Abstract: Biofuels are receiving increased scientific attention, and recently different biofuels have been proposed for spark ignition engines. This paper presents the state of art of using biofuels in spark ignition engines (SIE). Different biofuels, mainly ethanol, methanol, i-butanol-n-butanol, and acetone, are blended together in single dual issues and evaluated as renewables for SIE. The biofuels were compared with each other as well as with the fossil fuel in SIE. Future biofuels for SIE are highlighted. A proposed method to reduce automobile emissions and reformulate the emissions into new fuels is presented and discussed. The benefits and weaknesses of using biofuels in SIE are summarized. The study established that ethanol has several benefits as a biofuel for SIE; it enhanced engine performance and decreased pollutant emissions significantly; however, ethanol showed some drawbacks, which cause problems in cold starting conditions and, additionally, the engine may suffer from a vapor lock situation. Methanol also showed improvements in engine emissions/performance similarly to ethanol, but it is poisonous biofuel and it has some sort of incompatibility with engine materials/systems; its being miscible with water is another disadvantage. The lowest engine performance was displayed by n-butanol and i-butanol biofuels, and they also showed the greatest amount of unburned hydrocarbons (UHC) and CO emissions, but the lowest greenhouse effect. Ethanol and methanol introduced the highest engine performance and the best/lowest CO and UHC emissions. Acetone introduced a moderate engine performance and the best/lowest CO and UHC emissions. Single biofuel blends are also compared with dual ones, and the results showed the benefits of the dual ones. The study concluded that the next generation of biofuels is expected to be dual blended biofuels. Different dual biofuel blends are also compared with each other, and the results showed that the ethanol–methanol (EM) biofuel is superior in comparison with n-butanol–i-butanol (niB) and i-butanol–ethanol (iBE).

Keywords: biofuels; single blends; dual blends; spark ignition engines (SIE)

1. Introduction

The world is on the edge of an energy crisis, due to limited energy sources along with ever-increasing energy demand [1]. Statistics show that energy needs will increase by about 50% in 2025. Currently, the available sources of energy mainly depend on fossil fuel, which is limited with a non-renewable capability. The main sources of energy are oil (32%), coal (27%), and natural gas (22%) [2]. The problems of environmental pollution and global warming, related to fossil fuels, as well as the oscillation of oil prices can significantly support searching for alternative fuels for the future. Among the most promising alternatives, biofuels are recommended [3]. Biofuels are fuels produced from bio-origin sources, such as biomass.

Biofuels were used in the early decades of the last century but due to the low price of fossil fuels, biofuels were limited in entering into commercial play. Historically, at the beginning of the Second World War, biofuels, especially alcohols, were reused as fuel sources. Later on, in the beginning of the seventies of the last century, an oil crisis was revealed where the gulf countries refrained from exporting oil [2]. This led to a steep rise in the crude oil price, whereby the price of a barrel increased from USD 3 to USD 45.
This, in turn, led to the world being directed towards biofuels again [4]. Currently, several countries are using biofuels; in particular, the largest biofuel-producing countries are the United States of America, Brazil, China, and India, respectively, due to their benefits, as discussed later [5].

Despite the benefits of biofuels as a renewable source of energy, especially the reductions in greenhouse gases emissions and global warming, in comparison with fossil fuels, biofuels represent less than 1% of the global market for automobile fuels, and such biofuels depend strongly on governmental support [6,7]. Many countries have started to take serious steps toward producing and using biofuels as a main source of energy in their different energy applications, in order to meet the jump in their energy needs and reduce their imported energy dependency. In particular, Brazil is one of the leading countries in the production of biofuels, where 30% of the biofuels are used in its transport trucks [8]. The United States, for example, plans to replace 30% of liquid oil with biofuels in 2025 [6]. India increased biofuel rates from 5% to 20% [9]. India plans to reduce its dependency on oil by 10% in 2022 [10]. The European Union (EU) countries increased their dependency on biofuels [11]. Biofuel production doubled from 2003 to 2017 in some EU countries. The biggest producers of ethanol in the EU are Germany, France, and Poland. The greatest biofuel consumers in the EU are considered in Latvia (31.2%), Finland (26.7%) and Sweden (24.8%) [12]. China aims to increase its biofuel production capacity from 76 Mt in 2015 to 152 Mt in 2030 [13].

Biofuels are currently among the most important sources of renewable fuels, unlike other natural sources such as petroleum, coal, and other fossil fuels. Biofuels could be derived from plants and animal wastes (mostly horse and cow manures). The agricultural residues are also used for biofuels production. In detail, there are several sources of biofuels from agricultural residues, such as coconut and palm oils [14,15]. There are also available sources such as sunflower seeds, soybeans, peanuts, cones, wheat, sugar beet and maize [16,17]. In general, biofuels can be produced from dedicated crops, also called energy crops, or from wastes produced by agro-industry and agriculture, or from food waste or food by-product wastes. Biofuels are generated by a series of biological processes, such as hydrolysis, fermentation, and microbiological enzymes, which convert sugar molecules into fuels. Using such methods, hydrocarbons are extracted from the biomass sources; as such, biofuels are classified as natural organic compounds.

In comparison with fossil fuels, biofuels offer several benefits, as discussed next. Biofuel is a renewable source of energy; it turns the agriculture residues into energy; it makes an efficient use of residues with additional income instead of useless disposal; it helps towards a cleaner environment by turning residues into fuel instead of farmers burning them; and finally, it is an available source of energy in all countries, thus meeting strategy needs [18].

One of the main benefits of biofuels as promising future fuels includes their being carbon-free. Carbon dioxide, which is emitted from biofuels in combustion conditions, is extracted from the atmosphere while plants grow. This means that there is no emission of carbon dioxide in biofuel combustion. Biofuels also include oxygen in their structure, which makes fuel burn more completely, e.g., reduces the fuel pollutant emissions produced from volatile organic compounds [19,20]. Biofuels also have a high octane number, which eliminates the need to add lead to increase the octane number of regular fuels, as in the fossil fuel condition [21]. In addition, biofuels are degraded biologically, and are mostly non-toxic fuels [22].

Despite the several benefits of biofuels, as discussed above, there are some drawbacks. One of problems of biofuels is their production from food agriculture sources, such as maize and wheat; this, in turn, leads to an increase in food prices, and that can directly affect the lives of poor people [23,24]. Recently, this problem has been partially solved by imposing domestic legislation to prevent the production of biofuels from food sources, using agricultural and animal residues instead [25,26]. One further problem is the increased
costs of biofuel production; however, this problem gets better with time, and in the near future the price would be competitive with other fuels.

Biofuels are reviewed in the literature, and some studies have focused on biofuel types [27]. McDowall et al. [28] reviewed the future of biofuels. Global production methods of biofuels in recent utilizations were reviewed by Refs. [29–31]. Recent technologies for biofuel productions from different residues were reviewed by Ref. [32]. Biofuel production systems from the modeling point of view were reviewed by Ref. [33]. The future of biofuel as renewable energy sources is reviewed by Refs. [34–36]. In spite of all such review studies, there is still a gap in the reviewing of biofuels [37]. There are few studies focusing on the review of biofuels for Spark ignition engines (SIE) [13]. The current work aims at providing the state of art of using biofuels in spark ignition engines. Different fuels in single and dual blends are reviewed and compared under the same rates and engine conditions (Air to fuel ratio, ignition timing, spark timing, compression ratio, etc.). The benefits and weaknesses of using biofuels in SIE are considered. Future biofuels for SIE and the proposed method(s) to reduce engine pollutant emissions are highlighted. This study may help in evaluating the future of biofuels for SIE, and fill some gaps in the current study of biofuels, i.e., cover some topics not presented in the early review studies.

2. Biofuels for Spark Ignition Engines

Spark ignition engines (SIE) generally work based on the principle of receiving a mixture of air and gasoline fuel, compressing it, and igniting it using a spark-plug to produce a high temperature/pressure in the cylinder(s). At the time of the invention of the SIE (at the beginning of the last century), biofuels (from feed energy corps and food) were used as an energy source in the engine [38]. The first use of biofuels (ethanol) was in the 1800s. Later on, in 1826, the scientist Sawmill Morey worked to improve the engine’s performance using biofuels/bioethanol [38]. In 1860, the German engineer Nicholas Otto used biofuels (alcohols) in one of his engines [38]. In 1908, Henry Ford designed an engine using biofuels (ethyl alcohol) as an energy source [38]. In 1917, the famous scientist Alexander Graham Bell presented a paper in National Geographic about biofuels (ethanol) [38]. However, due to the low cost of fossil fuels, the using of biofuels was limited. Currently, researchers are directed toward biofuel blend technique. The first time gasoline was mixed with biofuels was in 1930 [38]. Biofuels were in development for the first time as fuels for transportation via a fermentation process of sugars into ethanol [39]. Several countries marketed biofuel blends for use in the SIE, such as Germany, Brazil, the Netherlands, France, United States of America and many other countries [40–42].

Biofuels are generally classified into four generations, according to early studies [43–49]. In the first generation, the biofuels were generated from food energy corps. This led to increased food prices due to food shortages [50] and, accordingly, the world moved into the next generation. In the second generation, the biofuels were from non-food corps, such as wheat, straw, and corn husk. The technology of biofuel production is scarce and complex, which makes biofuel production expensive and, in turn, the third generation was introduced. In the third generation, the biofuels were manufactured from microbial algae and cyanobacteria. In the fourth generation, the biofuels are generated from genetic microorganisms using thermochemical processing of CO$_2$. However, the fourth generation is still under development. In the following is a detailed discussion of using different biofuel blends in spark ignition engines.

2.1. Ethanol

Ethanol, which is usually a biomass-grounded renewable fuel (known as bio-ethanol), is formed by the alcoholic fermentation of animal and/or agricultural residues [51,52]. Ethanol is normally produced in two forms: hydrous and anhydrous ethanol. Hydrous ethanol is a wet ethanol, which is usually produced by distillation from organic biomass, and it is 95% ethanol and 5% moisture content; the hydrous ethanol is suitable as a fuel when mixed with 15% petroleum fuel. On the other hand, the anhydrous ethanol is formed
by drying the wet ethanol (hydrous one); the ethanol content in the anhydrous type is 100%, and it can be used as a fuel alone [53,54]. Ethanol, in both its types, is a colorless liquid fuel with a distinctive odor, and has a chemical formula of \( \text{C}_2\text{H}_5\text{OH} \). It is a lead-free fuel with a volatile composition content, so it should not be exposed to air at storage conditions. Ethanol contains oxygen in its chemical composition and, in turn, it is better than benzene and diesel fuels in combustion engines, especially in high altitude countries/cities where environmental oxygen is low. It has a high self-ignition temperature, in comparison with gasoline and diesel fuels [55]. It is also a nontoxic fuel and safe in drinking and inhalation conditions. It interacts with air during combustion, giving water, so it should be kept away from moisture in storage conditions to avoid reducing the fuel concentration, e.g., decreasing fuel efficiency. Sometimes ethanol is added to lead-free gasoline/diesel to improve fuel properties, such as octane/cetane number, fuel composition, oxygen content, etc. [56]. The oxygen-fueled ethanol has a positive effect on the pollutant emissions, as will be discussed later. Ethanol is known to have a high octane number. Referring to the different types of ethanol, it was noted that wet ethanol has a lower octane number than the dry one. The higher the octane number, the higher the compression ratio in the combustion chamber and the more engine propulsion. Ethanol would be used alone as a fuel (especially anhydrous type), and it could be mixed with gasoline (for both types) at any rate.

The most popular ethanol blend in the SI engine is 10% ethanol with 90% gasoline, which is known as E10. Additionally, ethanol 85% is broadly used (known as E85); this fuel mixture is used in some countries such as the United States, and it requires some changes in the engine, such as spark and ignition timing, AF ratio, etc., and it is known as a flexible-fuel technology (F.F.T) [57,58]. Ethanol blends at rates 24% and 20% (known as E22 and E24) are used also in some conditions, such as in Brazil, and they require some changes in the engine as well. Finally, ethanol 100%, known as E100, is alternatively used in Brazil, and it requires major modifications in the engine systems. The investigation of ethanol fuel showed many advantages in terms of engine efficiency, released emissions and high thermal proportions, which led to the development of the widespread use of such a fuel [59,60]. This is in addition to the improvement of pollutant levels as the proportion of ethanol to gasoline increases in the mixture [61–63]. However, there are also downsides to using ethanol. For example, it sometimes has a problem in starting the engine in cold weather, due to the evaporation problem [64–66]. Additionally, warm or hot weather may cause so-called steam/vapor lock. This is in addition to the fuel’s incompatibility with some parts of the engine’s metals [67,68]. Ethanol being miscible with water is one of its major drawbacks. However, despite all of these defects, it is currently the most applicable renewable fuel in gasoline engines in many countries of the world [69,70].

2.2. Methanol

Methanol, also recognized as methyl alcohol, is a liquid fuel containing the chemical formula \( \text{CH}_3\text{OH} \). Methanol consists of an “OH” group of alcohols bound to a single carbon atom (often shortened as MeOH). The carbon atom, which remains a bonding source, is formed by single carbon atom and triple hydrogen atoms [71,72]. Scientists have recognized that liquid methanol shares an origin word with methane gas. The component “meth” in both fuels refers to the single carbon, which is linked to hydrogen atoms. In methanol, this carbon is accompanied with the alcohol group; but in methane, the carbon is accompanied with four hydrogen atoms.

Methanol, as a fuel, is flammable, colorless, volatile and toxic to humans. Methanol could be generated from biomass (bio-methanol) as well as fossil fuels [73–75]. Traditionally, methanol was produced by the fermentation of bacteria in a cellulose compound found in wood and some supplementary plants [76]. This method led to the formation of methanol, which is deadly to drink, but it is useful as a fuel and as a solvent for scientific and industrialized purposes [77,78]. After the discovery of methanol, researchers began using it as a fuel for racing cars (in pure methanol form). It permitted high speeds, but it also contributed to a catastrophic fire that killed race car drivers in the past. Safety regulations
are currently in place to regulate the quality of methanol on the basis of the engine’s working conditions [79].

Methanol is extremely easy to ignite as a gas, and its fire is almost invisible. Methanol has a high octane rating as an ethanol fuel [80,81]. Some studies have looked at the use of methanol in SIE, but much less so than ethanol fuel [82,83]. In summary, the studies showed a significant improvement in engine performance and a decrease in pollutant emissions, in comparison with neat gasoline [84–86]. Compared to other biofuels, methanol has some advantages; it has the greatest hydrogen to carbon ration, and accordingly, low emission per energy unit [39]. It has also the greatest heat of evaporation and oxygen content, which enhances fuel combustion and emissions. A comparison between methanol and ethanol biofuels as regards engine performance and contaminant emissions of SIE is discussed afterwards.

2.3. Butanol

Recently, butanol (C$_4$H$_9$OH) as a promising biofuel type has been proposed. There are four different structures of this type, which are 1-butanol, 2-butanol, i-butanol, and t-butanol. The 2-butanol and t-butanol have not been confirmed yet [87], while the 1-butanol (also called n-butanol or normal butanol) and i-butanol (also called iso-butanol) were verified to be generated by different methods [88,89]. They were also produced commercially, (see, e.g., [90–92]). Accordingly, in the study, we will only present the investigation with these types. The use of n-butanol and i-butanol fuel in SIE showed approximately 39–56% savings in fossil fuels and could also minimize greenhouse gas emissions by approximately 32–48% [93]. The possible low hydrocarbon mole fractions and their oxygenated content would support both butanol isomers. The results of using neat and biofuel blends of either n-butanol or i-butanol with gasoline for spark ignition engines have been documented in the literature.

In what follows, the early analysis of n-butanol is briefly summarized. In the case of the addition of n-butanol, Farkade and Pathre [94] showed higher CO$_2$ and NOx emissions. Deng et al. [95] investigated 35 vol. percent n-butanol in gasoline; the results showed higher power, combustion efficiency, and fuel consumption, but also higher emissions of HC, CO, and NOx were obtained. Furthermore, 35 and 30% n-butanol mixed in gasoline were applied by Deng et al. [96], and the results showed that fuel blends can provide full combustion with a higher knock-resistance. Szwaia and Naber [97] tested n-butanol-gasoline blends using 100 to 20 vol. percent n-butanol in SIE; the findings showed that, compared to other tested fuels, neat n-butanol has the shortest combustion time and highest peak pressure. Up to 10% n-butanol in gasoline was investigated by Elfasakhany [98]; the emissions and mixed fuel efficiency were improved for mixed fuels compared to clean gasoline. With changing the spark timing, Dernotte et al. [99] studied 20 to 80 vol. percent n-butanol in gasoline. The findings showed higher CO, lower HC and no substantial improvement in 40 vol. percent blends; 60 and 80 vol. percent blends introduced higher HC emissions by 18 vol. percent. Yang et al. [100,101] analyzed the efficiency and emissions under cold start working conditions of 10 to 35 vol. percent n-butanol blended in gasoline. The results showed low CO/HC emissions, but higher NOx emissions. Engine power is not altered when butanol blends are below 20%, and cold start output is weak for all fuel blends. Wigg et al. [102] studied pure n-butanol emissions and found three times higher HC emissions; however, compared to clean gasoline, NOx and CO emissions are decreased by 17% and 12%, respectively. In large engine operating conditions, Martin et al. [103] analyzed n-butanol–gasoline blend emissions and reported lower CO and HC emissions but higher NOx emissions. The oxidation of 85% n-butanol blended into gasoline was studied by Dagaut and Togbe [104,105], and the authors presented a chemical kinetic mechanism for fuel mixtures. Furthermore, 60 and 80 vol. percent n-butanol blends were tested by Venugopal and Ramesh [106] and the findings showed a rise in CO/HC emissions for both fuel blends. Yacoub et al. [107] examined 22 and 11 vol. percent n-butanol–gasoline blends for each fuel blend with the modification of engine
working conditions. Both fuel blends show declines in CO/HC emissions and a rise in NOx emissions. Gu et al. [108] inspected n-butanol–gasoline blends of 10 to 40 vol. percent; the findings showed a decrease in the CO and unburned hydrocarbons (UHC) emissions of fuel blends. Park et al. [109] studied the efficiency and emissions of n-butanol–gasoline blend-fueled SI engines, and found a reduction in emissions. Additionally, 16% n-butanol–gasoline blends were tested by Cairns et al. [110], and the results showed comparable brake specific fuel consumption (BSFC) and maximum brake torque (MBT) values for both fuel blends and clean gasoline. Niass et al. [111] researched n-butanol–gasoline fuel blends and showed lower emissions of CO2 for fuel blends with higher knock resistance. Gautam and Martin [112,113] analyzed 10% n-butanol in gasoline, and showed lower emissions of CO, CO2, NOx and HC for fuel blends of about 16%, 18%, 5% and 17%, compared to clean gasoline, respectively. Williams et al. [114] analyzed n-butanol–gasoline blends, and the findings showed comparable thermal efficiency, combustion and emissions (with the exception of a reduction in CO2 emissions) for both fuel blends and neat gasoline. Furthermore, 85% n-butanol–gasoline blends were investigated by Cooney et al. [115] without any tuning conditions, and the results showed no improvement in fuel conversion efficiency at lower engine loads; however, fuel conversion efficiency decreased at higher load conditions by 4% for fuel blends. The flame velocity of n-butanol is higher than that of gasoline when the combustion timing is changed and, in turn, the faster combustion of n-butanol will improve the conversion efficiency of the fuel blends. Using 0, 10 and 15 vol. percent of n-butanol–gasoline blends, Mittal et al. [116] investigated engine efficiency and pollutant emissions; fuel blends can increase engine performance and HC and CO emissions. With the addition of n-butanol to gasoline, Pereira et al. [117] showed a faster burning velocity, but the flame growth between biofuel blends and clean gasoline was very similar. Broustail et al. [118] investigated n-butanol–gasoline blends using modified working conditions of the engine; their findings showed a close 12.8% decrease in CO emissions for fuel blends. The emissions, efficiency, and combustion of 40, 60 and 80 vol. percent n-butanol–gasoline blends were studied by Venugopal and Ramesh [119] and Broustail et al. [120]. The results showed low emissions of HC and CO for 40 vol. percent n-butanol; however, relative to clean gasoline, 60 and 80 vol. percent n-butanol showed higher HC and CO emissions. Lavoie and Blumberg [121] and Hu et al. [122] investigated SIE engine efficiency and emissions using n-butanol–gasoline blends; their findings reported unchanged but decreased NOx emissions in HC emissions, while BSFC increased marginally with fuel blends. Heywood [123] researched n-butanol–gasoline blends and demonstrated incomplete combustion and elevated fuel blend emissions. At engine speeds from 1000 to 4000 r/min and loads from 0 to 150 Nm, Wallner et al. [124] investigated engine outputs of 0 vol. and 10 vol. percent n-butanol–gasoline blends. The results registered higher fuel blend burning velocity, but with little change/improvement in CO, HC and NOx emissions and thermal efficiency. Then, 35% n-butanol in gasoline and pure gasoline was studied by Feng et al. [125] with the modification of ignition timing for each fuel. Fuel blends recorded a 38.3% rise in NOx emissions, a 13.8% decrease in CO emissions, an 11.8% decrease in HC emissions, a 7.7% increase in CO2 emissions, an 11.5% decrease in BSFC and a 1.2% increase in torque. Wigg [126] studied the application of n-butanol–gasoline blends and pure n-butanol biofuel combustion and emission appearances. The results showed twice the HC emission value for neat butanol compared to gasoline; for fuel blends, the results showed a 13.5% decrease in CO emissions, a 13.5% rise in NOx emissions, and a 4% reduction in HC emissions.

Heretofore, n-butanol fuel was reviewed and many researches have investigated it. In comparison, iso-butanol fuel has not received the same attention from researchers. The use of i-butanol is studied in spark ignition engines; it is much less prolific than n-butanol, and is summarized in the literature below. At engine speeds of 2600–3400 r/min, Elfasakhany [127] examined engine efficiency and pollutant emissions of 0 to 10 vol. percent i-butanol without any engine tuning conditions. The results registered higher CO and HC emissions for fuel blends at speeds above or equal to 2900 r/min, but contrary results
were obtained at speeds below 2900 r/min; the engine torque, fuel blend volumetric performance, and fuel blend brake power give lower values than with pure gasoline. In contrast to clean gasoline, a lower fuel conversion efficiency was shown for i-butanol–gasoline blends [128–133]. Rice et al. [134] analyzed 20 vol. percent i-butanol–gasoline blends, and declared lower HC emissions for the fuel blends; however, as the concentration of i-butanol increases, the HC increases rapidly. BQ et al. [135] tested the engine efficiency of 10, 30 and 50 vol. percent i-butanol–gasoline blends; their findings showed a 5% to 50% decrease in engine performance, relative to gasoline, for the fuel blends. In conclusion, in contrast to pure fuel, the results of the i-butanol–gasoline blends show decreases in engine efficiency and an improvement in some engine pollutant emissions.

2.4. Acetone

As a novel alternative fuel for compression ignition engines (CIE), acetone (C₃H₅OH) has recently been suggested [136–138]. In a couple of publications, the investigation of acetone in SIE was found by the author. Using 0, 3, 7 and 10 vol. percent acetone–gasoline blends, Elfasakhany [139] examined SIE pollutant emissions and engine efficiency. Compared to clean gasoline, the findings showed better engine efficiency and lower pollutant emissions for fuel blends; exhaust emissions decreased on average by around 32% for CO₂, 43% for CO and 33% for UHC compared to clean gasoline. In addition, engine output emissions varied with engine speeds; fuel mixes, in particular, showed an initial increase in UHC and CO emissions, followed by a steady decrease, while engine speeds increased. At moderate engine speeds (2900–3000 r/min), the peak emissions of blended fuel are seen, but these are still lower than those of clean gasoline. In addition, such fuel also needs further analysis by researchers.

3. Comparison between Single Biofuel Blends in SIE

Several biofuels have been proposed as promising alternative fuels for spark ignition engines, as discussed above. These biofuels yield significantly dissimilar performances and emissions results based on their different chemical compositions and structures. Ethanol and methanol showed higher engine performance and lower pollutant emissions, in comparison with neat gasoline. N-butanol and i-butanol, on the other hand, provided lower engine performance than neat gasoline, but butanol fuels showed some other benefits, in comparison with ethanol and methanol. The chemical structure of butanol provides some rewards, in comparison with ethanol and methanol, including its lower vapor pressure, which reduces the tendency toward the vapor lock condition and also enhances the cold engine starting condition. Butanol has a superior fuel economy due to its higher energy density [140–142]; it could be blended with gasoline at higher concentrations without (or with minor) retrofitting engines [143], and it has the capability of using existing gasoline fuel distribution pipelines. N-butanol and i-butanol showed lower tendencies toward solubility in water, upper flash point (29 °C) and boiling point (117.7 °C), which makes such butanol fuels safer to use than ethanol and methanol [144]; n-butanol and i-butanol, additionally, may cause less corrosive effects in engine materials and systems [145–147].

In the literature, Elfasakhany [148] examined the performance and pollutant emissions of SIE using ethanol, methanol, n-butanol, i-butanol, and acetone, at the same blend rates (3, 7, and 10 vol.%) and engine working conditions. The comparison focused on the engine emissions via CO₂, CO, and UHC, and performance via volumetric efficiency, brake power, and torque in a wide range of engine speeds from 2600 to 3400 r/min. It is important to define or clarify the physical meaning of volumetric efficiency, engine power, and torque, as follows. Volumetric efficiency (VE) is the real quantity of air flowing into the combustion chamber, compared to extreme conditions. Basically, it is a measure of how full the cylinders are. VE changes based on the environmental conditions, such as air density, temperature, and altitude changes. Engine power is the amount of energy or work obtained from the engine per unit of time. Torque is simply the measure of rotational effort applied on the engine crankshaft by the piston. The results showed that the
n-butanol and i-butanol provide a significant drop in volumetric efficiency, brake power and torque in comparison with ethanol, methanol, acetone and the neat gasoline, as shown in Figure 1. The greatest engine performance is obtained with ethanol and methanol; in detail, the highest volumetric efficiency is provided by methanol; ethanol can provide the greatest output power and torque from the engine. In conclusion, the lowest engine performance is introduced by n-butanol and i-butanol, in comparison with all test fuels. A moderate engine performance is obtained by acetone (AC). Regarding the pollutant emissions, acetone provided the lowest UHC and CO emissions, but n-butanol and i-butanol showed the highest UHC and CO emissions; in particular, n-butanol presented the highest CO and i-butanol presented the highest UHC emissions, but these are still lower than the neat gasoline fuel, as shown in Figure 2. The comparison also indicated that n-butanol and i-butanol can provide the lowest greenhouse effect among all test fuels. On the other hand, ethanol and methanol introduced the highest CO\textsubscript{2} emissions (even higher than the neat gasoline). In conclusion, in order to get a moderate great output torque, volumetric efficiency and brake power, as well as low UHC, CO\textsubscript{2} and CO emissions, one should apply AC fuel blends. It is important to highlight that i-butanol and n-butanol showed dissimilar results in engine performance and pollutant emissions, e.g., minor differences. This may be due to the similar chemical compositions of both fuels (C\textsubscript{4}H\textsubscript{9}OH). The slight difference appears due to dissimilar combustion characteristics and flame propagations. Both the fuels are different in terms of heating values, saturation pressures, stoichiometric A/F ratios, boiling points and auto ignition temperatures, as summarized in Table 1\textsuperscript{149,150}. One further difference is the structure of both fuels, whereby i-butanol is branched-chain but n-butanol is a straight-chain. There is a minor difference also in the relative reactivity of the both fuel blends, e.g., most reactive for n-butanol and least reactive for i-butanol\textsuperscript{127}. Finally, in the comparison of ethanol– and methanol–gasoline blends, ethanol showed a higher brake power and torque than those of methanol, although the later one (methanol) has a higher volumetric efficiency than the ethanol one. This may refer to the fact that ethanol’s heating value is greater than that of methanol by nearly 1.3-fold, as shown in Table 1, and that leads to an increase in the brake power and torque for ethanol blends. Regarding pollutant emissions, methanol presented lower CO and UHC emissions than the ethanol biofuel, but ethanol showed lower CO\textsubscript{2} emissions than methanol fuel. This may refer to the fact that the oxygen content of methanol is much higher than that of ethanol, as shown in Table 1; this without a doubt can enhance methanol’s combustion and emissions (CO and UHC) and, in turn, increase CO\textsubscript{2} emission.
Figure 1. Comparisons of volumetric efficiency, torque, and brake power for ethanol (E), methanol (M), n-butanol (nB), i-butanol (iB), and acetone (AC) blended with gasoline and neat gasoline (baseline) in %.

Figure 2. Comparisons of CO, CO$_2$, and UHC emissions for ethanol (E), methanol (M), n-butanol (nB), i-butanol (iB) and acetone (AC) blended with gasoline and neat gasoline (baseline) in %.
Table 1. Properties [149,150].

| Property                        | Gasoline | Ethanol | Methanol | I-Butanol | N-Butanol | Acetone |
|---------------------------------|----------|---------|----------|-----------|-----------|---------|
| Chemical formula                | C\(_8\)H\(_{15}\) | C\(_2\)H\(_{5}\)OH | CH\(_3\)OH | C\(_4\)H\(_9\)OH | C\(_4\)H\(_9\)OH | C\(_3\)H\(_8\)OH |
| Composition (C,H,O)(%)          | 86,14,0  | 52, 13, 35 | 37.5, 12.5, 50 | 65, 13.5, 21.5 | 65, 13.5, 21.5 | 62, 10.5, 27.5 |
| Lower H. V (MJ/kg)              | 43.5     | 27.0    | 20.1     | 33.3      | 33.1      | 29.6    |
| Heat of evap. (kJ/kg)           | 223.2    | 725.4   | 920.7    | 474.3     | 582       | 501.7   |
| Stoichiometric A/F ratio        | 14.6     | 9.0     | 6.4      | 11.1      | 14.6      | 11.2    |
| Oxygen content, mass %          | 0.0      | 34.7    | 49.9     | 21.6      | 21.6      | 9.54    |
| Density (kg/m\(^3\))           | 760      | 790     | 796      | 802       | 810       | 791     |
| Saturation pressure             | 31       | 13.8    | 31.69    | 2.3       | 2.27      | 53.4    |
| Flash point (°C)                | –45 to –38 | 21.1 | 11.1     | 28        | 35        | 17.8    |
| Auto-ignition temp. (°C)        | 420      | 434     | 470      | 415       | 385       | 560     |
| Boiling point (°C)              | 25–215   | 78.4    | 64.5     | 108       | 117.7     | 56.1    |
| Solubility in water             | <0.1     | Fully miscible | Fully miscible | 10.6      | 7.7       | Miscible |
| Vapor toxicity                  | Moderate | Very toxic | Toxic | Moderate | Moderate | Low     |

4. Comparison between Dual Biofuel Blends in SIE

Different dual blended biofuels are compared to each other in the literature. Elfasakhany [151] examined ethanol–methanol–gasoline, i-butanol–ethanol–gasoline and n-butanol–i-butanol–gasoline blends, as shown in Figures 3 and 4. The engine pollutant emissions, performance and combustion characteristics of the three dual blended biofuels are experimentally compared at the same rates and engine working conditions to establish the best prospective one as an alternative to fossil fuel. The results displayed that the engine behavior (volumetric efficiency, output torque, and brake power) were amplified, while engine emissions (unburned hydrocarbons and carbon monoxide) were decreased by using ethanol–methanol–gasoline blends, in comparison with other biofuel blends. However, n-butanol–i-butanol–gasoline blends demonstrated the maximum emissions and the lowermost performances among all tested biofuel blends; i-butanol–ethanol–gasoline blends can offer a reasonable performance and emissions among the three tested biofuel blends. It was also pointed out that the pollutant emissions of all dual biofuel blends are lower than the pure gasoline. Nonetheless, the engine performances of n-butanol–i-butanol–gasoline and i-butanol–ethanol–gasoline blends are inferior to pure gasoline, while ethanol–methanol–gasoline displayed a better performance than the pure gasoline. Elfasakhany [152] has examined, for the first time in internal combustion engines, a few new blended biofuels as possible alternatives to fossil fuels. I-butanol was blended in one fuel blend (iBM) with bio-methanol, and gasoline and n-butanol were blended in the other, with bio-ethanol and gasoline (nBE) at rates of 3–10 vol. percent of biofuels for both dual blends. As presented in Figures 5 and 6, the two dual blended biofuels for the engine pollutant emissions and combustion efficiencies in an SIE were contrasted with each other, as well as with pure gasoline. The results specified that, relative to conventional pure gasoline fuel, the two biofuel blends tested can achieve the objective of supplementary green sustainability. IBM fuel blends, which are 31%, 19% and 32% lower than pure gasoline for CO, CO\(_2\) and UHC emissions, respectively, obtained the most superior/best engine emissions. Nevertheless, when using plain gasoline, there are trivial advantages in engine efficiency over both iBM and nBM dual biofuel blends. The study also emphasizes that the combination of i-butanol–bio-methanol with gasoline results in higher engine efficiency than the combination of n-butanol–bio-ethanol with gasoline by about 6.2, 0.9, 2.6 and 1.47%, for in-cylinder pressure (ICP), exhaust gas temperature (EGT), brake power (BP) and torque (Torq), respectively. The nBE blended biofuel showed a slight decrease in engine performance, in comparison with pure gasoline, by approximately 3.4, 2.4, 5, 1.9 and 5.2% for EGT, volumetric efficiency (VE), ICP, Torq and BP, respectively.
and torque (Torq), respectively. The nBE blended biofuel showed a slight decrease in engine performance, in comparison with pure gasoline, by approximately 3.4, 2.4, 5, 1.9 and 5.2% for EGT, volumetric efficiency (VE), ICP, Torq and BP, respectively.

Figure 3. Comparisons of brake power, volumetric efficiency, and torque for ethanol–methanol (EM), n-butanol–i-butanol (niB) and ethanol–i-butanol (iBE) blended with gasoline and neat gasoline (baseline) in %.

Figure 4. Comparisons of CO, CO₂, and UHC emissions for ethanol–methanol (EM), n-butanol–i-butanol (niB) and ethanol–i-butanol (iBE) blended with gasoline and neat gasoline (baseline) in %.
Figure 5. Comparison of volumetric efficiency (VE), exhaust gas temperature (EGT), in-cylinder pressure (ICP), brake power (BP), and torque (Torq) for i-butanol–bio-methanol–gasoline blends (iBM), n-butanol–bio-ethanol–gasoline blends (nBE) and neat gasoline (baseline) on average basis.

Figure 6. Comparison of CO, UHC and CO2 emissions for i-butanol–bio-methanol–gasoline blends (iBM), n-butanol–bio-ethanol–gasoline blends (nBE) and neat gasoline (baseline) on average basis.

5. Comparison between Single and Dual Biofuel Blends in SIE

In a few publications, single and dual biofuels blended with gasoline were compared. A comparison between ethanol–methanol–gasoline blends (EM), bio-ethanol–gasoline blends (E) and methanol–gasoline blends (M) was carried out by Elfasakhany [153] on engine performance and emissions at similar rates of biofuel and engine working conditions, as shown in Figures 7 and 8. For the dual biofuel blends (EM), the results showed greater volumetric efficiency and output torque than ethanol–gasoline blends, and greater output brake power than that of methanol–gasoline blends. The author concluded that emissions (CO and UHC) and performance were improved by both dual and single biofuel blends compared to pure gasoline. In another study, Elfasakhany et al. [154] investigated...
pollutant emissions and engine efficiency using n-butanol–methanol–gasoline blends; as shown in the figures, the findings were contrasted with single n-butanol–gasoline blends and neat gasoline (from Figures 9 and 10). In the case of a high rate of biofuel blended into gasoline, the authors suggested dual biofuel blends, but single biofuel blends were needed at a low rate. Balaji et al. [155] investigated ethanol-i–butanol–gasoline mixtures’ outputs and exhaust emissions in SIE at constant engine speeds, but under different conditions of engine torque. The study contrasted dual biofuel blends (10% ethanol–2.5% i-butanol, 10% ethanol–5% i-butanol and 10% ethanol–7.5% i-butanol in gasoline) with single blends (10, 20 and 30% ethanol in gasoline), but there was no distinction between dual biofuel blends and i-butanol–gasoline blends in the study. The findings showed a decrease in CO and HC emissions and an increase in NOx emissions (dual and single) relative to pure gasoline for both fuel blends. The outcome also resulted in the growth of volumetric efficiency, braking power, thermal efficiency, and fuel consumption in dual and single blends relative to pure gasoline. Siwale et al. [156] compared dual biofuel blend efficiency, combustion and emission characteristics (53% methanol–17% n-butanol–30% gasoline) and a couple of single biofuel blends (70% methanol–30% gasoline and 20% methanol–80% gasoline). The study advocated the use of dual blends over single blends or pure gasoline. Nazzal [157] researched engine performance using dual biofuel blends of 6% ethanol–6% methanol–88% gasoline and a few single biofuel blends (12% methanol in gasoline and 12% ethanol in gasoline). In contrast to pure gasoline fuel, engine performance (thermal efficiency and brake power) showed an improvement in all fuel blends. In contrast with pure gasoline, it is also shown that brake-specific fuel consumption has been improved for all fuel blends. A comparison of engine efficiency and emissions using n-butanol–i–butanol–gasoline (niB) blends and i-butanol–gasoline blends (iB) and pure gasoline at two extreme engine speeds (2600 and 3400 r/min) was undertaken by Elfasakhany [158], as shown in Figures 11 and 12. The findings showed that the n-butanol–i–butanol–gasoline blends increased pollutant emissions more significantly than i-butanol–gasoline blends; in addition, the dual biofuel blends (niB) increased exhaust gas emissions by 15, 20 and 34% for UHC, CO and CO$_2$ respectively, compared to clean gasoline. The findings also showed that n-butanol–i–butanol–gasoline blends enhanced engine efficiency compared to single biofuel blends (iB), but that depends on the speed of the engine. As seen from Figure 11, the engine output using niB at both test speeds is better than that of iB (with the exception of torque at 2600 r/min, volumetric efficiency at 3400 r/min and EGT). In summary, positive n-butanol/i–butanol additions to gasoline fuel include engine efficiency reporting and emission reductions compared to i-butanol–gasoline under the same engine operating conditions, depending on engine speeds. In the end, the author favored the dual blends of biofuel as opposed to the single one and/or pure gasoline. Elfasakhany [159] also analyzed blends of ethanol–i–butanol–gasoline, and contrasted the findings with the gasoline and i-butanol–gasoline, as shown in Figures 13 and 14; the study explored the potential for the use of dual blends as a fossil fuel substitute for the next decade. The results have shown that ethanol–i–butanol–gasoline blends have increased emissions of contaminants and engine efficiency relative to i-butanol–gasoline blends. In addition, dual biofuel blends increased the emissions of contaminants by respectively 15, 34 and 20% for UHC, CO$_2$ and CO emissions relative to those of renewable gasoline. The author concluded that the dual biofuel blends may possibly offer the upcoming generation a fossil fuel alternative for gasoline engines; the author supported his conclusion by proving the many benefits of dual biofuel blends over single biofuel blends, as well as neat gasoline. The complete comparisons are summarized in Table 2 for engine performance and emissions of single and dual blended alcohols.
Figure 7. Comparisons of brake power, volumetric efficiency and torque for ethanol–methanol (EM), ethanol (E) and methanol (M) blended with gasoline and neat gasoline (baseline) in %.

Figure 8. Comparisons of CO, CO\(_2\) and UHC emissions for ethanol–methanol (EM), ethanol (E) and methanol (M) blended with gasoline and neat gasoline (baseline) in %.
Figure 9. Comparisons of brake power, volumetric efficiency and torque for n-butanol–methanol (nBM) and n-butanol (nB) blended with gasoline and neat gasoline (baseline) in %.

Figure 10. Comparisons of CO, CO$_2$ and UHC emissions for n-butanol–methanol (nBM) and n-butanol (nB) blended with gasoline and neat gasoline (baseline) in %.
Figure 11. Comparison of brake power (BP), torque (Tq), volumetric efficiency (VE) and exhaust gas temperature (EGT) for i-butanol–gasoline blends (iB), n-butanol–i-butanol–gasoline blends (niB) and neat gasoline (baseline) at two different speeds.

Figure 12. Comparison of CO, CO$_2$ and UHC emissions for i-butanol–gasoline blends (iB), n-butanol–i-butanol–gasoline blends (niB) and neat gasoline (baseline) at two different speeds.
Table 2. Engine Performance (%)

| Properties          | Biofuel | iB | iBE |
|---------------------|---------|----|-----|
| Tq                  | -60     | -40| -30 |
| VE                  | -20     | -20| -10 |
| EGT                 | -10     | -10| -10 |
| Engine Emissions (%)| -30     | -20| -10 |

Figure 13. Comparison of CO, CO2 and UHC emissions for i-butanol–bio-ethanol–gasoline blends (iBE), i-butanol–gasoline blends (iB) and neat gasoline (baseline) at two different speeds (2600 and 3400 r/min).

Figure 14. Comparison of brake power (BP), torque (Tq), volumetric efficiency (VE) and exhaust gas temperature (EGT) for i-butanol–bio-ethanol–gasoline blends (iBE), i-butanol–gasoline blends (iB) and neat gasoline (baseline) at two different speeds (2600 and 3400 r/min).
Table 2. Performance and emissions of single and dual alcohol blends.

| Biofuel | Properties | BP | Tq | VE | CO | UHC | CO₂ |
|---------|------------|----|----|----|----|-----|-----|
| E       |            | 8.5| 1.2| 16 | −20| −10 | 4.6 |
| AC      |            | 3.3| 1.6| 1.2| −32| −20 | −24.6|
| iB      |            | −5.6| −1.36| −2.1| −11.6| −6.8| −36|
| nB      |            | −3.6| −1.6| −2.6| −10| −16.2| −35|
| M       |            | 1  | 0.5| 21 | −30| −12.8| 10 |
| iBE     |            | −2.3| −1.7| −2.7| −14| −14| −14 |
| niB     |            | −3.1| −1.9| −3.3| −5| −13.5| −18 |
| EM      |            | 5  | 1.5| 17 | −21| −18| 6.3 |
| nBM     |            | −4.3| −2.3| −2.9| 10| 3.7| −5.8 |
| iBM     |            | −2.6| −0.43| −2.4| −31| −32| −19 |
| nBE     |            | −5.2| −1.9| −2.4| −18| −17| −27 |

6. Benefits and Weaknesses of Using Biofuels in SIE

Biofuels show many benefits, such as decreasing greenhouse gases (GHG) and global warming, and shortening the dependency on fossil fuels. In the literature, some studies have discussed the advantages of specific biofuels in terms of combustion and emissions. In particular, Ryojiro Minato [160] discussed the advantages of bio-ethanol; Liu et al. [161] discussed the advantages of bio-methanol; Veza et al. [162] discussed the advantages of butanol. In other studies, researchers discussed the disadvantages of biofuels [163]. One study summarized the advantages and disadvantages of different biofuel types. The benefits and weaknesses of using biofuels in SIE either in single or dual blended conditions with gasoline are summarized by Elfasakhany [164]. The study concluded that the biofuels can offer promising well-to-wheel CO₂ balance in our environment, and increase engine efficiency and output power. Biofuels’ oxygen content also offers benefits for the fuel combustion. Nevertheless, biofuels showed some weaknesses, such as minor carbon and hydrogen contents and heating values, and some corrosiveness of engine systems for some biofuel type(s). Boiling temperature, absorption with water, vapor toxicity and autoignition of biofuels showed benefits for some types and weaknesses for others; a summary of the benefits and weaknesses of using biofuels in cars is given in Table 3.

Table 3. Benefits and weaknesses of using biofuels compared to gasoline in SI engines.

| Properties         | Bio-Ethanol | Bio-Methanol | I-Butanol | N-Butanol | Acetone |
|--------------------|-------------|--------------|-----------|-----------|---------|
| Performance        | Ben.        | Ben.         | Ben.      | Ben.      | Ben.    |
| Emissions          | Ben.        | Ben.         | Ben.      | Ben.      | Ben.    |
| Oxygen content     | Ben.        | Ben.         | Ben.      | Ben.      | Ben.    |
| Hydrogen content   | Wek.        | Wek.         | Wek.      | Wek.      | Wek.    |
| Carbon content     | Wek.        | Wek.         | Wek.      | Wek.      | Wek.    |
| Absorption with water | Wek.    | Wek.         | Ben.      | Ben.      | Ben.    |
| Boiling Temp.      | Wek.        | Wek.         | Wek.      | Ben.      | Wek.    |
| Vapor toxicity     | Ben.        | Ben.         | Wek.      | Wek.      | Wek.    |
| Heating value      | Wek.        | Wek.         | Wek.      | Wek.      | Wek.    |
| Autoignition       | Ben.        | Ben.         | Wek.      | Wek.      | Ben.    |
| Corrosion          | Wek.        | Wek.         | Ben.      | Ben.      | Wek.    |

Ben: benefits, Wek: weaknesses.

7. Future Biofuels for SIE

The future fuel for SIE is gasoline, which will most probably be kept for the coming decade(s) [165]. This is because of its cost effectiveness and high heating value. The biofuels would be used as blended fuels with gasoline. The most promising biofuels are the second and third generations. The fourth generation biofuels are still under development and not fully dependable [37]. The first generation biofuels are no longer applied due to their food-dependency for production. Biofuels from second and third generations can reduce
the greenhouse gas life cycle. Among the promising second and third generation biofuels, bio-methanol, bio-ethanol, butanol, and bio-acetone are within the foreground.

The next-generation biofuels for SI engines are thought to be the dual biofuel blends. This conclusion is drawn from the early publications, as discussed earlier. Additionally, the conclusion of recommending dual biofuel blends as next-generation fuels is also motivated by the benefits and weaknesses of biofuels. In detail, many benefits are found for ethanol and methanol, but due to some drawbacks, as discussed earlier, researchers have moved towards new biofuel generations, which are n-butanol and i-butanol. However, the new generation showed also some drawbacks. Accordingly, researchers tried to investigate the benefits and weaknesses of different biofuels by mixing them together. For example, most of the issues with ethanol are advantages in i-butanol biofuels, and vice versa; difficulties in using bioethanol–gasoline blend fuels are regulated by the introduction of i-butanol to those blends, and there are similar approaches for i-butanol–gasoline blends, e.g., by the introduction of bio-ethanol. This method is believed to work because i-butanol has been used as a co-solvent to restore the stability of the ethanol–gasoline blend cycle [166].

8. A Proposed Method to Reduce Engine Pollutant Emissions

There are different methods or techniques proposed in the literature to reduce emissions from CIE [167–169]; however, these are rarely in the SIE. A proposed method to reduce engine pollutant emissions was introduced by Elfasakhany [170,171]. The method is based on reformulating the engine pollutant emissions into new fuels, and then re-using this new fuel in the engine again. The author applied exothermic partial oxidation using metal oxides of MgO, ZnO and/or Fe₂O₃ to instantaneously produce syngas from HC emissions. Such neutral thermo-reactions have the opportunity of creating syngas in autothermal and noncatalytic reactors, with significant avoidance of creating CO₂ emission. The CO emission stream can be treated using a water–gas shift reaction. Regarding CO₂ emission, the author used different oxide materials as sorbents for the CO₂, such as lithium zirconates, calcium oxide, lithium silicates and hydrotalcite (HTs)-like materials; the author recommends himself the use of hydrotalcite (HTs)-like materials as an attractive option for CO₂ sorption because of their high sorption capacity at a low temperature.

9. Conclusions

The state of the art of using biofuels in spark ignition engines is reviewed and discussed. Different biofuels, include ethanol, methanol, n-butanol, i-butanol, and acetone, are covered in the study, and compared with each other and with the commercial gasoline under the same rates and conditions. Ethanol and methanol showed many benefits and some drawbacks as alternative fuels for spark ignition engines, in comparison with gasoline. They have the ability to improve engine performance and pollutant emissions; however, they showed some problems in terms of engine starting condition in cold environments as well as a vapor lock in hot climate conditions. They showed also incompatibility with some engine material, and their miscibility with water is another disadvantage. On the other hand, i-butanol and n-butanol showed advantages in engine starting and vapor lock problems. However, they showed very low engine performance and great emissions (CO and UHC). They offer advantages for the greenhouse effect, e.g., low CO₂ emissions are produced from butanol. The ethanol and methanol biofuel blends introduced the highest CO₂ emissions. Regarding acetone blended fuel, it showed a moderate high performance and the lowest emissions (UHC and CO). The CO₂ values for different blends are 10, 4.6, −24.6, −35, and −36% for M, E, AC, nB, and iB, respectively. The CO and UHC for AC are −32 and −20%, respectively, which are the lowest, while the greatest are achieved by iB (−11.6 and −6.8% for CO and UHC, respectively). Other single blends introduced values in between. The greatest performance was introduced by AC for torque (1.6%), E for brake power (8.5%), and M for volumetric efficiency (21%). Blends of dual ethanol and methanol biofuel blends with gasoline showed the best performance and emissions among other dual biofuel blends (n-butanol–i-butanol, i-butanol–ethanol, i-butanol–methanol,
n-butanol–ethanol). However, n-butanol–i-butanol blended with gasoline demonstrated the highest emissions and the lowest performance among other dual biofuel blends. Based on the benefits and drawbacks of different biofuels, dual biofuel blends are thought to be the next generation of fuels for SIE. Finally, one may reduce engine pollutant emissions and reformulate the emissions into new fuels by using metal oxides to produce simultaneously syngas from CO, CO₂ and UHC emissions.

**Funding:** This work was funded by Taif University researchers supporting project number (TURSP-2020/40), Taif University, Taif, Saudi Arabia.

**Acknowledgments:** This work was supported by Taif University researchers supporting project number (TURSP-2020/40), Taif University, Taif, Saudi Arabia.

**Conflicts of Interest:** The author declares no conflict of interest.

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