energies

MDPI

Review

Ethanol/Gasoline Blends as Alternative Fuel in Last Generation Spark-Ignition Engines: A Review on CO and HC Engine Out Emissions

Paolo Iodice [1,*] and Massimo Cardone [2]

[1] Dipartimento di Ingegneria Industriale, Università degli Studi di Napoli Federico II, Via Claudio 21, 80138 Napoli, Italy
[2] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, 80138 Napoli, Italy; massimo.cardone@unina.it
* Correspondence: paolo.iodice@unina.it; Tel.: +39-081-7683277

Abstract: Among the alternative fuels existing for spark-ignition engines, ethanol is considered worldwide as an important renewable fuel when mixed with pure gasoline because of its favorable physicochemical properties. An in-depth and updated investigation on the issue of CO and HC engine out emissions related to use of ethanol/gasoline fuels in spark-ignition engines is therefore necessary. Starting from our experimental studies on engine out emissions of a last generation spark-ignition engine fueled with ethanol/gasoline fuels, the aim of this new investigation is to offer a complete literature review on the present state of ethanol combustion in last generation spark-ignition engines under real working conditions to clarify the possible change in CO and HC emissions. In the first section of this paper, a comparison between physicochemical properties of ethanol and gasoline is examined to assess the practicability of using ethanol as an alternative fuel for spark-ignition engines and to investigate the effect on engine out emissions and combustion efficiency. In the next section, this article focuses on the impact of ethanol/gasoline fuels on CO and HC formation. Many studies related to combustion characteristics and exhaust emissions in spark-ignition engines fueled with ethanol/gasoline fuels are thus discussed in detail. Most of these experimental investigations conclude that the addition of ethanol with gasoline fuel mixtures can really decrease the CO and HC exhaust emissions of last generation spark-ignition engines in several operating conditions.

Keywords: renewable energy; carbon monoxide; unburned hydrocarbons; ethanol/gasoline blends; SI engines

check for updates

Citation: Iodice, P.; Cardone, M. Ethanol/Gasoline Blends as Alternative Fuel in Last Generation Spark-Ignition Engines: A Review on CO and HC Engine Out Emissions. *Energies* **2021**, *14*, 4034. https://doi.org/10.3390/en14134034

Academic Editor: James W. G. Turner

Received: 28 May 2021
Accepted: 29 June 2021
Published: 4 July 2021

1. Introduction

Nowadays nations worldwide are strongly supporting research activity towards alternative renewable fuels both to supplant fossil fuels and to decrease harmful air pollutants. Currently, internal combustion engines give a crucial effect on air pollution; thus, alternative fuel research is accelerating to reduce the environmental problems due to fossil fuels. Really, fossil fuels still are the main source of worldwide energy and global energy consumption is estimated to rise by about 33% by 2050 [1,2]. Besides, the current amount of fossil fuel will decline quickly in the next five decades [3]. In this regard, dangerous air pollutants caused by the road transport sector, such as carbon monoxide (CO), particulate matter and unburned hydrocarbons (HC) sharply alter the air quality, also involving significant negative effects on human health [4]. Besides, nowadays, nearly 20% of worldwide greenhouse gas (GHG) emissions are the result of the growing number of circulating diesel and petrol cars [5,6].

Consequently, owing to large emissions from transportation sector, the growing need of energy and increased fuel prices [7], many countries are actively supporting research activity towards substitute fuels from renewable sources for their potential for reducing exhaust emissions and to supplant fossil fuels [8–10]. As an alternative compared to fossil fuels, alternative fuels from renewable sources can be produced from wastes and agricultural yields utilized as the feedstock [11–15].

Actually, among the renewable fuels existing for spark-ignition (SI) engines, ethanol is considered worldwide as an important renewable fuel when mixed with pure gasoline because of its good physicochemical properties [16–19]. Besides, in the last years, ethanol has attained growing attention as an alternative fuel for petrol cars owing not only to reduce toxic air pollutants in metropolitan areas, but also to decreased production prices [20]. Ethanol is typically utilized in spark-ignition engines by blending it with pure gasoline in specific percentages and then injecting it within the inlet manifold by direct injection.

Presently, EU legislation states that, as an automotive fuel, 10 vol% is the highest concentration of ethanol in ethanol/gasoline mixtures (E10), which can be really commercialized [21]. In fact, at this low percentage of ethanol in ethanol/gasoline mixtures, the engine design should not require substantial modification to perform well, while SI engines operating on 15 and 20 vol% of ethanol in ethanol/gasoline blends could lead to failure, reducing engine durability. In effect, the presence of ethanol fuel affects corrosion and wear mechanisms that involve poor sealing and high leakage, leading to loss of compression and cylinder misfires. In addition, since ethanol is basically corrosive, it may degrade the plastic, rubber and metal parts of the fuel system [22–24]. The use of ethanol fuel blends also affects tribological difficulties as the ethanol becomes contaminated with the lubricating oil, contributing to engine failure [25,26]. For all these reasons, at an ethanol fraction higher than 10 vol%, conventional SI engines necessitate broad modifications [27]. Really, 85 vol% ethanol in gasoline (E85), which is sold in Brazil, cannot be utilized on traditional petrol cars, and can be utilized in flex fuel vehicles (FFVs) only. In fact, presently, about 90% of new petrol cars sold in Brazil are FFVs [28–31].

However, many advantages are related to ethanol use in spark-ignition engines as compared to gasoline. First, the research octane number of ethanol fuel is higher than that of gasoline; as a result, to get more power from the engine, and ethanol/gasoline mixtures can tolerate higher pressures before detonating. The utilization of ethanol can also improve the thermal efficiency of spark-ignition engines because it depends on the compression ratio and, at the same time, ethanol accepts the utilization of high compression ratios without knocking [5]. Besides, in comparison with net gasoline, the higher oxygen fraction of ethanol entails a more complete combustion process. In fact, the use of ethanol in gasoline/ethanol-blended fuels deliver more oxygen than gasoline; thus, in these lean conditions, higher combustion efficiency can ensue [27,32,33].

Another benefit is the decrease of the GHG emissions when ethanol fuel is used in gasoline/ethanol mixtures. In effect, the lower carbon fraction of ethanol in comparison with net gasoline and the sort of renewable sources used during ethanol production process involve, as a net result, lower CO_2 exhaust emissions [34,35]. On the other hand, the main disadvantage of using ethanol as an alternative fuel in SI engines is related to the lower Reid vapor pressure of ethanol than that of gasoline, which makes a cold-start very tricky.

Previously, several researchers have worked with ethanol/gasoline mixtures as fuel substitutes for new generation spark-ignition engines [36–41]. Really, gasoline/ethanol-blended fuels should decrease exhaust emissions in SI engines compared to pure gasoline, but in scientific literature there are some incongruities in the explanations of CO and HC exhaust emissions, which make basic knowledge inadequate. Actually, there are several studies on exhaust emissions and engine performance of SI engines when ethanol/gasoline blends are used as a gasoline substitute; however, to the best of the authors' knowledge, there is only a restricted amount of research that focus on the effect of the compression ratio, the cold-transient phase and engine load on CO and HC engine out emissions. In fact, most of these experimental studies have focused on the engine out emissions of warmed SI engines when fueled with ethanol/gasoline-blended fuel, but without offering detailed investigation on the CO and HC emissions in real working conditions. Really, during the cold-start phase, SI engines need fuel-rich injections to prevail over the scarce mixing of the inlet charge. Besides, the efficiency of advanced catalysts adopted on last generation SI engines can be reduced due to both low temperatures and rich values of the air/fuel mixture that, therefore, produce a huge quantity of HC and CO engine out emissions during the cold phase.

Thus, since there is a gap of research results regarding the effect of cold-start phase, engine load and compression ratio on HC and CO emissions in spark-ignition engines fueled with gasoline/ethanol-blended fuels, this review article was planned to remedy this lack of knowledge. Besides, HC and CO emissions from SI engines fueled with gasoline/ethanol blends can become a potential barrier to market expansion of ethanol that has enormously increased in the last decade.

For all these reasons, an updated research on the issue of CO and HC exhaust emissions related to use of ethanol/gasoline blends in spark-ignition engines is necessary. In our recent studies based on experimental tests [5,27,32], CO and HC engine out emissions of a new generation four-stroke SI engine were measured in cold and hot operating conditions for several ethanol/gasoline blends. Starting from such results, the aim of this new investigation is to offer a complete literature review on the present state of ethanol combustion in last generation spark-ignition engines under real working conditions to clarify the possible change in CO and HC emissions. In the first section of this paper, a comparison between physicochemical properties of gasoline and ethanol is examined to forecast the potential effects on engine out emissions. In the second section, this article focuses on the effects of ethanol/gasoline blends on CO and HC formation; thus, numerous studies related to both combustion characteristics and exhaust emissions in spark-ignition engines fueled with ethanol/gasoline fuels are examined. Most of these experimental investigations conclude that the addition of ethanol with gasoline fuel blends can decrease the HC and CO exhaust emissions of new generation SI engines. The results obtained in this research can also help to guide the current research of emissions reduction systems related to use of ethanol in gasoline engines.

2. Physicochemical Properties of Gasoline and Ethanol: A Comparison

Ethanol is a flammable, volatile, transparent and colorless oxygenated liquid hydrocarbon. Moreover, it is also mixable in non-polar solvents and is characterized by a pungent odor [42–46]. Though, synthetic ethanol and bio-based ethanol (namely bioethanol) are essentially the same substance because they have the same molecular formula that is C_2H_5OH [47–51].

The characteristics of ethanol and gasoline/ethanol blends as fuels for last generation SI engines depend on numerous physicochemical properties such as heating value, density, oxygen content, stoichiometric air/fuel ratio, latent heat of vaporization and research octane number [52–55]. Besides, it is clear that engine performance and exhaust emissions of new SI engines strictly depend on these properties. Key chemical properties of gasoline and ethanol are assessed and exhibited in Table 1; thus, by comparing some of these characteristics, observations and differences between the two fuels can be itemized, as shown below.

Density. Usually, the density of a fuel influences fuel atomization efficiency and combustion characteristics. In fact, higher density can involve greater fuel flow resistance, which affects higher viscosity, resulting in a reduced fuel injection. Since the density of pure ethanol (equal to 795 kg/m^3) is higher than that of pure gasoline (equal to 755 kg/m^3), the volumetric fuel economy is enhanced because the volumetric fuel pump injects less mass of ethanol/gasoline-blended fuel than net gasoline [7,20].

Table 1. Physicochemical characteristics of gasoline and ethanol [27,38,47,56–71].

Property	Gasoline	Ethanol
Chemical formula	~$C_8H_{15.6}$	C_2H_5OH
C-fraction [mass %]	87.4	52.2
O-fraction [mass %]	0	34.7
H-fraction [mass %]	12.6	13.0
Lower heating value [MJ/kg]	44.0	27.0
Molar mass [kg/kmol]	100 ÷ 105	46.07
Kinematic viscosity [mm^2/s]	0.5	1.3
Reid vapor pressure (RVP) [kPa]	53 ÷ 60	17
Specific gravity at 20 °C	0.7392	0.7894
Research octan number (RON) [-]	91 ÷ 100	110
Density at 15 °C [kg/m^3]	750 ÷ 765	785 ÷ 810
Stoichiometric air/fuel ratio [-]	14.2 ÷ 15.0	9.0
Latent heat vaporization [kJ/kg]	380 ÷ 400	910
Water solubility [%]	0	100
Auto ignition temperature [°C]	257	425

Lower Heating Value. The energy content of ethanol (27,000 kJ/kg) is nearly 65% of gasoline energy content (44,000 kJ/kg). Therefore, ethanol fuel should involve higher fuel consumption in comparison with pure gasoline. Such a difference in the lower heating value between the two fuels similarly causes an increase in the fuel consumption of the gasoline/ethanol mixtures with the increase of the ethanol content in the mixtures. However, such consideration does not entail a substantial engine power reduction with a growing percentage of ethanol in the blended fuels. In effect, the heating value of the stoichiometric air/fuel mixtures (that is the ratio between the lower heating value and stoichiometric air/fuel ratio) can be calculated by using the data of Table 1; it is about 3 MJ/kg both for air/gasoline and air/ethanol mixtures. Besides this factor remains constant even considering several ethanol/gasoline-blended fuels. Really, since this value represents the energy content introduced in the engine with the unity mass of stoichiometric air/fuel mixture, the stoichiometric air/ethanol mixture holds the same amount of energy of the stoichiometric air/gasoline mixture [20,49].

Latent Heat of vaporization. The heat of vaporization of ethanol (around 910 kJ/kg) is higher than that of gasoline (around 390 kJ/kg). Consequently, since ethanol fuel needs more heat to vaporize in comparison with gasoline, the temperature of the intake manifold is reduced when ethanol is used as an alternative fuel in SI engines, thus improving the volumetric efficiency of the engine. However, higher heat of vaporization also results in lower burning velocity and combustion temperature, which can involve higher HC and CO engine out emissions. Moreover, high heat of vaporization of ethanol can also involve problems during the cold-transient phase chiefly during cold weather conditions owing to the severe cooling effect of the air/fuel blends under extremely low ambient temperature [47,72,73]. This item is better explained in the next sections of the paper.

Oxygen content. As shown in Table 1, ethanol has about 34.7% oxygen, which involves higher combustion efficiency. Really, because of the greater quantity of oxygen in ethanol/gasoline blends, a more complete and regular combustion process and higher combustion temperatures can be attained in comparison with the use of gasoline. Under such fuel-lean conditions, the CO and HC engine out emissions can also be decreased (leaning effect) and this reduction is connected to the rise in oxygen content in the ethanol/gasoline mixtures [20,27,74].

Reid vapor pressure. The Reid vapor pressure of ethanol is extremely low compared to that of net gasoline, as shown in Table 1 (17 kPa and around 55 kPa, respectively). Therefore, during the cold-start transient of the engine, higher HC and CO cold emissive levels can occur owing to the very low volatility of ethanol. However, the Reid vapor pressure of ethanol/gasoline-blended fuels does not depend linearly on the ethanol fractions in the blends. As a benefit, lower vapor pressure of ethanol compared to gasoline can decrease the evaporative emissions [75,76].

Research Octane Number. As explained in Table 1, the research octane number of ethanol (about 110) is higher than that of gasoline (about 95). For this reason, to get more power from the engine, gasoline/ethanol blends, in comparison with pure gasoline, can withstand higher compression ratios before detonating. Furthermore, since the thermal efficiency depends on the volumetric compression ratio and gasoline/ethanol mixtures can tolerate the use of high compression ratios without knocking, the use of ethanol can also boost the thermal efficiency of spark-ignition engines [20,77].

Stoichiometric air/fuel ratio. On analyzing the stoichiometric air/fuel equivalence ratios exposed in Table 1, combustion of ethanol obviously needs a lower amount of air in comparison with pure gasoline (about 1.7 times less). In addition, the air flow rate entering the cylinder remains constant for fixed engine speed and throttle valve opening. Consequently, to keep constant the air/fuel equivalence ratio, the ECU electronic control unit (ECU) must increase the consumption of the gasoline/ethanol-blended fuels [27,28].

Viscosity. On comparing the data shown in Table 1, it is clear that the viscosity of ethanol is higher than that of gasoline. In this regard, it is well known that viscosity of a fuel can normally affect spray characteristics, combustion quality and fuel drop size. In detail, since high viscous fuel forms larger droplets during injection, combustion quality in SI engines is damaged with the use of ethanol as alternative fuel, involving higher HC and CO exhaust emissions [7,78].

3. Effect of Gasoline/Ethanol Blends on HC and CO Exhaust Emissions

The combustion temperature, combustion duration and oxygen content are the main parameters affecting the HC and CO emissions in spark-ignition engines. The experimental investigations analyzed in this paper tested ethanol/gasoline mixtures from SI engines with different ethanol percentage in the blended fuels, from 3 vol% ethanol to as high as 100 vol% (that is pure ethanol). In the previous section, a comparison between fuel properties related to combustion of gasoline and ethanol has been shown. Clearly, the difference in physicochemical properties between ethanol and gasoline also affects the properties of different ethanol/gasoline mixtures, as already explained in detail in Table 1. From this table it can be detected that, with the growth in fraction of ethanol in the ethanol/gasoline fuels, the octane number, density and latent heat of vaporization increase while, at the same time, the heating value of the blends decreases. All the experimental studies selected for the purpose of the present paper are analyzed in detail to identify the effect of variations in physicochemical properties of ethanol/gasoline mixtures (resulting from variation in ethanol content) on the amount of CO and HC emissions produced inside the cylinder of SI engines.

The hydrocarbon emissions from the SI engines with about 200 organic compounds come from unburned mixtures of the fuel molecules owing to irregular mixing and incomplete combustion process. Exhaust emissions of this air pollutant are produced at the surface of the spray by the over-leaned fuel and at the nozzle sac through fuel effusing [47]. Generally, unburned HC composition in SI engines comprises aromatics, olefins and paraffins. Four basic mechanisms of HC formation in spark-ignition engines can be itemized as follows.

- Cyclic misfires and incomplete combustion of air/gasoline mixture.
- The unburned mixture of air/gasoline confined in the ring crevices causes rise in hydrocarbon formation.
- The flame-quenching layer that propagates at cold wall surfaces of the combustion chamber.
- The absorption process of unburned fuel by deposits in the combustion chamber and lubricating cylinder oil films [47].

Several experimental investigations have been performed by researchers to examine the impact of additional ethanol in gasoline fuel blends on HC emission; as described in this research, HC exhaust emissions decreased by adding ethanol in ethanol/gasoline blends compared to pure gasoline.

Hsieh et al. [79] examined the characteristics of gasoline/ethanol blends with different ethanol percentage (from 0% v/v to 30% v/v) on a multi-point injection SI engine equipped with air/fuel ratio closed-loop control. In these tests, the air/fuel ratios moved from rich toward stoichiometric ratios (leaning effect) as the ethanol fraction increased, resulting in a more complete combustion process and increased in-cylinder temperatures, which led to a decrease in HC exhaust emission.

In the experimental study performed by Singh et al. [80], by using gasoline blended with 10% v/v ethanol as test fuel, a decrease in HC emission was revealed as compared to gasoline due to high oxygen content of alcohol and the resulting leaning effect. The decrease in HC emission was also attributed to faster flame speed caused by the combustion of ethanol/gasoline blend as compared to gasoline; under such operating condition, the resulting quick and complete combustion process involves an increase in the cylinder temperature, which reduces HC formation. A similar experimental study was conducted by Yücesu et al. [81] by using gasoline blended with 60% v/v ethanol as test fuel; at 5000 rpm and 31.45% at 2000 rpm, a decrease in HC exhaust emission was measured up to 16.45% as compared to gasoline. Such reduction was due to the faster flame speed of ethanol compared to pure gasoline, which enhances the combustion process of alcohol fuel blends, thus affecting lower HC emissions.

Besides, by adding ethanol in ethanol/gasoline blends, HC emission levels can decrease especially under higher engine speeds in comparison with slower ones. Really, additional experiments [82] disclosed that the addition of ethanol can decrease HC exhaust emissions particularly under high engine speed (about 6000 rpm). Such a decrease in HC emission was due to a better homogenization of the air–fuel mixture at high engine speed, which tends to enhance combustion efficiency and increase the in-cylinder temperature.

Chen et al. [83] studied the effect of using ethanol/gasoline blends on CO and HC emissions as compared to pure gasoline in a multi-port fuel injection engine at a compression ratio fixed to 9.1. In accordance with the results obtained in this research, ethanol content in the blend higher than 20% decreased CO and HC emissions substantially as compared to pure gasoline.

CO exhaust emissions from SI engines, which are colorless, odorless and toxic air pollutants, result from incomplete combustion of hydrocarbon fuels above all in absence of air/fuel management system. Generally, in SI engines combustion becomes incomplete when there is time delay of the combustion cycle and insufficient quantity of air in the air/fuel mixture. For this reason, CO emissions in SI engines depend strictly on the oxygen fraction; the high content of oxygen in the ethanol/gasoline blends can effectively improve the combustion efficiency and involve the leaning effect in the fuel-rich zones of the engine, thus reducing CO exhaust emissions [84]. Decreases in CO exhaust emissions were found in experimental studies performed by Rice et al. [85] on SI engines by adding ethanol in gasoline; such decreases in CO emissions were caused by the faster flame speed of alcohols that enhances combustion process in SI engines. These reductions in CO emissions were also attributed to the lower stoichiometric value of ethanol compared to that of gasoline. Similar outcomes were found by He et al. [86]; by using gasoline blended with 10% and 30% v/v ethanol as test fuels, CO exhaust emissions decreased at idle speed compared to pure gasoline due to the high amount of oxygen, which efficiently improves the combustion in SI engines. In the study performed by Masum et al. [87], by adding ethanol in gasoline, a decrease in CO exhaust emission reached up to 12.4 % as compared to the use of pure gasoline due to the higher laten heat of vaporization of the alcohol/gasoline blends, which accelerates the combustion process.

Some experimental tests analyzed the effect of ethanol/gasoline blends on emissive behavior of two-wheelers. For example, Jia et al. [88] studied the influence of using E10 test fuel (10% ethanol v/v in gasoline) on engine out emissions of a four-stroke motorcycle (with engine displacement of 125 cm^3 and without catalyst). In this study, significant decreases in CO and HC emissions were found as compared to the use of commercial gasoline; these results were due to the oxygenated properties of ethanol in the blends, which are more effective in enhancing the combustion process and enhancing oxidation of hydrocarbons [5,17].

Yao investigated the impact of ethanol/gasoline-blended fuels on exhaust emissions of a four-stroke motorcycle equipped with carburetor system and engine displacement of 125 cm^3 [89]. The test fuels were prepared by blending ethanol with pure gasoline in different fractions (3, 10, 15, and 20% v/v) without changing the research octane number (RON was fixed to 95). Since the test engine was not equipped with a computerized fuel injection system, the content of fuel supply was not corrected instantly according to the combustion conditions. Under such operating conditions, the subsequent higher air/fuel ratios of ethanol/gasoline blends resulted in fuel-lean conditions (high amount of oxygen in the air/fuel mixture) that decreased CO emissions. However, with adding ethanol in the fuel blends, HC emissions did not decrease in the same way. In effect, with rising oxygen quantity in ethanol/gasoline blends over a specific lean limit (ethanol fraction >20% v/v) and for a constant RON gasoline, misfires and changes in the combustion conditions became more frequent, thus resulting in less emission decreases in HC emission than those of low ethanol fractions (<20% v/v).

Additionally, Yang et al. [90] examined the emissive behavior of regulated exhaust emissions of nine motorcycles equipped with four-stroke engine, carburetor system and two-way catalytic converter as an after-treatment system. In this experimental activity, the motorcycles were fueled with 3% ethanol v/v in gasoline/ethanol blends; CO and HC exhaust emissions reduced by about 20.0% and 5.3%, respectively, owing to improvement in the combustion process as result of the higher oxygen amount in ethanol/gasoline-blended fuels as compared to pure gasoline.

To evaluate the influence of turbocharger on engine emissions of last generation SI engines, in a recent publication [91], the exhaust emissions were measured in a turbocharged direct injection engine fueled with ethanol/gasoline blend (E10). This engine was operated under both cold-start and steady-state working conditions. As major results, several sharp increase and decrease in HC formation were detected under deceleration working conditions. In addition, enhancing the coolant water temperature in the jacket of the engine can benefit to decrease flame-quenching distance near the combustion chamber, thus reducing the HC exhaust emissions. CO exhaust emissions, during the cold-start transient phase, regularly reached peak levels under deceleration working conditions, whereas, under a steady-state working condition, CO emissions were very high under high engine load and high engine speed.

3.1. *Effect of Cold-Start*

In recent publications based on experimental results, several ethanol/gasoline test fuels were used to evaluate energy consumption and engine out emissions of a large-size motorcycle equipped with a last generation four-stroke spark-ignition engine (engine displacement of 1000 cm^3) and a three-way catalyst [5,27,32]. In one of these research studies [27], HC and CO exhaust emissions were measured in cold and hot working conditions over the execution of chassis-dynamometer tests.

In such experimental activity, as shown in Figures 1 and 2, CO and HC cold emissions were always higher than the emission levels measured within the hot operating conditions due to catalyst inefficiency, mixture enrichment and partial combustion, which characterize the cold-start transient for all test fuels. Throughout the cold-transient phase, the decrease in the CO emissions was significant for E20 test fuel (20% ethanol v/v) compared to both commercial gasoline CE0 and oxygen-free gasoline E0. Such a decrease was due to the rise in oxygen fraction in the gasoline/ethanol mixtures that enhances the oxidation of CO in the fuel-rich zones of the engine, thereby involving a more efficient combustion process under cold operating conditions. In contrast, in Figure 1 it is also obvious that CO emission factor of E30-blended fuel measured within the cold phase is higher than that of E20 fuel; in effect, with a growing ethanol fraction in the test fuels, the heating value reduces and concurrently the latent heat of vaporization rises. Under these operating conditions, the burning velocity and flame temperature of E30 fuel become lower than that of E20 fuel, leading to a less efficient and complete combustion and, therefore, to higher HC and CO cold emissive levels [27].

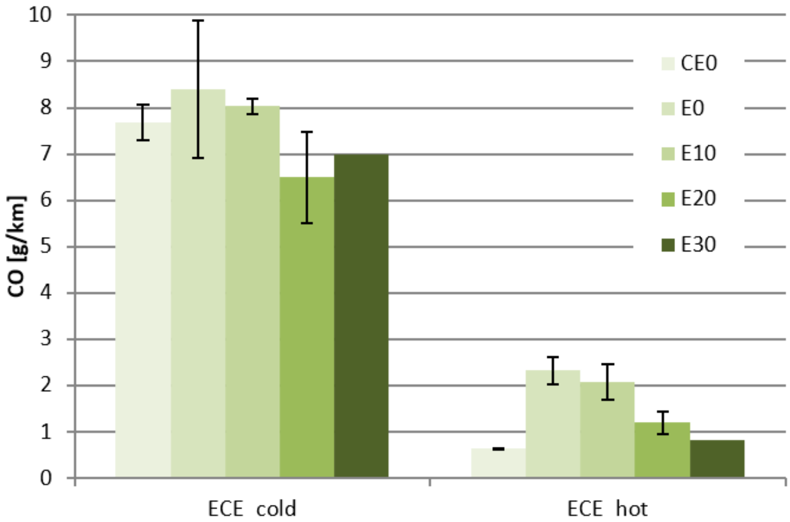

Figure 1. CO emission factors measured on the hot and cold phases of the ECE driving cycle: comparison between commercial gasoline (CE0), oxygen-free gasoline (E0), 10% ethanol v/v (E10), 20% ethanol v/v (E20) and 30% ethanol v/v (E30) [27]. Reproduced with permission from Applied Thermal Engineering; published by Elsevier, 2018. License Number: 5094070055330.

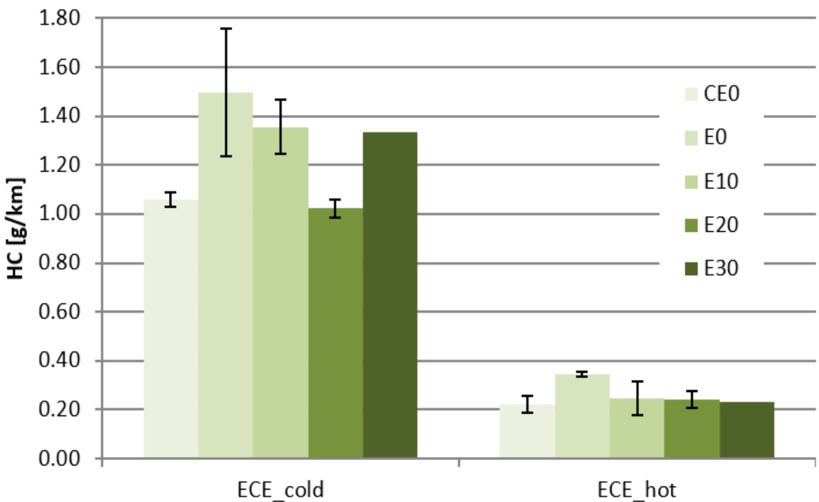

Figure 2. HC emission factors measured on the hot and cold phases of the ECE driving cycle: comparison between commercial gasoline (CE0), oxygen-free gasoline (E0), 10% ethanol v/v (E10), 20% ethanol v/v (E20) and 30% ethanol v/v (E30) [27]. Reproduced with permission from Applied Thermal Engineering; published by Elsevier, 2018. License Number: 5094070055330.

In general, during the cold-start transient phase, the higher oxygen fraction in the blended fuel is more efficient at enhancing oxidation of HC emissions compared to oxygen-free gasoline (E0), as exposed in Figure 2 for E10 and E20 test fuel. However, with a rising ethanol content in the blends, initially, the Reid vapor pressure rises (hence helping the fuel vaporization within the cold-transient phase), but at percentages of ethanol in the blend higher than 15% v/v, the volatility of gasoline/ethanol fuels declines. In effect, as already described in Table 1, the Reid vapor pressure of ethanol (around 17 kPa) is very low compared to that of pure gasoline (around 55 kPa). Hence, the level of HC emissions of E30-blended fuel measured during the cold-start transient phase is higher than that of

E20 test fuel due to the reduced volatility of the blends at ethanol concentrations higher than 20% *v*/*v* [27].

3.2. Effect of Engine Speed

Dogan et al. [92] examined CO and HC exhaust emissions in a four-stroke four-cylinder SI engine fueled with gasoline/ethanol blends in various ethanol concentrations, under different engine speed and at fixed compression ratio (CR = 8.8:1). In these experiments, as shown in Figure 3, the highest CO emissions were found with the E0 test fuel for each engine speed. Owing to both higher oxygen content in chemical structure and better volatility of ethanol compared to pure gasoline, a cleaner combustion can be ensured by using ethanol/gasoline blends. The lowest CO emissions were measured with the E10 test fuel for each engine speed due to increased volatility of the blends at ethanol fractions lower than 20% *v*/*v*. As explained in Figure 4, the same experiments disclosed that HC emissions decreased with increasing engine speed for all test fuels due to a better homogenization of the air–fuel mixture inside the cylinder at high engine speed, which enhances combustion efficiency and increases the in-cylinder temperature. However, in Figure 4 it is clear that the addition of ethanol in the blends increased HC exhaust emissions at each engine speed owing to the decreased temperature inside the cylinder when ethanol is added.

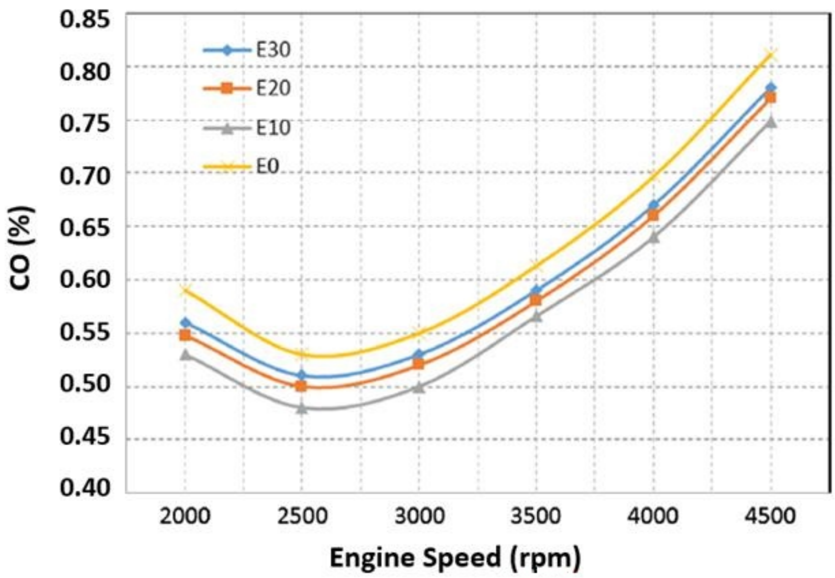

Figure 3. Variation in CO emissions with different engine speed and ethanol content in the blends: comparison between gasoline (E0), 10% ethanol v/v (E10), 20% ethanol *v*/*v* (E20) and 30% ethanol *v*/*v* (E30) [92]. Reproduced with permission from Applied Thermal Engineering; published by Elsevier, 2017. License Number: 5094070701800.

3.3. Effect of Compression Ratio

In the experimental tests performed by Celik [93] on a single-cylinder four-stroke engine, various ethanol ratios with gasoline (E25, E50, E75 and E100) were analyzed as test fuels at constant speed and load, while the compression ratio varied from 6:1 to 10:1. By using gasoline blended with 50% *v*/*v* ethanol, CO exhaust emissions were lower by 54% than those of gasoline at the same compression ratios owing to the increased oxygen concentration in the ethanol/gasoline blends, which improves the combustion process. Moreover, when using E50 as test fuel, CO emissions decreased at high compression ratios (10:1 and 13:1) up to around 50% as compared to low compression ratio (6:1) [3].

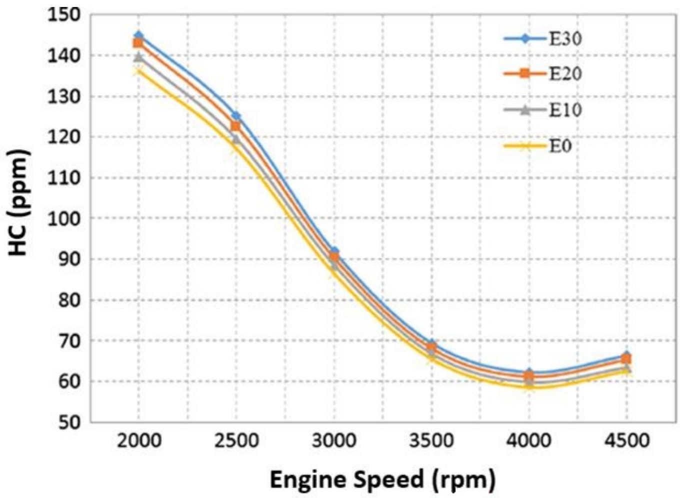

Figure 4. Variation in HC emissions with different engine speed and ethanol content in the blends: comparison between gasoline (E0), 10% ethanol v/v (E10), 20% ethanol v/v (E20) and 30% ethanol v/v (E30) [92]. Reproduced with permission from Applied Thermal Engineering; published by Elsevier, 2017. License Number: 5094070701800.

Koc et al. [94] examined the effect of various gasoline/ethanol blends (0%, 50% and 85% ethanol v/v) on HC and CO exhaust emissions of a four-cylinder SI engine within a wide range of engine speeds and compression ratios (from 5:1 to 13:1). Figure 5 shows the effect of ethanol addition on CO emissions; the CO concentration increased with increasing engine speed for all test fuels due to both resultant increased combustion temperature and insufficient time in the cycle for completion of combustion. The lowest CO emissions were found with the E85 test fuel for each level of engine speed and compression ratio due to oxygen enrichment in the gasoline/ethanol fuel, which enhances the oxidation of CO; really, CO formation is considerably affected even by negligible variations in the air/fuel ratio.

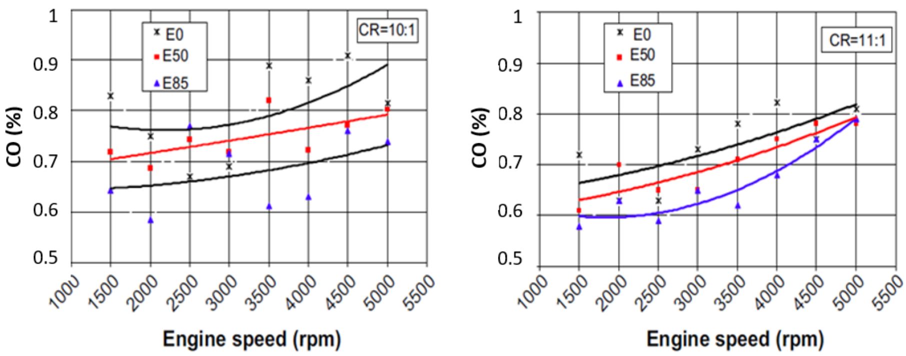

Figure 5. Variation in CO emissions with engine speed and ethanol content in the blends at different compression ratios (CR=10:1 on the left and CR=11:1 on the right): comparison between gasoline (E0), 50% ethanol v/v (E50) and 85% ethanol v/v (E85) [94]. Reproduced with permission from Renewable Energy; published by Elsevier, 2009. License Number: 5094080704915.

In Figure 6a, a decrease in HC formation was observed with increasing engine speed at both compression ratios because the resultant increased turbulence intensity enhances both the air/fuel mixing process and the combustion process. Besides, HC emissions resulted higher for higher compression ratio due to the lower cylinder temperature at the end of the expansion stroke, which results in an incomplete combustion process. However, HC emission decreased with the increase of ethanol in the blends; the minimum HC emissions were detected when using E85 test fuel, whereas the highest HC emissions were measured when using pure gasoline (E0). In effect, by increasing ethanol concentration in the blended fuels, higher oxygen fraction improves the combustion efficiency in the fuel-rich zones of the engine as result of the leaning effect, reducing HC formation.

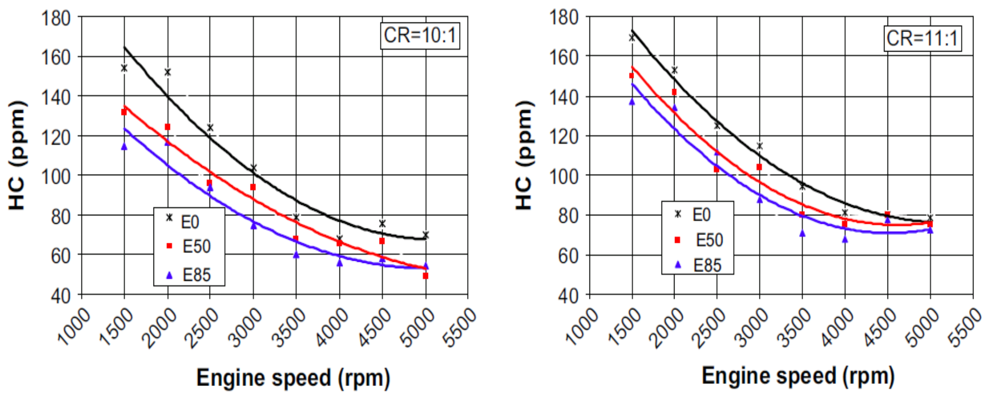

Figure 6. Variation in HC emissions with engine speed and ethanol content in the blends at different compression ratios (CR=10:1 on the left and CR=11:1 on the right): comparison between gasoline (E0), 50% ethanol v/v (E50) and 85% ethanol v/v (E85) [94]. Reproduced with permission from Renewable Energy; published by Elsevier, 2009. License Number: 5094080704915.

3.4. Effect of Engine Load and Equivalence Ratio

A comparative investigation on emissive characteristics and combustion of a multi-port fuel-injection SI engine was executed by Li et al. [95], by using different fractions of butanol, methanol and ethanol in gasoline-blended fuels. At an equivalence ratio fixed to 1 and 3 bar brake mean effective pressure (BMEP), as shown in Figure 7, with the rise of alcohol in the blends, the CO engine out emissions increased compared with pure gasoline. Normally, conditions of low combustion temperature, insufficient oxidizers and locally rich zones result in higher CO emissions; however, in this case, the shorter combustion duration of alcohols is the predominant mechanism for CO formation, leading to the insufficient oxygenation in the fuel-rich zones of the combustion chamber with the consequent rise in CO emission. Under the same operating conditions, as presented in Figure 8, HC emissions decreased with the rise of ethanol in the blends because the oxygen content in alcohols is helpful to improve combustion quality; the minimum HC emissions were detected when using E60 test fuel.

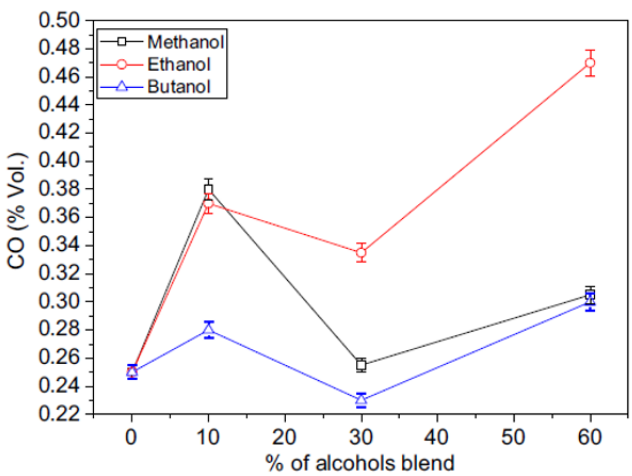

Figure 7. Variation in CO emissions with alcohol content in the blends at 3 bar BMEP and equivalence ratio ϕ = 1: comparison between methanol, ethanol and butanol [95]. Reproduced with permission from Applied Thermal Engineering; published by Elsevier, 2017. License Number: 5094081168292.

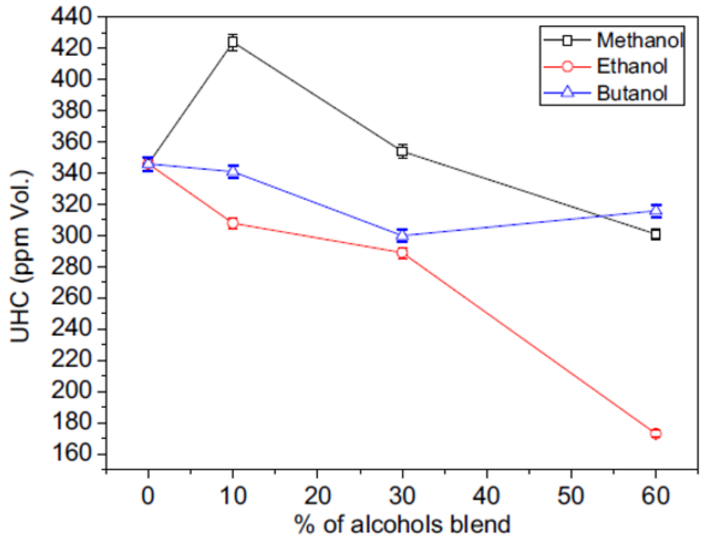

Figure 8. Variation in HC emissions with alcohol content in the blends at 3 bar BMEP and equivalence ratio ϕ = 1: comparison between methanol, ethanol and butanol [95]. Reproduced with permission from Applied Thermal Engineering; published by Elsevier, 2017. License Number: 5094081168292.

For the same multi-port fuel injection engine, the effect of gasoline blended with 30% v/v ethanol on the CO and HC emissions was also analyzed under different engine loads and equivalence ratios fluctuating from 0.83 to 1.25. It was found that, for each test fuel, the equivalence ratio controls CO emission only under reach conditions (Figure 9); on the other hand, under lean conditions, CO emissions do not vary significantly and are much lower compared to rich conditions due to the resultant high oxygen content, which improves the oxidation process. In Figure 9, it is also evident that, with adding ethanol in the fuel blends at 3 bar BMEP, CO emissions decrease at rich conditions while they increase at stoichiometric conditions. In Figure 10, HC exhaust emissions increase under rich conditions for each test fuel and for both engine loads due to the incomplete combustion process as the combustion quality worsens. E30 test fuel (30% ethanol v/v) revealed the 12.1–25.2% lower HC emissions owing to the enhanced combustion quality because of fuel-borne oxygen [95].

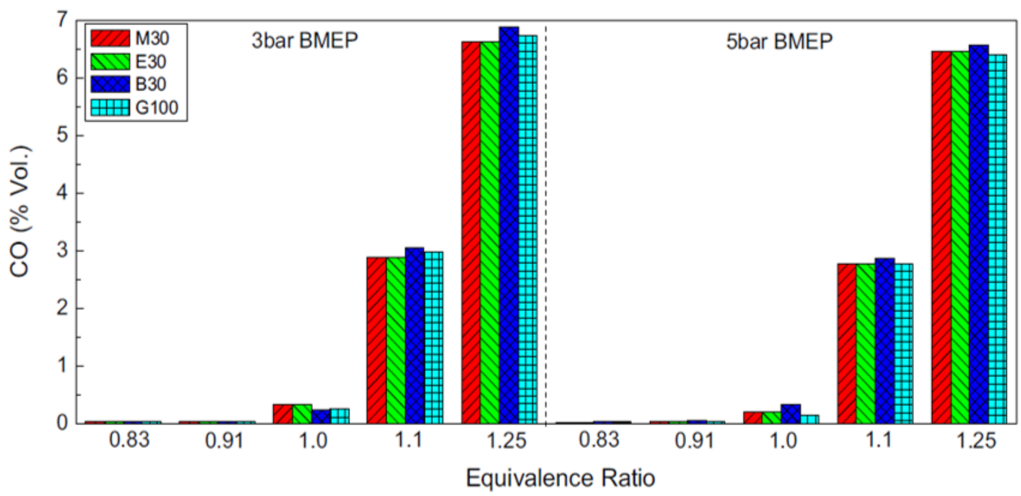

Figure 9. Variation in CO emissions with equivalence ratio, engine load and test fuel: comparison between gasoline (G100), 30% methanol v/v (M30), 30% ethanol v/v (E30) and 30% butanol v/v (B30) [95]. Reproduced with permission from Applied Thermal Engineering; published by Elsevier, 2017. License Number: 5094081168292.

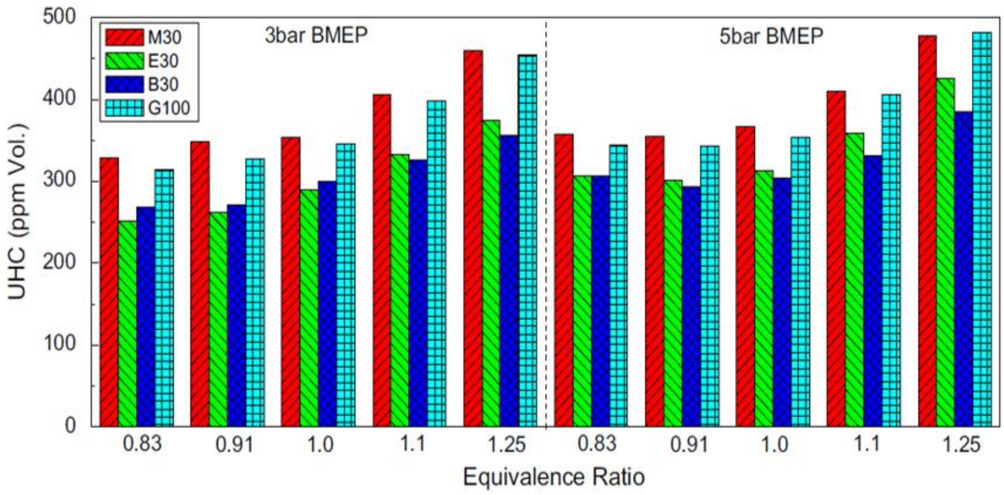

Figure 10. Variation in HC emissions with equivalence ratio, engine load and test fuel: comparison between gasoline (G100), 30% methanol v/v (M30), 30% ethanol v/v (E30) and 30% butanol v/v (B30) [95]. Reproduced with permission from Applied Thermal Engineering; published by Elsevier, 2017. License Number: 5094081168292.

To conclude, Table 2 summarizes the main experimental tests concerning the effect of ethanol addition into gasoline blends on CO and HC engine out emissions under different operating conditions.

Table 2. Main experimental tests concerning the effect of ethanol concentration and operating conditions on HC and CO emissions using gasoline/ethanol blends in SI engines.

Engine	Ethanol Concentration into Gasoline Blends	Operating Conditions	Ref.
1C, 4S, MFIE CR = 9.6:1	0%, 10%, 30%, 60%	Engine speed = 1200 rpm BMEP = 3 and 5 bar	[95]
4C, 4S, CR = 8.8:1	0%, 10%, 20%, 30%	Engine speed = 2000–4500 rpm	[92]
4C, 4S, EIS, WC	0%, 10%, 20%, 30%	Cold and hot conditions	[27]
1C, 4S, EIS	0%, 25%, 50%, 75%, 100%	Engine speed = 1500–4000 rpm, CR = 6:1 and 10:1	[93]
1C, 4S, CR = 5:1–13:1	0%, 50%, 85%	Engine speed = 1000–5500 rpm, CR = 10:1 and 11:1	[94]
4C, 4S, MIS, WC CR = 10.4:1	0%, 5%, 10%	WP = 5–20 kW Speed = 80–100 km/h	[84]
MFIE, CR = 9.8:1	0%, 10%, 20%, 30%, 40%	Cold-start condition	[83]
DI, CR = 12:1	0%, 25%, 50%, 85%	Steady-state conditions	[82]
4C, CR = 9.8:1	0%, 5%, 10%, 15%, 20%	Engine speed = 1000–5000 rpm	[88]
1C, 4S, AC, CR = 5.1:1	0%, 10%	Engine speed = 3000 rpm	[80]
4C, MIS, CR = 10:1	0%, 15%	Engine speed = 1000–6000 rpm	[87]
1C, 4S, WC	0%, 1.5%, 12%	Engine speed = 1500 rpm CR = 7.7:1 and 8.2:1	[28]
EIS, CR = 8.2:1	0%, 10%, 30%	Close-loop control at part engine load; Open-loop control at full engine load	[86]

E% = ethanol concentration, AC = air cooled, BMEP = brake mean effective pressure, C = cylinder, CR = compression ratio, DI = direct injection, EIS = electronic injection system, GPI = gasoline port injection, MFIE = multi-port fuel injection engine, MIS = multi-point injection system, WC = water cooled, WP = wheel power.

4. Conclusions

Ethanol is considered worldwide as an important renewable fuel when mixed with pure gasoline because of its favorable properties. The purpose of this study was to offer a complete literature review on the current state of ethanol combustion in SI engines to explain the difference in HC and CO emissions by using gasoline/ethanol blends. Most of experimental investigations conclude that the addition of ethanol with gasoline fuel mixtures can effectively decrease HC and CO exhaust emissions of new generation SI engines. In more detail, the key results obtained in this investigation can be summarized as follows:

- The high amount of oxygen in the ethanol/gasoline blends can effectively improve the efficiency of the combustion process and involve the leaning effect in the fuel-rich zones of engine, thus reducing CO and HC exhaust emissions. The decrease in exhaust emissions is also produced by faster flame speed due to the combustion of ethanol/gasoline blend as compared to gasoline; under such operating conditions, the resulting quick and complete combustion process involves a decrease in CO and HC formation.
- Throughout the cold-transient phase, the decrease in the CO and HC emissions compared to gasoline is significant for 20% ethanol v/v due to the rise in oxygen percentage in the gasoline/ethanol fuels, which enhances the oxidation of CO and HC, with a resulting more efficient combustion process in cold operating conditions. However, with a growing ethanol fraction in the test fuels, the heating value reduces, and simultaneously, the latent heat of vaporization rises. Under these operating conditions, the burning velocity and flame temperature of the blends decrease, leading to a less efficient and complete combustion process and, therefore, to higher HC and CO cold emissive levels. Besides, with a rising ethanol content in the blends (higher than 20% v/v), the Reid vapor pressure is reduced within the cold-transient phase, hindering the fuel vaporization; hence, under these operating conditions, HC cold emissions can increase due to reduced volatility of the blends.
- Regarding the effect of engine speed on emissive behavior, the lowest CO emissions can be reached at ethanol fractions lower than 20% v/v for several engine speeds; owing to both higher oxygen content in chemical structure and better volatility of ethanol compared to pure gasoline, a cleaner combustion can be ensured by using ethanol/gasoline blends. Besides, HC emissive levels decrease with increasing engine speed for different ethanol fraction in the blends due to a better homogenization of the air–fuel mixture inside the cylinder at high engine speed, which enhances combustion efficiency and rises the in-cylinder temperature. On the other hand, the CO concentration rises with increasing engine speed for several ethanol contents due to both increased combustion temperature and insufficient time in the cycle for completion of combustion.
- Regarding the effect of compression ratio on exhaust emissions, CO emissions decrease with increasing compression ratios under each level of ethanol fraction in the blends, whereas higher HC emissions result for higher compression ratios due to the lower cylinder temperature at the end of the expansion stroke, which results in incomplete combustion process.
- In relation to the effect of different engine loads and equivalence ratios, CO emissions decrease with adding ethanol in the fuel blends at rich conditions (due to the resultant high oxygen content, which improves the oxidation process) while they increase at stoichiometric conditions under different engine loads. By using ethanol/gasoline blends, HC emissions decrease as compared to gasoline due to the enhanced combustion quality because of fuel-borne oxygen. Besides, HC exhaust emissions increase under rich conditions for different engine loads and ethanol fractions in the blends due to the incomplete combustion process.

Author Contributions: Conceptualization, P.I.; methodology, P.I. and M.C.; formal analysis, P.I. and M.C.; investigation, P.I. and M.C.; data curation, P.I. and M.C.; writing—original draft preparation, P.I. and M.C.; writing—review and editing, P.I.; visualization, P.I.; supervision, P.I. and M.C.; project administration, P.I.; funding acquisition, M.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hosseini, S.E.; Wahid, M.A. Feasibility study of biogas production and utilization as a source of renewable energy in Malaysia. *Renew. Sustain. Energy Rev.* **2013**, *19*, 454–462. [CrossRef]
2. Saidur, R.; Abdelaziz, E.; Demirbas, A.; Hossain, M.; Mekhilef, S. A review on biomass as a fuel for boilers. *Renew. Sustain. Energy Rev.* **2011**, *15*, 2262–2289. [CrossRef]
3. Awada, O.I.; Mamata, R.; Alib, O.M.; Sidik, N.A.C.; Yusaf, T.; Kadirgama, K.; Kettnere, M. Alcohol and ether as alternative fuels in spark ignition engine: A review. *Renew. Sustain. Energy Rev.* **2018**, *82*, 2586–2605. [CrossRef]
4. Liaquat, A.; Kalam, A.; Masjuki, H.; Jayed, M. Potential emissions reduction in road transport sector using biofuel in developing countries. *Atmos. Environ.* **2010**, *44*, 3869–3877. [CrossRef]
5. Iodice, P.; Senatore, A.; Langella, G.; Amoresano, A. Effect of ethanol-gasoline blends on CO and HC emissions in last generation si engines within the cold-start transient: An experimental investigation. *Appl. Energy* **2016**, *179*, 182–190. [CrossRef]
6. Kumar, B.R.; Saravanan, S. Use of higher alcohol biofuels in diesel engines: A review. *Renew. Sustain. Energy Rev.* **2016**, *60*, 84–115. [CrossRef]
7. Mofijur, M.; Rasul, M.G.; Hyde, J.; Azad, A.K.; Mamat, R.; Bhuiy, M.M.K. Role of biofuel and their binary (diesel-biodiesel) and ternary (ethanol-biodiesel-diesel) blends on internal combustion engines emission reduction. *Renew. Sustain. Energy Rev.* **2016**, *53*, 265–278. [CrossRef]
8. Available online: https://www.e-education.psu.edu/egee439/node/720 (accessed on 20 March 2021).
9. Awad, O.; Ali, O.; Mamat, R.; Abdullah, A.; Najafi, G.; Kamarulzaman, M.K.; Yusri, I.; Noor, M. Using fusel oil as a blend in gasoline to improve SI engine efficiencies: A comprehensive review. *Renew. Sustain. Energy Rev.* **2017**, *69*, 1232–1242. [CrossRef]
10. Available online: https://www.thecropsite.com/articles/1781/biofuel-production-greater-shares-of-commodities-used/ (accessed on 20 March 2021).
11. Available online: https://ethanolrfa.org/wp-content/uploads/2020/02/2020-Outlook-Pocket-Guide-for-Web.pdf (accessed on 20 March 2021).
12. Available online: http://bioenergyinternational.com/markets-finance/us-tops-as-number-one-ethanol-producer-consumer-and-exporter (accessed on 21 March 2021).
13. Magnusson, R.; Nilsson, C.; Andersson, B. Emissions of Aldehydes and Ketones from a Two-Stroke Engine Using Ethanol and Ethanol-Blended Gasoline as Fuel. *Environ. Sci. Technol.* **2002**, *36*, 1656–1664. [CrossRef] [PubMed]
14. Erdiwansyah; Mamat, R.; Sani, M.; Sudhakar, K.; Kadarohman, A.; Sardjono, R. An overview of Higher alcohol and biodiesel as alternative fuels in engines. *Energy Rep.* **2019**, *5*, 467–479. [CrossRef]
15. Boulahlib, M.S.; Medaerts, F.; Boukhalfa, M.A. Experimental study of combustion performances and emissions of a spark ignition cogeneration engine operating in lean conditions using different fuels. *Int. J. Hydrog. Energy* **2018**, *43*, 3586–3596. [CrossRef]
16. Awad, O.I.; Mamat, R.; Ibrahim, T.K.; Hammid, A.T.; Yusri, I.; Hamidi, M.A.; Humada, A.M.; Yusop, A. Overview of the oxygenated fuels in spark ignition engine: Environmental and performance. *Renew. Sustain. Energy Rev.* **2018**, *91*, 394–408. [CrossRef]
17. Geng, P.; Cao, E.; Tan, Q.; Wei, L. Effects of alternative fuels on the combustion characteristics and emission products from diesel engines: A review. *Renew. Sustain. Energy Rev.* **2017**, *71*, 523–534. [CrossRef]
18. Leong, S.T.; Muttamara, S.; Laortanakul, P. Applicability of gasoline containing ethanol as Thailand's alternative fuel to curb toxic VOC pollutants from automobile emission. *Atmos. Environ.* **2002**, *36*, 3495–3503. [CrossRef]
19. Flavin, C.; Sawin, J.L.; Mastny, L.; Aeck, M.; Hunt, S.; MacEvitt, A.; Stair, P.; Podesta, J.; Cohen, A.; Hendricks, B. *American Energy: The Renewable Path to Energy Security*; Worldwatch Institute & the Center for American Progress: Washington, DC, USA, 2006.
20. Iodice, P.; Senatore, A.; Langella, G.; Amoresano, A. Advantages of ethanol-gasoline blends as fuel substitute for last generation Si engines. *Environ. Prog. Sustain. Energy* **2017**, *36*, 1173–1179. [CrossRef]
21. Boundy, R.G.; Diegel, S.W.; Wright, L.L.; Davis, S.C. *Biomass Energy Data Book*, 4th ed.; Department of Energy: Washington, DC, USA, 2011.
22. Coordinating, I. *Intermediate-Level Ethanol Blends Engine Durability Study*; Research Council: Alpharetta, GA, USA, 2012.
23. Tester, F. Gas-Caused (E10) Engine Damage and Performance Issues. Available online: http://www.fuel-testers.com/list_e10_engine_damage.html (accessed on 25 September 2020).

24. Wróblewski, P.; Iskra, A. Problems of Reducing Friction Losses of a Piston-Ring-Cylinder Configuration in a Combustion Piston Engine with an Increased Isochoric Pressure Gain. *SAE Tech. Pap.* **2020**. [CrossRef]
25. Wróblewski, P. The effect of the distribution of variable characteristics determining the asymmetry of the sealing rings sliding surfaces on the values of friction loss coefficients and other selected parameters of oil film. *Combustion Engines* **2017**, *171*, 107–116. [CrossRef]
26. Wróblewski, P.; Iskra, A. Geometry of shape of profiles of the sliding surface of ring seals in the aspect of friction losses and oil film parameters. *Combust. Engines.* **2016**, *167*, 24–38. [CrossRef]
27. Iodice, P.; Langella, G.; Amoresano, A. Ethanol in gasoline fuel blends: Effect on fuel consumption and engine out emissions of SI engines in cold operating conditions. *Appl. Therm. Eng.* **2018**, *130*, 1081–1089. [CrossRef]
28. Bayraktar, H. Experimental and theoretical investigation of using gasoline–ethanol blends in spark-ignition engines. *Renew. Energy* **2005**, *30*, 1733–1747. [CrossRef]
29. Vicentini, P.C.; Kronberger, S. Rating the performance of Brazilian flex fuel Vehicles. *SAE Tech. Pap.* **2005**. [CrossRef]
30. Carneiro, M.L.N.M.; Pradelle, F.; Braga, S.L.; Gomes, M.S.P.; Martins, A.R.F.; Turkovics, F.; Pradelle, R.N.C. Potential of biofuels from algae: Comparison with fossil fuels, ethanol and biodiesel in Europe and Brazil through life cycle assessment (LCA). *Renew. Sustain. Energy Rev.* **2017**, *73*, 632–653. [CrossRef]
31. Nadaleti, W.C.; Przybyla, G. Emissions and performance of a spark-ignition gas engine generator operating with hydrogen-rich syngas, methane and biogas blends for application in southern Brazilian rice industries. *Energy* **2018**, *154*, 38–51. [CrossRef]
32. Costagliola, M.A.; Prati, M.V.; Florio, S.; Scorletti, P.; Terna, D.; Iodice, P.; Buono, D.; Senatore, A. Performances and emissions of a 4-stroke motorcycle fuelled with ethanol/gasoline blends. *Fuel* **2016**, *183*, 470–477. [CrossRef]
33. Normann, F.; Andersson, K.; Leckner, B.; Johnsson, F. Emission control of nitrogen oxide sintheoxy-fuel process. *Prog. Energy Combust. Sci.* **2009**, *35*, 385–397. [CrossRef]
34. Lefebvre, A.H. The role of fuel preparation in low-emission combustion. *ASME J. Eng. Gas Turbines Power* **1995**, *117*, 617–654. [CrossRef]
35. Alasfour, F.N. NOx Emission from a spark ignition engine using 30% Iso-butanol-gasoline blend: Part 1—Preheating inlet air. *Appl. Therm. Eng.* **1998**, *18*, 245–256. [CrossRef]
36. Chong, J.; Tsolakis, A.; Gill, S.; Theinnoi, K.; Golunski, S. Enhancing the NO_2/NOx ratio in compression ignition engines by hydrogen and reformate combustion, for improved aftertreatment performance. *Int. J. Hydrog. Energy* **2010**, *35*, 8723–8732. [CrossRef]
37. Shahir, S.; Masjuki, H.; Kalam, A.; Imran, A.; Ashraful, A. Performance and emission assessment of diesel–biodiesel–ethanol/bioethanol blend as a fuel in diesel engines: A review. *Renew. Sustain. Energy Rev.* **2015**, *48*, 62–78. [CrossRef]
38. Masum, B.; Masjuki, H.; Kalam, A.; Fattah, I.R.; Palash, S.; Abedin, M. Effect of ethanol–gasoline blend on NOx emission in SI engine. *Renew. Sustain. Energy Rev.* **2013**, *24*, 209–222. [CrossRef]
39. Ganguly, A.; Chatterjee, P.; Dey, A. Studies on ethanol production from water hyacinth—A review. *Renew. Sustain. Energy Rev.* **2012**, *16*, 966–972. [CrossRef]
40. Ethanol Feedstocks. Available online: http://www.afdc.energy.gov/fuels/ethanol_feedstocks.htm (accessed on 1 October 2015).
41. Rizwanul Fattah, I.M.; Masjuki, H.H.; Liaquat, A.M.; Ramli, R.; Kalam, M.A.; Riazuddin, V.N. Impact of various biodiesel fuels obtained from edible and non-edible oils on engine exhaust gas and noise emissions. *Renew. Sustain. Energy Rev.* **2013**, *18*, 552–567. [CrossRef]
42. Varatharajan, K.; Cheralathan, M. Influence of fuel properties and composition on NOx emissions from biodiesel powered diesel engines: A review. *Renew. Sustain. Energy Rev.* **2012**, *16*, 3702–3710. [CrossRef]
43. Bowman, C.T. Kinetics of pollutant formation and destruction in combustion. *Prog. Energy Combust. Sci.* **1975**, *1*, 33–45. [CrossRef]
44. Fenimore, C.P. Formation of nitricoxide in premixed hydrocarbon flames. *Symp. (Int.) Combust.* **1971**, *13*, 373–380.
45. Fluent Inc. Prompt NOx Formation. 2001. Available online: http://combust.hit.edu.cn:8080/fluent/Fluent60_help/html/ug/node582.htm (accessed on 22 March 2021).
46. Miller, J.A.; Bowman, C.T. Mechanism and modeling of nitrogen chemistry in combustion. *Prog. Energy Combust. Sci.* **1989**, *15*, 287–338. [CrossRef]
47. Yusoff, M.N.A.M.; Zulkifli, N.W.M.; Masum, B.; Masjuki, H.H. Feasibility of bioethanol and biobutanol as transportation fuel in spark-ignition engine: A review. *RSC Adv.* **2015**, *5*, 100184–100211. [CrossRef]
48. Naik, S.; Goud, V.V.; Rout, P.K.; Dalai, A.K. Production of first and second generation biofuels: A comprehensive review. *Renew. Sustain. Energy Rev.* **2010**, *14*, 578–597. [CrossRef]
49. Szulczyk, K.R. Which is a better transportation fuel–butanol or ethanol? *Int. J. Energy Environ.* **2010**, *1*, 1–12.
50. Mohapatra, D.; Mishra, S.; Sutar, N. Chemical and Functional Properties of Local Banana Peel Flour. *J. Sci. Ind. Res.* **2010**, *69*, 323–329.
51. Tock, J.Y.; Lai, C.L.; Lee, K.T.; Tan, K.T.; Bhatia, S. Banana biomass as potential renewable energy resource: A Malaysian case study. *Renew. Sustain. Energy Rev.* **2010**, *14*, 798–805. [CrossRef]
52. Ashnani, M.H.M.; Johari, A.; Hashim, H.; Hasani, E. A source of renewable energy in Malaysia, why biodiesel? *Renew. Sustain. Energy Rev.* **2014**, *35*, 244–257. [CrossRef]
53. Ceres, I. *Carbon Dioxide/Net Energy*; Cares Inc.: California, CA, USA, 2015.

54. Hahn-Hagerdal, B.; Galbe, M.; Gorwa-Grauslund, M.F.; Liden, G.; Zacchi, G. Bio-ethanol – the fuel of tomorrow from the residues of today. *Trends Biotechnol.* **2006**, *24*, 549–556. [CrossRef]
55. Sims, R.E.; Mabee, W.; Saddler, J.N.; Taylor, M. An overview of second generation biofuel technologies. *Bioresour. Technol.* **2010**, *101*, 1570–1580. [CrossRef]
56. Lee, S.; Speight, J.G.; Loyalka, S.K. *Handbook of Alternative Fuel Technologies*; CRC Press: Boca Raton, FL, USA, 2014.
57. Aakko-Saksa, P.; Koponen, P.; Kihlman, J.; Reinikainen, M.; Skytta, E.; Rantanen-Kolehmainen, L.; Engman, A. *Biogasoline Options for Conventional Spark-Ignition Cars*; VTT Technical Research Centre of Finland: Vuorimiehentie, Finland, 2011.
58. von Sivers, M.; Zacchi, G. Ethanol from lignocellulosics: A review of the economy. *Bioresour. Technol.* **1996**, *56*, 131–140. [CrossRef]
59. Lynd, L.R.; Elander, R.T.; Wyman, C.E. Likely Features and Costs of Mature Biomass Ethanol Technology. *Seventeenth Symp. Biotechnol. Fuels Chem.* **1996**, *57*, 741–761.
60. D.S.D. Group. *Feasibility Study on an Effective and Sustainable Bio-Ethanol Production Program. by Least Developed Countries as Alternative to Cane Sugar Export*; Ministry of Agriculture, Nature and Food Quality (LNV): The Hague, The Netherlands, 2005.
61. Roozbehani, B.; Mirdrikvand, M.; Moqadam, S.I.; Roshan, A.C. Synthetic ethanol production in the Middle East: A way to make environmentally friendly fuels. *Chem. Technol. Fuels Oils* **2013**, *49*, 115–124. [CrossRef]
62. Nelson, R.; Taylor, M.A.; Davidson, D.D.; Peters, L.M. Olefin Hydration Process. U.S. Patent US2579601A, 25 December 1951.
63. Maki, Y.; Sato, K.; Isobe, A.; Iwasa, N.; Fujita, S.; Shimokawabe, M.; Takezawa, N. Structures of H3PO4/SiO2 catalysts and catalytic performance in the hydration of ethene. *Appl. Catal. A Gen.* **1998**, *170*, 269–275. [CrossRef]
64. Sugar Industry News. Available online: http://www.sugarinds.com/2011/08/worlds-top-20-ethanolproducing.html (accessed on 4 September 2015).
65. Park, C.; Choi, Y.; Kim, C.; Oh, S.; Lim, G.; Moriyoshi, Y. Performance and exhaust emission characteristics of a spark ignition engine using ethanol and ethanol-reformed gas. *Fuel* **2010**, *89*, 2118–2125. [CrossRef]
66. Kumar, S.; Cho, J.H.; Park, J.; Moon, I. Advances in diesel–alcohol blends and their effects on the performance and emissions of diesel engines. *Renew. Sustain. Energy Rev.* **2013**, *22*, 46–72. [CrossRef]
67. Chen, R.-H.; Chiang, L.-B.; Wu, M.-H.; Lin, T.-H. Gasoline displacement and NOx reduction in an SI engine by aqueous alcohol injection. *Fuel* **2010**, *89*, 604–610. [CrossRef]
68. Dernotte, J.; Mounaim-Rousselle, C.; Halter, F.; Seers, P. Evaluation of Butanol-Gasoline Blends in a Port Fuel-injection, Spark-Ignition Engine. *Oil Gas Sci. Technol.* **2010**, *65*, 345–351. [CrossRef]
69. Marketing Department, American Petroleum Institute; Refining Department, American Petroleum Institute. *Refining, Alcohols and Ethers: A Technical Assessment of Their Application as Fuels and Fuel Components*; American Petroleum Institute: Washington, DC, USA, 2001.
70. Owen, K.; Coley, T. *Automotive Fuels Reference Book*, 2nd ed.; Society of Automotive Engineers Inc.: Warrendale, PA, USA, 1995.
71. Yacoub, Y.M.; Bata, R.M.; Gautam, M. The performance and emission characteristics of C1-C5 alcohol-gasoline blends with matched oxygen content in a single-cylinder spark ignition engine. *Proc. Inst. Mech. Eng. Part A* **1998**, *212*, 363–379. [CrossRef]
72. Pischinger, S.; Günther, M.; Budak, O. Abnormal combustion phenomena with different fuels in a spark ignition engine with direct fuel injection. *Combust. Flame* **2017**, *175*, 123–137. [CrossRef]
73. Ramasamy, D.; Goh, C.; Kadirgama, K.; Benedict, F.; Noor, M.; Najafi, G.; Carlucci, A. Engine performance, exhaust emission and combustion analysis of a 4-stroke spark ignited engine using dual fuel injection. *Fuel* **2017**, *207*, 719–728. [CrossRef]
74. Larsen, U.; Johansen, T.; Schramm, J. Ethanol as a Future Fuel for Road Transportation: Main report. *DTU Mekanik*, 2009.
75. Bajpai, P. *Advances in Bioethanol*; Springer: Patial, India, 2013.
76. Szulczyk, K.R.; McCarl, B.A.; Cornforth, G. Market penetration of ethanol. *Renew. Sustain. Energy Rev.* **2010**, *14*, 394–403. [CrossRef]
77. Genchi, G.; Pipitone, E. Octane Rating of Natural Gas-Gasoline Mixtures on CFR Engine. *SAE Int. J. Fuels Lubr.* **2014**, *7*, 1041–1049. [CrossRef]
78. Hassan, N.; Rasul, M.; Harch, C. Modelling and experimental investigation of engine performance and emissions fuelled with biodiesel produced from Australian Beauty Leaf Tree. *Fuel* **2015**, *150*, 625–635. [CrossRef]
79. Hsieh, W.-D.; Chen, R.-H.; Wu, T.-L.; Lin, T.-H. Engine performance and pollutant emission of an SI engine using ethanol–gasoline blended fuels. *Atmos. Environ.* **2002**, *36*, 403–410. [CrossRef]
80. Singh, E.; Shukla, M.K.; Pathak, S.; Sood, V.; Singh, N. Performance Emission & Noise Characteristics Evaluation of n-Butanol/Gasoline Blend in Constant Speed SI Engine. *Int. J. Eng. Res. Tech.* **2014**, *3*, 993–999.
81. Yücesu, H.S.; Topgül, T.; Çinar, C.; Okur, M. Effect of ethanol–gasoline blends on engine performance and exhaust emissions in different compression ratios. *Appl. Therm. Eng.* **2006**, *26*, 2272–2278. [CrossRef]
82. Oh, H.; Bae, C.; Min, K. Spray and Combustion Characteristics of Ethanol Blended Gasoline in a Spray Guided DISI Engine under Lean Stratified Operation. *SAE Int. J. Engines* **2010**, *3*, 213–222. [CrossRef]
83. Chen, R.-H.; Chiang, L.-B.; Chen, C.-N.; Lin, T.-H. Cold-start emissions of an SI engine using ethanol–gasoline blended fuel. *Appl. Therm. Eng.* **2011**, *31*, 1463–1467. [CrossRef]
84. Canakci, M.; Ozsezen, A.N.; Alptekin, E.; Eyidogan, M. Impact of alcohol-gasoline fuel blends on the exhaust emission of an SI engine. *Renew. Energy* **2013**, *52*, 111–117. [CrossRef]
85. Rice, R.W.; Sanyal, A.K.; Elrod, A.C.; Bata, R.M. Exhaust Gas Emissions of Butanol, Ethanol, and Methanol-Gasoline Blends. *J. Eng. Gas. Turbines Power* **1991**, *113*, 377–381. [CrossRef]

86. He, B.-Q.; Wang, J.-X.; Hao, J.-M.; Yan, X.-G.; Xiao, J.-H. A study on emission characteristics of an EFI engine with ethanol blended gasoline fuels. *Atmos. Environ.* **2003**, *37*, 949–957. [CrossRef]
87. Masum, B.; Masjuki, H.; Kalam, A.; Palash, S.; Habibullah, M. Effect of alcohol–gasoline blends optimization on fuel properties, performance and emissions of a SI engine. *J. Clean. Prod.* **2015**, *86*, 230–237. [CrossRef]
88. Jia, L.-W.; Shen, M.-Q.; Wang, J.; Lin, M.-Q. Influence of ethanol–gasoline blended fuel on emission characteristics from a four-stroke motorcycle engine. *J. Hazard. Mater.* **2005**, *123*, 29–34. [CrossRef]
89. Yao, Y.-C.; Tsai, J.-H.; Chiang, H.-L. Effects of ethanol-blended gasoline on air pollutant emissions from motorcycle. *Sci. Total Environ.* **2009**, *407*, 5257–5262. [CrossRef]
90. Yang, H.-H.; Liu, T.-C.; Chang, C.-F.; Lee, E. Effects of ethanol-blended gasoline on emissions of regulated air pollutants and carbonyls from motorcycles. *Appl. Energy* **2012**, *89*, 281–286. [CrossRef]
91. Guo, T.; Duan, X.; Liu, Y.; Liu, J.; Zhou, X.; Li, Y.; Lai, M.-C.; Guo, G. A comparative experimental study on emission characteristics of a turbocharged gasoline direct-injection (TGDI) engine fuelled with gasoline/ethanol blends under transient cold-start and steady-state conditions. *Fuel* **2020**, *277*, 118153. [CrossRef]
92. Doğan, B.; EROL, D.; Yaman, H.; Kodanli, E. The effect of ethanol-gasoline blends on performance and exhaust emissions of a spark ignition engine through exergy analysis. *Appl. Therm. Eng.* **2017**, *120*, 433–443. [CrossRef]
93. Celik, M.B. Experimental determination of suitable ethanol–gasoline blend rate at high compression ratio for gasoline engine. *Appl. Therm. Eng.* **2008**, *28*, 396–404. [CrossRef]
94. Koç, M.; Sekmen, Y.; Topgül, T.; Yücesu, H.S. The effects of ethanol–unleaded gasoline blends on engine performance and exhaust emissions in aspark-ignition engine. *Renew. Energy* **2009**, *34*, 2101–2106. [CrossRef]
95. Li, Y.; Gong, J.; Deng, Y.; Yuan, W.; Fu, J.; Zhang, B. Experimental comparative study on combustion, performance and emissions characteristics of methanol, ethanol and butanol in a spark ignition engine. *Appl. Therm. Eng.* **2017**, *115*, 53–63. [CrossRef]