



Review Paper

A review on the effects of ethanol/gasoline fuel blends on NO_x emissions in spark-ignition engines

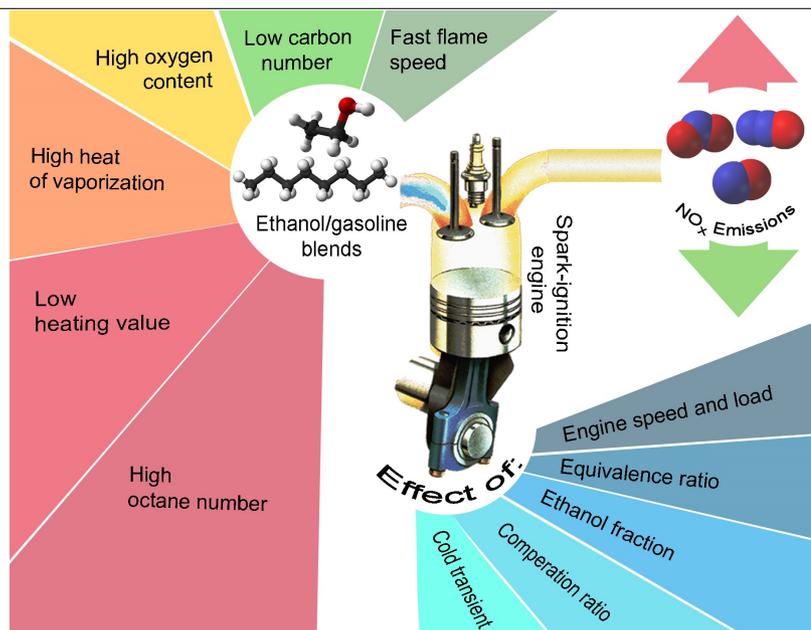
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HIGHLIGHTS

- Physicochemical properties of ethanol and gasoline are compared.
- NO_x formation pathways are reviewed and explained.
- Effects of ethanol/gasoline blends on NO_x formation in SI engines are reviewed and discussed.
- NO_x emissions are largely dependent on ethanol concentration and engine operating conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Ethanol can be used as an alternative fuel for spark-ignition (SI) engines to increase the octane number and oxygen content of ethanol/gasoline blends, thereby reducing dependence on fossil fuels and the exhaust emissions of incomplete combustion products. Although it is widely agreed that ethanol can reduce CO and HC exhaust emissions, the literature on ethanol and NO_x emissions is far from conclusive; hence there is a need for an in-depth, updated review of ethanol/gasoline blends in SI engines and the relative production of NO_x emissions. In light of that, the present work aims to provide a comprehensive literature review on the current state of ethanol combustion in SI engines to shed definitive light on the potential changes in NO_x emissions under various operating conditions. The first part of this paper discusses the feasibility of ethanol as an alternative transportation fuel, including world production and ethanol production processes. The physicochemical properties of ethanol and gasoline are then compared to analyze their effects on combustion efficiency and exhaust emissions. Then, the pathways of NO_x formation inside the cylinder of SI engines are discussed in depth. Finally, we review and critically discuss the effects of ethanol concentration in blends and different engine parameters on NO_x formation.

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Abbreviations

AC	Air-cooled
BMEP	Brake mean effective pressure
C	Cylinder
CE	Carbureted engine
CI	Compression engine
CO	Carbon monoxide
CR	Compression ratio
DI	Direct injection
E%	Ethanol concentration
ECU	Electronic control unit
EDI	Ethanol fuel direct injection
EI	Emission index
EIS	Electronic injection system
FFE	Flex-fuel engine
FFV	Flex-fuel vehicles
FIE	Fuel-injected engine
GHG	Greenhouse gas
GPI	Gasoline port injection
HC	Unburned hydrocarbons
HUCR	High useful compression ratio
IFI	Indirect fuel injection
IMEP	Indicated mean effective pressure
MFIE	Multi-port fuel injection engine
MIS	Multi-point injection system
NO _x	Nitrogen oxides
RON	Research octane number
SI	Spark ignition
TC	Turbocharged
WC	Water-cooled
WP	Wheel power

reducing global GHG emissions. Nevertheless, fossil fuels still represent the main source of the global energy supply (around 80%), with the world's energy consumption expected to increase by approximately 33% in the next three decades.

The road transport sector is undoubtedly one of the most energy-intensive sectors. Moreover, hazardous air pollutants produced by internal combustion engines widely used in this sector, such as nitrogen oxides (NO_x), unburned hydrocarbons (HC), particulate matters, and carbon monoxides (CO), can greatly affect air quality, causing significant negative impacts on human health (Taneja and Parmar, 2019). It is also worth mentioning that almost 20% of global GHG emissions come from the increasing number of circulating vehicles (Liaquat et al., 2010; Khan, 2017). Cleaner alternative fuels generated from renewable sources could replace conventional petroleum-based fuels and partially abate the associated harmful air pollutants in urban contexts (Elfasakhany, 2016; Saravanan et al., 2018). Moreover, these renewable energy carriers could be produced from waste and residues such as agricultural wastes, boosting rural economies and improving waste management (Yusri et al., 2017a).

Among the alternative fuels available for the road transport sector, the use of ethanol in spark-ignition (SI) engines in blended form with gasoline is accepted worldwide due to its favorable exhaust emission reducing properties (Flavin et al., 2006; Verma et al., 2018; Erdiwansyah et al., 2019). Moreover, the use of ethanol as a gasoline substitute has also obtained ample consideration due to reduced production costs over the years (Iodice et al., 2017).

Ethanol is usually used in SI engines by blending with pure gasoline in a well-defined percentage and is injected in the inlet manifold or directly into engine cylinders (Bae and Kim, 2017). At present, under the EU legislation, as a conventional vehicle fuel, 10 vol% is the maximum fraction of ethanol allowed (E10) in gasoline/ethanol blends; E10 is also sold in the United States as automotive fuel (Thakur et al., 2017a; Yusri et al., 2017b). No modifications to engine design would be required to use the gasoline/ethanol blend at such a low ethanol content. However, at higher ethanol concentrations in gasoline/ethanol blends, conventional SI engines require general modifications to perform well (Iodice et al., 2018). Indeed, 85 vol% ethanol in gasoline (E85), which has been sold in Brazil since 2003, cannot be used in conventional SI engines and can only be used in flexible fuel vehicles (FFVs) (Bayraktar, 2005). Currently, 90% of the new cars sold in Brazil are FFVs, while in the United States, almost 8 million vehicles, including passenger cars, vans, and pick-up trucks, are equipped with flexible-fuel engines which can run on E85 (Nadaleti and Przybyla, 2018).

The use of ethanol in SI engines confers several advantages over gasoline. First, the research octane number (RON) of ethanol is higher, obtaining more power from the engine, and ethanol/gasoline blended fuels can withstand higher pressures before detonating (Yusri et al., 2016). Since thermal efficiency depends on the volumetric compression ratio and ethanol fuel allows the use of high compression ratios without knocking, ethanol can also enhance the thermal efficiency of SI engines. Secondly, compared to gasoline, the oxygen content of ethanol leads to a more complete combustion phase within engine cylinders. Thus, under such fuel-lean conditions, higher combustion efficiency occurs. As a result, the oxidation of HC and CO in the fuel-rich regions of the combustion chamber is

1. Introduction

Anthropogenic activities are responsible for the annual emission of around 25 billion tons of carbon dioxide, a major greenhouse gas (GHG), closely linked to global warming and climate change (Hosseini and Wahid, 2013). The combustion of fossil fuels is regarded as the chief contributor to air pollution and GHG emissions. At the same time, the amount of readily available fossil fuels, such as natural gas and petroleum, is estimated to decrease rapidly in the next 50 years (Nocera and Cavallaro, 2016; Awad et al., 2018a). In light of these, much research has focused on improvements in exploiting renewables (biofuels, geothermal energy, solar power, etc.) to satisfy the world's growing energy requirements while meeting sustainable development goals and

improved by the high oxygen content of the ethanol molecules (Costagliola et al., 2016).

Besides, as the flame propagation speed and heat of vaporization of ethanol are higher than gasoline, gasoline/ethanol-blended fuels can guarantee faster combustions and higher volumetric efficiencies. A further advantage is a reduction in GHG emissions through using ethanol in gasoline fuel blends. In better words, the lower carbon number of ethanol compared to gasoline could result in lower global dioxide emissions, while it should also be noted that the origin of carbon contained in ethanol is biogenic (Normann et al., 2009). However, the main drawback of ethanol/gasoline blends as a fuel substitute for SI engines concerns the lower vapor pressure of ethanol than gasoline, making a cold-start difficult (Chansauria and Mandloi, 2018).

Ethanol production and its use as an alternative fuel in SI engines have been extensively studied. It has been shown that gasoline/ethanol blends, as for other oxygenated fuels, can significantly reduce CO and HC exhaust emissions in SI engines compared to neat gasoline up to the 20% ethanol ratio limit in blends. However, there are substantial inconsistencies in accounting for NO_x emissions, and the fundamental knowledge in this domain is still inadequate. As shown in Table 1, there are many comprehensive review articles on performance and exhaust emissions characteristics of SI engines using alcohols as alternative fuels. However, only a few provided detailed analyses concerning the effect of cold-start, compression ratio, and engine load on combustion characteristics and NO_x emissions when using ethanol as a gasoline substitute. Besides, some of the review articles tabulated in Table 1 are outdated and do not focus solely on ethanol fuel.

To the best of the authors' knowledge, most of the research and review articles are focused on engine performance and exhaust emissions of warmed and steady running SI engines, monitoring the air/fuel ratio, but without providing specific analysis of the NO_x emissions when the engine is fuelled with ethanol/gasoline blends under real operating conditions. In practice, during the warming-up process, SI engines require a fuel-rich injection to guarantee ignition and to overcome the low mixing of the inlet charge. In addition, the efficiency of sophisticated three-way catalytic converters is limited due to both their low temperature and rich air/fuel ratios. Hence, during the cold-start transient phase of last-generation SI engines, both the technological limits of three-way catalysts and the necessary rich air/fuel mixtures produce large amounts of exhaust emissions. Besides, NO_x emissions and combustion characteristics under real operating conditions are rarely

analyzed, which is noteworthy as exhaust emissions of SI engines depend on fuel combustion quality to a great extent.

Hence, given there are few review articles concerning the effect of cold-start transient, compression ratio, and engine load on NO_x emissions in SI engines powered by ethanol/gasoline blends, the present review article aims to fill this gap. It should be highlighted that NO_x emissions are classified by the Environmental Protection Agency (EPA) as one of the most harmful pollutants that can damage the respiratory system (Chong et al., 2010; Gonca, 2017). Therefore, NO_x emissions from SI engines fuelled with gasoline/ethanol blends could represent a considerable obstacle to further market expansion of bioethanol.

In this review article, the research on NO_x exhaust emissions related to the use of ethanol/gasoline fuel blends in last-generation SI engines under real operating conditions is comprehensively reviewed and critically discussed. The first part of this paper discusses the feasibility of using ethanol as an alternative transportation fuel, global ethanol production, potential sources, and ethanol production processes. In the next section, differences in ethanol and gasoline physicochemical properties are explained and compared to analyze their effects on combustion efficiency and NO_x exhaust emissions. The pathways of NO_x formation inside the cylinder of SI engines are also presented. Finally, the effects of both ethanol content in the blends and engine parameters on NO_x formation are discussed in detail.

2. World production, sources, and production processes of ethanol

Global ethanol production has increased steadily during the past decade thanks to the efforts made by many countries to decrease their dependence on crude oil reserves, boost agricultural-based economies, and improve air quality (Mahmudul et al., 2017). The total production of ethanol in 2019 reached around 155 billion L, as shown in Figure 1. According to the statistics provided by the Renewable Fuels Association, the USA is the world leader in the production, use, and export of ethanol, representing around 54% of global ethanol production (Fig. 2) (Ramli and Epplin, 2017). Ethanol is also widely produced and used in several other countries, including Brazil, the European Union, China, and India, where national programs for blending ethanol fuel into gasoline have been implemented (Masum et al., 2013; Shahir et al., 2015; Carneiro et al., 2017). In particular,

Table 1.
List of the latest review articles (2010-2021) published on performance and exhaust emissions characteristics of last-generation SI engines using alcohols as alternative fuels.

Focused on ethanol	Engine performance of SI engines	Engine performance of CI engines	Combustion characteristics of SI engines	Exhaust emissions of SI engines	Reference
×	✓	✓	×	×	Erdiwansyah et al. (2019)
✓	✓	×	✓	✓	Yusoff et al. (2015)
×	✓	×	✓	✓	Awad et al. (2018a)
×	✓	×	×	✓	Awad et al. (2018b)
✓	✓	×	×	×	Chansauria and Mandloi (2018)
×	×	✓	×	×	Kumar and Saravanan (2016)
×	×	×	×	×	Naik et al. (2010)
×	×	✓	×	×	Shahir et al. (2015)
✓	✓	×	×	×	Thakur et al. (2017a)
✓	×	✓	×	×	Verma et al. (2018)
✓	✓	×	✓	✓	Masum et al. (2013)
×	✓	✓	×	✓	Yusri et al. (2017a)
×	×	✓	×	×	Geng et al. (2017)
×	✓	×	×	✓	Gravalos et al. (2011)
✓	×	×	×	✓	Iodice and Cardone (2021)
✓	✓	×	✓	✓	Veza et al. (2020)
✓	✓	×	×	✓	Bharath and Selvan (2021)
✓	✓	×	✓	✓	The present review

✓: included
×: not included

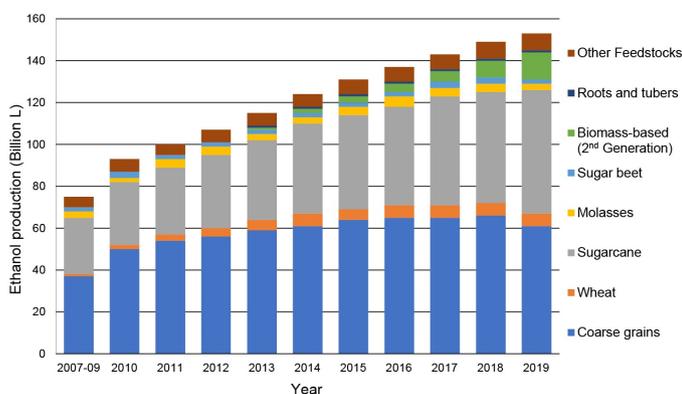


Fig. 1. Global ethanol production by feedstock from 2007 to 2019.

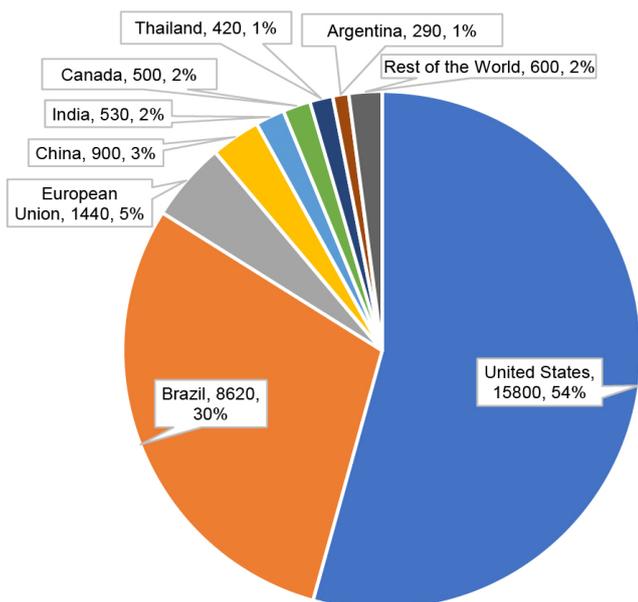


Fig. 2. Global ethanol production by country in 2019 (country; production in million gallons; percentage contribution) (Ramli and Eppin, 2017).

Brazil produced 8.62 billion gallons of ethanol in 2019, representing about 30% of world ethanol production. The Brazilian government has made the use of ethanol mandatory since the 1970s in pursuit of two main targets: obligatory use of gasoline-ethanol blends as a transportation fuel and gradual growth of the market of FFVs to the point that gasoline sold in Brazil now contains around 25% anhydrous ethanol and, at the same time, approximately 90% of new vehicles are equipped with flex-fuel engines (Flavin et al., 2006; Laurini, 2017).

Based on the various feedstock sources used in industrial operations, bioethanol can be classified into two main categories (Varatharajan and Cheralathan, 2012): first-generation bioethanol and second-generation bioethanol. First-generation bioethanol is the ethanol produced from both sugars (sugar beet, sugar cane, and fruit) and starch (milo, rice, potatoes, maize, and cassava) (Kumar and Saravanan, 2016), with nearly 50 billion L produced annually. However, the first-generation bioethanol feedstock is unsustainable because the growing demand for bioethanol has led to both the shortage and rising prices of sucrose-containing and starchy feedstocks, which have food and feed applications (Yusoff et al., 2015).

Second-generation bioethanol is the ethanol produced from non-food feedstocks such as lignocellulosic biomass (Naik et al., 2010) and agro-residues (Szulczyk and McCarl, 2010). As benefits, such feedstocks can enhance the energy balance of ethanol due to the decreased use of fossil fuel to produce

bioethanol. Also, being obtained from cheap, abundant, non-edible wastes and biomass, the produced ethanol is regarded as more environmentally friendly. Table 2 shows several potential biomass feedstocks to produce second-generation bioethanol and the related amounts of ethanol that can be potentially obtained per dry tonne of raw material (Naik et al., 2010). It should be highlighted that as reported by the United States Department of Energy's Centre for Transportation Research, the ethanol produced from lignocellulosic biomass reduces the life cycle of global GHG emissions further compared to its first-generation counterpart, e.g., maize-derived bioethanol (Fig. 3) (Yusoff et al., 2015).

Table 2. Several biomass feedstocks used to produce second-generation bioethanol and their potential ethanol yields (Naik et al., 2010).

Biomass type	Bioethanol (L/tonne feedstock, DMB)
Bagasse	437
Maize stover	428
Cotton gin trash	215
Forest thinnings	309
Mixed paper	440
Rice straw	416
Maize grain	470

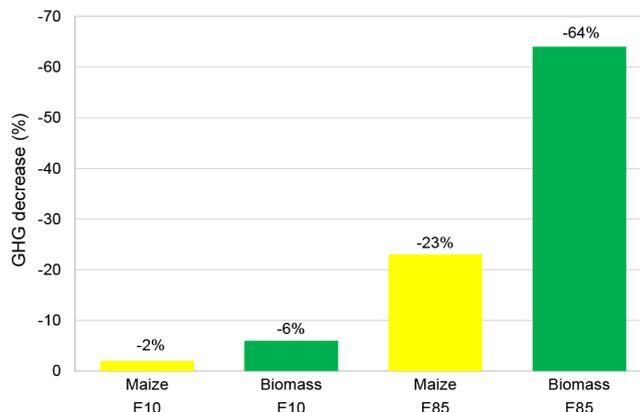


Fig. 3. Percentage decrease in GHG emissions from maize-derived and lignocellulosic-derived bioethanol for two different ethanol/gasoline blends (Yusoff et al., 2015).

Despite its advantages, the bioethanol produced from lignocellulosic biomass is still not economically viable. This is ascribed to the volatility of lignocellulosic feedstock prices and the high cost of pretreatments required, negatively affecting the overall production cost of lignocellulosic bioethanol (Hahn-Hagerdal et al., 2006). As a result, the main feedstocks for ethanol production are still coarse grains and sugar cane, with the second-generation bioethanol produced from lignocellulosic biomass contributing only 8% of the global ethanol production in 2019. Indeed, nearly 40% of the rise in world ethanol production over the last decade was due to increased sugar cane-based ethanol production mainly produced in Brazil.

As for the ethanol production process, first-generation bioethanol, such as maize-derived bioethanol, is obtained from the alcoholic fermentation of sucrose-containing and starchy feedstocks (Sims et al., 2010). The starchy [$n(C_6H_{10}O_5)$] feedstocks consist of long-chain glucose polymers and are first ground and mixed with water to break down into simpler sugars; subsequently, simple glucose ($C_6H_{12}O_6$) is fermented by yeast into bioethanol. The ethanol production process through alcoholic fermentation is shown in Equations 1 and 2. Three different kinds of microorganisms can be used in the fermentation of glucose into bioethanol, namely: yeast (*Saccharomyces* sp.), mold (mycelium), and bacteria (*Zymomonas* sp.) (Naik et al., 2010). In practice, 1000 kg of fermentable sugars produces

around 583 L of bioethanol. Thus, about 42-50% of glucose can be efficiently converted into ethanol.



The second-generation bioethanol (lignocellulosic bioethanol) production involved additional steps (Yusoff et al., 2015): (i) pretreatment (solubilization of hemicellulose), (ii) enzymatic hydrolysis process (conversion of cellulose into sugars), (iii) fermentation (conversion of sugars into ethanol), and (iv) distillation of pure ethanol. In addition to that, the high cost of the enzymatic hydrolysis process causes the bioethanol production process from lignocellulosic biomass to be much costlier compared with the first-generation bioethanol (Lynd et al., 1996).

Ethanol can also be produced via catalytic hydration of ethylene (C_2H_4) with steam, as shown in Equation 3:



The alcohol fermentation process contributes about 97% of the global ethanol production, whereas the catalytic hydration process contributes only 3% (Roozbehani et al., 2013). This is ascribed to the high cost of ethylene, making the synthetic ethanol production route less economically promising than alcoholic fermentation.

3. Physicochemical properties of ethanol and gasoline: a comparison

Ethanol contains about 34 wt% oxygen; it is transparent, neutral, colorless, flammable, volatile, and is easily mixable in non-polar solvents (Masum et al., 2013). The characteristics of ethanol and gasoline/ethanol blends as transportation fuels depend on several physicochemical properties such as density, viscosity, stoichiometric air/fuel ratio, heating value, latent heat of vaporization, RON, and oxygen content (Iodice et al., 2017; Awad et al., 2018a). Engine performance and exhaust emissions parameters, as well as the efficiency of the combustion process in last-generation SI engines, fuelled with gasoline/ethanol blends, rigorously depend on such physicochemical properties. The main chemical and physical characteristics of ethanol and gasoline and their differences are shown in Table 3.

Table 3.
Physicochemical properties of gasoline and ethanol.*

Property	Gasoline	Ethanol
Chemical formula	~ C ₈ H _{15.6}	C ₂ H ₅ OH
Molar mass [kg/kmol]	100-105	46.07
C-fraction [mass %]	87.4	52.2
H-fraction [mass %]	12.6	13.0
O-fraction [mass %]	0	34.7
Specific gravity at 20 °C	0.7392	0.7894
Density at 15 °C [kg/m ³]	750-765	785-810
Stoichiometric air/fuel ratio [-]	14.2-15.0	9.0
Kinematic viscosity [mm ² /s]	0.5	1.3
Reid vapour pressure [kPa]	53-60	17
Research octane number [-]	91-100	110
Lower heating value [MJ/kg]	44.0	27.0
Latent heat vaporization [kJ/kg]	380-400	910
Water solubility [%]	0	100
Boiling point [°C]	30-215	78
Flash point [°C]	-45	12-20
Auto ignition temperature [°C]	257	425
Adiabatic flame temperature [°C]	1970	1923
Freezing point [°C]	-40	-114

* Source: Chen et al. (2010); Dernotte et al. (2010); Masum et al. (2013); Mofijur et al. (2016); Jamuwa et al. (2016); Awad et al. (2017); Thakur et al. (2017b).

Density. Generally, density affects combustion characteristics and fuel atomization efficiency. In effect, higher density can bring about greater fuel flow resistance which causes higher viscosity, thereby resulting in lower fuel injection (Mofijur et al., 2016). Since the density of ethanol (around 795 kg/m³) is higher than that of gasoline (about 755 kg/m³), the volumetric fuel economy is improved because the volumetric fuel pump injects less mass of ethanol/gasoline blend than pure gasoline.

Lower heating value. The energy content of ethanol (27 MJ/kg) is around 65% of gasoline (44 MJ/kg). Hence, ethanol and gasoline/ethanol blends are associated with higher fuel consumption as compared to gasoline. However, this does not lead to a significant decline in engine power with increasing ethanol proportion in blends. The heating value of the stoichiometric air/fuel mixtures (which is equal to the ratio between the lower heating value and stoichiometric air/fuel ratio) is around 3 MJ/kg for both air/ethanol and air/gasoline blends, and this value remains constant even when considering different ethanol/gasoline mixtures (Iodice and Senatore, 2016; Deng et al., 2018). In effect, since this factor indicates the energy content introduced in the engine with the unit mass of stoichiometric air/fuel mixture, the stoichiometric air/ethanol mixture holds the same amount of energy as the stoichiometric air/gasoline mixture (Benajes et al., 2018; Boulahlib et al., 2018).

Latent heat of vaporization. The heat of vaporization of ethanol (910 kJ/kg) is much higher than that of gasoline (390 kJ/kg). Thus, since ethanol requires more heat to evaporate than gasoline, the temperature of the intake manifold is lower when ethanol is used as fuel, thereby increasing the engine's volumetric efficiency (Amirante et al., 2017). However, higher heat of vaporization also results in lower combustion temperature and burning velocity, which lead to higher HC and CO exhaust emissions (Awad et al., 2018b). Besides, high heat of vaporization of ethanol can also lead to difficulties during the cold-start transient of the engine, mainly during cold weather conditions because of the excessive cooling effect of the air/fuel blend at very low ambient temperature (Iodice et al., 2017).

Oxygen content. Ethanol has 34.73% oxygen which results in higher combustion efficiency. In effect, because of the greater amount of oxygen in ethanol/gasoline blended fuels, a more regular and complete combustion phase and higher combustion temperatures can be achieved than neat gasoline (Fajri et al., 2017). Under such fuel-lean conditions, the exhaust emissions of CO and HC can also be abated (leaning effect) (Geng et al., 2017).

Reid vapor pressure. The Reid vapor pressure of ethanol (17 kPa) is very low compared to neat gasoline (around 55 kPa). Hence, during the engine's warm-up phase, higher CO and HC cold emissions can occur due to the lower volatility of ethanol. As an advantage, the lower vapor pressure of ethanol can reduce evaporative emissions. However, the Reid vapor pressure of ethanol/gasoline blends does not depend linearly on the ethanol content in the blends.

Research octane number. The RON of ethanol (around 110) is higher than that of gasoline (approx. 95); as a result, to obtain more power from the engine, ethanol/gasoline blended fuels can withstand higher compression ratios before detonating in comparison with neat gasoline (Bhasker and Porpatham, 2017). Moreover, since the thermal efficiency depends on the volumetric compression ratio and ethanol fuel allows the use of high compression ratios without knocking, the use of ethanol can also enhance the thermal efficiency of SI engines (Genchi and Pipitone, 2014; Jamrozik et al., 2018).

Stoichiometric air/fuel ratio. On comparing the stoichiometric air/fuel equivalence ratios shown in Table 3, combustion of ethanol clearly needs a lower quantity of air compared to neat gasoline (around 1.6 times less). Also, the airflow rate entering the cylinder keeps constant for fixed throttle valve opening and engine speed. Therefore, to hold the air/fuel equivalence ratio constant, the electronic control unit (ECU) has to increase the consumption of the gasoline/ethanol blend (Masum et al., 2013).

Viscosity. Viscosity can generally affect combustion quality, spray characteristics, and fuel drop size (Mofijur et al., 2016). Since the viscosity of ethanol is higher than that of gasoline, larger droplets could be formed during injection, adversely affecting combustion quality, thus resulting in higher exhaust emissions (Hassan et al., 2015).

4. NO_x formation pathways

The oxides of nitrogen represent some of the most troublesome emissions from SI engines. NO_x in exhaust emissions comprises several chemical compounds: nitric oxide (NO), nitrogen dioxide (NO₂), nitrous oxide (N₂O), dinitrogen trioxide (N₂O₃), and dinitrogen tetroxide (N₂O₄). However, NO and NO₂ are predominant, whereas the other compounds are present in negligible quantities (Normann et al., 2009). The ambient concentration of NO, which is an odorless and colorless gas, is typically far less than 0.5 ppm. Nitrogen dioxide, a reddish-brown, toxic, and corrosive gas, is relatively visible in high ambient concentrations. Oxidation of nitrogen inside the cylinder of SI engines at high temperatures leads to NO_x formation (Chong et al., 2010). Hence, in effect, NO_x formation from SI engines greatly depends on the concentration of available oxygen, the peak temperature inside the cylinder, the equivalence ratio and the residence time for the reaction to occur between atmospheric oxygen and nitrogen molecules (Masum et al., 2013; Shahir et al., 2015). Two mechanisms of NO_x formation are discussed in this section: thermal and prompt NO_x.

Thermal NO_x formation is the predominant mechanism of total oxides of nitrogen. During combustion, nitrogen molecules react with the available oxygen inside the cylinder at temperatures higher than 1800 K through the following chemical reactions (Eqs. 4-7). Although the reactions leading to NO_x formation are many more, such kinetic equations represent the basic steps of the Zeldovich mechanism that describes thermal NO_x formation.



$$\frac{d[\text{NO}]}{dt} = \frac{k_1}{T^{1/2}} e^{-k_2/T} [\text{N}_2][\text{O}_2]^{1/2} \quad \text{Eq. 7}$$

However, thermal NO formation advances more slowly than the oxidation of hydrocarbons since NO production needs high temperatures to advance owing to its high activation energy (314 kJ/mole) (Fajri et al., 2017). Equation 7 describes the thermal NO production rate in which T is temperature, and k_1 and k_2 represent reaction constants. As defined in Equation 4, there is good evidence of a strong dependence of thermal NO production rate on temperature. In effect, high residence times for the reaction to occur, high available oxygen concentrations, and high peak temperatures lead to high formation rates of thermal NO_x (Varatharajan and Cheralathan, 2012).

The second mechanism leading to NO_x formation in exhaust emissions is termed prompt NO_x. Although the share of prompt NO_x on total NO_x emissions is lower than that of thermal NO_x, the presence of such prompt NO_x can be high in rich flames and the laminar premixed flame zone. Indeed, during the combustion of hydrocarbon fuels and before the production of thermal NO_x, prompt NO_x can be produced in a significant amount under specific operating conditions: fuel-rich conditions, short residence time, and low temperature. Prompt NO_x formation entails some intermediate compounds in a complex sequence of chemical reactions summarised in the following equations (Eqs. 8-12).



Normally, under both fuel-rich conditions and combustion temperatures lower than 750 °C, nitrogen molecules react with CH and CH₂ hydrocarbon fragments to produce amine species which are subsequently converted into prompt NO in exhaust emissions. Hence, as defined in the above equations, CH and CH₂ hydrocarbon radicals are the major contributors to producing prompt

NO_x, which is much more sensitive to fuel chemistry than thermal NO_x due to the high dependence of prompt NO_x on hydrocarbon radicals (Eqs. 5 and 6). However, the concentration of nitrogen-containing fragments (hydrogen cyanide; HCN) rises with the increasing quantity of CH and CH₂ hydrocarbon fragments, which in turn increases with growing equivalence ratios. Thus, prompt NO_x production grows with rising equivalence ratios while it decreases when a lack of oxygen occurs (Masum et al., 2013).

5. Effect of gasoline/ethanol blends on NO_x emissions

In the last three decades, SI engines have been extensively investigated to analyze the effect of varying ethanol concentrations in gasoline fuel blends on NO_x emissions. In most such experiments, a decrease in NO_x emissions was observed for ethanol-gasoline blends compared to neat gasoline. However, an opposite trend was also marked by other researchers (Song et al., 2007), while a few found no noteworthy differences in NO_x emissions between gasoline and ethanol/gasoline blends (Jia et al., 2005). This section discusses the causes of NO_x emissions for SI engines fuelled with ethanol/gasoline blends, focusing on different fuel compositions and engine parameters (i.e., compression ratio, equivalence ratio, engine load, and speed).

5.1. Effect of ethanol concentration in blends

The main parameters affecting NO_x emissions in SI engines fuels by ethanol/gasoline blends are combined with combustion temperature, combustion duration, and ethanol concentration. The experimental investigations reviewed in this work included studies on SI engines powered by ethanol/gasoline blends containing various ethanol concentrations ranging from 5 vol% to as high as 100 % v/v (i.e., neat ethanol). Owing to the differences in physicochemical properties of ethanol and gasoline (Table 3), the properties of resulting ethanol/gasoline blends also differ (Liu et al., 2016). More specifically, with increasing ethanol content in ethanol/gasoline blends, the octane number, latent heat of vaporization, and density increase while the heating value of the blends decreases (Li et al., 2018).

Turner et al. (2011) measured NO_x emissions of a direct injection SI engine fuelled with different ethanol/gasoline blends when the indicated mean effective pressure (IMEP) was set at 3.4 bar. They found that NO_x exhaust emissions decreased by increasing ethanol concentration from 30% to 85% in the test fuels. This decrease could be ascribed to the reduction in flame temperature, which was confirmed by the decline recorded in the exhaust gas temperature. Further increments in ethanol concentration in the blends beyond 85% v/v led to slight increases in NO_x emissions, possibly because of a more favorable combustion process resulting in higher maximum in-cylinder temperatures and pressures. Similar results were also reported by Bielaczyc et al. (2011), who used a vehicle with "Euro 4" European emissions standard (without engine modifications) and observed a linear decrease in NO_x emissions in response to increasing ethanol concentration from 10% to 85% v/v in the blends. These findings were in line with those of the study by Oh et al. (2010), in which a direct injection SI engine was fuelled with 25, 50, and 85% v/v ethanol blends. The authors attributed the decreases in NO_x emissions with increasing ethanol concentration to the reduced peak in-cylinder pressure and temperature due to combustion retardation.

As described in the previous section, the formation of NO_x emissions is strictly dependent on oxygen concentration, peak in-cylinder temperature, and residence time in the combustion chamber (Ozsezen and Canakci, 2011; Canakci et al., 2013; Masum et al., 2015). In an experimental study performed by Lin et al. (2010) on a small air-cooled engine, the decrease in NO_x emissions as a result of increasing ethanol concentration in the test fuels was justified by the lower combustion temperature due to the high oxygen content of ethanol. They claimed substantial reductions in NO_x emissions ranging from 77% to 86% when using gasoline/ethanol blends containing 6 to 9% v/v ethanol, attributing it to the higher heat of vaporization of ethanol in comparison with gasoline. In effect, with increasing ethanol concentration in the fuel blends, the temperature of ethanol/gasoline blends decreases at the end of the intake stroke, thus entailing a decrease in the maximum combustion temperature (Najafi et al., 2016).

Zervas et al. (2003) highlighted multiple reasons to explain the reductions observed in NO_x emissions of the investigated SI engine fuelled with ethanol-gasoline blends, including excess oxygen present in ethanol reducing the peak in-cylinder temperature, lower combustion temperatures owing to the lower heating value of the ethanol-containing blend, and higher latent heat of ethanol than gasoline. At an engine speed of 2000 rpm and in wide-open throttle conditions with different ethanol concentrations ranging from 5 to 80% v/v, Gravalos et al. (2011) found that NO_x emissions decreased with increasing ethanol percentage in the gasoline/ethanol blends. They also cited the higher heat of vaporization of ethanol than gasoline leading to a lower combustion temperature of the blends under investigation as the main reason behind these observations. The maximum percentage decrease in NO_x emissions was obtained with 80% v/v ethanol in ethanol/gasoline blends. Canakci et al. (2013), on a multi-port injection system engine, revealed that NO_x exhaust emissions decreased as the ethanol concentration in the blended fuels increased. Reduced peak in-cylinder temperatures owing to the higher latent heat of vaporization and lower heating value of ethanol as compared to gasoline were indicated as the underlying reasons. For 10% v/v ethanol, the percentage decrease in NO_x emissions was recorded at 15.5%.

Yao et al. (2009) revealed similar findings on a four-stroke motorcycle using ethanol blended with gasoline (at a constant RON) in variable percentages from 3 to 20% v/v with the lowest NO_x emission recorded for the 15% v/v ethanol concentration. Storey et al. (2010) and Broustail et al. (2012) also found a positive correlation between ethanol concentration in gasoline/ethanol blends and NO_x emission mitigation. Figure 4 depicts the variations in NO_x emission of a four-cylinder four-stroke SI engine under different engine speeds in response to various ethanol concentrations (0 to 30% v/v) in ethanol/gasoline blended fuels (Dogan et al., 2017). At all the investigated engine speeds, 30% v/v led to the most favorable NO_x emissions.

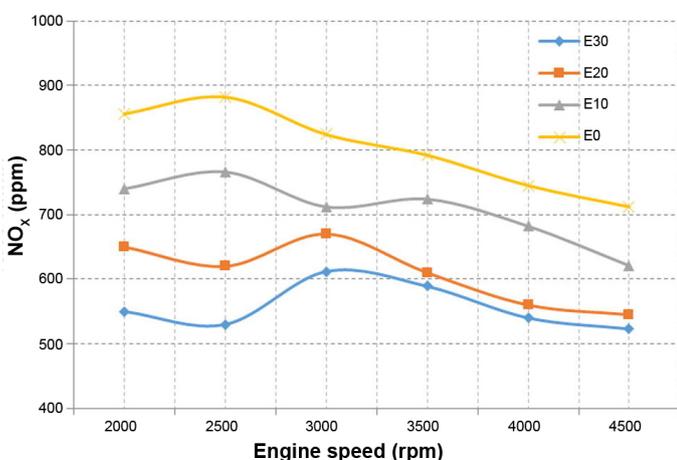


Fig. 4. Variation in NO_x emissions at different engine speeds and ethanol concentrations in the blended fuels. Neat gasoline (E0), 10% v/v ethanol (E10), 20% v/v ethanol (E20) and 30% v/v ethanol (E30) (Dogan et al., 2017). With permission from Elsevier. Copyright© 2017. License Number: 5040090337603.

While confirming the positive effects of ethanol inclusion (3 to 30% v/v) on mitigating NO_x emissions from a four-stroke motorcycle, Chen et al. (2010) argued that the best percentage reductions in NO_x emissions were obtained in ethanol concentrations lower than 15% v/v.

The effect of low ethanol concentrations in blends on NO_x emissions of SI engines was also investigated by Yang et al. (2012). They used nine four-stroke motorcycles equipped with carburetor systems tested on a chassis dynamometer using neat gasoline and gasoline blended with 3% v/v ethanol as test fuels but found no considerable differences between neat gasoline and the ethanol/gasoline blend. Jia et al. (2005) also found a slight reduction (6%) in NO_x emissions using gasoline blended with 10% v/v ethanol compared with neat gasoline.

Using 20% v/v ethanol concentration in the fuel blend, the emission performance of an in-use fuel-injected vehicle (without engine modifications) was analyzed by Tibaquirá et al. (2018). The authors reported reductions in

NO_x emissions ranging between 3 to 17.5% when E20 was used compared with neat gasoline under steady-state conditions (Fig. 5).

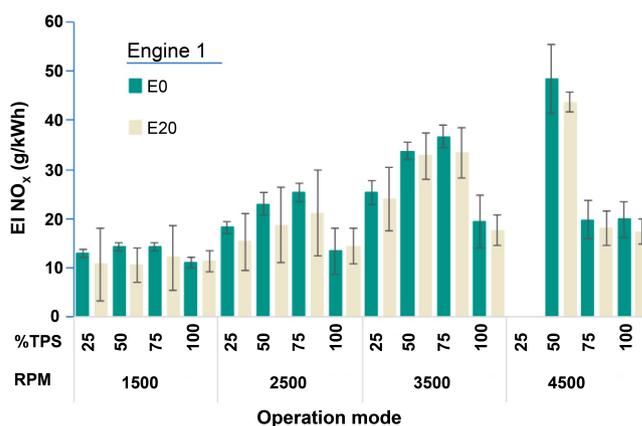


Fig. 5. Variations in NO_x emissions during the combustion of neat gasoline (E0) and 20% v/v ethanol (E20) at different engine speeds and throttle position sensor (TPS) (Tibaquirá et al., 2018).

In contrast to the findings presented above, there are also reports indicating increases in NO_x emissions in response to the addition of ethanol in gasoline. Schifter et al. (2011) examined the effect of ethanol blended with gasoline (in variable percentages ranging from 3 to 20% v/v) on NO_x emissions of a single-cylinder SI engine. They claimed that NO_x emissions were higher for ethanol/gasoline blends than neat gasoline, highlighting the higher heat release of ethanol as the underlying reason. Keskin and Guru (2011) also recorded higher NO_x emissions when ethanol concentration was increased in the blends, attributing their observations to the higher oxygen content of ethanol than gasoline. A similar justification was used by Schifter et al. (2005), who observed a slight increase in NO_x emissions using 9% v/v ethanol in gasoline. To explain the increased NO_x emissions with the addition of ethanol in gasoline/ethanol blends, Zervas and Tazerout (2000) pointed out the higher heat of vaporization of ethanol in comparison with gasoline, resulting in higher volumetric efficiency of the engine. Increased volumetric efficiency leads to more efficient and complete combustion, thus increasing cylinder temperature and pressure. Similar results were also obtained by Singh et al. (2014) using gasoline blended with 10% v/v ethanol. However, they attributed the increases in NO_x emissions to the faster flame speed caused by ethanol/gasoline blends combustion compared to neat gasoline. The resulting rapid and complete combustion process brings about an increased in-cylinder temperature and higher NO_x formation. Adding different alcohols (i.e., ethanol, butanol and methanol) to gasoline, Gautam et al. (2000) recorded increased NO_x emissions by around 14% compared to neat gasoline. They also attributed the observations made to the higher in-cylinder temperature caused by the high oxygen content of the alcohols.

Some studies have reported both increases and decreases in NO_x emissions depending on the ethanol concentration used in the fuel blend. For instance, Zhuang and Hong (2013), examining 0 to 60% v/v ethanol concentration, claimed that NO_x emissions increased for up to 24% ethanol concentration in gasoline, attributing it to improved combustion process inside the cylinder, resulting in an increased peak in-cylinder temperature. However, NO_x emissions decreased for ethanol concentrations higher than 24% v/v due to reduced peak in-cylinder temperature. The reduction observed could be ascribed to the higher latent heat of evaporation of the ethanol than gasoline's, lowering the peak in-cylinder temperature during vaporization of ethanol/gasoline blended fuels. Besides, for such high ethanol concentrations in the blends, the combustion temperature could also be reduced by more triatomic molecules in the combustion products of gasoline/ethanol-blended fuels than in those of neat gasoline (Schifter et al., 2013; Yao et al., 2013). Dhande et al. (2021) tested 10 to 25% v/v ethanol concentrations to investigate NO_x emissions of a single-cylinder, four-stroke SI engine at different engine speeds and constant engine load and

compression ratio. For the E10 test fuel and when the engine was operated at 1700 rpm, a 30% decrease in NO_x emissions was measured compared to neat gasoline. However, further increases in ethanol concentration of blended fuels increased NO_x emissions by 8.9%, 15.7%, and 76.9% for E15, E20, and E25, respectively.

5.2. Effect of transient cold-start

During the cold-start transient phase, fuel vaporization is slow due to the cylinder walls being cold. Consequently, the fuel flow increases with a resultant enrichment of the air/fuel mixture to overcome the poor mixing of the inlet charge, increasing unburned hydrocarbons. Furthermore, the gasoline forming a surface film inside the combustion chamber is weakly mixed and, therefore, weakly burned. Thus, during the warming-up process of the engine, until the cylinder walls warm up and the engine uses a rich mixture, CO and HC are increased. In addition, the efficiency of a three-way catalyst is also limited due to the rich values of the air/fuel ratio. Indeed, the best range of the air/fuel equivalence ratio for the optimum conversion efficiency of a catalytic converter is very narrow near the stoichiometric value. Hence, during the cold-start transient phase of last generation SI engines, both the technological limits of the three-way catalyst and the necessary rich values of the air/fuel mixture can produce higher CO and HC cold emission levels compared to hot operating conditions.

Iodice et al. (2018) compared NO_x emissions for cold and hot operating conditions and in response to different ethanol concentrations in the gasoline/ethanol blends. As presented in Figure 6, both in cold and hot operating conditions, NO_x emissions decreased with rising ethanol content in the test fuels as a result of the higher H/C atom ratio of ethanol compared to gasoline (See Table 3). NO_x emissions are produced in the combustion chamber owing to high peak in-cylinder temperature when the nitrogen reacts with oxygen. In this regard, the chemical combustion equations of ethanol and gasoline (Eqs. 13 and 14, respectively) show that ethanol/gasoline blends, under stoichiometric operating conditions, require a lower amount of air as compared to gasoline, with a subsequent decrease in NO_x hot emission levels (Dogan et al., 2017). Likewise, ethanol/gasoline blends also require less air under rich operating conditions during the cold-start transient phase.

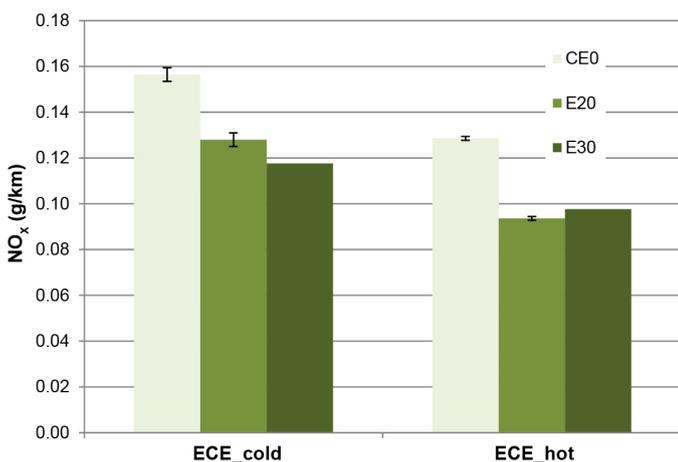
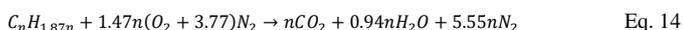
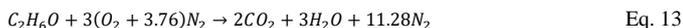


Fig. 6. NO_x emissions of commercial gasoline (CE0), 20% v/v ethanol (E20) and 30% v/v ethanol (E30) during the cold and hot phases of the ECE driving cycle (Iodice et al., 2018). With permission from Elsevier. Copyright© 2018. License number: 5040091034761.

In addition to the justification presented above, NO_x emissions decreased with the rise in ethanol content in the test fuels both in cold and hot operating conditions due to the higher latent heat of vaporization and lower heating value of gasoline/ethanol test fuels than those of commercial gasoline. Indeed, under

such operating conditions, the temperature of the air/fuel mixture drops at the end of the intake stroke, thereby lowering the combustion temperature and reducing the thermal NO_x.

To evaluate the effect of the transient cold-start on engine NO_x emissions of turbocharged SI engines, Guo et al. (2020) investigated the exhaust emissions of a DI TG four-cylinder engine fuelled with 10% v/v ethanol (E10) under steady-state and transient cold-start conditions. They argued that the NO_x transient cold-start emissions of the investigated DI TG engine fluctuated dramatically and strongly depended on the engine load. Besides, under steady-state operating conditions, the NO_x exhaust emissions were increased with increasing coolant temperature from around 40 °C to 100 °C.

5.3. Effect of compression ratio

The thermal efficiency of SI engines depends on the compression ratio. A fuel with a high octane number can withstand high compression ratios without knocking before detonating, thus improving the knock tolerance (Yücesu et al., 2006). The octane number of neat ethanol (around 108) is higher than gasoline (91-100). Hence, ethanol is particularly suitable for high compression ratios because it can improve the thermal efficiency of SI engines. For this reason, the fuel economy penalty resulting from the lower energy content of ethanol as compared to gasoline can be offset by an increase in the thermal efficiency of SI engines with high compression ratios when fuelled with gasoline/ethanol-blended fuels. However, NO_x emissions should increase with increasing compression ratios, especially at high engine loads due to the resulting high combustion temperatures.

In a study performed by Al-Baghdadi (2008), NO_x emissions were measured for an SI engine operated on ethanol/gasoline blends (ethanol concentration ranging between 0% to 30% v/v) at variable compression ratios (ranging between 8 to 9.25, proportional to the ethanol percentage in the blend). They confirmed decreases in NO_x emissions with rising ethanol proportion in the blends but also showed that increases in compression ratio caused an opposite effect. The latter could be justified, on the one hand, by the higher peak temperature and pressure and, on the other hand, by the reduction in the time needed for NO dissociation into N₂ and O₂ (Al-Baghdadi, 2008). Celik (2008) analyzed different ethanol/gasoline blends (E25, E50, E75, and E100) in a four-stroke single-cylinder engine at constant load and speed, while the compression ratio varied from 6:1 to 10:1. On using gasoline blended with 50% v/v ethanol at a high compression ratio of 10:1, NO_x decreased by 19% compared to neat gasoline under a compression ratio of 6:1. They attributed the reduced NO_x emissions to a lower heating value of ethanol than gasoline.

Koç et al. (2009) increased the compression ratio of a four-cylinder SI engine from 10:1 to 11:1 by using 0%, 50%, and 85% of ethanol in gasoline/ethanol blends. For the same ethanol percentage in the blends, NO_x emissions were higher for higher compression ratios due to the resultant high combustion temperatures (Fig. 7). Besides, NO_x emissions decreased with increasing ethanol concentration at both compression ratios. This phenomenon was due to the higher latent heat of vaporization of ethanol reducing the flame temperature, thereby resulting in lower NO_x emissions. In effect, on using neat gasoline at a compression ratio of 10:1, NO_x emissions were even higher than those of gasoline/ethanol blends at a compression ratio of 11:1.

5.4. Effect of equivalence ratio

The stoichiometric air/fuel ratio of ethanol is around 1.6 times lower than base gasoline. As is well known, for an SI engine, the airflow rate entering the cylinders remains the same for a given engine rotation speed and throttle valve opening. Hence, to obtain the same air/fuel equivalence ratio, the mass flow rate of the ethanol/gasoline blend is increased by the ECU as the ethanol content in the blended fuel increases. Following that, under fuel-rich operating conditions, the leaner effect caused by the high oxygen content of ethanol can shift the fuel/air ratio from rich to stoichiometric values, thus reducing the flame temperature and, consequently, NO_x emission levels.

Najafi et al. (2009) investigated the effects of 5, 10, 15, and 20% v/v ethanol blends on the NO_x emissions of a four-stroke SI engine and recorded higher NO_x emissions when the ethanol percentage in the blend

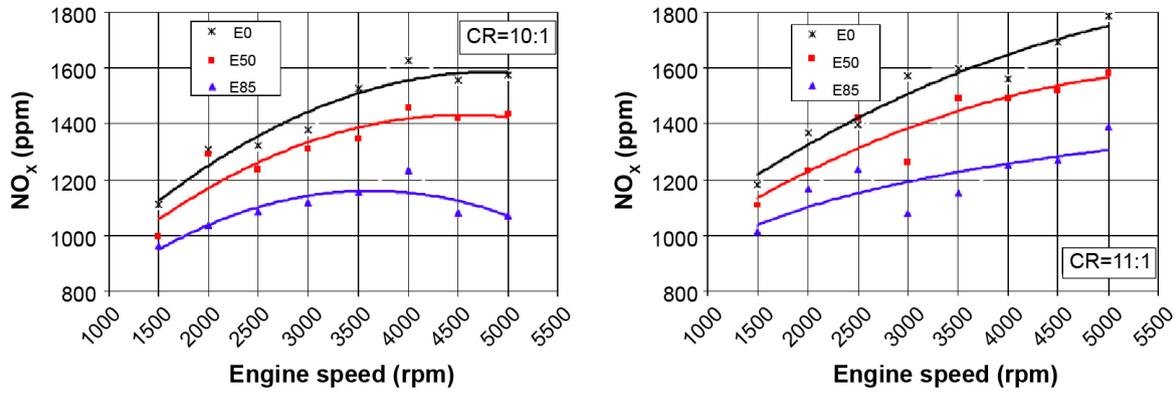


Fig. 7. Variations in NO_x emissions of gasoline (E0), 50% v/v ethanol (E50) and 85% v/v ethanol (E85) in response to engine speed and ethanol concentration in the blends at different compression ratios (Koç et al., 2009). With permission from Elsevier. Copyright© 2009. License number: 504009065550.

was increased. They attributed this finding to the higher oxygen content of the ethanol/gasoline blends than neat gasoline, increasing the air/fuel ratio in the fuel-rich regions of the engine. Hence, the air/fuel ratio moves from rich toward stoichiometric values as the ethanol fraction increases, thus bringing about a more complete and efficient combustion process (Thangavel et al., 2016). Finally, this efficient combustion process increases the in-cylinder temperature leading to an increase in thermal NO_x emissions. Similar results were also found by Al-Farayedhi et al. (2000) and Hsieh et al. (2002).

A comparative study on emission and combustion characteristics of a multi-port-fuel-injection SI engine powered by different fractions of butanol, methanol, and ethanol in gasoline-blended fuels was performed by Li et al. (2017). At equivalence ratios set at 1 and 3 bar BMEP, gasoline/ethanol blends (i.e., 10, 30, and 60% v/v) correspondingly decreased NO_x emissions by around 3%, 5%, and 12% as compared to gasoline (Fig. 8). In the same study, the effects of gasoline blended with 30% v/v ethanol on NO_x emissions were also analyzed under different equivalence ratios fluctuating from 0.83 to 1.25. The highest NO_x emission occurred when the equivalence ratio ranged between 0.9 and 1.0, which could be explained by the resulting rapid and complete combustion process leading to increased combustion temperature. Then, as shown in Figure 9, the NO_x emissions decreased as the equivalence ratio reached relatively leaner or richer values than the stoichiometric value due to the resultant reduced peak combustion temperatures.

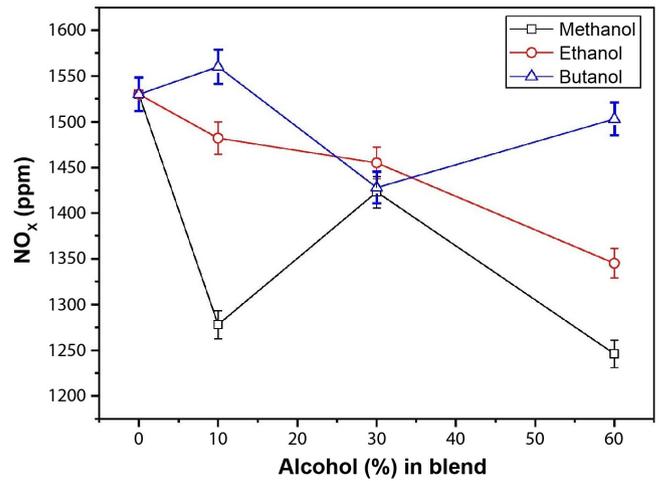


Fig. 8. Variation in NO_x emissions of methanol, ethanol, and butanol in response to alcohol concentration in the blends at $\phi = 1$ and 3 bar BMEP (Li et al., 2017). With permission from Elsevier. Copyright© 2017. License number: 5040081090704.

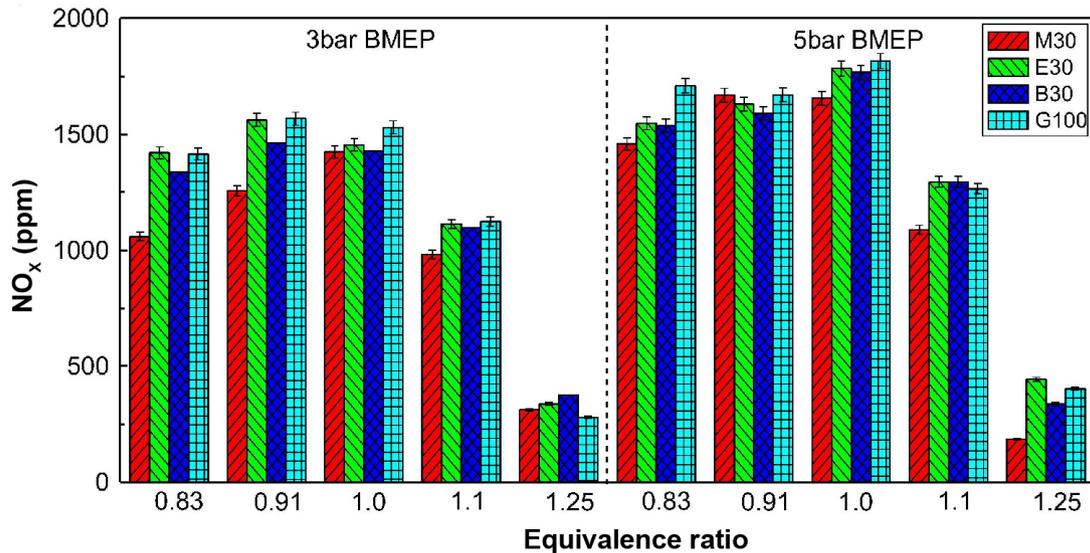


Fig. 9. Variations in NO_x emissions of gasoline (G100), 30% v/v methanol (M30), 30% v/v ethanol (E30) and 30% v/v butanol (B30) in response to equivalence ratio and engine load (Li et al., 2017). With permission from Elsevier. Copyright© 2017. License number: 5040081090704.

Zervas et al. (2003) also explored the effects of different equivalence ratios on NO_x emission of an SI engine fuelled with ethanol/gasoline blends. They argued that changing the equivalence ratio from 0.83 to 1.25 increased NO_x emissions from 15% to 30%, respectively.

5.5. Effect of engine load and speed

Engine load and speed are the main parameters affecting NO_x formation in SI engines: to increase the engine speed and load, a richer mixture is required, bringing about higher in-cylinder temperatures and hence higher NO_x emissions. In this context, the faster flame speed of ethanol than gasoline can play an important role in complete combustion in rich-mixture operating conditions, which results in higher NO_x emissions.

Melo et al. (2012) tested a flex-fuel SI engine fuelled with different ethanol percentages in the blends, from 5 to 100% v/v, at two different engine loads of 60 Nm and 105 Nm. They revealed that at the lower engine load, NO_x emissions decreased with increasing ethanol concentration in the blends. In contrast, NO_x emissions increased with the growing ethanol percentage in the blends at the same engine speed but at the higher engine load. The increase in NO_x emissions at the higher engine load was attributed to the faster flame speed caused by ethanol-gasoline blends compared to gasoline because, under such operating conditions, the resulting complete combustion process led to an increased in-cylinder temperature. Citing the same justification, Li et al. (2017) reported that at the engine load of 5 bar BMEP, higher NO_x emissions were generated compared to 3 bar BMEP (Fig. 9). However, compared to commercial gasoline, a reduced combustion temperature was caused by ethanol addition to the gasoline blends such that, under different equivalence ratios, the final NO_x emissions were 0.4–10.4% lower for E30 (30% ethanol v/v), despite the higher oxygen content supplied.

Keskin and Guru (2011) examined the effects of ethanol blended with gasoline (0% to 20% v/v) on NO_x emissions at different engine loads ranging between 800 and 2400 kW. NO_x emissions increased with increasing ethanol percentage in the blends at high engine loads, while at low engine loads, NO_x emissions were almost the same for all test fuels. Gomes et al. (2011) tested ethanol/gasoline blends (5% to 100% v/v) at engine loads of up to 30 bar IMEP. They concluded that at low engine loads, NO_x emissions were lower using ethanol concentrations >25% v/v owing to the reduced peak temperature. In contrast, NO_x emissions were almost the same for all blended fuels at higher engine loads as the faster flame speed of ethanol than that of gasoline leads to similar peak in-cylinder temperatures (Pischinger, 2017). Pang et al. (2008) investigated 10% v/v ethanol in blended fuel at two different engine loads, 3 and 160 Nm torque, but found no significant variations in NO_x exhaust emissions compared to neat gasoline.

NO_x formation in SI engines is known to rise with increasing engine speed due to higher in-cylinder temperatures when more fuel is burnt in less time available for combustion than at low engine speeds (Ramasamy et al., 2017). In this context, ethanol's faster flame speed than gasoline can play a major role in completing the combustion in rich-mixture operating conditions caused by high engine speeds, thereby leading to higher NO_x emissions than gasoline. Costa and Sodr  (2010) investigated the effect of 22 and 100% v/v ethanol in blends on NO_x emissions at low and high engine speeds. They claimed that at low engine speeds (2500–3000 rpm), there were no substantial variations in NO_x emissions between the tested fuels. On the contrary, higher NO_x emissions were observed at high engine speeds for neat ethanol than 22% v/v ethanol in the gasoline/ethanol blend due to the faster flame speed of ethanol than gasoline.

Koç et al. (2009) also examined the effect of 0, 50, and 85% v/v ethanol in gasoline/ethanol blends on NO_x emissions within a wide range of engine speeds ranging between 1500 and 5000 rpm. However, they observed opposite trends for gasoline-ethanol blends at high engine speeds compared to the previous reports. As shown in Figure 7, the increase in NO_x formation with engine speed was lower for the 85% ethanol (around 11%) than the value recorded for neat gasoline (approx. 42%). The lower increase in NO_x emissions as the ethanol content in the blended fuel increased under increasing engine speeds could be ascribed to the lower heating value and higher heat of vaporization of ethanol compared to gasoline.

In a recent study, Mohammed et al. (2021) assessed the effect of different ethanol inclusion rates (10, 20, 30, and 40%) in gasoline at various engine speeds ranging from 1500–2500 rpm. They found that with increasing engine speed, NO_x emissions increased. Moreover, the lowest NO_x emissions were

recorded at the highest ethanol level (E40) by 21%, which could be ascribed to the delayed ignition timing; this improvement did not decrease thermal efficiency, though. Taghavifar et al. (2020) added 20% bioethanol into gasoline at an engine speed of 1400 rpm and different engine loads and measured NO_x emissions under all conditions. Maximum NO_x emission reduction was recorded by 60% at 75% engine load but offered no explanations for the observations made. In another study aimed at understanding the effects of ethanol addition and exhaust gas recirculation (EGR), Biswal et al. (2020) used E20 at different engine loads and an EGR of 10%. They found that although ethanol inclusion in gasoline (without EGR) increased NO_x emission, using the EGR technique compensated for the ethanol effect, resulting in a 20% NO_x emission reduction compared to neat gasoline without EGR. However, it is worth noting that E20+EGR resulted in less NO_x emission reduction (17%) compared to E0+EGR (30%).

Rosdi et al. (2020) combusted three different ethanol/gasoline blends (10, 20, and 30%) on a four-cylinder turbocharged SI engine (Multi-Point Injection). NO_x emissions were proportionally decreased in response to increasing ethanol concentration in gasoline. For instance, NO_x emission stood at 800 ppm for E30 while it was considerably higher for neat gasoline at 1700 ppm. They attributed the findings obtained to the high latent heat of vaporization, low heating value, and high oxygen content of ethanol. Agarwal et al. (2020) studied some of the toxic exhaust gases, including NO and NO₂. They showed that the contribution of NO to NO_x emissions was significantly higher compared to that of NO₂. In their study, ethanol/gasoline blend (E10) showed various combustion behavior concerning NO_x emission depending on engine operation conditions. More specifically, at the lower engine load tested (i.e., 50%), ethanol inclusion decreased both types of NO_x emissions (NO and NO₂) by 1%. While at a full load of engine operation, E10 increased NO and NO₂ by 2%. They highlighted that at 50% load, the effect of ethanol's higher latent heat of vaporization was dominant over its oxygen, causing lower combustion temperature and NO_x formation. On the contrary, at a full load of engine operation, the fuel-bound oxygen played a major role leading to more complete combustion and increased in-cylinder temperature and NO_x emissions.

5.6. Effect of ignition timing

Little information is available in the published literature on the effect of ignition timing on the combustion behavior of ethanol/gasoline blends. In a very study, Liu et al. (2021) looked into the impact of ethanol port injection (25, 50, 75, and 100%) (ethanol injection using a separate injector) for different ethanol/gasoline blends (E0, E25, E50, E75, and E100) on engine performance and emission parameters at different ignition timings (10, 15, 20, 25, and 30 CA BTDC). Their results showed that retarding the ignition strongly reduced NO_x emissions. Minimum NO_x emission was obtained for E25 at all ignition timings investigated. On the contrary, E75 and E100 caused higher NO_x emissions than neat gasoline for all investigated ignition timings. In general, by increasing ignition timing from 10 to 30 CA BTDC, NO_x emissions were reportedly increased for all fuel blends. These findings could be explained by the fact that advancing ignition timing to 30 CA BTDC must have decreased the time for reaching the peak pressure, subsequently leading to higher engine temperature and higher NO_x emissions.

A summary of the main experimental results concerning the effect of ethanol addition in gasoline blends on NO_x emissions under different ethanol concentrations and operating conditions is provided in Table 4.

6. Conclusions and future research directions

Of the alternative fuels available for the road transport sector, ethanol is widely accepted as a renewable fuel for SI engines when blended with neat gasoline due to its favorable physicochemical properties. However, there are substantial inconsistencies in current findings regarding NO_x emissions from SI engines fuelled with gasoline/ethanol blends, which could represent a considerable obstacle to the market expansion of bioethanol. Therefore, we analyzed NO_x emissions related to the use of ethanol/gasoline blends in SI engines, providing a comprehensive literature review on the current state of ethanol combustion in SI engines to explain the reported inconsistencies.

Table 4.An overview of the main experimental results indicating the effect of ethanol concentration and operating conditions on NO_x emissions using gasoline/ethanol blended fuels in SI engines.

Engine type	Ethanol concentration in ethanol/gasoline blends	Operating conditions	Effect on NO _x emissions	Reference
1C, 4S, MFIE CR=9.6:1	0%, 10%, 30%, 60%	Engine speed=1200 rpm BMEP=3 and 5 bar	E% ↑ ⇒ NO _x ↓	Li et al. (2017)
4C, 4S, CR=8.8:1	0%, 10%, 20%, 30%	Engine speed=2000-4500 rpm	E% ↑ ⇒ NO _x ↓	Dogan et al. (2017)
4C, 4S, EIS, WC	0%, 10%, 20%, 30%	Cold and hot conditions	E% ↑ ⇒ NO _x ↓	Iodice et al. (2018)
1C, 4S, EIS	0%, 25%, 50%, 75%, 100%	Engine speed=1500-4000 rpm, CR=6:1 and 10:1	E% ↑ ⇒ NO _x ↓	Celik (2008)
1C, 4S, CR=5.1-13:1	0%, 50%, 85%	Engine speed=1000-5500 rpm, CR=10:1 and 11:1	E% ↑ ⇒ NO _x ↓	Koç et al. (2009)
4C, 4S, MIS, WC CR=10.4:1	0%, 5%, 10%	WP=5-20 kW Speed=80-100 km/h	E% ↑ ⇒ NO _x ↓	Canakci et al. (2013)
1C, 4S, EDI+GPI AC, CR=9.8:1	0%, 24.3%, 48.4%, 60.1%	Engine speed=3500-5000 rpm	E<24% ⇒ NO _x ↑ E>24% ⇒ NO _x ↓	Zhuang and Hong (2013)
4C, 4S, IFI CR=10.2:1	0%, 10%, 20%	Steady-state conditions	E% ↑ ⇒ NO _x ↓	Tibaquirá et al. (2018)
1C, CR=10.5:1	0%, 10%, 20%, 30%, 40%	Engine speed=2000 rpm	E% ↑ ⇒ NO _x ↓	Schifter et al. (2013)
4S, CE and FIE	0%, 15%	Constant engine speed	CE ⇒ NO _x ↓ FIE ⇒ NO _x ↑	Yao et al. (2013)
1C, CR=10.5:1, AC	0%, 100%	Engine speed=1600-3600 rpm	NO _x ↓	Balki et al. (2014)
1C, CR=9.5:1, GPI	0%, 25%, 50%, 75%, 100%	IMEP=3 and 5 bar	E% ↑ ⇒ NO _x ↓	Broustail et al. (2012)
4C, FFE, CR=10.35:1	25%, 30%, 50%, 80%, 100%	Load=60 and 105 Nm	60 Nm ⇒ NO _x ↓ 105 Nm ⇒ NO _x ↑	Melo et al. (2012)
1C, DI, CR=9.5:1	0%, 5%, 25%, 85%, 100%	Engine speed=2000 rpm	E<25% ⇒ NO _x ↑ E>25% ⇒ NO _x ↓	Gomes et al. (2011)
4C	0%, 10%, 25%, 50%, 85%	Constant engine speed	E% ↑ ⇒ NO _x ↓	Bielaczyc et al. (2011)
MFIE, CR=9.8:1	0%, 5%, 10%, 20%, 30%, 40%	Cold start condition	E<10% ⇒ NO _x ↑ E>10% ⇒ NO _x ↓	Chen et al. (2011)
1C, AC, CR=11.3:1	0%, 5%, 10%, 15%	Engine speed=2500, 5000, 6500 rpm	E% ↑ ⇒ NO _x ↓	Wen et al. (2010)
DI, TC	0%, 10%, 20%	Steady-state conditions	E% ↑ ⇒ NO _x ↓	Storey et al. (2010)
DI, CR=12:1	0%, 25%, 50%, 85%	Steady-state conditions	E% ↑ ⇒ NO _x ↓	Oh et al. (2010)
4C, CR=12:1	22%, 100%	Engine speed=2500-6000 rpm	E% ↑ ⇒ NO _x ↑	Costa and Sodr� (2010)
1C, CR=10.5:1	0%, 6%, 10%, 15%, 20%	Engine speed=2000 rpm	E% ↑ ⇒ NO _x ↓	Schifter et al. (2011)
4S, DI, CR=11.5:1	0%, 10%, 20%, 30%, 50%, 85%, 100%	Engine speed=1500 rpm; IMEP=3.4 bar	E% ↑ ⇒ NO _x ↓	Turner et al. (2011)
1C, HUCR, CR=8.1-9:25	0%, 5%, 10%, 15%, 20%, 25%, 30%	Engine speed=1500 rpm	E% ↑ ⇒ NO _x ↓	Al-Baghdadi (2008)
4C, CR=9.7:1	0%, 5%, 10%, 15%, 20%	Engine speed=1000-5000 rpm	E% ↑ ⇒ NO _x ↑	Najafi et al. (2009)
4C, CR=10.5:1	0%, 85%, 100%	Engine speed=3500 rpm	E% ↑ ⇒ NO _x ↓	Yoon et al. (2009)
3C, 4S, WC, CR=8.7:1	0%, 50%, 60%	Engine speed=2000-2800 rpm	E% ↑ ⇒ NO _x ↓	Srinivasan and Saravanan, (2010)
1C, 4S, AC, CR=5.1:1	0%, 10%	Engine speed=3000 rpm	E% ↑ ⇒ NO _x ↓	Singh et al. (2014)
4C, MIS, CR=10:1	0%, 15%	Engine speed=1000-6000 rpm	E% ↑ ⇒ NO _x ↓	Masum et al. (2015)
1C, 4S, AC, CR=8.5:1	0%, 3%, 6%, 9%,	Engine speed=3600 rpm WP=865, 1730, 2595 W	E% ↑ ⇒ NO _x ↓	Lin et al. (2010)
1C, 4S, WC	0%, 1.5%, 12%	Engine speed=1500 rpm CR=7.7:1 and 8.2:1	E% ↑ ⇒ NO _x ↑	Bayraktar (2005)
EIS, CR=8.2:1	0%, 10%, 30%	Close-loop control at part engine load; Open-loop control at full engine load	E% ↑ ⇒ NO _x ↓	He et al. (2003)

Table 4.
continued.

Engine	Ethanol concentration in ethanol/gasoline blends	Operating conditions	Effect on NO _x emissions	Reference
1C, CR=8:1	0%, 5%, 20%	IMEP=4.5 bar	E% ↑ ⇒ NO _x ↓	Zervas et al. (2003)
1C, 4S, CE	0%, 10%, 20%, 40%, 60%, 80%	Engine speed=2000 rpm Wide open throttle conditions	E% ↑ ⇒ NO _x ↓	Gravalos et al. (2011)
1C, 4S, CR=10:1	0%, 10%, 15%, 20%, 25%	Engine speed=1300-1800 rpm	E% ↑ ⇒ NO _x ↑	Dhande et al. (2021)
4C, 4S, CR=9.6	0%, 10%, and 20%	Engine speed=1000-5000 rpm, Different spark timing, and different throttle angle	Throttle angle ↑ ⇒ NO _x ↓, spark timing ↑ ⇒ NO _x ↓, RPM ↑ ⇒ NO _x ↓	Tian et al. (2020)
1C, 4S, CR=10.0	0% and 20%	Engine speed=1500 rpm, Loads: 33, 58, and 83%	Load ↑ ⇒ NO _x ↑	Biswal et al. (2020)
1C, 4S, MPFI, CR=8.8	0% and 10%	Engine speed=2000 rpm, Loads: 50 and 100%	Low load ⇒ NO _x ↓, High load ⇒ NO _x ↑	Agarwal et al. (2020)
4C, 4S, CR=7, carbureted	0% and 10%	Engine speed 1600-2400 rpm, full load	Max NO _x was recorded at 2500 rpm, E% ↑ ⇒ NO _x ↑	Örs et al. (2020)
1C, 4S, CR=8.5	0%, 10%, 20%, 30%, and 40%	Engine speed 1500-2500 rpm, Idle load	E% ↑ ⇒ NO _x ↓ Engine speed ↑ ⇒ NO _x ↑	Mohammed et al. (2021)
4C, 4S, CR=10.5	0%, 5%, 10%, 20%, 30%, and 50%	Engine speed 1000-6000 rpm (12 points), load 0-100%	Engine speed ↑ ⇒ NO _x ↑, E% ↑ ⇒ NO _x ↑	Iliev (2021)
4C, 4S, CR=9.5	0%, 10%, 20%, and 30%	Engine speed 3000 rpm, load 40%	E% ↑ ⇒ NO _x ↓	Rosdi et al. (2020)
1C, 4S, CR=7	0%, 5%, 10%, 15%, 85%, and 100%	Engine speed 2500 rpm, Engine load 2, 2.5, 3, 3.5, and 4 Nm	E% ↑ ⇒ NO _x ↑	Kul and Ciniviz (2021)
4C, 4S, CR=11	0% and 20%	Engine speed 2800 rpm, Engine load 25%, 50%, 75%, and 100%	E% ↑ ⇒ NO _x ↓, Engine load ↑ ⇒ NO _x ↓	Taghavifar, et al. (2020)
4C, 4S, CR=9.6	0%, 25%, 50, 75, and 100%	Engine speed 2100 rpm, 5 ignition timings	E% ↑ ⇒ NO _x ↓, Advancing ignition timing ↑ ⇒ NO _x ↑	Liu et al. (2021)

Overall, it is envisioned that such wide-ranging and, at times, conflicting data should provide a platform for future studies in all areas of alcohols application as alternative fuels and related exhaust emissions to steer advancements in techniques used for reducing emissions and, in particular, NO_x emissions.

The key conclusions which could be drawn from the present work can be summarised as follows:

- NO_x emission levels of SI engines decrease with the rise in ethanol concentration in ethanol/gasoline blends due to the higher latent heat of vaporization and lower heating value of gasoline/ethanol blends than commercial gasoline. More specifically, upon using gasoline/ethanol blends, the temperature of the air/fuel mixture drops at the end of the intake stroke, thus leading to reductions in the combustion temperature and hence in thermal NO_x emissions. Such decreases in NO_x emissions also result from the lower combustion temperature due to the high oxygen content in the ethanol molecules.
- It can also be argued that NO_x emissions decrease with increasing ethanol concentration in blended fuels due to the lower carbon number of ethanol than gasoline. In effect, the combustion process of ethanol/gasoline blends shows that, under stoichiometric operating conditions, a lower amount of air is required compared to neat gasoline.
- As the RON of ethanol is higher than that of gasoline, a higher compression ratio can be used in SI engines. Hence, the fuel economy penalty resulting from ethanol's lower energy content can be offset by an increase in the thermal efficiency of SI engines with high compression ratios when fuelled with gasoline/ethanol blends. However, NO_x emissions should increase with increasing compression ratios, especially at high engine loads due to the resulting higher combustion temperatures.
- The faster flame speed of ethanol than gasoline plays an important role in achieving more complete combustion in rich-mixture operating conditions. However, at the same time, an increase in NO_x emissions is

observed at high engine loads. In effect, to increase the engine speed and load, a richer mixture is required. The resulting complete combustion process of ethanol/gasoline blends increases in-cylinder temperature and, hence, thermal NO_x emissions. On the other hand, based on the experimental data available, under low engine speeds and loads, there are no considerable differences observed in NO_x emissions of SI engines fuelled by different gasoline/ethanol blends.

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