge of the composition of biodiesel fuels is necessary, in order to assess the performance of ignition and combustion in diesel engines. A list of the most commonly seen FA in biodiesel is provided in Table 1.

Table 1. Chemical structures of common FA [40].

Name of FA	**Structure (xx:y)** [1]	**Type** [2]	**Formula**
Lauric	12:0	S	$C_{12}H_{24}O_2$
Myristic	14:0	S	$C_{14}H_{28}O_2$
Palmitic	16:0	S	$C_{16}H_{32}O_2$
Stearic	18:0	S	$C_{18}H_{36}O_2$
Oleic cis-9-	18:1	US	$C_{18}H_{34}O_2$
Linoleic cis-9, cis-12-	18:2	US	$C_{18}H_{32}O_2$
Linoleic	18:3	US	$C_{18}H_{30}O_2$
Arachidic	20:0	S	$C_{20}H_{40}O_2$
Behenic	22:0	S	$C_{22}H_{44}O_2$
Erucle	22:1	US	$C_{22}H_{42}O_2$
Lignoceric	24:0	S	$C_{24}H_{48}O_2$

[1] xx—the number of carbon atoms in the FA chain; y—the number of carbon–carbon double bonds in the FA chain;
[2] S—saturated FA; US—unsaturated FA.

The physico-chemical properties of fats, oils, and esters derived from them vary with the amounts of each FA present in the feedstock. The FA profiles of the different feedstocks are presented in

Table 2 [40]. According to [85], it is generally assumed that FA compositional profiles remain constant during conversion of the feedstock to fuels through transesterification.

Table 2. Fatty acid (FA) composition of oil [40].

Vegetable Oil	**FA Composition (wt %)**					
	16:0	**16:1**	**18:0**	**18:1**	**18:2**	**18:3**
Cottonseed	28.7	–	0.9	13.0	57.4	–
Rapeseed	3.5	–	0.9	64.1	22.3	8.2
Rapeseed	3	–	1	64	22	8
Safflower-seed	7.3	–	1.9	13.6	77.2	–
Safflower	9	–	2	12	78	–
High oleic Safflower oil	5	–	2	79	13	–
Sunflower	6.4	0.1	2.9	17.7	72.9	–
Sunflower	6	–	3	17	74	–
Sesame	13.1	–	3.9	52.8	30.2	–
Sesame	13	–	4	53	30	–
Linseed	5.1	0.3	2.5	18.9	18.1	55.1
Linseed	5	–	2	20	18	55
Palm	42.6	0.3	4.4	40.5	10.1	0.2
Palm tree	35	–	7	44	14	–
Corn marrow	11.8	–	2.0	24.8	61.3	–
Corn	12	–	2	25	6	Tr
Soybean	13.9	0.3	2.1	23.2	56.2	4.3
Soya bean	14	–	4	24	52	–
Soya bean	12	–	3	23	55	6

As seen in Table 2, the main FA in the structures of the main glycerides of vegetable oils are: palmitic acid $C_{16}H_{32}O_2$, oleic acid $C_{18}H_{34}O_2$, linoleic acid $C_{18}H_{32}O_2$.

Different physico-chemical properties of feedstocks such as FA composition, free FA content, impurities, and moisture influence the production process of the biodiesel.

The biodiesel physico-chemical properties (CN, FP, oxidative stability, CP and LHV of biodiesel) are mostly influenced by the specific compositional profile of the FAME. As such, by knowing the FAME composition (e.g., FA chain length and degree of unsaturation), almost all of the biodiesel properties may be predicted [37,85]. Thus, as reported in many studies [8,85–88], the biodiesel properties may vary substantially from one feedstock to another. Moreover, Singh et al., in their review [40] state that "the biodiesel properties can even vary for the same raw materials, depending on the plant part used". This may be explained by the fact that the FA content is different in the same plant species in different parts of the plants. Mixed feedstock biodiesel production could be a good solution for providing biodiesel with improved physical properties; equally, this could be done the view of economic considerations.

FAME property values that are reported by different authors vary considerably. According to [85], this variation may be attributed to "the use of different analytical methods and different skill levels in applying these methods". The same authors explained in [85] that "additional sources of variability include the chemical process used to produce FAME"; also, "the storage time and conditions prior to analysis". In their review [85], Hoekman et al. presents the average values (calculated from a number of references) of the physico-chemical properties of biodiesel from different feedstocks (Table 3). In this table, the properties of cottonseed [8] and rice bran [86] were also added.

Table 3. Physico-chemical properties of biodiesel from different feedstocks [8,85,86].

Property	SAF-Flower	Soy	Sun-Flower	Tallow	Yellowgrease	Coco-Nut	Corn	Jotro-Pha	Palm	Rape-Seed	Cottonseed [8]	Rice Bran [86]
Sulfur content [ppm]	-	2	2	7	5	3	4	5	2	4	-	-
Kinematic viscosity [@40 °C, mm^2/s]	4.14	4.26	4.42	4.69	4.80	2.75	4.19	4.75	4.61	4.50	4.00	4.63
Cloud point, CP [°C]	-4	0	2	13	8	-3	-3	5	14	-3	-	-
Cloud Filter Plugging Point (CFPP) [°C]	−6	*−4*	*−2*	13	*1*	−5	*−8*	-	*9*	*−12*	-	-
Pour point, PP [°C]	−7	*−4*	*−2*	10	*3*	−9	*−2*	0	*13*	*−10*	-	3
Flash point, FP [°C]	174	159	175	124	161	113	171	152	163	169	-	165
Cetane number, CN	51.1	51.3	51.1	58.9	56.9	59.3	55.7	55.7	61.9 *65.8* [87]	53.7	52.0	56.2
Iodine value	141.0	125.5	128.7	65.9	89.9	18.5	101.0	109.5	54.0	116.1	-	102.0
Specific gravity	0.879	0.882	0.878	0.878	0.879	0.874	0.883	0.876	0.873	0.879	0.885	-
Lower heating value [MJ/kg]	-	37.0	35.3	37.2	37.6	35.2	39.9	37.7	37.3	37.6	37.5	38.725
Higher heating value [MJ/kg]	42.2	39.7	40.6	37.0	39.4	38.1	43.1	40.7	40.6	41.1	-	-
Average chain length	17.8	17.9	18.1	17.3	18.5	13.4	17.6	18.3	17.2	17.9	-	-
Average Unsaturation	1.63	1.50	1.59	0.59	1.06	0.12	1.46	1.15	0.62 *0.494* [88]	1.31	-	-
Boiling point [°C]	-	-	–	-	-	-	-	-	-	-	280–400	-
Stoichiometricair-fuel ratio	-	-	-	-	-	-	-	-	-	-	12.5	-
Number of references	4	59	20	12	37	7	6	23	44	39	1	1

In the studied papers, other values than those given in Table 3 were found, but if the differences were not substantial, the references were not quoted. However, in the table, those values that were very different from the usual ones are highlighted in italic, together with the references: this was the case for the cetane number for the biodiesel obtained from palm, and as presented by Shudo et al. [87], it was slightly higher than the value that was obtained by averaging 44 sources; equally, from the palm-obtained biodiesel, the average unsaturation was slightly different from the average value provided by Ali et al. [88].

Furthermore, an important observation arose from analyzing the values of CFPP and PP given by Hoekman et al. [85]: they were the result of averaging the data found in many references, and as seen in Table 3, the obtained values were not coherent, meaning that sometimes, the PP temperature was equal to or higher than the CFPP temperature; consequently, in order to highlight this aspect, they are italicized.

As mentioned by Hoekman et al. [85], when analyzing the properties of the biodiesel obtained from different feedstocks, it is important to keep in mind the standard specifications that have been established by various fuel standard-setting organizations, e.g., ASTM (in the U.S.) and the European Committee for Standardization (CEN). Table 4 shows the standard specifications for diesel fuel from US and Europe.

Table 4. Standard Specifications [37].

Properties Fuel	**Specifications**	
	(Fuel) Standard/Test Method	**Limits**
Density at 15 °C (kg/m^3)	(DIESEL) EN590/EN 3675	820–845
	(B100) EN 14214/EN 3675	860–900
Kinematic viscosity at 40 °C (mm^2/s)	(DIESEL) EN 590/EN 3104	2.0–4.5
	(B100) EN 14214/EN 3104-3105	3.5–5.0
	(B100) ASTM D 6751-08/D 445	1.9–6.0
Cetane number	(DIESEL) EN590/EN5165	Min. 51
	(DIESEL) ASTM D975-07/D613	Min. 40
	(B6–20) ASTM D7467-08/D613	Min. 40
	(B100) EN14214/EN5165	Min. 51
	(B100) ASTM D6751-08/D613	Min. 47
Water content (% *v*/*v*)	(DIESEL) EN590/EN12937	Max. 0.02
	(B6–20) ASTM D7467-08/D2709	Max. 0.05
	(B100) EN14214/EN12937	Max. 0.05
	(B100) ASTM D6751-08/D2709	Max. 0.05
Distillation characteristics, T90 (°C)	(DIESEL) ASTM D975/D86	Max. 338
	(B6-20) ASTM D7467-08/D86	Max. 343
	(B100) ASTM D6751-12/D7501; D1160	Max. 360
Lubricity, HFRR@60 °C Micrometer	(DIESEL) ASTM590/ISO12156-1	Max. 460
	(B6-20) ASTM D7467-08/D6079	Max. 460
	(B100) ASTM D6751-08/	-
Flash Point (°C)	(DIESEL) EN590/EN2719	Min. 55
	(B6-20) ASTM D7467-08/	Min. 38
	(B100) EN14214/EN2719; 3679	Min. 101
	(B100) ASTM D6751-12/D93	Min. 93
Sulfur content (mg/kg)	(DIESEL) EN590/EN20846; 20884	Max. 50
	(B6-20) ASTM D7467-08/	-
	(B100) EN14214/EN20846; 20,884	Max. 10

Note: Bx means a blend consisting of petroleum diesel fuel with x% biodiesel; also, used for B5 and below; also, used for B7 and below.

The viscosity of FAME reaches very high values; thus, it has to be brought to acceptable values in order to avoid negative impacts on the fueling system performance. Consequently, the biodiesel fuel blends feature higher viscosities than petroleum diesel fuel [8,37]. Yanuandri Putrasari et al. reported in their review [23] that “biodiesel has around 11 to 17 times higher viscosity than diesel”.

These striking values cannot be taken into discussion, because the standard EN 14214/EN 3104–3105 that limits the characteristics of pure biodiesel requires a viscosity between 3.5–5.0 mm^2/s, and for diesel, the standard EN 590/EN 3104 requires viscosity values between 2.0–4.5 mm^2/s [22]. Moreover, as seen from Table 3, according to a huge number of sources, the viscosity does not exceed 5 mm^2/s for any feedstock.

Generally, the densities of biodiesel fuel blends are slightly higher than those of petroleum diesel fuel. The density of the resulted fuel blend increases with the increasing of the percentage of pure biodiesel; the density values depend on the FA composition and purity [37].

Because biodiesel is largely composed of long-chain hydrocarbon groups, it has a higher CN than petroleum diesel fuel, whatever the feedstock that is used for its production; in the case of petroleum diesel fuel-biodiesel blends, increasing the amount of biodiesel increases the CN of the blend. Actually, the FAME composition considerably influences the CN of biodiesel fuels [37]. As seen in Table 3, the maximum CN is 65.8, according to reference [87]. However, as already mentioned, other values are also reported in the literature; for instance, CN values higher than 100 were reported in [23] by Yanuandri Putrasari. However, we think that these values cannot be accepted.

Distillation Characteristics. Generally, the boiling temperatures of components of biodiesel blends are higher than conventional diesel fuel [8]. The poor evaporation obstructs the early formation of an ignitable air–fuel mixture, generating a longer ignition delay (ID) and also, a lower peak of rate of heat release (RoHR) at a higher engine load [79].

The flash point of biodiesel is higher than fossil petroleum diesel [8]; it decreases as the amount of residual alcohol used in the transesterification process increases. Consequently, the biodiesel FP measurement also helps to show the presence of methanol/ethanol [37].

Because of the important variations in seasonal and geographic temperatures, neither the European biodiesel standards, nor the US have specifications for cold flow characteristics, even though these are the important properties for determining the suitability of biodiesel as a fuel. As stated before, according to [89], the presence of unsaturated FA in biodiesel and the length of the hydrocarbon chains influences the cold-flow properties of the biodiesel. Consequently, for biodiesel (no matter the feedstock), the cold flow properties are worse. Thus, by increasing the percentage of biodiesel in petroleum diesel-biodiesel blends, the cold flow properties become worse, and engine startability at low temperatures becomes difficult [8,9,22,24].

Water content. As mentioned in [37], "since FAME is capable of absorbing significantly more water than petroleum diesel fuel, it is especially important to dehydrate it during the production process and to minimize its potential to create free water during blending or distribution".

The biodiesel lower heating value (LHV) is lower than those of fossil diesel. The lower values for biodiesel's LHV are an obstacle to achieving the maximum torque under full load operation. Thus, the indicated specific fuel consumption (ISFC) of a biodiesel-fuelled CI engine could be up to 15% higher than that of a petroleum diesel fuelled CI engine, only because of the lower LHV [8,79].

3.2. Bio-Ethanol/Bio-Methanol Physico-Chemical Properties

Methanol and ethanol are oxygenated liquid hydrocarbon fuels. According to [79], "the hydroxyl moiety makes methanol and ethanol hydrophilic and has a dipole moment. This polarization by dipole moment affects the inter-molecular interactions and makes them hydrophilic and behave close to an azeotrope when blended with gasoline". An azeotrope or a constant boiling mixture is a mixture of two or more liquids whose proportions cannot be altered by simple distillation. This happens because when an azeotrope is boiled, the vapor has the same proportions for the constituents as the unboiled mixture [1].

Table 5 shows the standard specifications for ethanol and methanol from US and Europe.

Table 5. Standard Specifications.

Type of Fuel	**Standard Specifications**	
	US	**EN**
Ethanol	ASTM4806 ASTM5798	EN 15376 [1]
Methanol	ASTM D5797 [2]	EN 228-2008 (E) [3]

[1] "Automotive fuels—Ethanol as a blending component for petrol—Requirements and test methods"; [2] Available for methanol blends (70 to 85 vol % methanol) for the use in spark-ignition engines; [3] Standard contains a limit of 3 % methanol in gasoline.

In Table 6, the physical properties of ethanol and methanol, as values or a range of values, according to authors from 10 references cited in their paper review [1]. Also, values from [8,12,13,25,29,69,86–88,90–93] were taken into account.

Table 6. Physical property values of ethanol and methanol.

Property	**Methanol**	**Ethanol**
Formula	CH_3OH	CH_3CH_2OH
Molecular weight [kg/kmol]	32	46
Oxygen (wt %)	50.0	34.8
Density@20 °C [kg/m^3]	(787–792)	(780–820) *450* [93]
Lower heating value (LHV) [MJ/kg]	(19.9–22.7)	(26.4–26.9) *28,959* [93]; *29.38* [69]
Octane number, RON	(109–114)	(107–111)
Cetane number, CN	3	(5–8) *10* [86]; *11* [1,94]
Stoichiometric air–fuel ratio, A/F [kg/kg]	6.5	(8.9–9.0)
Latent heat of vaporization [kJ/kg]	(1101–1168)	(837–840) *880* [92]; *879* [13]
Boiling point [°C]	(64–65)	(78–78.3)
Flame speed [m/s]	-	0.39
Specific heat [kJ/kg K]	1.44	2.4
Vapor pressure@20 °C, [KPa]	12.9 *52* [13]	5.9 *21* [13]
Kinematic viscosity@20 °C [mm^2/s]	(0.759–1.01)	1.16–1.87
Flash point [°C]	(11–12)	9–17.2 *22* [86]; *24* [69]
Auto-ignition temperature, [°C]	(470–500)	(365–450) *636* [92]

As before, those values that go well beyond the range found in most of the references are italicized, together with their references. The following was concluded: a density of ethanol really lower than the usual values was found in reference [92]; equally, values of LHV, CN, latent heat of vaporization, vapor pressure, flash point, and auto-ignition temperature that were higher than the ones were found, as seen in Table 6.

Octane number (ON) is an indication of a fuel's ability to withstand auto-ignition, and is specific to SI engines. In case of this kind of engines, auto-ignition before and after the production of spark may lead to engine knocking, which can damage the engines. The alcohol fuels show higher ON, which makes the calibration of the spark advance possible, which is more favorable for achieving a higher indicated efficiency. Choongsik [79] cites results on fuel consumption behavior, considering the connection between a higher compression ratio (CR) and ON, which showed that an ON increment of four to six units is required per unit of CR increase.

The volatility expressed by the boiling point is lower than that for diesel fuels and therefore, alcohols represent a solution for improving their volatility.

Due to their low values of kinematic viscosity and surface tension, ethanol and methanol could influence the droplet size of the blended fuel in a negative manner.

The Lower heating value (LHV) of alcohols are lower than petroleum diesel and biodiesel fuels.

Alcohol fuels have high latent heats of vaporization; thus, improved charge cooling effects are to be expected, which can lead to an increase of the volumetric efficiency.

4. Use of Diesel–Biodiesel–Alcohols

4.1. Why Are Diesel–Biodiesel–Alcohols Blends Used?

For a more synthetic presentation, studies on this particular subject are presented in this section. Details of the influences of these kinds of mixtures on CI engine operation performance will be presented separately, in the following section.

Concerning the use of biodiesel in CI engines, as was already mentioned before, two main problems are associated with its use: its poor cold flow properties and thermal stability. The first aspect influences the startability of the CI directly, engines at below-zero ambient temperatures [22]. These drawbacks are associated mainly with a higher surface tension and viscosity of biodiesel fuels. So, the great challenge when using biodiesel for CI engines is the improvement of its poor cold flow characteristics [9,88].

The use of diesel and biodiesel blends is a way to improve the biodiesel properties and to benefit from its superiority. Moreover, CI engines do not require any modifications, for blends of up to 30% biodiesel blended in diesel fuel.

Ghadikolaei [25] has made an ample review on the effect of alcohol blends with petroleum diesel and fumigation on regulated and unregulated emissions of CI engines. He said that alcohol-based fuels may be used with diesel petroleum fuel, utilizing different dual fuel operation techniques. These methods are most often encountered within blending and fumigation. Thus, when talking about the blending method, the alcohol fuels are blended with the petroleum diesel fuel before the in-cylinder injection. This method implies some limitations regarding the stability of the mixture; therefore, additives are required. On the other hand, alcohol fumigation means that the alcohol fuel is sprayed or injected during the intake stroke into the intake manifold. The advantage of this method is that the alcohol will arrive inside the cylinder premixed with the intake air. From a technical standpoint, fumigation demands only the addition of the alcohol fuel supply system to the engine, i.e., a low-pressure fuel injector, a separate alcohol tank, pipelines and the associated command and control system. Consequently, according to Ahmadi Ghadikolaei [25], the engine's efficiency will be improved from the fumigation mode, compared to the blending method.

Zibin Zhang et al. [58] consider that the use of bioethanol has both advantages and disadvantages. They performed an economic analysis in that respect, and considered that the economic imbalances that bioethanol might create may be eliminated through appropriate policies (for example, by supplementing the supply on the market during the bad-weather years).

Combustion at a low temperature (LTC) is a novel combustion method in CI engines, which aims to reduce both nitrogen oxides (NO_x) and particulate matter (PM). In a CI engine, LTC may be applied by the addition of some combustible substances featuring higher vaporization characteristics and lower cetane numbers. In Putrasari et al. [23], the authors also explained the mechanism of the LTC concept and as a volatile combustible substance, they used gasoline mixed with biodiesel.

The other combustible substances used in order to operate a biodiesel fuelled engine in LTC mode are usually ethanol or kerosene [9]. For instance, as mentioned in [9], by blending the biodiesel with ethanol or kerosene at ratios up to 20% results in a reduction by 30% of the kinematic viscosity; furthermore, according to the same study, a very low content of around 0.03% of olefin-estercopolymers decreases by 33% the dynamic viscosity of soybean biodiesel.

Ali et al. in [88], said that the addition of 5% ethanol in pure palm oil biodiesel decreases the pour point by approximately 5 °C, the viscosity by 0.5 mm^2/s, and the density at 4 kg/m^3.

The addition of alcohols in biodiesel blends (methanol and/or ethanol) is practical, due to their miscibility with the pure biodiesel. Alcohols improve the physico-chemical properties of biodiesel blends (e.g., they reduce the viscosity and the density), leading to the improvement of combustion efficiency, and they generate less pollutants when used in a CI engine [37].

Bharadwaz et al. [95] optimized the parameters related to biodiesel–methanol (5, 10, 15%) blends, at a constant compression ratio and engine load, in order to maximize the engine's thermal efficiency, as well as minimizing the tailpipe emissions. They have presented the properties of biodiesel and methanol–biodiesel blends, and it can be observed that both the density and calorific value decreased with the increase in the amount of methanol.

Considering that palm oil has an important advantage of productivity compared with other vegetable oils such as rapeseed oil and soybean oil, even if its cold flow characteristics are poorer than other vegetable oil-based biodiesel fuels, Shudo et al. [87] performed an experimental study in order to simultaneously reduce CP, smoke, and NO_x emissions by blending bioethanol into biodiesel fuels and by also using exhaust gas recirculation (EGR). While the CP of neat biodiesel from palm oil is approximately 14 °C, by blending it with 40 vol % ethanol, it goes down to 8 °C. They also showed that the density decreases, and the volatility improves with an increasing amount of ethanol.

The possibility of utilizing blends of bioethanol (5%, 10%, and 15%) and fossil diesel with the help of a surfactant has been explored in a paper [69]. The density and the kinematic viscosity decrease, and the surface tension increases with the amount of bioethanol. CFPP and PP decrease, and the credible values shown are for blends with 15% ethanol.

Since ethanol is not miscible in fossil petroleum diesel fuel, Subbaiah et al. [86] explored the use of rice bran oil biodiesel as an additive in diesel–ethanol blends for CI engines, and the performance and emissions of the CI engine fueled with B10, B10E5, B10E10, and B10E15, compared to B100 and fossil diesel was shown. Tables 7–9 present some of these conclusions.

Rakopoulos et al., in [8], said that in the case of ethanol–fossil diesel blends, an emulsifying agent needs to be used in ratios of up to 1.5% (by vol.), to improve the mixture homogeneity, and to prevent phase separation. The mixing protocol consisted of first blending the emulsifier into the ethanol, and then blending the resulting mixture into the petroleum diesel fuel. Also, the authors mentioned that the use of low blending ratios of ethanol (i.e., 5, 10, 15%) is dictated by the necessity of avoiding any cyclic variability phenomena, which may occur in CI engines when very low CN fuels are used.

Regarding the pollutants of a CI engine, in the studies [92,96,97], it is argued that it is difficult to reduce nitrogen oxides (NO_x) and soot simultaneously. A promising method for solving this problem is to add oxygenated fuels (such as alcohols) to petroleum diesel fuel, in order to deliver more oxygen during combustion. Li et al. in [92] investigated oxygenated fuel combustion characteristics by adding 5, 10, 15, and 20 percent ethanol to petroleum diesel fuel with and without a CN improver. Soni et al. [96] considered that methanol has the potential to reduce NOx and soot emissions, and that it may be used in CI engines, due to its economic and environmentally friendly nature. More than that, Soni et al. explored the possibility of an even higher rate of reduction, especially for NOx and soot emissions. They cited authors that proposed different methods such as high-pressure multiple injections combined with the EGR technique. Their own study was focused on controlling the initial swirl, while using EGR, and by bringing water inside the cylinder in the form of a blend.

In order to decrease smoke and NOx emissions simultaneously in CI engines, Hasimoglu [97] has proposed the use of an ethanol-diesel fuel blend in a direct-injection turbocharged engine aiming at a so-called low-heat-rejection (LHR) application. Thus, a 10 vol % ethanol–90 vol % petroleum diesel fuel blend was used; the cylinder head, valves, and pistons of the test engine were coated with yttria-stabilized zirconia (Y_2O_3–ZrO_2) over a nickel–chromium–aluminum bond coat, by the atmospheric plasma spray coating method. The results of the engine test showed that NOx emissions decreased by up to 70%, and smoke by up to 39%, at 1200 r/min and 200 Nm, in comparison with the standard engine. Then, when increasing the engine speed at the same engine load, the NOx and smoke emissions were equally lower, but not at the same level.

However, the use of ethanol–diesel blends (i.e., e-diesel) has some drawbacks: reduced CN, lower lubricity and viscosity, higher volatility, which may generate an increased unburned hydrocarbons emission, and lower miscibility, which may lead to phase separations. Thus, the use of cetane improver additives is needed, to increase the potential of these blends as an alternative fuel for automotive CI engines [26]. As argued in [36], most blends of petroleum diesel fuels and ethanol are limited to 15% ethanol and 5% emulsifiers. According to [26], blends with a maximum of 10% (v/v) bio-ethanol may be used in CI engines in countries where ambient temperatures rarely decrease below −5 °C, but water contamination needs to be taken into account.

In conclusion, the biodiesel can be mixed with both ethanol and petroleum diesel fuel. This review paper [98] aimed to investigate the effects of biodiesel, alcohol, and petroleum–diesel fuel blends on the energetic and ecological engine performance of a CI engine.

M. Yasin et al. [90] declare that fuel properties are the parameters to be used, to understand the effects of the blended fuels on CI engine operation. They have conducted a study on the physical characteristics of biodiesel–diesel-blended fuels with alcohol as an additive. Practically, they have determined the properties of different blends: D75B20E5, D70B20E10, D75B20M5, and D70B20M10 (D75B20E5 means 20% biodiesel, 75% diesel, and 5% ethanol; D75B20M5 means a blend of 5% methanol with 75% diesel fuel and 20% biodiesel) and compared with petroleum diesel and pure biodiesel fuel properties. Although they sustain that "the measured properties of biodiesel and its alcohol blend fuels still meet the requirements of EN14214"; for example, the FP value is not in the limits; however, they are in concordance with the literature. Also, in our opinion, CN have a very high value and, because the equipment and method are not specified, this information is not credible. The study concluded that a concentration of alcohol of 5% to 10% by volume, diluted in B20 blended fuel significantly reduces the density and viscosity of the resulted blend.

The proper volatility of fuels is paramount to the operation of ICE, since it impacts both the performance and the emissions. The content of ethanol/methanol or other oxygenates improves the volatility, and as a result, the engine's performance and its tailpipe emissions. Shudo et al. [87] have studied the volatility of the blends used (40 vol % ethanol-blended biodiesel from palm oil) from the perspective of the volatility of each component, as estimated from the reference. They did not experimentally determine the volatility of the mixtures. Niculescu et al. [99] claim that for diesel–biodiesel–alcohols blends, the difference between each component's volatility generates difficulties when analyzing the overall volatility. They present an experimental method of distilling diesel–biodiesel–alcohols mixtures by adjusting the boiler pressure of an i-Fischer Dist. equipment using ASTM D1160 "Standard Test Method for Distillation of Petroleum Products at Reduced Pressure".

In their research study [100], H.G. How et al. investigated in a common-rail DI CI engine the effect of a small amount of bioethanol as an additive in biodiesel (obtained from coconut oil)—a diesel blend fuel (5% ethanol–20% biodiesel–75% diesel) on the engine performance, emissions, and combustion characteristics. They concluded that using the ethanol as an additive for the biodiesel–diesel blend does not imply any technical modification to a CI engine.

Yasin et al. [101] present a comparative study on biodiesel (20%)–methanol (5% or 10%)–diesel (75% or 70%) blends operating with a CI engine. They claim that combustion and emissions depend on methanol blend ratios and engine operating conditions. The results seem to be simultaneously favorable and contradictory, due to the oxygen content and the cooling effects of methanol. They have determined the physico-chemical characteristics of the mixtures, and it can be concluded that: a density measured at 20 °C decreased while increasing the methanol amount; the viscosity measured at 40 °C increased with an increase in the methanol amount, but it was lower compared to mineral diesel and B20; the flash point increased with the increase of methanol amount, but it was lower than that of B20 and mineral diesel; CN decreased with the increase of methanol amount; however, the CNs given for different blends seems to be too high to be correct, because they exceeded the CN of the

B20D80 blend and fossil petroleum diesel fuels obtained by the same authors (e.g., CN-B20D75M5 = 92.4 and CN-B20D70M10 = 91.2 were higher than CN-B20D80 = 78.2 and CN-D100 = 71.6). On the other hand, in our opinion, these values were unexpectedly higher than the ones usually known, and the authors did not explain this fact. Moreover, Table 3 shows that the highest value of CN was 65.8 for palm biodiesel, so that once again, the numbers given in reference [101] seemed not to be trustworthy, as the CN of the alcohols was very low, which would usually decrease the CN of the diesel fuels when they were mixed.

Seyed Mohammad Mousavi et al. cites a number of researchers in [102], and they reported that with an increase in the methanol fraction in diesel blends, the ID was influenced by the diesel and methanol fuel chemical reactions, and by the changes in the temperature inside the cylinders. Also, with an increasing percentage of all biofuels in the diesel fuel blends, this resulted in a significant reduction of smoke; furthermore, except for the vegetable oil blends, all of the other biofuels–diesel fuel blends featured lower CO emissions.

An experimental study has been devoted by Beatrice et al. in [91] to the characterization of an Euro 5 automotive CI engine, fueled by blend fuel consisting in 20 vol% bio-ethanol, 10 vol% rapeseed methyl ester, and 70 vol% fossil diesel underlining the impacts of bio-ethanol use. Emission measurements for an Euro 5 CI engine indicated the well-known effects of ethanol blending to petroleum diesel fuel: an important reduction of smoke in all tested conditions, NO_x reduction, and an increase of CO and HC, especially at low load conditions, compared with the B10 fueled engine. Starting from the obtained results, an optimized calibration was performed.

Alam et al. [82] cited many studies that have been performed with biodiesel and oxygenated diesel fuels, and most of them showed an important potential for reducing emissions. The higher CN of biodiesel and many oxygenates may enhance combustion performance in the CI engine. Moreover, they performed studies using 95% oxygenates (ether) in pure biodiesel. The combustion analysis and the visualization inside the cylinder used in this study made possible the understanding of the behavior of oxygenates in a CI engine.

Al-lwayzy et al. [103] reported that a mixture of 10% microalgae oil, 10% ethanol and 80% fossil diesel was found to be homogenous and stable without using a surfactant. In this study, microalgae oil was used instead of biodiesel to eliminate the transesterification cost and to further improve the properties of the resulted blend.

The alcohols (used like additives) have a relatively low FP and autoignition temperature compared to diesel and biodiesel fuels, and they may generate increased cyclic variability, which in turn, may result in a drop of engine output power and in higher emissions; therefore, effective methods to control the optimum additive ratio are needed [104].

In their paper [93], Sastry et al. reported a well-known observation, that a higher fuel injection pressure is effective in improving performance and in reducing emissions, and they performed an experimental investigation on a direct-injection CI engine, using iso-butanol and ethanol as additives (5–10% by volume) in diesel–biodiesel blends, at different injection pressures (200, 225, 250, and 275 bar).

Tutak et al. recently said that the ethanol is used as a fuel for CI engines under both methods: blended or dual-fuel combustion [94]. They have performed experimental works using ethanol with 11 wt % water content, analyzing two fuel supply systems: at 0.1 bar relative pressure, and at 1 bar relative pressure. They showed that the 1 bar fuel supply system allowed blends with higher ethanol fractions to be burnt; up to 45% [94].

Kowalewicz and Wojtyniak [13] compiled an ample review about alternative fuels such as biodiesel, bioethanol, and bio-methanol, and their use in ICE. The aim of their paper was to characterize alternative fuels by using the following criteria: their sources, properties, methods of production, and application for ICE; both SI and CI engine.

Table 7. Combustion characteristics (in this table, NA means "not available"; equally, being about blends, fuels are designated in the following manner: BxDy/EyDx/BxEyDz; B, E, D stand for biodiesel, ethanol, and diesel, respectively, while x, y, z stand for the corresponding percentages).

Fuels/Experimental Details	**Results**					**Reference Fuel**	**Ref.**
	Duration of Combustion DoC	**Rate of Heat Release RoHR**	**Injection Delay ID**	**In-cylinder pressure p_{cyl}**	**In-cylinder temperature T_{cyl}**		
B10D90; B20D80; B50D50; E5D95; E10D90; E15D85 - Biodiesel obtained from cottonseed	NA	Higher at the beginning of combustion and lower later on into the expansion stroke for BxDy blends	Slightly decreased for BxDy blends	Higher at the beginning of combustion and lower later on into the expansion stroke for BxDy blends	Higher at the beginning of combustion and lower later on into the expansion stroke for BxDy blends	Fossil diesel, D100	[8]
		The cumulative heat release values are lower at the beginning and catch up later on during the expansion stroke for ExDy blends	Slightly increased for ExDy blends	Unaltered for ExDy blends	Slightly reduced for ExDy blends		
E5D95; E10D90; E15D85 - Bioethanol obtained from Madhuca indica flower) - Fuels were emulsified with the help of a surfactant - Diesel operation at different loads (idle, 25%, 50%, 75%, 100%)	Decreases when increasing the bioethanol percentage	Higher. The maxi- mum value is found to be the highest for D85E15 followed by D95E5, D90E10	Higher at all loads	Higher at full load. The maximum cylinder pressure increases when increasing the amount of alcohol	NA	Fossil diesel, D100	[69]
B10E20D70 - Biodiesel obtained from rapeseed methyl ester	NA	NA	NA	A slight decrease	NA	B10D90	[91]
E5D95; E10D90; E15D85; E20D80 - With and without the CN improver (0.2% iso-amyl as the CN improver)	The total combustion duration decreases when increasing the ethanol amount or the oxygen mass fraction with and without a CN improver.	The maximum value increases with increasing the ethanol fraction in the blends	Increases with the increase of the ethanol fraction	Without the CN improver, it increases with an increase in the ethanol fraction	NA	Fossil diesel, D100	[92]
		NA	Decreases with the addition of a small amount of a CN improver to diesel–ethanol blends	With CN improver, it decreases, but it remains bigger than the case of neat diesel fuel			

Table 7. *Cont.*

Fuels/Experimental Details	Results					Reference Fuel	Ref.
	Duration of Combustion DoC	**Rate of Heat Release RoHR**	**Injection Delay ID**	**In-cylinder pressure p_{cyl}**	**In-cylinder temperature T_{cyl}**		
E5D95; E10D90; … E45D55 - Using two fuel supply systems (SS): HPSS@1bar and LPSS@0.1bar	Decreases in both cases with the increase of the ethanol fraction. LPSS—the decrease is linear. HPPS—combustion duration decreases to 15% ethanol in the diesel blend; after this, it remains near-constant of up to 35% ethanol	NA	Increases with the increase of the ethanol fraction. With the increase of pressure in the supply system (HPSS), it grows less	Higher with an increasing ethanol amount and supply pressure	NA	Fossil diesel, D100	[94]
B20E5D75 - At different engine loads.	NA	Slightly lower	NA	Slightly lower	NA	Fossil diesel, D100	[100]
B10E10D80 - Biodiesel obtained from microalgae oil - Variable compression ratio diesel engine at different speeds	NA	NA	NA	Very comparable	NA	Fossil diesel, D100	[103]
Diesel–Methanol dual-fuel - Separate injections	Decreases with an increase in methanol mass fraction	Increases with an increase in methanol mass fraction	Increases with an increase in methanol mass fraction	Higher with increasing in methanol mass fraction	NA	Fossil diesel, D100	[80]

Table 8. Engine performances (regarding the BxMy/BxMyDz notation, it refers to a blend containing y% of methanol; see also Table 7).

Fuels/Experimental Details	Results					Reference Fuel	Ref.
	BSFC	BTE	BP	EGT	IMEP		
B10D90; B20D80; B50D50; E5D95; E10D90; E15D85 - Biodiesel obtained from cottonseed	Increased with all bio-fuel blends	Slightly higher	NA	Slightly lower	NA	Fossil diesel, D100	[8]
Review on the effect of ethanol in the biodiesel-diesel blend	Higher	NA	NA	NA	NA	Fossil diesel, D100	[98]
B95M5, B90M10, B85M15 - Methanol–biodiesel blends - Biodiesel obtained from palm oil - Different compression ratios	Increases with methanol content in the blend	Increases with methanol content in the blend	NA	NA	NA	Fossil diesel, D100	[95]
B20M5D75, B20M10D70, B20D80, D100 - 20%, 40%, and 60% engine loads	Increases with methanol amount, especially at low engine loads	NA	NA	Increases with methanol amounts, especially at high engine loads	NA	Fossil diesel, D100	[101]
E5D95; E10D90; . . . E45D55 - Using two fuel supply systems (SS): HPSS@1bar and LPSS@0.1bar	NB. The authors did not specify the kind of SFC that was being reported (BSFC or ISFC?) When using HPSS: almost constant up to 35% ethanol fuel fraction in diesel blends; further increasing the ethanol percentage generates an increase in BSFC	Increases, the maximum increase is at 35% ethanol when using HPSS	NA	NA	Almost constant, until 35% ethanol. Cycle variation, expressed as COV_{IMEP}, increases with increasing ethanol amount	Fossil diesel, D100	[94]
	When using LPSS: it increases with the increase of ethanol fraction	It decreases when using LPSS			It slightly decreases. Cycle variation, expressed as $\text{left}_{\text{IMEP}}$, increases with increasing ethanol amount		

Table 8. *Cont.*

Fuels/Experimental Details	Results					Reference Fuel	Ref.
	BSFC	BTE	BP	EGT	IMEP		
Isobutanol/ethanol as additives in diesel biodiesel blends B20D70Alcohol10 B10D80Alcohol10 B30D70, D100, B100 - Biodiesel obtained from fish oil - Different injection pressure	For some blends, it increases, for others it decreases; however, there is a decreasing trend for all blends with the increase in injection pressure (200 to 275 bar)	Higher when the injection pressure is between 225–250 bar	NA	NA	NA	Fossil diesel, D100	[93]
		Smaller or almost equal at an injection pressure below 225 and above 250 bar.					
B20E5D75 - Biodiesel obtained from coconut - At 0.17, 0.69, and 1.20 MPa engine loads expressed as brake mean effective pressure (BMEP)	(2.0–2.7)% higher	(3.0–5.4)% higher	NA	NA	NA	Fossil diesel, D100	[100]
B10E20D70 - Biodiesel obtained from rapeseed methyl ester	Higher	NA	NA	NA	NA	B10	[91]
B100; B10E5D85; B10E10D80; B10E15D75 - Biodiesel obtained from rice bran oil - Single-cylinder diesel engine	Higher	A maximum BTE of 28.2% was observed with blend B10E15	NA	At B10E15 it was slightly lower	NA	Fossil diesel, D100	[86]
B95E5 - Biodiesel obtained from palm oil - Tests conducted at an increasing engine speed and 50% load.	Slightly lower	NA	Slightly higher	NA	NA	B100	[88]
	Higher	NA	Lower	NA	NA	Fossil diesel, D100	
B10E10D80 - Biodiesel obtained from microalgae oil, - Variable compression ratio diesel engine at different speeds	Very comparable	NA	Very comparable	Minor variations	NA	Fossil diesel, D100	[103]

Table 8. *Cont.*

Fuels/Experimental Details	Results					Reference Fuel	Ref.
	BSFC	BTE	BP	EGT	IMEP		
B30D70; B50D50 - Review paper - Biodiesel obtained from rapeseed methyl ester	Higher	NA	Lower	NA	NA	Fossil diesel, D100	[13]
D95E5; D90E10; D85E15 - bioethanol obtained from Madhuca indica flower emulsified with the help of a surfactant - Diesel operation at different loads (idle, 25%, 50%, 75%, 100%)	Higher for all loads (only at 25% load until 5% ethanol, it decreases)	NA	NA	Slightly increases with the increase of ethanol for all loads	NA	Fossil diesel, D100	[69]

Table 9. Emissions.

Fuels/Experimental Details	Results						Reference Fuel	Ref.
	NO_x	Smoke	CO	UHC	PM	CO_2		
B10D90; B20D80; B50D50; E5D95; E10D90; E15D85 - Biodiesel obtained from cottonseed	Decreases for all blends Increases with the percentage of biofuel in the blend	Decreases with an increase of the percentage of biofuel in the blend	Decreases for all blends Increases with the percentage of biofuel in the blend	Increases	NA	NA	Fossil diesel, D100	[8]
Review on the effects of ethanol in the biodiesel–diesel blend	Decreases significantly	Decreases with the increase of the percentage of ethanol	NA	Decreases significantly	Decreases	NA	Fossil diesel, D100	[98]
B95M5, B90M10, B85M15 - Methanol–biodiesel blends - Biodiesel obtained from palm oil - Different compression ratios	Decreases while adding methanol in biodiesel fuel	Decreases while adding methanol in biodiesel fuel	Increases while adding methanol in biodiesel fuel	Increases	NA	NA	Fossil diesel, D100	[95]
B20M5D75, B20M10D70, B20D80, D100 - 20%, 40%, and 60% engine loads	Decreases significantly Decreases while adding methanol	NA	Slightly increases while adding methanol	NA	NA	NA	Fossil diesel, D100	[101]
E5D95; E10D90; . . . E45D55 - Using 2 fuel supply systems (SS): HPSS@1bar and LPSS@0.1bar	Increases with the increase of the ethanol fraction in the blend until the combustion process starts to deteriorate	NA	Eight-times decrease (35, 45% ethanol), LPSS Five-times Decrease (35, 45% ethanol), HPSS	Increases with a higher ethanol fraction, or it was almost at a constant level. It improves for 20–35% ethanol in case of HPSS-1bar	NA	Decreases with the increase of the ethanol amount It is higher at HPSS	Fossil diesel, D100	[94]
Isobutanol/ethanol as an additive in diesel–biodiesel blends B20-D70-alcohol10 B10-D80-alcohol10 B30-D70 D100 B100 - Biodiesel obtained from fish oil	NOx emissions were decreased slightly; increase with an increase of the injection pressure (200 to 275 bar)	NA	NA	NA	NA	NA	Fossil diesel, D100	[93]

Table 9. *Cont.*

Fuels/Experimental Details	Results						Reference Fuel	Ref.
	NO_x	Smoke	CO	UHC	PM	CO_2		
B20E5D75 - Biodiesel obtained from coconutat all engine loads	Decreases	Decreases	Decreases	NA	NA	NA	Fossil diesel, D100	[100]
B10E20D70 - Biodiesel obtained from rapeseed methyl ester	Decreases	NA	Increases at low loads	Increases at low loads	Decreases	NA	B10	[91]
B100; B10E5D85; B10E10D80; B10E15D75 - Biodiesel obtained from rice bran oil - Single-cylinder diesel engine	Low emissions for biodiesel and for all of the other fuel blends at lower loads High emissions at higher loads	Decreases; the lowest value was obtained for the blend B10E15	Lower; minimum CO emissions for B10E15	Increases with the increase of the ethanol percentage, but lower than those of the diesel at higher loads	NA	Higher	Fossil diesel, D100	[86]
B80E20; B60E40 - 35% EGR (exhaust gas recirculation) (without deteriorating the thermal efficiency) - Biodiesel obtained from palm methyl ester	Decreases with the increase of ethanol amount	Decreases with the increase of ethanol (oxygen) amount	Slightly increases for B60E40These emissions are not very high and could be after-treated by oxidation catalysts	Slightly increases. These emissions are not very high and could be after-treated by oxidation catalysts	NA	NA	-	[87]
B10E10D80 - Biodiesel obtained from microalgae oil, - Variable compression ratio diesel engine at different speeds	Substantially lower	NA	Lower	Considerably lower	NA	Almost the same. Negligible reduction at low engine speeds	Fossil diesel, D100	[103]
E10D90 - A test engine modified for LHR (low-heat-rejection) conditions	Lower	Lower	NA	NA	NA	NA	Engine standard	[97]
B30D70; B50D50; B100 - Review paper - Biodiesel obtained from rapeseed methyl ester	Increases	NA	Decreases	Decreases	Decreases		Fossil diesel, D100	[13]

Table 9. *Cont.*

Fuels/Experimental Details	Results						Reference Fuel	Ref.
	NO_x	Smoke	CO	UHC	PM	CO_2		
Different blends of diesel–ethanol - Review Paper	NA	Decreases	Decreases	NA	NA	Drastically decreases with the fraction of ethanol	Fossil diesel, D100	
Different blends of diesel–ethanol - Review paper	Decreases when using alcohol fuels in fumigation mode	Decreases in both modes (fumigation and blended modes).	Increases in fumigation mode	Increases in fumigation mode	Decreases in both modes (fumigation and blended modes).	Decreases with using alcohol fuels in fumigation mode	Fossil diesel, D100	[25]
	Increases when using alcohol fuels in blended mode		Decreases with the use of alcohol fuels in blended mode	Decreases in blended mode		Increases with using alcohol fuels in blended mode		
E5D95; E10D90; E15D85 - Tests at full load	Lower Decreases with bioethanol amount increase	Decreases substantially with an increase in the amount of bioethanol (E5 decrease is 2.31%; E15 decrease is 20.8%)	NA	Lower for E5D95 Higher for E10D90	NA	NA	Fossil diesel, D100	[69]
D90M10; D80M20; D70M30	Decreases with an increase in the percentage of methanol in diesel blends	Increases with an increase in the percentage of methanol in diesel blends	Decreases with an increasing percent of methanol	Decreases with the increasing percent of methanol	NA	NA	Fossil diesel, D100	[96]
	15 vol % water addition reduces NO emissions by up to 95%	15 vol % water addition, the soot mass fraction could decrease by up to 14 %	15 vol % water addition, reduces CO emission up to 29%	15 vol % water addition in D70M30 results in a 36% reduction in HC emission		NA	D70M30	
	20% increase in the amount of EGR reduces NO by 36%	NA	NA	NA		NA		

Table 9. *Cont.*

Fuels/Experimental Details	**Results**						**Reference Fuel**	**Ref.**
	NO_x	**Smoke**	**CO**	**UHC**	**PM**	**CO_2**		
Diesel–methanol dual-fuel - Separate injections	Decreases with an increase of the percent of the injected mass of methanol	Decreases with an increase of the percent of the injected mass of methanol	Increases with an increase in the percent of the injected mass of methanol	Increases with increase of the percent of the injected mass of methanol	NA	NA	Fossil diesel, D100	[80]

Due to their higher CN, a shorter ID is obtained, and thus, the NO_x emissions are increased. At high idling operating conditions, for up to 5% biodiesel, the NO_x emissions decrease slightly, and they seem to increase for ratios that are higher than 5% [9].

In order to improve the properties of fossil diesel and biodiesel blends, Liu et al. [105], Ileri et al. [106] proposed other oxygenated compounds to be added as follows: compared to ethanol or methanol, *n*-butanol seems to be a better alcohol for applications in CI engines, due to its HHV, lower heat of vaporization, longer stability, and better inter-solubility with diesel fossil fuels, with no corrosion. Ileri et al. [106] who studied the effects of using a diesel–rapeseed oil–*n*-butanol blend showed that the high oxygen content of *n*-butanol and rapeseed oil decreased the LHV of the resulting blend; thus, producing a lower effective torque than the B20 case. On the other hand, the resulting blend generated lower UHC emissions than the diesel fuel.

Kumar et al. [107] elaborated in their review on the use of biofuel emulsions (diesel–water, biodiesel–water, diesel–biodiesel–water) for diesel engines, among other things, concluding that oxygen enrichment and oxygenate additions with emulsions can reduce the viscosity of emulsion, and it also reduces smoke, HC, and CO emissions. Chang et al. [108] have said that fuel blends that contain biodiesel are known to produce greater NO_x emissions than fossil diesel, which could be a barrier to a greater degree of adoption in the fuel market; one solution to this problem would be the addition of water with oxygenated compounds (acetone, butanol, and ethanol).

By summing-up, adding ethanol-based oxygen compounds (ethanol, methanol) to petroleum diesel fuels leads to the improvement of physico-chemical properties for the resulting blended fuel, which in turn, leads to improved combustion, with the benefit of reduced CO_2, NO_x, Smoke, HC, and PM emissions. The problems that arise with these blends are related to the miscibility of alcohols in petroleum diesel fuel, which can be solved by using some additives. Biodiesel itself helps to improve miscibility.

4.2. Influence of Different Diesel–Biodiesel–Alcohol Blends on CI Engine Operation

The papers that dealt with this subject were presented and briefly discussed in the previous subsection. Now, it is our intention to present in a simplified form the findings on the effects of different diesel–biodiesel–alcohol blends on CI engine operation (e.g., combustion characteristics, different performance parameters, and emissions).

4.2.1. Combustion Characteristics

Combustion is a very complex phenomenon that ultimately defines the energetic and ecologic performance of an IC engine. Concerning the effects of using a certain fuel, the combustion characteristics directly determine whether or not this fuel is suitable for proper engine operation [79].

Table 7 summarizes the conclusions of the various quoted authors on a number of combustion characteristics: the duration of combustion (DoC), the rate of heat release (RoHR), the ignition delay (ID); the cylinder pressure (p_{cyl}), and the cylinder temperature (T_{cyl}). The authors consider that it is not the case to discuss further on the reasons which explain the results that are introduced in Table 7. They are thoroughly discussed in the quoted references. Consequently, as said before, the authors' enterprise was to gather in one place the main conclusions on previous scientific studies about the subject that was approached by this review. The same was done in the following subsections (Sections 4.2.2 and 4.2.3).

4.2.2. Engine Performance

As before, the conclusions of the various quoted authors about different parameters defining engine performance are summarized in Table 8: brake-specific fuel consumption (BSFC), brake thermal efficiency (BTE), brake power (BP), exhaust gas temperatures (EGT), and the indicated mean effective pressure (IMEP). We chose to use the term "performance" because this is a generic term, and it may accept different parameters that may not be classified only in one explicit/dedicated category. Out of the above listed parameters, BSFC and BTE are actually images of the same key-feature of an IC engine:

energetic performance, BTE = $(\text{BSFC}\cdot\text{LHV})^{-1}$. Consequently, some of the results from Table 8 seem contradictory. However, we decided to still present these findings as it may be useful to others.

4.2.3. Emissions

As above, Table 9 summarizes the conclusions of the various quoted authors about the engine's gaseous and solid emissions: NOx, smoke, CO, UHC, PM.

5. Summary and Conclusions

The automotive industry is an important sector for the world economy, providing jobs and a positive contribution to trade balance, which is essential for world prosperity. However, today, road transport is the subject to many political debates, as it is responsible for an important part of GHG and pollutants that are emitted into the atmosphere. Therefore, any means which could reduce negative impacts on the environment are under intense scrutiny. Amongst these means, alternative biofuels have and will continue to have an important role in the future of road transport.

This being the context, this paper dealt with the impacts of some of the alternative fuels used as blended fuels on CI engine operation. The main findings of this review can be summarized as follows:

1. the importance of using alternative biofuels can be attributed to the following aspects:
    a. the need to pursue energy sustainability by increasing the use of renewable fuels, thus diminishing concerns of limited fossil fuel energy;
    b. improving the energetic and ecological performance of the IC engine through the better physico-chemical properties of these alternative fuels, compared to those of fossil fuels;
2. the effects of using diesel-biodiesel-alcohols blends fuels are:
    a. regarding combustion characteristics, compared to the case of using fossil diesel fuels: combustion duration decreases in all studied cases; the maximum rate of heat release increases with an increase in the ethanol fraction in the diesel–ethanol blends, and it is slightly lower for biodiesel–diesel–ethanol blends; the ignition delay increases with the increase of the ethanol fraction in diesel–ethanol blends, and it slightly decreases for biodiesel–diesel–ethanol blends or with the addition of a CN improver; cylinder pressure increases with the increase of the ethanol fraction in diesel–ethanol blends, and it slightly decreases or remains unaltered for biodiesel–diesel–ethanol blends;
    b. concerning engine performance, compared to the case of using fossil diesel fuel: the brake specific fuel consumption is higher in all studied cases; the brake thermal efficiency increases or is comparable; the brake power is very comparable or slightly lower; for exhaust gas temperatures, minor variations were observed; the indicated mean effective pressure has minor variations, or it decreases in cases of more than 35% ethanol in the fuel blends.
    c. while NO_X, smoke, and PM emissions seem to be lower, the improvement of HC and CO emissions depends considerably on the type of fuel blend (ratio and fuels used), and on the engine operating parameters.

Furthermore, this review equally points out that the massive use of alcohol–diesel blends may be limited by the following factors:

1. some properties of the alcohol blends, such as stability, lubricity, viscosity, and CFPP, which has a negative influence upon the injection system;
2. the low cetane number that affects the combustion process is another important limiting factor;
3. the fuel storage and handling problems that are derived from the high volatility of alcohol; in this respect, different technical modifications in the fueling system are necessary; for instance, to

avoid vapor locks, special systems for recovering of fuel vapors are necessary, especially when increasing the alcohol amount.

Finally, this review also showed that sometimes there are noticeable differences in the scientific literature for the same subject. For instance, some authors have argued positively for the effect of the use of biofuels, while others do not have the same viewpoint; different values for the same indicators (e.g., energy efficiency) were also found. The latter may be explained by the fact that bio-fuels are made from various types of biomass by using different processes for production; moreover, the features of bio-fuels (including their physico-chemical properties) are the result of different measurement techniques and different methods of calculation. Thus, perhaps in this field, there may also be a need for increasing the degree of standardization.

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Abbreviations

The following abbreviations are used in this manuscript:

ASTM	American Society for Testing and Materials
BEV	Battery electric vehicle
BP	Brake power
BSFC	Brake-specific fuel consumption
BSG	Brewers' spent grain
Bx	Biodiesel blend ratio (i.e., for x = 0, B0, meaning no biodiesel; for x = 100, B100, meaning no diesel fuel)
BTE	Brake thermal efficiency
CBG	Compressed biogas
C&D	Construction and demolition
CEN	Commission Européenne de Normalisation/European Committee for Standardization
CFPP	Cold filter plugging point, [°C]
CI	Compression ignition (engine)
CN	Cetane number
CNG	Compressed natural gas
CO	Carbon monoxide
CO_2	Carbon dioxide
COV	Coefficient of variance, [%]
CP	Cloud Point [°C]
Dx	Diesel blend ratio (i.e., for x = 0, D0, meaning no diesel fuel; for x = 100, D100, meaning pure diesel)
DxEyBz	x% pure diesel + y% ethanol + z% biodiesel blends
DxMyBz	x% pure diesel + y% methanol + z% biodiesel blends
Ex	Ethanol blend ratio (i.e., for x = 0, E0, meaning no ethanol; for x = 100, E100, meaning pure ethanol)
EC	European Commission
EGT	Exhaust gas temperatures
EN	European Norms
EROEI	Energy return and other energy related issues
EU	European Union
EV	Electric vehicles
FA	Fatty acids
FAME	Fatty acids methyl ester
FP	Flash point [°C]

GHG	Greenhouse gas
H_2	Hydrogen
HC	(Unburnt) hydrocarbons
HDV	Heavy-duty vehicles
HFC	Hydrogen fuel cell
HFRR	High-frequency reciprocating rig
HPSS	High pressure supply system
ICE	Internal combustion engine
ID	Ignition delay
ILUC	Induced land-use change
IMEP	Indicated mean effective pressure [bar]
ISFC	Indicated specific fuel consumption
LCA	Life-cycle assessments
LDV	Light-duty vehicles
LHR	Low heat rejection
LHV	Lower heating value
LNG	Liquefied natural gas
LPG	Liquid petroleum gas
LPSS	Low-pressure supply system
LTC	Low temperature combustion
LTFT	Low Temperature Flow Test
MSW	Municipal solid waste
Mx	Methanol blend ratio (i.e., for x = 0, M0, meaning no methanol; for x = 100, M100, meaning pure methanol)
NG	Natural gas
NO_x	Nitric oxides
PC	Passenger cars
PHEV	Plug-in hybrid electric vehicles
PM	Particulate matter
PP	Pour point [°C]
RON	Research octane number
SIE	Spark ignition engine
SO_2	Sulfur dioxide
SS	Supply systems
UHC	Unburned hydrocarbons
ULEV	Ultra-low emission vehicles
USA	United States of America
VHG	Very high gravity
ZEV	Zero–low emission vehicles

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