Chapter 3
Alcohol Fuels in Spark Ignition Engines

Giuseppe Di Luca, Michele Pipicelli, Roberto Ianniello, Giacomo Belgiorno, and Gabriele Di Blasio

Abstract Carbon dioxide (CO_2), nitrogen oxides (NOx) and soot emissions are primary concerns and the most investigated topics in the automotive sector. Indeed, recent governments directives push toward carbon–neutral mobility by 2050. In this framework, zero-carbon fuels, as hydrogen, or renewable low carbon alcohol fuels, play a fundamental role. To this aim, in this chapter, the main results on largely used alcohol fuels application in spark-ignition (SI) engines are discussed. Aspects inherent ethanol and methanol production processes, chemical-physical properties and their application in SI engines are presented. Different engine fuelling strategies, dual fuel and blend are analysed. Alcohols have higher enthalpies of vaporisation and research octane number (RON) values as well as excellent anti-knock ability compared to gasoline. This effect enhances in dual fuel mode. Ethanol and methanol have higher thermodynamic conversion efficiencies than gasoline combustion. Cycle to cycle variation is in line with gasoline values. In general, NOx decreases with alcohol fuels, and the best results are achieved in blend mode with a reduction of up to 30% with methanol compared to gasoline. Independently of the fuelling mode, significant benefits on particle number emissions are observed by using alcohol fuels. Carbon monoxide (CO) and hydrocarbons (HC) emission trends strongly depend on fuelling mode and engine operating conditions. Additionally, the lower carbon content of alcohol fuels reduces the CO_2 emissions up to 10% compared to reference gasoline.

Keywords Spark ignition · Methanol · Ethanol · Dual fuel · Fuel blend · CO_2 · Emissions

G. Di Luca (✉) · M. Pipicelli · R. Ianniello · G. Di Blasio
STEMS, Consiglio Nazionale Delle Ricerche, Via G. Marconi, 4, 80125 Naples, Italy
e-mail: giuseppe.diluca@stems.cnr.it

G. Belgiorno
PUNCH Torino S.p.A, Corso Castelfidardo, 36, 10129 Turin, Italy

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Abbreviations

API-GDI	Alcohol Port Injection—Gasoline Direct Injection
BMEP	Brake Mean Effective Pressure
BSCO	Brake Specific CO
$BSCO_2$	Brake Specific CO_2
BSHC	Brake Specific HC
BSNOx	Brake Specific NOx
BTE	Brake Thermal Efficiency
CO	Carbon monoxide
CO_2	Carbon dioxide
COV_{IMEP}	Coefficient of variation of IMEP
CR	Compression Ratio
DF	Dual Fuel
DI	Direct Injection
FSR	Fuel Substitution Ratio
GDI	Gasoline direct injection
GHG	Greenhouse Gases
GPI-ADI	Gasoline Port Injection—Alcohol Direct Injection
HC	Hydrocarbons
IMEP	Indicate Mean Effective Pressure
LHV	Lower Heating Value
NOx	Nitrogen oxides
PFI	Port Fuel Injection
pfp	Peak firing pressure
PM	Particulate Matter
PN	Particle Number
RON	Research Octane Number
SI	Spark Ignition
SOI	Start of Injection
TLV	Threshold limit value
WOT	Wide Opening Throttle

3.1 Introduction

The great concern related to global warming and greenhouse gas (GHG) emissions gives widespread attention to CO_2 reduction. In Europe, in the view of the Green Deal initiatives, most governments have set or are considering net-zero emissions targets (Soest et al. 2021). In this regard, the transport sector is responsible for about 23% of the global CO_2 emission (IEA 2021). Besides, the transition toward a cleaner form of propulsion, such as electric vehicles, is very far to be complete despite the rapid increase of the market share of electric vehicles (Hall et al. 2019) and its growth is expected to rise in the mid-long time frame. The lack of capillary electric fast-charging infrastructures and the production of electricity from renewable sources, especially outside cities, leave room for further developing internal combustion engines in the short-mid timeframe. In this context, SI engines are widely used in modern society in many operative fields such as passenger and commercial vehicles or other kinds of vehicles (Deng et al. 2018). Commonly thermal engines are recognised as a source of pollutant emissions. As a result, stringent regulation limits on CO_2 (EC 2020) and vehicle pollutant emissions push the research communities and industries to develop sustainable and effective solutions. Among the alternatives, in the short-mid timeframe, low carbon fuels, such as alcohol fuels, help to reduce the carbon footprint of the transport sector (Beatrice et al. 2020; Ianniello et al. 2021), especially if alcohols are produced in a renewable manner. Ethanol and methanol have drawn much attention in the last decade since they are considered renewable and cleaner fuels. Figure 3.1 shows a cumulative number of publications on SI engines fuelled with alternative fuels, methanol, ethanol in two different timeframes, based on research in the Scopus database.

Ethanol is a worldwide studied fuel, while interest in methanol fuel increased in the last decade (see Fig. 3.1).

The geographical regions where methanol and ethanol are mostly studied are shown in Figs. 3.2 and 3.3. The United States of America and China are the countries where this topic is most discussed and assessed. In the last decades, the interest is significantly growing in Eastern Asian Nations such as India.

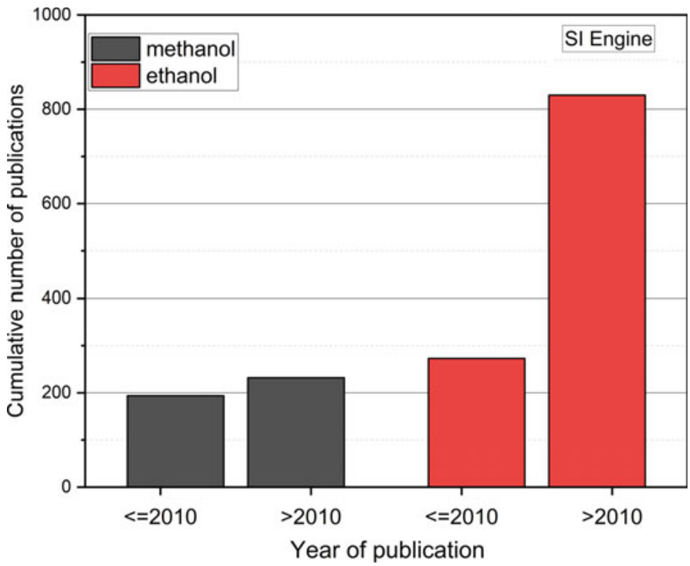

Fig. 3.1 The number of research papers on alcohols fuels (methanol and ethanol) in SI engines. *Source* Scopus database

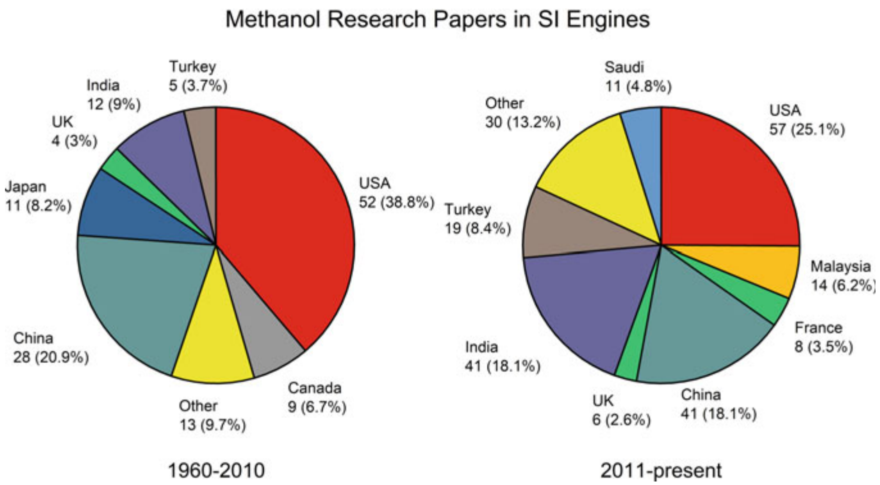

Fig. 3.2 Geographical distribution of the research papers on methanol usage in SI engines. *Source* Scopus database

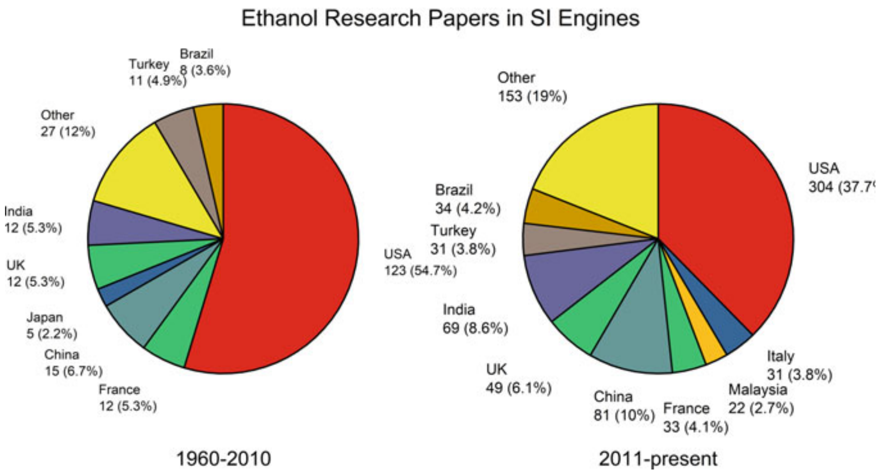

Fig. 3.3 Geographical distribution of the research papers on ethanol usage in SI engines. *Source* Scopus database

In this chapter, the application of ethanol and methanol fuels in spark-ignition engines is discussed. The chapter aims at assessing the use of ethanol and methanol in SI engines covering all fuelling technologies and injection strategies. Specific sections on combustion, emissions and engine performances are reported discriminating the effects of the technologies to those of the fuels.

3.2 Production and Properties of Alcohol Fuels

In this section, an overview on methanol and ethanol production is reported. The main chemical-physical fuel properties are discussed for both fuels and compared to conventional gasoline.

3.2.1 Alcohol Fuels Production

In this section, a brief overview on different fuel production processes for ethanol and methanol is reported below.

As mentioned, the attractiveness of methanol and ethanol fuels is related to the production processes based on renewable sources allowing carbon footprint reduction (Çelebi and Aydın 2019; Geng et al. 2017).

Ethanol can be produced by directly fermenting sugars, including sugarcane, sugar beet, sorghum, whey and molasses with yeast, from lignocellulosic materials, including woody materials, straws, agricultural waste and crop residues and catalytic hydration of ethylene (Çelebi and Aydın 2019). The ethanol produced by starch and sugar-based feedstock is known as first-generation ethanol. However, the increasing concern related to food feedstock production leads to alternative ethanol feedstock production (Popp et al. 2014). As an alternative, lignocellulosic materials seem to be more attractive due to their availability and the non-edibility of the feedstock (Isikgor and Becer 2015). Cellulosic-based ethanol is known as second-generation ethanol (Yun 2020). Recently, the so-called third-generation ethanol emerged as a candidate for future alcohol fuel production from microalgae. This ethanol production system gains increasing attention due to the simple process of converting microalgae into monosaccharides for biofuels production and their high growth rate and short harvesting cycle (Kim et al. 2020). Figure 3.4 shows the global ethanol production by top producer countries per year (2020). Brazil and the US are the two major ethanol producers, reaching about 85% of the world production.

Methanol can be synthesised from several carbon-containing feedstocks, including natural gas, coal, biomass, or CO_2 (Dalena et al. 2018). Methanol can be produced using renewable feedstocks such as forestry and agricultural waste, municipal solid waste, sewage, etc. In recent years, attention has been given to the methanol produced from CO_2. In this case, two different processes for methanol synthesis can be mentioned, a direct and indirect chemical CO_2 conversion. In the former case, CO_2 is directly converted into methanol, while in the second one, it is first converted into synthesis gas. The syngas produced is synthesised in methanol (Samimi et al. 2019). Generally, the primary use of methanol is in the chemical industry as either a feedstock, solvent, or cosolvent. Approximately 65% of the methanol produced worldwide is consumed for this purpose (Dalena et al. 2018). According to the IRENA Innovation Outlook (IRENA and Methanol Institute 2021),

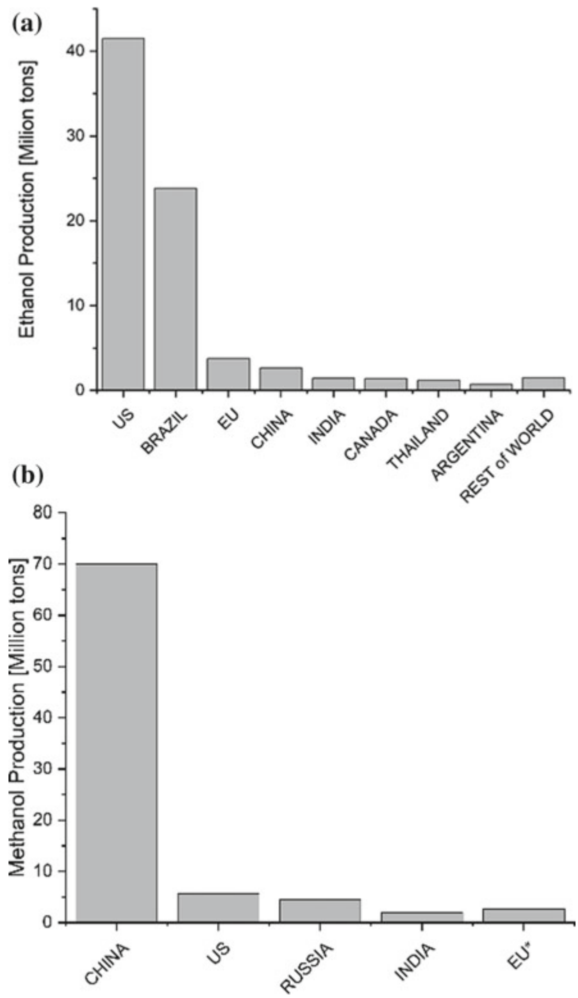

Fig. 3.4 **a** Global ethanol production by main production countries (2020). Sönnichsen (2020). *Source* data was rearranged from Sönnichsen (2020). **b** Global methanol production by different Countries (2018) (*2014)

in 2020, 30% of produced methanol has been used as a fuel feedstock and fuel additive. In Fig. 3.4b, the global methanol production by major Countries is depicted. As can be seen, China is the largest methanol producer in the world (about 70 million tons per year). Other countries produced much less methanol, e.g., the US produced 5.7 million tons per year (2018), and Russia produced 4.46 million tons per year (2018) (Bazaluk et al. 2020). India (2020) (Wikaspedia Domains 2021) and EU (2014) (Galadima and Muraza 2015) produced respectively 2 and 2.6 million tons.

3.3 Fuelling Mode, Combustion, and Emissions of Alcohol Fuels in Spark-Ignition Engines

In this section, a literature-based analysis on combustion process and emissions is carried out. The main alcohol fuels properties and the fuel injection system modes commonly applied for alcohols are also discussed.

3.3.1 Alcohol Fuels Properties

Alcohol fuels belong to the oxygenated family, and as inorganic compounds, a hydroxyl group substitutes a hydrogen atom. Ethanol (C_2H_5OH) and Methanol (CH_3OH) are primary alcohols because the carbon atom bound to the hydroxyl group is bonded with only one other carbon atom. In Table 3.1 are listed the main chemical-physical properties of gasoline, ethanol, and methanol fuels.

The molecular polarity generates a strong intermolecular hydrogen bond that led to a rise of the boiling point and the heat of vaporisation. It gives good miscibility with a substance characterised by a strong molecular polarity, such as water (Pearson and Turner 2012). The high values of heat of vaporisation promote a cooling effect on the air–fuel charge (Shamun et al. 2020).

Furthermore, oxygen content in the alcohol fuel lowers the stoichiometric air-to-fuel ratio. It influenced the combustion process, leading to higher brake thermal and

Table 3.1 Typical fuel properties (Heywood 2018; Ferguson and Kirkpatrick 2015; Noor El-Din et al. 2013; Sarıkoç 2020; Epping et al. 2002; Yates et al. 2010; Liu et al. 2015a)

Properties	Gasoline	Ethanol	Methanol
Research octane number [–]	≥ 95	108–109	107–109
Molar mass [g/mol]	~ 110	46.1	32.0
Carbon number [–]	4–12	2	1
H/C [–]	1.9	3.0	4.0
O/C [–]	0	0.5	1.0
LHV [MJ/kg]	42.6	27.0	20.0
(A/F)s [–]	14.6	9.0	6.4
Viscosity (@20 °C) [mPa/s]	0.6	1.21	0.54
Density (@15 °C) [kg/m^3]	720–775	794	796
Boiling point [°C]	40–200	78	65
Heat of vaporization [kJ/kg]	307	840	1160
ΔHvap/LHV [kJ/MJ]	7.14	31.23	55.22
Specific heat [kJ/kgK]	2.4	2.5	2.6
Adiabatic flame temp. [K]	2266	2197	2151
Specific CO_2 emissions [g/MJ]	75.1	70.7	68.8
Laminar flame speed [cm/s]	38.0	50.0	52.3

combustion efficiencies than conventional gasoline combustion (Çelebi and Aydın 2019; Kumar et al. 2020), but this aspect will be further discussed.

On the other hand, the presence of the carbon–oxygen bonds leads to a lower heating value (LHV) in comparison to gasoline (Table 3.1) and raising the mass fuel consumption at the same load conditions (Çelebi and Aydın 2019; Pearson and Turner 2012). Methanol and ethanol have similar properties, and their high-octane number rating makes them well suited for SI engines.

The material compatibility, density, oxidative stability, and viscosity strongly influence the functioning and life of the engine components. Methanol is more corrosive than ethanol. Aluminum and magnesium are subjected to aggressive corrosion, although with different chemical reaction rates. For these reasons, methanol concentration in blends is limited (Andersen et al. 2010). The EN228 regulation, which regulates the standard gasoline, set the methanol content limit to 3%. The higher methanol ratio tested is 85% v/v (Agarwal et al. 2020). The results show that high methanol concentration in blended fuel promotes engine wear and corrosion (Estefan and Brown 1990). The corrosive properties require modification to a state-of-the-art fuel injection system. Additives can be used with methanol to improve ignition, lubricity, and stability. Methanol is highly toxic in terms of ingestion, skin, or eye contact. According to Methanol Institute (Medina et al. 2017) and European Chemical Agency (ECHA) (van Leeuwenhoeklaan 2018), the threshold limit value (TLV) for time-weighted averaged (TWA) to methanol exposure is 200 ppm for an 8-h day and 40-h per week. The TLV as short-term limit rises to 250 ppm with skin notations. Intoxication by exposure to methanol initially manifests as temporary sickness and drowsiness. Nevertheless, methanol intoxication could have a latent period from 6 to 30 h. Methanol metabolisation could cause vomiting, dizziness, abdominal pain, diarrhea, difficulty breathing, blurred vision, etc. (Moon 2017).

Ethanol is less corrosive. The corrosive potential is in the percentage of water content, which is higher than in methanol and dielectric and conductive properties, leading to galvanic erosion. Matějovský et al. (2017) studied the corrosion effect of different ethanol-gasoline blends on different metallic materials, showing corrosion effect not linear with the ethanol content. According to the analysis conducted by the Royal Society and based on Brazilian experiences (Woods 2008), ethanol concentrations over 25% require an almost complete adaptation of the fuel delivering system.

Another aspect to consider is the cold starting, as one of the main issues affecting countries with average ambient temperature below the standard. Low air temperature influences the combustion process in the first running. The higher viscosity of alcohols determines poorer atomisation and air–fuel mixing. However, this phenomenon is less relevant for port fuel injection (PFI) modes (Gao et al. 2014).

The most commercialized gasoline-ethanol blend is the E10, characterised by 10% ethanol and 90% gasoline on a volume basis. It is commonly used in the US (Awad et al. 2018), and similarly, the EU Directive 2009/30/EC sets maximum ethanol concentration in gasoline to 10% v/v. Additionally, it sets also the maximum oxygen concentration to a 3.7% molar basis. Limited ethanol fractions do not require engine modifications, while neat ethanol requires specific materials to avoid corrosion.

Properties of alcohols strongly influence the combustion process. Indeed, they are characterised by a higher laminar flame rate (Glaude et al. 2010) and a slight increase in flammability limitis compared to gasoline. Methanol is generally safer than gasoline, and it is extinguishable with water thanks to its water solubility (Carpenter and Hinze 2004). On the contrary, ethanol poses significant fire safety concerns due to its solubility in water. Neat ethanol or blends requires custom fire-fighting foams (Naidenko 2009).

3.3.2 Fuelling Mode

This section describes the fuel injection system modes commonly applied for alcohol fuels in a SI engine: port fuel injection and direct injection (DI). The following nomenclatures are adopted in this chapter:

- the blends are reported on a volume basis, e.g., M85 is referred to a blend in which methanol and gasoline are in 85 and 15 v/v, respectively; E instead of M for ethanol;
- PFI-Blend refers to port-injected blend, while DI-Blend refers to direct-injected one. Dual Fuel (DF) mode, when the fuels are both injected in PFI and DI modes; alcohol port injection and gasoline direct injection (API-GDI) and vice versa (GPI-ADI);
- the fuel substitution ratio (FSR) is computed on an energy basis through the following equation:

$$FSR = \frac{m_a \cdot LHV_a}{m_a \cdot LHV_a + m_g \cdot LHV_g}$$

where m is the fuel mass while LHV is the lower heating value. To discriminate the alcohol fuel and gasoline, the *a* and *g* subscripts are utilised.

The most common fuelling approach is the alcohol-gasoline blend, which allows blending in any proportion with few or no modifications on the fuel injection system, notwithstanding cold start problems. Lower FSR, e.g., M85 instead of M100, is utilised to partially mitigate challenging cold starts issues at temperatures under 15 °C, and safety concerns such as in-tank flammability, low flame luminosity and odour (Awad et al. 2018).

The fuel properties cannot be fully exploited over the whole engine operating map at a fixed alcohol and gasoline blending ratio. Thus, a viable solution can be the DF mode, in which alcohol fuels can be injected in the intake manifold or directly into the cylinder depending on the SI engine baseline injection system.

3.3.3 Combustion

In this paragraph, the influence of alcohol fuels on combustion process is assessed. Details on the alcohols impact on knock are also reported.

Alcohol fuels in SI engines influenced the combustion process due to their high oxygen content and lower boiling point compared to gasoline.

The maximum in-cylinder pressure is evaluated as an important combustion control parameter and is limited by structural concerns at maximum engine loads. Figure 3.5 depicts a comparison among maximum peak firing pressure (pfp) as a function of engine speed for the different fuelling modes. The increments of pfp in PFI-Blend and DF modes are up to 5 bar, for DI-Blend up to 3 bar, and due to the higher latent heat and laminar flame speed, while the difference among the modes is related to the cooling effect. Kalwar et al. (2020) reported that increasing FSR in PFI mode further improves the combustion process, leading to slightly higher pfp than gasoline.

In contrast, Cho et al. (2015) investigated intermediate ethanol blends in a DI engine at different engine speeds and partial load. They found that the pfp decreases proportionally with the ethanol blend ratio at the constant energising time because of the reduced lower heating value than the gasoline fuel (Table 3.1). An increase in the combustion duration is observed, as confirmed by Balki et al. (2017).

The use of alcohol can reduce the combustion duration. Indeed, Li et al. reported a comparison among different alcohol-blends in a PFI SI engine at 1200 rpm and 3–5 bar of brake mean effective pressure (BMEP). They found a shorter ignition delay and combustion duration proportional to the FSR. This effect is confirmed by Singh et al. (2016) for different ethanol-gasoline blends (E5, E10, E20) at low engine speeds at wide opening throttle (WOT).

Ethanol and methanol generally increase the volumetric and Brake Thermal Efficiencies (BTE). Figure 3.6 reports the BTE values for the different fuelling modes, engine speeds, and engine types. As seen, a clear trend is not defined in the figures due to the different engine operating conditions. In general, the use of alcohol increases the BTE both in blend modes and in DF. This is partly explained by the higher

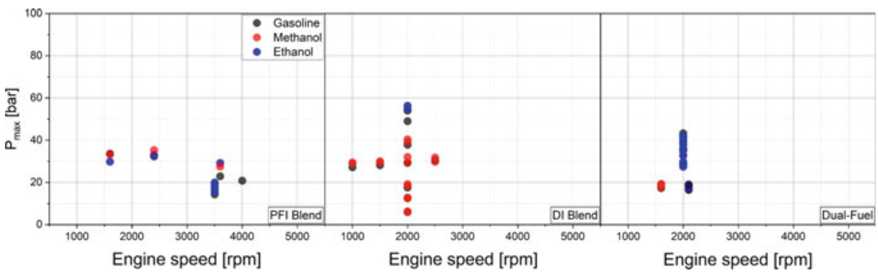

Fig. 3.5 pfp as a function of the engine speed, load, and engine type. Panel division based on PFI, DI and DF fuelling modes. *Source data* Zhang et al. (2014), Balki et al. (2014), Liu et al. (2015b, 2021), Zhuang and Hong (2013), Sharma et al. (2019), Edwin Geo et al. (2019), Qian et al. (2019)

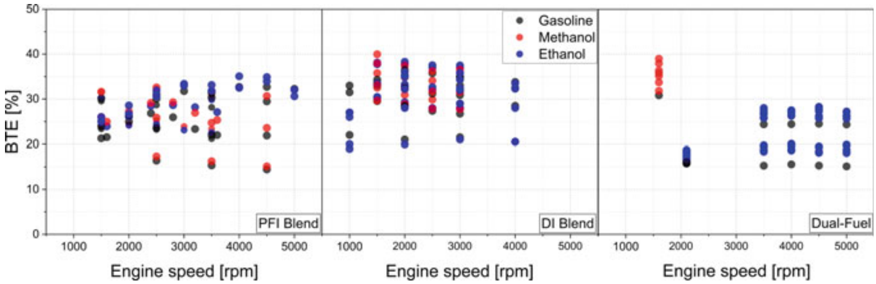

Fig. 3.6 Brake thermal efficiency as a function of engine speed, load, and engine type. Panel division based on PFI, DI and DF fuelling modes. *Source data* Deng et al. (2018), Balki et al. (2014), Liu et al. (2015b, 2021), Zhuang and Hong (2013), Turner et al. (2018), Sileghem et al. (2015), Wallner et al. (2009)

alcohol laminar flame speed and consequently reduced in-cylinder heat transfer losses compared to gasoline operation. In addition, the charge cooling effect with the use of alcohols and the consequent reduction of the exhaust gas temperatures can be considered another contributing factor. Turner et al. (2015) reported that a BTE gains up to 10% compared to gasoline for mid and high blend ratios. Balki et al. (2017) reported an increase of BTE with alcohols due to their oxygen content and higher heat of vaporization. Sileghem et al. (2014) confirmed this trend.

Based on indicated mean effective pressure (IMEP) recorded cycle by cycle, the combustion stability, and repeatability identified by the coefficient of variation of the IMEP (COV_{IMEP}) are discussed. Figure 3.7 reports the COV_{IMEP} values at different engine speeds and fuelling modes. A reference value of 5% has been considered as an acceptable limit for SI engines. Most COV_{IMEP} values are under the acceptable limit in a near stoichiometric operating condition. The outliers relate to ultra-lean conditions characterised by misfiring. In general, alcohol fuels do not influence combustion stability negatively in SI engines.

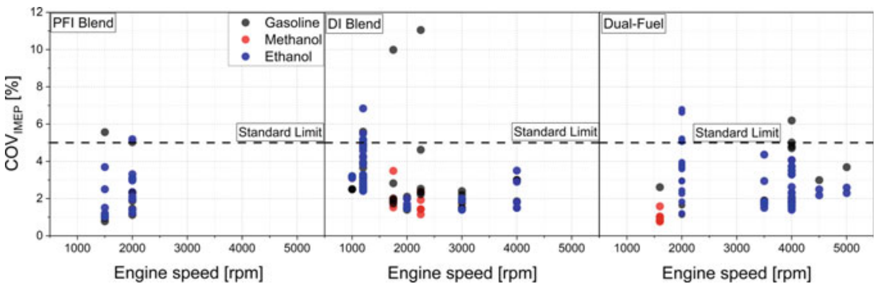

Fig. 3.7 COV_{IMEP} as a function of engine speed, load, and engine type. Panel division based on PFI, DI and DF fuelling modes. *Source data* Liu et al. (2015b), Qian et al. (2019), Wallner et al. (2009), Oh et al. (2010), Zhuang et al. (2018), Ceviz and Yüksel (2005), Nguyen et al. (2019), Ou et al. (2010

SI engine knock is one of the most critical phenomena limiting the efficiency increase. The anti-knock ability of fuel is described by RON number. As shown in Table 3.1, ethanol and methanol have higher RON than gasoline and can be recognised as anti-knock fuels (Wallner et al. 2009; Elfasakhany 2021). DF is the most effective mode to mitigate engine knock (Qian et al. 2019; Al-Muhsen et al. 2019). Liu et al. (Liu et al. 2015b) reported the advantages of the DF strategy in knock mitigation. The authors investigated the knock characteristics of methanol in the API-GDI engine reporting the effectiveness in suppressing engine knock, extending the high-load operating limit and improving fuel economy. Kim et al. (2015) investigated knock mitigation adding ethanol in API-GDI mode engine at different compression ratios (CR), 9.5 and 13.3. They found that at WOT and 1000 rpm, at most critical conditions, the required FSR to mitigate engine knock changes with CR, from 14 to 57%. It is also confirmed by Zhuang et al. (2018) in GPI-ADI mode. Engines operating at high FSR permits more advanced spark timing and higher boosting than gasoline only.

3.3.4 Emissions

In this section, the main engine-out regulated emissions of SI engines fuelled with alcohol in dual fuel and blend modes are discussed and compared to the conventional gasoline combustion.

In general, engine-out hydrocarbons production is related to different mechanisms: incomplete combustion, misfiring, flame quenching, and fuel trapped into crevices. Figure 3.8 shows the brake specific HC (BSHC) emissions as a function of the engine speed, load and fuelling modes. DF mode emits lower BSHC compared to blend ones. This behaviour can be ascribed to the ability to extend the lean burn limit (Huang et al. 2021). In blend mode, a clear trend does not emerge. Since HC emission is related to fuel not involved in the combustion process, the oxygen content of alcohols further improves the unburned fuel oxidation as reported by Silighem (2015). However, if the main mechanism is the charge trapped into crevices, the

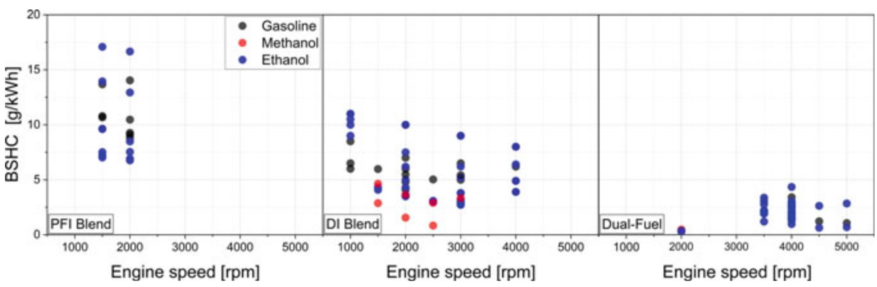

Fig. 3.8 Brake-specific HC emissions as a function of engine speed, load, and engine type. Panel division based on PFI, DI, and DF fuelling modes. *Source data* Kalwar et al. (2020), Sileghem et al. (2015), Wallner et al. (2009), Zhuang et al. (2018), Park et al. (2010)

use of PFI-Blend and DF modes can be worse than DI-Blend. This is confirmed by Kalwar et al. (2020) activities, who detected an increasing BSHC trend with FSR for both ethanol and methanol in DF mode compared to gasoline direct injection (GDI) baseline. Zhuang et al. (2018) found a non-monotonic BSHC trend related in particular to the lower in-cylinder temperature, lean air-to-fuel ratio, speed, and FSR. Park et al. (2010), investigating the effect of air to fuel equivalence ratio, found that E85 emits less HC than gasoline due to ethanol polar nature and its lower interaction with lubricating oil films. Moreover, an increasing trend was showed toward leaner conditions due to the incomplete combustion process. The HC phenomenology is particularly complex, but alcohols for some engine configuration and operation reduce the BSHC.

CO is essentially controlled by the local equivalence ratio (or air to fuel ratio) and temperature in the combustion chamber (Wallner et al. 2009). According to the literature review, using alcohol fuels potentially improves CO emissions, but it depends on the alcohol fuel employed and the engine operating conditions.

Figure 3.9 shows the brake-specific CO (BSCO) emissions as a function of engine speed, load, and fuelling modes. There is a lack of results in the technical literature regarding BSCO trends for the PFI blend. Therefore, no graphs are reported.

BSCO decreases adopting the DI fuelling mode. This trend is marked by adding methanol to gasoline due to the higher reactivity, with stratification in the combustion chamber and improved combustion process. Turner et al. (2018) evaluated the impact on engine-out emissions of blending ethanol at different ratios with gasoline in a DI engine, using a range of spark timings and start of injection (SOI). The greatest CO reduction has been observed adopting higher FSR, SOI advance, and retarded spark timing. The decreasing trend of BSCO emissions is also confirmed by Sileghem et al. (2015).

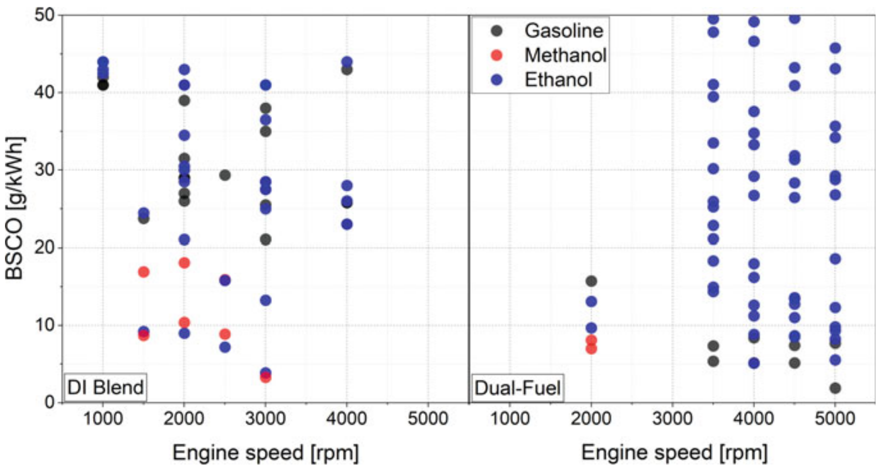

Fig. 3.9 Brake Specific CO emissions as a function of engine speed, load, and engine type. Panel division based on PFI, DI, and DF fuelling modes. *Source data* Kalwar et al. (2020), Zhuang and Hong (2013), Sileghem et al. (2015), Wallner et al. (2009)

Adopting DF mode, an opposite trend in BSCO can be noticed. As depicted in Fig. 3.9, for low engine speeds, the DF mode effectively reduces BSCO. Daniel et al. (2012) investigated engine emissions when ethanol and methanol are fuelled in GPI-ADI mode. The authors also compared the results with both a PFI and GDI baseline. They found for CO emissions a similar trend compared to the PFI baseline at lower loads and engine speeds, while lower CO emissions have been reported compared to the GDI reference. At higher loads, they observed a CO reduction compared to other fuelling modes. The improved oxidation was due to an improvement of the combustion process advancing the spark timing. The authors also estimated that further CO oxidation was related to the better vaporisation of the PFI gasoline, which helped the DI alcohol droplets to burn.

In Kalwar et al. (2020), the authors reported that at 2000 rpm, CO emission from DF engine with ethanol and methanol port-injected was lower than baseline. The oxygen content in the alcohol might be an important factor responsible for this trend due to the improved oxidation of CO in CO_2 in the stoichiometric fuel–air mixture. The authors also reported that increasing the premixed ratio of alcohols showed a different trend of CO emissions. At a higher premixed ratio, with an FSR of 30%, lower CO emissions can be observed employing ethanol/gasoline rather than methanol/gasoline dual-fuel. In this case, the methanol dominant charge cooling effect can be considered the driving factor for this trend.

At higher engine speeds, the DF strategy leads to an increase in BSCO. Particularly, at lower load, the increasing of FSR can cause an overmixing or low in-cylinder temperature, not guaranteeing optimal conditions for the oxidation of CO. This is coherent with the finding by Zhuang et al. (2013), that for FSR value greater than 48% reported an increase of BSCO.

Figure 3.10 shows the brake-specific CO_2 ($BSCO_2$) for blend fuelling mode.

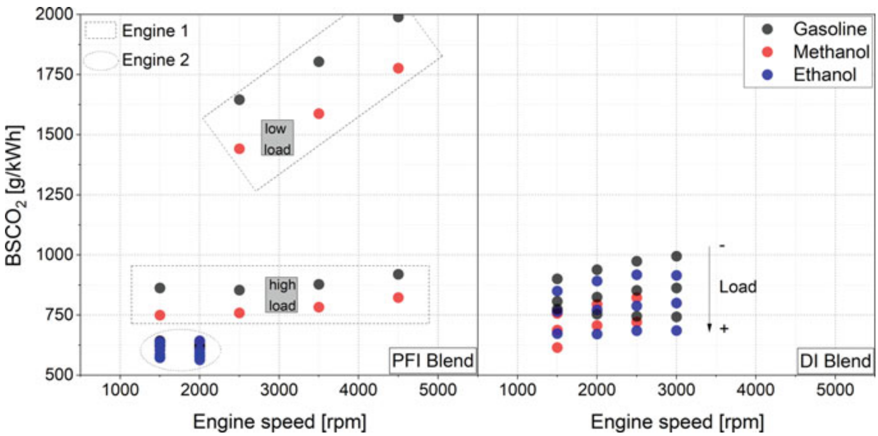

Fig. 3.10 Brake Specific CO_2 emissions as a function of engine speed, load, and engine type. Panel division based on PFI, DI and DF fuelling modes. *Source data* Turner et al. (2018), Sileghem et al. (2015), Park et al. (2010)

Few data are available in DF mode, and therefore no graphs are reported. Different engines characterised by different CO_2 baseline levels are identified. As can be seen, the results show a general decrease of $BSCO_2$ with alcohols. E.g., referring to the PFI-Blend chart, the operating points belonging to engine 1 show the methanol capability to reduce CO_2 at the same FSR, independently of the engine load and speed. In this case, the reduction is up to 10% compared to the baseline. In DI-Blend mode, for both alcohols considered, the CO_2 decreases as the load increases. At constant FSR, the CO_2 reduction is up to 20%.

Turner et al. (2018) reported a reduction of more than 10% in $BSCO_2$ for the gasoline-methanol blend compared to the gasoline baseline. The difference between methanol and ethanol CO_2 emissions is due to the methanol higher H/C ratio (Sileghem et al. 2015).

CO_2 emissions, through a well-to-wheel analysis, could be potentially further lower compared to gasoline due to the renewable nature of the alcohol fuels considered.

The NOx formation is strictly related to the in-cylinder temperature, which depends on the fuel properties and engine parameters, such as engine load and speed, equivalence ratio, coolant temperature, charge composition, etc. As previously discussed, alcohol fuels are characterised by higher heat of vaporisation and lower adiabatic flame temperatures compared to gasoline. Therefore, NOx emissions decrease according to the Zeldovich mechanism. Figure 3.11 shows the ethanol and methanol impact on NOx emissions at different engine speeds and fuelling modes. DI-Blend mode does not show a clear trend. In PFI-Blend one, NOx seems to rise as engine speed increases. However, the brake specific NOx (BSNOx) level is lower compared to the gasoline reference.

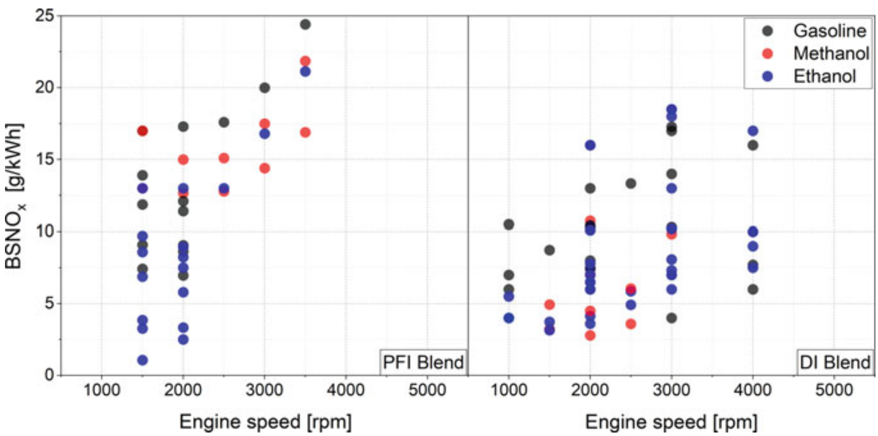

Fig. 3.11 Brake Specific NOx emissions as a function of engine speed, load, and engine type. Panel division based on PFI, DI, and DF fuelling modes. *Source data* Kalwar et al. (2020), Turner et al. (2018), Sileghem et al. (2015), Wallner et al. (2009), Park et al. (2010)

In the blend mode, the NOx emissions decrease as the fuel substitution ratio increases. Saikrishnan et al. (2018) investigated different ethanol blends (from E5 to E20) in a SI engine. The increase of ethanol fraction strongly influences the evaporation phase of the blend, thereby the in-cylinder temperature with a consequence NOx reduction.

The effect of the blending ratio enhances when it is directly injected instead of PFI. Turner et al. (2018) reported NOx emission in a DISI engine at 1500 rpm and 3.4 bar IMEP using ethanol-gasoline blends at different FSR. NOx emissions were reduced proportionally to the ethanol fraction because of the flame temperature reduction, which was corroborated by reducing the exhaust temperature.

In DI-blend mode, the alcohol charge cooling effect becomes the predominant parameter resulting in a further decrease of NOx emissions. In addition, the NOx concentration decreases as the increasing volume percentage of alcohol in the fuel mixture. As a result, the combustion process is more complete at leaner operating conditions, and the concentration of NOx emission is reduced (Thakur and Kaviti 2021).

GDI engines are recognised to emit lower CO_2 emissions, but with the disadvantage to generate more particulate matter (PM) emissions than conventional PFI configuration (Leach et al. 2013; Su et al. 2014). In addition, the particle number (PN) in a GDI is one order of magnitude higher than other ones. The fast fuel evaporation time and the wall impingement strongly influenced the PM emission (Raza et al. 2018), justifying the increase of small-sized particles fraction (Lee and Park 2020).

In Fig. 3.12, the impact of ethanol and methanol on the total PN number for DI-Blend and DF modes is depicted. As previously stated, the PFI data is not reported in this figure due to the lower PN production. As can be seen, alcohol fuel use reduces the total PN number for both injection modes thanks to the oxygen content of the alcohol, which improves the soot oxidation at the end-gas combustion phase.

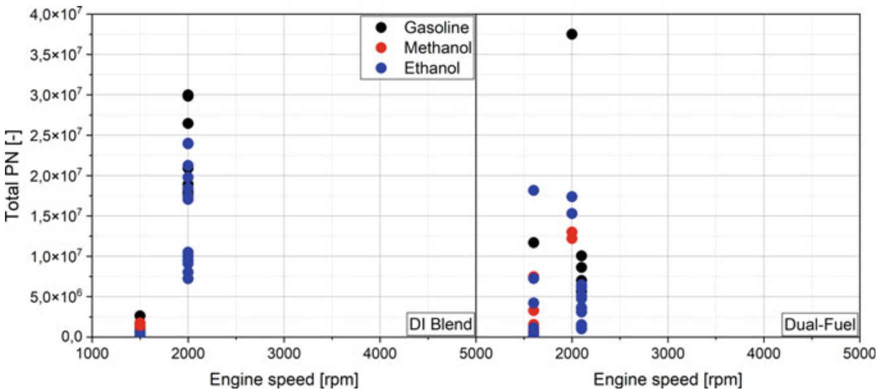

Fig. 3.12 Total particle number emitted as a function of engine speed, load, and engine type. Panel division based on PFI, DI and DF fuelling modes. *Source data* Liu et al. (2015a, 2021), Kalwar et al. (2020), Zhang et al. (2014), Turner et al. (2018)

The PN reduction is proportional to the percentage of alcohol used. This reduction can be observed also for lower FSR values as confirmed by Kalwar et al. (2020). They found that in a GDI-API engine, adding methanol in PFI at low FSR (15% on energy basis) reduced significantly total PN. In the same work, the authors assessed a further decrease of PN adding ethanol via PFI instead of methanol due to the higher oxygen content of ethanol. The increase of the premixed alcohol leads to lower PN emissions as confirmed in Liu et al. (2021). Liu et al. (2015a) found that PN significant reduction can be achieved by adopting DI-alcohol and PFI-gasoline strategy. The authors reported that the PFI-gasoline encourages fuel vaporisation, increases air–fuel mixing, and reduces wall wetting, strongly influencing the particles accumulation mode fraction. The DI-alcohol improves the combustion process leading to a reduction of locally rich regions due to the oxidant action of hydrocarbons by oxygen in the alcohol molecules.

In DI-Blend mode, the PN reduction is related to the FSR. In this case, the enhancement of the oxygen content adding alcohol fuels leads to a better combustion process and a reduction of particle formation. Turner et al. (2018) investigated particulate emissions from a single-cylinder DI engine operating on E85 and M56 fuels, confirming alcohol fuels characteristics to reduce PM emissions.

3.4 Conclusions

In this chapter, an assessment of alcohol fuels in a spark-ignition engine is carried out. This work evaluates the impact of methanol and ethanol fuels on SI engines and their advantages and drawbacks in combustion, emissions, and efficiency. The main outcomes are listed below:

- Ethanol and methanol are considered renewable fuels. Thanks to their physical and chemical properties, they are suitable for SI engines. The blending mode is the most common fuelling approach utilising alcohols. The use of a low FSR ratio in alcohols-gasoline blends needs no engines modifications.
- The alcohol FSR, in blends and DF fuelling modes, is not limited by the combustion process and miscibility issues. However, technical concerns are reported for high FSR blends regarding cold start, corrosion, and wear problems.
- The use of alcohol fuels shows a general increment of pfp in all the fuelling modes investigated and potentially reduces the combustion duration. Ethanol and methanol show better BTE compared to gasoline. According to the technical literature, in blend modes, alcohols lead to a slight increase in BTE. More evident is its increase in dual-fuel mode.
- COV_{IMEP} variation, using alcohol fuels is in line with gasoline independently by the fuelling mode and engine type. Alcohols with higher enthalpies of vaporisation and RON have greater anti-knock ability compared to gasoline. This effect is enhanced in DF mode.

- The HC phenomenology is particularly complex. The BSHC emissions are influenced by fueling mode and operating conditions. In blend mode, a clear trend does not emerge. In DF mode a reduction of BSHC is observed due to its ability to extend the lean burn limit.
- Specific CO emissions are lower adopting the DI-Blend mode. The decreasing trend is marked by adding methanol. An opposite trend can be noticed in DF mode depending on engine speeds and loads.
- Specific CO_2 emissions are lower for alcohol fuels due to their lower carbon content. The well-to-wheel CO_2 emissions could be potentially further improved compared to reference gasoline due to the renewable nature of the alcohols.
- Regarding NOx emissions, a clear trend cannot be noticed in DI-Blend mode, while in PFI-Blend one, NOx rises as engine speed increases. However, the BSNOx is lower compared to the gasoline reference.
- Alcohol fuels reduce the total PN number for all the fuelling modes investigated due to their oxygen content, improving the soot precursors oxidation.
- Based on the results above, it can be stated that the use of ethanol and methanol in SI engines can be considered, among the alternatives, a viable solution to reduce pollutant emissions in the short-mid term. Further work will be conducted by the authors extending literature-based research to explore further operating engine conditions adopting alcohol fuels.

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