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Review

Promising Bioalcohols for Low-Emission Vehicles

Manju Dhakad Tanwar [1,*], Felipe Andrade Torres [2], Ali Mubarak Alqahtani [3], Pankaj Kumar Tanwar [1], Yashas Bhand [1] and Omid Doustdar [4]

1 Organic Recycling Systems Limited, Navi Mumbai 400703, India
2 Department of Mechanical Systems, Center of Exact and Technological Sciences, Federal University of Recôncavo of Bahia, Cruz das Almas 44380-000, Brazil
3 Mechanical Engineering Department, Jubail Industrial College, Jubail 31961, Saudi Arabia
4 Department of Mechanical Engineering, School of Engineering, University of Birmingham, Birmingham B15 2TT, UK
* Correspondence: manju.tanwar@organicrecycling.co.in

Abstract: In recent decades, many kinds of research have been conducted on alternative fuels for compression ignition (CI) engines. Low/zero-carbon fuels, such as bioalcohols and hydrogen, are the most promising alternative fuels and are extensively studied because of their availability, ease of manufacturing, and environmental benefits. Using these promising fuels in CI engines is environmentally and economically beneficial. The most common alcohols are methanol, ethanol, isopropanol, propanol, butanol, n-butanol, tert-butanol, iso-butanol, and pentanol. The primary objective of this review paper is to examine the impact of bioalcohols and their blends with conventional diesel fuel in CI engines since these fuels possess characteristic properties that impact overall engine performance and exhaust emissions. This research also indicated that alcohols and blended fuels could be used as fuels in compression ignition engines. Chemical and physical properties of alcohols were examined, such as lubricity, viscosity, calorific value, and cetane number, and their combustion characteristics in compression ignition engines provide a comprehensive review of their potential biofuels as alternative fuels.

Keywords: alternative fuels; bioalcohols; fuel properties; emission; CI engines

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1. Introduction

According to *World Energy Balances*, fossil fuels provided around 81% of the total primary energy supply in 2019, with renewables providing nearly 14% [1]. Although the concern about oil reserve depletion has driven research into petroleum-based fuel substitutes, hydro, wind, and solar energies are aimed at large-scale power production. The transportation industry has the biggest need for petroleum-based derivatives, accounting for approximately 60% of total demand, with road transportation accounting for the majority [2,3]. Furthermore, scientists are investigating alternative fuel resources in response to rising fossil fuel prices, detrimental greenhouse gas emissions, and energy production diversity [4,5].

Conventional transportation infrastructure continues to be a major source of pollution, influencing overall greenhouse gas emissions and their impact on human health [6]. Although fully electric vehicles have been found to reduce pollutants, their extremely high cost and unreliability of energy output imply that they are not a short-term solution. This has resulted in a search for alternative fuels and lubricants, including low-carbon and zero-carbon fuels [7]. Solar energy, as an alternative source of energy, can still be used in a variety of ways. Solar rays are used by plants for photosynthesis, which converts them into stored energy in chemical bonds within plant tissue, which can be converted to fuel through different thermos-chemical processes [8]. Despite that electrification has been increasing for passenger vehicles fleet, both EVs (electric vehicles) and HEVs (hybrid electric vehicles), it is essential to focus on the development of advanced combustion and aftertreatment techniques as a short- and medium-term plan [9]. In this scenario, biofuel (low/zero-carbon fuels) produced from renewable sources is considered the most viable alternative, in a short-term scenario, for replacing conventional diesel fuel in compression ignition engines and is still and will continue to be necessary for cleaner mobility.

The industrial revolution resulted in the production of steam and waterpower, and since then, energy sources have changed to meet every increasing human demand. In 1900, Rudolph Diesel, the first diesel cycle engine designer, used vegetable oil (groundnut oil) as a fuel for his prototype [6]. His objective was to enhance efficiency and reduce the cost and size of engines in comparison to large steam engines so that smaller businesses could afford the machinery [8]. It was also suggested that using vegetable oil will significantly aid countries' agricultural efforts [10]. Many countries, such as Brazil and the United States, have diversified their biofuel production. For example, after the 1970s oil crisis, Brazil deployed ethanol fuel from sugar cane; however, the benefits began to fade due to an increase in ethanol fuel costs in 1989 [6]. Over the last few decades, there has been an increase in global warming and climate change caused by fossil fuels, specifically petroleum-based liquid fuels, natural gas, and coal [11]. This made biofuels derived from vegetable oils a promising alternative fuel [4].

Because of the oil resource, human health, and environmental impacts of fossil fuels, many researchers investigate the usage of vegetables to produce alternative fuels, usually edible vegetables. Most investigations have been done based on the use of fuels in diesel engines without any modification. Based on the literature, many researchers have attempted to review important investigations on biodiesel production processes, physical and chemical properties, and their performance and emissions characteristics as compression ignition engine fuels. Among the alternatives, alcohol fuels as low-carbon fuels possess certain advantageous properties that give them the potential to lower pollutants and CO_2 emissions from IC engines. However, alcohols also have some limitations in their application, such as miscibility, lower cetane number, and lower heating value than conventional diesel fuel. In this review paper, the potential future directions for bioalcohol fuels for low-emission vehicles have been comprehensively investigated in a way toward net-zero emission transportation.

2. Why Bioalcohols?

Alcohol fuels are once again becoming a popular keyword for clean fuel utilization as a means of mitigating global climate change and meeting the needs of less-used local energy sources. As raw feedstock, lignocellulosic biomass and algae could be derived from grain-based raw materials. It is critical to use locally available, underutilized feedstocks for local energy security and distributed energy infrastructure. Alcohols as low-carbon fuels such as methanol, ethanol, propanol, and butanol are the most common alcohols for automotive applications [12–14]. Investigations on the effects of propanol isomers (n-propanol and isopropanol) on combustion engines are uncommon and mostly limited to spark ignition (SI) engines. Although the above short-chain alcohols' high volatilities, low viscosities, and high oxygen contents could improve spray combustion and emissions, some disadvantages, such as high heat of transformation of vaporization, low heating values, and low cetane numbers (CNs), cause a lower proportion of applications in compression ignition (CI) engines.

Furthermore, when combined with diesel, a low alcohol concentration exhibits phase separation, cold start problems (i.e., ethanol-C_2H_5OH), stability issues, storage problems, and corrosion (i.e., methanol-CH_3OH) [15]. Even in the case of diesel/biodiesel/ethanol ternary blends, the proportion of ethanol in the mix should be kept as low as feasible because NO_x emissions from ternary blend combustion result in higher values than diesel fuel [16]. As a result, higher alcohol combined with diesel oil has recently received significant attention as an alternative fuel for diesel engines. Butanol (C_4H_9OH), pentanol ($C_5H_{11}OH$), hexanol ($C_6H_{13}OH$), octanol ($C_8H_{17}OH$), decanol ($C_{10}H_{23}OH$), dodecanol

($C_{12}H_{25}OH$), and phytol are all straight-chain alcohols with four or more carbon atoms ($C_{20}H_{41}OH$). Butanol and pentanol have lately gained significant attention as alternative fuels for diesel engines since they release fewer greenhouse gases and hazardous pollutants.

2.1. Methanol (CH_3OH)

CH_3OH is the simplest form of alcohol and is colourless, odourless, and poisonous. It is corrosive to some materials and is frequently created from a combination of sources, including synthetic gas (syngas), formic acid, formaldehyde, and methane. CH_3OH is hygroscopic, which causes phase separation in CH_3OH-gasoline blends [17]. Methanol is beneficial in the reduction of NO_x and particles due to its high oxygen content and also its high latent heat of evaporation.

Methanol has some disadvantages as a fuel additive: low lubricity, low viscosity, low cetane number, and ignitability. An enhancer of the cetane number and lubricity is needed to solve this problem. According to Cheung et al. [17], biodiesel and methanol-blended fuels have a higher fuel consumption because they have a lower heat value than oxygenated fuels. Compared to methanol, ethanol has a higher energy density, is nontoxic, and is available in large quantities, reducing racers' vulnerability to price increases and supply disruptions.

Additionally, when the proportion of methanol in mixed fuels increased, NO_x emissions were reduced. Researchers concluded that methanol's cooling impact dominated NO_x generation in blended fuels. Because of the reduction in soot generation, methanol-mixed fuels produce fewer particulates [18].

Methanol as an alternative fuel can be produced in a variety of sources, including natural gas, biomass [19], and coking plants. During the continuous manufacturing of biodiesel with supercritical methanol [20], the gas [21] can be recovered by flash evaporation. Many synthesis techniques have emerged, including low-pressure synthesis, novel designs, and sophisticated reforming processes [18]. Biomass processing is the most profitable method for producing methanol from renewable resources [22,23]. Reno et al. [24] conducted a life cycle assessment on the production of methanol from bagasse, and the results showed that the production of methanol from bagasse is a viable alternative in terms of output–input ratio. Holmgren et al. [25] developed the synthesis chain due to the interdependence of the various stages of the biomass and methanol gasification process; the results can be used to calculate energy efficiency and greenhouse gas emissions economic indicators for independent and integrated methanol synthesis plants with biomass gasification. Clausen et al. [26] investigated the viability of a methanol production system based on biomass gasification and water electrolysis. Methanol is a substance with numerous advantageous features that make it valuable as an energy source, chemical raw material, component, or intermediate in a variety of consumer products. Replacing existing generation fossil fuels with cleaner fuels has the potential to reduce demand as well as the economic expenses associated with traditional increased pollution [27,28].

2.2. Ethanol (C_2H_5OH)

C_2H_5OH can be a clear, colourless, poisonous liquid with a distinct odour. It has a higher octane rating than gasoline, making it ideal for combining as a liquid fuel. Ethanol has less energy per volume than gasoline while denatured ethanol (98% C_2H_5OH) has around 30% less energy per volume than gasoline [29]. Because C_2H_5OH includes oxygen, using it as a gasoline addition reduces carbon monoxide gas emissions by up to 25% [30]. It is also soluble in both polar and nonpolar solvents, has a higher vapour pressure than gasoline, and has a 35% oxygen content. C_2H_5OH has a limited half-life in surface water and subterranean aquifers, reducing the risk to aquatic organisms significantly. Furthermore, even when it is spilt, the environmental impact is minor. Because ethanol dissolves swiftly in the natural environment, biodegradation occurs quickly in soil, groundwater, and surface water, with projected half-lives ranging from several hours to ten days [31].

2.3. Butanol (C_4H_9OH)

Butanol has mostly been employed in the cosmetics and pharmaceutical sectors as a solvent, chemical intermediary, and extractant as well as in the assembly of butyl acrylate and methacrylate [32–34]. When created biologically through the fermentation of starchy and sugar feedstock, this alcohol class is commonly referred to as biobutanol.

The use of ethanol blended with gasoline increases the octane rating, including drawbacks such as metal component corrosion and vapour lock. Such troubleshooting is frequently resolved by modifying the engine and equipment, but the addition of alcohols with large carbon numbers, such as biobutanol, allows use in the existing system without requiring any changes. Alcohols with high carbon contents are frequently produced from syngas via a catalytic process involving modified Fischer–Tropsch or methanol catalysts. In recent years, researchers have taken an interest in n-butanol as an alternative biofuel to bioethanol. Even though most studies and enterprises have focused on ethanol as a fuel rather than butanol [35], butanol may be a significantly superior direct option.

Because n-butanol has a lower Reid vapour pressure than ethanol, it is less evaporative/explosive [7]. Because the air–fuel ratio and energy content of n-butanol are similar to those of gasoline, it is commonly mixed with gasoline in larger ratios than ethanol for use in existing cars without modification [8]. Furthermore, the high octane number makes the alcohol more appropriate for use in combustion engines. A fuel with a lower octane level is more prone to knocking (very quick and compression ignition) and can reduce efficiency. Engine damage might also result from knocking. Unlike other alcohols, the Environmental Energy Company (US) proved that n-butanol is frequently utilized as a full substitute for gasoline [10].

Although ethanol is promising as a biofuel, recent studies have shown that ethanol is a serious problem that must be solved before it can be used in engines. It is corrosive and can cause defects in the existing fuel line layout and injection system [36]. Ethanol also has a very low flash point and evaporation capacity, so extra precautions need to be taken when using it [37].

In addition to these shortcomings, ethanol can also reduce local air quality, thereby endangering human health. Compared with ethanol, butanol is a more promising choice [36,38,39]. For carbon atoms, the atoms can form a straight or branched chain [40]. The more carbon atoms, the higher the energy content of the alcohol fuel. In addition, compared with ethanol, butanol has less toxicity and higher energy consumption [36,41]. It can also be made from cellulose waste from agricultural products or even fibre residue from sugar factories [42,43].

Compared with ethanol, butanol is much less corrosive, which allows it to be transported through existing traditional fuel transportation systems [36,44]. Since butanol is less corrosive, it can also be used in automobiles without modification [45,46]. If it is contaminated by water, it is difficult to separate from the base fuel (gasoline/diesel). It also contains energy units similar to gasoline, but the specific energy per litre is 25% higher than that of ethanol [36]. The performance results in higher engine output, so the vehicle can easily increase butanol consumption. As we all know, due to the complexity of manufacturing, long-chain alcohol fuels have not been widely used; today, the production cost of butanol is gradually decreasing; rapid progress in production technology has made it possible to produce more butanol [47]. Butanol in gasoline engines is not as extensively studied as methanol or ethanol, despite the increasing number of publications. The following article examines the power, combustion, and performance effects of mixing butanol with gasoline. There are several loopholes in adding butanol to gasoline engines that deserve further study based on the comments in [47].

2.4. Pentanol ($C_5H_{11}OH$)

Pentanol blended with conventional fuels has fewer greenhouse gas emissions, leading it to gain a lot of attention as an alternative fuel for diesel engines. Because of pentanol's high potential as a blending component and its physicochemical features, binary blends, such as diesel/pentanol and biodiesel/pentanol, as well as ternary blends, such as diesel/biodiesel/pentanol, have been researched primarily within conventional diesel. Diesel, biodiesel, pure vegetable oil, and pentanol quaternary mixes were also studied. There is limited information available in the literature about the use of pentanol in advanced compression ignition (CI) engines. Diesel/pentanol mixes with exhaust gas recirculation (EGR) technology could lower NO_x and soot emissions from the CI engine at the same time. Furthermore, diesel/pentanol blends emitted more CO and hydrocarbon (HC) emissions than diesel oil. However, by combining the cetane improver with the blends, CO and HC emissions were dramatically reduced. Up to 45–50% n-pentanol/diesel blends can frequently be used safely in diesel engines with no engine modifications or additives. However, in terms of kinematic viscosity, lubricity, and oxidation stability of diesel/pentanol blends, pentanol concentrations should be kept below 10%. In general, investigations using biodiesel/pentanol blends in CI engines revealed a reduction in CO, HC, NO_x, and smoke emissions when compared to straight biodiesel. Researchers focused on diesel/biodiesel/pentanol blends for ternary blends. The emission characteristics of CO, HC, NO_x, and smoke opacity showed distinct trends that were consistent with the pentanol fraction in the ternary blends, particularly in [31].

2.5. Production of Bioalcohols

Alcohol fuels are frequently generated from all available organic elements, such as gas, coal, biomass, and organic waste. Alcohol fuels are primarily made from corn and sugar cane as raw materials, although the synthesis and manufacturing of alcohol fuels from nonfood crops and agricultural leftovers is a current focus. Energy crops, cellulosic residues, and wastes are examples of nonfood lignocellulosic biomass. Grain-based ethanol has been tried as the main generation to vary to second-generation cellulosic ethanol and other advanced cellulosic biofuels. After the 2000s, cellulosic ethanol was identified as a crucial biochemical method for converting biomass to fuels [48]. Third-generation algae-based feedstock for alcohol fuels emerged as a possibility as a big staple for the future alcohol fuel sector.

Figure 1 depicts the generations of raw feedstock used in the production of alcohol fuel as well as the most visible material used in different countries.

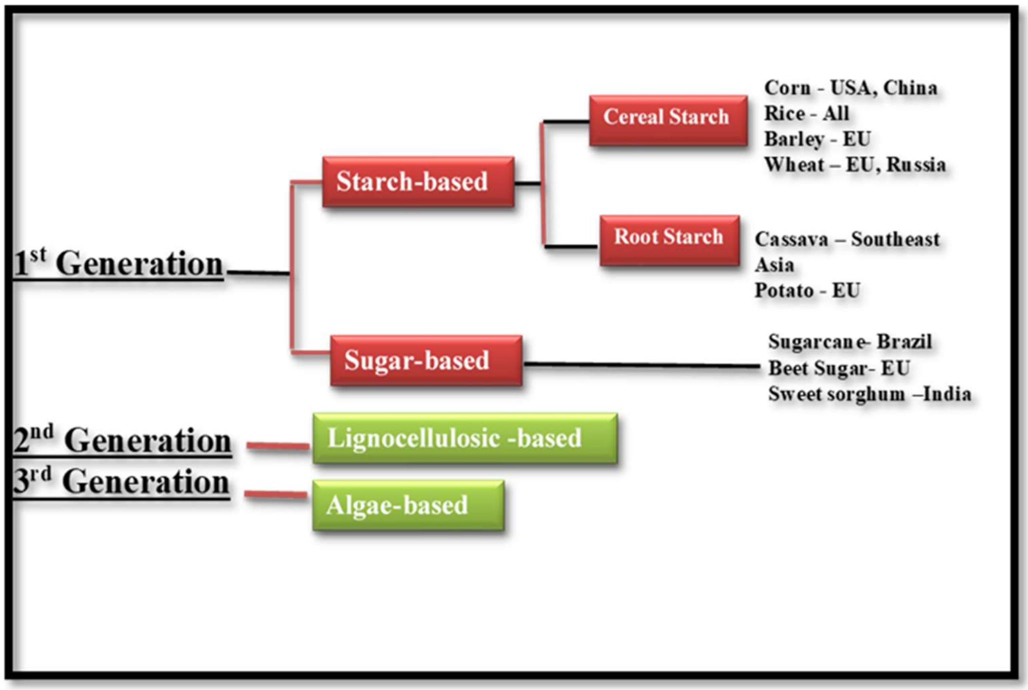

Figure 1. Raw materials used in the manufacturing of bioethanol in several nations (modified figure from Ref. [49]).

There is a clear difference between developing and developed countries in terms of priority selection, but the underlying notion should be the same: use locally accessible, underutilised feedstock, and choose feedstock that has a tipping fee to treat the feedstock as municipal/industrial wastes. However, when wastes are used as feedstock, it should be highlighted that the not-in-my-backyard (NIMBY) problem is now a common occurrence in nearly every country. The European Commission recently voted against the use of biofuels synthesised from biomass derived from food crop sources by 2030. For the timely commercialization of cellulosic bioethanol, a second-generation bioalcohol, intensive interdisciplinary efforts are expected.

Ethanol is made by either using coal and biomass syngas or synthesizing it from petroleum-based ethylene. It can also be obtained by fermenting sweet substances.

On the other hand, bioethanol is produced by fermenting regenerative biomass or through the procedures of distillation and purification. The United States and Brazil are the world leaders in the production of bioethanol, corresponding to roughly 85% of global production in 2021 [50]. The main feedstocks used for the production of bioethanol are corn in the United States and sugarcane in Brazil. Bioethanol Figures 2 and 3 show the overall manufacturing process of bioethanol. Pretreatment involves converting biomass into alcohol fuels. The first step to preparation is reducing the size and uniformizing the density/size. Often, steam, hot water, or slight carbonization is used as a pretreatment. Basically, saccharification (hydrolysis) is the process of breaking down cellulose/hemicellulose to produce sugars, such as glucose and xylose. Based on the concentration ratio and the adsorption ratio of the component enzymes, three distinct cellulase enzymes perform the overall hydrolysis. In fermentation, sugar and starch are converted into ethanol by microorganisms. Concentrating and cleaning the ethanol produced by distillation is called distillation and rectification and last is drying.

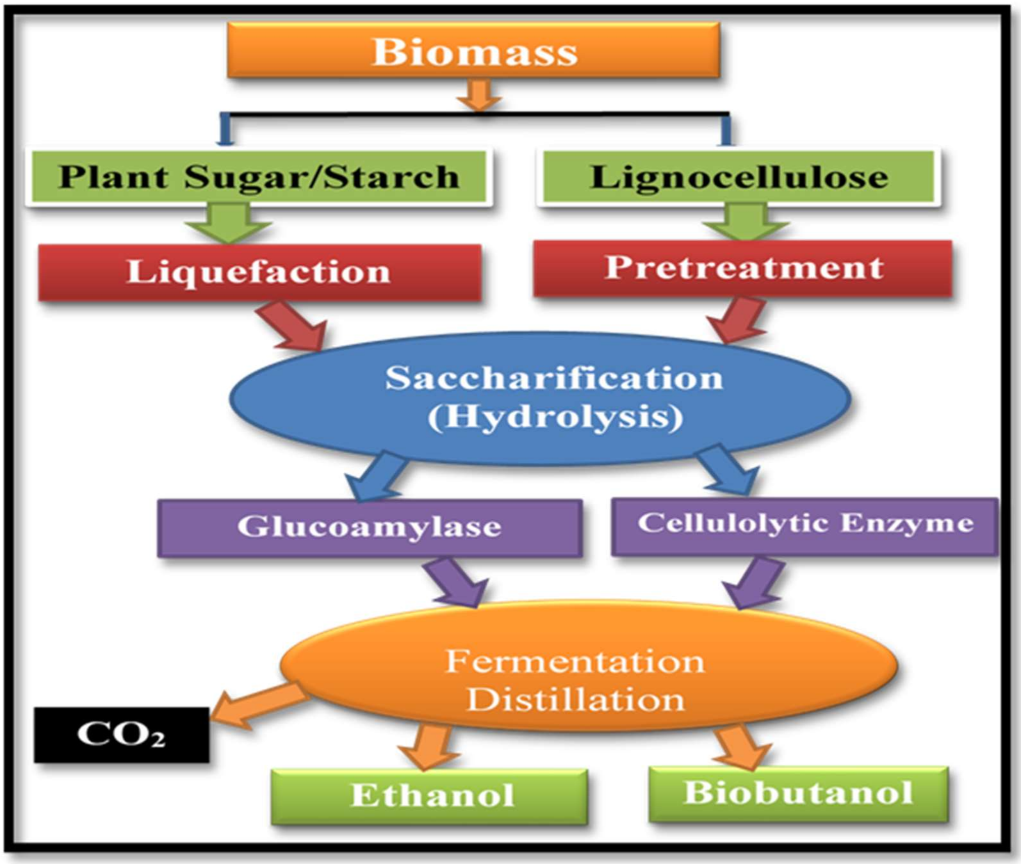

Figure 2. Biochemical conversion of biomass to alcohol fuels (modified from Ref. [30]).

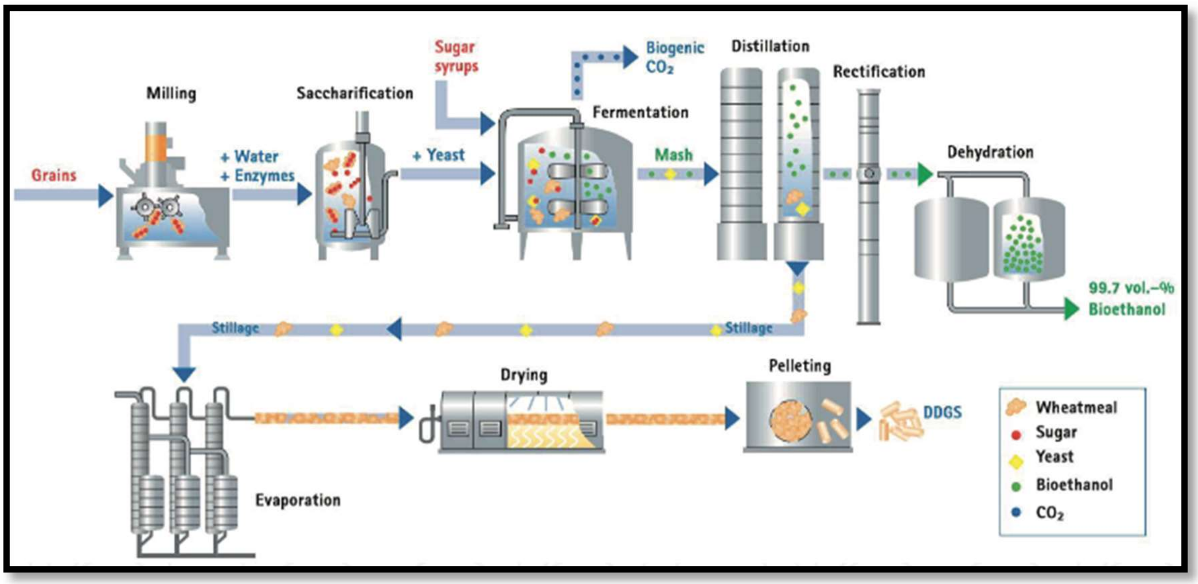

Figure 3. Bioethanol production process diagram [51].

Agricultural waste often comprises a high concentration of alkali metals (potassium and sodium) and other inorganic elements, such as calcium, magnesium, and, in rare cases, chlorine and sulphur. When converting these wastes to alcohol fuels using thermal techniques, alkaline metal components act to supply low-melting salts, causing clogging and other ash-related difficulties. In contrast, the fermenting approach can lessen the likelihood of ash issues, which may be a desirable component of the manufacturing process. Rice husk, in particular, contains over 90% ash, and rice straw contains almost 30% silica, though this varies depending on rice stock, climate, and geographical context.

These inorganic materials act as a barrier to the thermal conversion process, and fermenting is frequently a better technique to transform this biomass fuel. To supply ethanol, starch and carbohydrates are employed as first-generation raw materials. In 2013, about 90% of bioethanol was created from starch and carbohydrate. Major crops include corn, grain, and cassava (Figure 4). The degradation of the environment during crop cultivation and ethanol production as well as the exploitation of vital food resources as fuel production are disadvantages. As a result, significant agricultural countries such as the United States, Brazil, and China are currently major producers of biofuels, including alcohol fuels. In the United States, 95% of ethanol is derived from starch [52].

As the production of bioethanol from grain-based raw materials has recently been constrained, second-generation bioethanol production from non-grain-based biomass is now gaining a constantly growing importance. Bioethanol is quickly becoming a viable alternative to gasoline, and it is often made from the starch of corn and cassava or the sugary contents of sugar cane and sugar turnip. Bioethanol is also made from crop wastes that contain lignin and cellulose. Sugar and starch are easily converted to bioethanol, but their supply and cost are limited. As a result, efforts are being made to investigate various procedures for producing bioethanol from lignocellulose-based raw materials to capitalize on their vast supply in nature while also ensuring market viability [29].

Kandasamy et al. [53] investigated the ability to supply alcohol from lignocellulosic material; nevertheless, while not a protein chemical reaction degradation, the ultrasound technique produces more alcohol than that normally described in the literature [54].

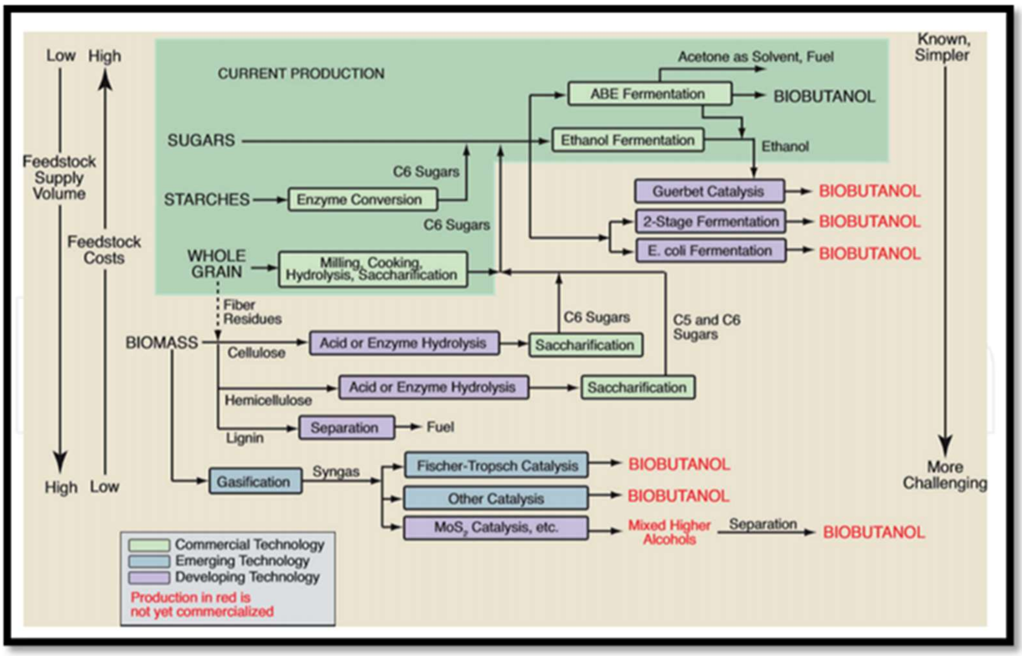

Figure 4. Biobutanol production process [53].

According to the authors, the bulk of plastic alcohol production units in the EU are only on a pilot or demonstration scale. According to Cotana et al. [55], in the context of a greater focus on the assembly of second-generation bioethanol, the use of lignocellulosic feedstock, monocot genus australis (common reed, which could be a perennial grass growing in wetlands or close to upcountry waterways), is an especially good option. In the mentioned research, a steam explosion was used to optimize the bioethanol production process from the monocot genus australis. The entire approach had a potency of sixteen and a 56 g ethanol/100 g staple. Eggert et al. [56] conducted a study to promote second-generation biofuels, specifically cellulose-based organic chemistry ethanol; additionally, the authors explore relevant regulations that could aid in the fight for those fuels. They believe that first-generation biofuels have been and continue to be heavily supported, which has contributed to the increased production and usage of such fuels.

The question is whether primary-generation biofuels pave the way for second-generation biofuels. Thus, they have the advantage that even if favourable conditions for innovation and scale efficiencies are created, necessary value reductions may not be realized. The GHG emissions from land-use change, which are linked to the large-scale increase of plastic feedstock, may counterbalance the gains from dynamic fuel.

Switchgrass (a warm-season grass) looks to have a high potential yield in marginal areas, making it an excellent nonfood bioenergy feedstock for bioethanol production in China [57]. Hansdah et al. [58] discussed the potential for producing bioethanol from the *Madhuca indica* flower, which is a tropical forest tree that grows abundantly in Asia and Australia. *Madhuca indica* seeds, on the other hand, are a potential feedstock for biodiesel production in India. Chen et al. [59] examined *Landoltia punctata* (a worldwide hydrophyte strain with the ability to collect starch) and its application as a novel feedstock for bioethanol production. To increase ethanol production, pectinase pretreatment was used, which resulted in the highest alcohol concentration reported to this date and a mistreatment hydrophyte because of the feedstock. Moreover, the invention of recent raw materials (filamentous fungi) and also the improvement of the method of obtaining bioethanol by integrating first- and second-generation alcohol production processes are described in [60], which that reports a discount of energy consumption by a pair of 5% and a rise of alcohol production by four-times. Connolly et al. [61] have elaborated different ways of manufacturing transport fuels, including alcohol and alcohol in terms of the resources and conversion processes used and the transport demands met. In keeping with the results of this study, the best answer at the present consists of liquid fuels, for instance, alcohol or dimethyl ether. Biomass chemical action and electrolysis area unit technologies require improvements. As introduced before, the third generation of bioethanol feedstocks area unit protoctist contains lipids, proteins, carbohydrates/polysaccharides, and skinny plastic walls. In keeping with [32], while "algal lipids area unit principally extracted and reworked into biodiesel, the left-over cake of starch (the storage component) and polysaccharide (the skinny wall component) may be reborn into bio-ethanol". Moreover, the ensuing combined biodiesel/bioethanol method additionally offers the advantage of manufacturing CO_2 fermentation, which might be captured and used.

2.6. Properties of Bioalcohols

Alcohols can be produced from fossil fuels and lignocellulosic biomass via synthesis gas. These alcohols can be used as neat or blended in current engines. From the early years of research in the area of alternative fuels, alcohol was evaluated as a fuel alternative for diesel vehicles [17]. Methanol (CH_3OH), ethanol (C_2H_5OH), propanol (C_3H_7OH), butanol (C_4H_9OH), and pentanol ($C_5H_{11}OH$) are five alcohols that will be reviewed in this section. Short-chained alcohols such as ethanol, propanol, and butanol have not been considered neat fuels for CI. However, they can be used as blends with fossil diesel fuels or biodiesel [62,63]. Generally, alcohols in CI engines reduce CO_2 and PM emissions with some changes in their cetane index and combustion process. Alcohol-based fuels can easily be used as blends in a diesel without any major changes and modifications to the engine [64].

Before using any new alternative fuels in an engine, it is fundamental to investigate their chemical and physical properties. This analysis shows how it is possible to use these new fuels without any major modification or property enhancer. The advantages of alcohol application in an engine regarding its reduction of soot formation and particle emissions make it more attractive than other alternative fuels.

In the 1970s in South Africa and in the 1980s in Japan, Germany, and the United States, ethanol was used as a fuel in diesel engines [62]. Ethanol combustion in diesel engines led to reductions in particulate matter emissions. Ethanol has low ignitibility, low lubricity, limited miscibility, and a low heating value, which makes its blending proportions limited. The best solution to use ethanol as an additive is to blend it with biodiesel to improve the stability, cetane number, and lubricity of blends [65]. Lapuerta et al. [63] reported that biodiesel fuel acts as a stabilizing component in ethanol-diesel bends. A higher ethanol content in blends increases the total hydrocarbon emissions, decreases smoke emissions, and may present a nuclei mode because the high THC emissions lead to the nucleation of hydrocarbons. Researchers concluded that the effect of the oxygen content in these blends on the particle size depends upon its functional group. Ethanol has low energy density and high hygroscopicity in comparison to gasoline.

Methanol is an alternative, renewable, and environmentally and economically attractive fuel; it is considered to be one of the most suitable fuels for traditional fossil fuels. Recently, methanol has been used as a substitute for traditional internal combustion engine (IC) fuel to solve some environmental and economic problems. Significant progress has been made in recent major research projects that is worth reporting. Methanol is considered to be one of the most suitable fuels for engines, for example: (a) it can be used in gasoline engines with high compression ratios and can replace diesel in some professional applications; (b) it can be used in intake manifold injection engines; (c) it can be used in high compression SI direct injection engines; (d) it can be used in direct injection engines; and (e) it can be used in medium power and high compression turbine engines with port injection [66–70].

Propanol as a possible alternative fuel can be produced from biomass through various kinds of processes. It has a higher energy density and cetane number compared to ethanol and methanol [71]. Low carbon chain length alcohols, such as methanol and ethanol, have been used extensively in SI engines because of their good antiknock properties and lower gaseous emissions, such as CO and THC [72–74]. Short-chain alcohols with a low cetane number in diesel engines result in a significant increase in the duration of ignition delay [75]. The addition of ethanol or butanol has been observed to have a longer ignition delay and a significant reduction in PM formation [76] because an increase in fuel ignition delay allows more time for fuel and air mixing before the start of combustion and leads to fewer fuel rich-zones and a decrease in PM emissions [75]. These fuels are not of good compatibility with diesel fuels due to their poor blending stability, poor cetane number, and lower heating value.

Butanol is a promising fuel with several advantages over ethanol, such as higher energy content, less corrosive, better miscibility than current fuels, and lower water absorption [77,78]. The same production process for ethanol can be adapted to produce butanol from different feedstocks. There are other technologies, such as fermentation and transesterification [79], with lower required energy, which lead to the production of desirable alcohols, such as butanol [71]. The THC emissions from ethanol blended with diesel are higher than butanol blended with diesel due to the higher heat of vaporization of ethanol [77] Longer chain alcohols are more suitable for blending with diesel fuel. They have proper lubricity, high calorific value, lower volatility, a high flash point, high viscosity, and cetane number compared to lighter alcohols [69,71].

It has been discussed that pentanol, butanol, and other higher alcohols have a low affinity for water and a higher energy density and fit well into current vehicles without any needed modification to the vehicle's engine [80]. The literature has shown that pentanol has good physical properties as an alternative fuel [80]. Pentanol is also an excellent alternative fuel because it can be produced from biological processes such as microbial fermentation using micro-organisms and biosynthesis from glucose [71]. Pentanol, a long-chain alcohol, requires even less production energy than butanol compared to other alcohols [81].

Heavier alcohols are more advantageous than light-chain alcohols due to their better blending stability, hydrophobic properties, higher cetane numbers, heating value, and low carbon counterparts [82–84]. Butanol as a blend with diesel fuel has been extensively studied in diesel engines [85–89]. It was concluded that the alcohol content in a diesel engine increased ignition delay due to its low cetane number. In-cylinder pressure and heat release rate increased due to an enhanced premixed combustion phase. The presence of oxygen improved the combustion process and reduced soot formation. Pentanol's similar properties to diesel and also the fewer emissions produced together with good engine performance make it advantageous as a short-term replacement in diesel engines. It has shown more advantages than butanol and other light alcohols [81,90].

The use of pentanol as an alternative fuel in a diesel engine is not as well-known as butanol, so it needs more investigation due to its properties being similar to diesel fuel. Generally, the low cetane number of alcohols increases ignition delay and so leads to a higher combustion temperature and then higher NO_x emissions [77]. However, the higher heat of vaporization in alcohols reduces the cylinder flame temperature and so reduces NO_x emissions [91]. It can be concluded from the different emissions analyses in the literature that engine operating conditions and injection strategies could affect the emission characteristics. A lower carbon-to-hydrogen ratio and the presence of oxygen in alternative oxygenated fuels lead to decreasing soot emissions from internal combustion engines [69]. According to Pinzi et al. [91], there is an increasing interest in employing long-chain alcohols, such as butanol and pentanol, in the transportation industry due to their potential production from residual biomass via fermentative methods. There is evidence that incorporating alcohol into diesel fuel allows for the well-known smoke-NO_x trade-off to be overcome in steady-state compression ignition engine running. However, the influence of long-chain alcohols under engine transient conditions is unknown, and their behaviour during the Worldwide Harmonized Light Vehicles Test Procedure (WLTP) cycle has not been recorded. The purpose of a recent study was to fill the research gaps mentioned above by characterising the noise and exhaust emissions (CO, total hydrocarbon content or THC, NO_x, and particulate matter or PM mass, PM number, and PM distribution) of a diesel engine running on ultralow sulphur diesel (ULSD) fuel and its mixtures with 1-pentanol and 1-butanol under stationary and transient conditions (WLTP). Dekati electrical pressure low impactor ELPI + paired with Dekati Fine Particle Sampler FPS-4000 monitored transient PM quantity, mass, and size distribution while Horiba Mexa 7100D assessed transient gaseous emissions. Increasing the long-chain alcohol concentration in gasoline blends reduces PM quantity and mass greatly in both stationary and WLTP tests, which is mostly due to the oxygen content of 1-butanol and 1-pentanol.

The addition of long-chain alcohols reduces NO_x emissions in stationary operation whereas the reverse tendency was observed under WLTP. The use of greater alcohol/ULSD fuel combinations appears to marginally increase noise levels. Overall, it is possible to infer that the use of greater alcohol/ULSD fuel mixes appears to be a better substitute for plain ULSD fuel [92].

Today, the scientific community is showing increasing interest in studying n-butanol as part of the mixture. Compared with ethanol, the safety of biobutanol in fuel transportation, processing, and storage [93] as well as its higher cetane index [94], higher calorific value [95], lower volatilization [96], higher flash point, improved lubricity [90], and better compatibility with diesel fuel (especially at low temperatures) have contributed to this interest. A summary of the some physical and chemical properties of alcohols fuels are listed in Table 1. Fernández-Rodrguez et al. [97] investigated and discovered, as in Figure 5 below, which shows scientific publications published in the previous few years linked to various fuels in diesel engines, ethanol in diesel engines and butyl alcohol in diesel engines. Schematic Diagram 5 demonstrates that the scientific community is aware of the eye-catching opportunities and situations resulting from the use of biofuels in diesel engines in road freight transportation, agricultural applications, such as tractors, harvesters, and self-propelled sprinklers, as well as cogeneration applications. Furthermore, Figure 5 indicates the growing interest in n-butanol as a mixing element for diesel engines, as evidenced by a growing number of papers in recent years.

Table 1. Physical and chemical properties of neat tested fuels [90].

Property	Diesel	Methanol	Ethanol	Butanol	Pentanol
Molecular formula	$C_{12}H_{22}$	CH_3OH	C_2H_5OH	C_4H_9OH	$C_5H_{11}OH$
Molecular weight (kg·kmol^{-1})	166.3	32.04	46.7	74.112	88.15
Cetane number	52	5	8	17	18.2
Density at 15 °C (kg·m^{-3})	834.8	791.3	789.4	811.5	814.8
Kinematic viscosity at 40 °C (cSt)	2.627	0.58	1.13	2.17	2.74
Lower heating value (MJ·kg^{-1})	45.97	19.58	26.83	33.81	34.65
Self-ignition temperature (°C)	254–300	463	420	345	300
Vapour pressure (mmHg)	0.4	127	55	7	6
Latent heat of evaporation (kJ/kg)	270–375	1162.64	918.42	581.4	656
Carbon (wt%)	86.44	37.48	52.14	64.86	68.13
Hydrogen (wt%)	13.56	12.48	13.02	13.51	13.72
Oxygen (wt%)	0	49.93	34.73	21.62	18.15
Water content (mg·kg^{-1})	41.7			11.46	29.7
Boiling point (°C)	180–360	64.7	78.3	117.4	137.9

Table 2 shows the main physical properties of C_2H_5OH and C_4H_9OH. However, the physiochemical properties of n-CH_4H_9OH are highly similar to those of diesel than to those of C_2H_5OH; it still cannot replace diesel at 100% [37]. The literature reports that alcohol–diesel blends are tested up to 40% butanol content (volume basis) while not requiring engine modifications [98,99].

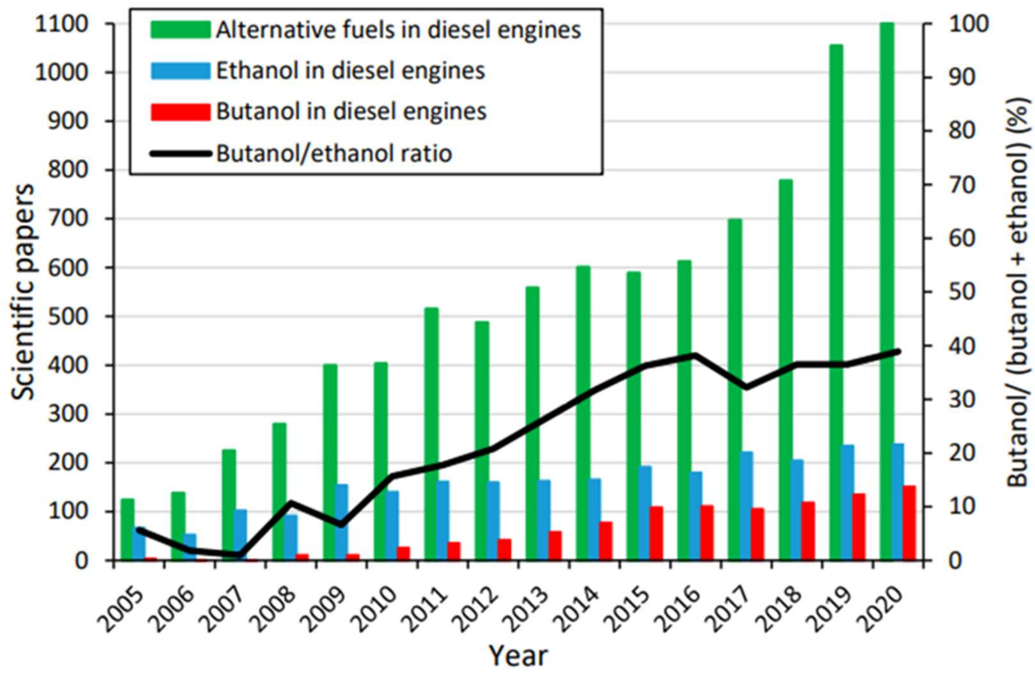

Figure 5. Bibliometric diagram ISI web of knowledge [97].

Table 2. Summary of ethanol and n-butanol properties [90].

Property	**Methods**	**Ethanol (C_2H_5OH)**	**Butanol (C_4H_9OH)**
Purity (% *v*/*v*)		99.7	99
Density at 15 °C (Kg/m^3)	EN ISO 3675	789.4	809.7
Kinematic viscosity at 40 °C (cSt)	EN ISO 3104	1.13	2.22
Lower heating value (MJ/kg)	UNE 51123	26.83	33.09
C (wt%)		52.14	64.82
H (wt%)		13.13	13.60
O (wt%)		34.73	21.59
Water content (ppm wt)	EN ISO 12937	2024	1146
Molecular weight (kg/kmol)		46.07	74.12
Boiling point (°C)		78.3	117.5
Stoichiometric fuel/air ratio		1/9.01	1/11.19
Cold filter plugging point (°C)	EN 116	<−51	<−51
Lubricity (WSD) (µm)	EN ISO 12156-1	1057	591
Cetane number		8 [100,101]	17 [94,102]

3. Effects of Bioalcohols on Emissions

The physical properties of the particles in this study are related to the quality, quantity, and size of the particles, the microstructure and agglomerates of the particles, and the nanostructure of the primary particles. Particulate matter is composed of soot and other liquids or solids, and soot accounts for the largest part of diesel particulate mass. Soot is usually a solid that contains carbon as a byproduct of fuel combustion. Various processes include fuel pyrolysis, nucleation, coalescence/cohesion, surface growth, coalescence, and oxidation. The first five steps from fuel pyrolysis to agglomeration must be carried out in sequence, and the oxidation process can be carried out at any time during the soot formation process [103].

In diesel engines, alcohol, especially methanol, has attracted more and more attention as an oxygen-rich and renewable fuel. Methanol fuel can be mixed with diesel in the engine; it can be mixed with diesel (85% methanol and 15% diesel) or other percentages. Huang et al. [104] examined the main combustion characteristics of the methanol/diesel fuel mixture by analysing the pressure in the cylinder of a compression ignition engine.

The results show that an increase of the methanol mass fraction in the methanol/diesel fuel mixture leads to an increase in the heat release rate of the premixed combustion stage and a decrease in the combustion duration and diffusion combustion stage.

Sayin et al. [105] investigated the influence of injection sites on exhaust emissions from direct injection (DI) single-cylinder four-stroke diesel engines running on a diesel/methanol mixture. The results demonstrate that using methanol-based diesel fuel reduces flue gas opacity, CO, and UHC emissions by 5–22%, 33–52%, and 26–50%, respectively, while reducing CO_2 and NO_x emissions by 14–68%. Depending on engine operating circumstances, this might range from 22 to 69%. Chao et al. [106] investigated the influence of methanol-containing additives (MCA) on carbonyl compound emissions from diesel engines. According to the findings, applying 10% and 15% MCA increased the emission factors of carbonyl compounds (CBC), acrolein, and isovaleraldehyde by at least 91%.

Zhang et al. [107] investigated the effects of controlled and unregulated exhaust emissions in four-cylinder direct-injection diesel engines powered by Euro V diesel and fumigated methanol. Fumigated methanol was injected under various engine circumstances to fulfil the engine load of 10%, 20%, and 30%. Methanol significantly increases HC, CO, and NO_2 emissions while decreasing NO_x. The use of methanol and diesel in combination is an efficient way to minimize PM and NO_x emissions from diesel cars in operation [108].

Cheng et al. [109] discovered that fumigated methanol can be utilized to reduce diesel consumption in part-load diesel engines. The greatest methanol utilization was discovered to be 43% of total fuel consumption. At low loads, BFC diminishes as the amount of fumigated methanol increases. It increases with the amount of fumigated methanol in the case of heavy exposure [110]. Lee et al. [108] developed an improved multidimensional model and detailed chemical kinetics mechanism to study the combustion and emission characteristics of controlled compression ignition (RCCI) engines operating with methanol/diesel. It has been found that burning methanol/diesel fuel can reduce emissions and improve fuel efficiency. Sayin et al. [111] studied the effects of injection pressure and injection time on the performance and emission characteristics of DI diesel engines using methanol (5%, 10%, and 15%) as mixed diesel fuel. The results show that as the proportion of methanol in the fuel mixture increases, BSFC, specific braking energy consumption (BSEC), and NO_x emissions increase as BTE, smog, CO, and THC decrease. It was also found that the increase in injection pressure and timing resulted in a decrease in smoke, CO, and THC emissions while increasing NO_x emissions.

Zhang et al. [112] studied the effect of methanol fumigation on the combustion and particulate emissions of diesel engines under various engine loads and fumigation levels. It was found that the fumigation of methanol would increase the ignition delay, but it would not significantly affect the combustion duration. Aeration with methanol can effectively reduce the particle mass and particle number concentration. Geng et al. [113] studied particulate matter emissions (PM) using the same engine; the results showed that PM number and concentrations were significantly reduced at low and medium loads and increased when the engine was operating at high loads. Wang et al. [114] assessed the working range and combustion behaviour of diesel engines treated with methanol and studied these in experimental tests. It was found that the operating range of methanol/diesel differs in load and methane displacement percentage; this is achieved in a load range of 6% to 100%. The scope of operation is limited by discovery: partial combustion, misfire, roaring combustion, and explosion.

Nagafi and Yusaf [115] studied the effect of a methanol-diesel mixture on diesel engine performance. In this study, a diesel engine was tested in which diesel fuel was mixed with methanol at specific mixing ratios of 10:90, 20:80, and 30:70. Experimental results show that the effective power and torque of diesel are less than that of diesel fuel mixed with methanol. The optimal mixing ratio to produce the lowest exhaust temperature is 10% to 90% methanol. Diesel engine exhaust temperature is higher than any mixed fuel mixture. A mixture of 30% methanol and 70% diesel reaches the minimum BSFC value.

Compared with any mixing ratio, the BSFC of diesel is much lower. Under almost all operating conditions where diesel fuel is mixed with methanol, BTE improved.

Zhang et al. [112] studied the effect of methanol and ethanol bleed on gas and particulate emissions in a four-cylinder DI diesel engine. Under various engine operating conditions, methanol or ethanol was injected to complete the engine loads of 10% and 20%. Diesel and fumigated methanol or ethanol can reduce nitrogen oxides and diesel particles and mass, and methanol fumigation is more effective, such as in fumigation with ethanol to reduce particles. Sayin et al. [116] studied the effects of methanol–diesel (M5, M10) and ethanol–diesel (E5, E10) mixtures on the performance and exhaust emissions of a single-cylinder four-stroke diesel engine with a naturally aspirated engine. Direct injection results show that when methanol–diesel and ethanol–diesel mixtures are used, BSFC and NO_x emissions increase while BTE, smog, CO, and THC emissions decrease.

After consulting the available literature on the effect of alcohol fuel (as most studies have proved and summarised in Tables 3 and 4) on the PM emissions of internal combustion engines, we can draw the following main conclusions (presented in Table 5):

- Both lower alcohols and higher alcohols can significantly change the composition and structure of fine dust, which leads to an average reduction of about 50% (weight) of fine dust, 60% (weight) of fine dust (TNC), and 30% (by weight) under various conditions of fine dust size (GMD). Under the same alcohol consumption (by volume or weight), lower alcohols, especially methanol and ethanol, are more effective than higher alcohols in reducing PM. This is because compared with the characteristics of higher alcohols, the difference in characteristics of lower alcohols significantly affects the formation of PM (especially when the carbon content is low, and the oxygen content is high).
- Mixed alcohol has a greater impact on PM reduction than fumigated alcohol, especially when running at low engine temperature (i.e., low speed or low torque). Evaporation of fumigation alcohol can cause poor combustion. In addition, part of the fumigated alcohol droplets will enter the low-temperature cooling area of the combustion chamber wall/tank, resulting in unburned fuel. In addition, spraying alcohol with a low-pressure fuel injection will produce large drops of alcohol, reducing the chance of complete combustion and further particle formation.
- Because alcohol has a lower weight, quantity, size, elemental carbon (about −60%) and flash point (about −8%) as well as higher fine dust oxidation reaction activity (about increased performance and service life) it can be used in a catalytic converter, especially a DPF.

Table 3. Reviewed investigations available in the literature about the PM physicochemical properties of internal combustion engines.

Reference Fuel	Alcohol Used	Fuelling Type	Engine Tested	Operating Conditions	Test Results	Ref.
Diesel	Methanol	Fumigation (achieving 10, 20, and 30% of desired engine load by fumigated methanol)	4-cylinder, NA, diesel engine	Japanese 13-mode test cycle	Decrease in PM mass (up to −21.2%, on average of different conditions for 30% fumigated methanol) with increase in methanol ratio	[117]
Diesel	Ethanol	Blend (mixing 5, 10, 15, and 20% of ethanol by volume with diesel)	6-cylinder, heavy-duty, turbocharged diesel engine	European 13-mode test cycle	Decrease in dry soot but increase in SOF resulting in no obvious effect of ethanol on the PM mass	[118]

Table 3. *Cont.*

Reference Fuel	Alcohol Used	Fuelling Type	Engine Tested	Operating Conditions	Test Results	Ref.
Diesel	Butanol	Blend (mixing 5, 10, 15, and 20% of butanol by volume with diesel)	Single-cylinder, DI stationary diesel engine	25, 50, and 75% of maximum engine power at a speed of 3000 rpm	Decrease in PM mass (up to −25%) with increase in butanol ratio	[119]
Diesel	n-Pentanol	Blend (mixing 10, 20, and 30% of n-pentanol by volume with diesel)	4-cylinder, NA, DI diesel engine	Five engine loads (BMEP of 0.84, 2.06, 4.15, 6.20, and 7.10 bar) at a speed of 1800 rpm	Decrease in PM mass (up to about −70%) with increase in pentanol ratio (on average of five loads, −42% reduction for 30% pentanol blend)	[120]

Table 4. Summary of the main parameters of the reviewed investigations available in the literature about the PM physicochemical properties of SI and CI engines.

Fuel Used	Engine Tested	Parameter Investigated	Ref.
Gasoline; diesel	SI and CI	PM mass; TNC; GMD; nanostructure of particles; OC-EC; ions; metal and elements	[121]
Gasoline; diesel	SI and CI	Micro- and nanostructure of particles	[122]
Ethanol	SI and CI	PM mass; PAHs	[123]
Methanol	SI and CI	PM mass; PAHs	[123]
Diesel	CI	PM mass; TNC; GMD; morphology, micro- and nanostructures of particles; OC-EC; metals and elements; ions; oxidation reactivity	[107]
Alcohol (methanol, ethanol, butanol, and pentanol)	CI	Soot; PAHs	[124]

Table 5. Summaty of the reviewed investigations available in the literature about the PM physicochemical properties of diesel engines.

Reference Fuel	Alcohol Used	Fuelling Type	Engine Tested	Operating Conditions	Test Results	Ref.
Diesel	CH_3OH	Blend (mixing 11.5% methanol by volume with 88.5% diesel)	4-cylinder, turbocharged diesel engine	One engine load (BMEP of 12 bar) at a speed of 1400 rpm	Decrease in the radius of gyration (−25%), fractal dimension (about −10%), number of primary particles (−51%), and primary particle diameter (7.5–42.5 nm for methanol and 9.5–50 nm for diesel)	[86]
Diesel	C_2H_5OH	Blend (mixing 10 and 20% of ethanol with diesel)	4-cylinder, supercharged diesel engine	One engine load (full load) at full engine speed	Decrease in the agglomerates and primary particles sizes with an increase in ethanol ratio	[114]
Diesel	n-Butanol	Blend (mixing 10 and 20% of butanol by volume with diesel)	4-cylinder, turbocharged diesel engine	One engine load (78.4 Nm) at a speed of 2000 rpm	Decrease in the agglomerates and primary particles sizes	[104]
Diesel	n-Pentanol	Blend (mixing 15 and 30% of pentanol by volume with diesel)	4-cylinder, turbocharged diesel engine	One engine load of 130 Nm at a speed of 2000 rpm	No significant differences in the overall morphology of particles (near-spherical shape) and agglomerates (branched-chain structures) for all the fuels tested; decrease in primary particles size (up to −8.2%) with an increase in pentanol ratio	[105]

In summary, in the future, zero-emission nonfossil energy vehicles will be fully introduced into today's fleet. However, the specific time is not clear. The combination of alcohol fuels, especially low-alcohol fuels, and emission catalysts may be effective. Methods to reduce the consumption of fossil fuels and emissions while reducing particulates, as illustrated in Figure 6, thereby improving the performance and service life of emission catalysts, must be developed.

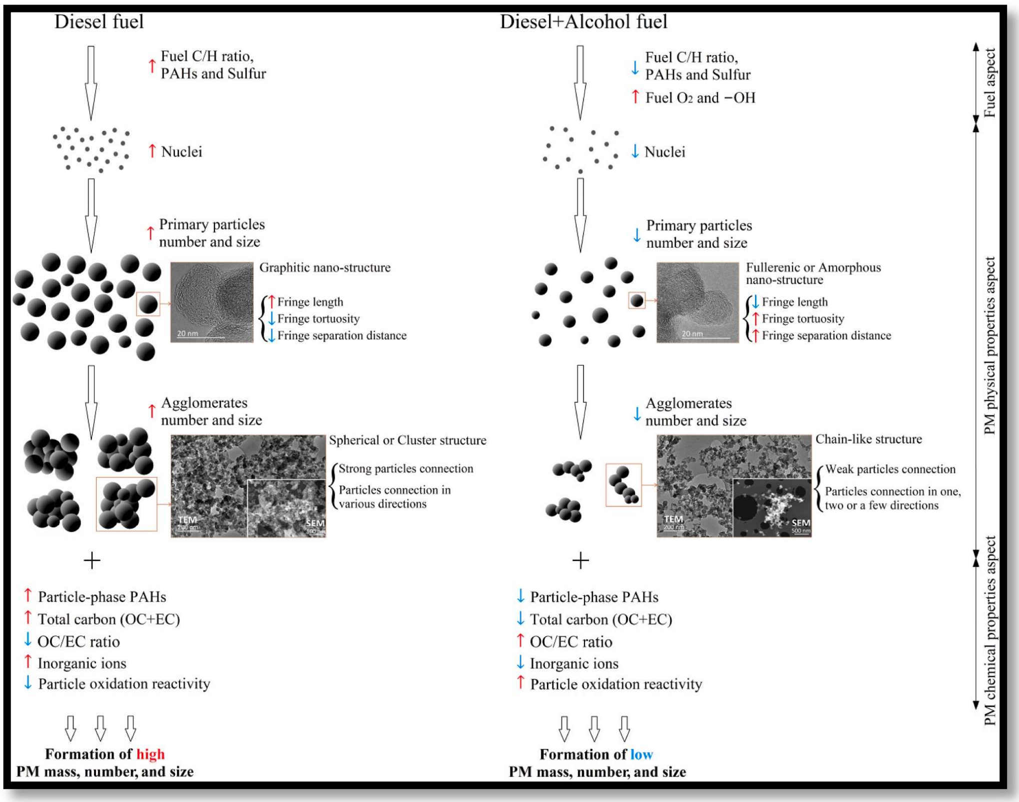

Figure 6. Effect of alcohol fuels on the PM mass, number, and size via several aspects, including fuel, PM physical, and PM chemical properties aspects.

4. Conclusions

There is no extraordinary super fuel that can meet all the requirements for the economy, maximum thermal efficiency, and engine performance while remaining clean enough to protect the environment. Each fuel has its advantages and disadvantages, and the choice of specific fuel depends on various parameters. The physical properties of fuel are shown in Table 1. If we start with the advantages of alcohol fuels, they can be summarized as follows:

- Compared to methanol, ethanol has a higher energy density, is nontoxic, and is available in large quantities, reducing racers' vulnerability to price increases and supply disruptions. Methanol can be made from organic materials, such as biomass and domestic waste; at some point, it may even be made from coal. The top five countries in the world's coal reserves are indeed the US, Russia, Australia, China, and India, and these reserves will be very abundant in the next few years. As compared with gasoline, the molar ratio of alcohol combustion products to reactants is higher, so higher combustion pressure is generated in the combustion chamber of the internal combustion engine, thereby improving energy production and thermal efficiency [125].
- Because alcohol fuel has higher volumetric efficiency, alcohol has better combustion characteristics and performance, making methanol the preferred fuel for racing cars. The acceleration time decreases as the power increases.
- Alcohol has better visibility in the event of a fire. It is used for evacuation, rescue, minor suffocation, cold flames, and low heat, resulting in minor burns, minor smoke

damage, and easy removal of residues. Water can be used to extinguish fires, and it is easier to use powder foam.
- Alcohol fuel has lower vapour emissions. When alcohol fuel is used, less harmful byproducts are released into the atmosphere.
- Because the carbon content in alcohol fuel is very low, the combustion of internal combustion engines will produce a small amount of soot, which is discharged into the atmosphere.
- Alcohol fuel is liquid, so it only needs to be modified slightly to use the same transportation and infrastructure management as traditional fuels.

This review paper focused on presenting the performance, combustion, and emission characteristics of CI engines using alternative alcohol-based fuels. The effects of alcohol fuels on the performance, combustion characteristics, and emissions, such as NO_x, CO, HC, and CO_2, were also investigated. This work also examined the PM emissions of CI engines when using conventional fuels and when alcohol was introduced. In general, to reduce PM emissions or reduce the harm to human health and the environment, it is necessary to determine their chemical properties. Since the internal combustion engine is the source of particulate matter in the atmosphere, it is better to understand the chemical properties of particulate matter, such as organic carbon, elemental carbon, inorganic ions, metallic elements, polycyclic aromatic hydrocarbons (PAH), and oxidation reactions in internal combustion engines and integrated circuit motors. TC consists of OC and EC, which is harmful to the environment and human health. OC is considered to be carcinogenic for humans because it consists of some nonvolatile hydrocarbons [37]. Due to the European Union affecting air pollution, the global carbon cycle, and OC's ability to absorb solar radiation, which leads to energy redistribution and climate change [126–129], some technologies are needed to reduce CO and EC emissions from electronic injection engines.

Biofuels, such as bioalcohols, are promising fuels that could be partially used in CI engines aiming to improve some combustion and performance characteristics of engines as well as to either reduce or control the exhaust emission and the particulate matter characterization of diesel engines. These biofuels can be used without requiring major modifications to the engine and could contribute to the dependence on fossil diesel. The compiled and detailed information about alcohol-based fuels is beneficial for conventional and also hybrid diesel vehicles to reach the forthcoming emissions regulations.

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