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The definitive publisher version is available online at [10.1016/j.renene.2022.05.132](https://doi.org/10.1016/j.renene.2022.05.132)

Evaluation of hydrous ethanol as a fuel for internal combustion engines: A review

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Abstract

Ethanol has been extensively used worldwide as a renewable biofuel to partly substitute fossil fuels, aiming to reduce pollutant and greenhouse gas emissions. However, due to the azeotropic points of water and ethanol, the production of anhydrous ethanol is energy intensive as significant energy is consumed in the distillation and dehydration processes. Therefore, the direct use of hydrous ethanol in engines can dramatically conserve energy and reduce costs. Under this background, this review focuses on the direct use of hydrous ethanol in internal combustion engines. This paper begins with a brief description of the fuel physicochemical properties relevant to engine applications. Furthermore, fundamental combustion characteristics, including the laminar burning velocity, ignition delay time and flame instability, are introduced. Then, the applications of hydrous ethanol or its blends with gasoline in spark ignition engines are summarized. Next, compression ignition engines running on hydrous ethanol in blended and dual-fuel modes are described. Subsequently, the use of hydrous ethanol in advanced combustion concepts, such as homogeneous charge compression ignition and thermally stratified compression ignition, is reviewed. Finally, the conclusions are presented and recommendations for future research are proposed.

Keywords: Hydrous ethanol; Internal combustion engines; Combustion; Emissions; Performance

Nomenclature			
aTDC	after top dead center	ECU	Electric control unit
BSFC	Brake specific fuel consumption	BTE	Brake thermal efficiency
CDC	Conventional diesel combustion	DOC	Diesel oxidation catalyst
CI	Compression ignition	FTP75	Federal test procedure 75
CO	Carbon monoxide	TWC	Three-way catalysts
DISI	Direct injection spark ignition	SCR	Selective catalytic reduction
DPF	Diesel particulate filters	ITE	Indicated thermal efficiency
GC	Gas chromatography	FTIR	Fourier-transform infrared spectroscopy
GDI	Gasoline direct ignition	PAHs	Polycyclic aromatic hydrocarbons
GHG	Greenhouse gases	HRR	Heat release rate
HC	Hydrocarbon	IMEP	Indicated mean effective pressure
HCCI	Homogeneous charge compression ignition	CR	Compression ratio
ICE	Internal combustion engine	MBT	Minimum advance for best torque
LBV	Laminar burning velocity	LNT	Lean-NO _x traps
LHV	Lower heating value	COV	Coefficient of variation
LTC	Low-temperature combustion	CFD	Computational fluid dynamics
LCA	Life cycle assessment	TEA	Technoeconomic assessment
RCCI	Reactivity control compression ignition	HWFET	Highway fuel economy test
RCM	Rapid combustion machine	DDFS	Direct dual-fuel stratification
SI	Spark ignition	GC-MS	Gas chromatography–mass spectrometry
SOI	Start of injection	MPRR	Maximum pressure rise rate
TNC	Total number concentration	GMD	Geometric mean diameter
TSCI	Thermally stratified compression ignition	WOT	Wide open throttle
λ	Air/fuel ratio	OOD	Octane-on-demand
YSI	Yield sooting index		

1. Introduction

In the foreseeable future, internal combustion engines (ICEs) will still power transportation, industry and other energy transformation areas owing to not only their convenience and affordability but also the high energy density of hydrocarbon fuels [1-4]. However, pollutants and greenhouse gases (GHG) produced by ICEs have brought the development of low-carbon, oxygenated alternative fuels into sharp focus [5, 6]. Ethanol has been extensively used worldwide as a biofuel to partly substitute fossil fuels. Particularly in Brazil, bioethanol can be used not only in gasoline/ethanol blends in conventional gasoline vehicles but also directly in flex-fuel vehicles.

In light of the life cycle assessment (LCA) of lignocellulosic bioethanol, regardless of the configuration of biorefinery, E10 (10 vol% ethanol + 90 vol% gasoline) can reduce GHG emissions by 1%–10% and cut human toxicity by 6%–7%, compared to conventional gasoline fuel. With a further increase of ethanol content, E85 (85 vol% ethanol + 15 vol% gasoline) can reduce GHG emissions by 5%–113% and cut human toxicity by as much as 72%–75% [7]. In addition, Daylan et al. [8] pointed out that the driving cost for E85 was 23% lower than that of gasoline.

Though fuel-grade ethanol production may vary in raw materials, production steps generally include fermentation, distillation and dehydration [9]. Notably, due to the azeotropic points of water and ethanol, dehydration with significant energy consumption is necessary for water removal to produce anhydrous ethanol [10, 11]. As shown in Figure 1, the energy required for water removal (i.e., the distillation and dehydration phases) accounts for 37% of the total output energy of corn ethanol [12]. According to Saffy et al. [13], producing 86 wt.% ethanol-in-water from corn can lower the thermal energy consumption from 7.7 to 6.9 MJ/L. Consequently, hydrous ethanol production can reduce energy costs and emissions by ~8% [13]. Since the energy consumption of anhydrous ethanol production is largely from non-renewable energy like fossil fuels, hydrous ethanol is more renewable and economic to produce than anhydrous ethanol. Generally, utilizing hydrous ethanol can not only eliminate the energy for dehydration but also reduce the distillation energy by about 80% [14]. In this respect, it is apparent that the direct use of hydrous ethanol in engines could dramatically lower energy and production costs, thereby increasing the sustainability of the overall process.

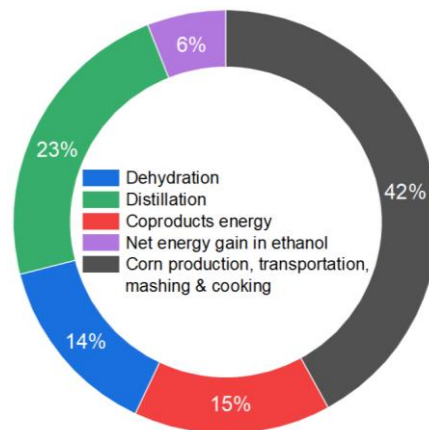


Figure 1. Net energy balance for corn anhydrous ethanol. Reproduced from Ref. [12].

Motivated by both energy and economic savings, the direct utilization of hydrous ethanol in ICEs has been widely evaluated. Due to its high octane number and heat of vaporization, hydrous ethanol is primarily considered as a spark ignition (SI) engine fuel, both in neat and blended forms. Hydrous ethanol has also been used in compression ignition (CI) engines in the form of hydrous ethanol/diesel emulsions because of its significant reduction effect on particulate matter (PM) emissions. With the development of advanced combustion concepts like dual-fuel reactivity control compression ignition (RCCI), port injection of hydrous ethanol may be a promising choice.

In spite of extensive investigations of hydrous ethanol in ICEs, a comprehensive summary of its applications is not available in the current literature. Therefore, this paper aims to review the state-of-the-art progress on direct use of hydrous ethanol in ICEs, including SI, CI and advanced combustion concept engines. This review begins with a brief description of the fundamentals of hydrous

ethanol, such as the fuel physicochemical properties and fundamental combustion characteristics (Section 2). The properties are compared with those of gasoline and diesel fuels, and their influences on engine performance are discussed. After this, a comprehensive discussion on the practical applications of hydrous ethanol in ICEs is presented, including i) the use hydrous ethanol and its blends with gasoline in SI engines (Section 3), ii) the use of hydrous ethanol in CI engines in both blended and dual-fuel modes (Section 4), and iii) the use of hydrous ethanol in advanced combustion concepts such as homogeneous charge compression ignition (HCCI) and thermally stratified compression ignition (TSCI) (Section 5). Finally, we highlight some current knowledge gaps for future research of hydrous ethanol (Section 6).

2. Fundamentals

2.1 Physical and chemical properties of hydrous ethanol

Indubitably, fuel properties greatly influence engine combustion quality, engine performance, and emissions. Therefore, it is critical to discuss the properties of hydrous ethanol and relate them to consequent engine parameter settings or engine performances. The physicochemical properties of hydrous ethanol, anhydrous ethanol, gasoline, and diesel fuels are listed in Table 1 .

Table 1. Physical and chemical properties of hydrous ethanol, anhydrous ethanol, gasoline, and diesel.

Fuel property	Gasoline [15,16]	Diesel [15,16]	Anhydrous ethanol [17]	Hydrous ethanol [18] ^a
Chemical formula	C ₅₋₁₂	C ₁₀₋₂₆	C ₂ H ₅ OH	-
Molecular weight [kg/kmol]	95–120	180–200	46.07	42.01-42.74
Cetane number	0–10	52	8	~12.7 ^b
Research octane number	88–100	-	109	~111.1
Motor octane number	80–90	20–30	90	91.8–103.3
Density @ 20°C [kg/m ³]	765	820	795	~810.9
Heat of vaporization [kJ/kg]	380–500	270	918.60	~948
Dynamic viscosity @ 20°C [mPa·s]	0.37–0.44	3.9	1.19	~1.454
Flash point [°C]	–45 to –38	65–88	8–13	~15.53
Boiling point [°C]	25–230	180–340	78.5	- ^c
Carbon content	87.4	86.1	52.2	50.59–50.7
Hydrogen content	12.6	13.9	13	12.89–13
Oxygen content	0	0	34.7	36.3–36.42
Lower heating value [MJ/kg]	42.9–43.4	42.5	26.84	24.76–25.235
Stoichiometric air–fuel ratio [kg/kg]	14.7	14.5	9	8.7–8.8
Autoignition temperature [K]	575	485	638	695–697
Yield Sooting Index (YSI)	111.4 ^d	48-115 ^e	10.3	-

Notes: a. Hydrous ethanol in Table 1 contains 4.0–5.0 vol% water.

b. The cetane number of hydrous ethanol was estimated by the method in Ref. [19].

c. “-” refers to no available data in the current publications.

d. The diesel refers to FACE Diesel #9 Batch A. The YSI was measured in Ref. [20].

e. The gasoline refers to the co-optima test gasoline. The YSIs were measured in Ref [21], and they vary depending on the components of the test gasoline.

Hydrous ethanol has a very low cetane number but a high octane number, which means that it is more suitable for SI engines [22]. Notably, hydrous ethanol has a higher octane number than gasoline, and thus, it is a good option to suppress engine knocking. Furthermore, it is favorable for hydrous ethanol–fueled engines to increase the compression ratio (CR) and thus the efficiency. Interestingly, in comparison to gasoline fuel, hydrous ethanol with a low water content has a higher sensitivity (defined

as the research octane number minus the motor octane number), which is favorable for application in highly boosted direct injection (DI) SI engines [23]. When applied in CI engines as diesel/hydrous ethanol blends, a small proportion is recommended due to its high autoignition resistance (see Section 4.1). However, it can be used as a low reactivity fuel in dual-fuel combustion operation at the expense of adding another port injection system into the diesel engine (see Section 4.2).

Ethanol's density falls between those of gasoline and diesel, and it generally increases with the addition of water. Compared to both gasoline and diesel, a higher latent heat of vaporization for hydrous ethanol brings about a significant charge cooling effect, which is beneficial for lowering the heat transfer losses and NO_x formation. In addition, it also lowers the intake air temperature, leading to an increase in the intake air density and mass flow into the cylinder, thereby increasing the volumetric efficiency. The higher latent heat of vaporization of hydrous ethanol can reduce the in-cylinder charge temperature, resulting in a better knock resistance. It can also easily induce thermal stratification in a new combustion concept named TSCI (see Section 5.2). However, this property also leads to cold start problems and increases the difficulty in preparing premixed mixtures and achieving autoignition for HCCI operation. At room temperature, hydrous ethanol has a higher boiling point than gasoline fuel, which indicates worse volatility. Therefore, under cold-start conditions, engine stability and emissions problems should be considered when using hydrous ethanol in SI engines [24]. Moreover, the lower flash point of hydrous ethanol makes it more difficult to safely transport and store.

The oxygen content of hydrous ethanol is as high as 36.3%, which can significantly reduce the emissions of pollutants, such as carbon monoxide (CO), unburnt hydrocarbons (HCs), and particulates. Due to the presence of oxygen, lower stoichiometric air is required for hydrous ethanol. Therefore, the fuel injection system needs to be re-calibrated with the addition of hydrous ethanol. A lower C/H ratio and aromatic-free nature are observed for hydrous ethanol, leading to a reduced lower heating value (LHV). To achieve comparable energy output to those of gasoline and diesel, more hydrous ethanol is needed. Additionally, hydrous ethanol has a relatively high autoignition temperature, which means that it is difficult to be spontaneously ignited under atmospheric conditions.

2.2 Fundamental combustion characteristics

From a fundamental combustion perspective, the laminar burning velocity (LBV) helps to describe combustion phenomena like flame stabilization and flame extinction and provides data for the validation of chemical kinetics mechanisms [25]. In terms of the engine combustion system, the LBV reflects the local unburned mixture composition and state [26]. Additionally, a higher LBV can shorten the total combustion duration, which has the potential to improve the thermal efficiency if a more ideal constant-volume combustion process can be achieved [27]. Figure 2 illustrates the laminar burning velocities of hydrous ethanol–air mixtures as functions of the equivalence ratio at various initial ambient conditions. As shown in Figure 2 (a), the LBV peaks of hydrous ethanol with 10 vol% water were located at the equivalence ratio of 1.1, independent of the measurement method. The experimental data of Treek et al. [28] at 358 K were comparable with those of Xu et al. [29] at 388 K, and both data were lower than the data of Liang et al. [30] at 383 K, without considering the experimental uncertainties. The discrepancies in the experimental data may have been caused by the variations in the experimental method, configuration, and uncertainty. At 358 K and atmospheric pressure, with increasing water content, the LBVs for water–ethanol–air mixtures generally decreased, as presented in Figure 2 (b) [28]. This may have been because the lower flame temperature and decreased radical production caused by the water addition suppressed the combustion reaction and LBV [31]. Notably, differences in the LBV for anhydrous ethanol and hydrous ethanol with 10% water fell within the experimental uncertainty, indicating that adding a small proportion of water (below 10 vol%) has a very low impact on the LBV of ethanol. As a result, when fueling hydrous ethanol with relatively higher water contents in practical combustion engines, it is necessary to increase the turbulence intensity of the mixture to avoid combustion durations that are too long. Furthermore, under fuel-rich conditions, water addition affects the LBV more significantly than under fuel-lean conditions. Figure 2 (c) shows that the LBVs of hydrous ethanol–air mixtures decreased as the initial pressure was increased from 2 to 4 bar.

Flame instabilities play a vital role in understanding the transition from laminar to turbulent

combustion. There are three types: hydrodynamic, diffusional–thermal, and buoyancy instabilities [34]. More recently, the results in Ref. [35] showed that increasing the water concentration from 0 to 30 vol% increased the flame thickness but decreased the thermal expansion ratio, regardless of the equivalence ratio, leading to reduced hydrodynamic instability. However, water addition increased the Lewis number, which indicated enhanced diffusional–thermal stability. Overall, the combined influences resulted in a significant decrease in flame instability with water addition.

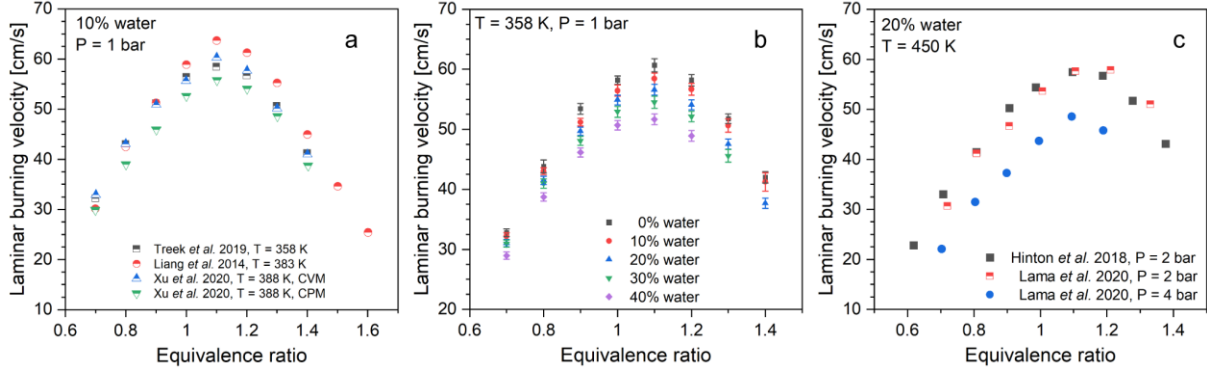


Figure 2. Laminar burning velocity of hydrous ethanol–air flames at various conditions: (a) hydrous ethanol containing 10% water at $P = 1$ bar (data collected from [28–30]; CVM: constant-volume method, CPM: constant-pressure method); (b) hydrous ethanol with various water proportions (data collected from [28]); (c) measured at various initial pressures at $T = 450$ K (data collected from [32, 33]).

The ignition delay time of a fuel is an important parameter in fuel and engine co-optimization. Figure 3 shows the ignition delay times of hydrous ethanol with various water contents at different conditions, as measured by Akih-Kumgeh et al. [36] in a shock tube. Over a high temperature range, 10% water addition had a negligible effect on ethanol ignition, while higher water contents shortened the ignition delay times at 2 and 12 atm. However, data for the low-temperature ignition delay times for hydrous ethanol was absent. Rahman et al. [37] studied the impacts of water addition on the laser ignition characteristics of ethanol–air flames. The results showed that a shorter laser ignition delay occurred as the water concentration was increased from 0% to 20%. Furthermore, the addition of water with relatively low concentrations (i.e., no more than 20%) accelerated both the flame growth rate and the flame propagation velocity. The reason behind this phenomenon was explained by Feng et al. [38], who stated that water addition advanced the ionization process and accelerated the radical production ratio, consequently enhancing the ethanol oxidation reaction. However, when the water concentration in ethanol was more than 30 vol%, the dilution effect of water significantly reduced the burning velocity and prolonged the laser ignition delay, especially under lean combustion conditions [39].

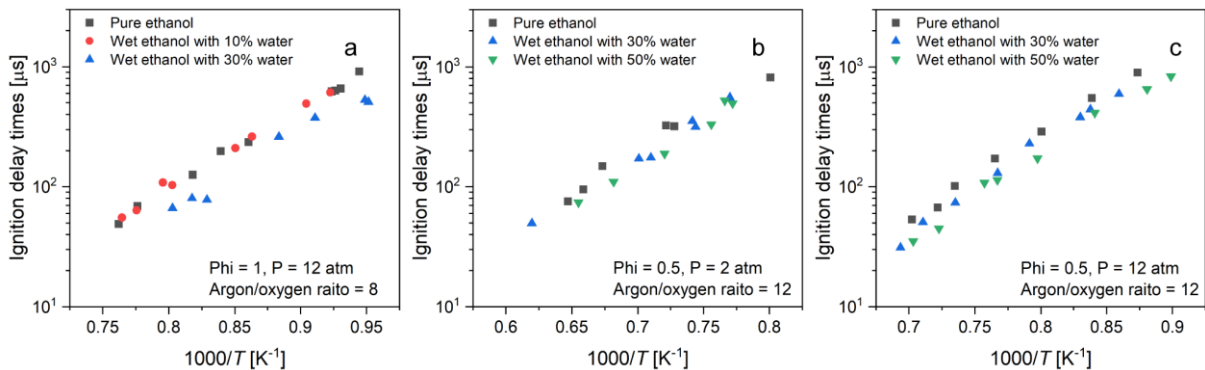


Figure 3. Ignition delay times of hydrous ethanol with various water contents at different conditions. Replotted from [36].

3. Using hydrous ethanol in SI engines

As evident from the high octane number listed in Table 1, hydrous ethanol can easily be used in SI engines, either standalone or as hydrous ethanol/gasoline blends. Considering the immiscibility of gasoline with hydrous ethanol, the direct utilization of hydrous ethanol in SI engines seems to be more popular, since it omits the preparation of stable gasoline–ethanol–water mixtures with co-solvents and emulsifiers. In Brazil, flex-fuel vehicles are extensively used, accounting for about 88.6% of the total number of vehicles in the Brazilian automobile market [40]. They burn pure gasoline, gasohol, hydrous ethanol, and any blends of the above fuels [41]. In addition to the commercial application in flex-fuel vehicles, many other studies have focused on the exploration of hydrous ethanol combustion on both gasoline-based port fuel injection (PFI) and direct injection (DI) engines. Compared with PFI engines, direct injection spark ignition (DISI) engines have higher CRs, larger volume efficiencies, and lower pumping losses. Consequently, they are superior in both power output and thermal efficiency and have been applied in passenger cars on a large scale. Therefore, investigations into DISI engines running on hydrous ethanol or its mixtures with gasoline have received more attention recently. Below, we summarize the applications of hydrous ethanol in SI engines and discuss how hydrous ethanol affects engine combustion, efficiency, and pollutant emissions. Note that earlier in 2016, El-Faroug et al. [42] previously reviewed the combustion and emissions of SI engines fueled with hydrous ethanol and its blends with gasoline. Therefore, in this sub-section, the up-to-date results are supplied in detail along with a summary of earlier publications.

For convenience, the tested fuels are abbreviated using the same convention. The letter "E" indicates anhydrous ethanol, and the number following the letter "E" means the volume fraction of anhydrous ethanol in the mixture. E22, for example, means a 78% gasoline–22% anhydrous ethanol mixture. The letters "HE" and "W" are the abbreviations for hydrous ethanol and water, respectively. For example, "HE100W5" indicates 100% hydrous ethanol (containing 5% water). Likewise, "HE20W5" means 80% gasoline–20% hydrous ethanol mixtures and hydrous ethanol containing 5% water.

3.1 Direct use in SI engines

3.1.1 Hydrous ethanol with fixed water content

Hydrous ethanol with a fixed water content varying from 4% to 8% is commonly used in the Brazilian market. In flex-fuel vehicles, the spark timing was optimized for each fuel to reach the minimum advance for best torque (MBT) or knock limit operation at each operating point. Due to the higher octane number and latent heat of vaporization, hydrous ethanol has a higher knock resistance, which allows the spark timing to be advanced. Advanced combustion phasing can increase the degree of constant volume combustion and thus the brake thermal efficiency [27]. As presented in Figure 4 (a), compared to E22 (78 vol% gasoline and 22 vol% anhydrous ethanol), an increase in thermal efficiency can be achieved for HE100W6.8 (hydrous ethanol containing 6.8 vol% water) at wide open throttle (WOT) and the whole speed range of the tested conditions [43]. In addition to the advanced spark timing, this phenomenon is partially attributed to the lower heat loss caused by a shorter combustion duration and the faster LBV of hydrous ethanol. This result was also confirmed by Rufino et al. [44], who reported that HE100W5 (hydrous ethanol with 5 vol% water) had higher first and second law efficiencies than E27 (73 vol% gasoline and 27 vol% anhydrous ethanol). Furthermore, exergy flow distribution analysis showed that hydrous ethanol exhibited lower in-cylinder, exhaust, and cooling irreversibilities. However, hydrous ethanol operation increased the peak in-cylinder pressure and induced more friction, leading to higher mechanical losses.

Figure 4 (b) compares the engine powers obtained using E22 and HE100W6.8. Compared to E22, HE100W6.8 yielded higher brake power at speeds over 4000 r/min, while it produced comparable power at low and medium speeds [43]. A similar observation was reported by Machado et al. [45], who stated that HE100W7.2 (hydrous ethanol fuel containing 7.2 wt.% water) exhibited a slightly higher brake mean effective pressure (BMEP) at both low and medium engine speeds but lower values at higher speeds (over 4000 r/min) than E25 (75 vol% gasoline and 25 vol% anhydrous ethanol). Under higher engine speeds, the more advanced ignition timing and the faster flame velocity of hydrous

ethanol offset the disadvantages caused by its lower LHV [43]. When the reference fuel changed from gasoline/anhydrous ethanol blends to E100 (100% anhydrous ethanol), additional research [46] showed that HE100W6.5 (6.5 vol% water-in-ethanol) produced a slightly lower brake power and torque as the water addition decreased the in-cylinder peak pressure and maximum heat release rate (HRR) and prolonged the combustion duration.

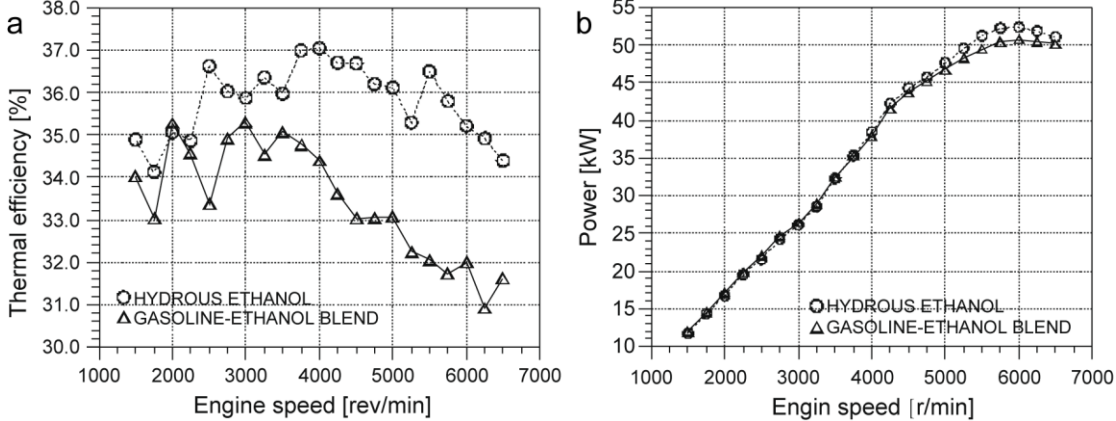


Figure 4 (a) Power and (b) thermal efficiency of the engine running on hydrous ethanol versus gasoline–ethanol blend [43].

Concerning the pollutant emissions, HE100W6.8 exhibited a higher in-cylinder peak temperature and thereby NO_x emissions than E22, throughout the engine speeds in ranges of 3000 – 6000 r/min. However, HE100W6.8 significantly reduced CO and HC emissions because of the more complete combustion caused by the higher oxygen content [43]. Compared with E100, HE100W6.5 produced higher CO and HC emissions but lower NO_x emissions [46]. The unregulated emissions of a PFI engine fueled with gasoline and HE100W4 (4 vol% water-in-ethanol) were evaluated using Fourier-transform infrared spectroscopy (FTIR) [47], as shown in

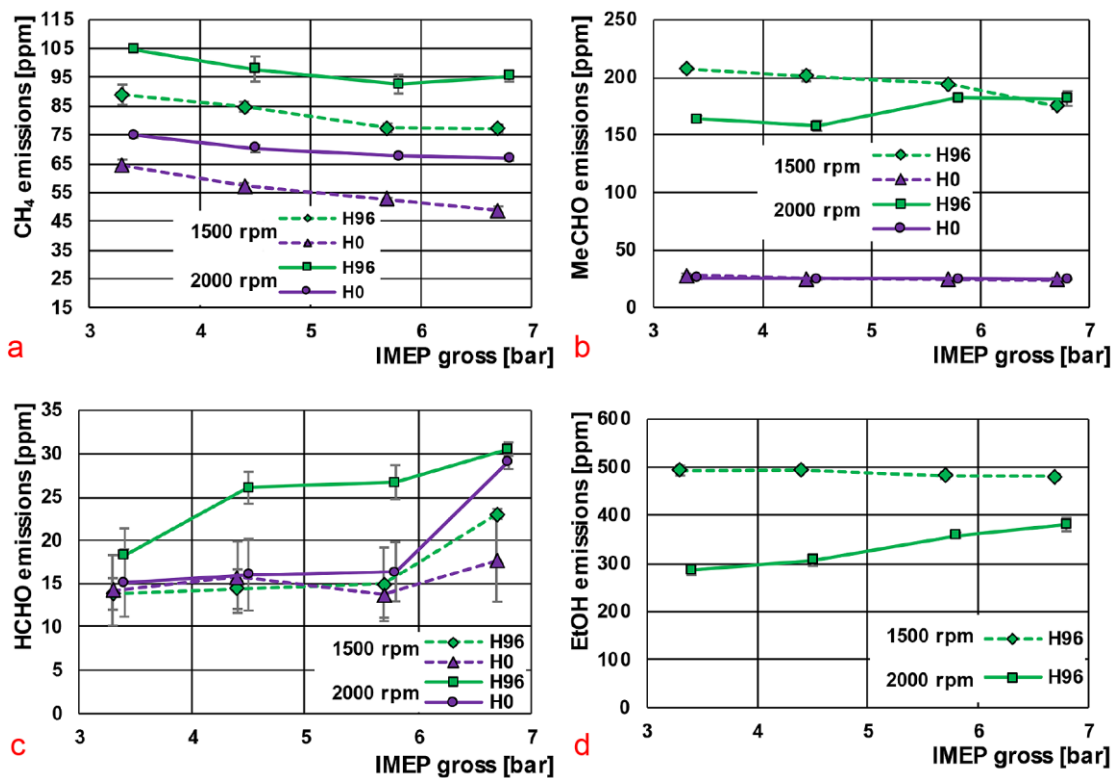


Figure 5. The concentration of unburnt ethanol was the highest for fueling with HE100W4 among the four unregulated emissions, independent of the operating point. HE100W4 also produced higher engine-out emissions of ozone precursors, including methane, acetaldehyde, and formaldehyde, than gasoline.

In addition to engine steady-state experiments, chassis dynamometer tests have been widely performed to assess the pollutant emissions emitted by flex-fuel vehicles running on hydrous ethanol. Over the whole Federal Test Procedure 75 (FTP-75) cycle, Martins et al. [48] found that HE100W6.8 emitted higher CO, HC, and NO_x but lower CO₂ emissions than E22. The same results were obtained under the cold start phase (the first 505 s) of the FTP-75 cycle. Under cold start condition, using heated intake air and fuel can significantly improve the engine-out HC and CO emissions but has a negligible effect on both NO_x and aldehyde emissions [49]. In Ref. [50, 51], analyzed by gas chromatography–mass spectrometry (GC-MS), it can be found that an HE100W4.9 (hydrous ethanol containing 4.9% water) fueled vehicle, ethene, ethyne, and ethane accounted for 95% of the non-methane hydrocarbons. Due to the high mass fraction and reactivity of ethene, HE100W4.9 tended to promote ozone formation more than E22. Silva et al. [52] found out that unburnt alcohol emissions increased with the increasing ethanol concentration, indicated by both methods of FTIR and GC. In addition, higher levels of unburnt alcohol emissions occurred at the first 100 s of the FTP-75 cycle, regardless of the test fuels. Combining the results from engine steady-state experiments, unregulated emissions like alcohols and aldehydes are much higher for hydrous ethanol operation. For this reason, the development of dedicated aftertreatments for hydrous ethanol-fueled engines is strongly encouraged. As for PM emissions, Daemme et al. [53, 54] showed that lower PM emissions were obtained for HE100W3.8 (hydrous ethanol containing 3.8 vol% water) under both FTP-75 and Highway Fuel Economy Test (HWFET) cycles, compared to E22. Quantitatively, PM emissions decreased from 2.14 mg/km for E22 to 0.79 mg/km for HE100W3.8 under the HWFET cycle, while they decreased from 0.63 mg/km for E22 to 0.56 mg/km for HE100W3.8 during the TFP-75 cycle. In addition, microscopy images further showed that particulates emitted from E22 over the FTP-75 cycle exhibited greater soot agglomeration than those generated from HE100W4.5 [55].

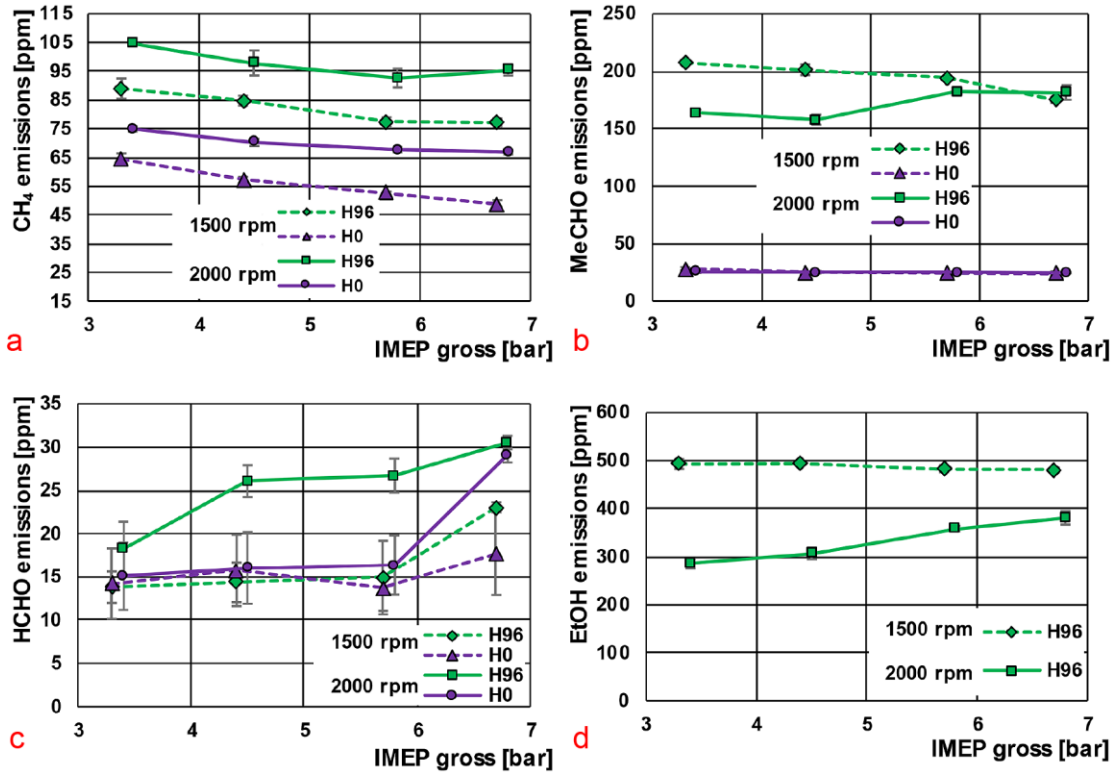


Figure 5. (a) Methane, (b) acetaldehyde, (c) formaldehyde, and (d) ethanol emissions of a spark ignition (SI) engine fueled with gasoline and HE100W4 [47]. In this figure, H0 = gasoline and H96 = HE100W4.

In SI engines, there are many strategies to improve the engine efficiency, such as elevating the CR, introducing exhaust gas recirculation (EGR), and adopting fuel-lean combustion. Increasing the CR enhances the fuel-air mixture density and flow turbulence in the combustion chamber, leading to a higher in-cylinder pressure and faster burning velocity. Limited by the gasoline knock resistance, however, the adoption of an intermediate volumetric CR in flex-fuel engines is not optimal for hydrous ethanol operation. da Costa et al. [56] figured out that the elevated CR from 10:1 to 12:1 increased the engine power and BMEP for E22 and HE100W6.8 fuels at high engine speeds. In particular, a higher thermal efficiency and lower specific fuel consumption were achieved for HE100W6.8 with the increase in CR. The same was observed by Malaquias et al. [57], who further pointed out that under the WOT and all the tested speeds, increasing the volumetric CR from 11.5:1 to 15.0:1 improved the fuel conversion efficiency of HE100W4 on average by 3.9% and 6.1% when injected into the PFI and DI systems, respectively.

The use of EGR is known to reduce the throttling loss and improve the thermal efficiency, and it also has the advantage of lowering NO_x emissions. However, the dilution and thermal effects of EGR slow the combustion process and thus increase the cycle-by-cycle variations. Increasing the in-cylinder turbulent energy may offset the undesirable effects of the EGR. Therefore, Malaquias et al. [58] studied the coupling effects of internal EGR and the in-cylinder primary flow structure in a flex-fuel DI engine burning HE100W4. The results showed that the use of internal EGR reduced the pumping losses, resulting in a 2% reduction of the fuel conversion efficiency for hydrous ethanol at CR = 15:1. With the acceptable combustion stability, the combination of internal EGR and in-cylinder tumble flow can further improve the fuel conversion efficiency up to 3.5% while lowering the gaseous pollutions for the hydrous ethanol case.

Another method of improving the thermal efficiency is fuel-lean combustion with excess air due to the higher specific heat ratios of lean mixtures. In addition, fuel-lean combustion not only reduces the pumping loss at partial-load conditions but also lowers the heat loss from cooling. Generally, fuel-lean combustion slows the burning rate and thereby prolongs the combustion duration. The combination of flame luminosity and OH* chemiluminescence confirmed that the flame propagation speed of hydrous

ethanol became slower with the increase in λ , and the edge of the flame was less wrinkled [59]. At high speeds, however, the higher turbulence caused faster flame propagation, so the lean combustion exhibited a similar combustion duration in comparison to stoichiometric combustion [60]. To maintain the overall engine thermal efficiency, the longer combustion duration of fuel-lean operation requires a more advanced spark timing than stoichiometric operation, which in turn leads to knocking. In this regard, hydrous ethanol is more suitable to be applied for fuel-lean combustion due to the higher knock resistance compared to ethanol/gasoline blends and pure gasoline fuel. As expected, within the lean limit, a higher fuel conversion efficiency and thermal efficiency were obtained for hydrous ethanol fuel-lean operation, together with the reduced engine-out CO, HC, and NO_x emissions [61-63].

Lean combustion suffers from combustion instability and the limitations of misfiring. So, it is important to study the lean limit of hydrous ethanol operation to improve the combustion stability and extend the lean limit. Under the speed of 2250 r/min and indicated mean effective pressure (IMEP) of 5 bar, Roso et al. [62] found that the fuel-lean operations in a PFI flex-fuel engine for E27 and HE100W4 fuels were limited to $\lambda = 1.5$, maintaining the coefficient of variation in IMEP (COV_{IMEP}) below 5%. As λ increased from 1.4 to 1.5, HE100W4 showed a much higher COV_{IMEP} than E27, revealing a slightly lower lean limit. Another study performed using a wall-air guided-type DI engine showed that the hydrous ethanol lean burn limit occurred at $\lambda = 1.4$ when the COV of net IMEP (COV_{NIMEP}) was under 3% [63]. In addition, Chuepeng et al. [61] compared the lean limits for hydrous ethanol (containing 5.0 wt% water) and anhydrous ethanol under steady-state idle conditions ($n = 900$ r/min). The results demonstrated that the lean limits would be $\lambda = 1.25$ for anhydrous ethanol and $\lambda = 1.49$ for hydrous ethanol, considering the combustion stability limit of COV_{IMEP} $\leq 10\%$.

The main reasons behind the combustion instability and even misfires of fuel-lean combustion are poor ignition and slow flame speeds [64]. One solution to these disadvantages is the use of a pre-chamber ignition system. The hot gas jets penetrate the main combustion chamber and ignite the lean mixture simultaneously as well as introducing turbulence. Using a pre-chamber ignition system not only provides a high ignition energy but also reduces the combustion duration [65]. In a torch homogeneous system, the fuel is injected by the only injector into the main combustion chamber and enters the pre-chamber during the compression stroke through the interconnection orifices. da Costa et al. [66, 67] developed a torch homogeneous system and found that this system improved the conversion efficiency of HE100W6 (hydrous ethanol containing 6% water) by 5.4% at $\lambda = 1.4$ when the baseline was stoichiometric conditions. The improved turbulent kinetic energy generated by the pre-chamber accelerated the burning velocity, which was also confirmed by the shorter ignition delay and combustion duration, resulting in a higher heat release rate. In turbulent jet ignition systems, the lean mixtures in the main chamber are ignited by injecting chemically active turbulent jets. Under 1200 r/min and WOT conditions, using a turbulent jet ignition system extended the lean limit to $\lambda = 1.77$ with HE100W10 (10% water in ethanol), on the premise of maintaining a COV_{IMEP} within 5% [68]. In addition, Roso et al. [69] and Duarte et al. [70] developed a stratified pre-chamber ignition system, which operated with hydrous ethanol in the main chamber together with hydrogen injected into the pre-chamber. The results showed that using a stratified pre-chamber ignition system was beneficial for burning lean hydrous ethanol mixtures, extending the lean limit with stable combustion, reducing fuel consumption, and controlling exhaust emissions. Almatrafi et al. [71] designed a narrow-throat pre-chamber system and evaluated the engine performance with HE100W4 as the main chamber fuel and methane in the pre-chamber. Equipped with this pre-chamber, burning HE100W4 as the main chamber fuel extended the lean limit by a global $\lambda = 2.7$. There are two approaches to extend the lean-burn limit: providing a stable flame kernel and improving flame propagation [72]. Therefore, further research is still necessary to extend the limit of hydrous ethanol lean combustion using the combination of advanced ignition systems (such as laser ignition) and tumble enhancement.

3.1.2 Hydrous ethanol with various water contents

In the preceding section, we discussed the combustion and emissions of SI engines burning hydrous ethanol with a fixed water content, and the water-in-ethanol concentrations mainly varied

from 4% to 8%. Aiming at using more low-cost ethanol, scholars have also focused on the performance of burning hydrous ethanol with higher hydration. Spark timing is a key parameter that affects flame formation and the early combustion processes in SI engines [73]. Under MBT spark timing conditions, water addition advances the spark timing without knocking. This may offset the disadvantage of the slow flame speed caused by adding water. Ambrós et al. [74] compared the engine performance of hydrous ethanol with various water contents under both adjusted spark timing for MBT and fixed spark advance conditions. For all fuels, the thermal efficiency under MBT conditions was higher than that under the fixed spark advance conditions. In this regard, when operating with hydrous ethanol, a spark advance at the MBT is necessary to maintain the engine efficiency.

Under the MBT condition, Lanzanova et al. [75] found that operating with a speed of 1800 r/min and a load of 34 N·m, advancing the spark timing from -20.5°CA to -6.5°CA after top dead center (aTDC) was achieved without knock occurrence when the water concentration in hydrous ethanol increased from 5 to 40 vol%. The water content can be increased to slow the combustion rate [76]. However, the combustion duration remained unchanged for up to a 30% water content [75], taking advantage of the advanced spark timing. This also led to a significant increase in the brake power, as shown in Figure 6. When the water concentration further increased from 30% to 40%, the combustion duration increased considerably, which resulted in an adverse impact on the brake power. This agreed with the observation of Ambrós et al. [74], who reported that by increasing the water content in ethanol from 10% to 40%, the specific fuel consumption decreased first but then increased, and the minimum value occurred for the hydrous ethanol containing 30% water. However, another study [77] found that when the water content in ethanol was increased from 20% to 40%, an increase in the brake specific fuel consumption (BSFC) by 75% as well as a 5% reduction in the overall efficiency occurred at a speed of 3300 r/min and a load of 72% condition. The authors attributed this result to the longer combustion duration with the increase in the water concentration, but the quantitative data of the combustion duration was absent in their work. It may be hypothesized that under MBT conditions, the positive effect of the spark timing advance on the combustion process may be related to the engine type and operating conditions. Moreover, the increase in the water content from 20% to 40% reduced the NO_x emissions by about 80% due to the lower combustion temperature, while considerably increasing the engine-out HC, CO, formaldehyde, and acetaldehyde emissions owing to the incomplete combustion [77]. Therefore, fueling hydrous ethanol with higher hydration requires the catalytic converter to eliminate the products of incomplete combustion.

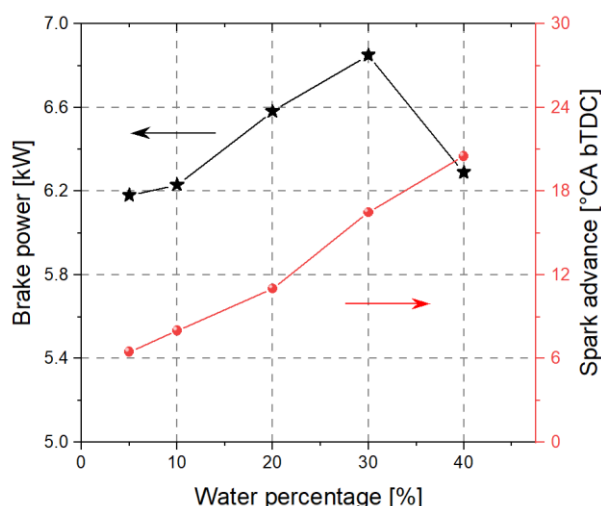


Figure 6. Effect of water addition on spark advance and brake power. Data from Ref. [75].

In addition to MBT conditions, the effect of the water ratio in hydrous ethanol on the combustion and emissions was evaluated under fixed spark timing conditions. At a fixed spark timing, the increase in the water percentage in hydrous ethanol slowed the burning velocity and consequently prolonged the combustion duration [78-80]. The optical experiments performed by Koupaie et al. [81] showed that at the fixed spark timing of -40°CA aTDC, the flame speeds decreased from 10.93 m/s for pure ethanol to 8.2 m/s for HE100W20 (hydrous ethanol with 20 vol% water). In addition, Fagundez et al.

[80] pointed out that at the fixed spark timing of -20°CA aTDC, the combustion duration of HE100W30 (hydrous ethanol with 30 vol% water) increased by over 50% compared to that of HE100W4. As a result, increasing the water ratio with a fixed spark timing later than the MBT reduced the engine output, thermal efficiency, and combustion stability [78]. A similar trend in which the fuel conversion efficiency decreased with increasing water content was observed by Fagundez et al. [80], who adjusted the ignition timing for a 50% mass fraction burned (MFB) at 10°CA aTDC.

Though the spark timing selection differed in various experiments, stable combustion can be obtained for hydrous ethanol with a hydration as high as 40%, under stoichiometric operation [74, 77, 82, 83]. The above discussions also showed well-defined trends related to the increase in the water content. Increasing the water ratio causes longer ignition delays, slower burning velocities, and higher combustion instability. Due to the cooling effect, water addition significantly decreases the combustion temperature, which is advantageous for the reduction of the NO_x emissions. However, the excessive wall wetting in PFI engines and fuel impingement in DI engines should be considered when running on hydrous ethanol with a relatively higher water contents [84]. These phenomena may increase the formation of HC and aldehyde.

Increasing the water-in-ethanol can mitigate the occurrence of knocking due to the higher latent heat of vaporization and heat capacity of water [80, 85]. The improved knock resistance allowed for higher compression ratios, which was beneficial for the engine power. Therefore, the impact of the compression ratio on the performance of an engine running on hydrous ethanol with various water contents was explored. Sari et al. [86, 87] concluded that adopting higher compression ratios shifted the maximum indicated efficiency conditions towards hydrous ethanol with a higher water concentration. A similar trend was observed by Fagundez et al. [88], who reported that HE100W30 showed higher indicated fuel conversion efficiencies than HE100W4 at compression ratios of 13.5 and 14.5.

As mentioned previously, dilution combustion technology is an effective strategy to enhance the thermal efficiency of SI engines. Lanzanova et al. [84] studied the influences of the water percentage in ethanol and fuel-lean operation on the combustion and emissions of a DISI engine. For HE100W20 fuel, stable combustion (i.e., $\text{COV}_{\text{IMEP}} \leq 5\%$) can be achieved under the lean condition of $\lambda = 1.3$. Independent of the water content, with the increase in λ , lower fuel consumption and NO_x emissions can be observed at the cost of increased HC emissions. For a given λ , increasing the water ratio decreased the combustion efficiency. Fuel-lean operation with hydrous ethanol can significantly decrease the in-cylinder temperature and extend the initial flame development process, which results in a higher cyclic variability. As suggested by DeFilippo et al. [89], this problem can be solved by adopting microwave-assisted spark, to some extent, which promotes faster early flame kernel development and decreases the COV_{IMEP} . Subsequently, Lanzanova et al. [90] evaluated the effect of the residual gas trapping on the combustion and emissions of a DISI engine fueled with hydrous ethanol with various water percentages. The results showed that for HE100W20, stable combustion (i.e. $\text{COV}_{\text{IMEP}} \leq 5\%$) could be achieved with a 40% residual gas fraction. As the water content increased, the tolerance of the maximum residual gas fraction for stable combustion decreased. Water addition slowed the flame speed, which resulted in the increase in flame development and propagation phases, and this effect became more significant as the residual gas fraction increased. Meanwhile, compared to the residual gas fraction, water addition to ethanol was more effective for the suppression of NO_x formation.

3.2 Hydrous ethanol/gasoline blends in SI engines

In addition to its use standalone in SI engines, hydrous ethanol is also used to blend with gasoline. However, gasoline-ethanol-water blends suffer from phase separation due to both gasoline and water's presence. Because of the larger possibility of phase separation at low temperatures, it is more important to evaluate the water tolerances at the lower temperature. Larsen et al. [91] reported that hydrous ethanol can contain up to 5 wt% water for gasoline-hydrous ethanol blends at low temperature down to -25°C before phase separation occurs, in the absence of any co-solvents. Since increased water percentage makes blends more economic but worsens the miscibility, the phase separation for hydrous ethanol-gasoline blends with relatively higher water contents should be a concern [92, 93]. Therefore,

the use of suitable co-solvents is necessary for the preparation of stable gasoline-ethanol-water mixtures. Kyriakides et al. [94] proved that the use of *tert*-amyl methyl ether (TAME) or methyl-*tert*-butyl ether (MTBE) as additives promoted water tolerance in gasoline–ethanol–water mixtures at temperatures of 2, 10 and 18 °C. In this regard, more work would be needed to determine the water tolerance levels of gasoline-ethanol-water mixtures at low temperatures in the presence of various co-solvents.

The effect of hydrous ethanol addition on the combustion and emissions of flex-fuel engines was studied when E22 and E25 were selected as the reference fuels [95, 96]. As stated earlier, hydrous ethanol addition advanced the spark timing without knocking. Therefore, under MBT conditions, higher in-cylinder peak pressures were observed for hydrous ethanol addition compared to those with E25. In addition, mixing with hydrous ethanol at four different contents uniformly decreased the cyclic variations of the combustion parameters [96], which was related to the higher latent heats of the blends [97]. Furthermore, hydrous ethanol addition generally produced a higher energy efficiency than E25, despite the reduction of the LHV. Adding hydrous ethanol with various concentrations to E25 or E22 reduced the CO and HC emissions, while unburned ethanol and aldehyde emissions significantly increased [95, 98]. Differently, the changes in the NO_x emissions with the hydrous ethanol ratios were sensitive to operating conditions. Due to the cooling effect, the NO_x emissions decreased at a torque of 60 N·m with the increase in the hydrous ethanol content in blends. However, at the torque of 105 N·m, the oxygen effect of hydrous ethanol seemed to be predominant, which led to an increase in NO_x formation [95].

In addition to flex-fuel vehicles, the effect of hydrous ethanol addition on the combustion and emissions of conventional PFI and GDI engines was explored. Generally, these experiments were performed under the control of an original electric control unit (ECU), and comparisons were made between hydrous ethanol/gasoline blends and gasoline fuel. Burning HE10W5 and HE20W5 together yielded slightly better brake powers and torques at full throttle and various engine speeds [99]. Though blended fuels have a reduced the lower heating value, their higher volumetric efficiency and oxygen content benefitted the combustion processes and combustion efficiency. In contrast, Venugopal et al. [100] reported that HE10W8.3 had a negligible impact on the power output at WOT operation compared to pure gasoline. However, under partial-throttle and lean-mixture conditions, a higher torque was observed for HE10W8.3 due to its higher combustion rate. For a given equivalence ratio of 0.83 at 25% throttle condition, HE10W8.3 exhibited lower exhaust energy loss and other energy losses, such as incomplete combustion and heat transfer losses, than gasoline. With the reduced lower heating values, hydrous ethanol concentrations in the blends showed a positive effect on the BSFC [99, 101]. However, improvements in the brake thermal efficiency (BTE) were obtained for hydrous ethanol/gasoline blends [99, 100], particularly under lean mixture conditions [100].

Variants in the in-cylinder pressures for HE10W5 and gasoline fuels are related to the engine loads [102]. That is, at low and medium loads, HE10W5 exhibited lower peak pressures than gasoline, which was attributed to the cooling effect caused by the higher latent heats of the blends. Similar results reported by Luo et al. [103] showed that HE20W5 lowered the peak in-cylinder pressure at engine loads of 20 and 50 N·m. However, at high loads, HE10W5 had the higher peak pressure than both E10 and gasoline fuels. This can be explained by the effect of the accelerated flame propagation and combustion speeds caused by oxygen-containing blends being dominant. Notably, peak in-cylinder pressures of HE10W5 were higher than those of E10 under the test loads, which demonstrated that the presence of water in hydrous ethanol enhanced the combustion process [102]. Similarly, the effect of hydrous ethanol addition on the cycle-to-cycle variations is highly related to operating conditions [104]. Generally, under relatively higher engine speed and load conditions, hydrous ethanol addition may restrain the cyclic variations [100, 104]. As the gas temperature in the combustion chamber is lower under low engine speed and load conditions, adding hydrous ethanol with a higher latent heat of vaporization worsens the early stage of combustion, which can further cause misfires and partial combustion in some cycles and increase the cyclic variations. With the increase in the engine speed and load, the combustion process is improved, and the presence of ethanol and water accelerates the flame propagation [104], which decreases the impact of turbulence and thus cycle-to-cycle variations [26, 42].

According to previous studies [94, 99-103], in contrast to pure gasoline, the impact of adding hydrous ethanol on NO_x emissions is still not conclusive. The variation of NO_x emissions with hydrous

ethanol addition might be due to two competing effects. The oxygen effect of hydrous ethanol provides relative oxygen enrichment in the reaction regions, which promotes the formation of NO_x. In contrast, due to the higher latent heat of vaporization, the cooling effect of hydrous ethanol decreases the in-cylinder gas temperature, which limits the NO_x formation. Notably, compared to adding anhydrous ethanol, mixing hydrous ethanol with the same ratio reduced the NO_x emissions because of the lower combustion temperature in the presence of water [94, 101-103]. Moreover, it is worth noting that the addition of hydrous ethanol generally decreases both CO and HC emissions [99, 101-103]. These results may provide evidence that hydrous ethanol addition promotes more complete combustion. In addition to the gaseous pollutants above, hydrous ethanol addition significantly decreases the concentrations of particles in the nucleation and accumulation modes, leading to reductions in the total number concentration and count median diameter compared to both pure gasoline and anhydrous ethanol/gasoline blends [103]. Furthermore, the impact of blending hydrous ethanol on the exhaust noise emissions is sensitive to the engine speed, and blended fuels reduce the exhaust noise at low engine speeds (below 2500 r/min) [99].

Recently, Duan et al. [105] found that an increase in the hydrous ethanol concentration in mixtures advanced the CA₅₀ and reduced the combustion duration of a gasoline direct ignition (GDI) engine. The presence of oxygen in hydrous ethanol increased the adiabatic flame temperature and therefore accelerated both the flame propagation speed and burning speed. This phenomenon was confirmed by their later observation from an optical single-cylinder engine [106]. Figure 7 shows a comparison of the flame development images for HE10W5, HE20W5, and HE100W5 [106]. With the increase in the hydrous ethanol concentration, both the flame development and propagation speeds increased, and the flame color changed from blue to yellow. Additionally, a reduced poor fire caused by fuel film on the impingement was observed for mixtures with higher hydrous ethanol concentrations. In GDI engines, pool fires are the dominant source of particulate emissions [107]. Therefore, this may be evidence that hydrous ethanol addition reduced the PAH and soot formation as well as the particulate number concentrations [105, 108, 109]. Similar to PFI engines, a reduction in both CO and HC emissions of a GDI engine was observed for mixtures at the expense of higher NO_x emissions. However, when the engine was fueled with hydrous ethanol–gasoline blends, the combination of EGR or a double injection strategy can simultaneously reduce the NO_x and soot emissions [105, 108, 109].

As mentioned before, hydrous ethanol/gasoline blends suffer from immiscibility. In addition, for blended modes, hydrous ethanol/gasoline should maintain a fixed blending ratio, which is not optimal for variable engine operating conditions. Therefore, hydrous ethanol–gasoline dual injection technology, which can provide flexible control for both fuels, should be considered. Currently, numerous studies have been conducted to evaluate the performances of ethanol/gasoline dual-fuel engines, and the results have indicated that the gasoline PFI plus ethanol DI strategy achieved better thermal efficiency than the ethanol PFI plus gasoline DI strategy [110]. For this reason, the evaluation of the dual-fuel engine performance of gasoline PFI plus hydrous ethanol DI is highly encouraged. During the entire driving cycle, a high octane fuel is usually needed only in a very narrow operating region in SI engines. Therefore, the octane-on-demand (OOD) concept was proposed, which combines the high volumetric energy density of gasoline at low to medium engine loads with the high anti-knock quality of high-octane fuels at higher engine loads [111, 112]. Morganti et al. [113] evaluated synthetic hydrous ethanol as the high-octane fuel for the OOD concept, with gasoline (RON 90) used as the low-octane fuel. In their study, E30 (70% gasoline and 30% anhydrous ethanol, RON 101) was used for the single-fuel baseline. The results showed that fueling with gasoline fuel could maintain the MBT spark timing at loads below about 7 bar, while hydrous ethanol should be added to increase the octane quality of the fuel and suppress knocking at higher loads. Using OOD was beneficial at lower loads for the gasoline fuel due to the higher LHV, which provided a 10% reduction in the BSFC compared to that of the E30. By adopting the peak efficiency strategy, at higher loads, OOD showed an 8% increase in the BSFC but resulted in 10% lower specific CO₂ emissions compared to E30.



Figure 7. Flame development images for various test fuels ($n = 1200$ r/min, indicated mean effective pressure (IMEP) = 0.4 MPa, injection timing: -280°CA) [106].

4. Using hydrous ethanol in CI engines

Although hydrous ethanol with high octane numbers has been extensively used in SI engines, the approaches for employing hydrous ethanol in CI engines have also been widely explored because of the increasing demand for energy savings and emission reductions of CI engines. Here, we discuss the use of hydrous ethanol in the applications of the hydrous ethanol/diesel blended mode and the hydrous ethanol/diesel dual-fuel combustion mode in the following section.

4.1 Hydrous ethanol/diesel blends in CI engines

Due to its high autoignition resistance, hydrous ethanol itself cannot be directly burnt in CI engines. One option for employing hydrous ethanol in CI engines is to use hydrous ethanol/diesel blended fuels. In blended mode, diesel and hydrous ethanol are mixed previously and then directly injected into the combustion chamber. This mode takes advantage of only requiring one injector, and no further modification to the engine is needed. However, the hydrophilic nature of hydrous ethanol prevents it from directly blended with diesel to form a stable mixture. To ensure the utilization of hydrous ethanol in CI engines in blended mode, the phase stability of hydrous ethanol/diesel blends should be initially addressed. Adding co-solvents [114] or emulsification [115] may be the common option to prevent the separation of hydrous ethanol/diesel blends. Liu et al. [114] found that using *n*-hexanol and *n*-octanol as co-solvent additives can improve the phase stability of hydrous ethanol (containing 10 vol.% water)/diesel blends. Generally, hydrous ethanol/diesel emulsion have a better miscibility than its solution counterpart [91]. Li et al. [115] successfully prepared the emulsions of 20 wt% water-containing ethanol and diesel fuel with the co-emulsifiers of Span 80 and *n*-butanol. Results showed that at the temperature of 25 °C, hydrous ethanol/diesel emulsified fuels with the hydrous ethanol mass ratios of 10%, 20%, and 30% can be stable for 1440 h (~ 60 days), 696 h (~ 29 days), and 103 h (~ 4.29 days), respectively. However, since phase separation occurs more easily at low temperatures, the miscibility limits of hydrous ethanol/diesel blends should be examined at lower temperatures, which is recommended in the future.

When diesel mixes with hydrous ethanol, the changes in fuel properties affect the fuel spray morphology and characteristics, which plays a vital role in the combustion process in the cylinder. Li et al. [115, 116] prepared emulsions of diesel mixed with hydrous ethanol (containing 20 wt.% water) with volume fractions of 10%, 20%, and 30% (denoted as D90HE10, D80HE20, and D70HE30, respectively) and explored their spray and combustion characteristics. Under both conditions of evaporating (ambient temperature = 800 K or above) and non-evaporating sprays (ambient temperature = 293 K), the influence of the hydrous ethanol addition on the spray tip penetration length and cone angle were negligible. However, under the evaporating conditions, the maximum liquid penetration length greatly increased with the increase in the hydrous ethanol content in the emulsions, which was attributed to the higher latent heat of vaporization of hydrous ethanol [115]. Note that liquid phase spray with an over-penetration length may impinge on the combustion chamber wall, which increased the exhaust emissions [117]. In this regard, fueling with emulsions with larger hydrous ethanol concentrations may require the optimization of the combustion chamber geometry to avoid spray impingement. As for burning sprays, flame images showed that the intensity of the natural luminosity significantly decreased with the increase in the hydrous ethanol content in the mixture, revealing a lower soot volume fraction in the spray flames. In addition, with the decrease in the ambient oxygen concentration, the effect of hydrous ethanol addition on the soot reduction became more pronounced [115].

In a diesel engine, the effects of blending hydrous ethanol (containing 11 vol% water) on the combustion and emission characteristics were evaluated, as reported in Ref. [118]. As the hydrous ethanol concentration was increased from 0 to 45 vol%, the ignition delay gradually increased, but the combustion duration decreased. Meanwhile, the hydrous ethanol addition increased COV_{IMEP} , indicating higher cyclic variations. Considering the lower ignitability but rapid combustion caused by blending a large concentration of hydrous ethanol, Setiaprada et al. [119] evaluated the influence of pilot injection on the combustion and emissions characteristics of a diesel engine with cooled EGR. The results showed that pilot injection strategies can effectively improve the combustion smoothness. In addition, a significant improvement in the NO_x -smoke trade-off was observed when the engine was fueled with emulsified blends, especially for D47E40W10 coupled with suitable EGR, as shown in Figure 8. As mentioned above, higher carbon alcohols can improve the stability of hydrous ethanol/diesel blends. Therefore, Nour et al. [120] prepared ternary blends of pentanol/hydrous ethanol/diesel and octanol/hydrous ethanol/diesel and further evaluated their impact on the combustion and performances of a diesel engine. Both ternary blends prolonged the ignition delay due to the lower cetane number and decreased the peak in-cylinder pressure. In addition, the combustion of hydrous-ethanol-containing blend significantly decreased the smoke and NO_x emissions.

Direct injection of a hydrous ethanol/diesel emulsion has two advantages. First, no modification of

the engine configuration is required with the application of the emulsified blends in the CI engines. Moreover, hydrous ethanol addition could significantly reduce the soot emission. In combination with EGR, fueling with an emulsion may improve the NO_x–soot trade-off relationship with comparable BTEs [119]. However, the hydrous ethanol/diesel blended mode also has some significant drawbacks. Due to the insolubility of the diesel and hydrous ethanol, blending hydrous ethanol with diesel fuel requires an emulsifier and/or a co-solvent to ensure stability during storage, delivery, and use, which may increase the usage cost. Another notable disadvantage is the limited content of hydrous ethanol in mixtures because of the high resistance to autoignition, especially for low-load and cold-start conditions, and therefore the improvement in the engine performance is small. Furthermore, adding higher fractions of hydrous ethanol greatly reduces the lower heating value, which results in a decrease in the engine power output.

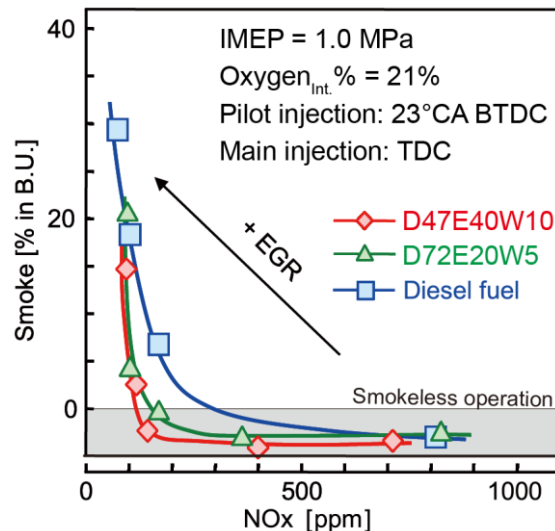


Figure 8. Improvements of the smoke-NO_x trade-off with hydrous ethanol-diesel emulsions (D72E20W5: 72% diesel +20% ethanol +5% water, by volume; D47E40W10: 47% diesel +40% ethanol +10% water, by volume). [119]

4.2 Hydrous ethanol in dual-fuel engines

Fortunately, dual-fuel combustion can overcome the above obstacles to the utilization of hydrous ethanol/diesel emulsions. Currently, dual-fuel operation, in which the second fuel with low reactivity is introduced into the intake manifold of a CI engine, seems to be more common [121-125]. Based on the methods of introducing hydrous ethanol, the dual-fuel combustion mode can be divided into four types: intake fumigation, port injection, exhaust manifold injection, and direct injection. Thus, the use of hydrous ethanol in dual-fuel combustion is summarized below.

4.2.1 Intake fumigation hydrous ethanol

Intake fumigation with hydrous ethanol eliminates the challenge of preparing a stable diesel/hydrous ethanol mixture at the expense of requiring engine intake system modifications. A separate fuel tank is required to store the hydrous ethanol, and an additional vaporizer or injector must be installed in the intake manifold. Under an engine speed of 1800 r/min and full-load condition, the maximum hydrous ethanol (containing 4.5 vol% water) substitution was up to 52.3% of the fuel energy [126]. A hydrous ethanol energy ratio higher than 52.3% was limited by a misfire and knocking effect. The energy substitution of hydrous ethanol fumigation increased with the increase in hydrous ethanol mass flow [126], while it decreased with the rising water concentration in ethanol [127].

López et al. [128] pointed out that fumigated hydrous ethanol (containing 5.8 wt%) with an energy substitution of 10% reduced the in-cylinder pressure peak compared with conventional diesel combustion (CDC) mode, which was attributed to the lower intake manifold pressure and cooling effect

of hydrous ethanol. Hydrous ethanol fumigation prolonged the ignition delay and exhibited higher peaks of the premixed combustion phase at two operating loads (0.216 and 0.478 MPa, BMEP), which resulted in higher cyclic variations. Goldsworthy et al. [129] also reported that with the increase in the hydrous ethanol ratio, the average knocking intensity increased. In diesel engines, adopting the pilot-main injection strategy has the potential of lowering the pressure rise rate and thereby the combustion noise. However, diesel with pilot-main injection is not suitable for dual-fuel combustion with larger ethanol energy substitution, as suggested by Goldsworthy [129]. When higher hydrous ethanol is used, the mixture is more easily ignited by the pre-injection, and knocking may occur due to the earlier combustion of the mixture before the main-injected diesel fuel.

Hydrous ethanol fumigation exhibits higher BSFC because of the significant reduction in the lower heating value of hydrous ethanol. However, slight improvements in both the thermal and exergy efficiencies were observed when the engine was operating with ethanol/water fumigation [130]. Similarly, Rosa et al. [127] and Telli et al. [126] reported that fumigated hydrous ethanol with various substitutions increased the energetic and exergetic efficiencies. Quantitatively, the maximum improvements of 26.2% in thermal efficiency and 22.9% in exergy efficiency were achieved with a hydrous ethanol energy ratio of 52%, under the engine speed of 2600 r/min [126]. Furthermore, for a given hydrous ethanol substitution, both efficiencies decreased with the increase in the water fraction in hydrous ethanol, which was attributed to the deficiency during the combustion process due to the presence of water. Nevertheless, fumigated hydrous ethanol with a larger water fraction is still desirable due to the economic viability and great reduction in smoke emissions [127].

The effect of hydrous ethanol fumigation on NO_x emissions may vary for different operating conditions. Some publications reported that fumigated ethanol/water decreased the exhaust temperature and NO emissions [130], and thereby reduced NO_x emissions due to the decrease in the intake airflow [131]. However, other researchers pointed out that adding hydrous ethanol to the intake manifold decreased the NO emissions but increased the NO₂ emissions [132, 133], resulting in a negligible effect on the NO_x emissions [132]. However, it is agreed upon that hydrous ethanol/diesel dual-fuel operation increases both CO and HC emissions [130, 133]. This phenomenon is attributed to the incomplete combustion caused by the quenching reaction of unburnt ethanol, which occurs close to the cylinder walls and crevices. Fortunately, in terms of increasing HC and CO emissions, the combinations of hydrous ethanol fumigation and diesel oxidation catalyst (DOC) can be considered to further diminish the engine-out emissions. Nord et al. [132] compared the emissions of hydrous ethanol/diesel dual-fuel combustion with or without heating. The results revealed that heated hydrous ethanol yielded modest benefits in the exhaust emissions.

In addition to gaseous emissions, hydrous ethanol addition reduced the smoke opacity [134], particle number concentration, and the total number concentration (TNC) [133]. However, the geometric mean diameter (GMD) of the particles from hydrous ethanol/diesel dual-fuel combustion depends on the engine load [128]. It is well known that a profound understanding of soot features and genotoxicity plays a vital role in exploring PM mitigation measures and assessing health impacts [135]. Thus, Agudelo et al. [136, 137] systematically studied the influences of hydrous ethanol fumigation on the physicochemical features and genotoxicity of diesel exhaust particulates. Based on thermogravimetric analysis, soot particulates emitted by hydrous ethanol fumigation are more easily oxidized and have higher volatile organic fractions and active surface areas. However, the impacts of fumigated hydrous ethanol on the PM morphology and soot nanostructure are negligible [136]. Furthermore, the soluble organic material extracted from exhaust particulates emitted by hydrous ethanol fumigation exhibits more genotoxicity and produces more deoxyribonucleic acid (DNA) damage than diesel fuel [137]. In this regard, particulates from hydrous ethanol fumigation can be considered to be beneficial for diesel particulate filter (DPF) regeneration, while their higher biological activities may be a hurdle for the further application of hydrous ethanol fumigation in CI engines.

4.2.2 Port injection hydrous ethanol

Recently, RCCI was proven to a promising dual-fuel combustion strategy due to its simultaneous reduction of NO_x and soot emissions while retaining a high indicated efficiency [122, 138]. In RCCI

combustion mode, a low-reactivity fuel (e.g., gasoline or ethanol) is port-injected in the cylinder by a port fuel injector, and a high-reactivity fuel (e.g., diesel and biodiesel) is directly injected into the combustion chamber through the direct injector [139, 140]. Using two such fuels with different reactivities, in combination with the direct injection timing, RCCI introduces a reactivity gradient in the cylinder. Different from the fumigation method, where diesel fuel is injected close to the top of the compression stroke, RCCI applies an early direct injection of diesel fuel to promote more homogenous mixtures [141]. Furthermore, port injection of hydrous ethanol in RCCI can be accurately controlled and provides a more rapid transient response than fumigation of hydrous ethanol.

Dempsey et al. [14] explored by three-dimensional simulations showed that for port-injected hydrous ethanol with a water content of 30% by mass, a peak gross cycle efficiency of 55% was achieved for RCCI operation along with very low NO_x and soot emissions. However, the intake temperature was reasonably increased for RCCI combustion in their work due to the significant charge cooling of premixed wet ethanol. Heavy-duty engine experiments showed that RCCI combustion using the above hydrous ethanol yielded gross indicated efficiencies of just over 50%, while it was subject to lower combustion efficiency caused by the incomplete combustion of impinged diesel fuel [142]. Considering the remarkable cooling effect of the above hydrous ethanol, a dryer hydrous ethanol with a water content of 10 vol.% was examined in a light-duty engine as the lower-reactivity fuel in RCCI combustion. The results showed that RCCI had a higher fuel conversion efficiency but lower combustion efficiency than CDC under both medium and high loads. Figure 9 displays the distribution of the input fuel energy over the net indicated cycle for CDC and RCCI, at an IMEP of 10.5 bar. The heat transfer losses and thermal exhaust losses for RCCI were lower than those for CDC, which was attributed to the lower peak combustion temperatures of RCCI combustion. The reduction in both the heat transfer losses and thermal exhaust losses for RCCI also accounted for the higher fuel conversion efficiency. However, incomplete combustion located in the squish region should be still improved for hydrous ethanol/diesel RCCI combustion to achieve a higher combustion efficiency [142]. Chuepeng et al. [143] reported that an increase in the hydrous ethanol (containing 5 vol% water) content increased the HC and CO emissions while it decreased the NO_x and soot emissions. In addition, soot particulates of all test cases exhibited a log-normal distribution located in accumulation mode (i.e. ~50-500 nm). Compared to the diesel particulates, particles from RCCI combustion with higher hydrous ethanol substitutions were smaller in size but larger in number, leading to a higher TNC.

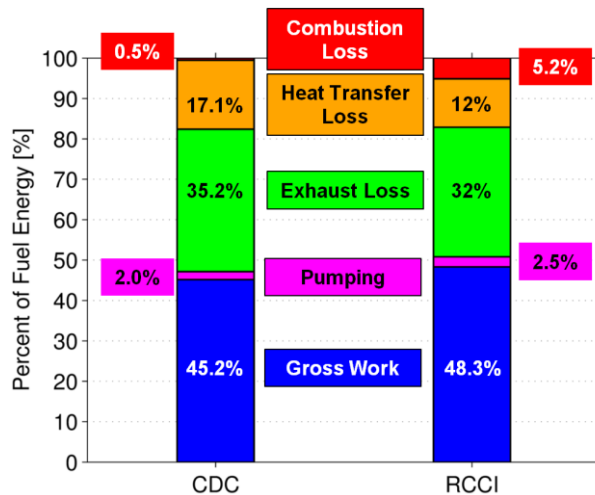


Figure 9 Distribution of the input fuel energy over the net indicated cycle for conventional diesel cycle (CDC) and reactivity control compression ignition (RCCI) at an IMEP of 10.5 bar. Reproduced from Ref. [142].

Liu et al. [144] evaluated the effect of water contents in hydrous ethanol on dual-fuel RCCI combustion characteristics. The rise of the water content in hydrous ethanol from 0% to 20% had little effect on the indicated thermal efficiency (ITE), whereas, when the water concentration further increased from 20% to 40%, the ITE dramatically decreased. For a given water content, increasing the hydrous ethanol fraction along with advancing the start of injection (SOI) can increase the ITE [145].

When the water content in hydrous ethanol increases, the maximum pressure rise rate (MPRR) first decreases and then increases [144]. At a fixed operating condition of $n = 1800$ r/min and $IMEP = 6$ bar, Rosa et al. [145] determined that the COV_{SIMEP} values for three water-in-ethanol concentrations under various hydrous ethanol substitution ratios were within 3%. However, the highest MPRR was observed for the highest water contents in hydrous ethanol (containing 36% water by volume), with a value of over 10 bar/°CA. Generally, the overshoot MPRR can be effectively avoided by the employment of the pilot-main injection of diesel fuel [146]. Thus, with the port injection of hydrous ethanol, the diesel pilot injection strategy including the pilot-main interval and pilot injection rate, can be further optimized.

The impacts of the operating parameters on hydrous ethanol/diesel RCCI operation were widely explored. An appropriate increase in the intake temperature can increase the reactivity of port-injected fuel, which is beneficial for both combustion improvement and pollutant reduction [144]. When a slightly high ratio of EGR was introduced, the ignition delay was prolonged, resulting in more homogeneous in-cylinder changes and higher combustion efficiency. Subsequently, NO_x , CO, and HC emissions decreased while maintaining the soot emissions to less than 0.008 g/(kW·h). With the improvement in the formation of homogeneous mixtures, a higher injection pressure also increased the combustion efficiency accompanied by lower CO and HC emissions [144].

For premixed hydrous ethanol (containing 25 vol% water) with an energy fraction of 76%, Fang et al. [147] studied the influence of the second diesel injection timing on the combustion and emission characteristics of hydrous ethanol/diesel RCCI operation. In their experimental work, the injection timing and mass fraction of the first diesel injection were respectively fixed at $-60^\circ CA$ aTDC and 60% total diesel fuel, and the second diesel injection timing (SOI2) was swept at different operating conditions. For each engine load, an optimal SOI2 was observed for the highest cycle efficiency. Too advanced of an SOI2 caused a portion of the diesel fuel to spray at the squish area, resulting in wall impingement and incomplete combustion. Conversely, too retarded of an SOI2 increased the local reactivity and equivalence ratio in the piston bowl, leading to more delayed CA50. If the SOI2 were optimally timed, such that the fuel jet targeted the piston bowl lip, the jet would be split and the diesel droplets could be well distributed in both the piston bowl and squish region, which consequently would result in an improvement in the combustion efficiency and a reduction in the HC and CO emissions. In subsequent work of Fang et al. [148], the operating parameters were optimized by response surface methodology to reduce the engine-out emissions of hydrous ethanol/diesel RCCI combustion. The results showed that the operating parameters sensitive to the RCCI emissions were highly linked to the engine load conditions. At low loads, the most significant factors for HC and CO emissions were the premixed energy fraction and intake air pressure, respectively. However, at a high load, both the first diesel injection mass and diesel rail pressure greatly affected the HC emissions, and the CO emissions were still sensitive to the intake air pressure.

The above discussions widely confirm the feasibility using hydrous ethanol as the low-reactivity fuel in CI engines operating with RCCI combustion. A simultaneous reduction of NO_x and soot emissions and a relatively high engine efficiency can be achieved for hydrous ethanol/diesel RCCI operation on the premise of an appropriate water concentration in hydrous ethanol. From the perspective of entirely replacing fossil fuels, studies on dual-fuel combustion with hydrous ethanol PFI and biodiesel DI are required, as suggested by [146].

4.2.3 Exhaust manifold injection hydrous ethanol

Due to the considerable cooling effects of port-injected fuel, intake air is always heated to ensure combustion stability and improve the combustion efficiency, which consumes extra energy. In this respect, the appropriate substitution ratio of hydrous ethanol with a suitable water content for RCCI operation should be explored without heated intake air. From another perspective, when higher hydrous ethanol is port-injected, the utilization of engine exhaust gas waste heat energy can be considered to heat the intake air. To eliminate the endothermic effect of port-injected hydrous ethanol, Nour et al. [149] proposed the exhaust manifold injection of hydrous ethanol, which can evaporate hydrous ethanol using the waste heat of the exhaust gases with a variable valve actuating system. In their work, the impact of ethanol/water mixture addition on diesel combustion was initially examined on a rapid combustion

machine (RCM). The RCM results indicated that adding water to ethanol prolonged the ignition delay and enhanced the premixing combustion phase compared to pure ethanol addition. Soot formation, therefore, can be significantly inhibited. Furthermore, the addition of water led to a decrease in the flame temperature and further NO_x emissions. Then, the influences of injecting hydrous ethanol into the exhaust manifold on the combustion and emissions of diesel engines were evaluated. When hydrous ethanol was injected from the exhaust manifold to the combustion chamber, some exhaust gases were also introduced, namely, the exhaust manifold injection brought about EGR. Compared to 25% EGR without introducing hydrous ethanol, lower soot and NO_x emissions along with an improved combustion efficiency were observed for hydrous ethanol with water contents below 10% by volume. Further, EL-Seesy et al. [150] compared the effect of the injection of hydrous ethanol into the intake or exhaust manifold on the combustion and emissions of a diesel engine. The results showed that the exhaust port injection exhibited a shortened ignition delay, higher NO_x emissions, and lower soot formation compared to the intake port injection. However, different from the RCM results of Nour et al. [149], EL-Seesy et al. [150] stated that hydrous ethanol addition showed higher soot and NO_x emissions than anhydrous ethanol injection.

4.2.4 Double direct injection of hydrous ethanol and diesel

Dual-fuel combustion with the double direct injection of diesel and hydrous ethanol was also explored. Teixeira et al. [151] compared the combustion and emissions of a double direct injection engine running with two various injection strategies, namely, an ethanol–diesel strategy (ethanol injected at -170°CA aTDC and diesel injected at -8°CA aTDC) and a diesel–ethanol strategy (diesel injected at -8°CA aTDC and ethanol injected at 4°CA aTDC). They pointed out that the ethanol–diesel injection strategy exhibited a higher apparent heat release and engine efficiency. However, this operation suffered from detonation when a higher ethanol fraction was injected. As for the diesel–ethanol injection strategy, the start of combustion occurred after the TDC, and as anticipated, an extremely low efficiency was observed. It can be inferred that double direct injection has two possible advantages. First, the lower cooling effect of the intake air by directly injecting hydrous ethanol might allow a higher hydrous ethanol substitution ratio. Additionally, direct injection of hydrous ethanol in the combustion chamber can be more effective in decreasing the maximum in-cylinder temperature, which would improve the combustion roughness and reduce NO_x emissions. However, to the best of our knowledge, comparative studies on the combustion and emissions of dual-fuel operation using hydrous ethanol as a low-reactivity fuel with direct injection and port injection are absent in the literature, which can be further considered to highlight the value of dual-fuel combustion with double direct injection. Alternatively, with double direct injection of two fuels with different reactivities, the direct dual-fuel stratification (DDFS) strategy was proposed by Wissink et al. [152], which could simultaneously benefit both RCCI and partially premixed combustion. Recently, methanol/diesel DDFS, E10 (10% ethanol in gasoline by volume)/diesel, and E85 (85% ethanol in gasoline by volume)/diesel DDFS have been studied through numerical simulations by various researchers [153, 154]. In particular, Li et al. [153] highlighted that methanol/diesel DDFS needs a lower initial temperature to retard the combustion phasing compared to methanol/diesel RCCI. Therefore, hydrous ethanol/diesel DDFS can also be explored and further optimized in the future.

Generally, dual-fuel operation with a higher premixed ratio reduces both the NO_x and soot emissions, while its emissions of incomplete combustion products, including CO and HC, are higher than those of the CDC mode. Such a problem can be effectively solved by coupling with a DOC. Note that a higher light-off temperature of the DOC is required in dual-fuel operation than in conventional diesel operation [155]. Therefore, it is suggested to adopt the advanced thermal management control strategies to improve the performances of catalysts [156]. In addition, the operation range of dual-fuel operation is still limited by misfires and excessive pressure rise rates. More investigations are therefore required to extend the operating ranges. Note that dual-fuel combustion requires two separate fuel injection systems, which increases the cost and complexity. This may restrict the commercial application of dual-fuel combustion, as heavy-duty diesel engines are originally more expensive [157].

5. Hydrous ethanol as fuel in advanced combustion engines

Current efforts in engine research focus heavily on advanced combustion strategies to achieve higher thermal efficiency and lower pollutant emissions. As an emerging technology, the low temperature combustion (LTC) concept is mainly achieved by the spontaneous ignition of homogeneous lean (and/or dilute) mixtures. Such a concept with low global equivalence ratios attempts to maintain the in-cylinder temperature below the thermal NO_x production threshold, which allows a higher efficiency while minimizing both NO_x and soot emissions [158]. HCCI is one type of LTC that takes advantage of both the homogeneous mixture of an SI engine and the lean mixture along with compression ignition of a CI engine. Therefore, HCCI engines running on hydrous ethanol, in particular, ethanol/water mixtures with high concentrations of water, have been evaluated. However, HCCI has a narrow operation range as it suffers from a lack of controllability in the heat release process. Therefore, researchers at Stony Brook University proposed a new advanced LTC concept, called TSCI, with the purpose of controlling the heat release process [159]. In this section, we will discuss the application of hydrous ethanol in both HCCI and TSCI engines. Though hydrous ethanol/diesel RCCI is also a type of LTC, discussions on its combustion and emissions have been presented as a part of the hydrous ethanol in dual-fuel engine discussion in Section 4.2.

5.1 Hydrous ethanol in HCCI engines

The main principle of HCCI is that a premixed charge is initially prepared and then ignited upon compression. Thus, preparing a homogeneous fuel–air mixture is the first step for achieving hydrous ethanol HCCI combustion. Generally, homogeneous charge preparation affects the start of combustion, and the mixture preparation, in turn, depends strongly on the physicochemical features of the fuel itself. Given that hydrous ethanol has a lower viscosity but higher volatility, port fuel injection may be a suitable choice. Since water injection retards the combustion phase for HCCI operation [160], increasing the intake temperature is more important for hydrous ethanol than fueling with anhydrous ethanol. Additionally, higher intake air is conducive to controlling the ignition timing and also extends the operating range of hydrous ethanol HCCI combustion. Four methods have been applied to heat the intake charge: the use of an electrical heater [161, 162], exhaust heat recovery [163, 164], external EGR [165-167], and negative valve overlap [168, 169].

Mack et al. [161] reported that elevated intake temperatures by an electrical resistance heater allowed stable hydrous ethanol HCCI operation with 40% water by volume. However, running hydrous ethanol with a higher water concentration was limited by incomplete combustion and excessive intake temperatures. Though using electrical heating provides the energy for vaporizing and autoigniting the hydrous ethanol, it consumes a great amount of electrical energy input. Allowing for HCCI operation without external energy addition, Saxena et al. [163] conducted exhaust gas heat recovery to heat the intake temperature instead of using an electrical heater. Specifically, a counterflow heat exchanger was installed to preheat the intake air using heat from the exhaust gases. The results showed that blends of 80% ethanol and 20% water (by volume) could be used in HCCI combustion without any external heat addition, which improved the energy balance for the utilization of wet ethanol as a fuel. In their subsequent work, the HCCI operation with 30% water-in-ethanol was optimized. A gross IMEP of 7.25 bar along with low ringing and NO_x emissions was achieved under the conditions of a 2-bar intake pressure, an equivalence ratio of 0.55, and CA50 located at 8°CA aTDC [164].

Employing EGR in HCCI combustion can not only recycle heat to the surrounding mixture but can also control the burning phase. An external EGR approach proposed by Martins et al. [165] is to recycle hot exhaust gases from the diesel cylinders to the hydrous ethanol cylinder without an EGR cooler. Since the diesel cylinder works with lean combustion, hot exhaust air is supplied to promote the autoignition of hydrous ethanol via sensible heat transfer [166]. HCCI operation with a high combustion stability was observed for 40% water-in-ethanol and had a comparable indicated efficiency with that of a diesel cylinder [165, 166]. Another EGR approach is internal EGR, also called residual gas trapping, which increased the residual gas within the combustion chamber with a high in-cylinder temperature by controlling the negative valve overlap [170]. However, HCCI combustion was achieved by intake boosting and residual gas trapping by Megaritis et al. [168, 169]. It was pointed out that water in hydrous

ethanol was counterproductive for the reduction of the pressure rise rates at higher loads and thus reduced the operating range compared to anhydrous ethanol HCCI combustion.

In addition to port injection, adding a vaporizer is also an approach to prepare a homogeneous mixture via the full vaporization of fuel before it enters the cylinder [12, 171]. Generally, a fuel vaporizer is used to atomize and homogenize high viscous fuels like diesel and biodiesel. However, some studies also explored the hydrous ethanol HCCI combustion using a fuel vaporizer. As reported by Martinez-Frias et al. [12], the utilization of wet ethanol in an HCCI engine was achieved by adding a vaporizer to evaporate the mixtures and a regenerator to heat the intake temperature from the exhaust, aiming at improving the ethanol life-cycle energy efficiency. Modeling results showed that the HCCI engine could operate on 35% ethanol in water by volume with a high efficiency of 38.7% and extremely low NO_x emissions of 1.6 ppm. In addition, exergy analysis showed that heat transfer processes in the fuel vaporizer and heat exchanger accounted for 4.39% of the total exergy destruction [171].

Generally, ethanol HCCI combustion, with or without water addition, exhibits single-stage autoignition. Introducing water reduces the in-cylinder gas temperature and retards the combustion phase. Though the water in hydrous ethanol provides the advantage of controlling the reaction rates, it also introduces ignition difficulty as a relatively high autoignition temperature is required due to the increased latent heat of vaporization. A higher intake air temperature for hydrous ethanol HCCI combustion is therefore needed, and the intake air heating methods without external energy input are explored and optimized to maximize the advantages of the direct utilization of hydrous ethanol in HCCI engines in terms of energy savings. Previous studies showed that hydrous ethanol with a high water volume fraction of 40% can be stably burnt in HCCI mode, but it also suffers from unacceptable HC and CO emissions due to incomplete combustion. Moreover, water addition decreases the exhaust temperature, which creates catalytic difficulties during aftertreatment. Hence, effective strategies for decreasing HC and CO emissions from hydrous ethanol HCCI are required. Regarding HCCI combustion, the limited operation range due to misfires at low engine loads, knocking at high engine loads, and a lack of control of the combustion phase are still obstacles for commercial application.

5.2 *Hydrous ethanol in TSCI engines*

Based on optical chemiluminescence and planar laser-induced fluorescence images, research has shown that the heat release process in HCCI combustion exists an in-cylinder temperature distribution, also called thermal stratification, which means that various regions in the cylinder auto-ignite sequentially depending on their local temperature [172]. Based on this finding, Lawler et al. [159] recently proposed a novel advanced low-temperature combustion mode, named TSCI, aimed at controlling the heat release rate in LTC via temperature stratification. Initially, they accomplished TSCI by water direct injection, and the results showed that the load range was extended from a gross indicated mean effective pressure (IMEP_g) of 2.3–3.6 bar for HCCI without water injection to an IMEP_g of 2.3–8.4 bar for TSCI with water injection [159]. Because employing direct water injection in TSCI requires a separate direct injector and has commercial application limits, the research team of Stony Brook University further introduced the split injection of wet ethanol to control the combustion process due to its low equivalence ratio sensitivity and high heat of vaporization. Below, we discuss the scientific contributions related to the employment of hydrous ethanol in TSCI engines.

Multiple injection strategies provide a high degree of flexibility in selecting the number of injection pulses, injection timing, and dwell time between injections, and they have also been used in advanced combustion concepts to improve the combustion phenomena [173]. A well-organized split injection strategy in TSCI plays an important role in governing the fuel–air mixing and thermal stratification, and consequently, the combustion and heat release processes. To realize TSCI with wet ethanol, Gainey et al. [174] used a split injection strategy with the first injection of a large portion of fuel and the second injection of the remaining fuel. The first injection during the intake stroke (−350°CA aTDC) provided sufficient time to premix the wet ethanol and air, while the second injection during the compression stroke (−60°CA aTDC) created thermal stratification in the cylinder. Benefitting from the thermal stratification by the second injection, the high load limit was extended from a 3.93 bar IMEP_g for HCCI to 6.97 bar IMEP_g for TSCI under naturally aspirated conditions. Combined with the intake boost, a

further load range extension up to a 7.64 bar IMEP_g was achieved [175]. As water-in-ethanol altered the latent heat of vaporization of the mixture, the effect of wet ethanol with various water contents on TSCI combustion was studied. The simulation results showed that a longer combustion duration along with a lower peak pressure and HRR were observed for the higher water contents. Furthermore, wet ethanol with a larger water content also brought about evaporation difficulty when it was injected at the intake stroke, while small water fractions of 10% or 20% were able to induce thermal stratification and had the ability to control the combustion phase [176]. Therefore, in the following studies on wet ethanol TSCI operation, wet ethanol with 20% water by mass was generally selected.

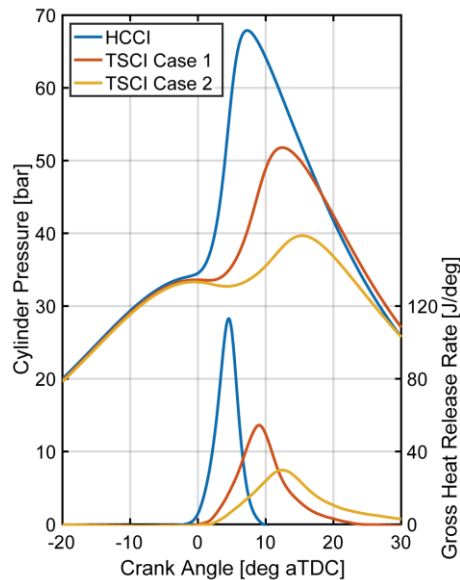


Figure 10. Cylinder pressure and gross heat release rate (HRR) for homogeneous charge compression ignition (HCCI) and thermally stratified compression ignition (TSCI) with wet ethanol at a fixed global equivalence ratio of 0.5 (HCCI: the second injection fraction of 0%, TSCI Case 1: the second injection fraction of 8%, TSCI Case 2: the second injection fraction of 13%) [174].

The timing and quantity of both injections can affect the heat release process. Therefore, Gainey et al. [174, 177-179] conducted a series of experiments and simulations to assess how both injection strategies affect the wet ethanol TSCI operation. Figure 10 shows the in-cylinder pressure and gross HRR for HCCI and TSCI with wet ethanol. At a fixed global equivalence ratio of 0.5, with the increase in the second injection fraction from 0% to 13%, both the in-cylinder pressure and gross HRR gradually decreased along with the retarder combustion phase, which indicated that the second injection of wet ethanol provided local cooling and thus thermal stratification. That is, injecting a larger fraction of wet ethanol in the second injection resulted in higher thermal stratification and had better controllability of the initiation and rate of combustion [176]. In addition to the split injection fraction, the TSCI combustion process was proven to be sensitive to the injection timing during both the intake and compression strokes. Numerical simulation results showed that before the start of combustion, the intake stroke injection timing affected the level of wet ethanol–air mixing [179]. Specifically, the wet ethanol–air mixture was homogeneous for the earliest injection, while the mixture became more stratified with retarded injection timing. In particular, for the later intake stroke injection timing, the insufficient mixing results showed an inverse relationship between the temperature and equivalence, namely, higher-temperature regions had higher equivalence ratios [179]. Experimental results indicated that the combustion efficiency decreased from 92.2% to 84.1% when the intake stroke injection timing was retarded from $-350^{\circ}\text{CA aTDC}$ to $-330^{\circ}\text{CA aTDC}$. Such a phenomenon can be explained by the evaporative cooling of the wet ethanol and its effects on the spray dynamics and wall impingement. Therefore, the injection timing of $-350^{\circ}\text{CA aTDC}$ may be optimal for the single injection strategy, providing a more homogeneous mixture of wet ethanol and air in the combustion chamber. Additionally, in terms of a high combustion efficiency, a double intake stroke injection strategy had no advantage [177].

During the compression stroke, the direct injection of wet ethanol introduced thermal stratification and decreased the mean in-cylinder temperature. Therefore, varying the compression stroke injection timing changed the local and global cooling effects. The results showed that in the compression stroke, injection too early ($-150^{\circ}\text{CA aTDC}$ to $-100^{\circ}\text{CA aTDC}$) lowered the mean in-cylinder temperature and thus retarded the start of combustion. In contrast, injection too late ($-20^{\circ}\text{CA aTDC}$) resulted in a high pressure rise rate due to the insufficient evaporation and mixing of the fuel spray. The midway injections with the timing varying from $-90^{\circ}\text{CA aTDC}$ to $-30^{\circ}\text{CA aTDC}$ increased the thermal stratification and allowed for good control in the combustion phase. Using a double compression stroke injection strategy can improve combustion efficiency due to the better breakup and less wall wetting [175, 179].

Numerical simulation analysis showed that for the engine configuration when an included angle as broad as 150° was used, the wet ethanol spray targeted the squish region (i.e., outside the piston bowl) and the thermal stratification was higher, which led to better control of the heat release rates. In contrast, targeting inside the piston bowl, an included angle as narrow as 60° had a lower thermal stratification [180]. However, it can be speculated that using the included angle of 150° might decrease the combustion efficiency but increase the CO and HC emissions due to the larger incomplete combustion of the fuel injected at the squish region. Furthermore, the coupling influences of the spray and piston geometries on wet ethanol TSCI combustion were explored [181]. The results demonstrated that for a split fraction of 80% with the 150° injector, using the shallow bowl piston produced lower CO and HC emissions than using the re-entrant bowl piston. In addition, lower heat transfer could be achieved for the shallow bowl piston with a lower surface-to-volume ratio, which led to a higher thermal efficiency. However, this also suffered from lower natural thermal stratification and thus higher pressure rise rates. Therefore, in terms of the control of the combustion process, a re-entrant bowl piston geometry coupled with a broader spray angle injector may be the optimal choice [181].

6. Conclusions and recommendations

6.1 Conclusions

Fuel decarbonization, i.e., the use of a low-carbon fuel to complement and partly substitute conventional fossil fuels, is critical for GHG emission reduction. Under this background, the direct use of hydrous ethanol in ICEs has attracted extensive attraction in recent years since hydrous ethanol is less expensive and more CO_2 friendly to produce compared to anhydrous ethanol. Therefore, this paper provides a systematic review on the use of hydrous ethanol standalone or as a blend component for ICEs including SI, DI and advanced combustion engines.

First, the physical and chemical properties of hydrous ethanol were described, and comparisons were made with both gasoline and diesel fuels. The properties related to the engine parameter settings or engine performance were introduced briefly. In addition, the fundamental combustion characteristics of hydrous ethanol, including the LBV, ignition delay times and flame instabilities, were summarized. Water addition with less than 10 vol% negligibly affects the LBV of ethanol fuel while further increasing water content suppresses the LBV. Adding water decreases flame instability and shortens the ignition delay times.

Hydrous ethanol has been widely used in commercial SI engines, especially as a fuel for flex-fuel vehicles in the Brazilian market. The hydrous ethanol used in Brazil mainly contains water with contents varying from 4% to 8%. Due to the higher octane number, enhanced knock resistance of hydrous ethanol allows for advancing the spark timing and elevating the compression ratio. Compared to gasoline or gasoline/ethanol blends (containing no more than 30% ethanol), hydrous ethanol combustion has a shorter or comparable combustion duration due to the advanced spark timing, which results in a slightly increased thermal efficiency at some operating points. The benefits of thermal efficiency reached a maximum improvement of 14.1% based on the previous publications. When combined with higher CR, internal EGR, and fuel-lean technology, hydrous ethanol operation can be further optimized. In comparison with gasoline/ethanol blends, hydrous ethanol produces greater NO_x emissions due to the advanced spark timing but lower HC and CO emissions. There is no doubt that unregulated emissions, such as alcohols and aldehydes, are higher for hydrous ethanol operation, and

future research needs to be carried out to reduce them. The combustion and emissions of hydrous ethanol with relatively higher water contents were also evaluated in the laboratory. Increasing the water percentage prolongs the flame development phase and slows the burning velocity. The cooling effect of water addition reduces the NO_x emissions, but hydrous ethanol with higher water contents emitted higher CO and HC emissions. Increasing the water-in-ethanol percentage may mitigate the knock occurrence, which indicates that the thermal efficiency can be improved by coupling with a higher CR.

Research on the combustion and emissions of SI engines running on hydrous ethanol/gasoline blends is relatively scarce. The main reason may be the restriction of the phase stability of the mixture. Differences in the combustion processes between fueling with hydrous ethanol/gasoline blends and anhydrous ethanol/gasoline blends are not significant and are dependent on the operating points. Hydrous ethanol/gasoline blend combustion decreases HC and CO emissions under most conditions, but the impact on the NO_x emissions is related to the operating conditions. It is recommended that using dual-fuel SI combustion with gasoline PFI plus hydrous ethanol DI may overcome problems such as fuel immiscibility and insignificant improvements of the engine performance with the blended mode.

In DI engines, operation with diesel/hydrous ethanol blends can significantly reduce PM emissions. Combining with optimized combustion strategies, smokeless operation can be reached along with very low NO_x level. However, diesel/hydrous ethanol blends also suffer from phase stability issues. Therefore, the hydrous ethanol/diesel dual fuel mode has attracted significant attention from the perspectives of intake fumigation, RCCI, and double direct injections. As expected, compared to CDC, dual-fuel operation reduces both NO_x and soot emissions at the expense of greater emissions of incomplete combustion products, such as CO and HC. In addition, the hydrous ethanol/diesel dual-fuel mode suffers from other problems, such as narrower operating ranges and higher cost and complexity.

The application of hydrous ethanol in advanced combustion engines was also explored. A higher efficiency and lower NO_x emissions can be achieved for hydrous ethanol HCCI operation, at the cost of higher HC and CO emissions. In addition, the presence of water reduces the in-cylinder temperature and provides the advantages of controlling the reaction rates. However, a higher latent heat of vaporization of hydrous ethanol also brings about ignition difficulty, and consequently, intake air heating is needed. Moreover, the limited operation range and lack of control of the combustion phase are still obstacles. To take advantage of the higher latent heat of vaporization, hydrous ethanol TSCI operation was introduced, which aimed to control the heat release rate via thermal stratification. Compared to the HCCI mode, the high load limit was extended up to 7.64 bar IMEPg by hydrous ethanol TSCI combustion.

6.2 Recommendations

Though the utilization of hydrous ethanol in ICEs has been widely explored and optimized, there are still some recommendations for future research, which are listed as follows.

- 1) As discussed, hydrous ethanol blending with gasoline or diesel is an important way of its applications in ICEs. Considering this, the phase separation of hydrous ethanol and gasoline/diesel is a challenge and must be avoided. Therefore, more work on the effects of blending ratios, water concentrations and co-solvents on miscibility characteristics of the blended fuels are needed, especially for hydrous ethanol/diesel blends at low temperatures.
- 2) Fuel injection systems are typically lubricated by the fuel being used. However, both ethanol and water are not effective lubricants. Therefore, long-term negative impacts, such as lubricant deterioration and fuel system corrosion should be considered, especially for diesel fuel injection systems. In addition, experiments on engine wear and durability should be performed when engines are fueled with hydrous ethanol or its blends to establish the viability of employing hydrous ethanol.
- 3) Generally, in SI engines, adding hydrous ethanol with a relatively low water content increases the

NO_x emissions. In dual-fuel engines, using hydrous ethanol as a low reactivity fuel mainly increases the CO and HC emissions. Therefore, under various combustion modes and different engine types, combinations of hydrous ethanol addition with the employment of various after-treatment systems should be considered to further reduce the pollutants.

- 4) In addition to regulated pollutants, unregulated emissions, such as ethanol and aldehydes, from the hydrous-ethanol-fueled operation are much higher than those from petroleum-based fuels. Therefore, clarification of these unregulated emissions, including the engine-out emissions and the aftertreatment efficiency, is required.
- 5) Considerable research on the hydrous-ethanol-fueled operation by experiments has been reported, while studies based on numerical simulations have been relatively few. Thus, more simulation work is needed to illustrate the physical and chemical roles of hydrous ethanol addition in practical combustion processes. Regarding this issue, additional work should be considered to elucidate the fundamental combustion characteristics of hydrous ethanol, such as low-temperature ignition delay times and spray characteristics. This work plays a vital role in computational fluid dynamics (CFD) simulations.
- 6) LCA is a method for evaluating the potential environmental impacts of the entire life cycle of a product. However, the environmental life cycle impacts of hydrous ethanol addition (or hydrous ethanol alone) on ICE-powered vehicles have not been evaluated. The life cycle approach is needed to assess the environmental impacts of hydrous ethanol from various raw materials. Moreover, comparative studies should be conducted on the environmental impacts of anhydrous ethanol or even fossil fuels. In addition to LCA, technoeconomic assessment (TEA) is a foundational tool in understanding cost benchmarks for the feasibility of hydrous ethanol in ICEs. Therefore, the comparative TEA of hydrous ethanol with the wide range of water percentages and various engine configurations is required, which provides a reference of the appropriate choice of hydrous ethanol as a fuel in ICEs.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (52106191, 51866002, 52006014), the China Postdoctoral Science Foundation (2020M683396, 2021T140584), the Natural Science Basic Research Program of Shaanxi Province (2021JQ-273), the Innovation Capability Support Program of Shaanxi (2021TD-28), the Youth Innovation Team of Shaanxi Universities, and the Fundamental Research Funds for the Central Universities, CHD (300102222104, 300102222509).

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