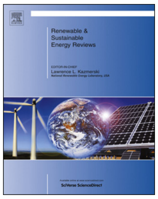
Renewable and Sustainable Energy Reviews 24 (2013) 209–222

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



Effect of ethanol–gasoline blend on NOx emission in SI engine

B.M. Masum*, H.H. Masjuki, M.A. Kalam, I.M. Rizwanul Fattah,
S.M. Palash, M.J. Abedin

Centre for Energy Sciences, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

ARTICLE INFO

Article history:
Received 25 July 2012
Received in revised form
10 March 2013
Accepted 15 March 2013
Available online 16 April 2013

Keywords:
Ethanol
Nitrogen oxide
SI engine
Renewable energy
Emission

ABSTRACT

The stricter worldwide emission legislation and growing demands for lower fuel consumption and anthropogenic CO_2 emission require significant efforts to improve combustion efficiency while satisfying the emission quality demands. Ethanol fuel combined with gasoline provides a particularly promising and, at the same time, a challenging approach. Ethanol is widely used as an alternative fuel or an effective additive of gasoline due to the advantage of its high octane number and its self-sustaining concept, which can be supplied regardless of the fossil fuel. As a result, vast study has been carried out to study its effects on engine performance and emission.

The first part of this article discusses prospect of fuel ethanol as a gasoline substitute. Then it discusses comparative physicochemical properties of ethanol and gasoline. The slight differences in properties between ethanol and gasoline fuels are enough to create considerable change to combustion system as well as behaviors of SI engines. These effects lead to several complex and interacting mechanisms, which make it difficult to identify the fundamentals of how ethanol affects NOx emission. After that, general NOx forming mechanisms are discussed to create a fundamental basis for further discussion. Finally, the article discusses different fuel composition, engine parameter and engine modification effects on NOx formation as well as mathematical approach for NOx prediction using ethanol.

Contents

---

* Correspondance to: Department of Mechanical Engineering, University of Malaya, 50603, Kuala Lumpur, Malaysia. Tel.: +603 79674448; fax: +603 79675317.

E-mail addresses: masum05me@gmail.com, masum079@yahoo.com (B.M. Masum).

http://dx.doi.org/10.1016/j.rser.2013.03.046

1. Introduction

The consumption of energy has ever-increasing trend mainly due to two reasons: (1) changes in lifestyles and (2) the significant growth of the population. Petroleum-based fossil fuels presently provide the major portion of the energy supply; however, their sources are limited on this Earth. In the twentieth century, the research emphasis was on the development of fossil crude oil, coal, and natural gas based refinery to exploit the cheaply available fossil feedstock to meet the growing demand of the population [1]. In the 21st century, the adverse effect of greenhouse gas emissions on the environment, together with declining petroleum reserves and future energy security, is pronounced well. The combustion of fossil fuels is a big contributor to carbon dioxide (CO_2) emission, which is a direct contributor to global warming. Every year about 25 billion ton of CO_2 are generated worldwide by anthropogenic activities [2]. Therefore, the present research is focused on alternative energy sources for sustainable development of the economy and society [1]. Fossil fuels still represent 80% of total energy supply whereas biofuel contribute only 1% [3].

The main alternative fuels utilized so far are oxygenates (alcohol, ether etc.), vegetable oils and their esters, gaseous fuel (hydrogen, liquefied petroleum gas etc.), gas to liquids (GTL) and coal derivatives. Ethanol has attracted attention worldwide because of its potential use as an alternative automotive fuel [4]. Use of ethanol as a fuel is not a new concept. In 1826, Samuel Morey developed an engine that ran on ethanol [5]. The use of ethanol blended with diesel was a subject of research in the 1980s. At that time, it was shown that ethanol blends were technically acceptable as a fuel for existing engines. However, the relatively high production cost of ethanol at that time hindered its regular use and made it a backup fuel in cases of fuel shortages. However, the economics have become much more favorable for the production of ethanol and it is now able to compete with standard petroleum-based fuel [6].

Ethanol is a green fuel because the growing sugarcane crops function as a CO_2 sink, thereby contributing to the reduction of greenhouse gases (GHG) [7]. Recently, ethanol has been used extensively as a fuel additive or an alternative fuel in spark ignition (SI) engines as well as in diesel engines as it is a high octane, clean-burning fuel [8,9]. Burning of ethanol in SI engines also reduces emissions of carbon monoxide (CO), hydrocarbon (HC), and so on, but there are some inconsistencies in NOx emissions as shown by many researchers. The Environmental Protection Agency (EPA) listed NOx as one of the critical pollutants that can affect the respiratory system. As the use of ethanol has increased enormously, NOx emission could become a significant barrier to its market expansion.

The objective of this report is to provide a thorough literature review on the current state of ethanol combustion in SI engines and to guide the continuing study of NOx emissions reduction techniques using ethanol. Previously many researchers worked with ethanol production [3,4,10–12] and its use in a gasoline engine [13–15]. Many review articles are also available on the effect NOx emission for different biofuels [16–20]. This article exclusively focuses on the issue of NOx emissions related to use of ethanol in gasoline engine. There are many published studies on ethanol use as an alternative fuel in SI engines, as will be summarized next, to explain the potential change in NOx emissions with ethanol fuels. However, there are considerable inconsistencies in the explanations, which make fundamental understanding incomplete.

2. Ethanol fuel as a gasoline substitute

Ethanol (C_2H_5OH) is an ecological fuel, as it is obtained from renewable energy sources. It is a colorless, transparent, neutral, volatile, flammable, oxygenated liquid hydrocarbon, which has a pungent odor and a sharp burning taste [4]. At present, however, blends of bioethanol and gasoline are more common in vehicles with fuel injection engines. Bioethanol and ethanol is practically the same product. They have the same molecular and structural formula, and are the same substance. In other words, bioethanol is just plain ethanol, which is produced from sugar derived from plants. Usually, it is produced from various feed stocks such as sugar cane, sugar beet, sorghum, grain, switch grass, barley, hemp, kenaf, potatoes, sweet potatoes, cassava, sunflower, fruit, molasses, corn, stover, grain, wheat, straw, cotton, and other biomass, as well as many types of cellulose wastes and harvests.

Generally, ethanol or bioethanol is more reactive than hydrocarbon fuels, such as gasoline [21]. It contains hydroxyl radicals as the polar fraction and carbon chains as the non-polar fraction; hence it can be easily dissolved in both non-polar (e.g. gasoline) and polar (e.g. water) substances [21]. Because of the regenerative and biodegradable characteristics of ethanol, it is widely used as an alternative fuel at present. The use of gasoline containing 3–10 vol% bioethanol is being promoted in many parts of the world for last few years [22]. The use of pure ethanol requires some modifications to SI engines; thus low concentration blends of ethanol are usually used without any modification of the SI engine [23]. Tables 1 and 2 show the advantages and disadvantages of using ethanol over gasoline.

Worldwide ethanol production in terms of feedstock can be categorized into three major groups [23]:

1. Ethanol from sucrose-containing biomass such as sugar cane, sugar beet, sweet sorghum and fruits.
2. Ethanol from starchy biomass such as corn, milo, wheat, rice, potato, cassava, sweet potatoes, and barley.
3. Ethanol from lignocellulosic biomass such as wood, straw, and grasses.

Ethanol produced from above-mentioned feedstocks is classified into two groups [23,24]:

1. First generation bioethanol that consists of both ethanol from sucrose-containing biomass and ethanol from starchy biomass.
2. Second generation bioethanol or ethanol from lignocellulosic biomass.

Table 1
Advantages of ethanol fuel over gasoline.

Ethanol is a renewable fuel	[32]
Ethanol could reduce petroleum imports, improve the balance of payments, improve national energy security, and reduce the reliance on petroleum from unstable areas of the world.	[32]
Bioethanol if cheaply produced can reduce demands for fossil fuels and the growth in fossil fuel prices.	[32,33]
Bioethanol could create stronger demands for feedstocks, thus boosting agricultural prices and producers' incomes.	[32]
Ethanol has high octane number	[34–37]
Higher latent heat of ethanol increases volumetric efficiency.	[38,39]
Ethanol provides more oxygen in the combustion process, which assists in complete burning.	[8,40]
Lower vapor pressure of ethanol reduces the evaporative emissions.	[41]
Ethanol has high laminar flame propagation speed, which makes combustion process to be finished earlier and broadens its flammability limit.	[39,42–45]
Ethanol increases thermal efficiency.	[36,41,46,47]
Ethanol increases engine torque output.	[48]
Ethanol allows the use of high compression ratio without knocking.	[34–36,49]
As oxygenated produce cleaner emission	[33,34,37,39,50,51]
Ethanol is used in direct injection gasoline engine to avoid knocking.	[52]
Ethanol burn reduces greenhouse gas emission significantly.	[4,41,53,54]
Ethanol is easily miscible in gasoline.	[55]
Ethanol is used widely as an oxygenated portion in gasoline.	[56]
Ethanol is less toxic than gasoline.	[49]

Table 2
Disadvantages of ethanol fuel over gasoline.

Energy content of ethanol is lower.	[34,50,57,58]
Lower vapor pressure of ethanol can contribute to produce unregulated pollutants like aldehydes.	[59]
Ethanol use can enhance corrosion on ferrous components such as fuel tank.	[60]
Ethanol is a triatomic molecule that results in higher gas heat capacity and lower combustion gas temperature.	[35]
Low vapor pressure of ethanol makes starting cold engine difficult.	[32,57]

Bioethanol production is achieved through fermentation of glucose in sugars and starchy biomass. There are two main ways to produce ethanol: one is alcoholic formation and another is the reaction of ethane with steam, as shown in Eqs. (1)–(3) [25,26].

Alcoholic fermentation [21]:

$$\underset{\text{(Glucose)}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow x\underset{\text{(Glucose)}}{C_2H_{12}O_6} + (2-x)\underset{\text{(Fructose)}}{C_6H_{12}O_6} \quad (1)$$

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

Reaction of ethane with steam:

$$\underset{\text{(Ethane)}}{C_2H_4} + \underset{\text{(Steam)}}{H_2O} \rightarrow \underset{\text{(Ethanol)}}{C_2H_5OH} \quad (3)$$

World ethanol production as a fuel increased steadily throughout last decade (Fig. 1). In 2012, the total production of ethanol fuel reached 85.985 billion L. The United States is the largest ethanol producer in the world with 88.4% of the total production level. Fuel ethanol production has increased remarkably, because many countries are now looking for reducing oil imports, boosting rural economies and improving air quality. Ethanol–gasoline blends are used in many parts of the world such European Union, Brazil, Thailand and Canada [27,28]. The Brazilian government has made the use of ethanol obligatory since 1976. They follow two approaches with regard to ethanol use: one is the mandatory use of ethanol–gasoline blends and the other one is expansion of the market of flex-fuel cars. Approximately, 90% of new cars which are sold in Brazil have flex-fuel engine and gasoline sold contains 20–25% anhydrous ethanol [29]. Many countries have already implemented or implementing programs for addition of ethanol to gasoline (Table 3). Most of the vehicles run on up to 10% ethanol blends. Additionally, manufacturers design vehicles to run with higher ethanol blends [30].

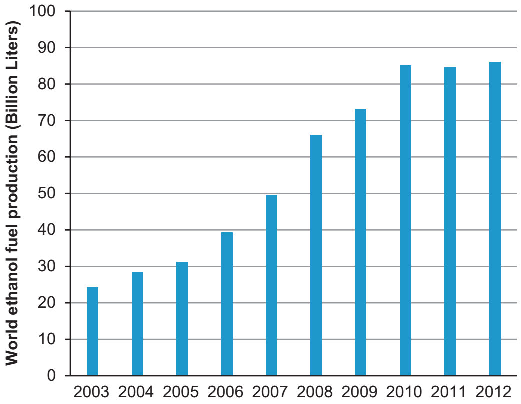


Fig. 1. World ethanol fuel production [31].

Table 3
Forms of ethanol use in different countries [61].

Country	Feedstock	Percentage of ethanol in gasoline blends, (%) (v/v)
Brazil	Sugar can	24
USA	Corn	10
Canada	Corn, wheat, barley	7.5–10
Colombia	Sugar cane	10
Spain	Wheat, barley	–
France	Sugar beet, wheat, corn	–
Sweden	Wheat	5
China	Corn, wheat	–
India	Sugar cane	5
Thailand	Cassava, sugar cane, rice	10

3. Comparison of physicochemical properties

The physical and chemical properties indicate the quality of fuel to be combusted in an engine. Engine combustion quality, performance and emission characteristics are dependent on them. Some of the properties related to combustion of gasoline as well as ethanol are compared in Table 4. The comparative features of ethanol and gasoline are presented below:

1. Heating value of ethanol is approximately 1/3 times lower than that of gasoline. Thus, to achieve same engine power output more amount fuel is required for ethanol.
2. An oxygen content of 34.7 wt% in ethanol promotes combustion efficiency as well as high combustion temperature.
3. Heat of vaporization of ethanol is higher than gasoline. Thus, charge requires more heat to evaporate which is taken up from in-cylinder environment. This in turn increases the volumetric efficiency of the engine.
4. Ethanol has slightly lower density than gasoline, thus volumetric-operating fuel pumps inject lower mass of alcohol than gasoline fuel.
5. Ethanol has no mono-aromatic or poly-aromatic hydrocarbons.
6. Lower C/H atom ratio of ethanol reduces the adiabatic flame temperature.
7. Ethanol has higher octane number (ON) than gasoline. The higher the octane number, the more compression the fuel can withstand before detonating. Premature fuel ignition can damage engine, which is a common phenomenon for lower ON fuel.
8. Ethanol has a higher laminar flame propagation speed than gasoline, which makes combustion process finish earlier and thus improving the engine thermal efficiency.
9. Using ethanol with gasoline can reduce costs of petroleum refineries as they can produce low-grade gasoline with lower ON.

4. Formation of NOx

NOx is a mixture of such compounds: nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), dinitrogen trioxide (N_2O_3), dinitrogen tetroxide (N_2O_4), and dinitrogen pentoxide (N_2O_5) [67]. Among them, nitric oxide (NO) and nitrogen dioxide (NO_2) are most prominent [68]. The other five nitrogen oxides are known to exist, but in very small quantities. Nitric oxide is a colorless, odorless gas. Its ambient concentration is usually far less than 0.5 ppm. Nitrogen dioxide is a corrosive, toxic, and reddish-brown gas. It is quite visible in sufficient amounts [69,70]. Oxidation of nitrogen molecules at high temperature inside the

Table 4
Comparison of gasoline and ethanol fuel properties [8,49,50,56,62–66].

Property	Unit	Gasoline	Ethanol
Chemical formula	–	C_5–C_{12}	C_2H_5OH
Molecular weight	kg kmol^{-1}	114.15	46.07
C-fraction	mass %	87.4	52.2
O-fraction	mass %	0	34.7
H-fraction	mass %	12.6	13.0
H/C	atom ratio	1.795	3
O/C	atom ratio	0	0.5
Specific gravity	–	0.7–0.78	0.794
Density (at 15 °C)	kg m^{-3}	750–765	785–809.9
Stoichiometric air–fuel ratio	w/w	14.2–15.1	8.97
Kinematic viscosity	mm^2/s	0.5–0.6	1.2–1.5
Reid vapor pressure at 37.8 °C	kPa	53–60	17
Research octane number	–	91–100	108.61–110
Motor octane number	–	82–92	92
Cetane number	–	8	5–20
Enthalpy of formation			
(a)Liquid	kJmol^{-1}	−259.28	−224.1
(b)Gas	kJmol^{-1}	−277	−234.6
Higher Heating Value	MJ kg^{-1}	47.3	29.7
Lower Heating Value	MJ kg^{-1}	44.0	26.9
LHV at stoichiometric mixture	MJ kg^{-1}	2.77	2.70
Latent of vaporization	kJ kg^{-1}	380–400	900–920
Specific heat			
(a)Liquid	kJ/kgK	2.4	1.7
(b)Vapor	kJ/kgK	2.5	1.93
Freezing Point	°C	−40	−114
Boiling Point	°C	27–225	78
Flash point	°C	−45 to −13	12–20
Auto ignition temperature	°C	257	425
Vapor Flammability Limits	vol%	0.6–8	3.5–15
Laminar flame speed at 100 kPa, 325 K	cm/s	~33	~39
Distillation			
(a)Initial boiling point	%	45	78
(b)10	%	54	78
(c)50	%	96	78
(d)90	%	168	79
(e)End boiling point	%	207	79
Water solubility	%	0	100
Aromatics volume	%	27.6	0
Vapor toxicity	–	Moderate irritant	Toxic in large doses
Smoke character	–	Black	Slight to none
Conductivity	–	None	Yes
Color	–	Colorless to light amber glass	Colorless

cylinder is the cause of NOx formation as a byproduct [71]. The pathways of formation of oxides of nitrogen such as Thermal, Prompt, Fuel NOx and N_2O intermediate mechanisms are discussed here.

4.1. Thermal NOx

During combustion, at temperatures above 1800 K, atmospheric nitrogen reacts with oxygen through a series of chemical steps known as the Zeldovich mechanism [72]. This mechanism of thermal NOx formation is believed to be the predominant contributor of total NOx [73]. The Eqs. (4)–(6) are the basic kinetic equations for thermal NOx formation.

$$O+N_2 \leftrightarrow NO+N \tag{4}$$

$$N+O_2 \leftrightarrow NO+O \tag{5}$$

$$N+OH \leftrightarrow NO+H \tag{6}$$

The first step determines the NOx formation as it requires high temperatures to proceed due to its high activation energy (314 KJ/mole). NO production by thermal mechanism proceeds at a slower rate than the oxidation of hydrocarbons. The NO formation rate can be written using Eq. (7) [74].

$$\frac{d[NO]}{dt} = k\,e^{-K/T}[N_2][O_2]^{1/2}t^{-1/2} \tag{7}$$

Here k and K is reaction constants, t is time and T is absolute temperature [75]. Eq. (7) represents a strong dependence of NO formation rate on temperature. High temperatures, high oxygen concentrations, and longer residence time results in high NO formation rate.

4.2. Prompt NOx

The presence of a second mechanism leading to NOx formation was first identified by Fenimore [76] and was termed “prompt NOx”. During combustion of hydrocarbon fuels, some NOx is quickly formed before formation of thermal NOx, in the laminar premixed flame zone, which is known as prompt NOx [77]. There is a good evidence that prompt NOx can be formed in a significant quantity in some combustion environments; such as in low-temperature, fuel rich conditions and where residence time is short. Prompt NOx is most prevalent in rich flames. The actual formation involves a complex series of reactions and many possible intermediate species. Generally, in low temperature (below 750 °C) and fuel rich condition, nitrogen molecules react with hydrocarbon radicals to form amines or cyano compound. After that, these nitrogen-containing fragments react with atmospheric nitrogen to form NO. The prompt NOx is generally formed through the following reactions (8)–(12).

$$CH+N_2 \leftrightarrow HCN+N \tag{8}$$

$$CH_2+N_2 \leftrightarrow HCN+NH \tag{9}$$

$$N+O_2 \leftrightarrow NO+O \tag{10}$$

$$HCN+OH \leftrightarrow CN+H_2O \tag{11}$$

$$CN+O_2 \leftrightarrow NO+CO \tag{12}$$

Here, CH and CH_2 are the significant contributors to form prompt NOx (Eqs. (8) and (9)). Prompt NOx is more sensitive to fuel chemistry than thermal NOx because of the dependence on hydrocarbon fragments. The amount of HCN increases with increasing the concentration of hydrocarbon radicals, which enhances with increasing equivalence ratio. Prompt NOx formation increases with an increasing equivalence ratio and then reaches a peak and decreases because of a shortage of oxygen. Compared to thermal NOx formation, the contribution of prompt NOx is less in entire combustion system. However, in combustion modeling studies, without considering prompt NOx mechanism, total NOx is underestimated [78].

4.3. Intermediate N_2O

The NOx formation by this pathway is another essential mechanism in a combustion process under high pressure and lean air–fuel ratio or low temperature condition compared to Fenimore NO, and a minor contribution to the formation of NOx related to the thermal NO mechanism [79]. Three steps of this NOx formation mechanism are shown in Eqs. (13)–(15).

$$O+N_2+M \leftrightarrow N_2O+M \tag{13}$$

$$H+N_2O \leftrightarrow NO+NH \tag{14}$$

$$O+N_2O \leftrightarrow NO+NO \tag{15}$$

Here, M is a general third body that is required to complete this reaction [73]. Reaction rates strongly depend on O, OH and H radial concentrations, which makes the mechanism favored for oxygen-rich conditions or lean condition [80].

4.4. Fuel NOx

When nitrogen-containing fuel compound are oxidized to NOx during combustion process, fuel NOx is formed [81]. Fuel NOx increase with the amount of nitrogen content of the fuel. Moreover, it is co-related with oxidation of the hydrocarbon and its chemical kinetics. However, the nitrogen level in the gasoline or ethanol fuel is extremely low; hence, fuel NOx formation is negligible.

5. Effect of ethanol–gasoline blend on NOx emission

Many studies have been done on SI engines as well as flex-fuel vehicles using either pure ethanol or ethanol–gasoline blends as a fuel. Section 3 shows some dissimilarity in properties between ethanol and gasoline. These properties may affect in fuel consumption, combustion speed, combustion temperature, mass burn fraction etc. as well as NOx emission. Many literatures [56,82–87] have shown increase in NOx emission for ethanol. Opposite trend was also observed by many researchers [29,88–90] as well. Few literatures [91,92] also found irregularity in NOx emission with ethanol. In this section, NOx emission causes will be discussed for ethanol–gasoline blends, emphasizing on different fuel blends, different engine parameters and engine modifications as well as different vehicle conditions.

5.1. Effect of fuel composition

5.1.1. Effect of blend concentration

Researchers have tested ethanol–gasoline blends from 5 vol% ethanol to as high as 100 vol% i.e. pure ethanol in SI engines. The physicochemical properties of different ethanol–gasoline blends are summarized in Table 5. These results presented have been obtained by different test methods as done by the researchers. From Table 5 it can be seen that the addition of ethanol to gasoline simultaneously increases the octane number, density, and latent heat of vaporization and decreases the heating value of the ethanol–gasoline blend. Many investigations have been carried out to identify the effect of these changes on emission characteristics especially on NOx emission due to variation in ethanol contents.

Table 5
Properties of different ethanol–gasoline blended fuels [36,40,50,56,62,82,93–96].

Property	E0	E5	E10	E15	E20	E25	E30	E40	E50	E60	E85
Density (kg/m^3)	757.5	759.1	760.8	776	764.5	775	768.2	780.6	751	789.5	
RVP (kPa)	53.7	59.3	59.6	58.8	58.3		56.8	63	45.3	57.4	37.85
RON	95.4	96.7	98.1	98.5	100.7	100	102.4	90.9	101.2	92.7	101.7
Sulfur (wt%)	0.0061	0.0059	0.0055	0.0063	0.0049	0.0246	0.0045	0.026	< 0.001	0.032	< 0.001
Distillation temperature (°C)											
(a) Initial boiling point	35.5–38.8	36.5	37.8	37.9	36.7–38.6		37.2–39.5	39.6	328.3		
(b) 10 vol%	54.5–56.1	49.7	50.8–52.9	51.7	51.3–52.8	58.1	52.1–54.8	53.4			73.9
(c) 50 vol%	94.4–109.6	88	71.1–95.8	72.6	70.3–73.8	71.7	72.4–74.6	72.5	521		78.0
(d) 90 vol%	167.3–206.3	167.7	157–166.4	165.3	165.2–163		154.6–159.3	152.7	547		78.7
(e) End point	197.0	202.5	197.5–208.4	198.1	198.6–203.6	177.9	198.3–205.1	204.1			79.9
Heating value (MJ/kg)	42.58–42.7	40.55–41.78	39.79–41	41.61	38.98–39.5	38.2	36.32–37.8	33.34–36.2	33.34	26.74	29.2

RVP = Reid vapor pressure, RON = Research Octane Number.

Many literatures have showed that, NOx emission decreases with the increase in content of ethanol. Turner et al. [66] investigated NOx emission in a direct injection spark ignition (DISI) engine on a 1500 rpm and 3.4 bar indicated mean effective pressure (IMEP) with ethanol–gasoline blends. When the ethanol portion increased up to 85% in the blend, NOx emission was reduced. They attributed this reduction to reduction in flame temperature, which was corroborated by a reduction in exhaust temperature. The NOx level then increased slightly for pure ethanol because combustion was advanced, leading to a higher in-cylinder pressure and temperature compared to those of 85% ethanol. Here the maximum in-cylinder pressure was reduced with an ethanol blend of up to 85% and then increased for pure ethanol. Bielaczyc et al. [62] also found decreased NOx for 10–85% ethanol blends. They evaluated the possibility of using gasoline–ethanol blends in a modern Euro 4 vehicle without substantial engine modification. NOx emission from the engine was found to give a perfect linear fit with the ethanol content of the blend over the range 10–85%. Oh et al. [65] studied a DISI engine with 25%, 50% and 85% ethanol–gasoline blends. They found that HC emissions increased and NOx emissions decreased with increase of ethanol percentage in blend due to the decreased peak in-cylinder temperature resulting from the combustion retardation.

Ioannis et al. [97] investigated NOx emission with different blends at 2000 rpm in wide open throttle (WOT) condition. From Fig. 2, it is seen that, NOx emission decreased with increasing ethanol concentration. Because of the higher heat of vaporization of ethanol compared to gasoline, the combustion temperature of the blend decreases. In case of HC emission, up to certain conc. of ethanol, HC emission is reduced as the oxygen content of ethanol causes the reaction to move towards complete combustion. However, a greater concentration of ethanol in the gasoline reduces the flame temperature, which increases HC emission. It is seen that E40 is a good option for reduced HC emission and E80 is suitable for lower NOx emission.

In a four-cylinder, multi-port injection system engine, Canakci et al. [50] found that NOx emission decreased as the ethanol percentage of the blend increased. With the use of alcohol in gasoline, the combustion temperature decreased due to the high latent heat and lower heating value, which led to the reduction of NOx emission. When comparing the exhaust emission of gasoline with pure ethanol, Balki et al. [98] found lower NOx emission for ethanol than gasoline. They attributed this reduction to the higher heat of vaporization of ethanol, which reduces the combustion temperature. However oxygenated fuel ethanol enhances combustion efficiency, which results in lower CO_2 emission and higher HC and CO emission for ethanol than gasoline. Using a lower percentage of ethanol, Yao et al. [99] found similar results. They ascribed this to lower flame temperature because of the higher latent heat of evaporation of ethanol.

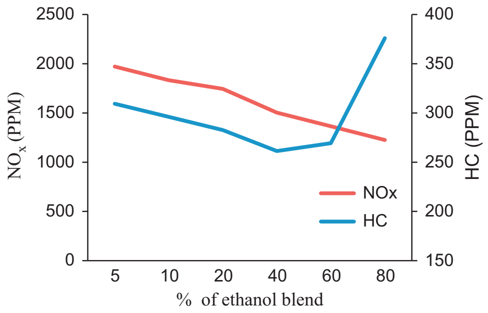


Fig. 2. Correlation of NOx and HC emission with ethanol percentage at 2000 rpm [97].

Considering a DISI engine, Storey et al. [100] analyzed the effect of ethanol addition and concluded that NOx emission decreased with increased ethanol concentration because of the lower energy density of the ethanol blend. Lin et al. [101] experimented on a small engine generator to observe the effect of ethanol–gasoline blend on exhaust emission and efficiency. Ethanol–gasoline blend led to a significant reduction in NOx emissions by approximately 35%, 86% and 77% on average with E3, E6, and E9 fuels respectively. The best results were obtained with E6 fuel in term of exhaust emissions and E9 fuel for engine performance.

Wu et al. [63] explained that NOx emission decreased with increases in the H/C atom ratio of fuel. From Table 4, it is seen that H/C atom ratio is higher for ethanol than for gasoline. In his experimental results, NOx emission was lower for ethanol than for gasoline. Broustail et al. [102] found a slight reduction in NOx using ethanol with gasoline than compared to pure gasoline.

Using a motorcycle engine Chen et al. [103] investigated the effect on emission of ethanol–gasoline blends (E3, E5, E10, E15, E20, E25 and E30). With an increase in the ethanol concentration, the particle diameter of the accumulation mode becomes smaller. The aerosol number concentration decreases with increases in ethanol concentration which causes combustion to become complete. For this reason, CO and NOx emissions decreased with increases in ethanol concentration. The emission reduction rate was high in low ethanol concentration blend ($<$ E15) compared to high ethanol concentration blend ($>$ E20). Using E3 fuel, Yang et al. [104] also found a 5.22% increase in NOx compared to gasoline.

In contrast, some researchers have found increased NOx emission. Using a single cylinder SI engine, Schifter et al. [105] investigated the effect of using gasoline–ethanol mid-level blends (0–20% ethanol) on engine performance and exhausts emissions. It is seen that NOx emission increased with the addition of ethanol to gasoline compared to gasoline. With the addition of ethanol, NOx emission is higher for a higher heat release of ethanol compared to gasoline. However, HC emission increased for shorter burn durations with ethanol addition in blend compared to pure gasoline. The performance and the pollutant emissions of a four-stroke SI engine operating on ethanol–gasoline blends of 0%, 5%, 10%, 15% and 20% were investigated by Najafi et al. [82]. They also found a higher NOx concentration when the ethanol percentage increased, as shown in Fig. 3. Another significant reason for this increase is that the oxygen content in the ethanol blended fuels increased the oxygen-to-fuel ratio in the fuel-rich regions. The most significant parameter affecting NOx concentration is the relative air–fuel ratio. The actual air–fuel ratio approaches to stoichiometric as the ethanol content of the blended fuel increases, and consequently combustion becomes complete. This complete combustion increases the in-cylinder temperature as well as NOx emission while the HC emission decreases. With a higher oxygen concentration in ethanol, Keskin and Guru [106] also found higher NOx emission with the addition of ethanol.

Zhuang et al. [35] varied the ethanol/gasoline energy ratio from 0% to 60.1%. NOx emission increased with the addition of up to 24.3% ethanol to gasoline after which it decreased with increasing ethanol percentage. With regard to increasing NOx, they reported that, ethanol improved the combustion inside the cylinder resulting in an increased in-cylinder temperature. In the case of reduced NOx they explained that a higher percentage of ethanol in gasoline reduces the in-cylinder temperature. They attributed this reduction to two factors. One is the high latent heat of vaporization of the ethanol fuel, which decreases the in-cylinder temperature when it vaporizes. The other factor is that there are more triatomic molecules in the combustion products of ethanol fuel than in those of the gasoline fuel. The more triatomic molecules are produced, the higher the gas heat capacity and the lower the combustion gas temperature will be. However the low in-cylinder temperature can also lead to an increment in the unburned combustion product.

5.1.2. *Effect of hydrous ethanol*

The water absorbs heat and lowers the pressure as the charge is compressed reducing the compression stroke work. Additionally, during the combustion itself, water absorbs heat as it vaporizes reducing the peak temperatures and then reducing NOx emissions. This peak temperature reduction diminishes the heat flux to the cylinder wall [95]. As a result of the reduced intake air temperatures and the effects on the combustion process itself, fuel blends of gasoline with hydrated ethanol present slightly lower exhaust gas temperatures. As distillation of hydrous ethanol to get anhydrous ethanol is costly, there is scope for hydrous ethanol. Also, few researches have dealt with hydrous ethanol so far [14,21,107–111].

Schifter et al. [95] compared mid-level (0–40% volume water) hydrous ethanol–gasoline blend with anhydrous gasoline blend. They found 2% lower NOx emission for hydrous ethanol–gasoline blends than for anhydrous ethanol–gasoline blend. Water in the hydrated ethanol decreases the temperature, combustion speed, and peak pressure compared to the anhydrous ethanol, therefore improving the NOx emission, especially for 30% and 40% ethanol contents. Water slows the combustion process but keeps the quantity of energy produced per cycle constant, the amount of work obtained is therefore the same and the same amount of heat is released, but more efficiently. Kyriakides et al. [112] also get lower NOx for 40% hydrous ethanol blend compared to 40% anhydrous ethanol. They explained, water content of hydrous ethanol lowered the peak temperature and slowed the combustion rate that resulted lowers NOx emission.

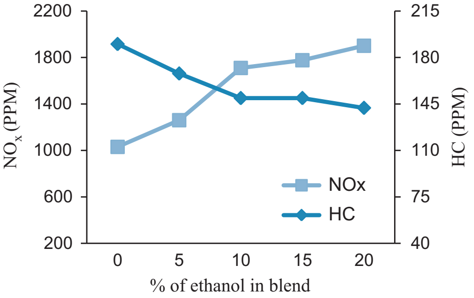


Fig. 3. Correlation of NOx and HC with the percentage of ethanol at 3500 rpm [82].

Costa and Sodre [21] compared the performance and emissions of E22 with hydrous ethanol (6.8% water content in ethanol). The NOx emission of hydrous ethanol was more than those of E22. For higher NOx of hydrous ethanol, they explained, a faster flame speed of hydrous ethanol favors the production of higher peak pressure and, therefore a higher peak temperature in the combustion chamber.

Considering a small SI engine, Munsen et al. [111] studied the effect of hydrous ethanol (up to 40% water in ethanol) on performance and emission. The addition of 20–40% water to ethanol resulted in incomplete combustion, which increased CO and HC emission and reduced NOx emission. They determined the combustion temperature by measuring the spark plug temperature. The spark plug temperature was found to decrease with increases in the water content in ethanol. The lower combustion temperatures of hydrous ethanol affect the thermal NOx formation.

5.2. *Effect of engine parameters*

5.2.1. *Effect of compression ratio*

A high compression ratio (CR) is desirable because it allows an engine to extract more energy from a given mass of air–fuel mixture due to its higher thermal efficiency. Higher CRs permit the same combustion temperature to be reached with less fuel while giving a longer expansion cycle. The detonation increases, when a lower octane number fuel is used a high compression ratio engine [93]. The octane number of ethanol is 108.6 (mentioned in Table 4), which is higher than that of gasoline. The high octane number offers a high compression ratio without knocking and improves the knock tolerance. It was also found that a high CR can increase the efficiency of ethanol fuel blends, and as a result, the fuel economy penalty associated with the lower energy content of E85 can be reduced by about 20% [113]. High combustion temperatures lead to higher NOx emissions, and thus forced induction can give higher NOx fractions. Especially at high engine load, NOx emission increase with increases in CR. The relatively high burning rate of the overall rich mixture combustion and a high-temperature environment contribute to the increase in the NOx emissions with increasing CR at high engine loads [114].

To improve engine power, Al-Baghdadi [96] used the high useful compression ratio (HUCR), which is a variable compression ratio that is directly proportional to the ethanol percentage in the blend. The compression ratio varies from 8 to 9.25 as the ethanol percentage increases from 0% to 30%. The NOx emission decreased with increases in ethanol although the CR was increased. It is also observed that thermal efficiency, power, HC, and CO emissions were better for ethanol with HUCR than for gasoline with constant CR 8:1. Celik et al.[34] increased the compression ratio from 6:1 to 10:1 by adding 50% ethanol to gasoline. When running with E50 at a high compression ratio (10:1), NOx decreases by 19% compared to the case of E0 fuel at a compression ratio of 6:1. NOx emission is reduced here owing to the fact that the heating value of ethanol is lower than that of gasoline. Koc et al. [38] used 0%, 50% and 85% ethanol with gasoline on compression ratios of 10:1 and 11:1. NOx emission decreased with the increase of ethanol. NOx emission of gasoline at CR 10:1 is also higher than those of ethanol–gasoline blend at a CR of 11:1. The high latent heat of vaporization of ethanol lowers the flame temperature, which results in lower NOx emissions. However, the NOx emission may change depending on the percentage of ethanol in the blend and operating conditions. The oxygen concentration and combustion temperature and combustion duration are the main parameters affecting the NOx emissions. However, for the same blend, NOx was higher for a higher CR.

5.2.2. *Effect of engine load*

Engine load plays a very important role in NOx formation. More fuel or a richer mixture is needed to increase the engine load, which results in a higher in-cylinder temperature as well as higher NOx formation. The flame speed of fuel is an important factor for complete combustion in rich-mixture conditions as well as high engine load.

Using a 1.4 L flex-fuel engine, Melo et al. [108] tested 0–100% hydrous ethanol with gasoline at two different loads. At a low load (60 Nm), NOx emission decreased with ethanol addition. But at the same speed with a higher load (105 Nm), NOx increased with the addition of ethanol. They explained that the higher flame speed of ethanol compared to gasoline was the cause of the NOx emission increase when using ethanol at high load. A higher flame speed assists in complete combustion. It is also seen that the CO emission reduction with the addition of ethanol at high loads is higher than that at low loads. At a high load, Keskin and Guru [106] also found higher NOx emission for adding ethanol. They did experiment with 0%, 4%, 8%, 12%, 16%, and 20% ethanol in gasoline at different loads (800, 1600, 2400 kW). At lower load conditions, NOx emissions were the same for all blends. But at higher loads, NOx emissions were higher for ethanol blended fuel.

Gomes et al. [115] focused on the operation of ethanol blends up to E100 at high loads of up to 30 bar IMEP. At comparatively lower loads, NOx emissions were lower for high ethanol content blends. They explained that ethanol lowered the peak temperature slightly, which reduces NOx at lower loads. However, at comparatively higher loads, NOx emissions were the same for all of the blends as high flame speed of ethanol fuel results in similar peak temperatures. No significant change in NOx emissions was observed at different engine loads (3–161 Nm torque) by Pang et al. [9], when they compared gasoline and 10% ethanol blended gasoline. However, for lower heating values, fuel consumption was greater for ethanol blended fuel.

5.2.3. *Effect of equivalence ratio*

The stoichiometric air–fuel-ratio of gasoline is 1.6 times higher than that of ethanol (as in Table 4). Since at fixed throttle opening and a fixed engine speed, the amount of air intake is a constant; to obtain the same λ, more volume flow rate of ethanol–gasoline blend is required than base gasoline which produces the leaning effect. Leaning of fuel/air ratio causes the flame temperature to be low enough to reduce NOx as well as other emissions [14]. Theoretically, the hottest flame comes from stoichiometric air/fuel mixtures; however, NOx peaks at slightly leaner fuel/air ratios. Leaning of fuel/air ratio causes the flame temperature to be low enough to reduce NOx as well as other emissions.

Najafi et al. [82] reported that the oxygen content of ethanol produces a leaner effect in fuel-rich conditions. This leaner effect shifts the air–fuel ratio to stoichiometric condition and helps in completing combustion hence increasing NOx emission. Hsieh et al. [56] also found higher NOx emission in stoichiometric air–fuel ratio as complete combustion leaded to a high combustion temperature. However, at an equivalence ratio lower than 1.0, the effect of addition of ethanol on NOx emissions was insignificant. They concluded that NOx emissions depend on the engine operating conditions rather than on the ethanol content. Using a six-cylinder test engine, Al-Farayedhi [116] found maximum NOx emission in the equivalence ratio of 0.9 for using gasoline, E10, E15, and E20 as fuel. NOx emissions increased as the ethanol concentration of the blend increased except at the equivalence ratio of 0.8. The availability of oxygen and high combustion temperature were the cause of these NOx emissions. However, for very lean mixtures, NOx concentration decreased for higher content of ethanol.

Zervas et al. [117] investigated the effect of different equivalence ratios ($\lambda = 0.83$–1.25) on exhaust emissions. They found, the difference in equivalence ratios did not lead to a large change in NOx emissions. With different values of λ, NOx varied from 15% to 30%. In stoichiometric and lean conditions, emissions of CO decreased. The addition of an oxygenated compound is more important than the percentage of oxygen in the fuel, which means that CO emissions decreased because the oxygen concentration was higher. However, for E5 fuel, HC emissions are almost independent of λ. For E20 there are two zones: a 9–28% decrease in HC emissions in the lean condition and a 46–48% decrease in HC emissions in the stoichiometric and rich conditions.

5.2.4. *Effect of speed*

Engine speed also affects NOx emissions. Some authors [82,116] have reported that NOx increases with engine speed as more fuel is burnt resulting in high in-cylinder temperature at high speeds. Few authors [38,99] have also reported low NOx emission because of less available time for combustion at high speeds.

At higher speeds, lower combustion time is available for burning higher amount of fuel than lower speeds. Flame speed is an important factor to complete the combustion in short time. As flame speed of ethanol is higher than that of gasoline, it assists in completing the combustion at high speeds, which results in higher NOx emission for ethanol. Costa and Sodré [21] found higher NOx emission for 100% hydrous ethanol than E22 at high speeds as it has more ethanol content than E22. However, at low speeds (2500–3000 rpm) there was no significant change for these fuels. Koç et al. [38] found different results for ethanol blended fuel at high speeds. They found 42%, 41% and 11% NOx increase for E0, E50 and E85 respectively within speed range of 1500–5000 rpm. Increase in NOx emission with speed was relatively lower for E85 than E0. Lower heating value combined with low combustion time can be the reason of lower NOx for ethanol in high speeds.

5.2.5. *Effect of cold-start*

The properties of ethanol cause difficult cold start and warm-up operations, which impact on engine emissions. The RVP (Reid Vapor Pressure) of ethanol is 17 kPa, far lower than that of gasoline, which is 53.7 kPa. But their mixture does not have an RVP value linearly proportional to the volume fraction. A volume fraction of 5–10% ethanol can achieve the maximal RVP and thus facilitate cold-start [118]. The vaporization temperature of ethanol is 78 °C, while that of gasoline is 40 °C. On the other hand, ethanol vaporization requires twice the energy required by gasoline. Therefore, ethanol-fueled engines do not start at temperatures below 13 °C, while gasoline-fueled engines can start at temperatures as low as −40 °C [119].

The effects of ethanol–gasoline blended fuel on cold-start emissions were studied by Chen et al. [120] using an ECU (electronic control unit) controlled SI engine. They compared the emissions of different ethanol–gasoline blends (E0, E5, E10, E20, E30, E40), keeping the intake air temperature around 20 °C. At cold start, E5 and E10 performed indistinguishably, while E20–E40 clearly had lower HC, CO, and NOx emissions. In the open-loop control, the fuel injection is roughly the same for all fuels (E0–E40). However, the stoichiometric air–fuel ratios for ethanol and gasoline are 9 and 14.7 respectively. The amount of air required to create a stoichiometric air–fuel mixture for gasoline (E0) would be excessive for ethanol–gasoline blended fuels, which helps in reducing HC and CO emissions. NOx decreases for lower flame temperatures produced by excess air. In the case of E40, the operation was unstable because the constant amount air supply makes the air–fuel mixture very thin. Liao et al. [121] also found lower HC, CO and NOX emission for ethanol blended fuel than those of gasoline in cold start.

Sales and Sodré [119] used a flexible fuel engine with heated intake air–fuel and compared the results with that of a conventional cold start system. Using hydrous ethanol, they found lower HC, CO, and NOx emissions for heated intake air–fuel than for a conventional cold start. Heating of ethanol and intake air improves fuel vaporization, thus reducing the formation of emissions in the first engine cycles.

Table 6 represents a complete overview of different experimental results on the effect of ethanol–gasoline blends on NOx as well as other emissions based on above-mentioned causes.

5.3. *Engine modification*

5.3.1. *Application of thermal barrier coating*

A thermal barrier coating (TBC) is applied to minimize heat transfer from the combustion chamber by insulating the piston and cylinder wall with an adherent layer of a low thermal conductivity material. This type of engines is known as a low heat rejection (LHR) engine. This insulation reduces the heat flux into the piston and thus heat transfer to the coolant is reduced [125]. Because of the lower heat loss, TBC affects the combustion process and hence changes the performance and emission characteristics. NOx emission is significantly higher in the coated pistons engine, which is evident due to the higher cylinder temperature due to the lower heat loss. As the heating value of ethanol is a lower, there is growing interest in thermal barrier coated engines with ethanol blended fuel and a few works have already been done [118,125–127].

Srinivasan and Saravanan [128] investigated the use of gasoline, E60 + 2.0 Iso-heptanol, and E50 + 1.0 Isoheptanol blends in a multi-cylinder gasoline engine with and without alumina titania coated pistons. In both cases, they found lower NOx emissions for ethanol blends than for gasoline. Moreover, ethanol blends in the coated pistons condition produced lower NOx emissions than gasoline fuel in the non-coated pistons condition. The lower heating value of ethanol is the reason for its lower NOx emissions compared to gasoline.

Kumar and Nagarajan [127] investigated the emissions and performance of an SI engine using E20 fuel with and without TBC on the cylinder head, inlet, and exhaust valves. As TBC reduced the heat loss from the combustion chamber, it increased the peak in-cylinder temperature as well as NOx formation. As a result, NOx emissions were higher for the coated than the uncoated cylinder for all types of fuel blend. However, the additional oxygen of E20

Table 6
Factors affecting NOx emission from different ethanol blends at different operating condition.

Engine	Ethanol concentration in blend	Adjustment and/or modification and test condition	NOx	Effect on other emission	Ref.
4S, 1C CR: 6/1–10/1, EIS	0%, 25%, 50%, 75%, 100%	CR 6:1 and 10:1 Varying speed (1500–4000 rpm)	E↑ and NOx↓	CO, HC, CO_2 ↓	[34]
4S, 1C CR: 5/1–13/1	0%, 50%, 85%	CR 10:1 and 11:1 Varying speed (1000to 5500 rpm)	E↑ and NOx↓	CO, HC↓ BSFC↑	[38]
4S, 4C, MIS, WC	0%, 5%, 10%	WP = 5–20 kW Speed = 80and 100 km/h	80 km/h: 11% and 15.5% NOx↓ 100 km/h: 10.5% and 13.5% NOx↓	HC and CO_2↓	[50]
1C, 4S, AC, EDI + GPI, CR 9.8/1	0%, 24.3%, 48.4%, 60.1%	Speed = 3500–5000 rpm	E < 24.3% NOx↑ E > 24.3% NOx↓	HC↑, CO↑	[35]
4S, motorcycle, carbureted engine (CE) and Fuel injected engine (FIE)	0%, 15%	Constant speed	CE 36% NOx↓ FIE 3%NOx↑	CE HC and CO↓ FIE HC and CO↓	[122]
1C, SI, CR 10.5/1	0%, 10%, 20%, 30%, 40% And H10%, 20%, 30%, 40%	Constant speed (2000 rpm)	NOx↓	HC and CO↓	[95]
1C, AC, CR 8.5/1	0%, 100%	Speed: 1600–3600 rpm	NOx↓	CO, HC↓, CO_2 ↑	[98]
1C, GPI, CR 9.5	0%, 25%, 50%, 75%, 100%	IMEP = 3 and 5 bar	NOx↓	HC ↓	[102]
4C, FFE, PFI, CR 10.35/1	25% and H 30%, 50%, 80%, 100%	Load = 60 and 105 Nm	At 60Nm NOx↓[a] At 105Nm NOx↑	At 60 Nm HC↓ At 105 Nm CO↓ HC↓	[108]
1C, DISI, CR 9.5	0%, 5%, 25%, 85%, 100%	Constant speed (2000 rpm)	E < 25% NOx↑ E > 25% NOx↓	–	[115]
4C, MIS, WC, CR 10.4/1	0%. 5%, 15%	Wheel power 5–20 kW Speed 80 km/h	E5: 11% NOx↓ E10 15.5% NOx↓	CO, HC↓	[50]
MFIE, CR 9.8/1	0%, 5%, 10%, 20%, 30%, 40%	Cold start condition, intake air temperature 20 °C	E5, E10 NOx↑ E > 10% NOx↓	E5, E10 CO, HC↑ E > 10% CO, HC ↓	[120]
4C, SI,	0%, 10%, 25%, 50%, 85%	Constant engine speed	NOx↓	CO, HC ↓	[62]
1C, SI, AC, CR 11.3/1	0%, 5%, 10, 15%	Idle, 2500, 5000, 6500 rpm	NOx↓	–	[123]
DISI, turbocharged	0%, 10%, 20%		NOx↓	–	[100]
DISI, CR 12/1	0%, 25%, 50%, 85%	End of injection CAD 45-5 BTDC	NOx↓	HC↑, smoke↓	[65]
4C, SI, CR 12/1	22%, H100%	Engine speed 2500–6000 rpm	NOx↑ (compared with E22)	HC & CO↓	[21]
1C, CR 10.5/1	0%, 6%, 10%, 15%, 20%	Speed 2000 rpm	NOx↓ (except E6)	HC↑ & CO↓	[105]
DI, CR 11.5/1	0%, 10%, 20%, 30%, 50%, 85%, 100%	Speed 1500 rpm IMEP = 3.4 bar	NOx↓	HC↓	[66]
1C, CR: variable	0%, 5%, 10%, 15%, 20%, 25%, 30%	Speed 1500 rpm CR; 8 and HUCR	NOx↓	CO, HC↓	[96]
4C, CR 9.7/1	0%, 5%, 10%, 15%, 20%	Speed: 1000–5000 rpm	NOx↑	HC & CO↓	[82]
4C, CR 10.5	0%, 85%, 100%	Speed: 3500 rpm	NOx↓	CO, HC↓	[124]

EIS = electronic injection system, EDI = Ethanol fuel direct injection, GPI = gasoline port injection, C = cylinder, CR = compression ratio, MIS = Multi-point injection system, WC = water cooled, AC = air cooled, DI = Direct injection, FFE = Flex fuel engine, MFIE = multi-port fuel injection engine, HUCR = High useful compression ratio, E = Ethanol, H *xx%* = *xx%* hydrous ethanol in gasoline, ↓ = decrease, ↑ = increase.

[a] compared with E25.

fuel accelerates NOx formation with higher in-cylinder temperature for thermal coating. Therefore, they found a 46% increase in NOx emission for E20 than for gasoline.

5.3.2. *Effect of separate aqueous ethanol injection*

It was hypothesized that the primary effect of the water was to reduce flame temperatures, thereby obstructing the thermal formation of NOx. From previous literature, it was seen that avoiding the phase separation of ethanol–gasoline blend requires high purity ethanol so it is costly, and better performance of the engine depends on the best ethanol–gasoline ratio, which varies for different engine speeds and torques. To solve this problem, an independently controlled separate set of aqueous alcohol injector was used. Chen et al. [64] installed a set of independently controlled separate aqueous alcohol injectors alongside the gasoline injector at the manifold. Aqueous ethanol with a high water content (ethanol purity: 99.7%, 75% and 50%) was injected as a fuel substitute through them. They selected two operating regimes: highway running and high load running. During highway running, engine control unit cut down the flow of gasoline when aqueous ethanol was injected by receiving feedback from the exhaust oxygen sensor, but in high load running, nothing happened. Aqueous alcohol reduced the combustion temperature and thus reduced NOx formation. They concluded that the water content in the fuel mixture dominated the NOx reduction rather than the ethanol content. With a 16% water content in the fuel mixture, NOx emission can be reduced by 30% with little adverse effect on the torque compared to gasoline.

On the other hand, to compare the effect of different injection strategies on engine emissions, Anderson et al. [129] performed two sets of experiments using premixed ethanol–water blends and separately injecting water and ethanol into the blends on a modified Co-operative Fuels Research (CFR) engine at a constant compression ratio of 10:1. Three types of ethanol–water blended fuels were used: 20 vol% water+80 vol% E100 (80/20), 10 vol% water+90 vol% E100 (90/10), and 30 vol% water+70 vol% E100 (70/30). They measured NOx emissions, first by injecting the premixed blend and then injecting water and ethanol separately. Premixed ethanol–water blends showed a higher reduction in NOx compared to separate injection of water and ethanol for blends with ethanol/water ratios of up to 70/30, as shown in Fig. 4. More immediate contact between the water molecules and ethanol under premixed conditions appears to have a strong influence on combustion chemistry, which in turn produces better NOx emission characteristics.

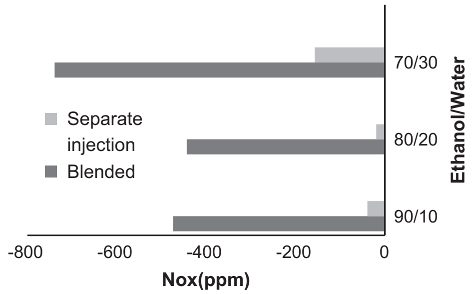


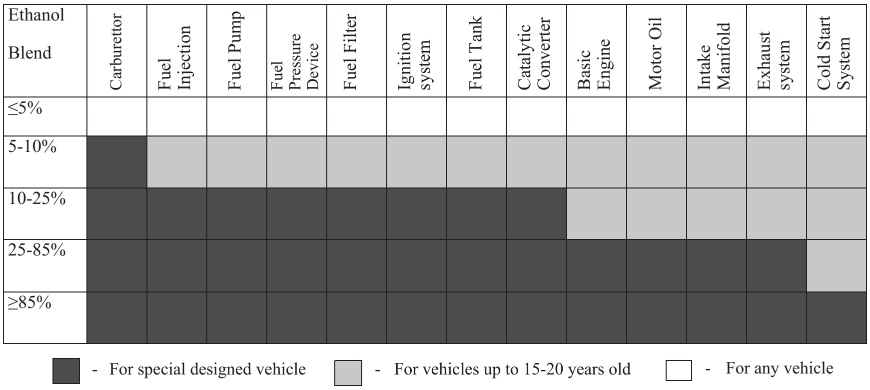
Fig. 4. NOx emission changes for ethanol/water fuel with respect to gasoline [129].

5.4. *Effect of different vehicles*

The use of ethanol in vehicles is increasing day by day. More than 95% of the gasoline in the U.S. contains ethanol in an approximately 10% blend [130]. Ethanol is also available in higher concentration blends marketed as E85 (also known as flex-fuel). The use of low concentration ethanol is possible in ordinary vehicles without any problem. However, use of higher concentration ethanol is somewhat questionable. Because of its corrosiveness, it degrades a range of the materials found in specific components of the engine, and fuel supply systems [60].

New generation engines are designed to work with higher biofuel blends, which allow the engine to be modified to maximize the benefits of the higher oxygen content and improved fuel efficiency with low emissions. Fig. 5 shows the variation of different generations of Flexible fuel vehicle (FFV) in Brazil. FFVs are among the modern vehicles designed to use up to 85% ethanol, and they were developed with better fuel efficiency with higher compression ratios. The speciality of this vehicle is that its fuel sensor automatically detects the ethanol–gasoline ratio to adjust fuel ignition and injection timing according to the ethanol–gasoline ratio [131]. In the US vehicle market alone, more than 10 million FFVs were in operation in mid-2012 [132]. This section will discuss the effect of ethanol blended fuels' NOx emission from these vehicles.

Zhai et al. [131] compared the fuel consumption and emission of FFVs with E85 and gasoline fuel. They used data from different data sources, such as portable emissions measurement system (PEMS) data, Environmental Protection Agency (EPA) certification data, and US Department of Energy (DOE) dynamometer tests. In higher vehicle specific power (VSP) modes, from PEMS data, NOx emission was found to be higher for E85 than for gasoline. From the dynamometer and certification data, NOx emission was seen to depend on the vehicle condition and not on the fuel. On a fleet basis, NOx and other emissions were lower for E85 than for



Ethanol Blend	Carburettor	Fuel Injection	Fuel Pump	Fuel Pressure Device	Fuel Filter	Ignition system	Fuel Tank	Catalytic Converter	Basic Engine	Motor Oil	Intake Manifold	Exhaust system	Cold Start System
≤5%	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
5-10%	■	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
10-25%	■	■	■	■	■	■	■	■	▨	▨	▨	▨	▨
25-85%	■	■	■	■	■	■	■	■	■	■	■	■	▨
≥85%	■	■	■	■	■	■	■	■	■	■	■	■	■

■ - For special designed vehicle ▨ - For vehicles up to 15-20 years old ☐ - For any vehicle

Fig. 5. Necessary modification to the engine to increase ethanol–gasoline blend [133].

gasoline. On a life-cycle basis, NOx emission was 82% higher for E85 than for gasoline.

Karavalasik et al. [94] investigated the impact of ethanol blends on different vehicle models ranging from 1984 to 2007 including FFVs. NOx emission increased with increase in ethanol content for a few old model vehicles, which can be attributed to differences in catalyst technology, aging or effectiveness. As old model vehicles do not have sophisticated engine control technology, the leaning effect cannot be very pronounced with the change of fuel type here. Yao et al. [134] tested various ethanol–gasoline blends (E0, E3, E10 and E20) in a low mileage (about 21750 mile) and a high mileage (about 87,000 mile) passenger car. Both cars operated well with ethanol blends of up to 20%. In this experiment, it was seen that NOx emission was lower when using ethanol blend, especially in the low-mileage vehicle fueled with E20. The low mileage vehicle had NOx emission of 0.072 g/km, 0.71 g/km, 0.068 g/km, and 0.061 g/km respectively, for E0, E3, E10 and E20 fuels, while the high-mileage vehicle's NOx emission was 0.471 g/km, 0.472 g/km, 0.451 g/km and 0.417 g/km, respectively, for E0, E3, E10 and E20 fuel. Durbin et al. [135] used 12 different vehicles to find the effect of different ethanol–gasoline blends and volatilities on emission. The vehicles included present day technologies with California low-emission vehicle (LEV), ultralow emission vehicle (ULEV) and super-ultralow-emission vehicle (SULEV) certification. They found an increase in NOx emission with a 10% ethanol–gasoline blend compared to gasoline. Mayotte et al. [136] investigated emission in a 1990 model or equivalent vehicles. They found that the sulfur concentration of fuel affects the HC and NOx emission of these vehicles.

Some authors reported that the operation of small engines using a lower ethanol percentage (10–15%) with gasoline causes HC and CO emissions to decrease and NOx emissions to increase [137]. The US DOE reported that in small engines using ethanol contents of 10–15% with gasoline, NOx emissions increased by 50–70%. Small engines have no oxygen-sensing feedback control like modern cars. When ethanol is added to gasoline, an engine operated under lean or oxygen-rich conditions experiences overheating [138]. This high temperature causes more NOx formation. Knoll et al. [139] compared some small non-road engines and observed the emissions for different ethanol–gasoline blends. From Fig. 6 it can be seen that NOx increases with the increase in ethanol percentage. In a Stihl Line Trimmer engine, NOx emissions were lower when using E20 due to poor combustion. Emissions were lower in a Poulan Blower engine as it was equipped with a three-way catalyst. Hilton and buddy [140] used 10 cars (1994 to 2004 models) to compare the tailpipe emissions of E20 and gasoline. Among the 10 cars, five produced higher NOx emissions and five produced an average of 2.4% lower NOx emissions when using E20 compared to gasoline. For most of the cars, HC and CO emissions were lower for E20 than for gasoline. They discussed some reasons for emissions degradation of vehicles such as degradation of the catalyst, material compatibility of fuel system components, and so on.

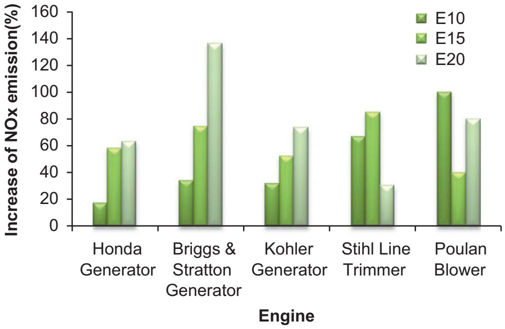


Fig. 6. Increase of NOx emission than gasoline fuel versus different engines for ethanol–gasoline blend [139].

6. Prediction of NOx emission by Artificial Neural Networks

As experimental studies are costly and time consuming, Artificial Neural Networks (ANNs) have been preferred in recent studies in order to minimize the time and money spent on experimental studies. ANNs were developed based on the working principle of the human brain. Without having the whole information of the system but only information on some input variables, an ANN can provide a good prediction close to that obtained using experimental data [141]. ANNs are an alternative technique for obtaining the relationship between different variable quantities of interest. An ANN requires only a set of experimental results which are numerical in nature and describes the relation by analyzing them [142]. With new experimental data, it can continuously retrain prediction that is more accurate. Some researchers have applied ANNs to predict the characteristics of IC engines. ANN models have been used recently in many studies to predict engine fuel consumption [142], performance [143], and different exhaust emissions [144–146] as well as NOx emission [147].

Deh Kiani et al. [148] trained the network with 80% of the experimental data obtained using a four cylinder fuel-injection SI engine. In this network, the fuel blend, engine load, and engine speed were used as input data and the torque, power, CO, CO_2, HC, and NOx were obtained as the output. The ANN provided the best accuracy in modeling the emission indices with correlation coefficient of 0.98, 0.96, 0.90 and 0.71 for CO, CO_2, HC and NOx respectively. However, the addition of 20% ethanol increased the engine torque, brake power, thermal and volumetric efficiency, while the BSFC decreased. As ethanol is an oxygenated fuel, NOx emission was found to be higher for ethanol–gasoline blend than for gasoline.

Najafi et al. [82] developed an ANN model to find the correlation between brake power, torque, brake specific fuel consumption, brake thermal efficiency, volumetric efficiency and emission components by using different gasoline–ethanol blends and speeds as inputs data. To train the ANN, 70% experimental data obtained from a four cylinder SI engine were used. In the experiment, it was found that when ethanol content increased, NOx increased and HC and CO emission were decreased. Comparing the experimental data with the ANN model, they found a good consistency, as the value of the correlation coefficient (R) was close to one and the root mean square error (RMSE) was very low. For NOx emission, the values: $R=0.973$ and RMSE$=89.85$ (ppm). They also presented the same explanation for NOx emission with ethanol addition.

7. Conclusion

Alternative fuels are becoming more and more important for vehicles because of the limited reserves of fossil fuels and environmental issues. Ethanol is one of the alternative fuels that have been used in several countries for several years as it is produced from renewable sources and produces cleaner emission. Burning of ethanol in SI engines reduces the emissions of CO, HC and so on, but there are some inconsistencies in NOx emission as shown by many researchers. A systematic review of the published literatures on the effect of fuel properties, composition and operating conditions, which influence ethanol NOx emission, has been carried out and the main findings are summarized below.

(1) The physicochemical properties of ethanol–gasoline blends such as heating value, latent heat of vaporization, oxygen content, laminar flame velocity etc. dominate in the NOx formation in SI engine.

(2) Thermal NOx formation is the dominant mechanism for NOx emission from SI engines for gasoline as well as ethanol fuel, as suggested by many researchers.

(3) Ethanol blended fuels can utilize a higher CR in SI engine due to their higher octane number. Using the higher percentage ethanol blend, a higher CR can be applied without increasing the NOx emission.

(4) Higher flame speed of ethanol helps in achieving complete combustion for rich mixtures attained during higher engine loads as well as higher engine speeds. This results in higher NOx emission for ethanol–gasoline blends than that of gasoline. No significant change or a small decrease in NOx emission is observed at low engine load for ethanol.

(5) Pure ethanol fuel is not suitable for engine cold-start. Engine can easily start in cold condition with lower HC, CO and NOx emission with use of ethanol blended gasoline fuel than gasoline. However, heated air–fuel mixture is more effective in cold start condition.

(6) As the water content absorbs heat and lowers the peak in-cylinder temperature, hydrous ethanol blends is more efficient in NOx emission reduction compared to gasoline as well as anhydrous ethanol blends.

(7) Separate alcohol injection is used in order to use higher water content with ethanol without having the problems of phase separation. Water content reduces NOx emission significantly but premixed water with ethanol is more efficient in NOx reduction than separate water injection.

(8) TBC is used to suppress the heat rejection to coolant and to restore the energy in the form of useful work but its use increases NOx emission. Low concentration of ethanol blend along with TBC accelerates the combustion as well as NOx formation as ethanol is an oxygenated fuel. However, TBC can be applied using higher ethanol–gasoline blend without further increase in NOx emission because of lower heating value of the blend.

Ethanol–gasoline blend is a proven technically feasible alternative fuel for SI engine. It is suitable to use in modern engines such as high compression ratio engines or low heat rejection engines. Application of hydrous ethanol instead of anhydrous one may produce better results in these engines i.e. lower NOx emission with better engine performance. The problem of ethanol is its lower heating value. Use of butanol may solve this issue. However, economical consideration will continue to favor the use of ethanol. Thus lowering the production cost of other alternatives can be a good field to carry out research.

Acknowledgment

The authors would like to appreciate University of Malaya for financial support through High Impact Research grant titled: “Clean Diesel Technology for Military and Civilian Transport Vehicles” having Grant no. UM.C/HIR/MOHE/ENG/07.

References

[1] Chandra R, Takeuchi H, Hasegawa T. Methane production from lignocellulosic agricultural crop wastes: a review in context to second generation of biofuel production. Renewable and Sustainable Energy Reviews 2012;16(3):1462–76.
[2] Abbasi T, Abbasi SA. Decarbonization of fossil fuels as a strategy to control global warming. Renewable and Sustainable Energy Reviews 2011;15(4):1828–34.
[3] Azadi H, de Jong S, Derudder B, De Maeyer P, Witlox F. Bitter sweet: how sustainable is bio-ethanol production in Brazil? Renewable and Sustainable Energy Reviews 2012;16(6):3599–603.
[4] Ganguly A, Chatterjee PK, Dey A. Studies on ethanol production from water hyacinth—A review. Renewable and Sustainable Energy Reviews 2012;16(1):966–72.
[5] Hardenberg HO. Samuel Morey and his atmospheric engine. Warrendale, PA: Society of Automotive Engineers, Incorporated; 1992.
[6] Hansen AC, Zhang Q, Lyne PW. Ethanol–diesel fuel blends-–a review. Bioresource Technology 2005;96(3):277–85.
[7] Turdera MV. Energy balance, forecasting of bioelectricity generation and greenhouse gas emission balance in the ethanol production at sugarcane mills in the state of Mato Grosso do Sul. Renewable and Sustainable Energy Reviews 2013;19:582–8.
[8] Park C, Choi Y, Kim C, Oh S, Lim G, Moriyoshi Y. Performance and exhaust emission characteristics of a spark ignition engine using ethanol and ethanol-reformed gas. Fuel 2010;89(8):2118–25.
[9] Pang X, Mu Y, Yuan J, He H. Carbonyls emission from ethanol-blended gasoline and biodiesel-ethanol-diesel used in engines. Atmospheric Environment 2008;42(6):1349–58.
[10] Amore A, Faraco V. Potential of fungi as category I consolidated BioProcessing organisms for cellulosic ethanol production. Renewable and Sustainable Energy Reviews 2012;16(5):3286–301.
[11] Faraco V, Hadar Y. The potential of lignocellulosic ethanol production in the Mediterranean Basin. Renewable and Sustainable Energy Reviews 2011;15(1):252–66.
[12] Sorapipatana C, Yoosin S. Life cycle cost of ethanol production from cassava in Thailand. Renewable and Sustainable Energy Reviews 2011;15(2):1343–9.
[13] García CA, Manzini F, Islas J. Air emissions scenarios from ethanol as a gasoline oxygenate in Mexico City Metropolitan Area. Renewable and Sustainable Energy Reviews 2010;14(9):3032–40.
[14] Kumar S, Singh N, Prasad R. Anhydrous ethanol: a renewable source of energy. Renewable and Sustainable Energy Reviews 2010;14(7):1830–44.
[15] Niven RK. Ethanol in gasoline: environmental impacts and sustainability review article. Renewable and Sustainable Energy Reviews 2005;9(6):535–55.
[16] Dwivedi G, Jain S, Sharma MP. Impact analysis of biodiesel on engine performance—A review. Renewable and Sustainable Energy Reviews 2011;15(9):4633–41.
[17] Saleh HE. Effect of exhaust gas recirculation on diesel engine nitrogen oxide reduction operating with jojoba methyl ester. Renewable Energy 2009;34(10):2178–86.
[18] Sun J, Caton JA, Jacobs TJ. Oxides of nitrogen emissions from biodiesel-fueled diesel engines. Progress in Energy and Combustion Science 2010;36(6):677–95.
[19] Tschanz F, Amstutz A, Onder CH, Guzzella L. Feedback control of particulate matter and nitrogen oxide emissions in diesel engines. Control Engineering Practice, http://dx.doi.org/10.1016/j.conengprac.2012.09.014, in press.
[20] Arbab MI, Masjuki HH, Varman M, Kalam MA, Imtenan S, Sajjad H. Fuel properties, engine performance and emission characteristic of common biodiesels as a renewable and sustainable source of fuel. Renewable and Sustainable Energy Reviews 2013;22:133–47.
[21] Costa RC, Sodré JR. Hydrous ethanol vs. gasoline–ethanol blend: engine performance and emissions. Fuel 2010;89(2):287–93.
[22] Yunoki S, Saito M. A simple method to determine bioethanol content in gasoline using two-step extraction and liquid scintillation counting. Bioresource Technology 2009;100(23):6125–8.
[23] Balat M, Balat H. Recent trends in global production and utilization of bio-ethanol fuel. Applied Energy 2009;86(11):2273–82.
[24] Rass-Hansen J, Johansson R, Møller M, Christensen CH. Steam reforming of technical bioethanol for hydrogen production. International Journal of Hydrogen Energy 2008;33(17):4547–54.
[25] Okada O, Tabata T, Kokitsu M, Ohtsuka H, Sabatino LMF, Bellussi G. Advanced catalyst for NOx reduction using hydrocarbons from lean-burning gas engine. Applied Surface Science 1997;121–122:267–72.
[26] O'Leary D. Ethanol; 2000. Available from: 〈http://www.ucc.ie/academic/chem/dolchem/html/comp/ethanol.html〉. [21.02.2012].
[27] Magnusson R, Nilsson C, Andersson B. Emissions of aldehydes and ketones from a two-stroke engine using ethanol and ethanol-blended gasoline as fuel. Environmental Science and Technology 2002;36(8):1656–64.
[28] Leong ST, Muttamara S, Laortanakul P. Applicability of gasoline containing ethanol as Thailand's alternative fuel to curb toxic VOC pollutants from automobile emission. Atmospheric Environment 2002;36(21):3495–503.
[29] Tavares JR, Sthel MS, Campos LS, Rocha MV, Lima GR, da Silva MG, et al. Evaluation of Pollutant Gases Emitted by Ethanol and Gasoline Powered Vehicles. Procedia Environmental Sciences 2011;4:51–60.
[30] Flavin C, Sawin JL, Mastny L, Aeck M, Hunt S, MacEvitt A, Stair P, Podesta J, Cohen A, Hendricks B. American energy: the renewable path to energy security. Worldwatch Institute & the Center for American Progress 2006, Washington, DC.
[31] Brown R. Full planet, empty plates: the new geopolitics of food scarcity. E.P. Institute; 2012 Editor.

[32] Szulczyk KR, McCarl BA, Cornforth G. Market penetration of ethanol. Renewable and Sustainable Energy Reviews 2010;14(1):394–403.

[33] Maurya RK, Agarwal AK. Experimental study of combustion and emission characteristics of ethanol fueled port injected homogeneous charge compression ignition (HCCI) combustion engine. Applied Energy 2011;88 (4):1169–80.

[34] Celik MB. Experimental determination of suitable ethanol–gasoline blend rate at high compression ratio for gasoline engine. Applied Thermal Engineering 2008;28(5–6):396–404.

[35] Zhuang Y, Hong G. Primary investigation to leveraging effect of using ethanol fuel on reducing gasoline fuel consumption. Fuel 2013;105:425–31.

[36] Eyidogan M, Ozsezen AN, Canakci M, Turkcan A. Impact of alcohol–gasoline fuel blends on the performance and combustion characteristics of an SI engine. Fuel 2010;89(10):2713–20.

[37] Çelik MB, Özdalyan B, Alkan F. The use of pure methanol as fuel at high compression ratio in a single cylinder gasoline engine. Fuel 2011;90 (4):1591–8.

[38] Koç M, Sekmen Y, Topgül T, Yücesu HS. The effects of ethanol–unleaded gasoline blends on engine performance and exhaust emissions in a spark-ignition engine. Renewable Energy 2009;34(10):2101–6.

[39] Sayin C. Engine performance and exhaust gas emissions of methanol and ethanol–diesel blends. Fuel 2010;89(11):3410–5.

[40] Keskin A. The Influence of ethanol–gasoline blends on spark ignition engine vibration characteristics and noise emissions. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 2010;32(20):1851–60.

[41] Harijan K, Memon M, Uqaili MA, Mirza UK. Potential contribution of ethanol fuel to the transport sector of Pakistan. Renewable and Sustainable Energy Reviews 2009;13(1):291–5.

[42] Beeckmann JRO, Peters N. Numerical and experimental investigation of laminar burning velocities of iso-octane, ethanol and n-butanol. SAE paper 2009-01-2784; 2009.

[43] Farrell JTJR, Androulakis IP. Molecular structure effects on laminar burning velocities at elevated temperature and pressure. SAE paper 2004-01-2936, 2004.

[44] Hara TTK. Laminar flame speed of ethanol, n-heptane, iso-octane air mixtures. SAE paper no. 2006-05-0409; 2006.

[45] Broustail G, Seers P, Halter F, Moréac G, Mounaim-Rousselle C. Experimental determination of laminar burning velocity for butanol and ethanol iso-octane blends. Fuel 2011;90(1):1–6.

[46] Latha KM, Badarinath KVS. Correlation between black carbon aerosols, carbon monoxide and tropospheric ozone over a tropical urban site. Atmospheric Research 2004;71(4):265–74.

[47] James Szybist, Matthew Foster, Wayne R.Moore, Keith Confer, Adam Youngquist, and Robert Wagner, Investigation of Knock Limited Compression Ratio of Ethanol Gasoline Blends. SAE Technical Paper 2010-01-0619; 2010.

[48] Wu C-W, Chen R-H, Pu J-Y, Lin T-H. The influence of air–fuel ratio on engine performance and pollutant emission of an SI engine using ethanol–gasoline-blended fuels. Atmospheric Environment 2004;38(40):7093–100.

[49] Kumar S, Cho JH, Park J, Moon I. Advances in diesel–alcohol blends and their effects on the performance and emissions of diesel engines. Renewable and Sustainable Energy Reviews 2013;22:46–72.

[50] Canakci M, Ozsezen AN, Alptekin E, Eyidogan M. Impact of alcohol–gasoline fuel blends on the exhaust emission of an SI engine. Renewable Energy 2013;52:111–7.

[51] Pourkhesalian AM, Shamekhi AH, Salimi F. Alternative fuel and gasoline in an SI engine: a comparative study of performance and emissions characteristics. Fuel 2010;89(5):1056–63.

[52] Blumberg PN, Bromberg L, Kang H, Tai C. Simulation of high efficiency heavy duty SI engines using direct injection of alcohol for knock avoidance. SAE International Journal of Engines 2009;1(1):1186–95.

[53] Huang J, Crookes RJ. Assessment of simulated biogas as a fuel for the spark ignition engine. Fuel 1998;77(15):1793–801.

[54] Bai Y, Luo L, van der Voet E. Life cycle assessment of switchgrass-derived ethanol as transport fuel. The International Journal of Life Cycle Assessment 2010;15(5):468–77.

[55] Rehnlund B, AB AE. Blending of ethanol in gasoline for spark ignition engines. In: Proceedings of ISAF XV, San Diego, CA; Sept. 2005. p. 26–8.

[56] Hsieh WD, Chen RH, Wu TL, Lin TH. Engine performance and pollutant emission of an SI engine using ethanol–gasoline blended fuels. Atmospheric Environment 2002;36(3):403–10.

[57] Aydin H, İlkılıç C. Effect of ethanol blending with biodiesel on engine performance and exhaust emissions in a CI engine. Applied Thermal Engineering 2010;30(10):1199–204.

[58] Lemaire R, Therssen E, Desgroux P. Effect of ethanol addition in gasoline and gasoline–surrogate on soot formation in turbulent spray flames. Fuel 2010;89(12):3952–9.

[59] Williams PRD, Cushing CA, Sheehan PJ. Data available for evaluating the risks and benefits of MTBE and ethanol as alternative fuel oxygenates. Risk Analysis 2003;23(5):1085–115.

[60] Wu TN, Chang CP, Wu TS, Shen YH. Emission characteristics of ethanol blending fuels from a laboratory gasoline engine. Applied Mechanics and Materials 2013;253:2227–30.

[61] Sánchez ÓJ, Cardona CA. Trends in biotechnological production of fuel ethanol from different feedstocks. Bioresource Technology 2008;99 (13):5270–95.

[62] Bielaczyc P, Szczotka A, Woodburn J. The effect of various petrol–ethanol blends on exhaust emissions and fuel consumption of an unmodified light-duty si vehicle. SAE Technical Paper 2011:24–0177.

[63] Wu X, Daniel R, Tian G, Xu H, Huang Z, Richardson D. Dual-injection: the flexible, bi-fuel concept for spark-ignition engines fueled with various gasoline and biofuel blends. Applied Energy 2011;88(7):2305–14.

[64] Chen RH, Chiang LB, Wu MH, Lin TH. Gasoline displacement and NOx reduction in an SI engine by aqueous alcohol injection. Fuel 2010;89(3):604–10.

[65] Oh H, Bae C, Min K. Spray and combustion characteristics of ethanol blended gasoline in a spray guided DISI engine under lean stratified operation. SAE International Journal of Engines 2010;3(2):213–22.

[66] Turner D, Xu H, Cracknell RF, Natarajan V, Chen X. Combustion performance of bio-ethanol at various blend ratios in a gasoline direct injection engine. Fuel 2011;90(5):1999–2006.

[67] Cooper C, Alley F. Air pollution control: a design approach 1994. Boston: PWS Inc; 1986.

[68] Normann F, Andersson K, Leckner B, Johnsson F. Emission control of nitrogen oxides in the oxy-fuel process. Progress in Energy and Combustion Science 2009;35(5):385–97.

[69] Lefebvre AH. The role of fuel preparation in low-emission combustion. ASME Journal of Engineering for Gas Turbines and Power 1995;117:617–54.

[70] Alasfour FN. NOx Emission from a spark ignition engine using 30% Iso-butanol–gasoline blend: Part 1—Preheating inlet air. Applied Thermal Engineering 1998;18(5):245–56.

[71] Chong JJ, Tsolakis A, Gill SS, Theinnoi K, Golunski SE. Enhancing the NO2/NOx ratio in compression ignition engines by hydrogen and reformate combustion, for improved aftertreatment performance. International Journal of Hydrogen Energy 2010;35(16):8723–32.

[72] Rizwanul Fattah IM, Masjuki HH, Liaquat AM, Ramli R, Kalam MA, Riazuddin VN. Impact of various biodiesel fuels obtained from edible and non-edible oils on engine exhaust gas and noise emissions. Renewable and Sustainable Energy Reviews 2013;18:552–67.

[73] Varatharajan K, Cheralathan M. Influence of fuel properties and composition on NOx emissions from biodiesel powered diesel engines: a review. Renewable and Sustainable Energy Reviews 2012;16(6):3702–10.

[74] Heywood JB. Internal combustion engine fundamentals. New York: McGraw-Hill Book Co; 1988.

[75] Bowman CT. Kinetics of pollutant formation and destruction in combustion. Progress in Energy and Combustion Science 1975;1(1):33–45.

[76] Fenimore CP, Formation of nitric oxide in premixed hydrocarbon flames. In: Proceedings of the 13th international symposium on combustion. The Combustion Institute; 1971. p. 373–80.

[77] Fluent Inc. Prompt NOx formation; 2001. Available from: 〈http://combust.hit.edu.cn:8080/fluent/Fluent60_help/html/ug/node582.htm〉.

[78] Miller JA, Bowman CT. Mechanism and modeling of nitrogen chemistry in combustion. Progress in Energy and Combustion Science 1989;15 (4):287–338.

[79] Gardiner WC. Gas-Phase Combustion Chemistry. 175, Fifth Avenue, New York, NY 10010, USA: Springer-Verlag New York, Inc.; 2000.

[80] Yang W, Blasiak W. Mathematical modelling of NO emissions from high-temperature air combustion with nitrous oxide mechanism. Fuel Processing Technology 2005;86(9):943–57.

[81] Galbiati MA, Cavigiolo A, Effuggi A, Gelosa D, Rota R. Mild Combustion For Fuel-Nox Reduction. Combustion Science and Technology 2004;176 (7):1035–54.

[82] Najafi G, Ghobadian B, Tavakoli T, Buttsworth DR, Yusaf TF, Faizollahnejad M. Performance and exhaust emissions of a gasoline engine with ethanol blended gasoline fuels using artificial neural network. Applied Energy 2009;86(5):630–9.

[83] Song CL, Zhou YC, Huang RJ, Wang YQ, Huang QF, Lü G, et al. Influence of ethanol-diesel blended fuels on diesel exhaust emissions and mutagenic and genotoxic activities of particulate extracts. Journal of Hazardous Materials 2007;149(2):355–63.

[84] Reuter R, Benson J, Burns V, Gorse R, et al. Effects of oxygenated fuels and RVP on automotive emissions—auto/oil air quality improvement program. SAE Technical Paper 1992;920326.

[85] Board CAR. Comparison of the effects of a fully-complying gasoline blend and a high rvp ethanol gasoline blend on exhaust and evaporative emissions: CEPA; November 1998.

[86] Naman TMA, JR. Exhaust and evaporative emissions from alcohol and ether fuel blends. SAE paper 800858; 1980.

[87] Stump FDK KT, Ray WD. Influence of ethanol-blended fuels on the emissions from three pre-1985 light-duty passenger vehicles. 19961149–61Journal of the Air and Waste Management Association 1996;46:1149–61.

[88] Furey RLK JB. Evaporative and exhaust emissions from cars fueled with gasoline containing ethanol or methyl tert-butyl ether. SAE Paper 1980;800261.

[89] Rajan S. Water–ethanol–gasoline blends physical properties, power, and pollution characteristics. Journal of Engineering for Gas Turbines and Power 1984;106:841–8.

[90] Rice RWS AK, Elrod AC, Bata RM. Exhaust gas emissions of butanol, ethanol, and methanol–gasoline blends. Journal of Engineering for Gas turbines and Power 1991:113.

[91] Lapuerta M, Armas O, Ballesteros R, Fernández J. Diesel emissions from biofuels derived from Spanish potential vegetable oils. Fuel 2005;84(6):773–80.

[92] Lapuerta M, Armas O, Herreros JM. Emissions from a diesel–bioethanol blend in an automotive diesel engine. Fuel 2008;87(1):25–31.

[93] Yücesu HS, Topgül T, Çinar C, Okur M. Effect of ethanol–gasoline blends on engine performance and exhaust emissions in different compression ratios. Applied Thermal Engineering 2006;26(17–18):2272–8.

[94] Karavalakis G, Durbin TD, Shrivastava M, Zheng Z, Villela M, Jung H. Impacts of ethanol fuel level on emissions of regulated and unregulated pollutants from a fleet of gasoline light-duty vehicles. Fuel 2012;93:549–58.

[95] Schifter I, Diaz L, Gómez JP, Gonzalez U. Combustion characterization in a single cylinder engine with mid-level hydrated ethanol–gasoline blended fuels. Fuel 2013;103:292–8.

[96] Al-Baghdadi M. Measurement and prediction study of the effect of ethanol blending on the performance and pollutants emission of a four-stroke spark ignition engine. Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering 2008;222(5):859–73.

[97] Gravalos I, Moshou D, Gialamas T, Xyradakis P, Kateris D, Tsiropoulos Z. Performance and Emission Characteristics of Spark Ignition Engine Fuelled with Ethanol and Methanol Gasoline Blended Fuels. Alternative Fuel 2011.

[98] Balki MK, Sayin C, Canakci M. The effect of different alcohol fuels on the performance, emission and combustion characteristics of a gasoline engine. Fuel 2012.

[99] Yao Y-C, Tsai J-H, Chiang H-L. Effects of ethanol-blended gasoline on air pollutant emissions from motorcycle. Science of The Total Environment 2009;407(19):5257–62.

[100] Storey JM, Barone T, Norman K, Lewis S. Ethanol blend effects on direct injection spark-ignition gasoline vehicle particulate matter emissions. SAE International Journal of Fuels and Lubricants 2010;3(2):650–9.

[101] Lin WY, Chang YY, Hsieh YR. Effect of ethanol–gasoline blends on small engine generator energy efficiency and exhaust emission. Journal of the Air and Waste Management Association 2010;60(2):142–8.

[102] Broustail G, Halter F, Seers P, Moréac G, Mounaim-Rousselle C. Comparison of regulated and non-regulated pollutants with iso-octane/butanol and iso-octane/ethanol blends in a port-fuel injection Spark-Ignition engine. Fuel 2012;94:251–61.

[103] Chen YL, Chen S, Tsai CY, Sun RH, Tsai JM, Liu SY, et al. Effects of ethanol–gasoline blends on engine performance and exhaust emissions in motorcycle. In: Proceedings of the 5th international symposium on machinery and mechatronics for agriculture and biosystems engineering. Fukuoka, Japan; 2010.

[104] Yang H-H, Liu T-C, Chang C-F, Lee E. Effects of ethanol-blended gasoline on emissions of regulated air pollutants and carbonyls from motorcycles. Applied Energy 2012;89(1):281–6.

[105] Schifter I, Diaz L, Rodriguez R, Gómez JP, Gonzalez U. Combustion and emissions behavior for ethanol–gasoline blends in a single cylinder engine. Fuel 2011;90(12):3586–92.

[106] Keskin A, Gürü M. The effects of ethanol and propanol additions into unleaded gasoline on exhaust and noise emissions of a spark ignition engine. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 2011;33(23):2194–205.

[107] Costa RC, Sodré JR. Compression ratio effects on an ethanol/gasoline fueled engine performance. Applied Thermal Engineering 2011;31(2–3):278–83.

[108] TCCd Melo, Machado GB, Belchior CRP, Colaço MJ, Barros JEM, de Oliveira EJ, et al. Hydrous ethanol–gasoline blends—Combustion and emission investigations on a Flex-Fuel engine. Fuel 2012;97:796–804.

[109] de Doz MBG, Bonatti CM, Solimo HN. Liquid–liquid equilibria of water plus ethanol plus reformate. Fluid Phase Equilibria 2005;230(1–2):45–50.

[110] Alzate CAC, Toro OJS. Energy consumption analysis of integrated flowsheets for production of fuel ethanol from lignocellulosic biomass. Energy 2006;31(13):2447–59.

[111] Munsin R, Laoonual Y, Jugjai S, Imai Y. An experimental study on performance and emissions of a small SI engine generator set fueled by hydrous ethanol with high water contents up to 40%. Fuel 2013;106:586–92.

[112] Kyriakides A, Dimas V, Lymperopoulou E, Karonis D, Lois E. Evaluation of gasoline–ethanol–water ternary mixtures used as a fuel for an Otto engine. Fuel 2013;108:208–15.

[113] Szybist J, Foster M, Moore WConfer K, Youngquist A, and Wagner R, Investigation of knock limited compression ratio of ethanol gasoline blends. SAE Technical Paper; 2010. p. 01–0619.

[114] Zheng J, Wang J, Wang B, Huang Z. Effect of the compression ratio on the performance and combustion of a natural-gas direct-injection engine. Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering 2009;223(1):85–98.

[115] Gomes P, Ecker R, Kulzer A, Kufferath A. Study on boosted direct injection si combustion with ethanol blends and the influence on the ignition system. SAE Technical Paper; 2011. p. 36–0196.

[116] Al-Farayedhi A, Al-Dawood, A., Gandhidasan, P. Effects of blending crude ethanol with unleaded gasoline on exhaust emissions of SI engine. SAE Technical Paper 2000-01-2857; 2000.

[117] Zervas E, Montagne X, Lahaye J. Emissions of regulated pollutants from a spark ignition engine. Influence of fuel and air/fuel equivalence ratio. Environmental Science and Technology 2003;37(14):3232–8.

[118] Lawrence P, Mathews PK, Deepanraj B. Experimental investigation on Zirconia coated high compression spark ignition engine with ethanol as fuel. Journal of Scientific and Industrial Research 2011;70:789–94.

[119] Sales LCM, Sodré JR. Cold start emissions of an ethanol-fueled engine with heated intake air and fuel. Fuel 2012;95:122–5.

[120] Chen R-H, Chiang L-B, Chen C-N, Lin T-H. Cold-start emissions of an SI engine using ethanol–gasoline blended fuel. Applied Thermal Engineering 2011;31(8–9):1463–7.

[121] Liao S, Jiang D, Cheng Q, Huang Z, Wei Q. Investigation of the cold-start combustion characteristics of ethanol–gasoline blends in a constant-volume chamber. Energy and Fuels 2005;19(3):813–9.

[122] Yao Y-C, Tsai J-H, Wang IT. Emissions of gaseous pollutant from motorcycle powered by ethanol–gasoline blend. Applied Energy 2013;102:93–100.

[123] Wen L-b, Xin C-Y, Yang S-C. The effect of adding dimethyl carbonate (DMC) and ethanol to unleaded gasoline on exhaust emission. Applied Energy 2010;87(1):115–21.

[124] Yoon S, Ha S, Roh H, Lee C. Effect of bioethanol as an alternative fuel on the emissions reduction characteristics and combustion stability in a spark ignition engine. Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering 2009;223(7):941–51.

[125] Velliangiri M, Krishnan A. An experimental investigation of performance and emission in ethanol fueled direct injection internal combustion engines with zirconia coating. Journal of Energy Technologies and Policy 2012;2(2):42–53.

[126] Murali Krishna M, Kishor K, Murthy P, Gupta A, Narasimha Kumar S. Comparative studies on Performance evaluation of a two stroke copper coated spark ignition engine with alcohols with catalytic converter. Renewable and Sustainable Energy Reviews 2012;16(8):6333–9.

[127] Ramesh Kumar C, Nagarajan G. Performance and emission characteristics of a low heat rejection spark ignited engine fueled with E20. Journal of Mechanical Science and Technology 2012;26(4):1241–50.

[128] Srinivasan CA, Saravanan C. Emission reduction in SI engine using ethanol–gasoline blends on thermal barrier coated pistons. International Journal of Energy and Environment 2010;1:715–26.

[129] Anderson E., Cyr J., Cordon D, Steciak J, Beyerlein S, and Budwig R, Compression ratio and catalyst aging effects on aqueous ethanol ignition (Year 2): Part 1. Compression Ratio Effects on Aqueous Ethanol Ignition; 2009.

[130] Yanowitz J, Knoll K, Kemper J, Luecke J, McCormick RL. The impact of adaption on flex-fuel vehicle emissions when fueled with E40. Environmental Science and Technology 2013;47(6):2990–7.

[131] Zhai H, Frey HC, Rouphail NM, Goncalves GA, Farias TL. Comparison of flexible fuel vehicle and life-cycle fuel consumption and emissions of selected pollutants and greenhouse gases for ethanol 85 versus gasoline. Journal of the Air and Waste Management Association 2009;59:8.

[132] Motavalli J. Flex-fuel amendment makes for strange bedfellows; 2012. Available from: 〈http://wheels.blogs.nytimes.com/2012/03/01/flex-fuel-amendment-makes-for-strange-bedfellows/〉 [20.02.13].

[133] Pickett J. Sustainable biofuels: prospects and challenges. Policy 2008:1–90.

[134] Yao YC, Tsai JH, Chou HH. Air pollutant emission abatement using application of various ethanol-gasoline blends in high-mileage vehicles. Aerosol and Air Quality Research 2011;11(5):547–59.

[135] Durbin TD, Miller JW, Younglove T, Huai T, Cocker K. Effects of fuel ethanol content and volatility on regulated and unregulated exhaust emissions for the latest technology gasoline vehicles. Environmental Science and Technology 2007;41(11):4059–64.

[136] Mayotte S, Lindhjem C, Rao V, Sklar M. Reformulated gasoline effects on exhaust emissions: phase i: initial investigation of oxygenate, volatility, distillation and sulfur effects. SAE Technical Paper 1994;941973:1994, http://dx.doi.org/10.4271/941973.

[137] Association AL. Testimony of A. Blakeman early presented on behalf of the American Lung Association before the Senate Environment and Public Works Committee Subcommittee on Clean Air and Nuclear Safety; 2009.

[138] Naidenko OV. Ethanol–gasoline fuel blends may cause human health risks and engine issues. Environmental Working Group; 2009: Washington, DC.

[139] Knoll K, West B, Clark W, Graves R, Orban J, Przesmitzki S, Theiss T. Effects of intermediate ethanol blends on legacy vehicles and small non-road engines, Report 1—Updated. Oak Ridge, TN: National Renewable Energy Laboratory; 2009.

[140] Hilton B, Duddy B. The effect of E20 ethanol fuel on vehicle emissions. Proceedings of the Institution of Mechanical Engineers. Part D: Journal of Automobile Engineering 2009;223(12):1577–86.

[141] Özgören YÖ, Çetinkaya S, Sarıdemir S, Çiçek A, Kara F. Predictive modeling of performance of a helium charged Stirling engine using an artificial neural network. Energy Conversion and Management 2013;67:357–68.

[142] Kara Togun N, Baysec S. Prediction of torque and specific fuel consumption of a gasoline engine by using artificial neural networks. Applied Energy 2010;87(1):349–55.

[143] Oğuz H, Sarıtas I, Baydan HE. Prediction of diesel engine performance using biofuels with artificial neural network. Expert Systems with Applications 2010;37(9):6579–86.

[144] Yusaf TF, Buttsworth DR, Saleh KH, Yousif B. CNG-diesel engine performance and exhaust emission analysis with the aid of artificial neural network. Applied Energy 2010;87(5):1661–9.

[145] Tütüncü K and Allahverdi N Modeling the performance and emission characteristics of diesel engine and petrol-driven engine by ANN. In: Proceedings of the International Conference on Computer Systems and Technologies and Workshop for PhD Students in Computing, ACM; 2009.

[146] Yap WK, Ho T, Karri V. Exhaust emissions control and engine parameters optimization using artificial neural network virtual sensors for a hydrogen-powered vehicle. International Journal of Hydrogen Energy 2012.

[147] Obodeh O, Ajuwa C. Evaluation of artificial neural network performance in predicting diesel engine NOx emissions. European Journal of Scientific Research 2009;33(4):642–53.

[148] Deh Kiani MK, Ghobadian B, Tavakoli T, Nikbakht AM, Najafi G. Application of artificial neural networks for the prediction of performance and exhaust emissions in SI engine using ethanol- gasoline blends. Energy 2010;35(1):65–9.