C3-C4 Alcohols Blending Effect on Motor Gasoline Properties and Performance of Spark Ignition Engines: A review

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Abstract

Supplementing petroleum fuels with sustainable and renewable alternatives is a good option for increasing the sustainability of transportation fuels. Alcohols are particularly attractive blendstocks for spark ignition (SI) engines, mainly due to their desirable fuel properties such as high octane, good charge cooling and reduced sooting propensity. Although the use of SI engines is widespread around the world, predominately for light duty vehicles due to sustainability concerns such as air and CO_2 emissions, the consensus is that SI engines need to be more efficient and lower emitting, and the intelligent blending of C2-C4 alcohols into motor gasoline is a viable method for achieving that goal. There are a multitude of ways to produce renewable alcohols such as through fermentation from first-generation feedstocks (sugar and corn) and second-generation feedstocks (lignocellulosic biomass), or by gasification and mixed alcohol fuel synthesis routes from lignocellulosic biomass. Currently ethanol is extensively used in motor gasoline fuels worldwide and although many have proposed the use of C3 and C4 alcohols in motor gasoline as an improvement over ethanol, the higher cost of production and lack of clear definition as to their benefit over ethanol when blended into motor gasoline have led to slow acceptance into the market. In this review, special emphasis is placed on C3 and C4 alcohols blending effects on motor gasoline in terms of physicochemical properties, volatility behavior, and engine performance when compared to ethanol blends. Furthermore, the C3, C4 alcohol blending effect on emission (particulate matter, nitrogen oxides, carbon monoxide, hydrocarbons, and unregulated oxygenates) and combustion (volumetric efficiency, thermal efficiency, fuel consumption, and cold performance) characteristics is discussed. Although there are some disagreements in the literature over the effect of alcohols predominately around the type of SI engine, i.e., port fuel injected versus direct fuel injected and engine operating mode, generally it is stated that alcohols can potentially reduce soot, unburned hydrocarbons and CO emissions while increasing thermal efficiency. Thus, further research must be conducted to find the optimum combination of alcohol blends and engine configurations and this review will explore this concept in depth.

Keywords: *Alcohol, Higher alcohols, Gasoline, Blend, Combustion, Biofuel*.

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1. Introduction

Motor gasoline is defined as the final product that is delivered to the customer most commonly by the fuel pump at a fueling station. Motor gasoline is fully blended and contains all blendstocks, i.e., E10 the most common transportation fuel for (SI) engines [1] in the United States which is 10% ethanol and 90% Reformulated Blendstock for Oxygenate Blending (RBOB) or Conventional Blendstock for Oxygenate Blending (CBOB). RBOB and CBOB are the two base gasoline stocks produced by the petroleum refinery and most commonly transported by pipeline that get splash blended with ethanol at the fuel terminal to produce motor gasoline which gets delivered to the fuel stations for ultimate delivery to the customer. Desires for higher efficiency and lower emitting SI engine powered vehicles are driving interest for optimized motor gasoline formulations and the informed and rational blending of C3 and C4 alcohols into CBOB or RBOB is a potentially attractive approach towards achieving optimum fuel properties for motor gasoline [2–4]. This approach can reduce the fossil fuel consumption, improve the efficiency and reduce emissions of SI engines, and contribute to rural society economic wealth by creating new jobs in the agricultural sector [5].

Ethanol has been used as a blendstock in motor gasolines initially to replace MTBE as an oxygenate. Ethanol has many desirable fuel properties such as high Research Octane Number (RON) and good charge cooling properties, and since it is commercially produced in large quantities in many parts of the world, it has a relatively low cost of production [1]. However, ethanol has some issues when blended into motor gasoline including exhibition of azeotropic behavior [6,7], low energy density, high corrosivity [8], and poor stability in the gasoline when the fuel is in contact with water [9]. Given the dissimilarities between ethanol and gasoline, the use of ethanol in the fuel supply requires modifications in the handling, distribution, and storage infrastructure and depending on the volume percent of ethanol used in the fuel, i.e., E85, engine systems modifications may be required. An option for reducing the modifications required is to make biofuel blendstocks that are more infrastructure compatible [9,10]. Higher alcohols (alcohols with higher molecular weight than ethanol) are more compatible for existing fuel distribution infrastructures than ethanol [8]. In comparison to ethanol, higher alcohols offer higher energy density [11], lower water affinity, lower (or no) corrosivity, enhanced material compatibilities [11], better stability in the motor gasoline [12], and lower (or no) azeotropic behavior [7].

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The influences of C3, C4 alcohols on SI engine performance have been investigated by several groups, however, a comprehensive review of the effects of these alcohols on the physicochemical properties, emissions, combustion, and other aspects is not available in the literature. In this review, blends of C3, C4 alcohols to produce an optimized motor gasoline were scrutinized with ethanol provided as a benchmark. Methanol is excluded because it has low potential to produce a better motor gasoline than ethanol blends. Alcohols with five or more carbons (especially branched alcohols) are much less studied in the literature; thus, they are excluded as well. In this paper, the focus is on the effects of blending C3 and C4 alcohols in motor gasoline in terms of physicochemical properties, volatility behavior, and engine performance, benchmarked to ethanol blends. Furthermore, the C3, C4 alcohol blending effect on emissions (particulate matter, nitrogen oxides, carbon monoxide, hydrocarbons, and unregulated oxygenates) and combustion (volumetric efficiency, thermal efficiency, fuel consumption, and cold performance) characteristics is discussed.

2. An introduction to C2-C4 alcohols

Physiochemical properties of C2-C4 alcohols are provided in Table 1, 2-methyl-2-propanol (tert-butyl alcohol) is excluded because its melting point is too high (about 25 °C) which makes it unfit for fuel applications although it has been used as co-solvent in trace amounts to increase the water-tolerance of ethanol blends with motor gasoline. In this section, a brief introduction to these alcohols are provided.

Table 1 Physicochemical properties of alcohols [a, b]

Properties	Ethanol	1-propanol	2-propanol	1-butanol	2-butanol	Sec-butanol
Molecular weight (kg/kmol)	46.0684	60.10	60.10	74.12	74.12	74.12
C (%wt)	52.14	59.96	59.96	64.82	64.82	64.82
H (%wt)	13.13	13.42	13.42	13.60	13.60	13.60
O (%wt)	34.73	26.62	26.62	21.59	21.59	21.59
Boiling point (°C)	78.30	97.20	82.30	117.80	99.60	107.90
Water Solubility at 25 °C (Kg/L) [c]	1000	1000	1000	63	181	85
Research octane number (RON)	109.00	104.00	106.00	98.00	105.00	105.00
Motor octane number (MON)	90.00	89.00	99.00	85.00	93.00	90.00
Flash point (°C)	17.00	11.70	11.67 [f]	36.00	26 [f]	27.78 [f]
Reid vapor pressure (kPa)	16.00	6.20	12.40	2.20	5.30	3.30
Density at 20 °C (g/cm^3)	0.789	0.804	0.786	0.810	0.807	0.802
Viscosity at 20 ^{O}C (cSt)	1.5	2.7	3.1	3.6	3.7	8.3
Surface tension at 25 °C (dyne/cm) [f]	21.97	23.32	20.93	24.93	23.73	22.54
Heat of evaporation at 25 °C (kJ/kg)	919.6	792.1	756.6	707.9	671.1	686.4
Lower heating value (MJ/L)	21.4	24.7	24.1	26.9	26.7	26.6

[a] *All boiling points, Reid vapor pressures, and densities are from* [7]. [b] *All heat of vaporizations, lower heating values, research and motor octane numbers, and viscosities are from* [13]*, unless otherwise noted.* [c] *All water solubility values are from* [14]. [d] *Obtained from* [15]. [e] *All flash points are obtained from* [16]*, unless otherwise noted.* [f] *Predicted via Toxicity Estimation Software Tool (T.E.S.T)* [17].

2.1. Ethanol

Ethanol with molecular formula of C_2H_5OH has seen extensive use as a transportation worldwide. The world biofuel markets are dominated by ethanol (74% of global biofuel production) and its worldwide production has almost doubled from 2007 (13,123 million gallons) to 2016 (25,583 million gallons) [18].

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Brazil and United States are major producers of ethanol in the world and account for 58% and 27% of the overall production, respectively in 2016 [19]. Ethanol in Brazil is mainly produced from sugarcane while in the united states, ethanol is mainly generated from corn. Since the production of first-generation liquid biofuels where the feedstock comes from food crops (like corn ethanol in US and sugarcane ethanol in Brazil) this has raised some arguments such as food versus fuel issues. More recently a greater emphasis has been placed on second-generation biofuels produced from lignocellulosic feedstocks and although great progress has been achieved there are still some technical and economic obstacles towards wide scale commercialization[20]. Second-generation biofuel production is being deployed worldwide, for instance, in 2016, United States produced 38 million liters of second-generation ethanol while Brazil produced six million liters of cellulosic origin ethanol and EU produced approximately five million liters [21].

Ethanol obtained from fermentation was first offered as a potential fuel in 1930s but was rapidly overtaken by gasoline from petroleum that was perceived at that time as a superior fuel. It was reintroduced to the market in the 1970s mostly in response to the oil price and supply shocks of the 1970s [22]. Ethanol is predominately produced through three main pathways [23]: 1) Biological pathway: Fermentation of sugary, starchy, and lignocellulosic feedstocks; 2) Chemical pathway: Direct hydration of ethylene; 3) Thermochemical pathway: High temperature catalytic conversion of synthesis gas produced from lignocellulosic biomass to a mixture of alcohols via mixed alcohol synthesis.

Today, fermentation is the primary method for ethanol production which uses sucrose-containing biomass such as sugar cane, sugar beet, and sweet sorghum in addition to starchy biomass such as corn, milo, wheat, rice, potato, cassava, sweet potatoes, and barley. Ethanol from sugar and starch biomass is commonly referred to as first-generation ethanol [22,23,24] .

Furthermore, synthesis gas obtained from gasification can be converted catalytically to a mixture of alcohols continuing ethanol through a continuous flow process with relatively high yield. It has been considered an advantageous method in some parts of the world because synthesis gas can be obtained from a wide range of biomass and residues such as forest or agricultural surplus and household waste [23].

E10 is the predominant motor gasoline in use in the US, current estimates that almost 97% of motor gasoline used in the US is E10. In the United States, Environmental Protection Agency granted a waiver for low concentration blends of ethanol (up to 15% ethanol volume) for use as an automotive spark-ignition engine fuel and for up to 85 vol % for flexible-fuel engines [25]. Ethanol has some advantages over motor gasoline as an SI engine fuel. Ethanol has a better antiknock property compared to base gasoline which allows higher compression ratio engines to be used leading to higher thermal efficiencies [1,22,26]. In addition, this feature of ethanol can decrease costs of petroleum refineries because they are no longer obliged to produce high octane RBOBs and CBOBs. Additionally, the HoV of ethanol is much higher than motor gasoline, thus, more energy is required to vaporize the fuel which effectively cools the cylinder prior to the combustion and allows for higher compression ratios [22,27,28]. Furthermore, higher flame propagation speed of ethanol relative to base gasoline makes combustion occur faster [22]. Also, lower C/H atom ratio of ethanol can potentially cause a reduction in CO_2 emissions [27,29]. Neat ethanol has a higher flash point and lower vapor pressure compared to base gasoline which makes it safe for transportation and storage in the current systems [29].

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Ethanol also exhibits some disadvantages. Ethanol contains only two-thirds of motor gasoline's heating value which can result in increased volumetric fuel comsumption. Low vapor pressure of neat ethanol can cause cold start problems while high vapor pressure of ethanol-gasoline blends (low to medium blending ratios) increases evaporative emissions [27,30,31]. High HoV of ethanol may cause poor cold startability and increases intake valve deposits [28]. Polarity and hydrophilic nature of ethanol can cause corrosion on ferrous components such as fuel tank [32].

Given that large experience base with ethanol in motor gasoline, the use of ethanol has been extensively reviewed [22,33–36] and as such it is only included in this review as a benchmark.

2.2. Propanol isomers

Propanol (C_3H_7OH) is a 3-carbon alcohol with higher energy density than ethanol which makes it a potential alternative for blending with motor gasoline. Propanol has two isomers: n-propanol and isopropanol. 1-propanol (n-propanol) is a straight chain molecule that is currently used as a solvent in the paint and cosmetics industries [37] as well as a diluting agent to reduce viscosity of biodiesel [16]. Isopropanol is the simplest secondary alcohol. It is a colorless and flammable liquid with a strong odor [38]. It is a very valuable chemical with many industrial applications whose worldwide production exceeds 10^6 tons per year [39]. Isopropanol can be used as the catalyst instead of methanol in transesterification process for biodiesel production and it can also be dehydrated to yield propylene which is currently derived from petroleum for polypropylene production [40]. In the automotive fuel segment, propanol isomers have not seen widescale use predominantly because their large-scale production is more expensive than ethanol and their use is hard to justify. Thus, studies on these alcohol fuels are very limited compared to ethanol and butanol isomers.

Syngas obtained from gasification of biomass or municipal wastes can be converted to 1-propanol with certain species of *Clostridium* (*Clostridium ljungdahlii* and *Clostridium ragsdalei*) through threonine catabolism, but none of these pathways can yield more than 70 mg/L [37,41]. So far, no existing microorganism has been identified to produce 1-propanol naturally from glucose in substantial amount suitable for industrial scale production [16]. Hence, some researchers have proposed a switch to bio-synthetic pathways instead of using the pathways naturally evolved for alcohol production in microorganisms. They devised a systematic approach to synthesize higher alcohols (1-propanol and 1-butanol) with the use of native amino acid available in all organisms as alcohol production precursors aiming to minimize metabolic perturbation caused by toxic intermediates. In these studies, engineered *Escherichia coli* strain which is more easily can be manipulated compared to *Clostridium* species has been shown to be able to produce 1-propanol via 2-ketobutyrate with relatively high yield [37,42]. Furthermore, recently some metabolic engineering strategies have been exploited to improve the amount of 1-propanol production from the engineered *Escherichia coli* [43].

Several species of *Clostridium* including 52 strains of *Clostridium beijerinckii* and *Clostridium isopropylicum* have been evaluated for isopropanol production. However, these species produce isopropanol together with butanol and titers of isopropanol are very low; therefore, they have not been considered feasible pathways to produce substantial quantity of isopropanol [40,44]. Some studies produced isopropanol through a synthetic metabolic pathway by using engineered cyanobacteria (*Synechocystis elongates* PCC 7942) from cellular acetyl-CoA via a four step process and reported 26.5

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mg/L production of isopropanol after 9 days under the optimized conditions [40,45,46]. The highest level of isopropanol production was suggested by Inokuma et al. [40]. They improved isopropanol production by metabolically engineered *Escherichia coli* strain TA76, the optimization of fermentation conditions and isopropanol removal by gas stripping. They reported 143 g/L of isopropanol after 240 h with a yield of 67.4 mol %.

2.3. Butanol isomers

Butanol has the chemical formula of C_4H_9OH and occurs in four isomeric structures based on the location of the hydroxyl group. 1-Butanol or n-butanol ($CH_3CH_2CH_2CH_2OH$) has a straight-chain structure and hydroxyl group is located at the terminal carbon. 2-Butanol or sec-butanol (CH_3CH (OH) CH_2CH_3) also has a linear structure but the hydroxyl group is located at the internal carbon. However, iso-butanol ($(CH_3)_2CHCH_2OH$) and tert-butanol ($(CH_3)_3COH$) are branched with the hydroxyl group at the terminal carbon for iso-butanol and internal carbon for tert-butanol. The difference in the chemical structures result in different thermodynamic properties. Main applications of butanol isomers are [47]:

- n-butanol: solvents, plasticizers, chemical intermediate, cosmetics
- iso-butanol: solvents, paint additive, ink ingredient, industrial cleaners
- sec-butanol: solvents, chemical intermediate, industrial cleaners, Perfumes
- tert-butanol: solvents, denaturant for ethanol, industrial cleaners, chemical intermediate

Among the different isomers, sec-butanol, and tert-butanol are not qualified as fuels for SI engines because sec-butanol has a very low motor octane rating (32), and tert-butanol has a high melting point (about 25°C) [48]. However, n-butanol and iso-butanol (i-butanol) have been considered as potent pote3ntial blendstocks for SI fuels. Thus, from this point forward, we use the terminology that butanol isomers refer to n-butanol and i-butanol.

Typically, the lower heating value (LHV) of alcohols increases with increase in carbon atom number. Hence, the LHV of both n-butanol and i-butanol are greater than ethanol and closer to that of motor gasoline. In addition, due to the closer stoichiometric air-fuel ratio of butanol isomers to base gasoline, allow their introduction to the fuel system at higher blending ratios than ethanol without changes in the current vehicle systems [49]. In addition, the distribution of butanol isomers is much easier than ethanol because they have low tendency to separate from the motor gasoline if contaminated with water. High tolerance to water contamination makes the use of these fuels feasible in the existing distribution pipelines with no corrosivity to aluminum or polymer components in the fuel system and no need for transportation via rail, barge or truck which is the case for ethanol [50–52]. Lower HoV and autoignition temperature of butanol isomers relative to ethanol can improve the atomization and avoid cold start and ignition problems [49,51]. Lower polarity of butanol eliminates the problem of increased RVP specific for ethanol when blended with motor gasoline. This causes lower evaporative emissions during the fueling as well as lower tendency for cavitation and vapor lock [53]. Low volatility also makes them safer to use at high ambient temperatures especially by taking the high flash point into account [47].

The auto-ignition temperatures for i-butanol and n-butanol are 415 and 385 °C, respectively [54]. Studies on reaction pathways of iso-butanol and n-butanol also confirm that i-butanol is less reactive than n-butanol at low temperatures [55–57]. In these studies, it was shown that the combustion reaction of both

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isomers is initiated by H-atom abstraction. However, burning n-butanol generates mostly H radicals while i-butanol forms mostly methyl radicals which are less reactive than H radicals. Thus, n-butanol has a shorter ignition time compared to i-butanol. Furthermore, n-butanol has a faster flame propagation speed relative to i-butanol at all equivalence ratios and pressures [58]. Hence, it can be concluded that differences in emissions and performance of theses isomers have its roots mainly in the different flame propagation speeds and combustion characteristics.

Isomers of butanol can be produced from fossil fuel sources via various methods. However, to meet the goal of reducing greenhouse gas emissions, production of butanol through biological pathways is of interest. One of the major obstacles of bio-butanol introduction into market is the cost of production which is currently less competitive with gasoline and ethanol mainly due to the low efficiency of industrial fermentation. In addition, the biological pathway generates some by-products such as hydrogen, acetic, lactic and propionic acids, acetone, isopropanol, and ethanol which makes the purification even more costly [59,60]. Currently, many biotechnology companies around the world are working on solutions to increase the efficiency of ABE (acetone, butanol, and ethanol) fermentation to commercialize bio-butanol [47].

Bio-butanol is naturally produced from a number of clostridia via fermentation from feedstocks that are the same as other biofuels; i.e., sugar beets, wheat, corn, sugar cane, straw, sorghum, and cassava [61]. Microorganisms of the genus Clostridium are spore-forming anaerobes and the fermentation of these microorganisms consists of two phases: acidogenic phase and solventogenic. In acidogenic phase, pathways for acid formation are activated which results in products such as acetate, butyrate, hydrogen, and CO_2. In the next phase (solventogenic), acids are re-integrated and produce mainly butanol, ethanol and acetone and in some cases iso-propanol [47].

ABE fermentation of Clostridium currently suffers from some drawbacks. Clostridium are not able to metabolize more than 20 g/L of sugars which significantly limits the amount of carbon substrate in the fermentation and subsequently reduces the final productivity [62]. One of the major problems is product toxicity because Clostridium species produce butanol during the phase of sporification in which the functionality of these organisms becomes suspended temporarily as a result of butanol presence. This is because butanol damages the cell membrane initiating a rise in membrane fluidity [64]. Thus, in order to realize the idea of industrial production of butanol, series of studies have been conducted to improve major aspects of butanol production process including substrate cost, production yield, solvent toxicity, and downstream processing cost [47,65] . To meet these goals, several scientific efforts have focused on metabolic engineering of *Clostridium acetobutylicum* [66–69], improvements in fermentation and recovery process [70–73], finding economic and non-food biomass as a substrate for fermentation [74], and studying of *Escherichia coli* as an alternative host for bio-butanol synthesis [37,75,76].

3. Storability of ethanol and C3, C4 alcohol-gasoline blends

Ethanol is a strong solvent and is corrosive to some metallic and non-metallic parts of the engine. Ethanol can cause corrosion in three ways [9,77]:

- General corrosion (due to the ionic impurities such as chloride ions and acetic acid in low quality commercial oxygenates)

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- Dry corrosion (due to the relatively high polarity of ethanol)
- Wet corrosion (due to the ethanol absorption by the surrounding water)

To avoid general and dry corrosion, in locations where fuel supply chain is designed for motor gasoline, modifications in handling, distribution, storage, and engine systems are required. For example, in Brazil location of the most developed technology for alcohol-powered automobiles, regular gasoline engines and infrastructures have been redesigned to make alcohol engines more functional and economical. Some of these modifications are as follow [78]:

- The intake manifold was redesigned to provide more heat for evaporation due to the high HoV of ethanol.
- Fuel tanks were coated by pure tin.
- Cadmium brass was used for fuel lines instead of zinc steel alloy.
- Compression ratio (CR) of engines was increased to about 12:1.
- Palladium and rhodium were replaced by palladium and molybdenum in the catalytic converters.

One of the major concerns for the introduction of alcohol–gasoline blends to the existing system is achieving a stable homogeneous liquid fuel to avoid wet corrosion. Ethanol and propanol isomers are completely miscible in water, but miscibility decreases for larger alcohols [79]. Base gasoline and water are not soluble with each other; however, when an alcohol is blended into gasoline, some measurable water can also dissolve [13]. Based on ASTM D8418, water-tolerance is defined as the ability to absorb small quantities of water without creating a separate phase in the fuel. Water can enter the fuel system in a variety of ways. A fuel with sufficiently high water-tolerance can absorb the water to avoid formation of the secondary phase. A trace amount of water dissolved in the fuel has no notable effect on the engine components and only acts as an inert diluent in the combustion process [79].

However, water as a separate phase has serious issues. If lower alcohols with high affinity towards water are blended with gasoline, the separated water phase can subsequently absorb the alcohol and decrease the alcohol concentration in the fuel blend. Therefore, the antiknock property of the fuel blend deteriorates, and volatility is changed due to the reduced oxygen content. Furthermore, the separated alcohol-water phase is highly corrosive to the engine and fuel systems [80]. However, in case of higher alcohols, phase separation is less damaging because the separated phase mostly consists of water which sinks to the bottom of the fuel tank due to its higher density which at worst will stall the engine but not result in significant damage to the engine. Solubility of water in alcohol-gasoline blends depends on parameters such as alcohol concentration, temperature, humidity, fuel composition, and co-solvent [12]. For example, fuels containing high concentration of aromatics and olefins are more miscible in the water due to the Pi-bonding in their structures [80]. Water-tolerance of alcohol blends increases rapidly from ethanol to propanol, but 1-butanol and t-butanol provide almost the same water-tolerance as propanol [79,81]. However, i-butanol blends have lower water-tolerance compared to the corresponding ethanol blends (same alcohol concentration) [30,82].

4. C3, C4 alcohols blending effect on volatility

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Fuel volatility is one of the key fuel properties required for optimal SI engine operation and driveability and is usually characterized via vapor pressure and distillation curve. In this section, the effect of alcohol blending on these properties are reviewed.

In SI engines, the vapor pressure of a fuel accounts for the cold-start and warm-up driveability. A fuel with low vapor pressure may cause cold-start problems while a fuel with high vapor pressure increases the risk of evaporative emissions and vapor lock [83]. Reid vapor pressure (RVP) is the vapor pressure over the liquid level at a temperature of 100°F (37.8 °C) while the volume ratio of the vapor and liquid phase of the sample is 4:1 (ASTM D 323). RVP is usually used to address fuel-related issues because it is not temperature dependent. RVPs of C3,C4 alcohols are far less than motor gasoline, but when ethanol, and propanol isomers are blended with motor gasoline, RVP values are greater than the base motor gasoline up to a certain concentration due to the azeotropic behavior [7]. In general, non-polar hydrocarbons and polar compounds with similar volatility can form positive azeotropes. For example, ethanol can form azeotropes with C5-C8 hydrocarbons (alkanes, olefins, aromatics) with boiling points in the range from 30 °C to 120 °C [80]. The highest RVPs are observed with relatively low concentrations of ethanol (5-10 vol %) [7,82].

However, all C4 alcohols except tert-butanol led to RVPs less than the base gasoline, regardless of alcohol concentration because the effect of hydroxyl group is dissipated due to the relatively long hydrocarbon chain [13]. Figure 1 shows the RVPs of the C2-C4 alcohols blends with gasoline. It is worth noting that the RVP of blends is also a function of motor gasoline composition. For example, in case of a heavy hydrocarbon with high boiling point, more ethanol is required to form an azeotrope and the resultant azeotrope would exhibit a higher boiling point compared to azeotropes derived from ethanol and lighter hydrocarbons. This explains why alkanes can lower the azeotrope boiling point more than aromatics of similar volatility while saturated cyclic hydrocarbons lie between the alkanic and aromatic azeotropes [80]. Formation of azeotropes is also a function of pressure such that higher pressures result in more azeotrope production and vice versa [80].

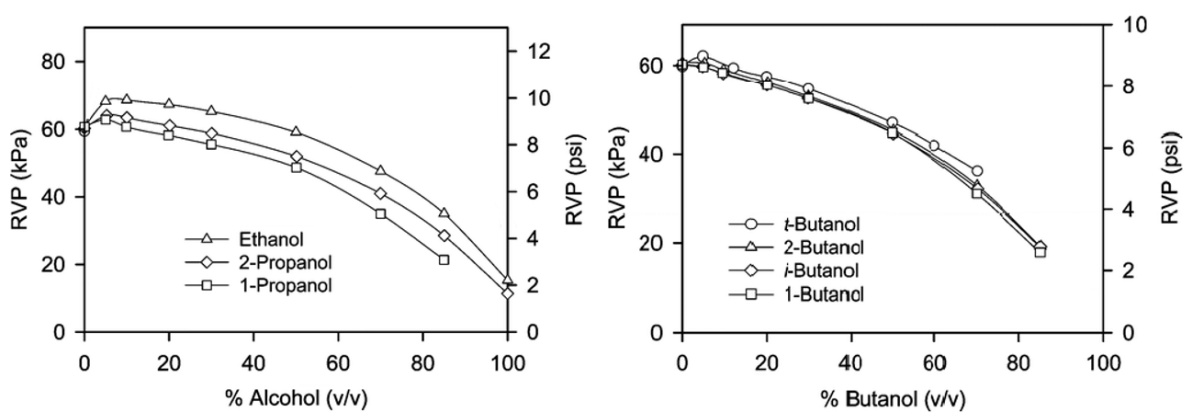

Fig. 1. RVPs of the C2-C4 alcohols blends with motor gasoline [7].

The distillation curve is a plot of the boiling temperature of a fluid mixture versus the volume fraction distilled. Front-end volatility (T_0 to T_{20}) gives information about the cold start, engine warm-up, evaporative emissions, and vapor lock. Midrange volatility (T_{20} to T_{90}) can be used to interpret warm up,

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acceleration, and cold weather performance ability of a fuel. Information regarding tail-end volatility (T90 to end-point) is used to estimate propensity for deposits formation and oil dilution [84–86]. The distillation curve of a typical motor gasoline has a smooth and steadily increasing fashion in the range of 20 to 225 °C. However, addition of ethanol causes a significant reduction in boiling temperatures at early stages of distillation due to the formation of positive azeotropes [87]. In the United States, refiners vary butane concentrations in ethanol blends to meet summer and winter front-end distillation specifications. In contrast, C3 and C4 alcohols exert smaller changes to the distillation characteristics due to the lower polarity, higher boiling point, and lower RVP of these alcohols compared to the ethanol [82,87]. For illustration, Figure 2 shows a comparison between the distillation curves of ethanol blends and n-butanol blends. To sum up, the effect of C2-C4 alcohols on T_{10} is minor for low to medium blending ratios; however, changes in T_{10} become considerable when high concentrations of alcohols are used. The impact on T_{50} is also considerable, but changes in T_{90} are negligible [23,87,88].

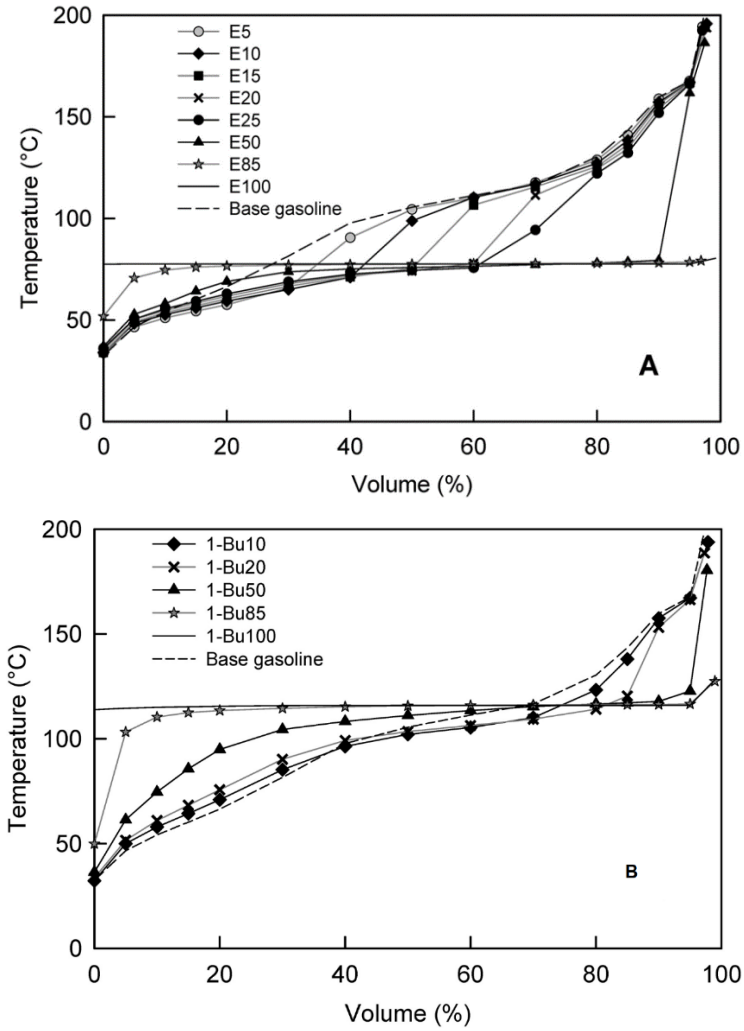

Fig. 2. Distillation curves for blends of ethanol (A) and n-butanol (B) [87].

5. C3, C4 alcohols blending effect on knock performance

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Knock is a sharp rise in pressure that is not synchronized with the combustion event and can result in severe damages to the engine. Knock performance can be studied from a combustion chemistry point of view. Combustion is a complex process in which fuel molecules produce intermediates which are subsequently transformed to stable products. The combustion process develops according to a radical chain mechanism. The evolution of combustion process and operating kinetic mechanism depend highly on temperature. In a combustion process, an end-gas undergoes a two-stage ignition process where a cool flame proceeds to hot ignition. Cool flames appear in a temperature range that transition from low temperature to high temperature mechanism occurs [89]. Mechanisms at low and high temperatures should be studied distinctly because different branching agents are effective at each condition. High temperature chemistry accounts for combustion efficiency and pollutant emissions [1] while low temperature chemistry accounts mainly for ignition quality of a fuel. If an air-fuel mixture undergoes a transition to high temperature chemistry prior to consumption by the propagating turbulent flame, knocking would occur. Hence, differences in reactivity arise from differences in low-temperature combustion chemistry of fuels; i.e., fuel knock performance is directly related to the fuel's ability to undergo cool flame reactions to allow autoignition at lower temperatures [1]. Therefore, fuels with higher reactivity have more propensity to undergo an ignition process at low-temperature conditions.

At low temperature, there is a convoluted competition between multiple chemical reactions [90]. Westbrook et al. [90] developed a detailed chemical kinetic reaction mechanism including both high and low temperature reaction pathways to describe oxidation of n-alkanes larger than n-heptane. In this study, it was shown that at temperatures below 1200 K, for all hydrocarbons the reaction is initiated by H-abstraction from the alkane by oxygen molecules to generate alkyl (•R) and hydroperoxy (•OOH) radicals. At a temperature range between 500 to 600 K, alkyl radicals react quickly with oxygen molecules to produce peroxyalkyl radicals (ROO•) which can isomerize to form peroxide species . Peroxides play an important role because they have an O-OH bond which can be severed to form OH radicals. Subsequently, these radicals attack alkane molecules to generate additional alkyl radicals which can undergo the similar pathways. The increase in the number of active radicals causes an exponential acceleration of reaction rates to a certain temperature at which point peroxyalkyl radical (ROO•) formation is no longer favored and alkenes are formed which led to overall reaction rate reduction. Once temperatures reach this critical point in which alkene formation is favored, the system temperature remains relatively constant until sufficient quantities of hydrogen peroxide (H_2O_2) are formed to trigger the high temperature radical chain branching ignition. This behavior is responsible for the negative-temperature coefficient (NTC) which describes the temperature region where ignition delay time increases as temperature increases; i.e., the fuel is less reactive in this region [91]. It typically occurs in a temperature range from 500 to 850 K [92].

In contrast to alkanes, neat ethanol shows no significant H- abstraction below 725 K; thus, the presence of ethanol reduces alkylperoxy and hydro-peroxy-alkyl reactions (cool-flame reactions) such that the rapid auto-ignition of CH_3CHO will occur at temperatures above conditions often experienced in the end-gas. Furthermore, ethanol when present as a blend component along with hydrocarbons such as paraffins that are known to exhibit low temperature chemistry can also inhibit low temperatures ignition. For instance, oxidation of the mixture of ethanol and n-heptane (ethanol 85 vol%+ n-heptane 15 vol%) at 628 K and 12.5 atm begins with oxidation of the paraffins to produce HO_2 radicals that subsequently react with ethanol to form C_2H_5O radicals. These radicals rapidly react with O_2 to form acetaldehyde while

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regenerating HO2. The HO2 stimulates a near-straight chain HO2 induction cycle (the two latter reactions) to produce CH3CHO and H2O2 as intermediate products. However, low temperature reactions of CH3CHO are not significant channels of carbon flux; instead, low temperature reactivity is imparted by slower radical propagation and branching reactions associated with n-heptane which serves to slow the rate of radical pool growth[93]. It shows that blends of ethanol with hydrocarbons exhibit no global low temperature reactivity. Therefore, it can be stated that ethanol provides a sink of reactive species (OH radicals) that disturb the chain branching of the hydrocarbon fuels at low temperature conditions [1] and consequently decreases the reactivity of the blend compared to the base-gasoline.

Isomers of propanol and butanol also exhibit low reactivity at low temperatures. Pentanol is the lowest molecular weight alcohol that exhibits measurable reactivity at low temperatures because the inhibiting effect of hydroxyl group is decreased due to the longer hydrocarbon chain, which can participate in the ROO low temperature chemical pathways described earlier [13,23]. However, similar to behaviors seen in iso-parrafins, the highly branched higher alcohols, such as 3-methyl-1-butanol, 3-methyl-3-pentanol and 2-methyl-1-butanol, exhibit less low temperature reactivity than their straight chain counterparts due to their inability to rapidly undergo the isomerization reactions needed to form peroxide species [10,82,94,95]. The fuel's high temperature chemistry is important in flame propagation and is more important to SI combustion efficiency and emissions than its low temperature reactivity. In contrast to low temperatures, alcohols have higher reactivity than their corresponding hydrocarbon at high temperatures [96] resulting in a higher turbulent premixed flame speed [55]. It is shown that high temperature reactivity of all linear normal alcohols longer than methanol (ethanol to n-octanol) is similar [97].

An appropriate fuel for SI engines must be resistant to autoignition to avoid knock. The index usually used for ignition quality of a fuel for SI engines is referred to as octane rating. Research octane number (RON) is used to simulate city driving speed with frequent acceleration while motor octane number (MON) tends to simulate highway driving at higher engine speeds [9]. Generally, octane number increases when a fuel contains molecules with methyl branching, double bonds, aromatic rings [10], and oxygen content [98] which impact low temperature combustion pathways described earlier. The major attraction of alcohols is the notable anti-knock performance. Ethanol and propanol isomers have higher octane numbers than regular gasolines while octane number of butanol isomers is very close to that of conventional gasoline [13,98]. The octane ratings of larger linear alcohols are lower than that of gasoline. Therefore, blending of these alcohols (i.e., straight chained < C5 or larger iso-alcohols) with gasoline can decrease the risk of knock in SI engines [23]. In some cases, the blending effect is synergistic, meaning that the octane number of the blend is greater than what obtained by linear interpolation from the pure constituents [99]. However, in other studies an antagonistic blending effect was observed [100]. These differences have their roots in ethanol concentration and composition of motor gasoline. Some measurements have shown a non-linear dependence of RON on the ethanol content because Cooperative Fuel Research (CFR) engines are sensitive to the charge cooling [99–101]. Motor gasoline composition is also important. For instance, antagonism of ethanol and aromatics (such as toluene) can act against synergism of ethanol and paraffins with respect to the octane number [100]. Figure 3 illustrates this opposite behavior.

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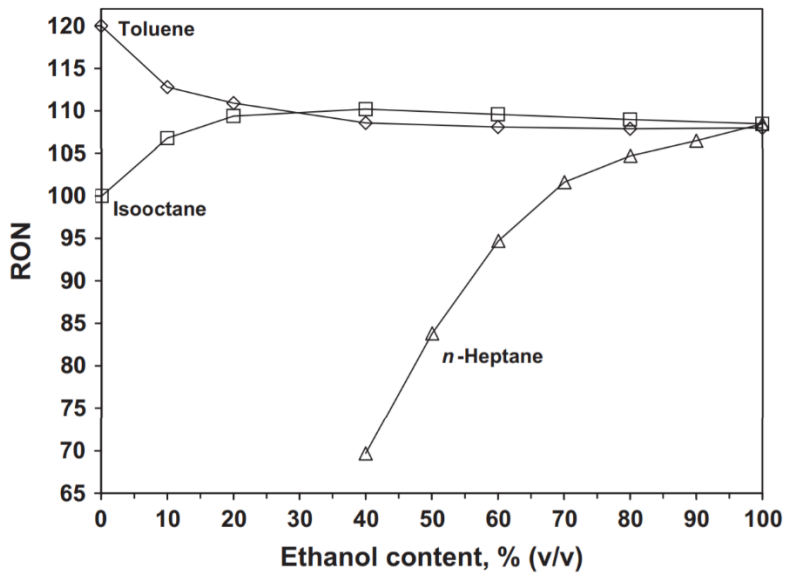

Fig. 3. RONs for blends of ethanol-isooctane, ethanol-n-heptane and ethanol-toluene (volume basis) [102] .

Anti-knock properties and high HoV of alcohol blends allow using higher compression ratios and advanced spark timings relative to motor gasoline which may improve the brake thermal efficiency and power-output despite the lower energy density of alcohol blends [88,98,103–105]. For example, in [106] an effort was done to identify the knock limited compression ratio for ethanol blends (E10, E50, and E85) in a single-cylinder engine operated at wide open throttle (WOT). Knock did not occur for blends with high ethanol content (E50 and E85) at any operating condition, but motor gasoline and E10 became knock-limited at high CRs requiring retarded spark timings to avoid knock which decreased the indicated mean effective pressure. Therefore, at substantially similar engine conditions, using blends with higher ethanol content results in a higher engine efficiency and power-output. In another study [65], an experiment was conducted in a single-cylinder SI engine fueled with a n-butanol–gasoline blend (35 vol %) and gasoline under WOT condition. Ignition timing corresponding to the maximum brake torque (MBT) were obtained for both fuels. It was observed that advanced ignition timing is possible without knocking for B35 due to the higher-octane number. Advanced MBT ignition timing causes the combustion to occur closer to the top dead center (TDC) which increases the power output and thermal efficiency. They also reported that advanced ignition timing resulted in a superior torque, fuel consumption, and hydrocarbon/CO emissions while deteriorated NO_x emissions.

6. C3, C4 alcohols blending effect on emissions

6.1. Particulate matter

Particulate matter (PM) from *combustion* refers to solid particles in the exhaust stream. Particles smaller than 10 microns can easily penetrate deep into lungs and cause serious health issues. PM emissions can vary significantly with engine configurations. Fuel direct injection (DI) (Figure 4) is a critical enabling technology for these performance improvements, in which fuel is injected directly into the cylinder rather than at the intake valve (as in older port fuel injection technology engines). DI causes an effective

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increase in fuel knock resistance because of evaporative cooling of the fuel-air charge, enabling higher compression ratios and improving efficiency by reducing pumping work and heat transfer [110,111]. However, the use of DI raises the potential for the fuel spray to impinge on the piston or cylinder wall during cold start or high load conditions, leading to pool fires or regions of locally poor fuel-air mixing and an increase in particulate matter (PM) emissions over earlier port fuel injection engines [112–118]. PM, or colloquially "soot," is the aerosolized agglomeration of carbon, typically polyaromatic hydrocarbons, derived from incomplete combustion or pyrolysis and has been linked to human health and life expectancy concerns [119], as well as climate-warming [117,120–123]. The United States Environmental Protection Agency Tier 3 regulations require the reduction of light-duty vehicle PM emissions from nominally 10 mg/mi to 3 mg/mi, phased in between 2017 and 2021 [124], posing a potential challenge for DISI (Direct Injection Spark-ignition) engine technologies and highlighting a potential trade-off between achieving higher fuel efficiency and the health and climate effects of PM.

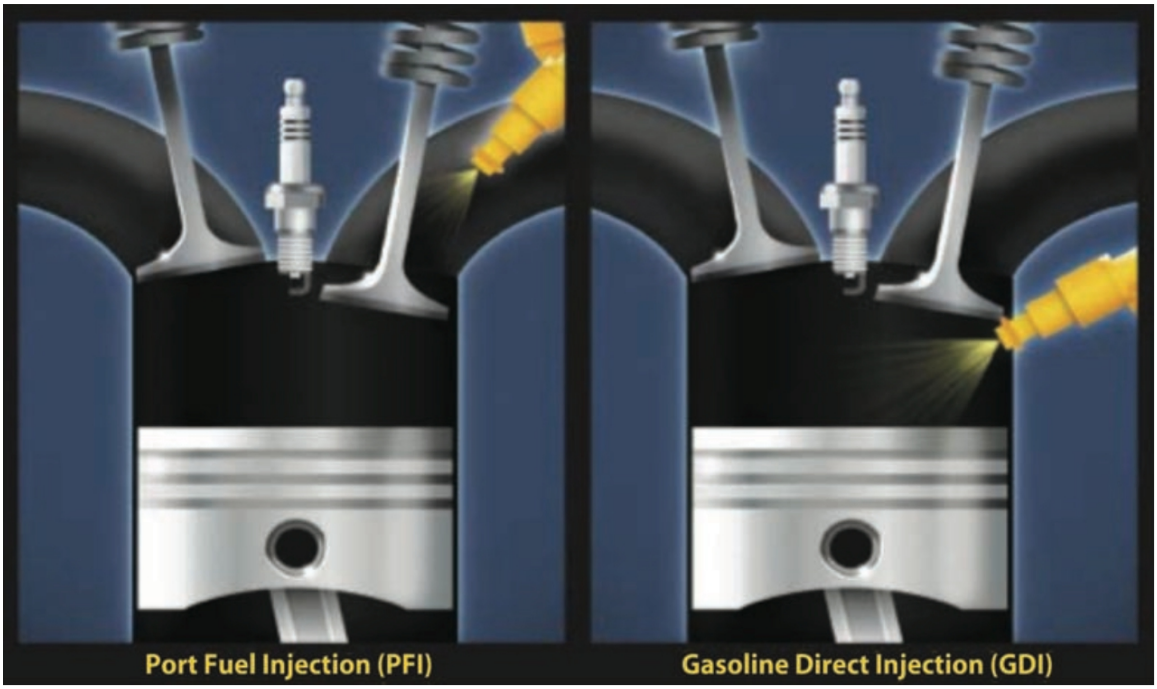

Fig.4. Fuel injection in PFI (left) and GDI (right).

In theory, the presence of oxygenated functional groups in fuels should reduce the possibility of soot formation in DISI engines, because oxygen atoms follow their respective carbon atoms down kinetic pathways towards oxidation and away from poly-aromatic soot precursor pools. Bergthorson et al. [1] in a review article of the combustion and emissions properties of advanced transportation biofuels summarized the work that has been done on alcohols (methanol, ethanol, butanol, n-pentanol, n-hexanol, and n-octanol) to state that in general these alcohols reduce PM emissions since the carbon–oxygen bonds in the alcohols reduce the number of carbon atoms that are active in the radical pool responsible for PM formation [125]. Highly synergistically with the Bergthorson work, Westbrook [126] describes a comprehensive overview of the combustion processes involved for lower molecular weight biofuels, primarily alcohols and their impact on soot reduction.

However, in practice the data that has been collected on this points to a more complex impact. Specifically, for DISI applications, there has been a number of studies that have tested oxygenated

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biofuels for sooting behavior [127,128], and both increases and decreases in PM formation have been observed. Engine operational strategies can greatly alter the rate of PM formation, often masking the effect of fuel composition on sooting tendency.

As perhaps the best studied example of fuel oxygenates, blending short-chain alcohols such as ethanol into a petroleum-derived gasoline blendstock has led to a reduction of PM emissions in many studies. For example, He et al. [129] compared emissions from ethanol (10 vol%, E10 and 20 vol%, E20) and butanol (12 vol%, B12) blends in neat gasoline in a DISI engine. They observed little change in PM emissions for E10 but measured reductions for B12 and E20, with B12 being the most significant with up to 50% reduction relative to neat gasoline. The authors proposed that this reduction is likely because of the dilution of high boiling olefins and aromatic hydrocarbons in the gasoline blendstock. Other work on alcohols (methanol, ethanol, butanol, n-pentanol, n-hexanol, and n-octanol) indicate that, in general, these alcohols reduce PM emissions (reviewed in Bergthorson et al. [1]), likely because carbon–oxygen bonds in the alcohols reduce the number of carbon atoms that are active in the radical pool responsible for PM formation [125] .

However, these oxygenates have also been shown to increase PM under some engine operating conditions, specifically from fuel impingement on the cylinder and piston walls. In a follow-on study, He et al. [130] varied start of injection (SOI) and observed increased PM for an E20 blend at conditions with liquid fuel impingement. When liquid fuel impinges on the piston, ethanol's high heat of vaporization slows the evaporation process and leads to a more heterogeneous fuel-air mixture near the piston or even pool fires during the combustion process, thus producing higher PM emissions. Butler and coworkers also observed PM to increase for ethanol blending in a study of vehicles equipped with PFI engines and speculated that the evaporative cooling effect was the cause [131]. He et al. also looked at the impact of engine loads on PM emissions and observed that higher engine loads resulted in higher PM emissions for all SOIs. They theorized that this may be caused by the long injection durations required for high loads that in turn leads to fuel impingement on the piston and/or cylinder walls leading to the negative impact of the high heat of vaporization of ethanol on PM emissions noted above. They went on to show that multiple injection cycles could correct this issue. A recent study by Ratcliff et. al. showed that PM emissions for ethanol gasoline blends in a single cylinder DISI engine depended on the relative amount of ethanol in the blend and the aromatic composition and molecular weight in the gasoline. The study showed that due to dilution, ethanol has a tendency to reduce PM emissions when gasoline with high volatility aromatic content is used, but due to slowed evaporation stemming from HoV effects, PM emissions would increase when ethanol was blended with a gasoline with heavy aromatic fractions [132].

A number of studies have been conducted looking at the impacts of ethanol on PM emissions in real world drive tests. Interestingly, the limited data indicate that ethanol may be more effective in reducing PM in DI engines than in PFI ones. For PFI engines, Butler et al [131] tested 15 high sales cars and light trucks from the 2008 model year over a representative fuel matrix. In 10 of the vehicles tested, higher PM emissions were observed for the ethanol blends. The remaining 5 of the 15 test vehicles showed little or no sensitivity of PM emissions to ethanol, providing further indication of the interaction between fuel properties and engine design. For DI engines, several studies showed a reduction in PM emissions resulting from the use of ethanol blends. Maricq et al. [117] investigated PM emissions in a light duty truck for ethanol blends up to E45 using the Federal Test Procedure (FTP) including cold start and reported little, if any change in PM below 20% ethanol but a significant reduction for E30 - E45. Similarly, Storey et al. [122] measured PM emissions for a mid-size 2.0L DISI equipped car during an FTP urban drive cycle at 30 MPH and 80 MPH using E10 and E20 and measured particle reductions

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relative to standard test gasoline. Their data showed that the ethanol blends reduced the PM mass and number concentration emissions for both transient and steady-state cycles.

The reduction in PM emissions is mainly attributed to three factors: 1- Oxygen content effect including a more compete combustion and reduced number of carbons in the radical pools responsible for soot formation [1,133]. 2- Dilution effect ; i.e., reduction in the concentration of key intermediate species known as soot precursors such as aromatics [134,135]. 3- Soot particles are oxidized faster in the presence of alcohols [133]**.** As an example, Figure 5 shows the reduction in the total nucleation mode and accumulation mode concentration of particles when ethanol and n-butanol are blended with gasoline at 10 and 20 vol% at different EGR rates.

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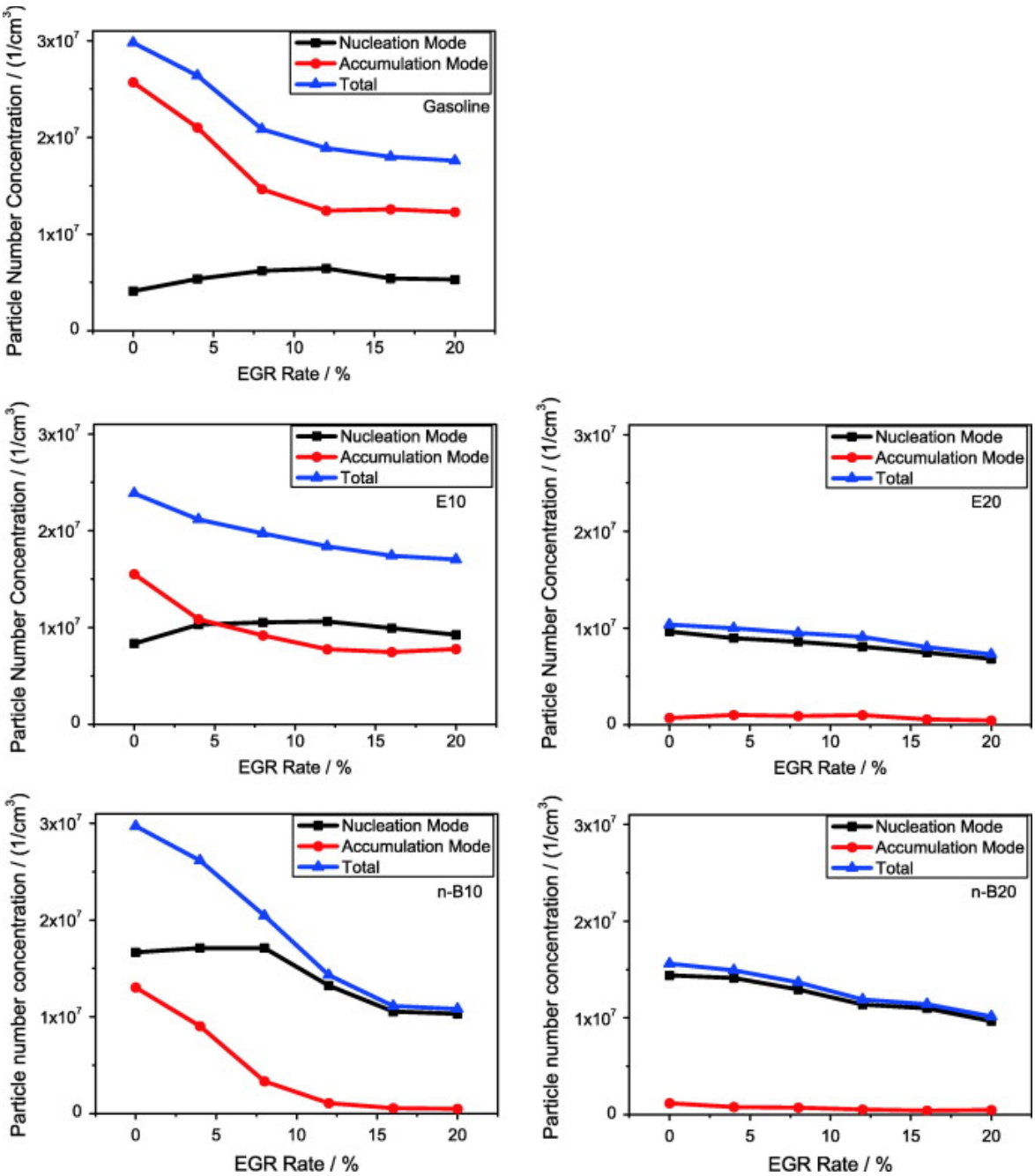

Fig. 5. Particle number concentration of gasoline vs. ethanol and n-butanol blends [136].

6.1.1. Fuel factors that will likely lead to soot formation

6.1.1.1. Effect of a fuel's chemical properties on soot formation

When burned, fuel molecules have different tendencies to form soot depending on their molecular structure. In this section, we review the main chemical mechanisms by which soot is formed, and how they are altered by differences in molecular structure.

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The formation of soot particles proceeds via many chemical reactions and physical processes spanning varying length and time scales. These processes can be generally divided into four major steps: (1) formation of polyaromatic hydrocarbons (PAHs), the precursors to soot formation, (2) nucleation of soot particles, (3) mass growth of particles, and (4) particle agglomeration [137–139]. The first step, formation of PAHs, is largely dependent on the chemical properties of the fuel. During combustion, the fuel is consumed by unimolecular or bimolecular reactions, and the resulting fragments can undergo subsequent reactions that lead to the formation of either the desired combustion products (CO_2 and H_2O) or undesired small aromatic hydrocarbon soot precursors. To quantitatively determine the contributions of competing pathways, detailed kinetic models of combustion must be combined with experimental data. Well-established kinetic models have been developed for various small hydrocarbon molecules, such as acetylene, methane and ethylene [140–144]. A detailed review by Richter and Howard outlines many of the possible pathways proposed for the formation of the first aromatic ring for varying classes of hydrocarbon fuel molecules [138].

However, the complete mechanism for formation of the first aromatic ring is not well-established for many classes of fuel molecules, including most oxygenates. Detailed analyses are lacking for the combustion and soot precursor formation pathways in oxygenates; and new kinetic studies can require the addition of thousands of possible reaction steps to the existing models [145,146]. However, some general trends related to soot formation mechanisms for specific functional groups have emerged from experimental measurements, discussed in more detail in section (bench-scale metrics) [147,148].
For simple n-alkane fuel molecules, increased aromatic hydrocarbon formation is generally observed with increasing carbon number. Small n-alkanes decompose to primarily ethylene and methyl radical, which are slow to react in addition reactions to form aromatics. In contrast, the combustion products of longer chain alkanes include a greater fraction of C_3H_x and C_4H_x species that undergo fast coupling and cyclization reactions to form benzene [140,148,149]. The reactivity of the double-bond groups in olefins can also lead to faster cyclization reactions [150]. Aromatic hydrocarbon fuel molecules can completely circumvent the cyclization steps needed to form aromatic soot precursors from aliphatic fuel molecules, and therefore tend to have high sooting tendencies. The ability of hydrocarbon decomposition products to form other resonance stabilized cyclic species besides benzene, such as cyclopentadienyl radical, which can go on to form naphthalene has also been cited as a mechanistic explanation for increased soot formation [138].

In the case of oxygenates, decomposition products often also include oxygen containing species that do not lead to soot (e.g., CH_2O, CO), and therefore oxygenates in general tend to have reduced sooting tendencies. However, the propensity of any specific oxygenate to form soot can be highly dependent on the specific functional groups present [147]. In the case of ethers and ketones, the oxygen atom interrupts the carbon chain resulting in small decomposition products that are less effective at forming benzene. In contrast, secondary alcohols can undergo four-center reactions, such as the elimination of H_2O from 2-butanol (Figure 6), which remove the oxygen atom and produce an olefin that can easily undergo cyclization reactions as described above [150]. Primary alcohols have sooting tendencies similar to alkanes, because fewer hydrogen atoms are available to form the four-membered ring transition state [126]. Propyl, butyl and pentyl esters can also show increased sooting compared to the analogous n-alkanes due to six-center reactions converting the carbon-chain on the ether side of the molecule into propene (Figure 6) [150].

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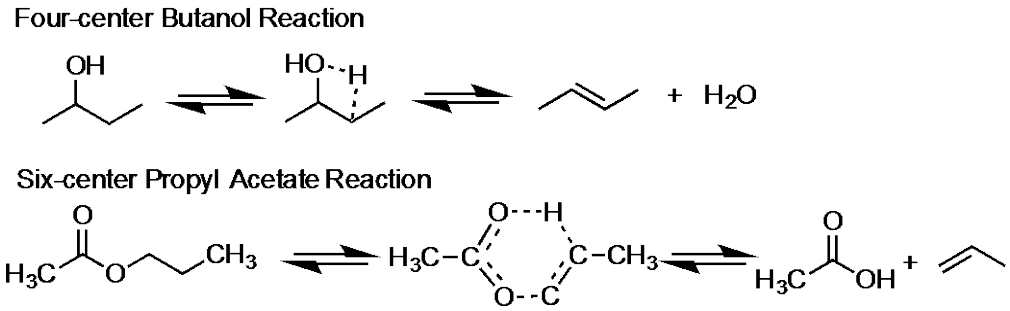

Fig. 6. Examples for four-center and six-center reactions of oxygenates to produce C_3+ olefins.

After the formation of primary sooting precursors, additional growth steps are required to convert the aromatic hydrocarbons to larger (>3 ring) polyaromatic hydrocarbons. The H-abstraction, acetylene addition (HACA) mechanism (Figure 7) proposed by Frenklach is commonly accepted as the major pathway for aromatic hydrocarbon ring growth [138–141,151]. In this mechanism, the repetitive two-step reaction sequence involves formation of a radical via abstraction of a H atom followed by the addition of acetylene to the aromatic radical formed. If the concentrations of aromatics are sufficiently high, polyaromatic hydrocarbon growth can also occur through ring-ring condensation reactions (Figure 7) [143,152]. At sufficiently high temperatures, PAHs can decompose through the reverse reactions along many of these formation pathways. Oxidation reactions of aromatics and aliphatic precursors are important to determining the net rate of formation of PAHs, as these reactions compete with aromatic formation and growth reactions. The main oxidation reactants are OH·, O· and O_2, the relative importance of which changes as the combustion reaction proceeds [138]. Frenklach suggested that, in particular, the oxidation of C_2H_3 is a key branching point in the removal of PAH precursors prior to aromatic formation [151]. How these various growth and oxidation steps are impacted by fuel chemistry, specifically by oxygen in the fuel, remains an open question.

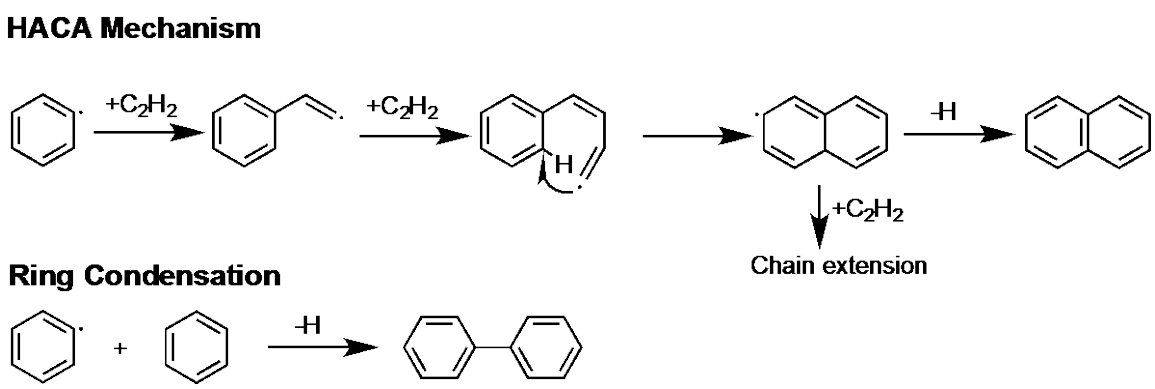

Fig. 7. Reaction pathways for ring growth in PAH formation.

A final step in the formation of PM emissions is the conversion of gas phase PAHs to solid particles, and is one of the least understood aspects of soot formation [138,142]. Fine particles are often defined as growth above a specific mass (i.e., 2000 amu or particle diameter of 1.5 nm). Further growth of soot particles competes with their decomposition via gas-particle surface reactions analogous to those involved in gas phase PAH growth (e.g., HACA, oxidation). Larger particles are formed with a concomitant decrease in particle numbers through sticking collisions between particles during particle coagulation. In the particle coalescence regime spherical particles collide and coalesce completely to form new spherical particles. Eventually, these particles begin to agglomerate into chain-like fractal aggregates. The

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molecular structure of the fuel effects the concentration of various gas species that can react with the particles. Outside of this effect the particle coagulation processes would be impacted by the physical properties of the fuel but most likely not by the chemical properties of the fuel.

6.1.1.2. Effect of a fuel's physical properties on soot formation

Combustion in DISI engines is heterogeneous process in which the physical behavior of the fuel spray has a significant effect on sooting tendency by inhibiting fuel-air mixing. The fuel spray is a transient two-phase turbulent flow exhibiting complex effects as the fuel evaporates [153,154]. Increased soot formation is typically caused by spray impingement on the piston top, cylinder wall, or other surfaces; by increased fuel droplet size; or by slowing of evaporation. Fuel impingement is a major contributor to soot formation in DISI engines leading to fuel rich regions near surfaces or pool fires [112,129,130,155]. Since oxygenates can differ substantially from their hydrocarbon counterparts with the same carbon number in properties relevant to these mechanisms, blending with oxygenated fuels has the potential to vastly change a fuel's combustion behavior.

Spray penetration depends on how rapidly the spray breaks up into individual droplets, which is a function of turbulence energy and shearing forces between fuel and air. In fuels of higher density, fuel penetration length can be significantly longer, increasing the potential for surface impingement [156]. Hydrocarbon gasoline typically has a density of 700 to 750 kg/L (at 20°C), while many gasoline boiling range oxygenates exhibit densities over 800 kg/L or in some cases even 900 kg/L [157].

A fuel with higher viscosity will require a higher pressure to inject the same fuel mass through the fuel injector nozzle, or alternatively will require a longer time to inject the same volume of fuel. Under both scenarios spray penetration could increase. However, higher viscosity may also cause the spray angle to increase [158]. Spray angle is the angle of divergence of the spray from the nozzle. Wider spray angles have been shown to reduce particle emissions for early fuel injection timing (when the piston is just beginning to descend at the start of the intake stroke) by reducing impingement on the piston. However, for late fuel injection timing wide spray angle can cause increased wetting of cylinder, valve, and other surfaces. Hydrocarbon gasoline viscosity is on the order of 0.40 to 0.65 cSt (at 20°C) while viscosities for oxygenates can be considerably higher – as high as 8.3 cSt for isobutanol, for example.

Increases in gasoline viscosity of roughly 10 to 20 percent have been reported for 15 volume percent alcohol blends [13]. Surface tension can also be important in spray development. Increased surface tension, along with increased viscosity, causes resistance to fuel breakup into smaller droplets [158–160]. In the studies we reviewed surface tension effects were frequently confounded with viscosity effects. Gasoline surface tension has been reported to range from 22 to 26 nN/m in the studies cited above [158–160], with values for isooctane, o-xylene, ethanol, and n-butanol of 14.7, 29.6, 22.4, and 25.4 nN/m, respectively.

Volatility of the fuel components can have a significant impact on PM emissions, where low volatility can lead to increased soot production [161]. Mechanistically, vapor pressure plays a key role in the fuel injection process, and specifically in evaporation of the fuel spray. A component with low volatility will evaporate from the fuel spray considerably slower than more volatile components and will be more likely to stick to injector nozzles or metal surfaces within the combustion chamber – both areas that experience low air-to-fuel mixing and can lead to increased soot production. Leach et al. [162] suggested that low volatility

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compounds could hinder the breakup or evaporation of the fuel spray, again providing weak air-fuel mixing and leading to increase soot emissions. Both explanations result in increased soot due to poor air-fuel mixing: the former case places the blame of increased soot solely on the low-volatile components of the fuel, while the latter allows for all fuel molecules within the spray to contribute. In a recent study involving vehicle emissions with ethanol and butanol blended gasoline, Barrientos et al. [163] showed that the most volatile half of the fuels contributed <3% of the total PM, whereas the 5% of the fuel that made up the least volatile fraction resulted in 44% of the observed PM.

Additionally, under some conditions the fuel is injected into an in-cylinder environment where the air temperature is above the boiling point of the most volatile fuel components at the cylinder pressure (or pressure below the saturation pressure). For example, the normal boiling point of the common hydrocarbon gasoline component n-pentane is 36°C. This leads to what is known as flash boiling where the well-defined spray can disintegrate into a mist of fine droplets, enhancing fuel-air mixing [164,165]. This phenomenon can occur at idle, light-load, and part-load conditions. Zeng and coworkers [166] have described three regimes for multiple hole injectors based on the ratio of ambient (in-cylinder) pressure to saturation pressure, Pa/Ps. For Pa/Ps ≥1 flash boiling does not occur. For 1 > Pa/Ps > 0.3 is the transition flash boiling region where spray penetration and droplet mean diameter decrease and spray angle increases with decreasing Pa/Ps.

When Pa/Ps reaches 0.3 the spray plume collapses and shows a dramatic increase in spray penetration and decrease in spray angle with further decreasing of Pa/Ps – via a mechanism that does not appear to be well understood. The intentional use of flash boiling has been widely discussed as a strategy to increase rates of fuels air mixing, reduce spray penetration length, and reduce spray impingement on engine surfaces [167]. However, there do not appear to have been detailed studies of the effect of flash boiling or of spray collapse at Pa/Ps<0.3 on particle emissions. Heat of vaporization (HoV) appears to also play a role in the formation of soot, where fuels that have higher HoVs may not completely vaporize in the combustion chamber. Some cases in which fuel impingement occurs was previously covered in the section on soot formation in DISI engines. However, it has been put forth that the observed detrimental effects of excessive HoV may be due to using engines not designed for ethanol blends above 10% [163].

Fuel droplet size from the spray injector also can play a large role in the formation of soot [1,168,169] . Hayashi et al. [168] demonstrated that soot formation is directly impacted by the initial fuel droplet size in spray flames. They concluded that as droplet size increases, vaporization of the fuel droplet decreases, resulting in a shift in both the location and shape of the spray flame and an increase in the soot formation area. As noted above, increasing viscosity and surface tension can hinder spray breakup and droplet formation. For example, Bergthorson et al. [1] indicated that the use of pyrolysis liquids (which contain a significant quantity of oxygenated compounds) can lead to increased viscosity and/or surface tensions of the liquid droplet. These properties in turn can lead to poorer breakup of the droplet and increased soot formation.

While physical effects have been investigated regarding their impact on sooting tendency and several correlations are apparent, the exact mechanisms are poorly understood. Furthermore, only limited studies have examined real gasoline-oxygenate blend spray properties and how these might affect fuel-air mixing and particle formation. Ultimately, the general consensus in the literature is that properties such as heat of vaporization, vapor pressure, viscosity, and surface tension impact sooting largely through their influence on spray penetration, mean droplet size, and potentially flash boiling and related spray collapse. Oxygenates have, and can impart to their blends with hydrocarbon gasoline, substantially different values

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of these properties, an aspect of the fuel effect on particle formation that has not yet been adequately studied.

6.2. NO_x

Oxides of nitrogen produced during the combustion are NO, NO_2, and N_2O and referred to as NO_x. NO_x can cause acid rains and acidification of lakes and streams. Moreover, NO_x can react with volatile organic compounds and form ozone which is the major cause of urban smog [170]. NO is a major product of combustion and produced mainly by two mechanisms: Zel'dovich NO (thermal route) and Fenimore NO_x (prompt route). NO is the only nitrogen oxide formed through Zel'dovich route, but the Fenimore NO_x mechanism can produce NO, N_2O, and/or NO_2 [171]. The thermal mechanism consists of three reactions with atomic nitrogen formation acts as the rate-limiting step. Favorable conditions for Zel'dovich NO formation are slightly lean regimes and high peak flame temperatures (greater than 1800 K) [172,173]. In the Fenimore NO_x route, CH radicals are initiators and react with nitrogen molecules. Thus, hydrocarbons such as straight chain alkanes have more potential to produce NO_x through this mechanism. Fenimore mechanism is more complicated compared to the Zel'dovich and is not strictly limited to high temperature conditions. Favorable conditions for this mechanism are fuel rich regimes and low to medium temperatures [174]. Alcohols produce less NO_x in comparison to the corresponding alkanes under the same condition for two reasons: 1) Alcohols have lower energy densities and produce lower peak flame temperatures which decrease the NO_x emissions through the thermal mechanism [175] ; 2) The presence of hydroxyl group reduces the number of CH radicals for Fenimore NO_x route [125].

The effect of neat alcohol and alcohol-gasoline blends on NO_x emissions is complicated and many factors must be considered at the same time. Most of the studies reported that NO_x emissions are decreased with addition of alcohols [26,27,182–191,63,94,176–181]. In these studies, the reduction in NO_x emissions was mainly attributed to the high HoV and lower LHV of alcohols relative to gasoline which reduce the exhaust gas temperature in addition to the presence of OH group which reduces the number of CH radicals for NOx production through the prompt route. Figure 8 clearly shows the correlation between exhaust gas temperature and NO_x emissions for ethanol blends at different equivalence ratios in an electronic fuel injection 4-cylinder SI engine running at 3000 rpm and maximum brake torque ignition timing.

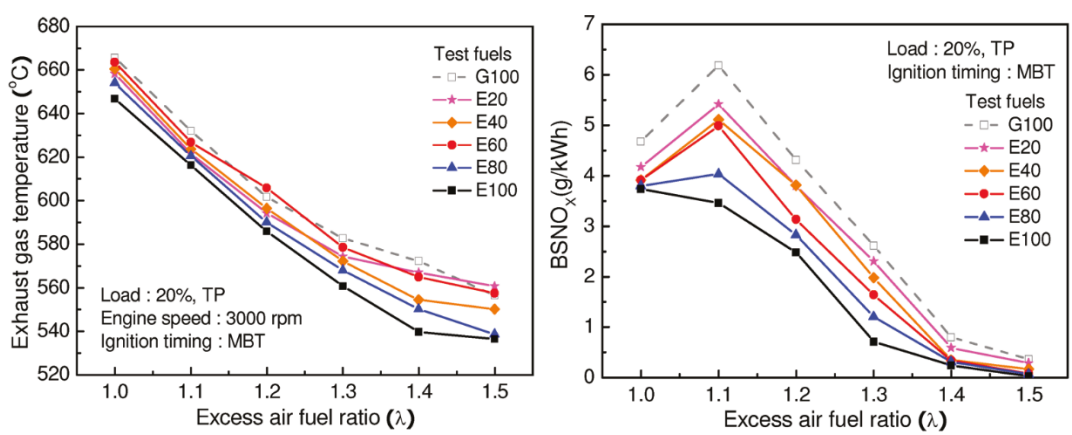

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Fig. 8. NO_x emissions of ethanol blends and the correlation between exhaust gas temperature and NO_x emissions for ethanol blends at different equivalence ratios [192].

In contrast, some researchers reported increased NO_x emissions [11,38,193–197] according to the following reasonings: 1) The high anti-knock effect of C3,C4 alcohols allows higher compression ratios to be used resulting in a higher end-gas temperature and pressure. The high temperature at the end of the compression stroke provides an appropriate condition for Zel'dovich NO formation. 2) Oxygen content of alcohols results in a more complete combustion and accordingly more heat is released. 3) More oxygen is available for NO_x production. 4) Faster flame propagation speed of C3, C4 alcohols results in a higher combustion temperature. 5) Leaning effect of C3, C4 alcohols accelerate the production of NO_x, especially when engine control unit is not able to confine lambda within an appropriate range due to the limitations dictated by the three-way catalytic converters. For example, Figure 9 shows that how iso-propanol blends produced higher NO_x emissions than unleaded gasoline at various engine speeds in a Multi-Point Fuel Injection (MPFI) SI engine at a load of 2.53 bar.

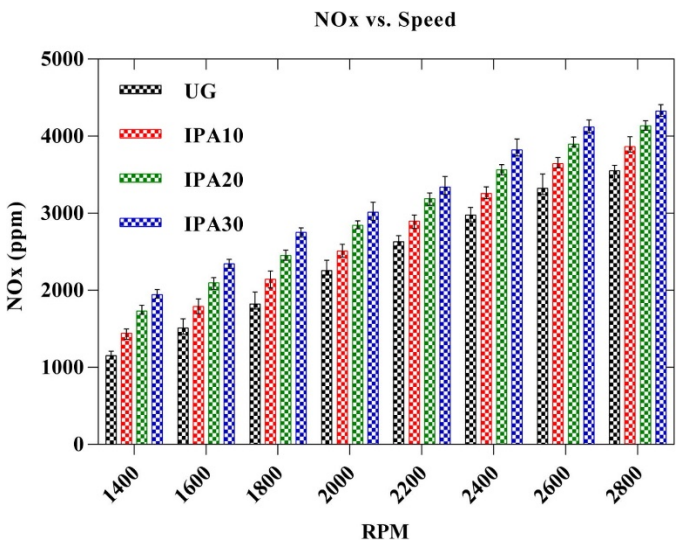

Fig. 9. NOx emissions of iso-propanol blends vs. gasoline [38].

Given the inconclusive results for NO_x emissions, it appears that the level of NO_x in the exhaust stream is a strong function of engine operating conditions. Engine speed, air-fuel ratio, spark timing, EGR rate, compression ratio, intake air temperature, and ambient temperature [25,186,205,192,198–204]. For example, Figure 10 shows variations in NO emissions at different engine speeds and loads for n-butanol blends. At high speeds, the engine thermal load is high and the effect of high HoV might be negligible [186]. In [192], the lean combustion (air-fuel equivalence ratio from 1 to 1.5) in a 4-cylinder SI engine fueled with ethanol-gasoline blends (0 to 100 vol %) was investigated. Results showed that although all ethanol blends produced lower NO_x compared to gasoline at each air-fuel equivalence ratio, the NO_x emissions were linearly decreased as air-fuel equivalence ratio increased. Spark timing is also important. Early spark timing increases the cylinder temperature and pressure substantially before top dead center and increases NO_x emissions [200,203]. In another study [202], it was shown that high HoV of ethanol combined with the temperature reduction effect of EGR lowered the temperature in the cylinder which

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favors NO_x reduction. The effects of cold-start and preheating inlet air have been also investigated on alcohol-gasoline blends [201,204]. Several studies investigated the effect of hydrogen addition on combustion and emissions performance of ethanol engines at different conditions because presence of hydrogen improves the fuel-air mixture homogeneity and shortens the combustion duration due to the widened flammability range and rapid flame speed [206–212]. Different hydrogen volume fractions were adopted in the intake in these studies. Although the overall effect of this strategy is positive on engine performance and emissions, in most of the studies, peak cylinder temperature was raised after the hydrogen enrichment and nitrogen oxides were slightly increased accordingly.

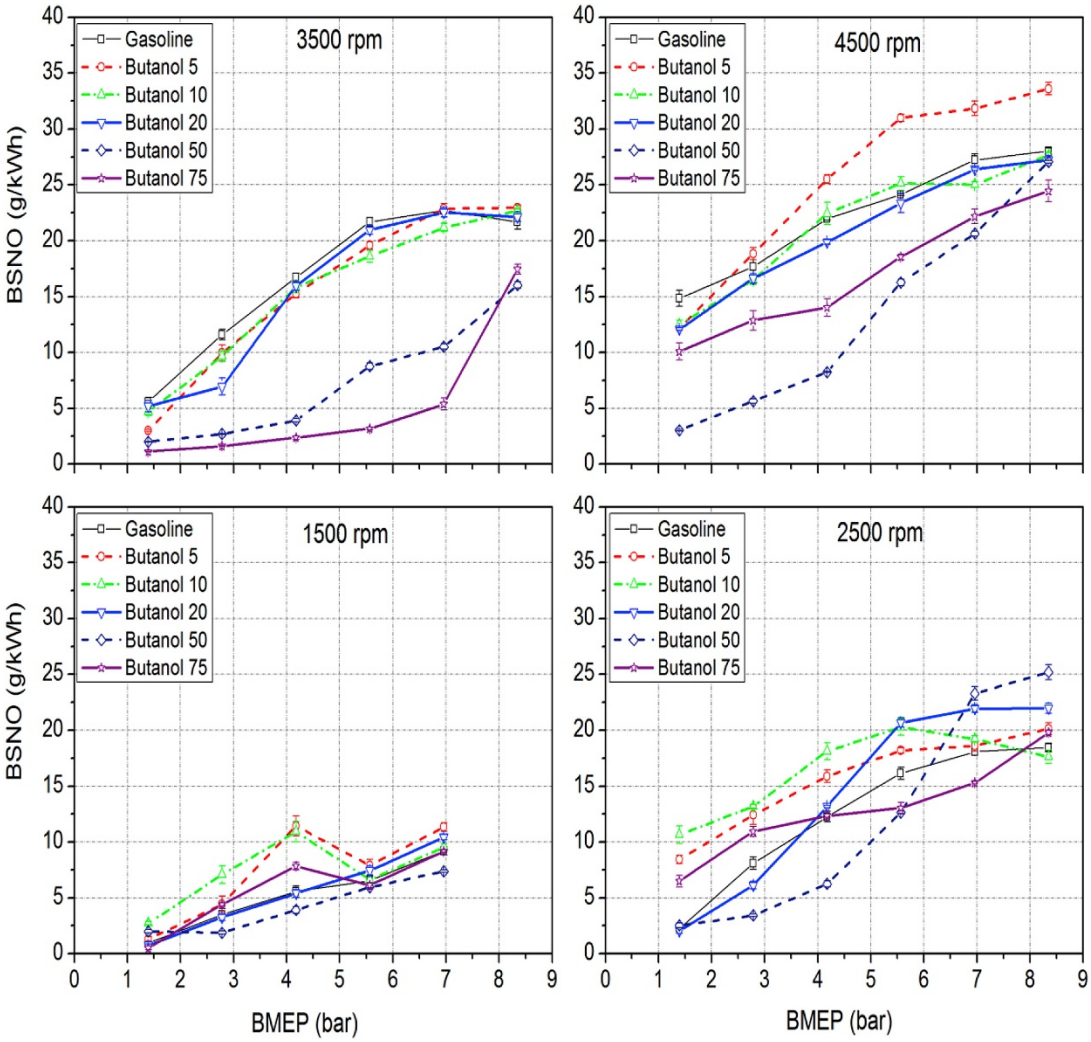

Fig. 10. Rapid increase in NO emissions with increasing load and rpm for gasoline and 1-butanol blends [190].

6.3. CO and hydrocarbons

CO emissions are controlled primarily by the air-fuel equivalence ratio. Unburned hydrocarbons (UHC) emissions are mainly caused by the unburned air-fuel mixture because of poor mixing and incomplete

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combustion. Since both CO and UHC emissions represent incomplete combustion and lost chemical energy, improving the combustion process can cause reduction in both [197].

Generally, observations suggest that the effect of blending alcohols with motor gasoline has a positive effect of on CO and UHC emissions [26,27,189,190,193–198,205,213,38,214–223,48,224–226,63,180,182,184–186] which is mainly explained by the following reasons: 1- Oxygen content increases the oxygen-to-fuel ratio and contributes to an easier oxidation of CO into CO_2 specially in the fuel-rich regions. 2- Lower stoichiometric air-fuel and C/H ratios of alcohols compared to motor gasoline reduce the demand for oxygen and avoid formation of fuel-rich zones. 3- Faster flame speed of C3,C4 alcohols relative to motor gasoline contributes to a more complete oxidation. 4- Dilution effect significantly reduces UHC emissions due to the reduced concentration of high boiling point compounds in the motor gasoline. 5- Blends containing low to medium level of ethanol have high vapor pressures due to the azeotropic effect. This contributes to the reduction of UHC emission specially during the open-loop cycle.

On the contrary, some studies reported negative or mixed results specially for UHC [54,177,179,191,203,217,224,227]. These studies stated that these results have their roots in the high HoV of alcohols such that cooling effect causes misfire or partial burn in the regions near the cylinder wall under certain conditions and increases UHC emissions. Furthermore, cooling effect coupled with heterogeneous effects of alcohols can increase UHC by decreasing the oxidation during the expansion and exhaust strokes. Low volatility also mentioned as an effective parameter for blends with high alcohol content and neat alcohols.

Although the overall positive effects of alcohols on CO and UHC emissions has been proved, design and operating factors such as air-fuel ratio, engine speed, ignition timing, and load can make significant differences. For example, effect of alcohols on CO and UHC emissions is more notable during the open-loop mode (fuel-rich regime) than closed-loop mode (stoichiometric ratio) [103,197]. CO and UHC also have functionality of engine speed such that sometimes at low engine speeds high HoV causes misfire and partial combustion [176]. Engine load is also an important factor because in some cases there is not enough time for alcohol blends and neat alcohols to evaporate completely when engine operates at high loads which can adversely impact the UHC and CO emissions [94,134]. CO and UHC emissions highly depend on air–fuel equivalence ratio. Generally, lean operation is desired to reduce UHC emissions, but at low speeds there is a risk of incomplete combustion [199]. Some studies tested alcohol blends at variable equivalence ratios [192,228,229]. For example, in [229], although n-butanol-gasoline blends (20, 40, 60 vol.%) produced lower CO compared to gasoline at stoichiometric condition, the results were opposite at lean regimes. The effect of spark timing has been also investigated [200,205,230]. In general, delayed ignition timing caused poorer combustion and higher UHC emissions given the high HoV of alcohols. Larsson et al. [231] have done a comprehensive research and collected data from different literature for CO and UHC emissions for DISI engines at various loads at 1500-2000 rpm for alcohol blends presented here in Figure 11.

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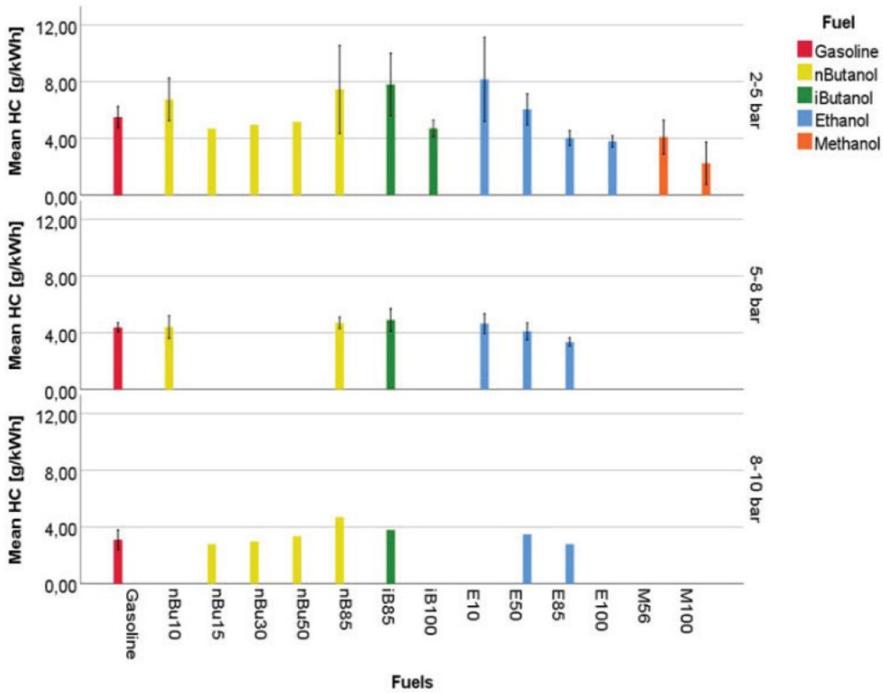
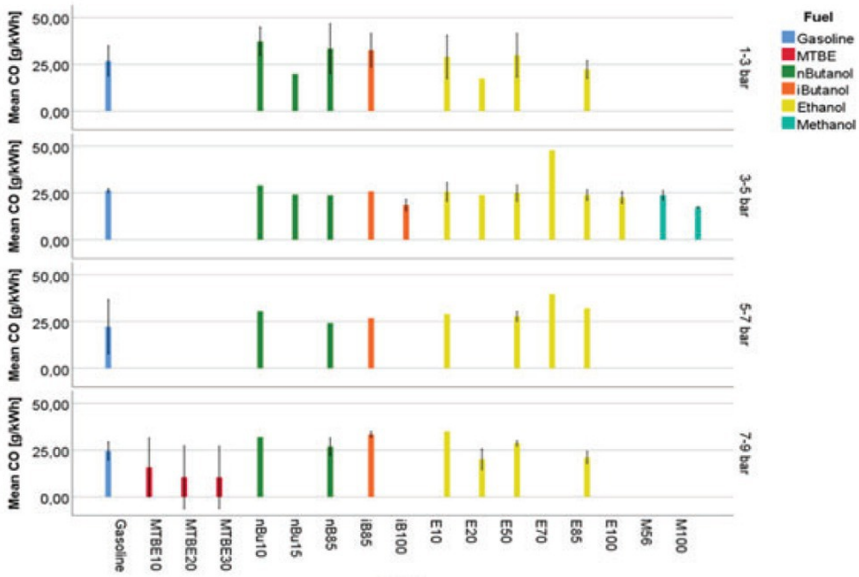


Fuel	n-Butanol			i-Butanol			Ethanol			Methanol		
BMEP [bar]	2-5	5-8	8-10	2-5	5-8	8-10	2-5	5-8	8-10	2-5	5-8	8-10
HC/vol%	0.01	0.005	0.025	-0.005	0.005	0.005	-0.03	-0.01	-0.005	-0.035	-	-
R^2	0.08	0.14	0.71	0.00	0.42	1	0.34	0.56	0.60	0.85	-	-



Fuel	MTBE	n-Butanol				i-Butanol				Ethanol				Methanol
BMEP [bar]	7-9	1-3	3-5	5-7	7-9	1-3	3-5	5-7	7-9	1-3	3-5	5-7	7-9	3-5
CO/vol%	-0.2 (-0.09)	0.04	-0.01	-0.06	-0.1	0.04	-0.06	-0.04	-0.01	-0.05	0	0.05	-0.05	-0.09
R^2	0.031 (0.59)	0.02	0.38	0.90	0.57	0.04	0.53	1	0.26	0.03	0.00	0.28	0.05	0.78

Fig. 11. CO and UHC emissions at 1500-2000 rpm at different loads for direct injection spark ignition engines [231].

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6.4. Unregulated emissions

Although oxygenates are not regulated emissions, potential increase in such emissions is an ongoing concern because oxygenates such as aldehydes and ketones are known as toxic air contaminants, mutagens, and carcinogens [232]. In general, use of alcohols in the motor gasoline changes the combustion pathway toward the production of oxygenates such as formaldehyde, acetaldehyde, and ketones [11,178,180,195,215,233–237] because generation of such carbonyls from alcohol oxidation is easier compared to motor gasoline [195,234]. This is because the formation and oxidation of carbonyls highly depends on the exhaust gas temperature and residence time and the oxidation of C3, C4 alcohols is initiated at higher temperatures than most of the hydrocarbons present in motor gasoline. However, it was also observed that these compounds are effectively oxidized by the three-way catalytic converters (TWC) and the pipe-out emissions are not sufficient to cause acute or chronic symptoms [178,180,215,234].

7. C3, C4 alcohols blending effect on combustion characteristics

Volumetric efficiency is often improved by blending C3, C4 alcohols with motor gasoline mainly because of higher stoichiometric air–fuel ratio of alcohol blends compared to motor gasoline. In addition, high HoV and heat capacity of alcohol blends provide a high charge cooling effect in the intake manifold (in PFI systems) which increases the density of the charge and consequently improves the volumetric efficiency [182,211,218,219,238]. Higher volumetric efficiency then leads to a higher output torque from the engine. However, a few cases reported negative impact of C4 alcohols on volumetric efficiency [54,205,223] possibly due to the lower HoV and stoichiometric air–fuel ratio of butanol isomers compared to ethanol.

Due to the high oxygen content of ethanol and C3,C4 alcohols, the energy per unit mass is lower than corresponding alkane and motor gasoline [79]. Blending ethanol and C3,C4 alcohols with motor gasoline often increases the brake specific fuel consumption (BSFC) due to the significant lower LHV combined with the higher stoichiometric air-fuel ratio of these alcohols compared to motor gasoline [94,176,243,182,192,214,220,239–242]. However, optimization of engine parameters specially compression ratio and MBT spark timing for alcohol blends usually have a positive effect on engine efficiency. Given a more complete combustion of alcohol blends coupled with their higher volumetric efficiency, laminar speeds, antiknock values, and HoVs, it is possible to obtain even lower BSFC with alcohol blends than motor gasoline depending on engine operating conditions [189,210,216,244].

Most of the studies on neat alcohol fuels and alcohol-gasoline blends have been reported that brake thermal efficiency (BTE) is increased with addition of ethanol and C3,C4 alcohols to gasoline [26,27,186,189,194,198,218,221,222,224,238,239,38,245,52,176,178,179,182,184,185]. Better BTE is explained by the following reasons: 1- Alcohols' oxygen content contributes to a more complete combustion. 2- Faster flame speed of C3,C4 alcohols causes the combustion to be completed earlier than base gasoline reducing heat losses to the cylinder walls and hence less work is required for compression. 3- High octane rating of alcohols allows engine to operate at higher CRs which releases more energy from the fuel. 4- Relative to base gasoline, higher HoV of alcohol absorbs more heat from the cylinder in the compression stroke decreasing required work for the compression. Few studies [63,241,242] reported neutral/deteriorating effect of alcohols on BTE mainly because sometimes high HoV of alcohols has

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negative impact on the combustion by inhibiting mixing of alcohols with air at low temperatures (e.g. low engine speeds). In addition, at high temperatures (e.g. high engine speeds), the role of HoV is relatively faint. It is worth noting that optimization of engine parameters for alcohols blends (e.g. advance MBT ignition timing and CR) in addition to exploiting strategies such as hydrogen addition [209–212] and EDI+ GPI [246,247] can significantly improve the BTE.

Although blending alcohols with motor gasoline decreases the fuel's heating value, it generally improves the brake power (indicated mean effective pressure and torque) [179,187,188,194,218,219,240,248–250] because: 1- Better anti-knock behavior of alcohol blends allows advancing ignition timing to gain the MBT. In addition, higher CRs can be used. 2- The combustion of alcohol blends is more complete than gasoline due to the oxygen content. 2- Higher volumetric efficiencies of alcohol blends lead to a higher output torque. 3- The combustion velocity of alcohol fuels is faster than gasoline. Moreover, optimizing engine operating factor such as air-fuel ratio, CR, and ignition timing can positively affect the engine power-output [192,200,228]. However, lower LHV of alcohol blends can be the dominant factor at some engine conditions and reduces the engine power [54,63,94,178,205,214,223,251].

Peak pressure and heat release of C2-C4 alcohol blends occur usually sooner and the magnitudes are higher than the neat-gasoline due to the faster flame propagation speed [38,52,196,224,241,252]. A few studies reported opposite results for magnitudes of peak pressure and heat release rate [205,253]. For example, sometimes the peak pressure and heat release rate are increased at low loads but decreased at high loads because at low loads, there is enough time for evaporation and the cylinder temperature is not significantly high; therefore, HoV is dominant. However, at high loads, since the cylinder temperature is high, and fuel can easily atomize and evaporate, flame propagation speed plays the leading role. Also, sometimes at low engine speeds the magnitude of peak pressure and heat release rate are lower for alcohols compared to motor gasoline because the high octane rating is dominant over higher laminar flame speed, but at high engine speeds, it is vice versa [182,216].

Figure 12 shows the variation of some of the combustion characteristics with engine speed for gasoline blends containing 20 vol% of linear C2-C4 alcohols. This is in consistency with the general trend of increase in brake thermal efficiency, power, peak pressure and brake specific fuel consumption by alcoholic gasoline blends.

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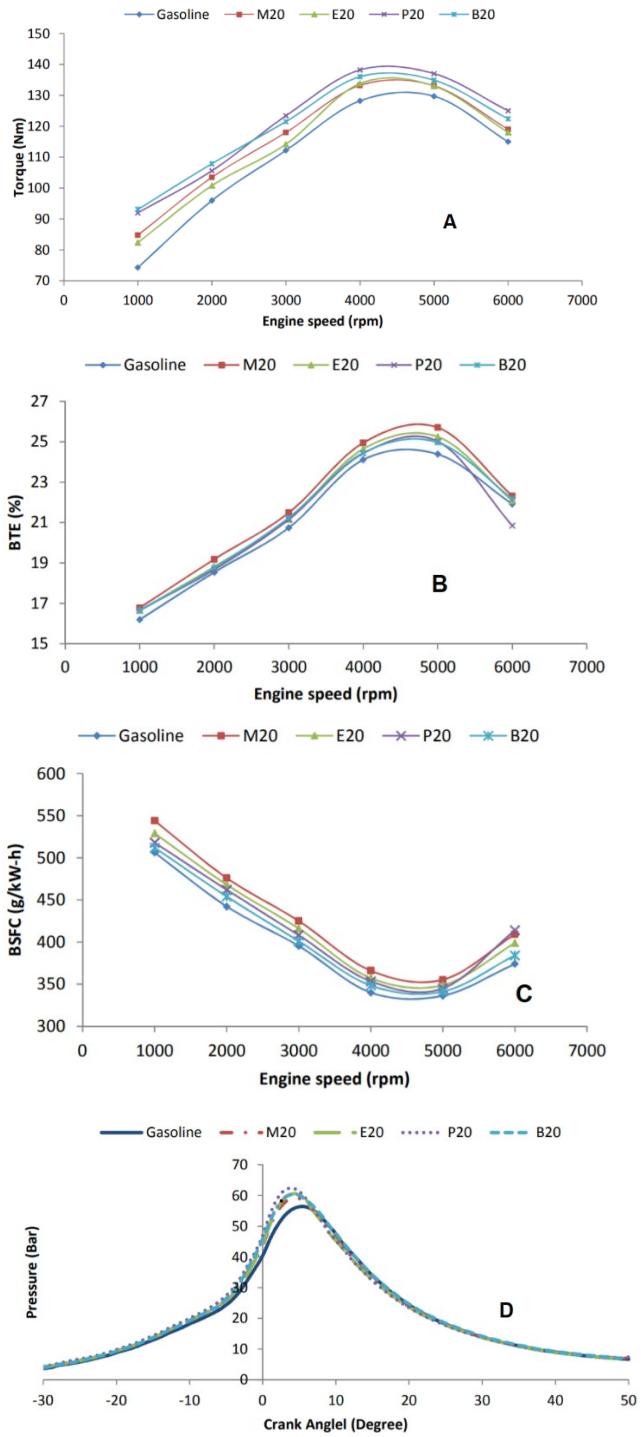

Fig. 12. Variation of torque (A), brake thermal efficiency (B), and brake specific fuel consumption (C) with engine speed for gasoline blends containing 20 vol% of linear C2-C4 alcohols and comparison of in-cylinder pressure at 4000 rpm (D) [194]

8. C3, C4 alcohols blending effect on Cold-start performance

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Cold-start mostly influences CO, UHC and NO_x emissions. Since catalytic converter is not able to efficiently reduce these pollutants until it reaches the light-off operating temperature, usually the overall emissions are high during the cold-start and warm-up (first 90 s). Most of the UHCs are formed during the cold-start and warm-up period but reduced approximately 40% in average afterward. CO emissions depend primarily on the equivalence ratio and hence is increased during the cold-start due to the mixture enrichment. However, NO_x is reduced because of the low chamber temperature and rich fuel regime [201].

Several studies investigated the cold-start performance of ethanol-gasoline blends. One study suggested that the best ethanol-gasoline blends for smooth driveability during the cold-start are blends containing 20 to 30 vol% of ethanol [254]. In contrast, another study recommended blends containing up to 20 vol% ethanol[255]. They observed that CO and UHC emissions were decreased with the increase in ethanol up to 20 vol% due to the high volatility but increased with more ethanol (up to 30 vol %) because of the low LHV and high HoV of these blends. In [256], the engine out particular matter number (PN) distributions from a DISI engine was investigated under the cold fast idle conditions (engine coolant temperature of 0° C to 40° C) when ethanol-gasoline blends (E0 to E85) were used as the fuel. It was observed that that total PN was increased with the reduced coolant temperature for all the test fuels. At coolant temperatures above 20° C, the trend of increase in the total PN was insensitive to ethanol content and was the same for all the fuels. However, blends containing ethanol produced lower PN compared to motor gasoline at coolant temperatures below 20° C.

Conventionally, an auxiliary gasoline injection system (a small gasoline reservoir, an electronic fuel pump and an electronic valve) is used to avoid the cold start difficulties in the ethanol-fueled vehicles. Auxiliary gasoline injection system injects motor gasoline during the cold start and warm-up period. Some recent efforts have been done to eliminate the motor gasoline reservoir by heating the ethanol [257,258]. However, the time required to heat the injected ethanol was too long in these attempts. A new cold start system which provides hydrous ethanol-fueled engine start in less than 2 seconds under temperatures as low as 0 °C was presented in [201] . In the other study [259], authors tested the cold-start emissions of an ethanol fueled engine with this new heated intake air and fuel system. Results showed a significant reduction in the raw exhaust UHC and CO emissions and a slight reduction in the raw exhaust NO_x emissions compared to the conventional cold-start system. It was also shown that catalytic converter efficiency was increased with this new system.

In [260], it was shown that it is not possible to ignite the engine with neat i-butanol at ambient temperatures below 20 °C, but blends of i-butanol performed well enough to be used as a drop-in fuel although showed poorer cold start performance than gasoline.

9. Conclusions

In this paper, an extensive review was conducted on the blending effect of C3, C4 with gasoline on the fuel properties and engine performance.

In general, in comparison to motor gasoline, the oxygen content of C3, C4 alcohols usually results in cleaner combustion, especially with regard to emission of CO, UHC, and NO_x. In addition, the faster

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laminar flame speeds can improve the combustion phasing. Furthermore, the HoV of C3, C4 alcohols is significantly higher than that of motor gasoline, leading to improved thermal efficiencies through the charge cooling although this feature may cause cold start problems under certain operating conditions and particulate matter formation due to the poor fuel atomization evaporation. Stemming from the oxygen content and the shorter hydrocarbon chains, their heating value and stoichiometric air-fuel ratios are lower than motor gasoline which may adversely impact the fuel economy if the engine is not optimized for such fuel blends. In comparison to ethanol, C3, C4 alcohols have lower oxygen content, higher energy density, lower octane value, lower octane sensitivity, lower HoV, and better solubility in gasoline. Depending on the operational conditions and combustion strategies, these can have either improve or deteriorate the combustion and emission characteristics. This article reviewed such matters comprehensively.

While most of the studies have been conducted on binary blends of gasoline and a pure alcohol, the potential of multiple component biofuel blends is missing in the literature. Some studies showed that the best motor gasoline might be the correct blend of ethanol, C3, and C4 alcohols (or other types of biofuels) which is able to provide the best optimum between fuel properties for high efficiency and low emitting engines. Such blends have potential to provide a better physiochemical property, volatility, octane sensitivity, and equivalence ratio sensitivity. Thus, there is a need for systematic studies on multiple component biofuel blends

Given the overall positive blending effects of C3,C4 alcohols, the main thrust areas required further work are research on co-optimizations of the fuel and engine by first understanding the desired fuel properties that will be required by future advanced engines that will be more efficient and lower polluting and then what fuel properties will be required that can be enabled by blends of C3 and C4 alcohols, identifications of the best multi-alcohol blends, better understating of C3 and C4 alcohol blends on cold start, high load, and other engine performance criteria, better kinetic mechanisms for C3 and C4 alcohols especially oxygenates to better enable efficiency gains and emission reductions, the low-cost sustainable production of C3,C4 alcohols from low-cost feedstocks by using genetically modified organisms, and optimization of conversion technologies. Furthermore, long-term compatibility of these fuel blends with the existing infrastructures and engines must be ensured.

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