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Review

Sustainable Biofuels from First Three Alcohol Families: A Critical Review

Muhamad Norkhizan Abdullah [1], Ahmad Fitri Yusop [1,2,*], Rizalman Mamat [1], Mohd Adnin Hamidi [1,2], Kumarasamy Sudhakar [1,2,3] and Talal Yusaf [4]

[1] Faculty of Mechanical & Automotive Engineering Technology, Universiti Malaysia Pahang, Pekan 26600, Malaysia
[2] Automotive Engineering Center, Universiti Malaysia Pahang, Pekan 26600, Malaysia
[3] Energy Centre, Maulana Azad National Institute of Technology, Bhopal 462003, India
[4] Faculty of Engineering and Surveying, National Center for Engineering in Agriculture, Central Queensland University, Norman Gardens, QLD 4701, Australia
* Correspondence: fitriy@ump.edu.my

Abstract: With its unique qualities, such as infinite supply, high octane number, and capacity to cut greenhouse gas emissions, alcohol is a viable alternative fuel for SI engines. This review article aims to reveal to readers the effects of alcohol on the performance, combustion behavior, and emission characteristics of SI engines by collecting the outcomes from previous research. This article looks at methanol, ethanol, and butanol fuel qualities. The performance of SI engines with butanol, ethanol, and methanol combined with gasoline is investigated in terms of brake torque, brake power, fuel consumption, thermal efficiency, volumetric efficiency, mean effective pressure, and coefficient of variation under various conditions. Second, in-cylinder pressure, mass fraction burnt, ignition delay, pressure increases, and heat release rates are also used to evaluate the combustion characteristic. Finally, the article discusses pollutant emissions such as CO, CO_2, NO_x, UHC, and exhaust gas temperature. Methanol, ethanol, and butanol mixed with gasoline increased fuel consumption and lowered spark-ignition engines' thermal efficiency. When alcohol was combined with gasoline, most research found that CO, NO_x, and UHC emissions were reduced due to improved combustion.

Keywords: alcohol; spark-ignition engine; alternative fuels; performance; combustion; emission

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1. Introduction

Internal combustion engine development has been practised since the 1860s. Generally, the working operation of the internal combustion engine is to convert chemical energy to mechanical energy via the combustion process in the combustion chamber [1,2]. Generally, the working mechanism for SI engines depends on the engine's stroke, whether two-stroke or four-stroke [3]. The undesirable gases emitted from the engine exhaust, such as carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxide (NO_x), and unburned hydrocarbon (UHC), have many adverse implications. Since the last decade, numerous studies have been performed on the emissions from internal combustion engines [4–8]. Other than lower-emission engines, performance is also an important criterion in designing an engine. The performance of an engine is dependent on many factors. Firstly, high engine power is the number one criterion that people survey. The higher the engine power, the faster the car can travel. Another factor that people consider is fuel consumption. The combustion quality inside the combustion chamber closely affects the performance, combustion behavior, and emission characteristics. Generally, there are three combustion process regions in the combustion chamber: ignition and flame development, propagation, and termination. Besides that, engine geometry can affect SI engines' performance, combustion behavior, and emission characteristics. However, engine modification is very challenging because it requires high amount of investment. In addition, engine operating conditions, such as engine load, speed, equivalence ratio, ignition timing, injection timing, and compression ratio, highly affect the engine performance, combustion, and emission characteristics of SI engines. Therefore, the effects of engine operating conditions on engine performance, combustion, and emissions were discussed further throughout this paper.

As a result, the primary goal of this review article is to study more about the potential of methanol, ethanol, and butanol as alternative fuels in SI engines. This review article is divided into five sections. The introduction is the first portion of this article, covering the basics of internal combustion engines. The second section covers general information and the manufacturing of methanol, ethanol, and butanol. Meanwhile, the physical and chemical characteristics of methanol, ethanol, and butanol are discussed in the third part. The fourth section of this article discusses the performance and emission characteristics of SI engines that operate on methanol, ethanol, or butanol combined with gasoline. The final part reviews the exhaust emissions of SI engines running on methanol, ethanol, or butanol combined with gasoline. Finally, in the concluding part, all of the material that was evaluated is summarized and concluded.

2. Alcohols as Alternative Fuels

The rise in the world population has resulted in a significant increase in fossil fuel usage. Fossil fuels, on the other hand, are becoming scarce and expensive. Today, the majority of energy consumed in the world comes from fossil fuels, at 80%, and 58% of it comes from the transportation sector [9–11]. To protect the environment, alternative fuels have been proposed to replace or minimize the usage of fossil fuels [12–15]. Biomass-based, eco-friendly, and renewable fuels are globally available from forests, agriculture, and waste. Figure 1 shows the classification of various biofuels [9]. The suitability of green fuels in engines must follow the criteria for improving engine efficiency, engine performance, pollutant emission reduction, and renewable and biodegradable resources [16–18].

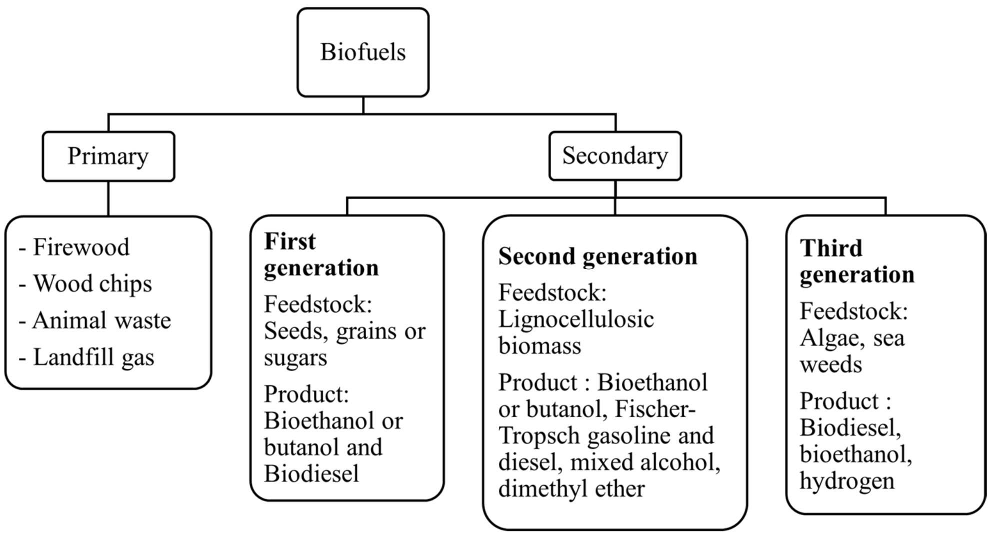

Figure 1. Classification of biofuels [9].

Alternative fuel research for internal combustion engines, especially for transportation sectors, consists of several types of fuel, such as methanol, ethanol, butanol, biodiesel, dimethyl ether, diethyl ether, synthetic natural gas (SNS), straight vegetable oils (SVO), and hydrogen [19–22]. However, because of their application potential, only three alcohol (methanol, ethanol, and butanol)-based fuels will be discussed in this review paper. Further, the performance and emissions are close to or even better than conventional fuels.

2.1. Methanol

Methanol is the first alkane in the family, having the molecular formula CH_3OH. Methanol, also known as methyl alcohol, is manufactured from biomass, natural gas, and coal. Methanol and methanol–gasoline mixtures have been used in several research works on SI engines [23–26]. Today, methanol can be produced by a catalytic process directly from hydrogen, carbon dioxide, and carbon monoxide [12]. In addition, methanol can be made by a new gasification method from the fermentation of carbohydrates such as rice husks, straws, and sawdust [27]. Syngas is produced by steam reforming, while methanol is made via the water–gas shift process. Syngas is converted to methanol in the presence of a zinc-based catalyst at a high temperature, as described in Equations (1)–(3) [9].

Steam reforming reaction:

$$\underset{\text{(Methane)}}{CH_4} + \underset{\text{(Steam)}}{H_2O} \xrightarrow[\text{800−1000 °C, 20−30 atm}]{\text{Zinc based catalyst}} CO + 3H_2 \tag{1}$$

Water–gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

Methanol synthesis reaction:

$$2H_2 + CO \xrightarrow[\text{800−1000 °C, 20−30 atm}]{\text{Zinc based catalyst}} \underset{\text{(Methanol)}}{CH_3OH} \tag{3}$$

Methanol has a high octane number and low carbon-to-hydrogen ratio, oxygen ratio, and flammability limit, and it is renewable. SI engines fueled with methanol give such benefits as higher efficiency, specific power, and fewer emissions. Engines with high compression ratios can use methanol as fuel without knocking or engine damage because of its high octane number compared to gasoline [28]. Furthermore, the higher oxygen content (50%) in a methanol molecule leads to faster combustion speeds and runs with rich air–fuel mixtures without any problems [29].

2.2. Ethanol

Ethyl alcohols, or ethanol, are the second family of alcohols, with a chemical formula of C_2H_5OH. Ethanol can be fermented by biomass feedstocks derived from plant biomass and agricultural residues. In comparison to the other alcohol families, the most widely used alternative fuel is ethanol. However, the limitation of ethanol usage is the high cost of production, but, with the mass production of ethanol, the price is decreasing. Ethanol can be easily obtained and compete with conventional fuels [30].

The primary sources of bioethanol are glucose in sugars and starch, which go through fermentation processes. Ethanol can be produced using two methods: alcoholic formation and the reaction of ethane with steam. Equations (4)–(6) represent the chemical reactions of ethanol production [31].

Alcoholic fermentation:

$$\underset{\text{(Glucose)}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{(Glucose)}}{xC_2H_{12}O_6} + \underset{\text{(Fructose)}}{(2-x)C_6H_{12}O_6}\ 0 \leq x \leq 1 \tag{4}$$

$$\underset{\text{(Fructose)}}{C_6H_{12}O_6} \rightarrow \underset{\text{(Ethanol)}}{2C_2H_5OH} + 2CO_2 \tag{5}$$

The reaction of ethane with steam:

$$\underset{\text{(Ethane)}}{C_2H_4} + \underset{\text{(Steam)}}{H_2O} \rightarrow \underset{\text{(Ethanol)}}{C_2H_5OH} \tag{6}$$

World ethanol production across countries reached 26,500 million gallons in 2018, with the United States first, followed by Brazil, the European Union, China, and Canada. Also noteworthy is that India, Thailand, Brazil, China, and Pakistan are the world's major sugarcane producers. Furthermore, ethanol production was divided into three sectors: fuel, beverage, and industrial use, with proportions of 73%, 17%, and 10%, respectively [32].

In general, ethanol offers excellent performance when utilized as a fuel in SI engines. However, because ethanol consumes less energy, it consumes more gasoline and produces low mileage. Furthermore, due to the constraints mentioned above, ethanol's capacity to be extensively employed is quite limited [33,34]. As a result, numerous researchers have studied the performance and emissions of SI engines that run on ethanol–gasoline blends [35–38]. Ethanol also has a higher latent heat of vaporization, which may result in cold start issues due to poor evaporation.

2.3. Butanol

Butanol contains a carbon atom chain that is either straight or branched. The four isomers of butanol are normal butanol (n-butanol or 1-butanol), secondary butanol (s-butanol or 2-butanol), iso-butanol (i-butanol), and tertiary butanol (t-butanol). Furthermore, because of the low hydrocarbon mole fraction and high oxygen concentration in butanol isomers, they have a high potential for reducing pollutant emissions. Various studies on internal combustion engines fueled with butanol have been carried out because of its potential and properties that resemble conventional fuels [39–42]. Butanol is a hydrophobic solvent that provides smooth transportation in pipelines. As a result, when mixed with water, butanol will not separate from the base fuel [43]. In addition, fossil fuel energy can be saved by up to 56% and pollutant emissions reduced by up to 40% when butanol is used as transportation fuel [44].

Bio-butanol is formed through the fermentation of acetone butanol ethanol (ABE). The production of n-butanol was primarily based on acetaldehyde aldol condensation, accompanied by dehydration and hydrogenation of crotonaldehyde [45]. Based on Figure 2, Step 1 is called dehydrogenation, which enables hydrogen removal in a chemical reaction, followed by a process called aldol condensation to produce a β-hydroxyaldehyde or β-hydroxyketone. Aldol condensation is a standard organic synthesis method that has the benefit of forming carbon–carbon bonds. Following aldol condensation, aldol-adducts are hydrogenated (Step 3) to increase their aqueous-phase solubility. Furthermore, in HMF and furfural, selective hydrogenation of the furan ring can result in additional carbonyl-containing compounds that can self-condense to form larger alkanes via aldol self-condensation [45].

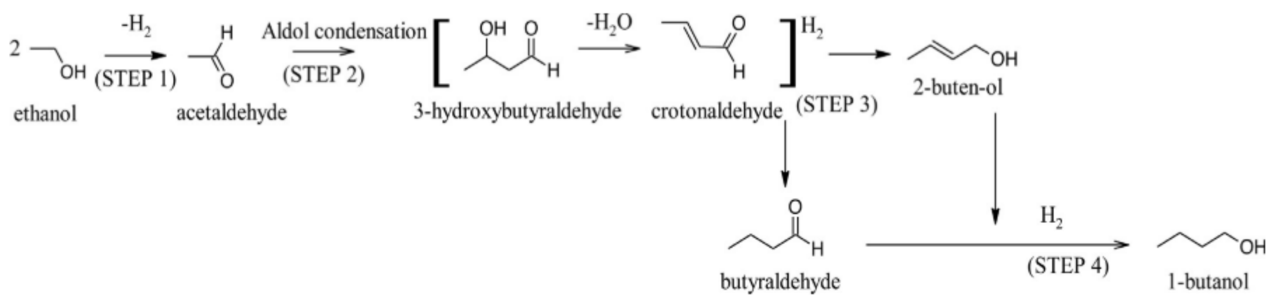

Figure 2. The reaction mechanism of n-butanol formation [45].

3. Properties of Fuels

Performance, combustion characteristics, and engine emissions are strongly related and influenced by the working fuel properties. The essential features of fuels are the density, dynamic viscosity, boiling point, heating value, octane number, flash point, autoignition temperature, stoichiometric air–fuel ratio, and laminar flame speed.

3.1. Density

The fuel density is determined by its molecular weight, which may be measured using a digital density meter following ASTM D4052-16 [46–48]. Typically, higher-density fuel tends to result in weak engine performance, which is believed to be due to big fuel droplets that increase the inertia of injected fuel. High fuel-injection inertia causes high penetration in the combustion chamber [49]. The volumetric-operating pump imparts a lower fuel mass flow rate and a higher pressure drop with higher-density fuel. [50]. Figure 3 shows the density meter model DA-640 series that is typically used to measure the density of fuels.

Figure 3. Density Meter model DA-640 series.

3.2. Viscosity of the Fuel

One of the essential engine fuel parameters is viscosity, which measures a fuel's resistance to flow at a specific temperature. The ASTM D445-01 standard can be used to determine the viscosity of a fuel [51,52]. The mixture formation, combustion process, and fuel spray strongly depend on fuel viscosity [53–55]. Usually, fuel with higher viscosity creates a bigger droplet, lower atomization quality, and lower combustion quality or combustion completeness [51,56]. Furthermore, increased fuel viscosity can cause combustion delays because of a lack of fuel flow in the combustion chamber. On the other hand, low-viscosity fuel can cause fuel system leakage [57,58]. The fuel viscosity can be measured using the equipment in Figure 4, called Anton Paar SVM model 3001.

Figure 4. Anton Paar SVM model 3001.

3.3. Heating Value

The heating value is the quantity of heat delivered into the combustion chamber by chemical reactions during combustion, indicating the amount of energy accessible in the fuel. As it is the quantity of heat provided to the combustion chamber by chemical reactions during combustion, the heating value reflects the amount of energy accessible in the fuel [49]. The heating value can also be called the calorific value, which directly influences the engine's power output. The heating value is directly related to an operating engine's fuel consumption and thermal efficiency or fuel conversion efficiency [7,28,59]. This means that lower heating values can cause high fuel consumption. For example, because ethanol has a lower heating value than regular gasoline, ethanol–gasoline blends consume more fuel than gasoline [50]. Heating values are often divided into lower and higher heating values. A greater heating value is used when all of the H_2O created is condensed to the liquid phase, whereas a lower heating value is used when all of the H_2O formed is in the vapor phase. The heating value is usually expressed in MJ/kg, which can be measured using an oxygen bomb calorimeter according to ASTM D240 [60]. The heating value for alcohol is lower (20–33 MJ/kg) compared to conventional gasoline fuel (44 MJ/kg) [61–63]. Figure 5 shows the typical machine used to measure the heating value of fuels.

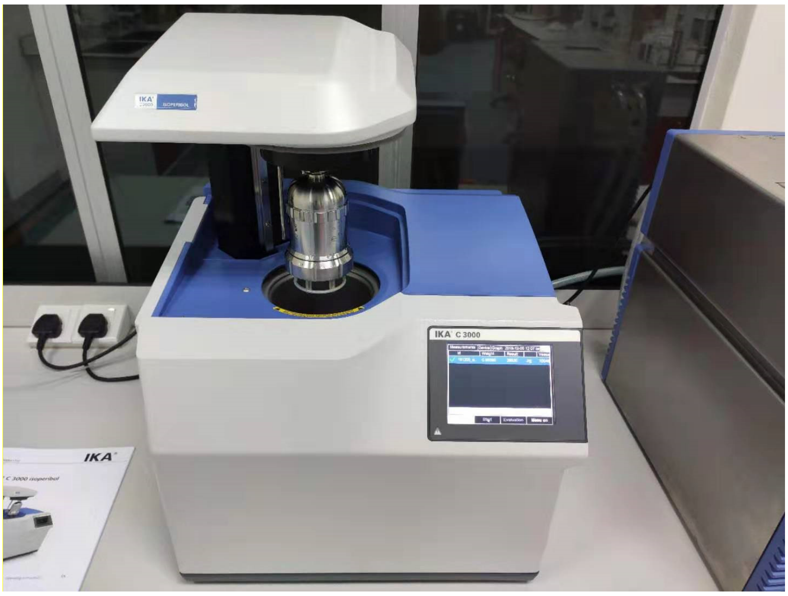

Figure 5. IKA calorimeter C600.

3.4. Octane Number

The octane number of gasoline is an essential feature that describes the fuel's capacity to avoid engine knocking or breakdown [64–66]. The resistance to engine knocking increases when the octane number is higher. However, it also depends on the engine design, weather conditions, engine condition, and type of fuel used previously. Furthermore, there are two methods for measuring octane numbers: research technique and motor method, with the values denoted as research octane number (RON) and motor octane number (MON) [67,68]. The values of RON and MON can be measured following ASTM D-2700 and ASTM D2699 [67–69]. Almost all fuels have a distinction between their RON and MON. The RON is mostly higher than the MON. The differences between RON and MON are called fuel sensitivity [70,71]. The advertised octane number is the average between the RON and MON.

3.5. Stoichiometric Air–Fuel Ratio

The air–fuel stoichiometric ratio is the effective ratio of fuel combined with oxygen required to burn in combustion chambers totally [1,2]. All carbon is transformed into CO_2 in complete combustion, and all hydrogen is converted to water (H_2O). Theoretically, the air–fuel stoichiometric ratio for conventional gasoline is 14.7 to 1 [72–74], while the range of the stoichiometric air–fuel ratio for alcohol is normally below the value for gasoline, at about 6:1 to 11:1, due to its different molecular structures. Furthermore, this ratio compromises maximum power and maximum economy [75]. Combustion is most efficient at stoichiometric air–fuel ratios because nearly all of the oxygen in the air is combined with the fuel in the engine and burned in the combustion chambers [1]. In addition, the oxygen sensor voltage will vary between 0.3 and 0.8 volts if the ratio is at or near stoichiometric [76]. Table 1 compares the properties of commonly used alternative fuels and gasoline.

Table 1. Properties of alcohol-based alternative fuels and gasoline fuels.

Properties	Gasoline [31]	Methanol [61]	Ethanol [31]	N-Butanol [63]	Iso-Butanol [77]
Chemical formula	C_2–C_{14}	CH_3OH	C_2H_5OH	C_4H_9OH	C_4H_9OH
Oxygen content (wt.%)	0	50	34.7	21.5	21.6
Density, kg/m^3	700–780	792	785–810	810	802
Viscosity, mm^2/s	0.5–0.6	0.6 [a]	1.2–1.5	2.63	4.58 [b]
Boiling point, °C	27–225	64	78	118	108
Lower heating value, MJ/kg	44.0	20	26.9	33.1	33.3
Research octane number (RON)	91–100	110	109–110	96	105 [b]
Stoichiometric air–fuel ratio	14.2–15.1	6.47	8.97	11.2	11.1
Autoignition temperature (°C)	257	465	425	343	415
Laminar flame speeds, m/s	0.33	0.52	0.39	0.59	-

[a] ref [78], [b] ref [79].

4. Alcohol-Based Fuel Blend: Performance in SI Engines

The impacts of engine speed, engine load, and equivalency ratio were covered in the first subsection. Furthermore, the second subsection discusses the effects of compression ratio, spark timing, and injection timing.

The performance of an engine is usually quantified in terms of brake power (BP), brake torque (BT), coefficient of variation for IMEP (COVIMEP), indicated mean effective pressure (IMEP), brake thermal efficiency (BTE), and brake specific fuel consumption (BSFC). Internal combustion engine combustion parameters are frequently evaluated in terms of in-cylinder pressure, in-cylinder temperature (Pcyl), combustion duration (CD), mass fraction burnt (MFB), rate of heat release (ROHR), and rate of pressure rise (ROPR). When comparing engine sizes, torque is employed, whereas power is used when engine speed is needed. A dynamometer is often used on a test bed to measure engine torque, with the shaft attached to the dynamometer rotor. Using a flow meter, fuel consumption in engine testing may be calculated from the flow rate of fuels per unit of time. Furthermore, brake-specific fuel consumption (BSFC) is a helpful measure frequently used to examine an engine's performance where a lower BSFC is preferable.

Aside from fuel consumption, one of the essential elements is the engine's thermal efficiency. Thermal efficiency is commonly referred to as brake thermal efficiency (BTE) or indicated thermal efficiency (ITE). Thermal efficiency is the ratio of work performed each cycle to the quantity of fuel energy released per cycle during combustion. BTE is calculated by dividing brake power by the fuel energy delivered every cycle, whereas ITE is calculated by substituting indicated power for brake power. The mass of fuel delivered to the engine each cycle multiplied by the heating value of the fuel yields the fuel energy supplied by combustion [80]. The pressure within the cylinder during the combustion process is referred to as in-cylinder pressure. In-cylinder pressure varies due to different types of operating fuel and engine configuration. Crank angle and cylinder volume both affect in-cylinder pressure. A spark plug-type piezoelectric pressure transducer linked to the cylinder can measure the in-cylinder pressure of a SI engine [81,82]. Figure 6 shows the image of a typical engine setup on a dynamometer. The engine is coupled to an eddy current dynamometer, which controls both engine torque and speed throughout the test. The fuel flow meter is connected to the fuel inlet line to measure fuel consumption. The crank angle position can be obtained from a crank encoder. Pressure sensors and the crank encoder are connected to the data acquisition system to measure and record the in-cylinder pressure against the crank angle. The dynamometer measures the brake power and brake torque. The CO, CO_2, UHC, NO_x, and air–fuel ratio can be measured using a gas analyzer, where the sampling probe is linked to the exhaust manifold and flow to the gas analyzer occurs via a flexible hose. It is crucial to ensure that the hose is located below the analyzer level to avoid excessive condensation into the filter. Zhang et al. [7] investigated the performance of a hydrogen–methanol mix (0 and 3% volume fraction of hydrogen) in a 1.6 L SI engine under various load circumstances ranging from 38 kPa to 83 kPa and at a speed of 1400 rpm. The authors discovered that increasing the amount of hydrogen enhanced their thermal efficiency.

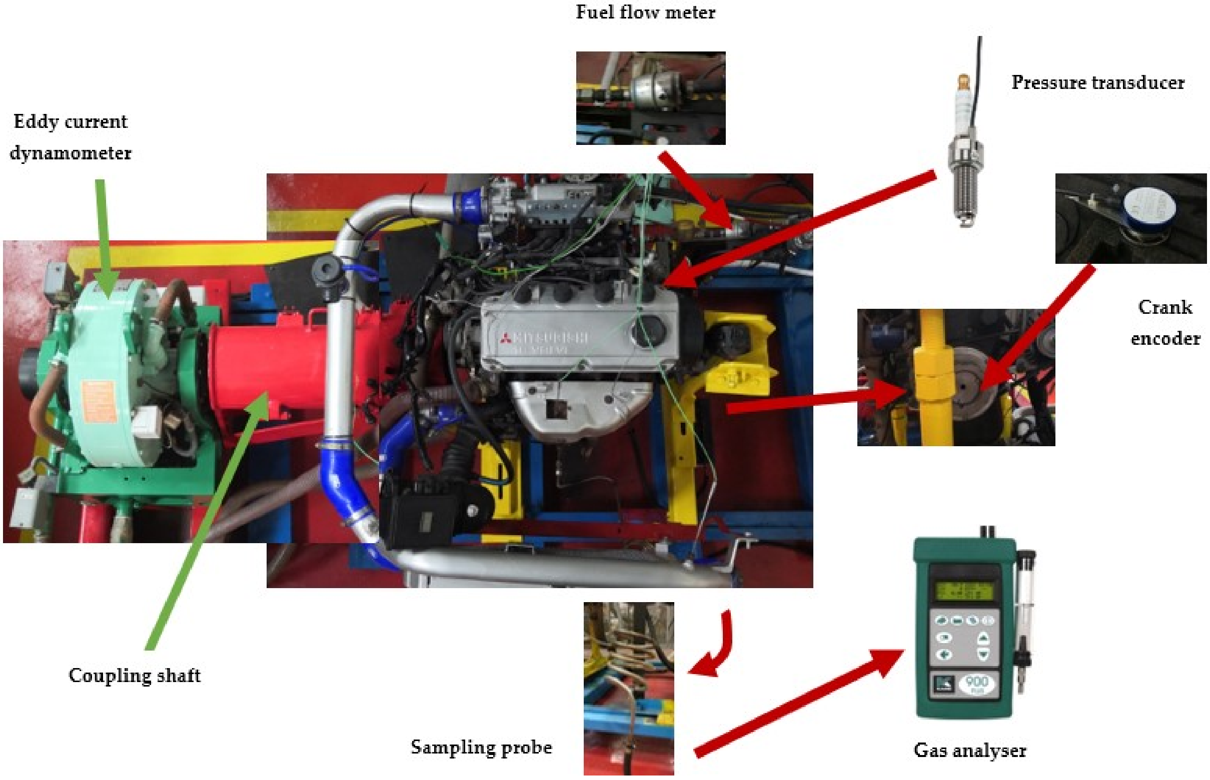

Figure 6. Typical experimental setup for engine performance, combustion, and emissions.

4.1. Effects of Different Engine Speeds, Engine Loads, and Equivalence Ratios

He et al. [83] performed research in SI engines using n-butanol and gasoline and separate intake port injection systems. The effects of gasoline–ethanol mix % on the performance of a four-stroke, four-cylinder SI engine at different engine speeds were studied (1000–4000 rpm) [84]. In general, the study concluded that blending gasoline with ethanol increased braking power (BP), brake torque (BT), and volumetric efficiency (VE) and decreased the BSFC and equivalency air–fuel ratio in the 20 vol.% ethanol sample.

Elfasakhany [85] investigated the performance of SI engines utilizing dual n-butanol (50%) and iso-butanol (50%) mixes at 3%, 7%, and 10%. The study found that 10% n-butanol–iso-butanol–gasoline created the maximum in-cylinder pressure related to engine production. Ozsezen and Canakci [86] also determined that, when engine power grew, then so did the pressure within the cylinder of SI engines powered by ethanol and methanol. Lanzanova et al. [87] investigated the effect of water content in ethanol on the performance of a single-cylinder DISI engine with 5–20% water at stoichiometric lean air–fuel ratios at loads of 3.1 bar, 6.1 bar, and 1500 rpm.

The equivalency ratio's effect on the performance and combustion characteristics of a 0.6 L SI engine running on a water-containing acetone–butanol–ethanol–gasoline mix was investigated [88]. The initial combustion duration (ICD), major combustion duration (MCD), torque, and fuel consumption were all compared by the authors (ISFC). The results indicated that when the equivalency ratio fell, ICD and MCD declined. Furthermore, due to the low LHV of ABE and water, the ISFC for ABE29W1 was 5.6–8.9% greater than pure gasoline. Table 2 summarizes the impacts of different engine speeds and loads on engine performance, combustion characteristics, and emissions of SI engines powered by alcohol and/or alcohol–gasoline blends.

Table 2. Effects of varying engine speeds and loads on engine performances and combustion characteristics.

Author	Fuel	Speed, RPM	Load, Bar	Eq. Ratio	Output
He et al. [83]	n-Butanol Gasoline	1500 2000	-	-	▲CD, ▲COV_{IMEP}, ▲ITE
Mourad et al. [89]	Ethanol-Butanol	1000–3500 (▲500)	-	-	▲BP, ▲BTE, ▼BSFC, ▼CO, ▲NO_x, ▲UHC, ▼CO_2
Elfasakhany [62]	Iso-butanol Gasoline	2600–3400 (▲100)	-	-	▲BP, ▲VE, ▼BT, ▲EGT, ▲CO_2, ▼CO, ▼UHC
Ozsezen and Canakci [86]	Ethanol Methanol Gasoline	40–100 km/h (▲20 km/h)	-	-	▲BP, ▲BSFC, ▲EGT, ▲CO, ▼CO_2, ▼UHC, ▼NO_x
Yusri et al. [82]	2-Butanol Gasoline	1000–4000 (▲500)	-	-	▲NO_x, ▲EGT, ▲CO, ▼CO_2, ▲UHC
Pourkhesalian et al. [19]	Methanol Ethanol Methane Propane Hydrogen	1500–5000 (▲500)	-	-	▲VE, ▲BP, ▲P_{incyl}, ▲BSFC
Elfasakhany [85]	n-Butanol Iso-butanol Gasoline	2600–3400 (▲100)	-	-	▲BP, ▼VE, ▼BT, ▲EGT, ▲CO_2, ▼CO, ▼UHC
Masum et al. [30]	Ethanol Iso-butanol Iso-propanol Iso-pentanol n-Hexanol Gasoline	1000–6000 (▲1000)	-	-	▲BT, ▼BSFC, ▲CO, ▲BTE, ▼UHC, ▲EGT, ▲NO_x
Eyidogan et al. [90]	Methanol Ethanol Gasoline	80 km/h 100 km/h	-	-	▲BSFC, ▲EGT, ▲P_{incyl}, ▼ROHR
Hsieh et al. [47]	Ethanol Gasoline	1000–4000 (▲1000)	-	-	▲BT, ▲BSFC, ▼UHC, ▼CO_2, ▲CO, ▼NO_x
Nour et al. [91]	Butanol, Octanol, and Heptanol	900 and 1500	-	-	▲BSFC, ▲BTE, ▼NO_x, ▲Soot
Nour et al. [91]	Butanol, Octanol, and Heptanol	-	25–100% (▲25%)	-	▼BSFC, ▲BTE, ▲EGT, ▲NO_x, ▼NO_x (75%), ▲Soot
Edwin Geo et al. [92]	Ethanol, Benzyl Alcohol	-	20–100% (▲20%)	-	▲BTE, ▲EGT, ▲ NO_x, ▲CO_2, ▼UHC, ▼CO
Irimescu et al. [93]	Butanol Gasoline	-	0.3 1	-	▲IMEP, ▲COV_{IMEP}, ▲P_{incyl}, ▲ROHR, ▼CO, ▲UHC, ▲NO_x
Li et al. [61]	Methanol Ethanol Butanol Gasoline	-	3 5	-	▲BTE, ▼BSFC, ▼CO, ▲NO_x, ▲UHC
		-	-	0.83 0.91 1.0 1.1 1.25	▼BTE, ▲BSFC, ▲CO, ▲UHC, ▲NO_x (0.83–1.0), ▼NO_x (1.0–1.25)
Nithyanandan et al. [43]	Acetone Butanol Ethanol Gasoline	-	3 5	-	▼ID, ▼CD, ▲EGT, ▲UHC, ▲CO, ▲NO_X

Table 2. *Cont.*

Author	Fuel	Speed, RPM	Load, Bar	Eq. Ratio	Output
		-	-	0.83 0.91 1.0 1.11 1.25	▲BSFC, ▼BTE, ▲UHC, ▲CO, ▲NO_x (0.83–1.0), ▼NO_x (1.0–1.25)
Munsin et al. [94]	Ethanol Gasoline	-	0.75 1.89 3.77 5.66 7.54	-	▼BSFC, ▲BTE, ▼CO, ▼UHC, ▲NO_x
Zhang et al. [3]	Hydrogen Methanol	-	0.38–0.83	-	▲BTE, ▼COV_{IMEP}, ▼CO, ▼UHC, ▲NO_x
Li et al. [88]	Acetone Butanol Ethanol Gasoline	-	-	0.83 0.91 1.0 1.11 1.25	▲BT, ▲ISFC, ▲CO, ▲UHC, ▼NO_x (after 1.0)

(▲) Increase or higher, (▼) decrease or lower.

4.2. Effect of Compression Ratios, Ignition Timing, and Injection Timing

Compression is calculated by dividing the maximum cylinder volume at the bottom dead center (BDC) by the minimum cylinder volume at the top dead center (TDC). Engines with a higher compression ratio reduce fuel consumption significantly [95]. Several research works have been published on the influence of the compression ratio on SI engine performance, combustion parameters, and emissions [96–99]. Szwaja and Naber [100] investigated the combustion properties of n-butanol in SI engines with various volume fractions of n-butanol blends with gasoline in percentages of 0%, 20%, and 60%. The authors concluded that a greater compression ratio resulted in shorter ignition delays. However, higher in-cylinder temperatures and compression ratios enhanced the likelihood of autoignition.

Balki and Sayin [27] investigated the effects of compression ratios on the performance, combustion, and emissions of pure methanol in SI engines compared to unleaded gasoline as a control. They discovered that using methanol enhanced in-cylinder pressure, brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), brake mean effective pressure (BMEP), and emission reduction at all compression ratios. A year later, in 2014, Sayin and Balki [101] investigated the properties and emissions of an iso-butanol–gasoline mix in gasoline engines with CRs of 9:1, 10:1, and 11:1. They also reported comparable results compared to prior works. Gonca [102] investigated the influence of engine design parameters such as compression ratio and spark timing on the performance of SI engines. The author determined that engine design parameters significantly impacted brake power (BP) and brake thermal efficiency (BTE).

Yousufuddin and Masood [95] examined the effect of spark timing and compression ratios (7:1, 9:1, and 11.1) on the performance of SI engines fueled with 0%, 20%, 40%, 60%, and 80% volume fractions of hydrogen blended with ethanol blends. The authors reported that the BMEP and BTE increased as the addition of hydrogen increased. The BSFC for all combinations decreased with increasing compression ratios, while the value for BMEP increased when compression ratios increased from 7:1 to 11.1.

Spark timing is a critical aspect of the performance and efficiency of SI engines. The spark timing and injection timing adjustment is significant to establish efficient air–fuel mixtures near the spark plug, but an overall lean air–fuel mixture is required [64]. Alcohol has an advantage in this matter, due to its unique properties of high octane number, higher latent heat of evaporation, and lower calorific value when linked to conventional gasoline [103]. Research on the influence of spark timing and injection timing on SI engines with alcohol and alcohol–gasoline blends has been conducted [102–105]. Deng et al. [106]

investigated and simulated the effect of ignition and valve timing on conventional SI engines running on n-butanol–gasoline blends. The GT-Power simulation model was used to examine the effect of valve timing on engine performance. Researchers found that increasing valve timing overlaps did reduce the fuel consumption.

Li et al. [64] investigated the performance of methanol-fueled SI engines under different injection and ignition timing conditions. When a SI engine runs on methanol fuel with optimized injection and ignition timings, it has more significant in-cylinder pressure, a higher rate of heat release (ROHR), a shorter ignition delay, a higher BTE, and less cycle-by-cycle variance than when the injection and ignition timings are not optimized. Another study of methanol in SI engines was conducted by other researchers, such as Xie et al. [29]. The experiment was conducted under spark timing of 18, 15, and 12 °CA bTDC. They found that performance improvement and lower emissions at full load were established as soon as the ignition timing was adjusted. Table 3 summarizes the outcome of various compression ratios, ignition timings, and injection timings on SI engines.

Table 3. The effects of various compression ratios, ignition timings, and injection timings on SI engines.

Author	Fuel	CR	ST, °CA	IT, °CA	Output
Gonca [102]	Ethanol Methanol Gasoline	10–20 (▲2)	-	-	▲BP, ▲BTE, ▲NO.
		-	35 to 5 bTDC (▲5)	-	▼BP, ▼BTE, ▼NO
Samet Uslu [107]	Isoamyl alcohol	8–9 (▲0.5)	-	-	-
Yousufuddin and Masood [95]	Ethanol Hydrogen	7:1 9:1 11:1	-	-	▼BSFC, ▲BMEP, ▲BTE
		-	10 15 20 25 30 bTDC	-	▼BSFC (10–25), ▲BSFC (25), ▲BMEP, ▲BTE
Yucesu et al. [69]	Ethanol Gasoline	8:1 9:1 10:1 11:1 12:1 13:1	-	-	▲BT, ▼BSFC, ▼CO, ▲UHC, ▼EGT
Kim et al. [8]	Ethanol Gasoline	9.5:1 13.3:1	-	-	▲ROHR, ▼UHC, ▼CO, ▼NO_x
		-	-	270 305 540 bTDC	▼ROHR, ▲CO, ▲UHC, ▲NO_x
Sayin and Balki [101]	Iso-butanol Gasoline	9:1 10:1 11:1	-	-	▼BSFC, ▲P_{incyl}, ▲ROHR, ▲BTE, ▲CO_2, ▼CO, ▼UHC
Szwaja and Naber [100]	n-Butanol Gasoline	-	4 8 10 14 18 bTDC	-	▲P_{incyl}, ▲MFB rate
Li et al. [64]	Methanol	-	13 16 18 21 23 bTDC	-	▲ITE (13–18), ▼ITE (21–23), ▼ID (13–18), ▲ID (21–23), ▼COV (13–18), ▲COV (21–23), ▲P_{incyl}, ▲ROHR, ▲CO, ▲NO_x, ▲UHC.

Table 3. *Cont.*

Author	Fuel	CR	ST, °CA	IT, °CA	Output
		-	-	34 37 39 41 42 bTDC	▲ITE (34–39), ▼ID (34–39), ▲ID (39–42), ▲P_{incyl} (34–39), ▼P_{incyl} (41–42), ▲ROHR (34–39), ▼ROHR (41–42), ▲CO, ▲NO_x, ▲UHC
Gu et al. [108]	n-Butanol Gasoline	-	5 10 15 20 25 30 35 40 bTDC	-	▲BT (5–25), ▼BT (30–40), ▼BSFC, ▼CO, ▲UHC, ▲NO_x
Xie at al. [29]	Methanol	-	12 15 18 bTDC	-	▼BSFC, ▲BMEP, ▲P_{incyl}, ▲ROHR

(▲) Increase or higher, (▼) decrease or lower.

Kim et al. [8] evaluated the impact of compression ratios and ignition timing on SI engines with ethanol–gasoline blends as the working fuel. The authors concluded that the knock tendency decreased as ethanol injection timing overlapped with intake valve timing. Table 3 summarizes SI engine performance and combustion characteristics influenced by different compression ratios, spark timings, and/or injection timings.

Li et al. conducted comparative research on methanol, ethanol, and butanol combined with gasoline [61]. The three different percentages of blends used (10, 30, 60%) are denoted by M10, M30, M60, E10, E30, E60, B10, B30, and B60. Conventional gasoline is used for comparison. As shown in Figure 7a, the BTE for all three alcohol blends was lower than traditional gasoline (21.26%). The authors concluded that the low BTE of the three alcohol blends was due to the vapor pressure of gasoline, as it is a compound. For E60, the most advanced combustion phasing resulted in the lowest BTE. Besides, for ethanol– and butanol–gasoline blends, the BTE was improved when the ratio was increased to 30 vol.% and 60 vol.%, probably because the fuel-borne oxygen offset the net work loss owing to improper combustion phasing. As shown in Figure 7b, the BSFC for alcohol blends increased with the blend percentages due to the lower LHV of alcohols compared to gasoline.

Table 4 summarizes data on the performance and combustion of alcohol and alcohol–gasoline blends versus conventional gasoline.

Table 4. Previous findings with alcohol and alcohol–gasoline blend fuels.

Fuel	% Blend	Engine	P_{incyl}, Bar	ROPR, bar/°CA	ROHR, J/°CA	IMEP, Bar	BP, kW	BSFC, g/kW·h	BTE, %	Ref.
Methanol	10, 30, 60	1C,4S, SI, 0.575L, 9.6CR	~35.4, ▲1.14%	-	-	-	-	~413, ▲8.28%	~21.37, ▼0.93%	[61]
Methanol	20, 70	4C, 4S, SI, 1.6L, 11.1CR	~45, ▲12.5%	-	~28.1, ▲15.2%	-	-	~380, ▲10.14%	~0.25, ▲4.17%	[28]
Ethanol	10, 20	4C,4S, SI, 1.8L, 9.6CR, EGR	-	-	~295, ▲14.6%	-	-	~284, ▲7.2%	-, ▲1.3%	[34]
Ethanol	5, 10, 20, 30	1C, 4S, SI, 1.0L, 13CR	22.17, ▼3.61%	-	-	-	-	-	-	[109]
Ethanol	10, 30, 60	1C, 4S, SI, 0.575L, 9.6CR	~35.3, ▲0.86%	-	-	-	-	~410, ▲6.51%	~21.27, ▼1.35%	[61]

Table 4. *Cont.*

Fuel	% Blend	Engine	P_{incyl}, Bar	ROPR, bar/°CA	ROHR, J/°CA	IMEP, Bar	BP, kW	BSFC, g/kW·h	BTE, %	Ref.
2-Butanol	5, 10, 15	4C, 4S, SI, 1.8L, 9.5CR	20.8, ▼6.3%	0.32, ▼20%	15.5, ▼8.3%	7.87, ▼1.5%	-	-	-	[82]
Iso-butanol	3, 7, 10	1C, 4S, SI, 0.147L, 7CR	22.5, ▼8.16%	-	-	-	1.58, ▼0.63%	-	-	[62]
Butanol	10, 30, 60	1C, 4S, SI, 0.575L, 9.6CR	~35.3, ▲0.86%	-	-	-	-	~405, ▲4.96%	~21.40, ▼0.76%	[61]
50%-n-Butanol 50%-Iso-butanol	3, 7, 10	1C, 4S, SI, 0.147L, 7CR	~23.4, ▼5.26%	-	-	-	~1.56, ▼4.6%	-	-	[85]
30%-Iso-propanol 60%-Butanol 10%-Ethanol	30	1C, 4S, SI, 0.6L, 9.6CR	~35.4, ▲1.2%	-	17.3, ▼1.14%	-	-	418.8, ▲9%	21.6, 0%	[33]
30%-Acetone 60%-Butanol 10%-Ethanol	100	1C, 4S, SI, 0.575L, 9.6CR	~33.0, ▲6.45%	-	-	-	-	~524, ▲39.36%	~22.0, ▲0.92%	[43]
Acetone	10, 20	1C, 4S, SI, 0.575L, 9.6CR	~37.75, ▲3.42%	-	~36.76, ▲6.37%	-	-	~437, ▲4.55%	~20.5, ▲3.54%	[66]
Acetone	3, 7, 10	1C, 4S, SI, 0.147L, 7CR	-	-	-	-	-, ▲3.3%	-	-	[77]

(▲) Increase or higher, (▼) decrease or lower.

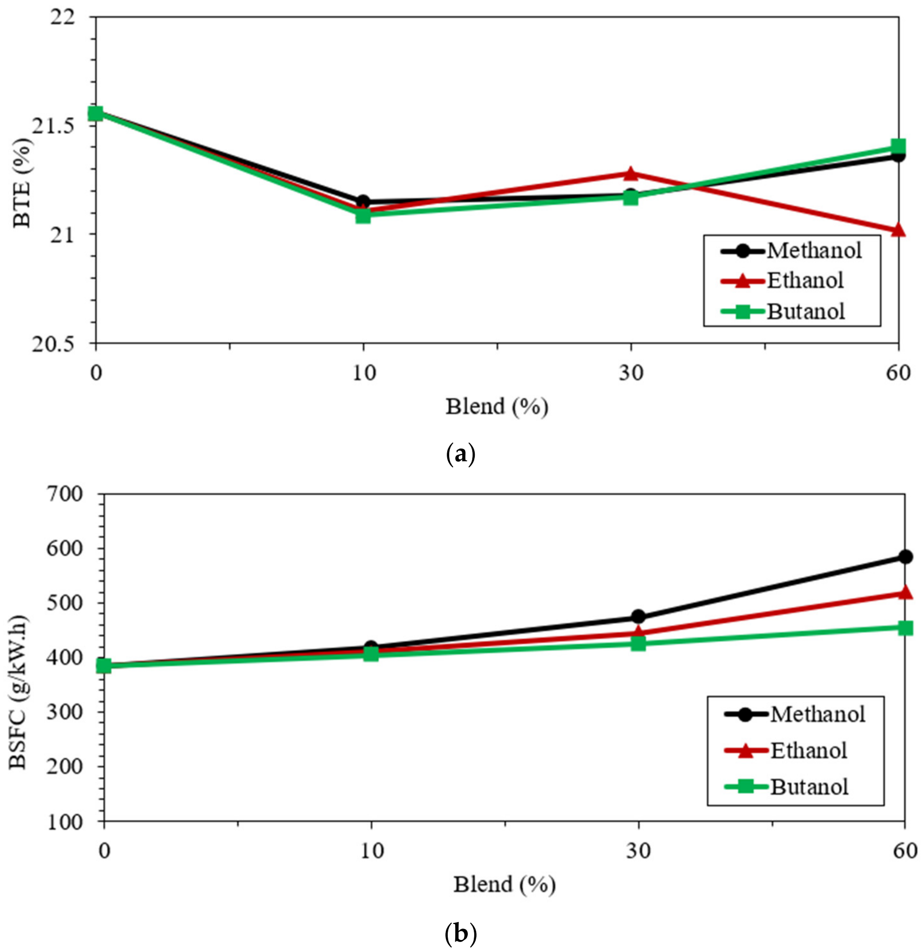

Figure 7. (**a**) BTE and (**b**) BSFC comparison between methanol, ethanol, and butanol blended with conventional gasoline [61].

5. Pollutant Emissions Study of Alcohol-Based Fuel Blend

The gas emitted from vehicle exhaust consists of a lot of undesired gases, such as carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxide (NO_x), and unburned hydrocarbon (UHC). CO is a colorless, odorless, and poisonous gas. Normally, CO is formed when the engine is operated with a fuel-rich equivalence ratio, which means that the formation occurs when there is insufficient oxygen to convert all of the carbon to CO_2. Therefore, some fuel is not burned, and some carbon becomes CO. The typical content of CO in exhaust gases is about 0.2% to 50%. The lost chemical energy not fully utilized in the engine can also cause CO formation [86]. In conclusion, CO is formed when there is poor fuel–air mixing and incomplete combustion. In summary, excessive CO emissions may be caused by excessively rich air–fuel ratio equipment failure, such as faulty injectors, dirty air filters, and engine oil diluted with the working fuel [110].

CO_2 levels steadily climb from roughly 6% to 13.5% when the air–fuel ratio is raised from 9:1 to 14.7:1. CO_2 levels are maximum when the air–fuel ratio is slightly less than stoichiometric. At the stoichiometric air–fuel ratio, CO_2 levels begin to decrease. Spark failures, incomplete combustion, engine mechanical problems, exhaust system leaks, and an insufficient air–fuel mixture can all result in abnormal CO_2 emissions [110]. Nitrogen oxide (NO_x) is the most undesirable gas from the exhaust, and regulations limit the amount of NO_x that can be produced. The in-cylinder temperature, pressure, air–fuel ratio, combustion time, and chemical reactions all impact NO_x formation [1]. When the combustion temperature reaches more than 1370 °C, the N and O_2 in the air combine to form these oxides of nitrogen. Photochemical smog is the main product of NO_x formation when released into the atmosphere. The smog is formed from the reaction between exhaust gases (NO_x) with sunlight energy. Higher than normal NO_x emissions may be caused by the overheated engine, lean air–fuel mixture, over-advanced spark timing, and too high compression [110].

The formation of UHC depends on the original fuel components, which are different for each gasoline blend. The UHC exposed to the atmosphere will act as irritants and odorants. Some UHC components are also carcinogenic. The primary cause of UHC formation is a non-stoichiometric air–fuel ratio. When fuel is richer than air, insufficient oxygen to react with carbon will increase UHC formation. However, poor combustion typically occurs due to misfire if the mixture is lean. A single misfire in 1000 cycles can produce 1 L gm kg of UHC. Unfortunately, even if the fuel and air enter at a stoichiometric ratio, the combustion is not perfect. Some hydrocarbon will end up in the exhaust, often called incomplete combustion. The incomplete mixing of air and fuel is the criterion of incomplete combustion because some fuel particles cannot find oxygen to react within the combustion chamber. In summary, excessive HC emissions may be caused by misfiring in the ignition system, improper ignition timing, low cylinder compression, and engine oil diluted in working fuel [110].

Several investigations have been performed on the pollutant emissions from SI engines to discover the potential of alcohol to be used in SI with less pollution output. Yusri et al. [82] examined the combustion, emission, and thermal balance of 2-butanol–gasoline blends in SI engines at different engine speeds ranging from 1000 to 4000 rpm. According to the findings, increasing the amount of 2-butanol reduces NO_x emissions.

In contrast, the studies of Elfasakhany [62] on SI engines using iso-butanol–gasoline blends (3%, 7%, 10% of iso-butanol) at engine speeds of 2600–3400 rpm found that iso-butanol–gasoline blends emitted less CO than pure gasoline at engine speeds of 2600–2900 rpm. However, the CO content was higher than pure gasoline at engine speeds of 3000–3400 rpm. The same results were found for UHC emissions. In contrast to [60], the CO_2 emissions from iso-butanol–gasoline blends were up to 43% lower than pure gasoline. Dhamodaran et al. [59] examined the characteristics of n-butanol blends (10%, 20%, and 30% n-butanol) in SI engines operating at speeds between 1400 and 2800 rpm. The findings revealed that using n-butanol blends reduced CO and UHC emissions compared to engines running on pure gasoline fuel. In contrast to [60,65], they discovered that the NO_x emissions from n-butanol–gasoline blends were higher than pure gasoline at both low and high engine speeds. Table 5 represents the previous findings on the emissions of SI engines fueled in comparison between alcohol–gasoline blends and conventional gasoline.

Table 5. Previous findings on emissions of SI engines fueled with alcohol–gasoline blend fuels.

Fuel	% Blend	Engine	EGT, °C	CO, %	CO_2, %	NO_x, PPM	UHC, PPM	Ref.
Methanol	10, 30, 60	1C, 4S, SI, 0.575L, 9.6CR	-	~0.257, ▲0.125%	-	~1245, ▼18.56%	~301, ▼13.01%	[61]
Methanol	20, 70	4C, 4S, SI, 1.6L, 11.1CR	~570, ▼6.9%	~0.11, ▼9.8	~12.27, ▼4.29	~800, ▼20%	~300, ▼40%	[28]
Ethanol	10, 30, 60	1C, 4S, SI, 0.575L, 9.6CR	-	~0.338, ▲34%	-	~1350, ▼12.09%	~170, ▼50%	[61]
2-Butanol	5,10,15	4C, 4S, SI, 1.8L, 9.5CR	680, ▼2.86%	2.75, ▼22%	7.5, ▲14%	890, ▼20%	64, ▼20%	[82]
n-Butanol	10, 20, 30	4C, 4S, SI, 1.0L, 9.4CR	-	0.02, ▼17.64%,	-	4750, ▲64.2%	167, ▼15.51%	[63]
Iso-butanol	3, 7, 10	1C, 4S, SI, 0.147L, 7CR	-, ▼5.2%	-, ▲2.5%	-, ▼43%	-	-, ▲7%	[62]
Butanol	10, 30, 60	1C, 4S, 0.575L, 9.6CR	-	~0.23, ▼8%	-	~1426, ▼13.29%	~300, ▼13.29%	[61]
50%-n-Butanol 50%-Iso-butanol	3, 7, 10	1C, 4S, SI, 0.147L, 7CR	~618, ▼6.8%	~3.86, ▼2.5%	~8.39, ▼31%	-	~218, ▼25%	[85]
30%-Iso-propanol 60%-Butanol 10%-Ethanol	30	1C, 4S SI, 0.6L, 9.6CR	-	0.24, ▼4%	-	1450, ▼3.3%	291, ▼20.3%	[33]
30%-Acetone 60%-Butanol 10% -Ethanol	30, 85	1C, 4S, SI, 0.575L, 9.6CR	-	33.1 g/kWh, ▲60%	-	10.5 g/kWh, ▼16%	4.5 g/kWh, ▼37%	[88]
30%-Acetone 60%-Butanol 10%-Ethanol	0	1C, 4S, SI, 0.575L, 9.6CR	~360, ▲1.12%	~0.21, ▼16%	-	~1850, ▼7.04%	~230, ▼30.3%	[43]
Acetone	3, 7, 10	1C, 4S, SI, 0.147L, 7CR	-	-, ▼46.7%	-, ▼35.5%	-	-, ▼31.8	[77]
Acetone	10, 20	1C, 4S, SI, 0.575L, 9.6CR	-	~0.33, ▼23.26%	-	~3880, ▲10.86%	~240, ▼20%	[66]

(▲) Increase or higher, (▼) decrease or lower, (CR) compression ratio, (C) cylinder, (S) stroke, (SI) SI engine, (EGT) exhaust gas temperature.

In a SI engine experimental research work, the combustion, performance, and emission properties of several alcohols (methanol, ethanol, and butanol) were examined at different equivalence ratios and engine loads, as shown in Figure 8. They discovered that all alcohol–gasoline mixes produced more CO than pure gasoline, with the exception of a 30% butanol–gasoline blend (B30), which emitted 8% less CO [61].

Figure 9 depicts the percentage increase in CO, NO_x, and UHC exhaust emissions from a SI engine running on various blend percentages of three alcohol families (methanol, ethanol, and butanol) and gasoline [61]. The equivalence ratio significantly affects the emissions emitted from the exhaust. The researchers discovered that the equivalence ratio regulated CO emissions. Furthermore, the UHC emissions increased as the equivalence ratio increased. The other cause of UHC emission is incomplete combustion. Even if the fuel and air enter at stoichiometric ratios, but the combustion is not perfect, some UHC will still end up in the exhaust. In addition, they concluded that the highest NO_x emission occurred at equivalence ratio ranges of 0.9–1.0 and would decrease when the ratio entered a richer fuel mixture ratio [6]. Other than the equivalence ratio, temperature, pressure, combustion duration, and chemical reaction influence NO_x formation. Zhang et al. [7] identified the SI engine combustion and emission characteristics using a hydrogen–methanol blend (0 and 3% hydrogen addition) under a lean mixture (λ = 1.20) and different engine loads (38 kPa to 83 kPa). They discovered that the formation of UHC for a 3% hydrogen-methanol blend was inversely proportional to engine loads. In addition, the UHC formation of 3% hydrogen–methanol is about 50% lower than pure methanol.

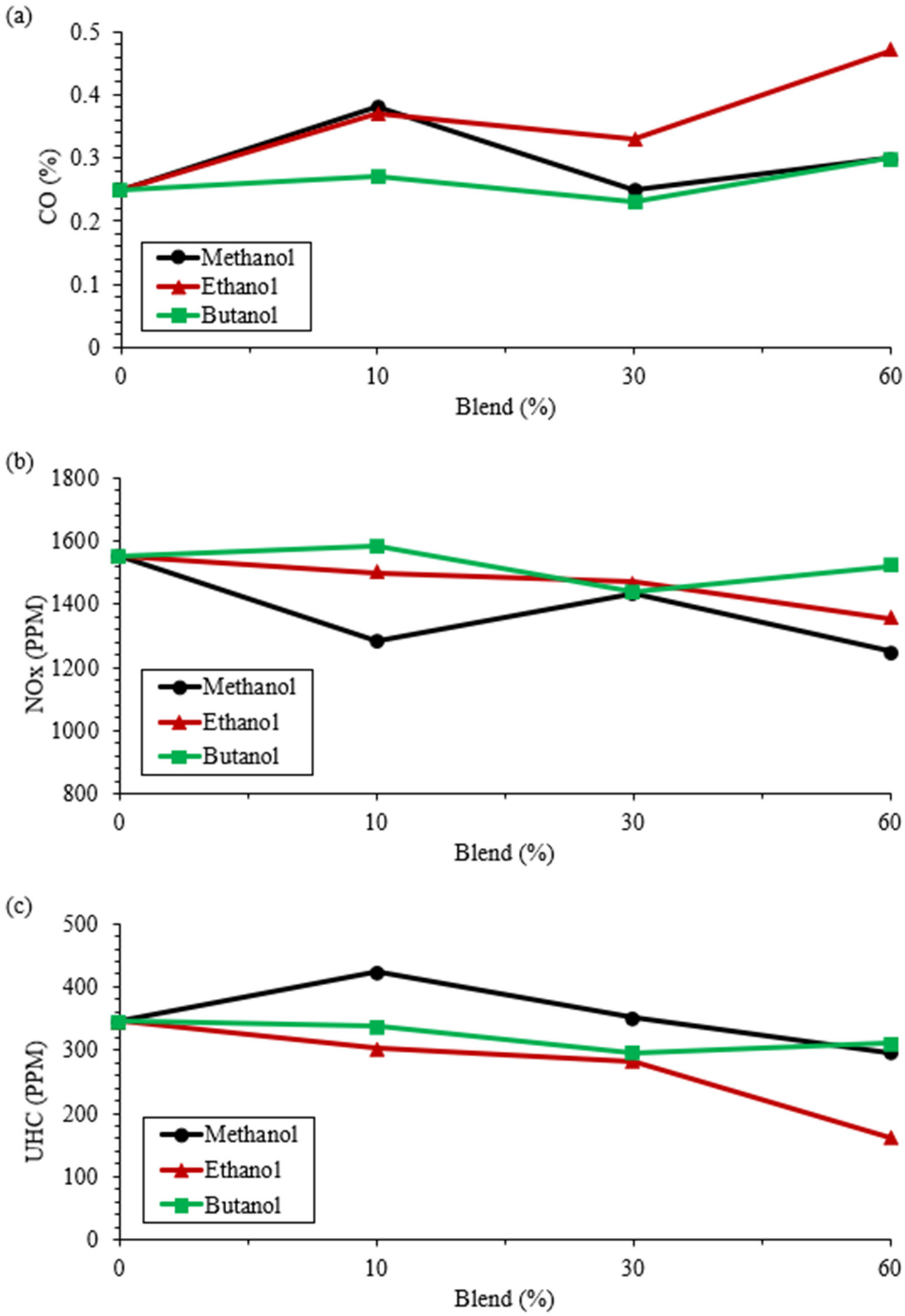

Figure 8. Effect of blend percentages of methanol, ethanol, and butanol on exhaust emissions of SI engine (**a**) CO, (**b**) NO_x, and (**c**) UHC [61].

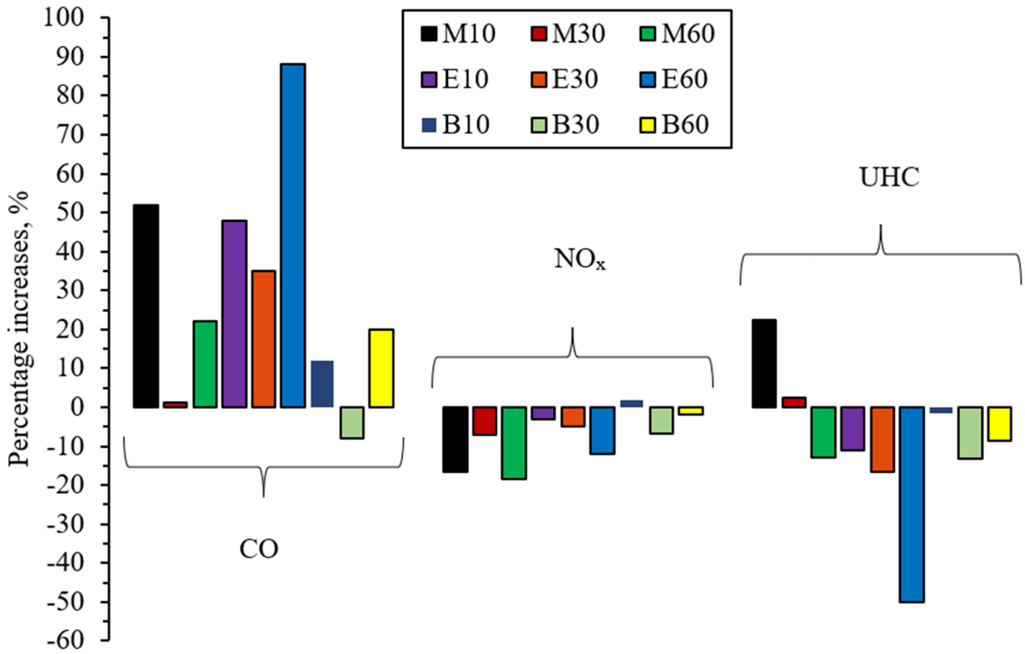

Figure 9. Percentage increases in CO, NO_x, and UHC for methanol, ethanol, and butanol blends [61].

6. Conclusions

Alcohol is the most promising solvent as an alternative fuel due to its properties that closely resemble conventional gasoline. Three alcohol families often used as alternative fuels are methanol, ethanol, and butanol. All of those alcohols were produced from renewable and biodegradable resources. The performance and exhaust emissions of SI engines powered with alcohol–gasoline blends have been widely explored. The engine's performance, combustion behavior, and exhaust emissions depend on the fuel properties and engine conditions and design. All of those aspects were discussed in this review, and the major conclusions were summarized. The properties of alcohols and engine designs significantly impact performance, combustion properties, and pollutants released by internal combustion engines.

A higher octane number of alcohols provides higher resistance to engine knocking. As a result, alcohol could be used without modification of SI engines. However, the calorific value for alcohol is significantly lower than conventional gasoline. This matter could cause high fuel consumption. SI engines' performances and emissions were typically investigated under operating conditions or parameters such as engine speed and load. Most of the studies on varied engine speeds on SI engines fueled with alcohol-based fuel blends concluded that the fuel consumption and brake power were increasing as the engine speed increased. Besides that, the compression ratio could also affect the performance and emissions of an engine fueled with alcohol. Most studies concluded that increasing the compression ratio improved the thermal performance or combustion efficiency. In addition, adjusting spark timing and ignition timing was very important in obtaining better combustion.

The spark timing is often adjusted to either advanced or retarded. Advanced spark timing reduces fuel consumption, increases combustion efficiency, and increases in-cylinder pressure. Most researchers found a reduction in CO, NO_x, and UHC emissions when alcohol was blended with gasoline, due to better combustion. CO was formed when the engine was operated with a fuel-rich equivalence ratio, which meant that CO formation occurred due to insufficient oxygen to convert all of the carbon to CO_2. Therefore, the oxygen content in alcohol can enhance CO_2 formation and reduce CO formation. Finally, based on the review, among all three alcohols, butanol is the most promising alcohol for automotive fuels, with enhanced performance and lesser emissions. However, it is influenced by the properties and blending ratio of that alcohol with gasoline.

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